CEM V based special cementitious materials investigated by means of SANS method. Preliminary results

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Abstract. The management of the radioactive waste assume 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 waste packages. 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. For conditioning wastes containing radioactive aluminum new formulas of low basicity cements, using coatings as a barrier between the metal and the conditioning environment or introducing a corrosion inhibitor in the matrix system are required. Preliminary microstructure investigation of such improved CEM V based cement matrix is reported.

1. Introduction

Cementitious materials are much more complex than it might seem. Cement paste contains many crystalline and non-crystalline phases in various ranges of sizes. New analysis tools for concrete study, which allows the understanding of the mechanisms regulating the processes needed in different applications, have been used lately [1-11]. One of these analysis tools is the small angle neutron scattering method (SANS). Small angle neutron scattering represents a powerful tool for the characterization of the inner structure of technically relevant porous materials, e.g. hydrating cement pastes. Various parameters can be obtained by this non-destructive method, allowing repeated measurements as well as long term investigations, such as particle size distribution, specific surface of grains, etc. [3, 11]. The QENS technique was also applied and showed, among other things, that the hydrated cement paste contains C-S-H in a gel form and C-H in the form of colloidal particles imbedded in the C-S-H matrix. The water molecules incorporated in the colloidal particles appear immobile while the water molecules dispersed in the C-S-H gel matrix behave as interfacial water showing some slow dynamics, quite different from that of bulk water. Over time, the interfacial water in C-S-H gel penetrates into the colloidal particles [9].
The management of the radioactive waste assume 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 waste packages. Chemically, after mixing with water and additives, 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. Adjusting the phase fractions of the individual compounds of dry cement is one of the few ways to change the structural and mechanical properties of the matrix.

In the present paper, results on SANS measurements accomplished on CEM V samples for identification of microstructural changes induced in the special prepared cement samples are reported.

2. Experimental
2.1. Sample description
The wastes produced as result of nuclear activities are divers and sometimes incompatible with ordinary Portland cement based encapsulation matrices. A type of radioactive waste that cannot be embedded in Portland cement matrix is the radioactive aluminum [11, 12]. New formulas of low basicity cements, using coatings as a barrier between the metal and the conditioning environment or introducing a corrosion inhibitor in the matrix system [12, 13] are required.

Using CEM V with chemical composition given in Table 1, following special cementitious samples were prepared (see Table 2).

### Table 1. Chemical composition CEM V

| Formula | Z  | Concentration  |
|---------|----|----------------|
| CaO     | 20 | 54,65%         |
| SiO2    | 14 | 27,12%         |
| Al2O3   | 13 | 9,45%          |
| MgO     | 12 | 2,81%          |
| Fe2O3   | 26 | 4,14%          |
| K2O     | 19 | 0,96%          |
| TiO2    | 22 | 0,56%          |
| MnO     | 25 | 0,22%          |
| SrO     | 38 | 0,05%          |
| ZnO     | 30 | 0,02%          |
| ZrO2    | 40 | 0,01%          |

### Table 2 Description of the cement samples

| Sample  | Sample description                                                                 |
|---------|-------------------------------------------------------------------------------------|
| Sample 1| CEM V + H2O                                                                          |
| Sample 2| CEM V + H2O + Al(powder)                                                             |
| Sample 3| CEM V + H2O + Al(powder) + Al2(SO4)3 + citric acid + pantarhol                        |
| Sample 4| CEM V + H2O + Al(powder) + Al2(SO4)3 + citric acid + pantarhol + LiNO3              |

For SANS measurements the cement samples were prepared in the form of round plates (Fig.1).
Figure 1 Cement samples: 1, 2, 3, 4 (see Table 2)

2.2 Scanning electron microscopy (SEM)
For the investigation of the morphology of the samples, a JEOL type JSM-840 scanning electron microscope was used.

2.3 Small angle neutron scattering (SANS)
SANS measurements on cement sample gives an intensity of scattered neutrons, I(Q) as a function of the momentum transfer \( Q = (4\pi/\lambda) \sin(\theta/2) \), with the scattering angle being \( \theta \); and \( \lambda \) the wavelength. In the case of cement paste studies, it was shown that for populations of approximate similar small pores and/or particles the Guinier approximation could give the pore size and shape [15]. Analysing the SANS intensity using the power-law approach very interesting features of cements can be distinguished [1-3].

Small angle neutron scattering (SANS) experiments were performed at the time-of-flight YuMO spectrometer [16] in function at the high flux pulse IBR-2 reactor, JINR Dubna. The Sonix+ software control system provides spectrometer operation [17]. The experiments were carried out at a sample-to-detector distances of 5.28 m and 13.04 m, resulting in a Q range of 0.007÷0.2 Å⁻¹. The sample diameter and thickness in the beam were 14 mm and respectively 1 mm. The measured neutron scattering spectra are corrected relative to the transmission and thickness of the sample, background scattering due to the experimental scotch tape support and the vanadium reference sample using the SAS software [18], providing a neutron scattering intensity in absolute units of cm⁻¹.

Further, in the present paper, first steps in the SANS investigation of CEM V cementitious compounds are presented.

3. Results and discussions
In Figure 2, scanning electron microscopy (SEM) images of CEM V series samples are presented. The recorded images have the same magnification (x500) and evidence quite different morphology. The presented images give the possibility to observe changes in the microstructure of matured cement paste as a consequence of adding the following components one at a time: Al(powder), Al₂(SO₄)₃ + citric acid + pantarhol and LiNO₃. In the first image (Fig.2a), clumps of quite large grains of CEM V can be noticed. In the next image (Fig.2b), agglomeration of smaller particles is visualized. Next (Fig.2c) we remark combined agglomeration of big grains and fine needle-shaped particles. In the final image (Fig.2d), some morphological similarity with first image (Fig.2a) is observable.
In Figure 3 SANS curves of samples 1, 2, 3, 4 measured at 20 °C temperature are depicted. From the beginning, a likeness between the curves aliasing is evident for samples 1 and 4, and respectively for samples 2 and 3. In the Q domain up to the value of 0.1 Å\(^{-1}\) the power law behavior of the curves for all the samples (1-4) suggests the fractal approach to be used for the data treatment. More information will be obtained after detailed analysis of the experimental data.

In Figure 4 SANS curves of sample 2 measured at several values of the temperature (20 °C, 30 °C, 40 °C, 50 °C, 20 °C) are given. The curves present different features in the Q range higher than 0.1 Å\(^{-1}\). This fact may be due to the different content of water molecules that with the increase of the temperature could evaporate from the sample. Detailed analysis is in progress.

Figure 2 Scanning electron microscopy images of CEM V cement series samples: (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4.
Figure 3. SANS curves of: (a) samples 1, 2, 3; (b) inset of figure 1: SANS curves for samples 1, 2, 3, 4 (see the table 2).

Figure 4. SANS curves of sample 2 (CEM V + H2O + Al(powder)), measured at several temperature: 20a °C; 30 °C; 40 °C; 50 °C; 20b °C. a – means that temperature is increasing; b- means that temperature is decreasing.
4. Conclusions

By admixture of additives during the cementitious material preparation the microstructure is changing at different length scales. Both scanning electron microscopy and small angle neutron scattering gives useful information about the forming processes.

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