Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1359

Poster session abstract

Supercritical CO_2 carbonation of cemented radioactive waste-forms Influence on leachability and structure

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Received 11 August 1998; accepted 29 January 1999

The traditional practice of cementing transuranic (TRU) low-level waste poses several technical problems, the most serious of which is that many of the legacy TRU waste-forms do not meet Department of Transportation (DOT) prohibitions on decay heat and/or free liquid [1]. To address these problems, a treatment of cemented waste-forms with supercritical CO_2 ($SCCO_2$) has been proposed [2,3]. This treatment method alters the bulk chemical and structural properties of cast cement by accelerating natural carbonation reactions, while at the same time reducing both free and bound water. Reducing the amount of the hydrogenous content of a cemented waste-form to below 30 wt% simultaneously fulfills the DOT free-liquid requirement and increases the maximum allowable decay heat of the TRUPACT-II drums by a factor of 4 [3,4]. The effect of $SCCO_2$ treatment applying different CO_2 pressure and temperature conditions (8.4 MPa $< p <$ 28 MPa, 35°C $< T <$ 62°C) on the leachability, phase constitution, and microstructure of surrogate-doped Portland cement type I/II samples was investigated. Leaching studies were performed using a synthetic groundwater leaching procedure [5]. The treatment-related changes in phase constitution of the major crystalline phases as well as the microstructure were assessed by Rietveld structure refinement using X-ray diffraction data and scanning electron microscopy.

$SCCO_2$ treatment was shown to significantly improve the chemical durability of hydrated Portland cement paste. The releases of ^{232}Th and $^{151/153}Eu$ were strongly related, indicating in first order a closely related sorption mechanism, as well as similar chemical interaction between the surrogates and the calcium silicate hydrate (C-S-H) cement phases. Using X-ray diffraction techniques and Rietveld structure refinement, the carbonation of portlandite to calcite was determined quantitatively as a function of the radial distance from the sample rim to its core. After a 2-hour $SCCO_2$ treatment, significant carbonation of portlandite was only observed near the exposed rim of the cement section, to a depth of about 4 mm. $SCCO_2$ treatment has also affected the microstructure of the cement. In the first stage of the $SCCO_2$ treatment, water of the cement pores was extracted. As a consequence of this strong dehydration process, channels of about 50 μm diameter developed. Simultaneously, dissolved calcium crystallized with CO_2 as calcite along the channel walls and at the surface. In a second stage, structural bound water was extracted and carbonation of portlandite to calcite took place. Furthermore, the C-S-H gel that surrounded the partially hydrated cement clinker was partly replaced by carbonate. The short fibres of the C-S-H cement framework, which are also responsible for physical properties of cement, were most likely not affected by the $SCCO_2$ treatment using low pressure (8.4 MPa).

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PII: S0008-8846(99)00057-5