Journal of Hazardous Materials B135 (2006) 443–448

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Short communication

# Advances in cement solidification technology for waste radioactive ion exchange resins: A review

Junfeng Li, Jianlong Wang *

*Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China*

Received 10 June 2005; received in revised form 7 November 2005; accepted 14 November 2005
Available online 4 January 2006

**Abstract**

Treatment and disposal of waste radioactive ion exchange resins is one of the most urgent problems for nuclear industries in China. Cement solidification technology has many advantages, such as requiring simple equipment, easy scaling-up, low working temperature, no trouble of gas cleaning and low cost. It is a suitable technology for treatment of waste radioactive resins, and has been widely used. The new developments and theoretical basis of cement solidification of radioactive resins were introduced in this paper. The cement solidification technology suitable for China and the questions needed to solve were also discussed.


*Keywords:* Cementation; Solidification; Radioactive resins

## 1. Introduction

During the operation and decommissioning of nuclear facilities, lots of waste radioactive ion exchange resins were produced. The resins loaded with radioactive nuclides could not be reused. These waste resins should be properly treated and disposed in order to minimize the potential danger to the environments. Cement is a best material for resins solidification due to its good physical, chemical and mechanical properties. Cement solidification was developed in the 1950s, and it had been the only method for solidification of radioactive wastes before 1965s [1]. After that pitch, plastic, incineration and pyrogenation were used in solidification [2,3]. Compared with cement solidification, these new solidification technologies have the disadvantages such as high temperature operation conditions, flammable and hard handling. So they were seldom accepted and used in industry. Since cement solidification emerged, researchers from all over the world had committed themselves to improve this technique [4–15]. Resin is one the most difficult kind of radioactive wastes to be cemented. For resin cementation, the main researches focus on increasing loading of spent resins, reducing leaching of nuclides, improving compressing strength of the matrix and controlling hydration heat during cementation. Some new developments of cement solidification had been appeared. In this paper, the theoretic base and the new developments of resins cementation in China are introduced.

## 2. Compatibility between cement and waste resins

The purpose of solidification is to isolate radioactive ions or hazardous waste from the environment by fixing into cement-based or pozzolan-based solidification systems, where the wastes are physically contained and/or chemically bound. The solidified cement-matrix is a kind of porous matter. The cement compositions, water/cement ratio and molding condition determine the pore structures of the solidification products. The properties of the solidification products lie on the chemical compositions and the mechanical structures of the matrix. Generally, the solidification of contaminants by cements includes three aspects: (a) chemical fixation; (b) physical adsorption; and (c) physical encapsulation [16,17]. Recent researches found that the including of resins would not affect the hydration of cement, and would not change the main forms of hydration products [18]. Figs. 1 and 2 are pictures of scanning electron microscopy (SEM) of resins solidified in ASC (a kind of specific cement) and Ordinary Portland Cement (OPC). From these figures, it can be seen that the resins and cement had not solidified together, and the resins were only physically encapsulated.

* Corresponding author. Tel.: +86 10 62784843; fax: +86 10 62771150.
*E-mail address:* wangjl@mail.tsinghua.edu.cn (J. Wang).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.11.053

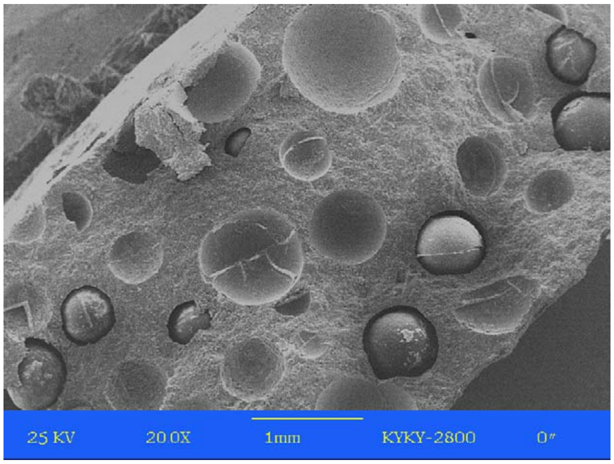


Fig. 1. ASC solidification products.

