

Composite absorbers consisting of inorganic ion-exchangers and polyacrylonitrile binding matrix

III. Options for treatment of spent composite absorbers for final disposal

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(Received September 16, 1996)

Both cementation and vitrification was shown by preliminary experiments to be applicable for treatment of the spent composite absorbers with polyacrylonitrile binding matrix for final disposal. Loadings of cement mix with composite absorbers up to 5-9% (w/w) were achieved. Admixtures of natural clinoptilolite were found to improve compressive strength of the samples. The presence of PAN binding polymer was found not to disqualify the composite absorber tested from final treatment by vitrification.

Introduction

Inorganic ion-exchangers may be immobilised by all the basic processes¹ (immobilisation in cement, bitumen, organic polymer, vitrification in glass). The quality of the resulting solidified product must be conforming to the fact that spent inorganic ion-exchangers may often be classified as intermediate- or high-level radioactive waste. Possibility of cementation of selected inorganic ion-exchangers was studied in Harwell Laboratory.² Because of high requirements towards the quality of final waste special processes are being developed. Among those in which ceramic waste is produced hot isostatic pressing,^{3,4} ceramisation of inorganic ion-exchangers at 1000 °C after their mixing with clay⁵ or Australian SYNROCK process may be listed.

PAN-based composite inorganic-organic absorbers represent a group of inorganic ion-exchangers modified by using polyacrylonitrile (PAN) binder to produce larger size particles.⁶⁻¹¹ From the point of view of stability and treatment for final disposal the composite absorbers represent a separate group of absorbers similar both to organic ion-exchange resins and inorganic ion-exchangers. Their main feature is that the organic binding polymer (PAN) is inert and all the radionuclides are bound to inorganic active component (inorganic ion-exchanger). Thus contrary to organic ion-exchange resins even in case of decomposition of organic binding matrix (radiation, chemical, thermal or biological decomposition) no radionuclides are released.

The primary process which has been considered for treatment of composite absorbers for their final disposal is immobilisation in cement. In the tests described below properties of cement samples loaded with increasing amount of composite absorbers and their water resistance after soaking for 1 week were studied. In addition influence of clinoptilolite admixtures to cement mix and freeze/thaw or soak/dry cycling on the quality of cement samples was studied.

Because of the high efficiency and selectivity of composite absorbers, the volume of treated waste can reach up to 10⁴ to 10⁵ times the bed volume of the absorber (concentration factor 10⁴-10⁵). In such applications, namely when treating higher level waste, spent composite absorbers represent high level waste. Immobilisation of such materials in cement may not be acceptable and/or safe enough. Therefore, the possibility of vitrifying NiFC-PAN absorber was tested in trial experiments.

Experimental

Cemented specimen preparation and testing

The samples were prepared from Portland Cement PC-400 (Pragocement Radotin, Czech Republic), selected composite absorbers, distilled water, and clinoptilolite (Czech origin, grain size <0.3 mm) admixtures. Characteristics of the composite absorbers used in these tests are given in Table 1. The cemented specimen were prepared by mixing the appropriate amounts of dewatered

Table 1. Characteristics of composite absorbers used in tests

Composite absorber	Active component	Grain size, mm	Dry residue of absorber, %
TiO-PAN	Titanium oxide	<0.18	19.4
MnO-PAN	Manganese dioxide	<0.18	21.1
Ba[Ca]SO ₄ -PAN	Barium sulphate activated by calcium	<0.18	19.6
KNiFC-PAN	Potassium-nickel hexacyanoferrate	<1.5	17.8
NiFC-PAN	Nickel hexacyanoferrate	0.18-0.63	21.6

Table 2. Characteristics of cement samples with encapsulated composite absorbers. All the cement mixes were prepared from 30 g of Portland Cement PC-400

Composite absorber	Cement mix				
	Water, g	Wet absorber, g			
		15	30	45	60
TiO-PAN	10	HS-WR	HS-WR	USS	USS
MnO-PAN	8	HS-WR	HS-WR	USS	USS
Ba[Ca]SO ₄ -PAN	8	HS-WR	USS	USS	USS
KNiFC-PAN	8	HS-WR	USS	NT	NT
NiFC-PAN	8	HS-WR	USS	NT	NT

HS-WR – Visually homogenous samples with no signs of cracking or powdering. Water resistant after soaking for 1 week.

USS – Unsatisfactory samples.

NT – Not tested.

Table 3. Influence of admixture of clinoptilolite on quality of cement samples with encapsulated composite absorbers. Composition of cement mix: 15 g wet absorber + 30 g PC-400 + 8 water + clinoptilolite

Composite absorber	Clinoptilolite, g					
	0		1		3	
	CS	CS	CS-5F	VQ-5SD	CS	VQ-5SD
TiO-PAN	9.8	28.7	15	GQ	27.3	GQ
MnO-PAN	8.5	23.6	28.4	GQ	34	GQ
Ba[Ca]SO ₄ -PAN	6.3	NM	NM	NM	25.9	GQ
KNiFC-PAN	~ 9	10.4	7.5	GQ	17.6	GQ
NiFC-PAN	~ 13	12.1	11.6	GQ	17.1	GQ

CS – Compressive strength after 28 days of curing, MPa.

