

STUDY OF THE STRUCTURE AND DYNAMICS RELAXATION PHENOMENA IN COMPLEX DISORDERED SYSTEMS, RESULTING FROM HYDRATION OF THE CEMENT PASTES, USING THE NEUTRON SCATTERING TECHNIQUES

C. A. DRAGOLICI¹, A. RADULESCU², GH. ROTARESCU¹, F. DRAGOLICI¹

¹*Institute of Research and Development for Physics and Nuclear Engineering “Horia Hulubei”,
077125 Bucharest-Magurele, Romania*

²*Institute for Solid State Research, Research Center Jülich, 52425 Jülich, Germany*

(Received January 15, 2010)

Abstract. Neutron scattering is a powerful and direct method for investigating the static and dynamic properties of materials manifesting disordered structure. Ordinary Portland cement hydrated with light and heavy water and mixed with specific precipitates used for conditioning of the radioactive waste, was used to be studied by INS. The obtained data allows us to draw conclusions regarding the behavior of H₂O and D₂O molecules in the structure of the investigated material and the influence of the additives to the general dynamics of the sample. In the following, we discuss the spectra obtained from the data accumulated during the experiments performed at the DIN-2PI spectrometer from JINR Dubna, Russian Federation. We'll show that some of the additives used in large or small quantities influence in a way or another the dynamic structure of the cement paste.

Key words: inelastic neutron scattering, INS, Portland cement, additives.

1. INTRODUCTION

Neutron spectrometry techniques provide a powerful tool for non-destructive evaluation and study of the structure and dynamics of the condensed matter. In the last time the neutron scattering methods, small angle neutron scattering (SANS), neutron diffraction (ND), quasielastic neutron scattering (QENS) and inelastic neutron scattering (INS), have been oriented to investigate the structure and the dynamics of hydrated cement pastes [1-10]. As it is known, when ordinary Portland cement (OPC) is mixed with water, a period of rapid reaction lasting only a few minutes is followed by an induction period during which the hydration reactions proceed at a much slower rate. After a period of a few hours the rate of reaction increases again and the cement paste begins to harden. The evolution of the inner structure of the hardened cement paste as well as the hydration kinetics is of great

interest. Many investigators have studied the process of cement hydration with a variety of tools, because understanding and control of the cement hardening process is obviously of great economic importance [11, 12].

Nevertheless many aspects of the cement hydration process remain unexplained. OPC is a heterogeneous material composed of four major and several minor crystalline compounds, the phase composition is highly variable. The structure and reactivity of the individual compounds are strongly influenced by the condition under which they are formed and started, the type and concentration of impurities, the nature and concentration of their structural disorder and their particle size distribution. The rate of hydration of cement compounds is normally measured by thermal calorimetry which gives the overall kinetics at early times but do not measure the rate of product formation directly. Quantitative x-ray diffraction analysis (QXDA) can be used to measure the rate at which the starting compound is consumed and ignition techniques can be used to measure the amount of chemically water, but neither of these techniques can be used to monitor the early kinetics.

These difficulties encouraged the development of new analytical tools such as: real time measurements of the progress of cement hydration using neutron diffraction [13], Raman scattering [14], synchrotron x-ray diffraction [15], quasielastic neutron scattering [16-18].

2. THEORETICAL BACKGROUND

Neutrons are scattered by a hydrating cement paste, both elastic and inelastic. The scattered intensity is dominated by the scattering from hydrogen due to its large incoherent cross section compared to other elements present in a cement paste [19]. The elastic scattered component of the spectrum has a Gaussian distribution in energy of a width determined by the energy resolution of the spectrum. The integrated intensity of this component is directly proportional to the number of hydrogen nuclei that are, chemically bound to the cement gel and hence immobile. The inelastic scattered neutrons exhibit a Lorentzian energy distribution with a width that is related to the diffusion state (translational and rotational) of the hydrogen atoms over the time on a scale given by

$$\Delta t \cong \frac{\hbar}{\Delta E}$$

and a distance scale

$$\Delta L \cong \frac{2\pi}{Q},$$

where $Q = (4\pi/\lambda)\sin\theta/2$.