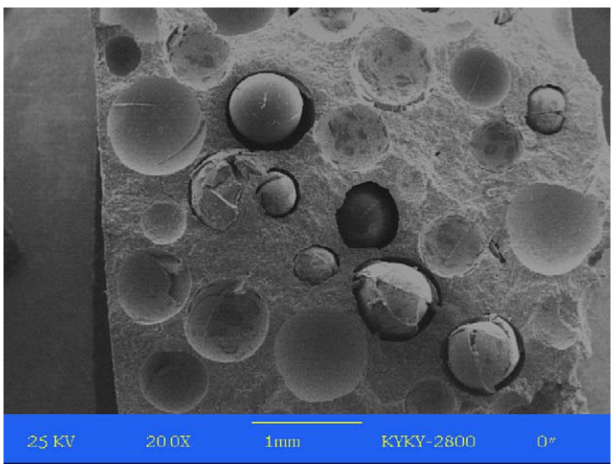


Fig. 2. OPC solidification products.

## 3. Research works on resin solidification

Cement compositions, cement proportion, resin properties, resin load, compositions of additive, water/cement ratio and solidification conditions are main factors that influence the properties of cement solidification products of resins. Various supplementary materials have been used with cements to enhance the efficacy of stabilization/solidification of contaminants. The supplementary materials often used in cementation of radioactive and hazardous wastes are listed in Table 1. Those supplementary materials were also used in cement solidification of radioactive resins.

### *3.1. Researches on reducing leaching rate of nuclides*

When radioactive ions diffuse into outer medium by conjoint pores, it is called leaching. Leaching rate of containments is determined by the properties of the waste form such as water content, pore structure, homogeneity and hydraulic conductivity. Lots of researches had been done to reveal the relations between ions leaching and the microstructure of the solidification products. These researches find that minimizing pore in solidification products and improving pore structures are effective methods in order to mechanically contain wastes in solid [32]. So, low water/cement ratio and compressive molding were used to minimize pore in solidification product, and surface painting was also used to clog pores in the products.

Exhausted ion exchange resins are favorably cemented for disposal. Heavy metals readily precipitate in the high pH environment of cements, but alkali metals, such as caesium (Cs), remain substantially soluble. Cementation of Cs-loaded resins does have its drawbacks. Cs-loaded resins, when cemented, show one or two orders of magnitude higher leaching rates in cement-matrix than in the resins themselves. Researches focusing on the reduction of significant Cs leaching (in terms of the total Cs adsorbed on the resin) by blending natural untreated and chemically treated zeolites to the cement were done by Bagosi [21]. They got the conclusion that addition of natural zeolites decreased Cs release by up to 70–75% (of the quantity originally bound in the resin) in the course of a 3-year leaching period.

In order to reduce the leaching rates, kaolin clay was added into cement by Osmanlioglu [23]. The effects of kaolin clay on the leaching properties of the cemented waste forms were evaluated, and the effect of addition of kaolin on the strength of the cemented waste form is also investigated. The long-term leaching tests showed that inclusion of kaolin in cement reduces the leaching rates of the radionuclides significantly. However, clay additions in excess of 15 wt.% caused a significant decrease in the hydrolytic stability of cemented waste form. It was found that

Table 1
Additives used in cement solidification

| Material | Intended purpose | Unfavorable effect | References |
|---|---|---|---|
| Fly ash | Decrease permeability, increase mix fluidity, lower initial heat evolution | Excess blend, reduce strength | [19,20] |
| Blast furnace slag | As above and lower initial Eh | As above | [17,20] |
| Natural pozzolan (zeolite) | Increase sorption | Excess blend, reduce strength | [21,22] |
| Clay minerals | Increase sorption | Reduce strength | [23,24] |
| Silica fume | Decrease permeability, increase sorption | Difficulty to mix homogeneously | [20,24,25] |
| Superplasticizers | Reduce water content and permeability | Unclear long-term effect on cement properties | [26,27,28] |
| Sodium silicate, calcium hydroxide, sodium hydroxide | Precipitate heavy metals, decrease permeability | Rapid set | [29] |
| Miscellaneous getters | Reduce solubility of special radwaste species, e.g. $Ag^+$, $Ba^{2+}$, for $I^-$, $IO_3^-$ | Unstable persistence of salts (e.g. AgI, $BaI_2$) in cement | [30,31] |

the best waste isolation, without causing a loss in the mechanical strength, was obtained when the kaolin content in cement is 5%.

