Influences of Additives on the Performances of the Cementation of Simulated Radioactive Fluoride Liquid Wastes

Zhenghua Qian, Xueyang Liu, Yanbo Qiao, Shuai Wang, Hongjun Ma and Yaping Sun

Abstract This paper studied the influences of additives with zeolite, vermiculite, silica fume and quartz sand on the performances of the cementation of simulated radioactive fluoride liquid wastes, which mainly contains Cs^{+}, Sr^{2+}, F^{-}, etc. Different additives were added into the cement formulation with water/cement ratio of 0.45, and then cemented waste forms were made in the $\Phi 50$ mm $\times$ 50 mm plastic molds. Our work investigated the setting time and fluidity of the cement paste, the 28 days compressive strength of the cemented waste form, and strength losses after water/freezing resistance tests. The shock resistance and leaching tests were also carried out. Through series of comparison, the study obtained the cement formulation with zeolite, silica fume and quartz sand which could satisfy the demands of cementation of simulated radioactive fluoride liquid wastes. The cement paste could set in 22 h, and its fluidity was 18.4 cm, so its performance could meet the requirements of cement solidification in the barrel. And the mechanical behavior of the cemented waste form could meet the demands of GB 14569.1-2011. Also the cemented waste form had a good anti-leaching capacity of fluorine ion, whose cumulative leaching rate was under 4.59×10^{-3} cm during 42-day leaching test.

Keywords Additive · Cementation · Performance test · Fluorine ion

1 Introduction

With the development of nuclear science, nuclear power plants and other nuclear facilities would produce a large amount of radioactive liquid wastes when they were in service. Cementation was a kind of frequently used method for the treatment of radioactive liquid wastes, and it made the radioactive liquid wastes stored in solid

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state safely and steadily [1–7]. Cementation had many advantages such as simple equipment, technology maturation, easy operation, safety, less energy intensive, low cost, and high mechanical strength of solidified waste form.

So far, most cement formulations were aimed at radioactive borated wastes of PWR [8, 9]. Molten salt reactor was different from PWR. Its coolant was molten fluorides and its fuel was mixed with the coolant. Molten salt reactor would inevitably produce radioactive fluoride liquid wastes when it was in service. In order to protect the safety of public and environment around nuclear facilities, the radioactive fluoride liquid wastes had to be solidified for storage. Research of cementation of radioactive fluoride liquid wastes had not been reported. In consideration of toxicity and leaching performance of fluoride, we needed to carry out the research of cementation of radioactive fluoride liquid wastes.

In this experiment, we used $CsNO_3$/$Sr(NO_3)_2$/NaF as constituents of the simulated radioactive fluoride liquid wastes. Cement formulations with additives like zeolite/vermiculite/silica fume/quartz sand were used to solidify the simulated liquid wastes. Then we measured the performance parameters of the cement paste and the cemented waste form, and chose the suitable additives through comparing these parameters [10–13]. Make sure that the cemented waste forms made by the cement formulation could meet the request of GB 14569.1-2011. If so, our research would provide technical support to the cementation of radioactive fluoride liquid wastes in the future.

2 Reagents and Equipment of the Experiment

2.1 Reagents and Material

$Sr(NO_3)_2$ and $CsNO_3$ were purchased from Xiya Reagent Co., Ltd.; NaF was obtained from Sinopharm Chemical Reagent Co., Ltd.; and clinoptilolite (mesh number is 200), vermiculite (2–3 mm, without any pretreatment), silica fume ($\sim$0.3 μm), quartz sand (mesh number is 1200), and 325 # ordinary Portland cement were obtained from Conch Cement in Shanghai.

2.2 Equipment and Instrument

NJ-160 cement paste mixer, NRJ-411A cement mortar mixer, ISO cement paste normal consistency and setting time testing apparatus, NLD-3 motorized cement mortar table, and cement mortar mold were purchased from Wuxi Jianyi Instrument & Machinery Co., Ltd.; YAW-300 electro-hydraulic cement compression testing machine was purchased from Ji'nan Zhong Lu Chang Testing Machine Manufacturing Co., Ltd.; YH-40B cement concrete standard curing box was obtained

Hebei Rong Chang Test Instrument Factory; and DX219-F fluorine ion electrode was bought from Mettler-Toledo International Inc.

3 Sample Preparation of the Cemented Waste Form

Constituents of the simulated radioactive fluoride liquid wastes are shown in Table 1.

A total of 0.5 L simulated radioactive fluoride liquid wastes was added into the cement mortar mixer (cement paste mixer) and mixed with cement and additives. Then after 3 min, the cement mortar (cement paste) was poured into the plastics cement mortar mold with size of $\Phi 50 \times 50\ mm^3$, and the cemented waste forms were finished.