Here h is Plank's constant, λ is the neutron wavelength, ΔE is the energy resolution of the instrument and θ is the neutron scattering angle [20].

Because the cement paste, pore water and hydration products contain hydrogen atoms, these characteristics make quasielastic neutron scattering ideal for the study of the rate of reaction in hydrating cements. QENS measurements of a hydrating cement paste can directly quantify the fraction of water in the sample that is chemically bound. If the stoichiometry of the reactions is sufficiently well understood, the bound water index (ratio of chemically bound water to total water) can be converted to the degree of reaction and the measurements used for detailed studies of the reaction kinetics. The problem becomes more complicated if various chemical components are added in order to improve the quality of the cement used for radioactive waste conditioning. To improve the safety of the disposal, it would be necessary to immobilize these wastes in order to produce a long term stable solid waste form. There is a limited knowledge of the chemical reactions and the products formed during the mixture of the cement with solid or liquid waste and water. The study of the precipitation products and their behavior during cementation and the long-term disposal is an extremely difficult task. More information related to the presence of various precipitations can be obtained by means of the inelastic neutron scattering. In this case INS technique can give the same information as QENS and even more data about the vibration states of the system in presence of these precipitates.

3. EXPERIMENTAL PERFORMANCE

The investigation of cementitious systems involving hydrated cement matrices prepared from anhydrous cement and fresh precipitate of calcium hydroxide, aluminum hydroxide, NaSiO₂ and bentonite in the presence of H₂O or D₂O, is the main goal of the present study.

An ordinary Portland cement powder having the specific Blaine fineness of 320 m²/kg and the composition shown in the table bellow has been used in performance of our experiments.

Table 1

Composition of the Portland cement used in the experiment

Oxide composition	%	Mineral composition	%
CaO	61.90	C ₃ S	57.64
SiO ₂	20.16	C ₂ S	13.17
Al ₂ O ₃	5.72	C ₃ A	8.72
Fe ₂ O ₃	3.81	C ₄ AF	11.58
SO ₃	3.00		
MgO	1.05		
Na ₂ O	0.45		
K ₂ O	0.91		

One-energy neutrons with $E_0 = 10.476$ meV and an experimental resolution of $\Delta E = 0.5$ meV, measured on a vanadium target was used to investigate the following samples:

Table 2

Samples composition and weights

No	Sample composition	w/c	Cement	Additives	H ₂ O/D ₂ O
1	Cement + D ₂ O	0.50	200g	-	100g
2	Cement + H ₂ O	0.30	200g	-	60g
3	Cement + Bentonite + D ₂ O	0.45	200g	10g	90g
4	Cement + Bentonite + D ₂ O	0.45	200g	2g	90g
5	Cement + Bentonite + H ₂ O	0.45	200g	10g	90g
6	Cement + Ca(OH) ₂ + D ₂ O	0.50	200g	50g	100g
7	Cement + Ca(OH) ₂ + D ₂ O	0.39	200g	10g	78g
8	Cement + Ca(OH) ₂ + H ₂ O	0.35	200g	10g	70g
9	Cement + Al(OH) ₃ + D ₂ O	0.25	200g	14g	50g
10	Cement + Al(OH) ₃ + D ₂ O	0.25	200g	35g	50g
11	Cement + NaSiO ₂ + D ₂ O	0.25	200g	10g	50g

The measurements have been performed at the time of flight spectrometer DIN-2PI, positioned at the second neutron channel of the reactor IBR-2 from JINR Dubna, Russian Federation. The time of flight spectra were taken within an angular range of 6° – 134° using He³ counters.

The time of flight spectra taken for some of the above mentioned samples are presented in Figs. 1–6. Only the most representative spectra were considered for this paper. In this figures the ordinate and the abscissa axes represent the intensities measured at various scattering angles as a function of time of flight. The intensity (counts) is proportional to the double differential time of flight cross section:

$$d^2\sigma/d\Omega dt,$$

where $d\Omega$ is the solid angle under which the sample is seen by detector, t is time of flight of the scattered neutrons from the sample to the detector. For each sample, 20 spectra have been measured corresponding to an angular range of $\phi_s = 6^\circ \div 134^\circ$ and an energy transfer range in the scattering process of $\hbar\omega = 0 - 200$ meV. The time of flight channel width was taken at 8 μ s.

