Journal of Nuclear Materials 483 (2017) 121–131

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Solidification of ion exchange resins saturated with Na^+ ions: Comparison of matrices based on Portland and blast furnace slag cement

E. Lafond [a], C. Cau dit Coumes [a,*], S. Gauffinet [b], D. Chartier [a], L. Stefan [d], P. Le Bescop [c]

[a] CEA, DEN, DTCD, SPDE, F-30207 Bagnols-sur-Cèze cedex, France
[b] Laboratoire Interdisciplinaire Carnot de Bourgogne UMR 6303 CNRS-Université de Bourgogne, Dijon, France, 9 Av Alain Savary, BP 47870, 21078 Dijon cedex, France
[c] CEA, DEN, DPC, SECR, F-91192 Gif-sur-Yvette, France
[d] AREVA, Back End Business Group, Dismantling & Services, 1 Place Jean Millier, 92084 Paris La Défense, France

HIGHLIGHTS

- Solidification of cationic resins in the Na^+-form is investigated.
- Portland and blast furnace slag cements are compared.
- Deleterious expansion is observed with Portland cement only.
- Resin swelling is due to a decrease in the osmotic pressure of the pore solution.
- The consolidation rate of the matrix is a key parameter to prevent damage.

ARTICLE INFO

Article history:
Received 27 June 2016
Received in revised form
15 September 2016
Accepted 1 November 2016
Available online 2 November 2016

Keywords:
Ion exchange resins
Swelling
Hydration
Portland cement
Blast furnace slag cement

ABSTRACT

This work is devoted to the conditioning of ion exchange resins used to decontaminate radioactive effluents. Calcium silicate cements may have a good potential to encapsulate spent resins. However, certain combinations of cement and resins produce a strong expansion of the final product, possibly leading to its full disintegration. The focus is placed on the understanding of the behaviour of cationic resins in the Na^+ form in Portland or blast furnace slag (CEM III/C) cement pastes. During hydration of the Portland cement paste, the pore solution exhibits a decrease in its osmotic pressure, which causes a transient expansion of small magnitude of the resins. At 20 °C, this expansion takes place just after setting in a poorly consolidated material and is sufficient to induce cracks. In the CEM III/C paste, swelling of the resins also occurs, but before the end of setting, and induces limited stress in the matrix which is still plastic.

1. Introduction

Ion exchange resins (IERs) are polymeric materials, usually in the form of spherical beads or ground grains, which are capable of exchanging particular ions within the polymer with ions in a solution that is percolated through them. Fig. 1 shows the typical structure of a cationic resin: it is made of a polystyrenic backbone, reticulated with divinylbenzene, and functionalized with sulfonic groups. These groups bear a negative charge that is compensated by exchangeable cations, such as H^+ in the shipped resins, or Na^+ in the spent resins considered in this study.

IERs are commonly used by the nuclear industry in the decontamination process of radioactive effluents. The spent resins become a low-level or intermediate-level radioactive waste. They not only contain radionuclides, but also chemical species present in the treated waste streams. For instance, cationic resins used to purify solutions originating from spent fuel reprocessing often contain high amounts of sodium. Such waste has to be stabilized and solidified, i.e. placed under a solid, stable, monolithic and confining form, before being sent to disposal. Calcium silicate cements are good candidates for resins encapsulation [1–4]. They can

---

* Corresponding author.
E-mail address: celine.cau-dit-coumes@cea.fr (C. Cau dit Coumes).

http://dx.doi.org/10.1016/j.jnucmat.2016.11.003

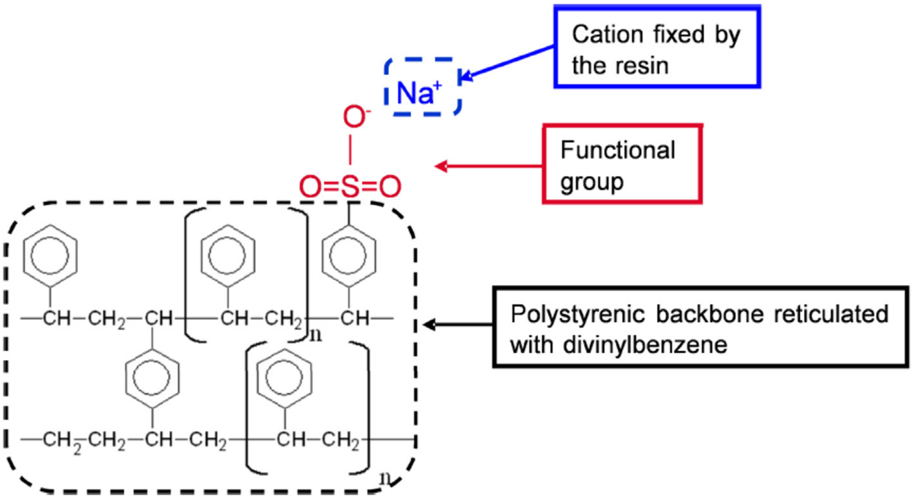

Fig. 1. Typical structure of a cationic resin in the Na^+ form.

