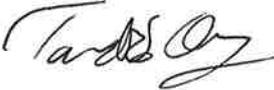


Review: Radionuclide leaching in concrete containment barriers

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<p>Exposure of concrete to ionizing radiation for prolonged periods is known to produce radionuclides, which can subsequently leach out of the concrete to the surrounding environment. However, the way in which such leaching is modelled is often overly simplistic, and the experimental results used to validate existing leaching models remain sparse. The current literature review clarifies existing knowledge gaps, and outlines how they might be addressed by using geochemical modelling to better estimate radionuclide leaching from its association with de-calcification of cement phases.</p>		
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Preface

The FiR 1 research reactor, located in Espoo, Finland, ceased operation in 2015. This has prompted several studies related to its decommissioning. The focus of these studies so far has been the activity of decommissioning waste, but the availability of concrete samples exposed to radiation also presents an opportunity to evaluate the ageing and durability of such materials, particularly as-relevant to radioactive waste storage repositories. Of primary interest to such applications is the leaching of radionuclides from active concrete, as may occur during disposal of decommissioning waste, or in concrete altered by radiation in-situ when used as a containment barrier for high level waste. However, although the resistance of concrete to such leaching has been a subject of recent research interest, few studies present detailed analysis of the long-term stability of cementitious hydration products, and how these may impact radionuclide leaching. Though currently available data also remain insufficient to distinguish between expected failure mechanisms of concrete containment barriers, i.e., between the formation of preferred diffusion pathways due to mechanical failure or diffusion of radionuclides through *intact* concrete, more detailed evaluation of radionuclide retention in the cement-based matrix of concrete would remain necessary to evaluate instances where the latter is the limiting factor for contaminant release. Based on the findings of this literature review, VTT's Structural Materials team has planned a series of experiments to elucidate the extent of leaching for the FiR 1 concrete, for a simplified reference case, in order to provide a foundation for future work. Outcomes will provide an improved basis for updating the leaching models prevalent in the literature, as well as for interpreting results of monitoring in waste repository structures.

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1. Introduction and background

Concrete is a common structural material, consisting of aggregates (rocks) within a porous matrix of hydrated cement paste. Due to its low cost and high capacity to shield against radiation, concrete has also been frequently used as a barrier in nuclear power plants (NPPs) and radioactive waste storage facilities.¹ The cement paste is composed of hydration products, mainly calcium-silicate-hydrates (CSH), aluminoferrites (AFt, AFm), and portlandite (CH). Hydration products are relatively soluble compared to aggregates, and both may be prone to dissolution over the timescales relevant to concrete barriers for radioactive waste disposal.^{2,3} Depending on the concrete characteristics, radiation exposure, and groundwater composition, temperature, and flow rate, this dissolution could be very rapid or negligibly slow. As such, better understanding of dissolution and degradation following radiation exposure is needed.⁴

Concrete dissolution is an incongruent process,⁵ meaning the composition of the dissolving phases changes throughout dissolution. The elements present in these phases may also be altered to radioisotopes following irradiation,⁶ potentially altering their chemical behaviour and the associated stability of cementitious phases of which they are a part. By this mechanism, transport properties of the concrete may also be altered, thus facilitating release of such radioisotopes to the surrounding environment. Such changes occur in parallel with other mechanical damage caused by irradiation,^{1,4,7,8} making it challenging to accurately model radionuclide retention in concrete. For these reasons, the current review has focused on improving understanding of *chemical* influences of radiation on concrete, and specifically on the cement hydration products, to establish a basis for necessary future study of potential coupling between the various chemical and mechanical concrete degradation mechanisms.⁹

2. State of the art in radionuclide leaching from concrete

Due to the inherent heterogeneity and variability of concrete materials, even the leaching behaviour of ordinary (non-irradiated) concrete remains an evolving field of research.¹⁰⁻¹² Most such efforts have focused on easily actionable solutions, such as generalizable simulations,¹⁰ or the development of new performance-based test methods.¹² As such, most studies typically limit their scope to the influence of leaching on degradation of concrete mechanical properties, with little concern with regard to the leachate solution.¹¹ These two factors have resulted in a dearth of basic understanding of the mechanisms driving leaching. Such lack of understanding is therefore reflected in attempts to model radionuclide leaching: simplifying assumptions are often made to enable this modelling, despite the likelihood that such assumptions are wildly inaccurate. For example, it has been standard for models of effective radionuclide diffusivity to assume that (1) surface concentration of the radionuclide is zero (i.e., ignoring groundwater flow rate), (2) surface area of the solid does not change (i.e., ignoring any chemical or physical alteration of the concrete during leaching), and (3) bulk diffusion is the rate-limiting process (i.e., ignoring the concrete pore structure, or potential time-dependent alteration thereof).¹³