4. RESULTS AND DISCUSIONS

The analysis of the dynamic processes which have place in the investigated samples can be done in terms of the neutron scattering spectra shown in Figs. 1–6. The starting point of this analysis is considered the spectra presented in Fig. 1 and Fig. 2. These are considered references because show the dynamic structure of the cement matrix obtained by hydration with light and heavy water.

On the figures are also indicated the quantities of each component used in the sample preparation. The two spectra shown in each figure is an average over first ten angles (small) and over the last ten angles (large) in the interval 6° – 134° .

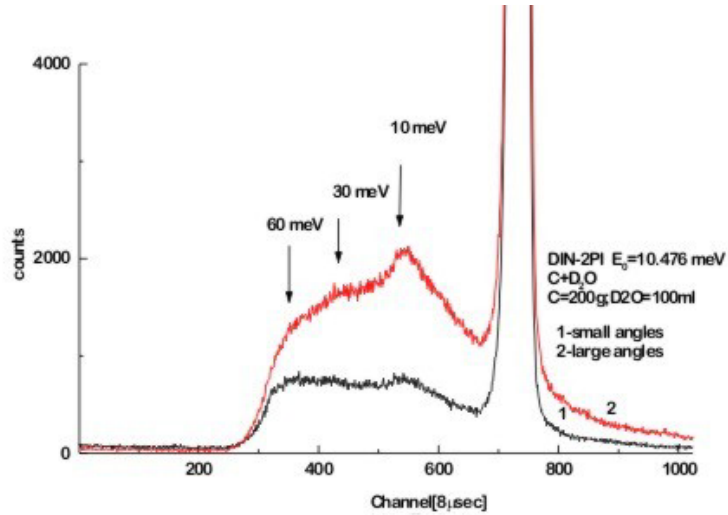


Fig. 1

All the dynamic changes observed as a result of various addition precipitates are discussed by comparing with the references from Fig. 1 and Fig. 2. Two main parts of the inelastic scattering spectra have to be distinguished: the elastic component ranged within time of flight channel number $670 \div 800$ and inelastic component ranged within channels $300 \div 670$.

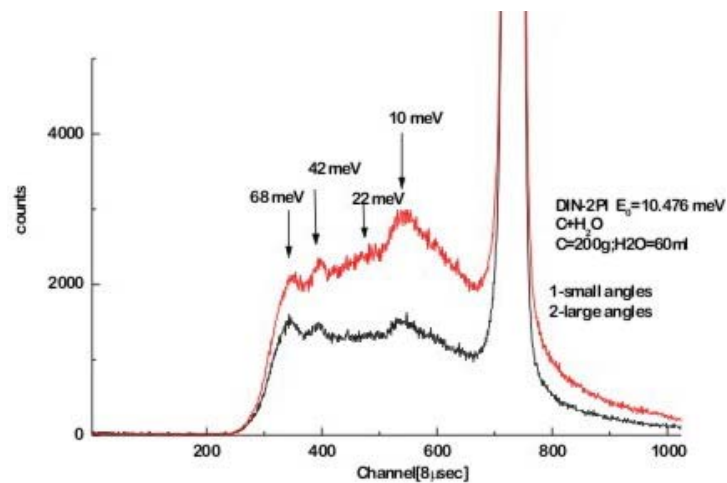


Fig. 2

As expected, the dynamics processes of these samples are dominated by the dynamics of water and heavy water. We'll see further how these dynamics are influenced by the presence of the added precipitates.

The energies corresponding to various dynamic processes are indicated on the figures and systematized in the table bellow.

Table 3

Energies of considered systems resulted from the INS spectra.

No	Sample composition	E [meV]			
1	Cement + D ₂ O	30	60		
2	Cement + H ₂ O	22	42	68	
3	Cement + Bentonite + D ₂ O	52			
4	Cement + Bentonite + D ₂ O	62			
5	Cement + Bentonite + H ₂ O	42	65		
6	Cement + Ca(OH) ₂ + D ₂ O	6	30	44	74
7	Cement + Ca(OH) ₂ + D ₂ O	42	68		
8	Cement + Ca(OH) ₂ + H ₂ O	42	70		
9	Cement + Al(OH) ₃ + D ₂ O	30	60		
10	Cement + Al(OH) ₃ + D ₂ O	28	66		
11	Cement + NaSiO ₂ + D ₂ O	30	46		

A general analysis of all obtained spectra, having as reference point the spectra measured on Cement + H₂O and Cement + D₂O let us share the results explained in the followings.

