UNIVERSITY OF NIŠ
The scientific journal "FACTA UNIVERSITATIS"
Series. "Physics, Chemistry and Technology" Vol.1, N^o 3, 1996. 219-222
Editor of Series. Predrag Dimitrijevic
Address: Univerzitetski trg 2 YU-18000 Niš Tel: +381 18 23953, Fax: +381 18 24488
http://www.grafak.ni.ac.yu/facta.html

SOME CONTRIBUTION TO INVESTIGATION OF THE HYDRATION MECHANISMS

UDK : 535.338

N. Popović[1]
L.A. Nasr[2]
Lj. Miljković[1]

[1] Department of Physics, Faculty of Science, Ćirila i Metodija 2, 18000 Niš, Yugoslavia
[2] Physics dept. University of Alexandria, Alexandria, Egypt

Abstract: The spin grouping method is used to consider protons dynamics during a hydration time of different cement type materials (different clinkers, with or without addings). NMR T_1 methods are used for recording the nature of hydration process. Multi-component analysis of magnitudes of proton spin-lattice relaxation time T_1 yield dynamical information about the proton environment, ie. the stage intervals, length of particular stages and their changes in time are determined. The results indicate a different structures of the new producing and forming materials and pores during the hydration.

Introduction

In recent years a great interest has been shown to product and to improve a new materials, including cement type. New methods of data collecting and analysing provide successful investigations of mutual dependence between processes of creating new materials and their specific properties. A variety of basic cement type materials (clinkers) has been made by different technological processes and different income natural materials.

It is already known that the ratios between the basic cement components [C_3S, C_2S, C_3A, C_4AF] determines the hydration process and physical characteristics of hydrated cement paste. An essential difference between ordinary portland cement (grey) and white cement is low content of Fe_2O_3 (below 0,4%) and resulting low C_4AF content in white cement.

Nuclear magnetic resonance (NMR) has been used very successfully to study for physical characterization of hydration process [6-10] using the T_1 spin-grouping method of analysing recorded data. According to *Zimmerman-Brittin* theory, proton spin-lattice relaxation time (T_1) have contributions from exchange between water molecules: (a) on the surface of the pore (T_{1s}) with percentages η and (b) in the bulk (T_{1b}) with percentages (1-η)[3]:

$$\frac{1}{T_1} = (\frac{1}{T_{1s}})(\eta) + (\frac{1}{T_{1b}})(1-\eta).$$

Received 15.July 1996.

Thus, relaxation rate (T_1^{-1}) depends on the ratio between the pore surface area and the pore volume.

The interaction of a water with the surface in a porous solid has been used to study the hydration of cement paste. It is a well known characteristic that the fluid in a porous solid has a faster nuclear spin-lattice relaxation rate than the corresponding bulk fluid, ie., $T_{1b} \gg T_{1s}$,

$$\frac{1}{T_1} \approx (\frac{1}{T_{1s}})\eta \sim r^{-1},$$

where, r is the average pore radius. The proton spin-lattice relaxation rate T_1^{-1} of "exchangeable water" (interlayer, micropore and gel adsorbed component) is proportional to the specific surface of hardened cement paste. In the slow exchange approximation, the distribution of pore sizes is proportional to a distribution of T_1 values.

Experimental

All investigated OPC clinker samples (P_1,P_2,P_3) are basic cement type materials with standard addings. White cement clinker sample (K1) and white Portland cement sample (BC) are made by different technological procedures. Sample PD was prepared adding 5% active inorganic admixture water glass (K_2SiO_3) to P_1 clinker sample.

The proton spin-lattice relaxation time T_1 was measured as a function of the hydration time, by a $90 - \tau - 90$ pulse sequence technique. The NMR measurements were performed with a IJS pulse spectrometer operating at the frequency of 16 MHz. All data were collected at room temperature up to 1000 hours (Fig.1). Typically 32 signals were accumulated to average using computer program for collecting and analysing recorded data. Multi-component analysis was used to select water behavior in different environments.

For the sample preparation the standard procedure was followed with w/c ratio (water/ cement)=40%. Double destilled water was mixed 3 minutes with the dry cement powder. The cement paste was then put into glass tubes and closed.

