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THE EFFECT OF CURING TEMPERATURE ON THE HYDRATION PROCESS OF CEM II CEMENT TYPE

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This paper presents the hydration kinetics at three different curing temperatures of a CEM II/B-M type Portland composite cement, used as main binder in the radioactive waste conditioning matrix. Information regarding the hydration kinetics are obtained by two methods: DTA/TGA analysis and software modeling. The results of these two approaches are correlated and compared in order to understand how modeling can be used in the estimation the long-time hydration evolution of this complex multicomponent-multiphase system of the cement-based materials.

Keywords: cement hydration, software modeling, DTA/TGA analyses, Portlandite

1. Introduction

In the context of the widespread use of cement-based materials in a lot of fields, but especially in the nuclear field (used as the main binder in the radioactive waste conditioning matrix, as a structural material for consolidation of access tunnels and disposal galleries in geological repositories and for construction of disposal cells in surface repositories) the study of the initial hydration products and their future stability is very important.

Cement hydration is a very complex process that involves a lot of chemical reactions leading to the formation of hydration products. A full understanding of the hydration process is crucial for the future assessment of cement-based materials' performance, because their main properties such as workability, setting behaviour, strength development, but also durability, are related to this process [1].

The hydration process is directly influenced by external and internal factors. There are a lot of publications [2-12] that mention the curing temperature as one of the most important external factors that influence the normal process of clinker phases dissolution, formation of the initial hydration products and future stability.

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The cement hydration process evolution can be studied with various experimental techniques such as thermal analysis, isothermal calorimetry, microscopy, electrical conductivity, nuclear magnetic resonance, etc. [13-19]

Besides these experimental techniques, software modeling using geochemical codes such as GEMS and PREEQCH was extensively used in the last years for investigating the cement-based materials hydration and hydration products formation [3,5, 19-24]

In the present work both approaches (experimental determination and software modeling) were used to assess the influences induced by different curing temperatures on hydration of hardened cement paste made from CEM II/B-M cement type at different hydration times and three different curing temperatures.

2. Materials and Methods

2.1 Samples preparation and composition

Cement pastes used for the experimental study were prepared with a water-cement (w/c) ratio of 0.5 at room temperature (22°C±2).

The cement used for specimens' is a commercial Portland composite CEM II/B-M (S-LL) 42.5 R which has in its composition, between 65-79% clinker and between 21-35% blast furnace slag and limestone mixed [25]. This cement type was selected for this study as it constitutes the main binder in concrete matrix used for the stabilization and the solidification of radioactive waste in our waste treatment department.

The oxide proportions and normative phase composition are shown in Table 1.

Table 1

Oxide proportions and normative phase composition of the cement

Chemical composition	**[%]**	**Mineralogical and chemical composition**	**[%]**
CaO	59.7	Alite (C_3S)	22.085
SiO_2	21.4	Belite (C_2S)	39.843
Al_2O_3	5.7	Aluminate (C_3A)	8.625
Fe_2O_3	3.4	Ferrite (C_4AF)	9.538
CaO (free)	0.5	CaO (free)	0.461
MgO	1.41	$CaCO_3$	13.838
K_2O	1.1	$CaSO_4$	4.308
Na_2O	0.2	K_2SO_4	1.14
CO_2	6.2	Na_2SO_4	0.09
SO_3	3.4	K_2O	0.25
(L.O.I)	7.1	Na_2O	0.07
Blaine surface area [m^2/kg]	432	MgO	1.3
Total Additive	27	SO_3	0.09

The oxide proportion was taken from the technical data sheet of the product. The clinker major phases (C_3S, C_2S, C_3A, C_4AF) was calculated using modified Bogue's Equations of Paul Stutzman *at al* [26] for the determination of the oxide component and modified Taylor's Models of Sang-Hyo Shim *at al* [27] for the determination of the sulfate component. Also Loss on ignition (L.O.I) and CO_2 was determined experimentally by thermal analysis.

After mixing the cement pastes, these were cast in cylindrical shapes with the size of diameter of 24 mm and height of 25 mm after which they were stored in three curing temperature ranges (3, 22 and 38℃) until there were subjected to DTA/TGA analysis (at the age of 1, 3, 7, 14, 21, 28, 60, 90 and 150 days) in order to estimate the degree of hydration. In this regard, the hardened cement pastes were crushed and sieved to analyse them by heating from room temperature to 800°C under nitrogen atmosphere using a DTG-60H analyser manufactured by Shimadzu Corporation.