The dynamics of the cement hydrated with H₂O and D₂O is dominated by the latter. The energy of 10 meV corresponds to the water molecules vibration taken as a whole entity. While the peaks observed at 60 meV respectively at 68 meV are assigned to be hydrogen rotation around the mass center of the water molecule which approximately coincide with the position of the oxygen atom. A small difference was observed due to the deviation from the isotropy of the harmonic oscillation behavior of the H and D. The difference observed from the spectra at small and large scattering angles demonstrate a highly anisotropy of the static structure of these samples.

The samples prepared with light water reveal more structural spectra and a more active dynamics at 22 meV and 42 meV that stands for the vibrations of the cement matrix. This dynamics is more attenuated in the case of heavy water.

Summarizing the observations above, we can draw the conclusion that the cement paste prepared with D₂O is more stable than the one prepared with H₂O. The D₂O molecules are more bounded than the H₂O.

The presence of bentonite in large quantities (10g) has an influence on the dynamics of deuterium (Fig. 3) while the vibrations of the D₂O molecules remain unchanged.

A small amount of bentonite (2g) has a favorable role on the dynamics of D (Fig. 4). Consequently, we can estimate that bentonite in large quantities has a positive role in the cement dynamics and its macroscopic properties.

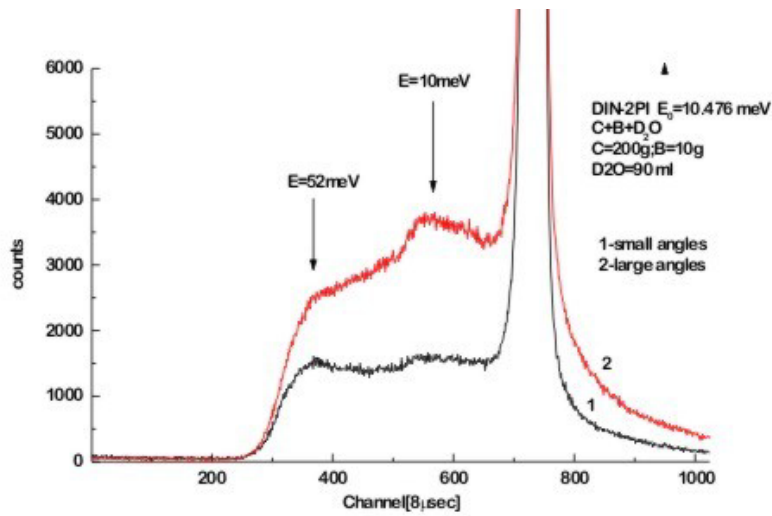


Fig. 3

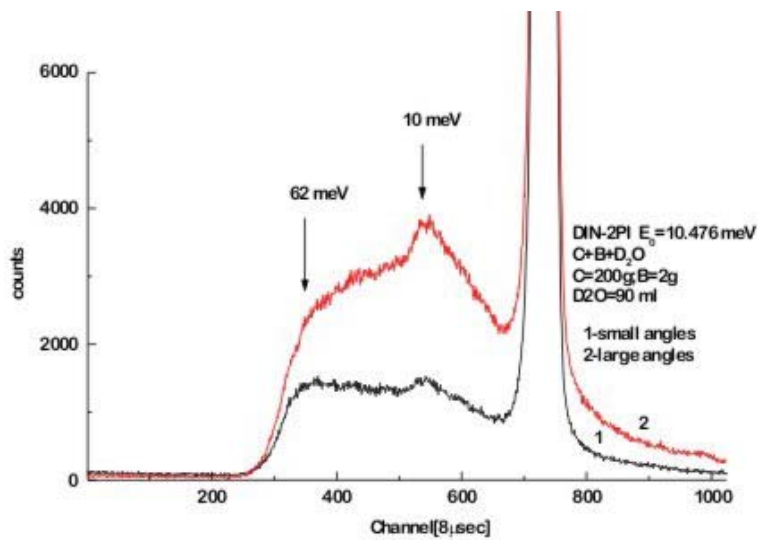


Fig. 4

The presence of bentonite has an insignificant influence on the dynamics of cement prepared with H_2O (sample no. 5 in Table 2 and 3).

