



INFLUENCE OF MINERAL ADDITIONS ON CEMENT HYDRATION INVESTIGATED BY NMR AND SEM METHODS

UDK : 543 : 547.21

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Abstract: In order to explore new cement type materials two mineral additions, kaolinite and mica, were used to replace a fraction of Portland cement in a small amounts. The hydration properties of obtained cement pastes were studied by means of $^1H T_1$ pulse NMR (Nuclear Magnetic Resonance) technique, with multicomponent analysis of spin-lattice relaxation. The values and evolution dynamics of T_1 (spin-lattice relaxation time) and M_0 (fraction in total magnetization) show that both kaolinite and mica accelerate the initial hydration of Portland cement to the extent depending on percentage of addition. The lowering of pastes fluidity in dormant caused by both additions is more apparent in the case of kaolinite. In advanced stages of hydration the retarding influence of kaolinite as well as mica is observed yielding to a higher final porosity of samples, where the effect is more pronounced for mica additions. The results of SEM (Scanning Electron Microscopy) investigation indicate the pozzolanic activity of kaolinite, not evidenced for mica, as a mechanism of slowly filling of pores in a hardened pastes.

1. Introduction

Currently, the research of cement based materials with clay minerals additions is of interest, since it was shown [1] that small amounts of clays might change the hydration course as well as the properties of final cement product. The applicability of clay minerals as additions to cement based materials is enabled dominantly by their large specific surface area, complex chemical composition and charged layer structure which provides the water immobilization and ions capturing effects in cement paste.

It is already known [2] that hydration progress could be examined by monitoring the 1H spin-lattice relaxation of exchangeable water in cement paste during its hydration time. In accordance with efficiency of the proton T_1 relaxation mechanisms the composite NMR signal can be resolved into spin groups [3]. Each component is characterized by its own relaxation parameters T_1 and M_0 (fraction in total magnetization). Therefore, the

influence of clay minerals on cement hydration may be explored by observing the changes in values and evolution dynamics of T_1 and M_0 of each component.

The SEM examination, utilized in this work, presents the standard method for investigation of cement paste microstructure. By this method it is also possible to evident the characteristic changes in pore sizes, structure of products, their distribution inside the cement paste etc. caused by effects of additions. Besides that, the SEM method is applicable in exploration of pozzolanic reaction of clay minerals, as it was shown in ref. [4].

2. Experimental

The type I Portland cement used in this study was produced by Cement Industry "Novi Popovac", Paraćin, Yugoslavia. The clay mineral kaolinite was supplied by "ECC International John Keay House", St. Austell, Cornwall, England. The mineral mica with granulometric composition from 63 to 90 μm , was obtained from "National Building and Civil Engineering Institute ZRMK", Ljubljana, Slovenia. The chemical composition of kaolinite and Portland cement is given in Table 1.

Table 1. The oxide content (in percentages) in kaolinite and in Portland cement

| Oxide | Kaolinite | Cement |
|-------------------------|-----------|--------|
| SiO_2 | 48.7 | 18.21 |
| Al_2O_3 | 36.0 | 5.61 |
| Fe_2O_3 | 0.82 | 2.79 |
| CaO | 0.06 | 64.76 |
| MgO | 0.25 | 2.82 |
| SO_3 | — | 2.88 |
| K_2O | 2.12 | — |
| Na_2O | 0.10 | — |
| TiO_2 | 0.05 | — |
| LOI | 1.9 | 1.3 |

The cement paste for T_1 investigation was prepared by mixing a cement powder with suspension of individual clay in water and sealed in a glass tube. The amount of each clay addition was 0, 1, 3 or 5% (per dry cement weight) where the water/solid ratio was equal to 0.42.

The NMR measurements were all made at hydration times ranging from a few minutes to 300 hours. The ^1H spin-lattice relaxation experiments were performed at 16 MHz on the IJS pulse NMR spectrometer applying the $\pi - \tau - \pi/2$ sequences. The data from each T_1 measurement were processed by the spin-grouping technique yielding the T_1 and M_0 parameters of particular components.

3. Results and discussion

The evolution of T_1 and M_0 , for decomposed spin groups (a), (b) and (c), during hydration of Portland cement samples containing 0, 1, 3 and 5% of kaolinite and mica is presented in Figures 1 and 2, respectively. The hydration time in Figures 1 and 2 and in further considerations is typically divided into stages.

The spin-lattice relaxation time and corresponding magnetization fraction for component (i), where $i = a, b, c$, are labeled as $T_1(i)$ and $M_0(i)$, respectively, in following text.