Results and discussion

The evolution of T_1 components with hydration time in different clinker samples is presented on Fig.1.(a) and Fig.1.(c) in a log-log presentation. The time evolution of corresponding magnetization fractions is presented on Fig.1.(b) and Fig.1.(d).

During the early hydration period (I) in all cement samples, with different T_1 values in each of them, only one spin-lattice relaxation time component is obzerved.

After few hours of hydration (~2-4 in OPC samples) there is a rapid decrease of T_1 values. The onset of the middle hydration period (II) is connected to the increase of the consistancy (setting) of cement paste. C_3S hydration rate increases, water gets more immobilized by strong adsorption on the growing surface of hydration products and T_1 decreases (1). Parameters, including starting time, length of the second stage and the slope of the T_1 curve give information about forming rate of the new structure in different samples. In this stage two T_1 componenets (T_{1l}, T_{1s}) are separated with corresponding magnetization components, Fig.1.(b) and (d). The time evolution of their percentages of magnetization ratio indicates how fast they arise, how great is their mutual ratio during hydration and where stable percentage ratio begins.

In white clinker cement sample (K1) second period starts after $1,2h$ of hydration, Fig.1.(c), with high T_1 values ($T_{1l} \sim 60\,ms$, $T_{1s} \sim 15\,ms$) and stable magnetization fraction between 70% and 90% for short component. The third component, with shortest T_1, probably starts to grow after $320\,h$.

White cement clinker (BC), Fig.1.(a), with standard addings (gypsum) is a very old sample, characterized with long first stage ($29\,h$) very fast second stage and high value of T_1. Magnetization component of T_{1s}, Fig.1.(b), increases very slow with small stable magnetization fraction ($\sim 40\%$) after $500\,h$.

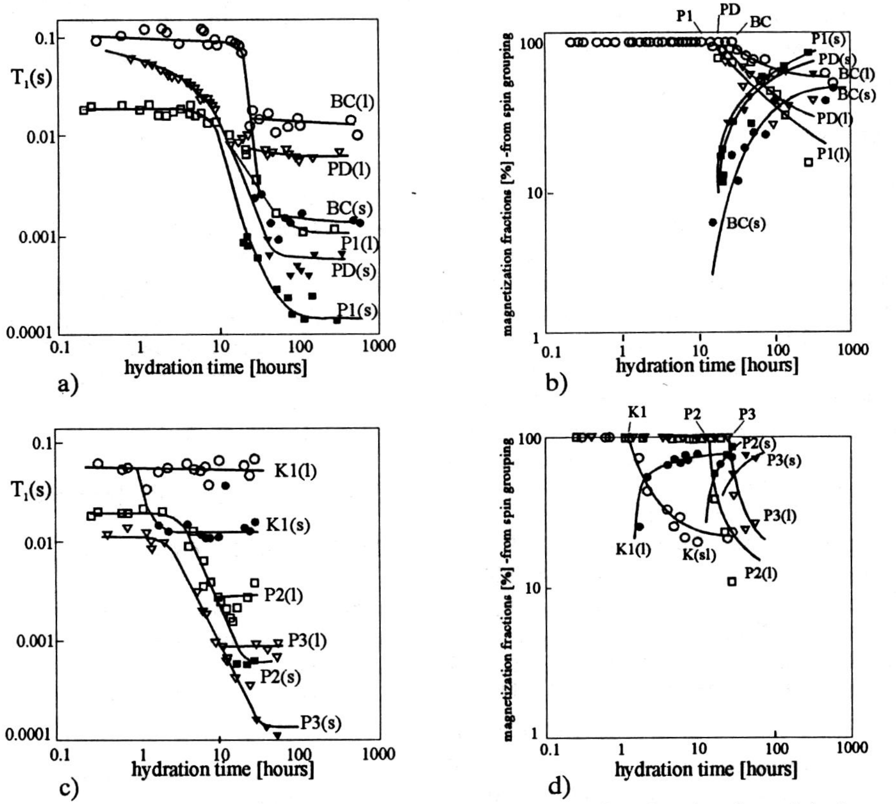

Fig 1. a. and c. The evolution of proton NMR spin-lattice relaxation time; b. and d. the evolution of component's magnetization fractions during hydration time. (o)-K1-clinker white cement, (•)-BC-white cement, (⊓)-P1, (⊓)-P2, (▽)-P3-different portland cements, (▽)-PD- portland cement P1 with 5% admixture-water glass ($Na_2\,SiO_3$), (l)-long component and (s)-short component.