A very interesting picture of the dynamic structure is given by the presence of the $Ca(OH)_2$ precipitate (sample no. 6) illustrated in Fig. 5. The dynamics of D_2O molecule remain unchanged while the presence of H in $Ca(OH)_2$ shows that the dynamic spectrum is very rich in details and the peaks are very well located. This dynamics is influenced by the quantity of $Ca(OH)_2$.

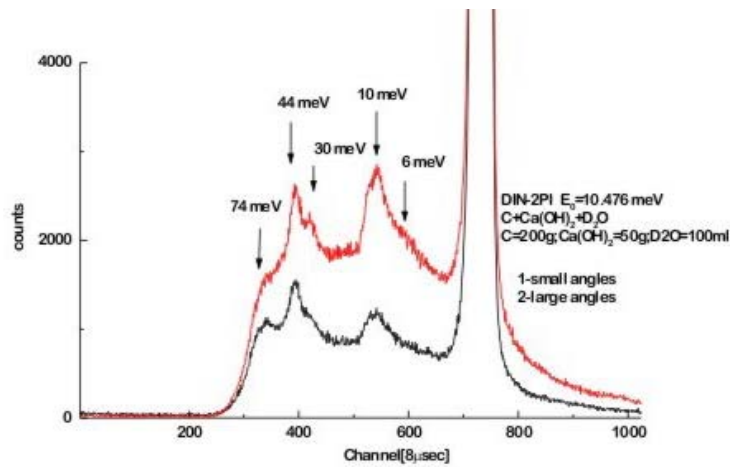


Fig. 5

A smaller quantity (10g) of $\text{Ca}(\text{OH})_2$ (sample no. 7 in Fig. 6) produce an attenuation of the vibration dynamics of the sample. Therefore we can appreciate that smaller quantities of $\text{Ca}(\text{OH})_2$ precipitate, if optimized, has a better consequence on the quality of cement paste.

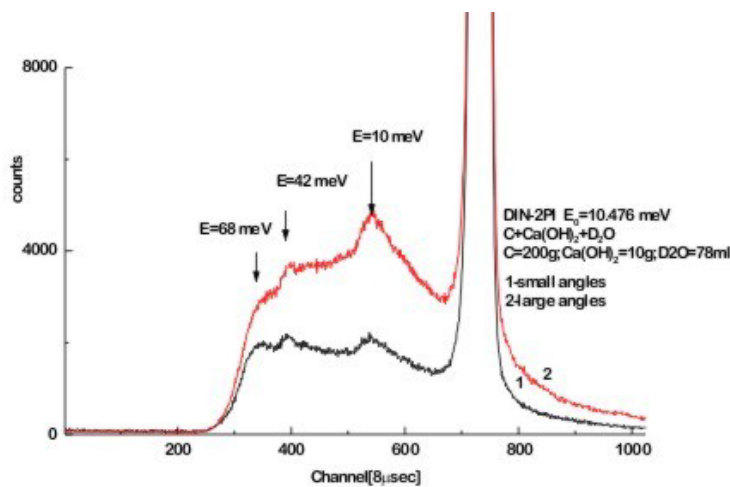


Fig. 6

From the comparison of the spectra for samples no. 7 and 8, where a specific quantity of $\text{Ca}(\text{OH})_2$ is present into the samples prepared with D_2O and H_2O , we can conclude that the dynamics of the sample containing H_2O is more active and rich in details. The spectrum of the sample prepared with D_2O is more flat and the static structure is in a more stable equilibrium.

The dynamics derived from the spectra of the samples no. 9 and no. 10 show that the $\text{Al}(\text{OH})_3$ precipitate compared to the $\text{Ca}(\text{OH})_2$ has a much less influence on the dynamical properties of the Cement + D_2O and do not depend in a obviously way like in the case of bentonite or $\text{Ca}(\text{OH})_2$.

