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Superplasticizers degradation in a deep geological disposal for nuclear waste cementitious matrix: an analytical investigation.

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Introduction

The conditioning by solidification in a cementitious matrix of radioactive waste coming from French nuclear industries is a widely used solution. For safety reasons it is important to evaluate and control the production of hazard flammable gas such as dihydrogen. Yet water in cementitious matrices exposed to ionizing radiation emitted by waste (radiolysis phenomenon) can contribute significantly to dihydrogen formation. The main objective of the Matrice project (Materials resistant to irradiation based on cement) with Leon Grosse, Vicat, CEA and Andra as partners is to optimize the formulations of cementitious materials to limit dihydrogen emissions to an acceptable level while optimizing the conditioning of highly radioactive waste. Most of investigated approaches require the addition of superplasticizers (SPs), which are water-reducing agents.
Thus, it is important to study degradation of these compounds in the nuclear waste context.[1] Radiolysis and/or alkaline conditions can potentially induce formation of small organic molecules that can form stable complexes with radionuclides or affect radionuclide mobility.[2] The objective of this study is to characterize the molecules degradation of two types of SPs: a polyaromatic sulphonate (radioresistant but with poor plasticizing properties) and a polyether based superplasticizer (less radioresistant but with excellent plasticizing properties). [3]

Hydrolysis and radiolysis degradation of superplasticizers

Solutions at 1% in weight of SPs in concrete simulated solutions porewater (0.114 mol.L^{-1} KOH, 0.18 mol.L^{-1} NaOH, 2.3 mmol.L^{-1} $Ca(OH)_2$, pH 13.4-13.5) were deaerated and sealed under inert atmosphere (nitrogen). Hydrolysis degradation was performed under inert atmosphere at 60°C. The solution was characterized after one month. The impact of radiolysis was evaluated after irradiation of the solutions under gamma rays irradiation (150-300 kGy; 1000 Gy/h; anaerobic conditions). After irradiation, gas analysis were performed. After degradation, the solutions were analyzed by infrared and ultraviolet-visible spectroscopies to highlight new chemicals functions, size exclusion chromatography to determine the evolution of the molecular weight, ionic chromatography to quantify small carboxylic acids and the gas chromatography – mass spectrometry coupling to identify the volatile organic molecules.

Conclusion

For both SPs, almost no impact of hydrolysis was observed. After irradiation, degradation and cross-linking are clearly observed. An evolution of the average molar mass of the polymer and small organic molecules are observed in solution. The impact of the identified SPs degradation molecules on radionuclide complexation will be discussed.

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