

Studies of the radioactive waste confinement matrix using neutron scattering methods

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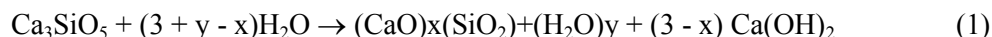
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Abstract. The management of the radioactive waste implies the conditioning in a cement matrix as an embedding, stable, disposal material. Cement matrix is the first and most important engineering barrier against the migration in the environment of the radionuclides contained in the packages. Chemically, after mixing with water, cement produces a reacting matrix with a porous microstructure. Knowing how the microstructure develops is therefore desirable in order to assess the compatibility of radioactive streams with cement and predict waste form performance during storage and disposal. This article highlights the work performed in SANS investigation of a new type of cements to be used for conditioning of aluminium waste coming from reactor decommissioning activities. It is well known that the expansion of corrosion products formed on aluminium can lead to cracking of the waste form.

1. Introduction

The set-up of the cement matrix begins as a mixture of water and cement powder. Adjustment of the phase fractions of the individual cement compounds in the anhydrous cement is one of the few means of altering its mechanical properties. The proportions of C_3S and C_2S in the anhydrous cement are important in determining the rate of hardening of the cement, as well as the heat released, which can cause micro cracking and long term durability problems. The main chemical reaction occurs between the water and the C_3S and can be written as:



where the calcium/silica ratio, x , goes from 0.7 to 1.7 over the course of the reaction [1]. The first term on the right-hand side is the calcium silicate hydrate gel that makes up the binder, usually abbreviated as C-S-H. Its water content, y , remains uncertain. Part of it is in the form of OH- groups in the structure of the gel, and the remainder is immobilized H_2O molecules. The most accepted conditioning process in accordance with the actual international disposal requirements and respecting the waste acceptance criteria for interim storage or/and final disposal is concrete embedding. The use of Ordinary Portland cement (OPC) or modified formula [2] by adding pozzolans as fly ash, silica fume or blast furnace slag developed a pore solution pH as high as 13.5. This research is focused on the development of CEM III and CEM V modified systems based on addition of aluminum sulfate in order to minimize the alkaline attack of cement hydrolysis products on metallic radioactive waste.

2. Materials & Methods



2.1. Materials

To obtain the decreasing of portlandite concentration in shorter time by a direct chemical reaction during the setting time was develop a modified system based on CEM III-A and CEM V-A by addition of aluminum sulfate. The materials used in the modified systems were Portland Cement (CEM-III and CEM-V from Lafarge Romania).

A number of 4 samples were prepared and investigated in a time interval of 232 to 247 hours from their date of production. The samples for this study were made from special types of cements, MKP, CEM V, CEM III and White Portland Cement with specific proprieties. All the samples were mixed with de-ionized water at 0.4 w/c (water to cement ratio) [3] by mass.

2.2. Methods

Electron microscopy studies made on the C-S-H gel phase have revealed the presence of significant fluctuations in the local Ca/Si ratio within the gel phase throughout the specimen. The presence of a bimodal distribution in the local Ca/Si ratio; however, as specimens matured it can be seen that the degree of bimodality decreased (Fig. 1 and 2).

X-ray diffraction was conducted on set and cured mixes (5 days) to ensure the hydration products are formed. The spectra for samples with 50% $\text{Al}_2(\text{SO}_4)_3$ (CM V-50 and CM III-50) shows that these samples hydrates to form ettringite and gypsum as a primary phases and portlandite as a minor phase.

SANS measurements were done at FLNP from JINR Dubna, using the YuMo instrument from the pulsed reactor IBR-2. As is known from the previous SANS experiments the microstructure of hydrated cement paste contains two fractal objects: volume and surface fractals.

3. Results & Discussion

3.1. Electron microscopy studies

Following the nanophasic model, subcrystalline regions would exist; however, they would be confined to small fragments of Ca-O layers (with attached silicate chain fragments) that are several nanometers long. This model can explain many of the crystal chemical observations, macroscopic properties, structural, and compositional trends. In particular, it takes into account the importance of the presence of strong fluctuations in the local Ca/Si ratio. The early presence of bimodality demonstrates that discrete regions exist which initially have different Ca/Si distributions but cannot establish the presence of short-range compositional and/or structural order.