The previous sample behavior lead us to the conclusion that the water dynamics, indicated by the position of the peaks at 10 meV and respectively at 60 meV, practically is not in a significant way influenced by the bentonite, $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$.

The experimental results for the sample no. 11 reveal that NaSiO_2 has a rather high role on the D rotation. The decreasing energy from around 60 meV to about 30–46 meV demonstrates that the rotation of the proton is hindered.

5. CONCLUSIONS

The role played by various investigated added precipitates, even in small quantities, is unexpected of high importance for the dynamics and microscopic properties on the cement matrix containing bounded H_2O or D_2O water. Bound H from the additives seems to have a direct influence on the INS spectra and on the overall dynamics of the sample only in the case of $\text{Ca}(\text{OH})_2$ where the dynamics is influenced by the quantity, while $\text{Al}(\text{OH})_3$ has a very weak influence. Also, the quantity of bentonite has a favorable influence on the dynamics of the samples prepared with D_2O but very less on the samples prepared with H_2O .

Generally, the cement matrix prepared with D_2O seems to be more stable than prepared with H_2O .

In order to clarify many observed features of the dynamic microscopic structure in these samples, first time investigated by inelastic slow neutron scattering, an extensive program of experimental research of these complex disordered systems has to be set up.

REFERENCES

1. F. Haussler, F. Eichhorn, H. Baumbach, *Physica Scripta*, **50**, 210–214 (1994).
2. F. Haussler, J. Schreilier, A. Hempel, F. Eichhorn, A. I. Ioffe, Experimental Report BENSC, No MAT-05019 (1996).
3. F. Haussler, M. Hempel, F. Eichhorn, A. Hempel, H. Baumbach, *Physica Scripta T57*, 184–189 (1995).
4. A. Heinemann, H. Hermann, K. Wetzig, F. Haussler, H. Baumbach, M. Kroning, *Journal of Materials Science Letters*, **18**, 1413 (1999).
5. A. J. Allen, *J. Appl. Cryst.*, **24**, 624 (1991).
6. A. J. Allen, *Philosophical Magazine*, B **56**, 263 (1987).
7. M. Kriechbaum, *Advances in Cement Research*, **6**, 93 (1994).
8. A. Heinemann, H. Hermann, F. Häußler, *SANS analysis of fractal microstructures in hydrating cement paste*, *Physica B*, **276–278**, 892–893 (2000).

9. R. Berliner, M. Popovici, K. W. Herwig, M. Berliner, H.M. Jennings, J.J. Thomas, *Cement and Concrete Research*, **28**, 231 (1998).
10. S. Eriksson, R.L. MC Greevy, P. Zetterstrom, J. Erikson, Experimental report NFL, No 225 (1999).
11. H.W.F. Taylor, *Cement Chemistry*, Academic Press, London, 1990.
12. G. Filoti, V. Spanu, C. N. Turcanu, International Conf. Appl. Mossbauer Effect, Sept. 10–14, Rimini, Italy, 1995.
13. R. Berliner, F. Trouw, H. Jennings, *Bull-Am., Phys. Soc.*, **40**, 665 (1995).
14. M. Tarrida, M. Madon, B. Le Rolland, P. Colombet, *Adv. Cem. Bas. Matter*, **2**, 15–20 (1995).
15. S.M. Clark, P. Barnes, *Cem. Concr. Res.*, **25**, 639 (1995).
16. NIST Reactor, Summary of Activities, October 1992 through September, 1993, p. 7.
17. NIST Reactor, Summary of Activities, October 1992 through September, 1993, p. 5.
18. R.A. Livingston, D.A. Newman, A. Allen, J.J. Rush, Application of Neutron Scattering Methods to Cementitious Materials, D. Neumann, T. P. Russel, B. J. Wuens (eds.), *Mater. Res. Symp. Proc.*, **376**, (1995).
19. G.E. Bacon, *Neutron Diffraction*, Clarendon Press, Oxford, 1975.
20. T. Springer, *Quasielastic Neutron Scattering for the Investigation of Diffuse Motions in Solids and Liquids*, Springer Tracts in modern Physics Springer-Verlag, Berlin, 1972, p. 64.