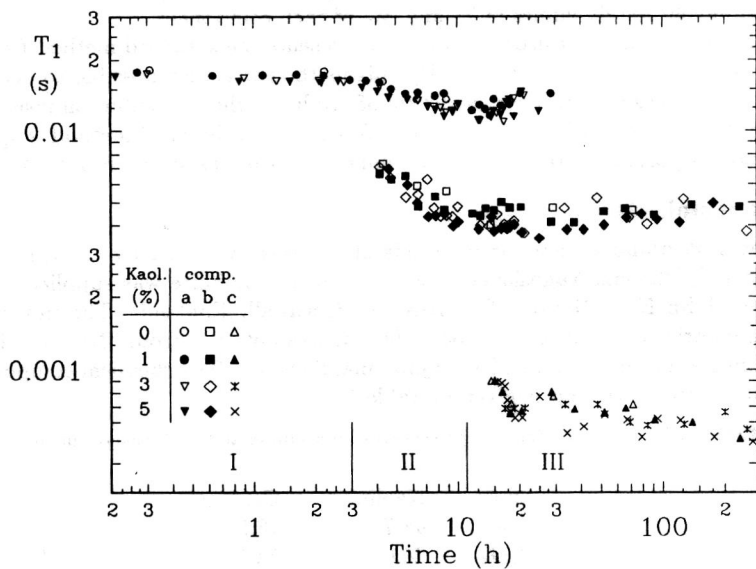


Fig. 1.1. Dependence of $T_1(i)$, $i = a, b, c$, on hydration time for Portland cement samples with 0, 1, 3 and 5% of kaolinite additions

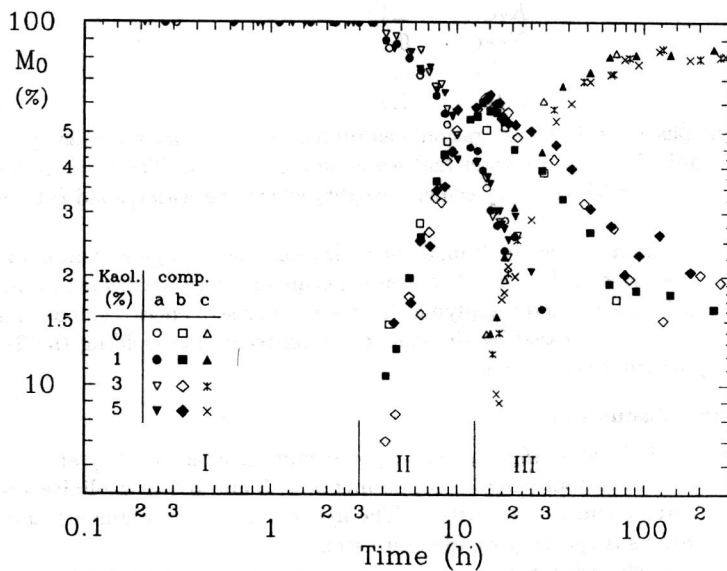


Fig. 1.2. Dependence of $M_0(i)$, $i = a, b, c$, on hydration time for Portland cement samples with 0, 1, 3 and 5% of kaolinite additions

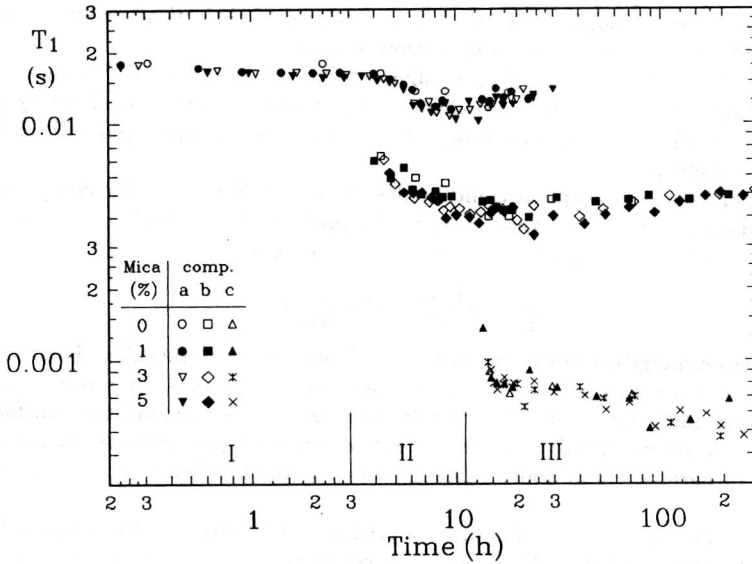


Fig. 2.1. Dependence of $T_1(i)$, $i = a, b, c$, on hydration time for Portland cement samples with 0, 1, 3 and 5% of mica additions