CS-5F – Compressive strength after 28 days of curing and five freeze/thaw cycles, MPa.

VQ-5SD – Visual estimate of the quality of sample after five soak/dry cycles.

GQ – Good quality.

NM – Not measured.

(swollen) composite absorbers and distilled water, adding cement, and thoroughly stirring the resultant cement mix for approximately 10 minutes. When preparing the series of samples with clinoptilolite admixtures, clinoptilolite was mixed into the suspension of absorber in water prepared as described above. After some 2 minutes cement was added and the grout homogenised in the same way as for samples without clinoptilolite. Exact composition of the samples prepared is given in Tables 2 and 3.

The grout was then poured into 4 × 4 × 4 cm³ cubic moulds and vibrated manually to remove any air bubbles. The samples were demoulded after 24 hours, concrete cubes were sealed into PE bags and cured for additional 27 days at ambient temperature. The dimensions of the cured samples were checked.

The strength tests were carried out using strength tester LZC following to Czech Standard¹² ČSN 722117. For freeze/thaw cycles the cement samples were frozen for 2 days at -25 °C and two days de-frozen at ambient temperature. Visual quality of cement samples during soak/dry cycles was evaluated after soaking the samples

for 2 days followed by 2-3 days' drying at ambient temperature.

Glass specimen preparation and testing

NiFC-PAN composite absorber with nickel hexacyanoferrate active component and glass frit type¹³ "LKU" was used. This glass frit was originally proposed for vitrification of "chrompick" type accident waste¹⁵ from NPP A-1 at Jaslovské Bohunice, Slovak Republic. The experiments were performed with fresh absorber and/or absorber containing ~ 1 mg · ml⁻¹ of stable caesium.

Dried NiFC-PAN absorber was mixed with glass frit in different ratios and melted in porcelain crucibles. Temperature increase gradient of 5 °C · min⁻¹ was used, the mixture was melted for 30 minutes at 1050 ± 10 °C.

Viscosity of the melts, visual quality and hydrolytic resistance of the resulting samples were examined. Hydrolytic resistance of the product was tested by leaching 1 g of crushed glass specimen (0.3–0.5 mm) in 50 ml of

distilled water for 24 hours. Electrical conductivity of the leach was measured.

Results and discussion

Cementation

From the results of tests performed (see Table 2) it can be concluded that loading of cement mix with dry composite absorber up to 5–9% (w/w) is acceptable. Maximum loading depends on the type of composite absorber and its grain size. The maximum loadings found are comparable to maximum loading of cement matrix with pure inorganic ion-exchangers.²

Solidification of radioactive wastes with cement has the disadvantage of relatively high leachability of ¹³⁷Cs. One possibility of improving leakage resistance of the resulting concrete is addition of suitable additives. Natural clinoptilolite is one of the possible candidates for such additives. This is why the influence of clinoptilolite admixtures on the quality of cement samples with encapsulated composite absorbers was studied. From the results shown in Table 3 it follows that admixtures of clinoptilolite improve compressive strength of the resulting cement samples. No significant deterioration of the quality of composite absorber-cement product with admixtures of clinoptilolite was observed after repeated freeze/thaw or soak/dry cycles.

Vitrification

The melts resulting from mixtures containing 10% (w/w) of absorber were highly viscous, it was hardly possible to pour them from the crucible. When only 5% (w/w) of dried absorber was added to the mixture, the melt could be easily poured out, and it was transparent and homogeneous.

One of the fast preliminary criteria of quality of the glass products is their hydrolytic resistance. Vitrified materials, which yield hydrolytic resistance lower than 20 $\mu\text{S} \cdot \text{cm}^{-1}$ in standard leaching tests, are usually considered to be prospective for long term storage as high level waste.

Hydrolytic resistance of the vitrified NiFC-PAN composite absorber was tested by leaching crushed glass specimen containing 5% of dried absorber, only. Electrical conductivity of the leaches ranged from 6 to 8 $\mu\text{S} \cdot \text{cm}^{-1}$.

Conclusions

Spent composite absorbers with polyacrylonitrile binding matrix were shown to be solidifiable by cementation. Maximum loadings of cement mix with composite absorbers and those with pure inorganic ion-exchangers are comparable. Admixtures of natural clinoptilolite were found to improve compressive strength of the resulting concrete products.

Preliminary laboratory experiments showed that vitrification may also be used for the final treatment of spent composite absorbers for their disposal in radioactive waste repositories. The test performed with NiFC-PAN absorber demonstrated that the presence of PAN binding polymer does not interfere with the possibility of obtaining vitrified products of satisfactory quality.

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This study is a part of broader research jointly supported by the Grant Agency of the Czech Republic, Award No. 104/94/0315, and the International Atomic Energy Agency under Research Contract No. 7381/RB.

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