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The potential effect of radiolyzed superplasticizers contained in cement-based materials on europium uptake

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I. INTRODUCTION

In the French nuclear waste management context, most of the intermediate-level long-lived waste will be stabilized in mortar or concrete packages. The cement-waste forms are used to immobilize radionuclides (RN) and provide a protection from radiations. In such cement-based materials, superplasticizers (SP) are used as admixtures to increase the workability of the early-age cement-water-aggregate mixture. In a deep geological repository situation, SP undergo coupled effect from both radiolysis and hydrolysis in the pore solution of cement-based materials leading to the formation of potentially complexing degradation products. Determining the impact of SP degradation products on RN transfer through cementitious materials is important for assessing the disposal concept [1]. This study is focused on two major families of SP used by French nuclear industry: polycarboxylate ether (PCE) and polynapthalene sulfonate (PNS) in the presence of europium(III) taken as chemical analogue of trivalent actinides. The main objectives of this work are i) a better understanding of the sensitivity of SP, and degradation products, to the coupled effect of radiolysis and alkaline hydrolysis; ii) to describe the interactions between Eu(III) and ligands resulting from the degradation of SP by radiolysis and alkaline hydrolysis; and iii) to evaluate the impact of these interactions on the reactive transport of Eu(III) in a compact cementitious matrix after radiolysis [2]–[4]. The study presented hereafter is more particularly focussed on parts i) and ii).

II. RESULTS AND DISCUSSION

A. Materials and method

The experimental part is focused on interactions between Eu(III) and ligands resulting from degradation of SP. SP alkaline solutions are prepared with respectively 1 and 2%w of PCE and PNS in alkaline medium under anaerobic conditions. The SP are commercial products whose density and dry extract are (1.05 ± 0.02) g cm^{-3}, (19.9 ± 2.0)% for PCE and (1.15 ± 0.03) g cm^{-3}, (32.5 ± 1.6)% for PNS. The alkaline medium contains 0.15 mol L^{-1} NaOH, 0.12 mol L^{-1} KOH and 10 g L^{-1} of crush mortar (CEM I 52.5 N - SR 5 CE PM-CP2 NF HTS Le Teil; water/cement ratio = 0.4; 2.51%w PCE or 5.03%w PNS). The SP alkaline solutions are at pH value of 13.3 ± 0.1. The SP alkaline solution are degraded by gamma-radiolysis, which is performed by Poséidon irradiator (LABRA, CEA). The irradiator is equipped with a ^{60}Co source: irradiation doses are 0, 50, 100, and 250 kGy, and the dose rate is 1 kGy h^{-1}. SP alkaline solutions are filtered through Thermo Scientific Nalgene syringe filters equipped with PES membrane (0.2 µm size pore × 25 mm ∅). SP degradation products are characterized by gas spectrometry, infrared spectroscopy, ionic chromatography (IC), size exclusion chromatography (SEC), and total organic carbon content (TOC). The interaction of Eu(III) by SP degradation products is investigated by the measurement of Eu solubility.

The TOC measurement is done with Elementar Vario TOC cube analyzer. The measuring principle is the oxidation of bound carbon and CO_2 measurement with IR detection. The total inorganic carbon (TIC) is measured by acidifing the sample with a 5% H_3PO_4 (85%, Merck). The total carbon (TC) is obtained by combustion of samples at high temperature catalytic combustion up to 850°C. The TOC is obtained by the difference between TC and TIC. The calibration is done using potassium hydrogen phthalate (Elementar S35.00-0151) for TOC and sodium carbonate (Elementar S35.00-0152) for TIC (from 1 to 25 mg_C L^{-1}). The SP alkaline solutions are diluted by 100 and 300 for PCE and PNS alkaline solutions, respectively, to remain in the calibration concentrations range. The injected volume is 0.1 mL and each sample is replicated 3 times. A blank is inserted between each sample to check the background and the system is rinsed with the sample prior to each injection.