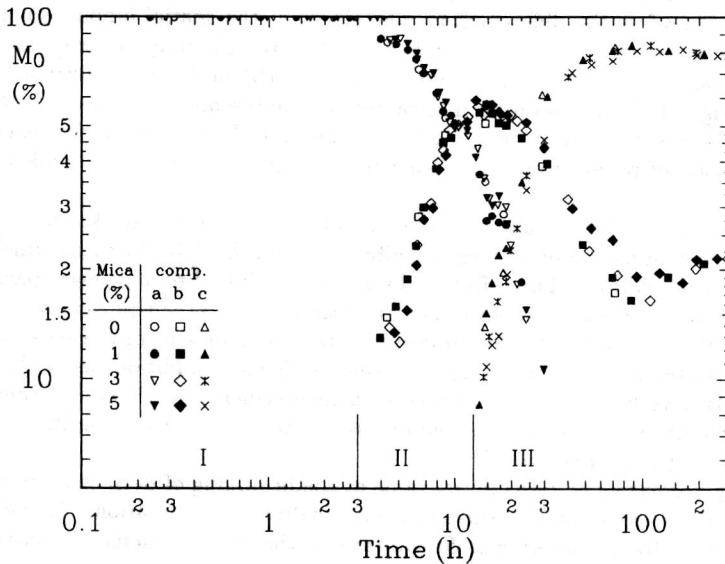


Fig. 2.2. Dependence of $M_0(i)$, $i = a, b, c$, on hydration time for Portland cement samples with 0, 1, 3 and 5% of mica additions

The origin of these components, referring to the spins with $T_2 \geq 45 \mu s$ i.e. to the protons of exchangeable water, could be deduced from analysis of their time evolution and by comparison with known facts about a hydration process.

From presented Figures 1 and 2 it is obvious that all samples exhibit similar time evolution features of corresponded components. Hence, the consideration about hydration process, based on T_1 components evolution, for pure Portland cement generally holds for all examined cement pastes.

As the cement paste in dormant could be described as a liquid gel, the component (a) in this time domain (stage I) is associated to the protons of this fluid [5]. According to *Zimmerman-Brittin* theory, the unique observed T_1 value, where:

$$\frac{1}{T_1} = \frac{1}{T_{1f}}(1 - \eta) + \frac{1}{T_{1b}}\eta \quad (1)$$

indicates a fast exchange process between free and bonded water molecules. Their inherent relaxation times T_{1f} and T_{1b} , respectively, are primarily determined by interactions with dissolved paramagnetic ions and with adsorptive centers and paramagnetics on surfaces [6]. Therefore, the existence of only one component (component (a)) demonstrates a spatial homogeneity of parameters in above relation including the fraction of bonded molecules, η .

The growth and participation of hydration products reflecting in active surface develop accounts for the general fall in T_1 values in stages II and III. The typical dimensions of spaces occupied with exchangeable water in cement paste allow holding the fast exchange approximation in each of them [7]. Thus, in a case of single cement pore the unique T_1 would be observable. Assuming the slow exchange between individual pores or that the pore system is connected only through narrow throats, the discrete pore model could be applied [8]. Therefore the differences in pore sizes i.e. the spatial inhomogeneity of η in cement paste is the main reason for crude separating the T_1 components of exchangeable water protons. In that sense, the components (a), (b) and (c) in advanced stages of hydration originate from protons in macropores, capillaries and gel pores, respectively [5]. This could be easily certified applying the simple model given in [7] for calculation of mean dimension of pores belonged to particular group, based on corresponded measured T_1 value.

As Figures 1.1. and 2.1. show, the influence of both clay minerals, kaolinite and mica, on Portland cement hydration in stage I exhibits through the $T_1(a)$ lowering which depends on percentage of addition. This effect could not be attributed to a stronger paramagnetic relaxation since the Fe_2O_3 content in both additions (due to their purity) was lower than that one in Portland cement. The observed influence comes from a greater amount of the bonded water [η , in relation (1)] in pastes with more addition, as both concerned clay minerals have higher specific surface area than cement [9]. A weaker effect of mica compared to that one of kaolinite is in accordance to the ratio of their specific surface areas and water absorption capability [9].

A slightly decreasing of $T_1(a)$ initial value at the beginning of dormant, caused by each of used additions, demonstrates the short-term hydration acceleration. This effect could be accounted for by the lowering of Si/Ca ratio in the cement grains protective layers as well as by introduction of Si rich material into the system [10]. According to some authors [11], the pointed acceleration is the consequence of initial acting of additions surfaces in provision the nucleation sites for hydrated phases growth.