Leaching of $^{137}Cs$ and $^{60}Co$ radionuclides fixed in cement and cement-based materials was studied by El-Kamash [25]. It was found that the leaching tests of $^{137}Cs$ and $^{60}Co$ radionuclides represent the leaching behaviour of some of the typical radionuclides encountered in low-level solid waste forms. Addition of 0–15% silica fume and ilmenite to cement decreased the leaching rate of each nuclide at different studied temperatures was concluded.

The leaching of heavy metal ions from cementitious waste had been investigated [33–39]. Various mathematical models were then used to assess the behaviour of embedded radioactive wastes. Krishnamoorthy et al. [40] proposed an iterative model to simulate the release rates of radionuclides from cylindrical cement blocks. Pescatore [41] derived two leach rate expressions for the diffusive release of radioactive constituents from both cylindrical- and rectangular-shaped waste forms.

### *3.2. Researches on improving resins load and compressing strength of the solidification products*

Lots of researches had been done by Natsuda [42,43] in order to improve resins load and compressing strength of the solidification products. It was concluded that resins load in the solidification products of OPC should be controlled bellow 20% (volume of wet resins to solidification product). 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. A model of expansion was also established. From this model, when capacities for ions and water of resins reach saturation, the expansion pressure should be zero and there should be no cracks and fractures. But experiments showed that when resins loads were higher there would be fractures in the solidification products even if the resins were saturated.

Furnace slag and fly ash were added by PAN [4]. 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 (w/w). Zeolite and OPC were used in cementation of radioactive resins [21]. Resins 24 ml, OPC 55.9 g and 37.3 g zeolite were used. Assuming the weight of 24 ml resins was 20 g, the resins to base ratio was about 20:100 (w/w).

In order to increase resins loads and stability of the products, fibers (usually stainless steel fibers, fiberglass or carbon fibers) were added. Research results showed that addition of fibers could improve stability of the products, but fiberglass and carbon fibers were not suitable to be used in cement solidification. Fiberglass were not alkali-resistant, and readily to be dissolved in cement. Carbon fibers were hard to uniformly disperse. Durafiber is a kind of fiber made of polypropylene, and it is widely used in cement to control cracks. To use this kind of fiber in solidification of spend radioactive resins, radiation-reduced degradation should be considered. Application of fibers in solidification certainly will increase the cost of treatment, so it is seldom used in industrial scale.

### *3.3. Researches on controlling of hydration heat*

Heat release during hydration of cement is one of the main factors resulting in cracks beside expansion of resins during resins cementation. Controlling the stress of temperature is a key problem that must be solved before the solidification technology is applied in industrial scale. Large-scale samples were seldom done in lab, so there were little experiences in temperature cracks control.

In order to prevent cracks resulting from hydration heat, controlling temperature and improving restrict conditions can be used. In the process of solidification, when containment were selected restrict conditions were determined, so controlling highest temperature was mainly considered. Following methods can be used in controlling highest temperature [44]:

1. Reducing ratio of cement in the products;
2. Using cement of lower hydration heat;
3. Adding ice into binders, or pre-cooling part or all of the materials;
4. Improving heat emit conditions;
5. Minimizing temperature grads in the products.

Addition of supplementary materials can reduce hydration heat, but in most conditions, the compressive strength will reduce. Measuring heat release curve can be used in comparing different prescription [45].

### *3.4. Researches on cement solidification of waste resins in China*

Researches on effective cement solidification of waste resins had been carrying out in China. A kind of special cement (ASC) was used in radioactive spent resins solidification. It was found that the best prescription was X ASC cement + 0.5X waste resins (dry) + 0.4X water from researches of prescription comparing. In this condition, the load of resins was about 45(v/v). The compressing strengths of the matrices were between 18–20 MPa [46,47].

By means of Mercury Intrusion Test, X-ray diffraction and SEM analysis, the properties corresponding to the microstructures of solidification products made by different type of cement has been studied. The results of Mercury Intrusion Test were showed in Figs. 3 and 4. From the curves it can be seen that the apertures of the pores were from 5 to 100 nm, and mercury intruded into the ASC matrices was hardly to release. The retarding capability of ASC matrices was larger than OPC matrices. Therefore, the ASC matrices had better apertures structures to reduce leaching of nuclides than OPC matrices. The interstitial rate of ASC matrices calculated by software was to be 1.17%, and the interstitial rate of OPC matrices was 2.26%.

