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Radioactive waste limits in cement to avoid leaching out

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Cement is a material that has been used for 7000 years or more, and its longevity is shown by, for example, the Pantheon and Colosseum built in Rome between 80 and 128 AD (Naus, 2007). Naturally then, mankind, in the modern need for energy in general and nuclear energy in particular, has once again turned to cement and concrete both to safely encapsulate a nuclear reactor and as a storage mechanism for the long-term containment of the radioactive waste products so produced (http://www.nukemgroup.com/fileadmin/pdf/Brochure_Cementation_Juni_2007.pdf). Cement and concrete do, however, show problems of 'wear and tear', for example, due to repeated cycles of weathering involving water getting into cracks in the concrete or cement and then freezing and thawing. There are also biological causes of degradation (see Naus, 2007). A particularly favoured modern day material is 'ordinary Portland cement', discovered in 1824.

Radioactive waste products, moreover, when mixed with cement–water paste, can hinder the cement hydration process. The presence of these foreign chemical elements can affect its hydration kinetics. In particular, an increase in the porosity of the microstructure of hydrated cement may give rise to more leachability, and this is a major concern in the radioactive waste management challenge because nuclear waste remains active for a long period of time. This can obviously cause radiochemical hazards to the environment. So, any modification of the mesoscopic structure of 'normal' hydrated cement needs investigating. A standard model for radioactive waste and a standard model for cement are also needed so as to allow reproducible scientific experiments and measurements.

The article by Das *et al.* (2014) (of the Bhabha Atomic Research Centre, Mumbai, India) reports a study of the mesoscopic structure of cement loaded with cerium waste using small-angle neutron scattering (SANS), transmission electron microscopy (TEM) and mercury intrusion porosity measurements. It is the mesoscopic structure that determines cement's important macroscopic properties such as its durability, porosity, strength, and permeability for liquids and gases. Specifically, this study investigated two types of pores, a short length scale one and a long length scale one (see Figs. 1*a* and 1*b*).

Using SANS data, the authors derived pore sizes (and distributions) and drew conclusions regarding the loading capacity of cement with nuclear waste. TEM was used to directly show the local structure within the samples for correlation with the SANS results and their validation. The measurement physics for the SANS is interesting, whereby repeat experiments, as a control, from a sample of twice the thickness of the first sample were made. Also, cement loaded with cerium waste is probably not the most typical of samples for SANS; one might more usually expect a molecule in solution rather than voids in a solid object like cement. The small-angle scattering (SAS) signal originates from the inhomogeneity of scattering length densities on typically 1–1000 nm length scales. The scattering intensity at small angles is basically the Fourier transform of the density fluctuations in the cement arising from the mesoscopic structure. As usual though, such scattering signal can be analysed to determine the morphological details like particle shape, particle size, particle size distribution and, as the authors explain, fractal characteristics by implementing an appropriate microstructural model. However, note that SAS theory is based on a single-scattering approximation, which means that the variation of the scattering intensity spectrum with scattering vector magnitude needs to be independent of the experimental sample thickness and the wavelength of the probing radiation, apart from a simple scale factor. Nevertheless, it is often observed that SAS data from porous materials are affected by multiple scattering. In theory, for the single-scattering approximation to hold good, it is necessary that the sample thickness should be infinitesimally small compared to the scattering mean free path (SMFP) of the probing radiation. However, in practice factors like strong contrast in the sample, long neutron