At the beginning of stage II the lowering of $T_1(a)$ and $T_1(b)$ values appears, which reflects the decrease in dimensions of water filled spaces, with increasing percentage of each addition, where the effect is more significant for kaolinite. This could be accounted for by previously accelerated hydration by added clay minerals and by corresponding faster developed hydrates as well as pore system.

The evolution of percentage fractions of magnetization in Figures 1.2 and 2.2. shows an decreasing slope of $M_0(a)$ and $M_0(b)$ with rising content of both kaolinite or mica. This means that additions of these materials decelerate the hydration of Portland cement in stage II. An explanation of observed deceleration could be the reducing nucleation effect of $Ca(OH)_2$ due to its promoted early crystallization in the presence of clay minerals [12].

It should be noticed from Figures 1.2 and 2.2 that in stage III some effect of $T_1(b)$ rising and $M_0(c)$ decreasing appears indicating a lowering of specific surface area of all aged pastes. This could be attributed, as done by some authors [2], to performances of apparatus i.e. to inability of observing a considerable part of strongly bonded water (with low enough T_2). A part of this effect could be ascribed to a real existence of specific surface area decreasing and to the lowering of a gel pores to capillaries percentage fractions ratio [13], in a gel stabilization process.

The dependence on time of $M_0(i)$, $i = b, c$, in Figure 1.2, regarding to the above discussed origin of particular components, shows the slower development of gel pores and corresponding decreasing in percentage of capillaries, in samples with higher kaolinite or mica content. Although the final $M_0(c)/M_0(b)$ ratio has the similar values for all samples, the decreasing of this parameter with rising percentage of kaolinite or mica can still be evident. This indicates the higher porosity of hardened cement pastes with greater amount of kaolinite and mica, where the influence is more apparent for mica.

The results of our SEM investigations confirm above conclusions about greater porosity of hardened pastes with more clay minerals additions. Figures 3.1. and 3.2. represent the typical SEM photographs of 28 days old paste with 5% of kaolinite addition. The large pores, which are not evidenced in pure Portland cement paste, can be seen. The pore in Figure 3.2. is the result of air entrapped during the preparation of the sample, which is characteristic for aggregates [13].

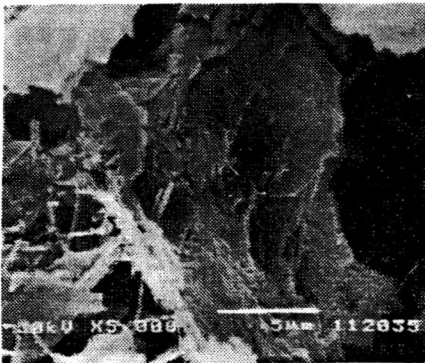


Fig. 3.1. A large pore in hydrated cement paste with 5% kaolinite

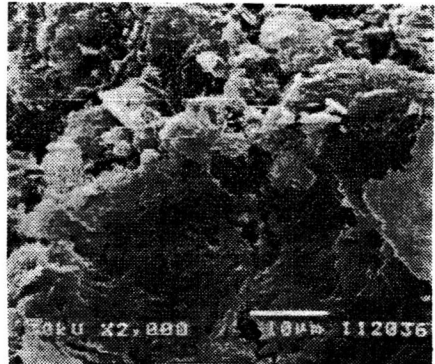


Fig. 3.2. An air pore in hydrated cement paste with 5% kaolinite

The effects of mica in cement paste are also closed to these of aggregates. Really, it seems that in cement paste of 28 days age the most of mica particles stay in unreacted form as Figure 4.1. show. In this Figure many small and large $Ca(OH)_2$ crystals in vicinity of mica particle can also be observed. The noticed mica effects are typical for aggregates [14] so the mica could be treated as the member of this class additions. SEM Figure 4.2. represents the partly unfenced mica particle (in addition to cement hydrates) which could be the consequence of AAR (alkali-aggregate reaction) [15] rather than pozzolanic activity.