The IC system used is an Integrion Ion Chromatography System (Thermofisher, Dionex) controlled by the Chromeleon software. The acetate, SO_4^{2-} and SO_3^{2-} anions

are detected by conductivity. The employed guard column is a Hydroxide-Selective Anion-Exchange Dionex IonPac AG15 RFIC 2 mm ∅ × 50 mm L and the column is an AS15 2 mm ∅ × 250 mm L, both maintained at 30°C. The elution is obtained by isocratic method at 38 mmol L^{-1} of KOH from 0 to 40 min. The flow rate is 0.3 mL min^{-1} and the sample injection volume is fixed at 10 µL. The calibration is performed by a acetate standard solution for IC TraceCERT at 1000 mg L^{-1} in water (Sigma-Aldrich 51791), a sulphate standard solution for Ion Pair Chromatography at 1000 mg L^{-1} in water (Fisher Chemical J/4564/05) and a power of anhydrous Na_2SO_3 (Sigma-Aldrich 31454). Standards are obtained from dilution of the standard solution to the following concentrations: 50; 30; 10; 5; 2; 1 and 0.5 mg·L^{-1}. Standards solutions are injected in triplicates and blanks of pure water are injected before each sample. Samples are also injected in triplicates to estimate measurement standard deviations (σ) and are diluted in pure water with a dilution factor from 0 to 50. The uncertainty is estimated as 2σ.

The SEC system used is U3000 Chromatography System (Thermofisher, Dionex) controlled by the Chromeleon software. The PCE is detected by ERC refractoMax 520 refractive index detector (RI) and the PNS by Dionex PDA-100 Photodiode Array Detector (UV-visible detector at 290 nm. The employed guard column is a Tosoh TSKgel superAW-L 4.6 mm ∅ × 3.5 cm L and two columns in series are Tosoh TSKgel superAW4000 6.0 mm ∅ × 15 cm L × 6 µm particle size, all maintained at 35°C. The elution is obtained by isocratic method at 10 mmol L^{-1} of ammonium acetate from 0 to 40 min. The flow rate is 0.2 mL min^{-1} and the sample injection volume is fixed at 20 µL. The standard calibration, although widely spread, is not applicable to SP so the irradiated samples are compared to each one.

The operational solubility of Eu(III) is measured as a function of SP degradation products. The Eu solubility limit in the medium is estimated at $10^{-(6.1 \pm 0.9)}$ mol L^{-1} at pH 13.3 by PhreeqC software using the PSI database [5] considering amorphous $Eu(OH)_3$; the formation of $Eu(OH)_4^-$ is not considered as explained elsewhere [6]. A total Eu concentration of 10^{-4} mol L^{-1} including a spike of radioactive ^{152}Eu solution (2 Bq g^{-1}) in anoxic conditions is added to SP alkaline solutions. After equilibration of one hour, solutions are ultra-centrifuged at 20,000 rpm for 1h (36,400 g), and aliquot of the supernatant are sampled. The supernatants are analysed by gamma counting in order to determine the residual amount of radioactive tracer dissolved in solution. At this initial concentration of Eu (10^{-4} mol L^{-1}), the Eu wall sorption is considered negligible.

B. Results

The TOC is quantified in SP alkaline solutions. The initial PNS alkaline solutions contains in average 3600 mg_C L^{-1}, *i.e.* three times more TOC as PCE alkaline solutions (1200 mg_C L^{-1}). These initial concentrations are not impacted by irradiation.

The average molecular weight of polymers is measured by SEC. The observed modifications of the average molecular weight of the polymers in solution after irradiation are for both SP as a function of the dose: a degradation by chain scissions for PNS (Figure 1) and also cross-linking for PCE (Figure 2).

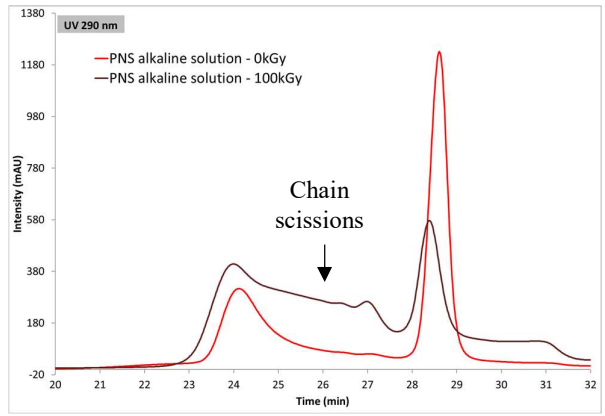

Figure 1. SEC chromatograms of PNS alkaline solution before (0 kGy) and after (100 kGy) irradiation – UV detection at 290 nm.