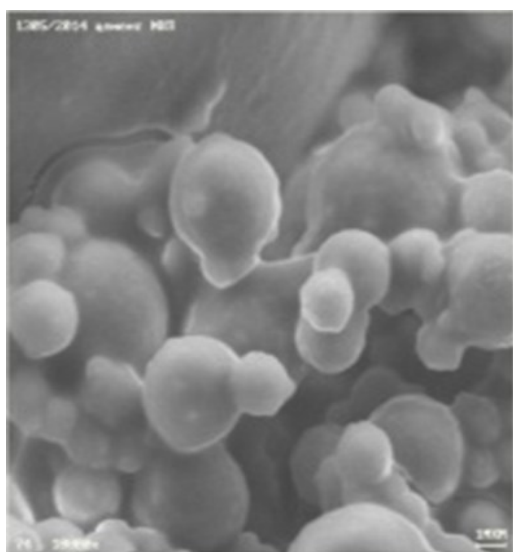


Figure 1. Bimodal distribution of Ca/Si.

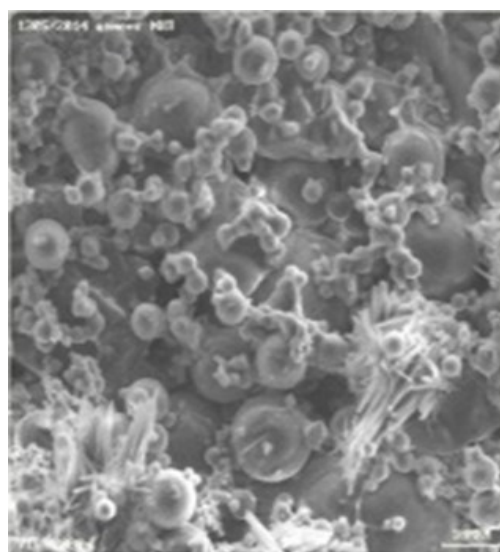


Figure 2. Discrete regions with bimodal distribution of Ca/Si.

3.2. X-ray diffraction studies

The hydration products were studied using a Bruker D8 – Advance x-ray diffractometer with Cu K α radiation, diffraction angle 2 theta ranged between 5° and 70°, a step size of 0.02° and an acquisition time of 4sec/step. The quantity of gypsum which is formed reduces the rate of the hydration reaction and complicates further the reactions that will occur. The spectra of modified cements with different Al₂(SO₄)₃ content (Fig. 3 and 4) show that the diffraction peaks intensity of portlandite decreased gradually with the increase of aluminum sulphate proportion.

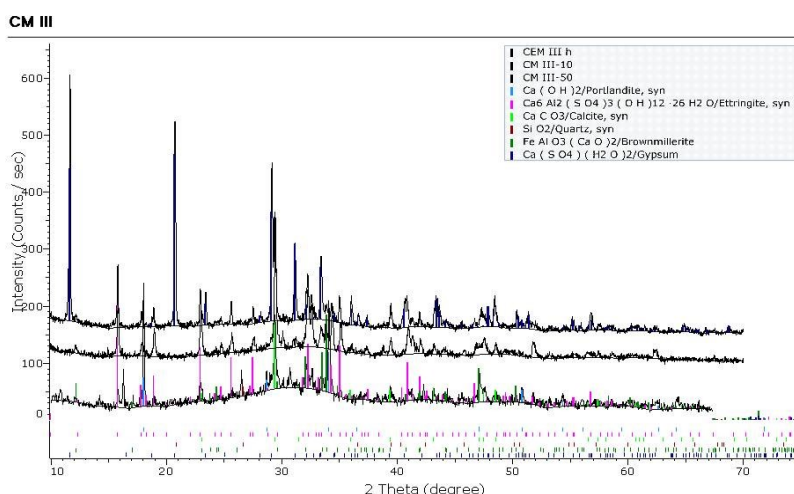


Figure 3. Diffraction spectra for modified cement systems based on CEM III-A.