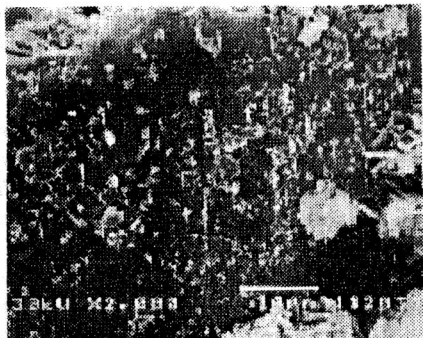


Fig. 4.1. A mica particle in hydrated cement paste



Fig. 4.2. A partly unfenced mica particle in hydrated cement paste

However, in spite of similarity with aggregates regarding to the influence on hydration dynamics and porosity of hardened paste, kaolinite exhibits the activity in pozzolanic reaction, which is not pointed in the case of mica [14]. To ratify this statement we have employed the SEM examinations of the mixture of kaolinite, CaO (analytically pure) and H_2O . The SEM Figures 5.1. and 5.2. of this mixture aged 3 and 28 days, respectively, show that besides unreacted material the weakly developed products exist. The fibrous product, which is absent in older sample, is very similar to one of the principal cement hydrates i.e. to $CSH(II)$, while the foliated one reminds of $CSH(I)$ [16].

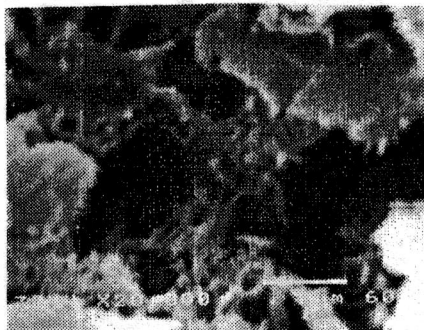


Fig. 5.1. The 3 days old mixture of kaolinite, CaO and H_2O

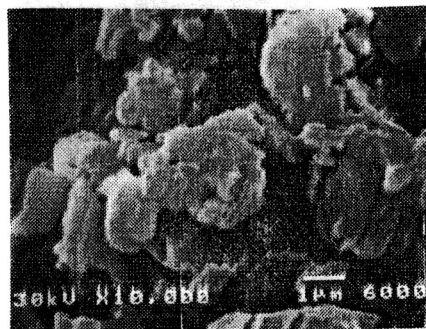


Fig. 5.2. The 28 days old mixture of kaolinite, CaO and H_2O

Since the slow pozzolanic reaction of kaolinite actually takes place, one can expect a further slowly filling of pores in hardened pastes with kaolinite addition by products of this reaction and consequent decreasing of porosity in a time longer than our investigation domain. In the pastes with mica addition such effect could not be expected since mica acts as aggregate.

4. Conclusions

It is shown that the addition of any of two concerned clay minerals lowers the fluidity of Portland cement paste in dormant to the extent depending on clay species. Each clay also accelerates the hydration in dormant, where the effect is more apparent for kaolinite. These effects are enhanced in samples with higher percentage of both additions.

In the advanced stages, the hydration of Portland cement is decelerated by addition of any of two used clay minerals. The retarding is depended on percentage of added clay i.e. it is more observable in samples with greater content of addition. The decelerating influence of both additions could be attributed to the reducing nucleation effect of $Ca(OH)_2$ due to its promoted early crystallization in the presence of clay minerals.

The final values of gel pores to capillaries percentage fractions ratio indicate a higher porosity of hardened samples with more kaolinite or mica addition. This is confirmed by results of SEM investigation which demonstrate the presence of many large pores in samples with additions as well as the belonging of mica to the aggregates class. However, as our SEM examination show, the filling of pores in the samples with kaolinite could be expected due to development of products of this clay pozzolanic reaction.

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NMR I SEM ISPITIVANJE UTICAJA MINERALNIH DODATAKA NA HIDRATACIJU PORTLAND CEMENTA

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Sadržaj: U cilju ispitivanja novih materijala cementnog tipa, mali iznosi dva mineralna dodatka, kaolinita i liskuna, korišćeni su kao zamena dela Portland cementa. Osobine hidratacije dobijenih cementnih pasti proučavane su korišćenjem 1H T_1 pulsne NMR tehnike, uz primenu multikomponentne analize spin-rešetka relaksacije. Vrednosti i dinamika evolucije T_1 (spin-rešetka vreme relaksacije) i M_0 (frakcija totalne magnetizacije) pokazuju da oba dodatka ubrzavaju inicijalnu hidrataciju Portland cementa u stepenu koji zavisi od njihovog procenta. Sniženje fluidnosti pasti u dormantu izraženije je u slučaju dodatka kaolinita. U kasnijim stadijumima hidratacije opaža se usporavajući uticaj kaolinita i liskuna, kao i veća finalna poroznost hidratiranih uzoraka, sa nešto izrazitijim uticajem liskuna. Rezultati SEM istraživanja ukazuju na pucolansku aktivnost kaolinita (koja nije evidentirana u slučaju liskuna) kao mehanizam sporog popunjavanja pora u hidratiranim pastama.