The SEM results of ASC matrices and OPC matrices were shown in Figs. 5 and 6. From the pictures, the structures of

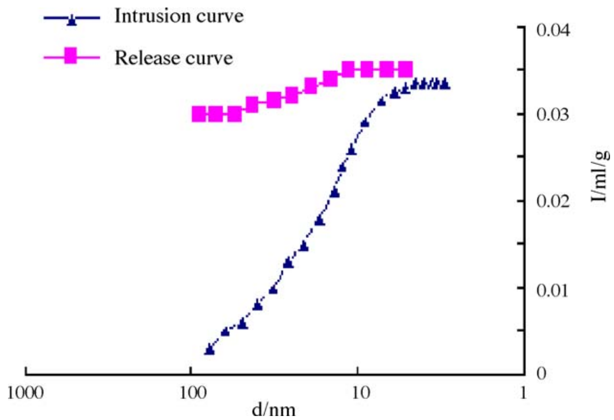


Fig. 3. Intrusion and release curve of ASC.

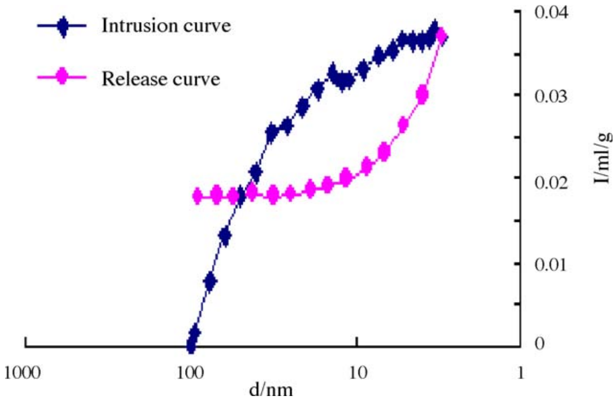


Fig. 4. Intrusion and release curve of OPC.

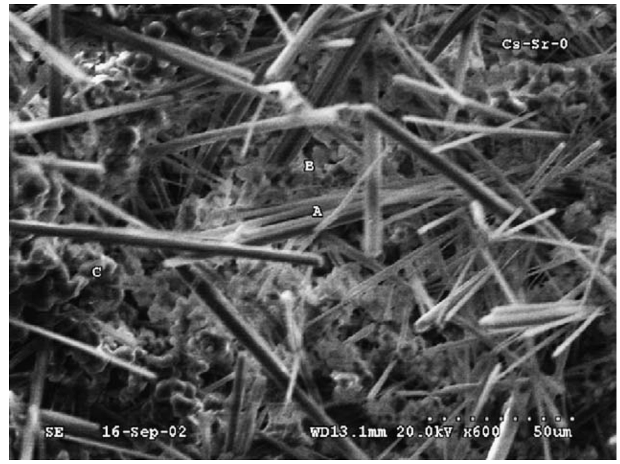


Fig. 5. SEM picture of ASC matrices.

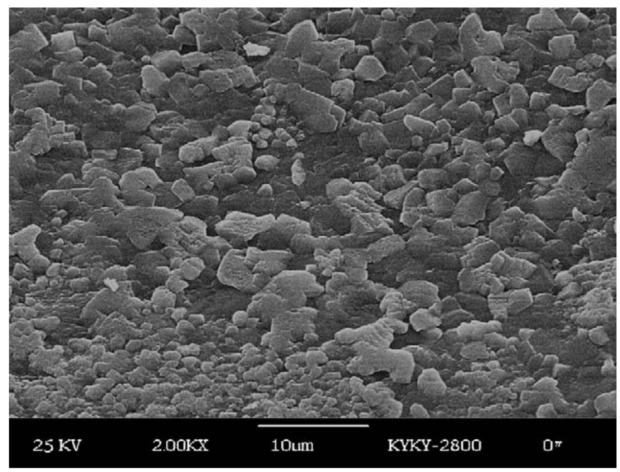


Fig. 6. SEM picture of OPC matrices.