Though fundamental mechanisms for radionuclide leaching are not currently incorporated in most models, a general understanding of aqueous reactivity of cement and mineral phases can at least provide some guidance on possible mechanisms for future study.² Leaching can be expected to constitute two, inter-dependent steps: (1) release of radionuclides to solution, and (2) transport of radionuclides out of the concrete, with each being driven by a transfer of radionuclides from areas of high concentration to low concentration. In theory, this should simplify future study of radionuclide leaching and allow for separate experimental investigation of (1) mechanisms of radionuclide release to solutions of fixed composition, and (2) transport of radionuclides out of the concrete in a similar manner to ordinary leaching. As the latter is not unique to irradiated concrete, and will necessarily remain dependent on assumptions of transport mechanisms, i.e., due to incomplete understanding of mechanical degradation,¹ focus is hereafter given to the former: mechanisms of radionuclide release to solution.

Most existing experimental studies of radionuclide solubility and migration in concrete have been limited to specific elements of interest.^{14–18} However, there appears to be a broad general trend that alkali (¹³⁷Cs), alkaline earth (⁹⁰Sr), and non-metals (¹⁴C) leach more rapidly than transition metals (⁶⁰Co), or rare earth elements (¹⁵²Eu).¹⁹ This release also is generally reported to slow over time,¹⁶ suggestive of a diffusion-limited process, as consistent with reports that porosity (and cracking and transport properties more generally) likely dominate such leaching behaviour in concrete.^{20,21} Likewise, factors that increase the abundance or surface area of hydration products, such as increased cement content or increased degree of reaction, are generally reported to improve immobilization of radionuclides.^{15,22,23}

With regard to solubilisation of radionuclides, two mechanisms have been the focus of recent work: (1) adsorption of radionuclides on cement hydrates, and (2) precipitation of radionuclides as distinct solid phases. The latter generally is reported for the transition metals and rare earth elements, and depends upon the alkaline pH of the cementitious matrix.²⁴ These elements are expected to precipitate as hydroxides,²⁵ but may be re-solubilized by heating or reductions in pH, the former potentially caused by radiative heat transfer from high-level nuclear waste, and the latter potentially occurring due to microbial activity.²⁶ These findings are consistent with the reported lower mobility of such transition metals and rare earth elements, but suggest that such elements would also be more sensitive to exposure conditions typical of near-surface waste repositories (e.g., acidification).

Adsorption of radionuclides on cement hydrates is most frequently reported for the calcium-silicate hydrate phase (CSH).^{15,17,19,27,28} This phase is the majority constituent of hydrated cement paste, and it may be that other phases have not been sufficiently studied. However, there is strong evidence that decalcification of the CSH phase trends similarly with the release of radionuclides from concrete, and thus this mechanism may still represent a very good first approximation for potential leaching risk. Similar dependence of contaminant precipitate solubility with calcium concentration has also been reported, though speciation changes caused by a variety of other environmental factors are also noted to play a role (e.g., redox conditions, presence of iron, etc.).¹⁸ From a modelling perspective as well, inclusion of CSH decalcification appears to be critical in obtaining accurate predictions when comparing against existing experimental data,^{28–30} in particular with the associated need to accurately model coupled electro-diffusion in solutions containing nitrates and sulfates,²⁸ calling into question several accelerated leaching test methods that employ ammonium nitrate as a CSH decalcification agent. Overall, geochemical modelling of cementitious phases under ordinary (non-irradiated) conditions has shown promise in its ability to predict multispecies reactive transport, i.e., as relevant to estimation of potential CSH de-calcification, thus representing an attractive area to direct future research on driving forces for radionuclide leaching.^{31–33}

3. Summary and conclusions

The bulk of current literature results that study radionuclide leaching are limited in scope, typically addressing either the solubility of specific radionuclide species (and stability of associated solid phases that bind them) or transport of species through cement paste pore structure, but rarely both. Existing attempts to produce generalizable radionuclide leaching models remain somewhat unreliable, likely because such models would need to account for several other factors, such as mechanical degradation, that also remain poorly understood. Because of the marked success of geochemical modelling of cement phase stability in other contexts, and the noted importance of de-calcification of such cement phases in correlating to radionuclide release, development of more robust datasets for input to such models is recommended as the most appealing option for continued study of radionuclide leaching.

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