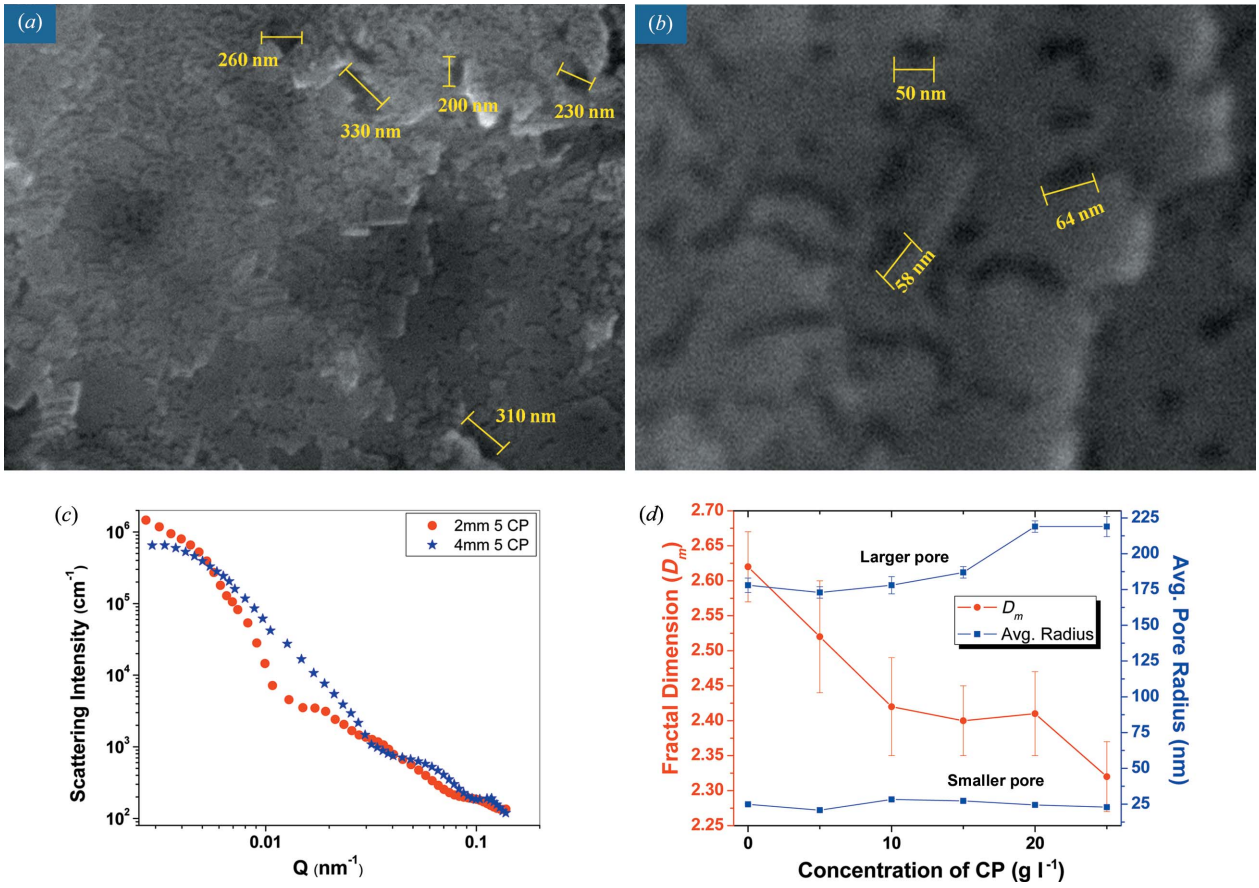

Figure 1
(*a*), (*b*) Pores present in the cement microstructure in (*a*) the larger length scale domain type (radius ∼150 nm) and (*b*) the smaller length scale domain type (radius ∼25 nm). (*c*) Scattering intensity profiles of specimens of the same chemical composition but for two different sample thicknesses. (*d*) The change of the fractal dimension and average pore radius of hydrated cement specimens loaded with different concentrations of cerium waste corrosion products. Reproduced from Das *et al.* (2014).

wavelength, significant sample thickness and/or large sample inhomogeneities cause the SMFP not to be insignificantly small in comparison to the sample thickness. Then the single-scattering approximation would no longer be valid. Fig. 1(*c*) depicts the SANS profiles for two samples of different thicknesses, which were the same as far as the chemical composition was concerned. It is evident from the figure that the scattering profile of the 4 mm-thick cement specimen was significantly broader than that of the 2 mm-thick specimen. This is the key signature of the presence of the multiple-scattering phenomenon and had to be taken into account in the data interpretation.

The results are important as they revealed a significant alteration of the mesoscopic structure in hydrated ordinary Portland cement due to the addition of the cerium waste. The degree of cement hydration did not remain homogeneous and the hydration process was hindered because of the presence of corrosion products, which reduced the homogeneity. Two sizes of pores were revealed. The size of the larger pores increased by 22% with the maximum loading (25 g l^{-1}) of waste investigated in comparison to the pore size of the virgin cement matrix (see Fig. 1*d*). Furthermore, the neutron scattering data revealed that the hydrated cement possessed a non-Euclidean fractal morphology, which became more branched with increased radioactive waste loading (see Fig. 1*d*). This fractal effect is expected to worsen (*i.e.* increase) the cement leaching rate property, clearly undesirable in radioactive waste management. Overall, this study suggests that cerium waste loading into a cement matrix should not exceed a concentration of 15 g l^{-1} of corrosion product, otherwise the incarceration technique may not provide the essential physical isolation of the nuclear corrosion products.

In summary, the work of Das and co-workers has tackled an important modern day challenge for the nuclear energy industry and used cutting edge, modern day, analytical techniques of neutron scattering and transmission electron microscopy as well as mercury intrusion porosimetry. The work is likely to be of wide interest and high impact.

References

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