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.

The X-ray diffraction of ASC matrices is shown in Fig. 7. The results showed that the hydration products of ASC are mainly $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, and the hydration products of OPC are mainly crystals of portlandite and gel of $3CaO{\cdot}2SiO_2{\cdot}3H_2O$.

The effects of addition of zeolite on the strength, hydration heat of cementation and leaching rates of the resins cementation

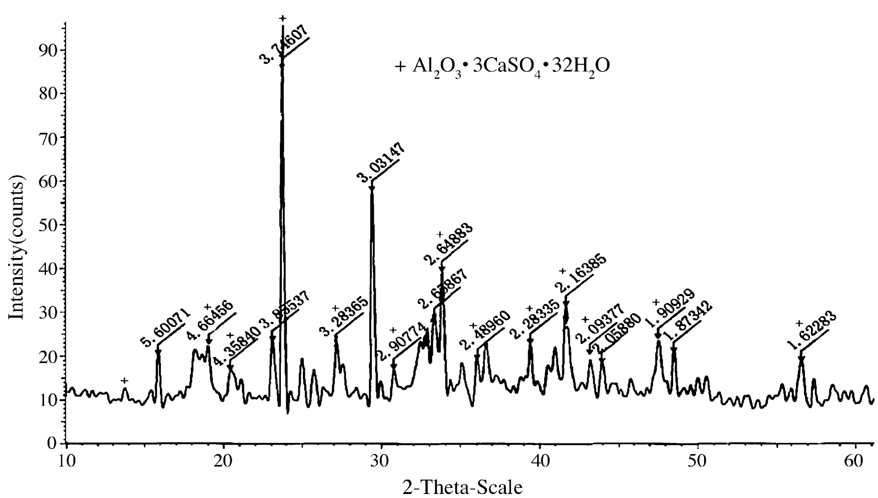


Fig. 7. XRD result of ASC matrices.

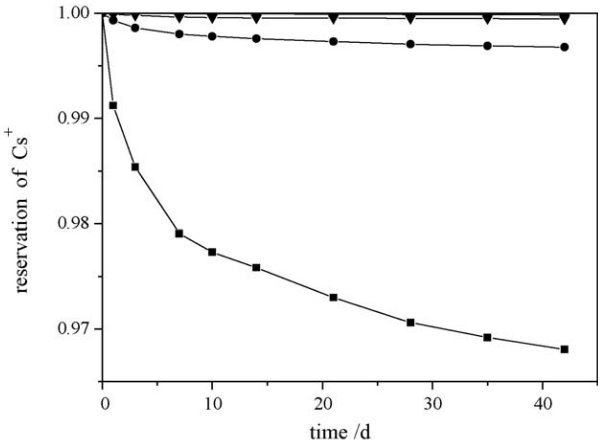


Fig. 8. Impact of zeolite addition on reservation $Cs^+$; (■) no zeolite added; (●) 10% zeolite added; (▲) 20% zeolite added; (▼) 30% zeolite added; (⧫) 40% zeolite added.

matrix were investigated. A superior combination was obtained as ASC 35 wt.%, zeolite 7 wt.% to mix 42 wt.% of resins with 16 wt.% of water, the moisture content of the resins was about 50%. The simulated leaching tests showed that inclusion of zeolite in ASC reduced the leaching rates of radionuclides significantly. Impact of zeolite addition on reservation of $Cs^+$ was shown in Fig. 8.

Compared with cement used in solidification processes before, the ASC cement is a promising material for cementation of radioactive spent resins due to its good properties, such as low nuclides leaching rates, high spent resin loadings in the matrices, excellent matrix stability during wet and dry cycling curing, high matrix strength, and easy solidification. However, there is still one problem to be resolved before this new technique can be used in industry. High hydration heat releasing rate of ASC will lead to high temperature in the solidification products. So controlling the stress of temperature is the main research aspect in using ASC in cement solidification of resins.

## 4. Conclusion

The main researches of resins solidification are focused on increasing loading of spent resins, reducing leaching of nuclides, improving compressing strength of the matrix. Zeolite is a kind of promising supplementary materials for reducing leaching rates. The new kind of specific cement used in China is a kind of promising cement for solidification radioactive resins for better apertures structures, low leaching rate and needles or spines like structures.