Additives mentioned in the experiment were zeolite, vermiculite, silica fume, and quartz sand. The weight of each cemented waste form was about 200 g. Contents of the additives in each cemented waste form are shown in Table 2.

4 Measurements and Analysis

4.1 Performance Test of the Cement Paste

Cement paste should meet the requests of cement solidification process. Fluidity of the cement paste should be greater than 13 cm. Initial setting time of the cement paste should be greater than 1.5 h, and final setting time should be less than 24 h.

Table 1 Components of the simulated radioactive fluoride liquid wastes

Constituent	$Sr(NO_3)_2$	$CsNO_3$	NaF
Content (g/L)	10.628	6.746	11.520

Table 2 Ratios of the additives in each cemented waste form

Number	Cement type	Cement/kg	Water–cement ratio	Additives/g			
				Zeolite	Vermiculite	Silica fume	Quartz sand
1	325 # ordinary Portland cement	1	0.45				
2		1	0.45	100			
3		1	0.45		100		
4		1	0.45			100	
5		1	0.45				300
6		1	0.45	100		100	300
7		1	0.45		100	100	300

Table 3 Influences of additives on the setting time and fluidity of the cement paste

Number	Additives	Fluidity/cm	Initial setting time/h	Final setting time/h
1	Cement paste	>30	13.5	22.5
2	Zeolite	26	9	22
3	Vermiculite	24.2	7	20
4	Silica fume	20.6	15	25.5
5	Quartz sand	26.6	10	23
6	Zeolite, silica fume and quartz sand	18.5	7.5	24
7	Vermiculite, silica fume and quartz sand	14.4	8	21

When the water–cement ratio of the cement formulation was 0.45, we studied the influence of additives on fluidity and setting time of the cement paste. We measured fluidity of the cement paste according to the regulations GB/T 2419-2005 and setting time of the cement paste according to the regulations GB/T 1346-2001 [14, 15]. Results of the test are shown in Table 3.

Table 3 showed that silica fume could obviously reduce the fluidity of the cement paste, the cement pastes with silica fume could reach the scope of 160–220 mm. Silica fume could increase the setting time of the cement paste, and other additives had little effect on this parameter.

4.2 *Mechanical Property Test of the Cemented Waste Form*

When curing time was over, we measured the compressive strength of the cemented waste forms according to the regulations GB 14569.1-2011 [16]. One group was tested for compressive strength directly, another group was tested after freezing resistance test, and the third group was tested after water test.

We used electrohydraulic cement compression testing machine to measure the compressive strength of the cemented waste forms. The results are recorded in Table 4.

The cemented waste forms were made to fall from height of 9 m to the concrete ground, and then each cemented waste form was broken (small pieces of edges and flaw were not treated as broken). The results are recorded in Table 5. All of specimens with quartz sand after the shock resistance test showed integrity which is given in Fig. 1.

Date in Table 4 showed that compressive strength of each cemented waste form was greater than 7 MPa. Compressive strength after freezing resistance test and water test could meet the request of national standard.

Table 4 Data of the compressive strength of the cemented waste forms

Number	Additives	28-day compressive strength/MPa	Compressive strength after freezing resistance test/MPa	Compressive strength after water test/MPa
1	Cement paste	11.2	12.7	14.6
2	Zeolite	16.1	15.5	16.2
3	Vermiculite	13.9	13.9	15.4
4	Silica fume	8.1	11.1	7.4
5	Quartz sand	21.7	19.2	21.6
6	Zeolite, silica fume and quartz sand	23.8	21	24.6
7	Vermiculite, silica fume and quartz sand	19.1	19.8	21.65

Table 5 Result of the shock resistance test of the cemented waste form

Number	Additives	Experimental result
1	Cement paste	Broken
2	Zeolite	Broken
3	Vermiculite	Broken
4	Silica fume	Broken
5	Quartz sand	Integrity
6	Zeolite, silica fume, and quartz sand	Integrity
7	Vermiculite, silica fume, and quartz sand	Integrity