be easily supplied, at low cost. The process is operated at room temperature and does not require any gas treatment. It is compatible with aqueous waste: water provided by the resins can be used up for cement hydration. The hardened material usually exhibits acceptable mechanical strength, good self-shielding, and high alkalinity which allows many radionuclides to be precipitated and thus confined. However, for certain combinations of cement and resins, the solidified waste forms can exhibit strong dimensional variation, possibly leading to cracking of the matrix [5,6].

To design a robust cement-based matrix, several features of the IERs have to be considered, such as their low intrinsic mechanical strength and the possible ionic exchanges with the pore solution [7,8]. It is also well known that IERs grains can exhibit strong volume changes in aqueous medium, depending on the composition of the solution. Two main processes are involved: *(i)* ion exchange and/or *(ii)* variations in osmotic pressure [9]. *(i)* Resin volumes change with conversion to ionic forms of differing degrees of solvation. *(ii)* In more concentrated solutions, less water is taken up owing to greater osmotic pressure. These volume changes can also occur in a cementitious matrix since its pore solution chemistry evolves with ongoing hydration. Under severe conditions, they can lead to cracking and disintegration of the matrix [10–12]. Knowledge about the chemical evolution of IERs in a cementitious environment is limited. For example, it is often mentioned in the literature that the encapsulation of IERs with Portland cement (CEM I) leads to strong expansion during the early stages of cement hydration, whereas no swelling is observed when Portland cement is blended with high amounts of blast furnace slag [13,14]. However, the reasons for these different behaviours are not understood.

To simplify the system under investigation, Portland cement was replaced in a previous study by its main component, tricalcium silicate [15]. The C_3S-waste form also exhibited a strong expansion and two main stages were observed during hydration at early age. In the first one, due to ionic exchange (fixation of calcium, release of sodium), the resins shrank. Then, in a second stage, as hydration accelerated, the sodium concentration in the pore solution rapidly decreased due to the precipitation of sodium-bearing C–S–H, whereas the resins continued to fix calcium ions. Swelling of the resins occurred during the second stage, and resulted from the decrease in the osmotic pressure of the pore solution due to the consumption of sodium ions. Despite its small magnitude, swelling seemed to be enough to deteriorate the hardened matrix during the second stage, just after setting, while the degree of hydration was still low and the matrix poorly consolidated.

To provide deeper understanding of real systems, this work aims at comparing the hydration of Portland cement and blast furnace slag cement (CEM III/C) pastes with cationic resins initially in the Na^+ form. The objective is to explain why cements containing high amounts of blast furnace slag are more appropriate than Portland cement to solidify and stabilize this waste.

2. Experimental

2.1. Materials

The two cements used in this study were referred as CEM III/C (32.5 N from Calcia Rombas) and CEM I (52.5 N from Calcia Couvrot). According to European standard EN 197–1:201204, CEM I comprises 95–100% Portland Cement clinker (without the necessary calcium sulfate) whereas CEM III/C corresponds to a Blast Furnace Cement consisting of 5–19% Portland cement clinker and 81–95% blast furnace slag. The compositions of the cements and clinker are reported in Tables 1 and 2. The two cements comprised the same Portland clinker, but in different amounts. 96.9 wt. % of the slag was vitreous.

IERs were supplied by Rohm&Haas under the trade name Amberlite IR120H in the physical form of spherical beads or ground grains. The IER beads had a diameter comprised between 620 and 830 μm, and the ground IERs had a particle size ranging from 0.4 μm to 300 μm ($d_{10} = 15$ μm, $d_{50} = 65$ μm, $d_{90} = 155$ μm). The exchange sites of the resins, shipped in the H^+ form, were saturated with Na^+ ions by percolating a solution of sodium hydroxide. The pH of the eluted solution was continuously monitored, and the percolation was stopped as soon as the pH exceeded 7. The resins were then rinsed with water to eliminate the excess of base and to recover a neutral pH. Finally, the suspension of water and resins was filtered under humid atmosphere and slight vacuum on a Buchner funnel to remove the free intergranular water (water between the resin grains). The dry extract of the wet resins was measured by gentle heating at 55 °C (to avoid any damage of the functional groups) until constant weight. Values of 54.3 ± 0.2% and 45.3 ± 0.2% (weight fraction of dried resins) were achieved for beads and ground grains respectively. This difference was explained by the fact that ground resins developed a larger surface area than bead resins. The volume of water adsorbed onto the surface of resin was thus more important. The wet resins were kept