## References

[1] Z.Q. Shi, D. Fang, et al., Environmental Effect of Nuclear Plants, Press of Water Power, 1984 (In Chinese).
[2] P. Pisciella, S. Crisucci, et al., Chemical durability of glasses obtained by vitrication of industrial wastes, Waste Manag. 21 (2001) 1–9.
[3] P.N. Bhat, D.K. Ghosh, et al., Immobilization of beryllium in solid waste (red-mud) by fixation and vitrification, Waste Manag. 22 (2002) 549–556.
[4] L.W. Pan, B.D. Chang, et al., Optimization for solidification of low-level-radioactive resin using Taguchi analysis, Waste Manag. 21 (2001) 767–772.
[5] X.D. Shen, Study on solidification technology of high level radioactive waste by alkali activated slag cement, Dissertation, Nanjing Chemistry Engineer institute, Nanjing, July 1994.
[6] R.J. Eijk, H.J.H. Brouwers, Modelling the effects of waste components on cement hydration, Waste Manag. 21 (2001) 279–284.
[7] T. Hartmann, P. Paviet-Hartmann, et al., The effect of supercritical carbon dioxide treatment on the leachability and structure of cemented radioactive wast-forms, Waste Manag. 19 (1999) 355–361.
[8] I. Serclerat, P. Moszkowicz, et al., Retention mechanisms in mortars of the trace metals contained in Portland cement clinkers, Waste Manag. 20 (2000) 259–264.
[9] G. Pecqueur, C. Crignon, et al., Behaviour of cement-treated MSWI bottom ash, Waste Manag. 21 (2001) 229–233.
[10] J. Paya, M.V. Borrachero, et al., Properties of Portland cement mortars incorporating high amounts of oil-fuel ashes, Waste Manag. 19 (1999) 1–7.
[11] M.S. Hernandez, A. Guerrero, et al., Effect of the temperature on the leaching performance of the cement-based immobilization systems: sulfate and chloride behavior, Cement Concrete Res. 27 (1997) 515–524.
[12] C. Venkobachar, L. Iyengar, et al., Release of U(VI) from spent biosorbent immobilized in cement concrete blocks, Cement Concrete Res. 25 (1995) 1639–1646.
[13] A. Macias, A. Kindness, et al., Impact of carbon dioxide on the immobilization potential of cemented wastes: chromium, Cement Concrete Res. 27 (1997) 215–225.
[14] M. Yousuf, A. Mollah, et al., The Interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems, Waste Manag. 15 (1995) 137–148.
[15] N.W. Wieslawa, M. Jan, Application of calorimetry in studies of the immobilization of heavy metals in cementitious materials, Thermochim. Acta 269/279 (1995) 613–619.
[16] C. Shi, R.L. Day, et al., Uptake of metal ions by autoclaved cement pastes, in: Proceedings of Materials Research Society 245, 1992, pp. 141–149.
[17] C. Shi, X. Shen, et al., Immobilization of radioactive wastes with Portland and alkali-slag cement pastes, Il Cemento 91 (1994) 97–108.
[18] Y.Z. Zhou, Study on cementation technology of radioactive spent resins and mechanism investigation, Dissertation, Tsinghua University, Peking, 2002 November (in Chinese).
[19] A. Katz, A.R. Brough, et al., Cement solidification of simulated off-gas condensates from vitrification of low-level nuclear waste solutions, Waste Manag. 21 (2001) 543–553.
[20] W.S. Chuang, C.P. Wang, Solidification of liquid radwaste by cement containing fly ash ground blast-furnace slag and silica fume, Nucl. Sci. J. 33 (1996) 417–427.
[21] S. Bagosi, L.J. Csetenyi, Immobilization of caesium-loaded ion exchange resins in zeolite-cement blends, Cement Concrete Res. 29 (1999) 479–485.
[22] J.F. Li, G. Zhao, et al., Solidification of low-level-radioactive resins in ASC-zeolite blends, Nuclear Eng. Design 235 (2005) 817–820.
[23] A.E. Osmanlioglu, Immobilization of radioactive waste by cementation with purified kaolin clay, Waste Manag. 22 (2002) 481–483.
[24] W.H. Huang, Properties of cement-fly ash grout admixed with bentonite silica fume or organic fiber, Cement Concrete Res. 27 (1997) 395–406.
[25] A.M. El-Kamash, A.M. El-Dakroury, et al., Leaching kinetics of $^{137}Cs$ and $^{60}Co$ radionuclides fixed in cement and cement-based materials, Cement Concrete Res. 32 (2002) 1797–1803.
[26] W.H. Huang, Improving the properties of cement–fly ash grout using fiber and superplasticizer, Cement Concrete Res. 31 (2001) 1033–1041.
[27] K. Yoshioka, E. Tazawa, et al., Adsorption characteristics of superplasticizers on cement component minerals, Cement Concrete Res. 32 (2002) 1507–1513.
[28] S.K. Agarwal, I. Masood, et al., Compatibility of superplasticizers with different cements, Construction Building Mater. 14 (2000) 253–259.