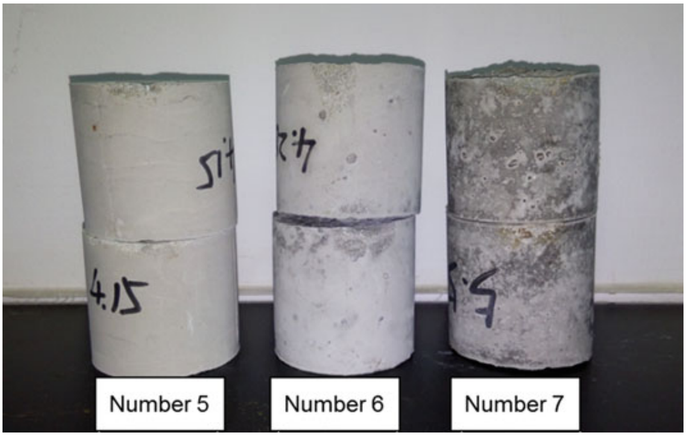

Fig. 1 Picture of the specimens with quartz sand after the shock resistance test

Zeolite slightly increased the compressive strength of the cemented waste form, vermiculite almost had no influence, and silica fume reduced the compressive strength of the cemented waste form.

The surface of the cemented waste forms which contained zeolite or vermiculite had some pores, big or small. In particular, the vermiculite without any pretreatment would create more pores for its hygroscopicity, leading to the decrease in water/cement ratio. Silica fume could well fill the gap between different particles. The compactness of cemented waste form was increased. Silica fume was advantageous to the early strength of cemented waste form, but it was disadvantageous to the long-term strength of cemented waste form because it replaced the main components of the cement.

Date in Tables 4 and 5 showed that quartz sand substantially increased the compressive strength and shock resistance of the cemented waste form. The main constitute of quartz sand was SiO_2, it took place secondary hydration with $Ca(OH)_2$ which was produced by hydration of cement. The secondary hydration promoted the formation of C–S–H gel. It was conducive to increase the strength of cemented waste form. The equation is:

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow C - S - H.$$

4.3 Leaching Performance Test of the Cemented Waste Form

We measured the leaching performance of Cs^+/Sr^{2+} of all the cemented waste form according to the regulations GB/T 7023-2011 [17]. The 42-day leaching rate and cumulative leaching rate of Cs^+/Sr^{2+} of all the cement formulations mentioned above are shown in Figs. 2 and 3.

As shown in Figs. 2 and 3, zeolite, silica fume, and quartz sand could reduce the leaching of Sr^{2+}, and vermiculite was just the opposite. Silica fume could reduce the leaching of Cs^+ too. The 42-day leaching rate and cumulative leaching rate of Cs^+/Sr^{2+} of all the cement formulations mentioned above were under 2.04×10^{-3} cm/d and 0.205 cm/1.17×10^{-4} cm/d and 4.96×10^{-3}cm. It could meet the request of GB 14569.1-2011.

4.4 Fluorine Ion Leaching Test

The mass percent of the fluorine ion in the simulated radioactive fluoride liquid waste was 0.5%. In this experiment, we used fluorine ion electrode to measure the leachate of each cemented waste form, whose 42-day cumulative leaching rate was