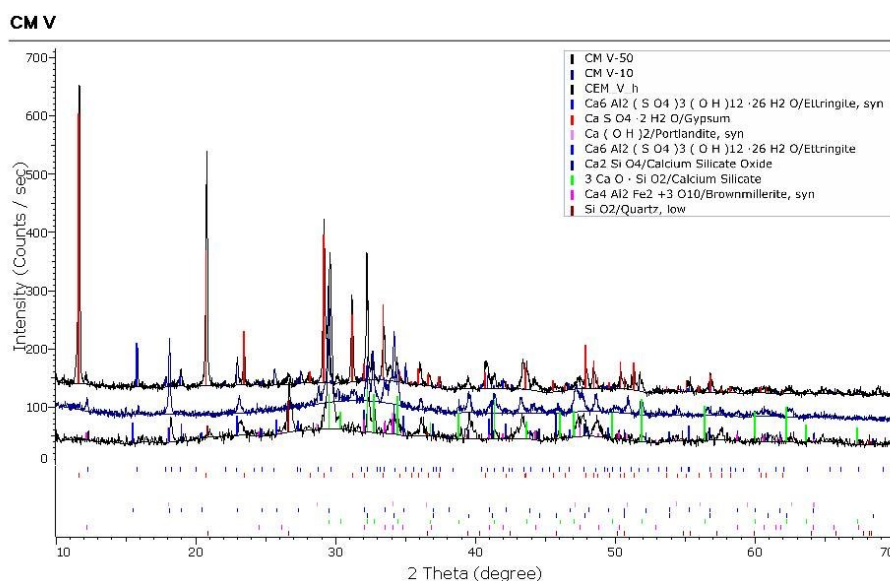


Figure 4. Diffraction spectra for modified cement systems based on CEM V-A

3.3. Small Angle Neutron Scattering studies

SANS measurements (Fig. 5 and Fig. 6) were carried out using the YUMO instrument installed at IBR-2 high pulsed reactor (JINR, Dubna, Russia), equipped with a two-detector system. The coverage interval of scattering vector Q was $0.006 \text{ \AA}^{-1} < Q < 0.3 \text{ \AA}^{-1}$. The measured neutron scattering spectra were corrected for the transmission and thickness of the sample, background scattering on the film substrate and on the vanadium reference sample using SAS software, yielding a neutron scattering intensity in absolute units of cm^{-1} . The volume fractal represents the gel network – (C–S–H) gel clusters consisting of nanometric globules (1–5 nm) and the surface fractal is supposed to be a gel deposit on the compact remains of unhydrated clinker cores. The gel clusters [4] contain very fine pores (gel pores with diameters less than about 50 nm) which form, however, only a minor part of the total porosity. The major part of the overall porosity consists of capillary pores (diameters larger than 50 nm up to millimeters). The fractal dimensions of the gel clusters are strongly dependent on the moisture content and vary from about 2.5 at 100% RH to 3.0 at 55% RH.