[29] A.K. Minocha, N. Jain, et al., Effect of inorganic materials on the solidification of heavy metal sludge, Cement Concrete Res. 33 (2003) 1695–1701.
[30] M.L.D. Gougar, B.E. Scheetz, et al., Ettringite and C-S-H portland cement phases for waste ion immobilization: a review, Waste Manag. 16 (1996) 295–303.
[31] M. Yousuf, A. Mollah, et al., Speciation of silver in cementitious environment, J. Hazard. Mater. 63 (1998) 163–177.
[32] C.J. Shi, R. Spence, Designing of cement-based formula for solidification/stabilization of hazardous radioactive and mixed wastes, Crit. Rev. Environ. Sci. Technol. 34 (2004) 391–417.
[33] S.R. Hillier, C.M. Sangha, et al., Long-term leaching of toxic trace metals from Portland Cement Concrete, Cement Concrete Res. 29 (1999) 515–521.
[34] J. Macsik, A. Jacobsson, Leachability of V and Cr from LDSlag/Portland Cement stabilised sulfide soil, Waste Manag. 16 (1996) 699–709.
[35] S. Trussell, B. Batchelor, Leaching of heavy metals from solidified wastes, Waste Manag. 13 (1993) 515–516.
[36] P.G. Baker, P.L. Bishop, Prediction of metal leaching rates from solidified/stabilized wastes using the shrinking unreacted core leaching procedure, J. Hazard. Mater. 52 (1997) 311–333.
[37] B. Batchelor, Leach models: theory and applications, J. Hazard. Mater. 24 (1990).
[38] K.Y. Cheng, P.L. Bishop, Developing a kinetic leaching model for solidified/stabilized hazardous wastes, J. Hazard. Mater. 24 (1990) 213–224.
[39] C.E. Halim, S.A. Short, et al., Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC, J. Hazard. Mater. A125 (2005) 45–61.
[40] T.M. Krishnamoorthy, S.N. Joshi, et al., Desorption kinetics of radionuclides fixed in cement-matrix, Nucl. Technol. 104 (1993) 351–357.
[41] C. Pescatore, Leach rate expressions for performance assessment of solidified low-level radioactive waste, Waste Manage. 11 (1991) 223–229.
[42] M. Natsuda, T. Nishi, Solidification of ion exchange resins using new cementitious material. (1) Swelling pressure of ion exchange resin, J. Nucl. Sci. Technol. 29 (1992) 883–889.
[43] M. Natsuda, T. Nishi, Solidification of ion exchange resins using new cementitious material. (2) Improvement of resin content fiber reinforced cement, J. Nuclear Sci. Technol. 29 (1992) 1093–1099.
[44] B.F. Zhu, Temperature and Stress Control of Cement Construction, Press of Water Power, 1976 (in Chinese).
[45] J.F. Li, G. Zhao, et al., Reduction of hydration heat during cementation of radioactive resins, J. Tsinghua Univ. Sci. Technol. 44 (2004) 1600–1602 (in Chinese).
[46] Y.Z. Zhou, Y.C. Ye, et al., Study on solidification of spent ion exchange resin using ASC cement, Radiation Protection 22 (2002) 225–230 (in Chinese).
[47] Y.Z. Zhou, G.C. Yun, et al., Solidification of spent ion exchange resin using ASC cement, J. Tsinghua Univ. Sci. Technol. 7 (2002) 636–640.