Changes in T_1 evolution curve components of OPC samples (P1,P2,P3) reflect differences in quality and properties of Portland cements manufactured from different clinkers. P1 sample has longer T_1 components and high stable magnetization fraction ($\sim 80\% - 90\%$) comparing to P2 and P3.

PD sample was prepared adding 5% water solution of K_2SiO_3 to P1. Comparing to P1, PD is characterized by shorter first period of hydration, longer second period and higher values of T_{1l} and T_{1s} components, which form later but faster, with smaller stable magnetization fraction ($\sim$ 70%). Taking into account the fact that the stable structure porouss forms have short and long T_{1s} and T_{1l} in PD sample correspond to larger pores.

Conclusion

Proton dynamics of different spin groups can be modeled from their inherent T_1 relaxation characterization in different environments. Apparently different results through stages of investigated cement samples are correlated with shaping of solid structure and radius of pores during hydration. Using another NMR methods (T_2, $T_{1\rho}$, IMR,..) it is possible to require considerable improvements over standard methods of characterization of hydration process and cement paste properties.

References

[1] Bye, G.C. (1983) Portland cement, PERGAMON PRESS
[2] Advances in cement technology (1983) *Cement Research Institut of India*, New Delhi
[3] Zimmerman, J.R., Brittin, W.E. (1957) *J.Phys.Chem.* **61**, 1328-33
[4] Halperin, W.P., D'orazio, F., Bhattacharja, S., Tarczon, J.C. (1989) Magnetic Resonance Relaxation Analysis of Porous Media, *Edited by Joseph Klafter and J.M. Drake*
[5] Double, D.D., Hellawell, A., Perry, J.S. (1978) *Proc.R. Soc. Lond. A* **359**, 435-451
[6] Schreiner, L.J., Mac Tavish, J.C., Miljković, Lj, Pintar, M.M., Blinc,R., Lahajnar, G., Lasič, D., Reeves, L.W. (1985) *J. Am. Ceram. Soc.* **68 (1)**, 10-16
[7] Blinc, R., Dolinšek, J., Lahajnar, G., Sepe, A., Zupančič, I., Žumer, S., Milia, F., Pintar, M.M. (1988) *Z. Naturforsch.* **43 a**, 1026-1038
[8] Mac Tavish, J.C., Miljković, Lj., Schreiner, L.J., Pintar, M.M., Blinc, R., Lahajnar, G. (1985) *Z. Naturforsch.* **40 a**, 32-36
[9] Miljković, Lj., Mac Tavish, J.C., Jin Jian, Pintar, M.M., Blinc, R., Lahajnar, G. (1986) *Cement and Concrete Research.* **16**, 864-870
[10] Milia, F., Bakopoulos, Y., Miljkovič, Lj. (1991) *Z. Naturforsch.* **46 a**, 697-699
[11] Popović, N., Nasr, L.A., Miljković, Lj. (1994) Karakterizacija rane hidratacije materijala cementnog tipa, XXXVIII Jugoslovenska konferencija za ETRAN

DOPRINOS ISTRAŽIVANJU MEHANIZAMA HIDRATACIJE

N. Popović[1], L.A. Nasr[2], Lj. Miljković[1]

[1] Studijska grupa za fiziku, Filozofski fakultet, Ćirila i Metodija 2, 18000 Niš, Jugoslavija
[2] Studijska grupa za fiziku Univerziteta u Aleksandriji, Aleksandrija, Egipat

Sadržaj: Metodom spinskog grupisanja studirana je dinamika protona u toku hidratacije različitih cementnih materijala (različiti klinkeri sa i bez dodataka). Proces hidratacije je praćen NMR T_1 metodama. Multi-komponentna analiza dobijenih vrednosti protonskog spin-mrežnog vremena relaksacije u funkciji vremena hidratacije T_1 daje dinamičku informaciju o protonskom okruženju, tj. o podeli na intervale, dužini pojedinih intervala i njihovoj vremenskoj evoluciji. Rezultati ukazuju na formiranje različitih struktura i pora materijala u toku procesa hidratacije.