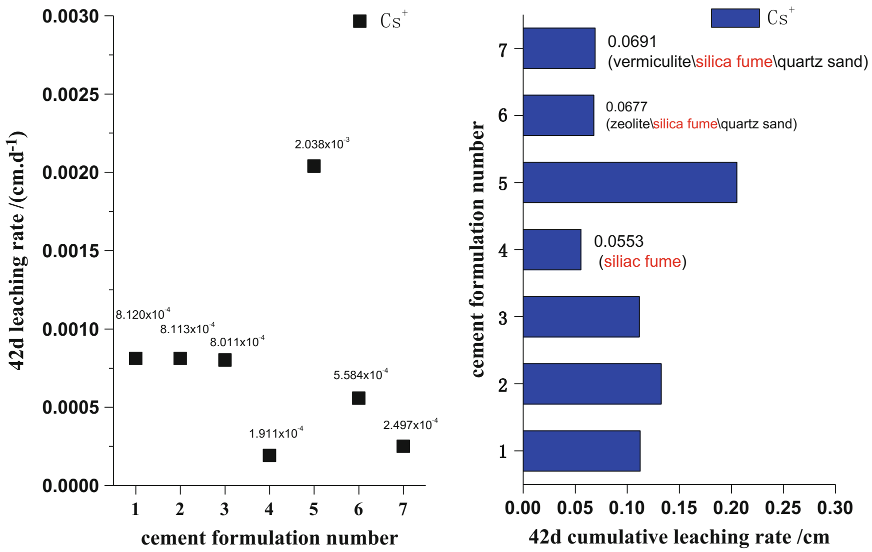

Fig. 2 42-day leaching rate and cumulative leaching rate of Cs^+

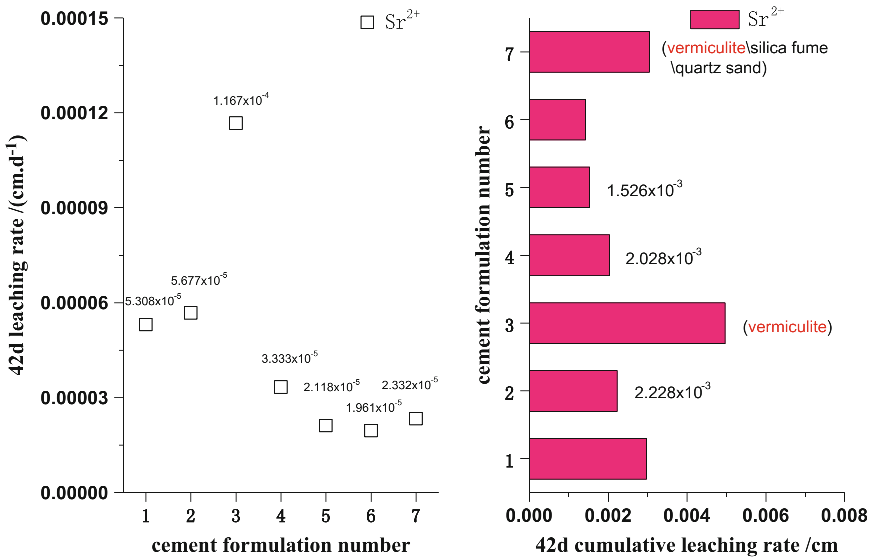

Fig. 3 42-day leaching rate and cumulative leaching rate of Sr^{2+}

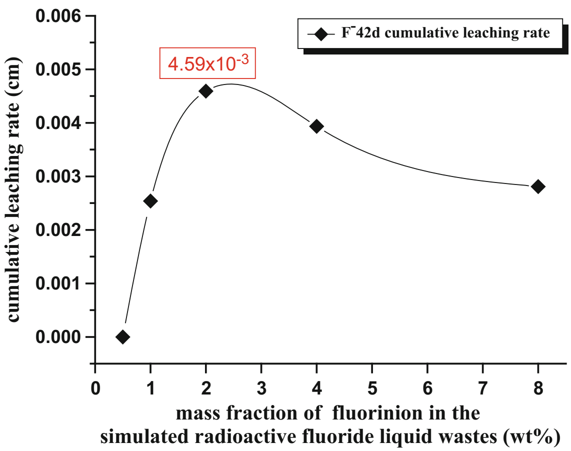

Fig. 4 Curve of cumulative leaching rate to mass fraction of the fluorine ion

all almost zero. It showed that additives had little effect on the leaching performance of fluorine ion.

Then we used the cement formulation whose additives were zeolite, silica fume, and quartz sand to make the cemented waste forms, in which mass percent of the fluorine ion in the simulated radioactive fluoride liquid wastes were increased twofold from 0.5 to 8 %. The cemented waste forms were maintained/soaked/taken samples as the leaching test. After 42-day leaching test, we measured the leachate of the fluorine ion in each cemented waste form. Curve of cumulative leaching rate to mass percent of the fluorine ion in each cemented waste form is shown in Fig. 4.

When the mass percent of the fluorine ion in the simulated radioactive fluoride liquid wastes was under 8%, the 42-day cumulative leaching rate of the fluorine ion rose at first and then decreased. The 42-day cumulative leaching rate was reached maximum 4.59×10^{-3} cm when the mass percent of the fluorine ion was 2%, and it was still very low. It showed that the cemented waste form made by the cement formulation mentioned above had a good anti-leaching capacity of fluorine ion.

5 Conclusions

(1) Silica fume reduced the fluidity of the cement paste and increased its setting time; it also reduced the compressive strength of the cemented waste form. Quartz sand substantially increased the compressive strength and shock resistance of the cemented waste form.

(2) Zeolite, silica fume, and quartz sand reduced the leaching of Sr^{2+}, vermiculite was just the opposite. Silica fume also reduced the leaching of Cs^{+}. Additives had little effect on the leaching performance of fluorine ion. All the cemented waste forms had a good anti-leaching capacity of the simulated radionuclide Sr^{2+}/Cs^{+}, also the fluorine ion.

(3) Cement paste was made by the cement formulation whose additives were zeolite, silica fume, and quartz sand, and its final setting time was 22 h and fluidity was 18.4 cm. Mechanical properties and leaching performance of the cemented waste form made by the cement formulation could meet the request of GB 14569.1-2011, and the 42-day cumulative leaching rate of the fluorine ion was under 4.59×10^{-3} cm when the mass percent of the fluorine ion was under 8%. So the cement formulation could be applied to the cementation of simulated radioactive fluoride liquid wastes.

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