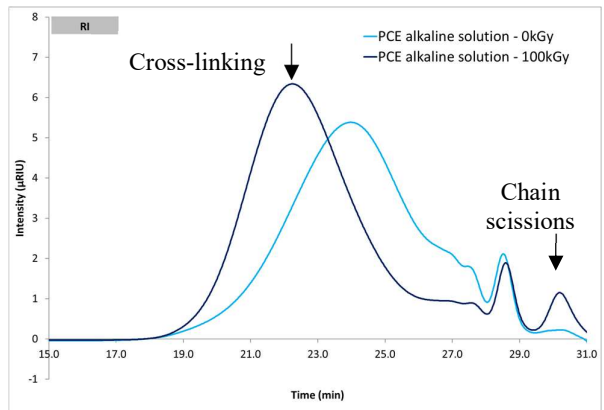

Figure 2. SEC chromatograms of PCE alkaline solution before (0 kGy) and after (100 kGy) irradiation – RI detection.

The SP alkaline solutions are analyzed by IC. Two SP degradation products are characterized in solution as marker of degradation: SO_3^{2-} (and SO_4^{2-}) for PNS, and acetate for PCE. Sulphate come from oxidation of sulphite. The formation of sulphites was also demonstrated without irradiation for PNS proving that this SP is sensitive to alkaline hydrolysis degradation. Formation yields are obtained, (0.017 ± 0.008) µmol J^{-1} and (0.061 ± 0.018) µmol J^{-1} in solution for sulphite and acetate, respectively. These yields, compared to polymer quantity, reach (2.7 ± 1.2) µmol J^{-1} and (30 ± 9) µmol J^{-1} for PNS and PCE, respectively. The corresponding conversion rates at 100 kGy are (11 ± 1.5)% for the two SP. As these values are too high to correspond to primary effects, we conclude that SP degradation products result mainly from the attack of oxidizing radicals resulting from the radiolysis of water [7].

Operational solubility shows a significant increase of dissolved Eu in presence of SP (Figure 3) compared to already available data without SP [3]. Eu solubility seems to increase further significantly after radiolysis degradation at 100 kGy for the PNS. This increase can be attributed to SP radiolysis degradation products.

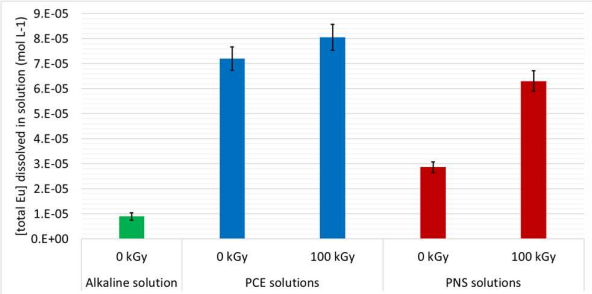

Figure 3. Concentration of total Eu dissolved (mol L^{-1}) in alkaline solution (without SP), PCE alkaline solutions and PNS alkaline solutions in function of dose (0 and 100 kGy) – solutions are without SP, 1 and 2 %w of PCE and PNS respectively in 0.15 mol L^{-1} NaOH, 0.12 mol L^{-1} of KOH and 10 g L^{-1} of crushed mortar (pH 13.3) – $[Eu]_{total} = 10^{-4}$ mol L^{-1}.

III. CONCLUSIONS

The main objectives of this work is to understand interactions between Eu(III) and ligands resulting from sensitivity of SP to the coupled effect of radiolysis and alkaline hydrolysis. These tests will make it possible to interpret the reactive transfer tests in progress on the cement matrices. The first experiments have shown a modification of the average molar weight of the polymer and the formation of SP degradation products in solution after irradiation for both SP as a function of the dose. The presence of SP seems to affect significantly Eu solubility. The degradation by chain scissions seems to affect more the Eu solubility in the case of PNS. Operational solubility measurements will be completed with those for SP alkaline solutions irradiated at 50 and 250 kGy, and for pore solution obtained by pressing of CEM I grout. The complexation of Eu(III) by SP and his degradation products will be investigated in detail using time-resolved laser-induced fluorescence spectroscopy. Eu(III)-sorption/desorption experiments will also be performed in order to highlight the impact of complexes on the uptake of Eu(III) in the cementitious matrix.

IV. ACKNOWLEDGMENT

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