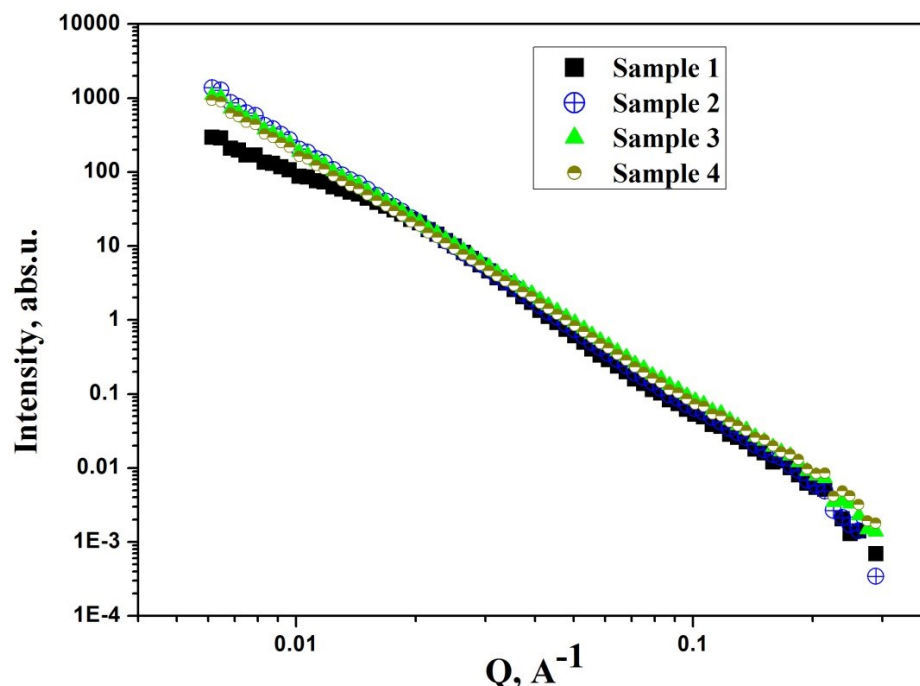


Figure 5. SANS data for MKP, CEM V, CEM III and Portland White Cement.

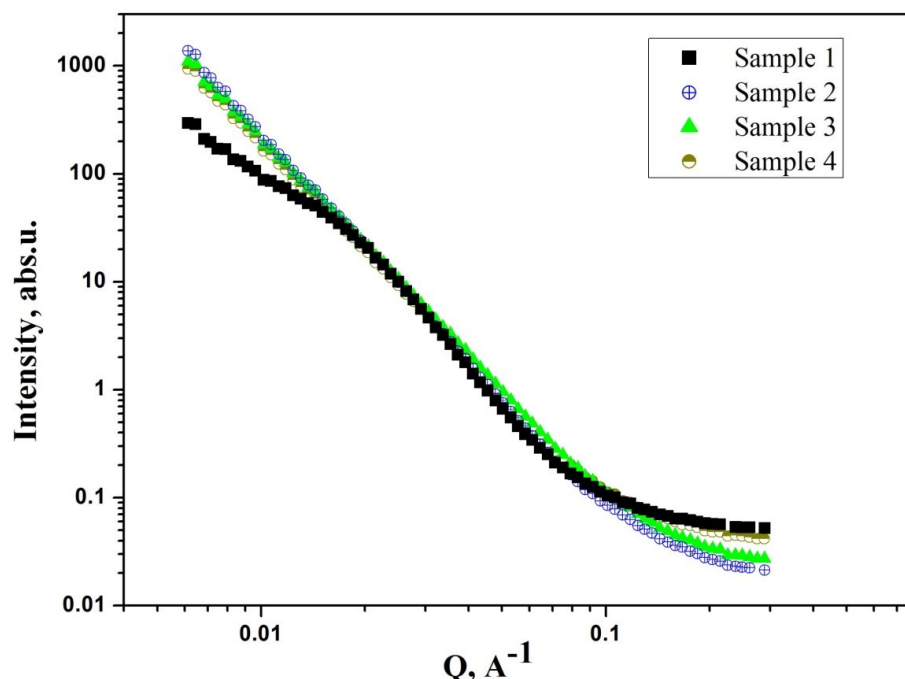


Figure 6. SANS data for MKP, CEM V, CEM III and Portland White Cement.

4. Conclusions

Based on the investigation results the main conclusions are the following:

There is some uncertainty concerning the scaling ratio (l/L) of the volume fractal structure of the gel.

A mix containing 50% $\text{Al}_2(\text{SO}_4)_3$ which hydrates to form ettringite [5] as a primary phase may be a potential candidate for meeting the aluminium conditioning requirements.

The modified cement grouts have developed a good mechanical structure and the compressive strength values are included in the accepted limits for the matrix durability.

Because of overlap with the surface fractal, the SANS technique is capable to explore the gel volume structure in rather limited interval (1nm, 50nm), the volume clusters may show certain fractal arrangement up to micrometric levels at which our measurements were performed.

References

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