2.2 Hydration process experimental approach

The experimental method for estimating the degree of hydration by using DTA/TGA analysis is based on Portlandite ($Ca(OH)_2$) quantification according to Equation (1) [13].

$$\alpha(t) = \frac{m_{Ca(OH)_2}}{m_C r_0} \tag{1}$$

where:

$\alpha(t)$: degree of hydration of the cement at time t;

$m_{Ca(OH)_2}$: amount of $Ca(OH)_2$ calculated using the equation (2);

m_C: mass of the initial cement calculated using the equation (3);

r_0: amount of $Ca(OH)_2$ produced upon complete hydration of the cement which can be determined by using the simplified equations proposed by Duc Chinh Chu *at al* [13].

$$m_{Ca(OH)_2} = \frac{\Delta m(400°C - 520°C) * M_{Ca(OH)_2}}{M_{H_2O}} \tag{2}$$

where:

$\Delta m(400°C - 520°C)$: the mass loss of the samples between 400°C and 520°C from the TGA analysis;

$M_{Ca(OH)_2}$: molar mass of $Ca(OH)_2$;

M_{H_2O}: molar mass of water .

$$m_c = \frac{m_{sample}}{\left(1 + \frac{w}{c}\right)(1 + LOI)} \tag{3}$$

where:

m_{sample}: mass of the samples;

w/c: the water to cement ratio of the paste;
LOI: loss of cement on ignition.

2.3 Hydration process modelling approach

The hydration of cements is presumed to take place via dissolution and precipitation processes [5]. To simulate these processes GEMS-PSI [28] geochemical modelling code and an Excel file developed by Lothenbach *et al* [20] were used. This are based on the well-known and widely used [4,5,20-24, 29] Parrot and Killoh model. This model is mathematically described by Eqs. (4)-(6) [4,5, 20, 22, 23] which represent nucleation and growth, diffusion, and formation of a hydration shell, respectively.

$$R_t = \frac{K_1}{N_1}(1 - a_t)\big(-ln(1 - a_t)\big)^{(1-N_1)} \tag{4}$$

$$R_t = \frac{K_2(1 - a_t)^{2/3}}{1 - (1 - a_t)^{1/3}} \tag{5}$$

$$R_t = K_3(1 - a_t)^{N_3} \tag{6}$$

where:
R_t the lowest value of hydration rate for any time step;
K, N and *H* empirical parameters of hydration of individual clinker*;*
a_t expressed as Eq. (7) is the hydration degree of clinker mineral at the time *t* calculated from the hydration degree of the mineral at the previous time step (a_{t-1}), the time interval (Δ_t), and hydration rate of the clinker mineral at the previous time step (R_{t-1}).

$$a_t = a_{t-1} + \Delta_t \cdot (R_{t-1}) \tag{7}$$

The influence of water to cement ratio is accounted by adding the factor *f(w/c)* as follows:

$$f\left(\frac{w}{c}\right) = \left(1 + 3.333 * \left(H * \frac{w}{c} - a_t\right)\right)^4 \; ; pentru \; a_t > H * w/c \tag{8}$$

$$\left(\frac{w}{c}\right) = 1; \, pentru \; a_t \leq H * w/c \tag{9}$$

The influence of temperature on the hydration process may be accounted by using the Arrhenius equation which is by far the most widely used relationship to describe the rate processes of chemical reactions and it is represented in the Equation (10) [4, 5, 30, 31].

$$k_T = Ae^{-\frac{E_a}{RT}} \tag{10}$$

where:
k_T is rate constant at temperature T;
R is the natural gas constant (8.314 J/mol/K);
T is temperature in K at which reaction occurs;
R_T equals the rate of hydration evolution at temperature T;
A is the proportionality constant (same units as R);
E_a equals activation energy (J/mol).

The rate at temperature of interest is then calculated by:

$$R_{t,T} = R_{t,T_0} e^{-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \tag{11}$$

where T corresponds to the temperature of interest in K, T_0 to 293 K (20 °C) and R_{t,T_0} to the rate at time *t* calculated at 20 °C (cf. Eqs. (4)-(6)).

3. Results and Discussion

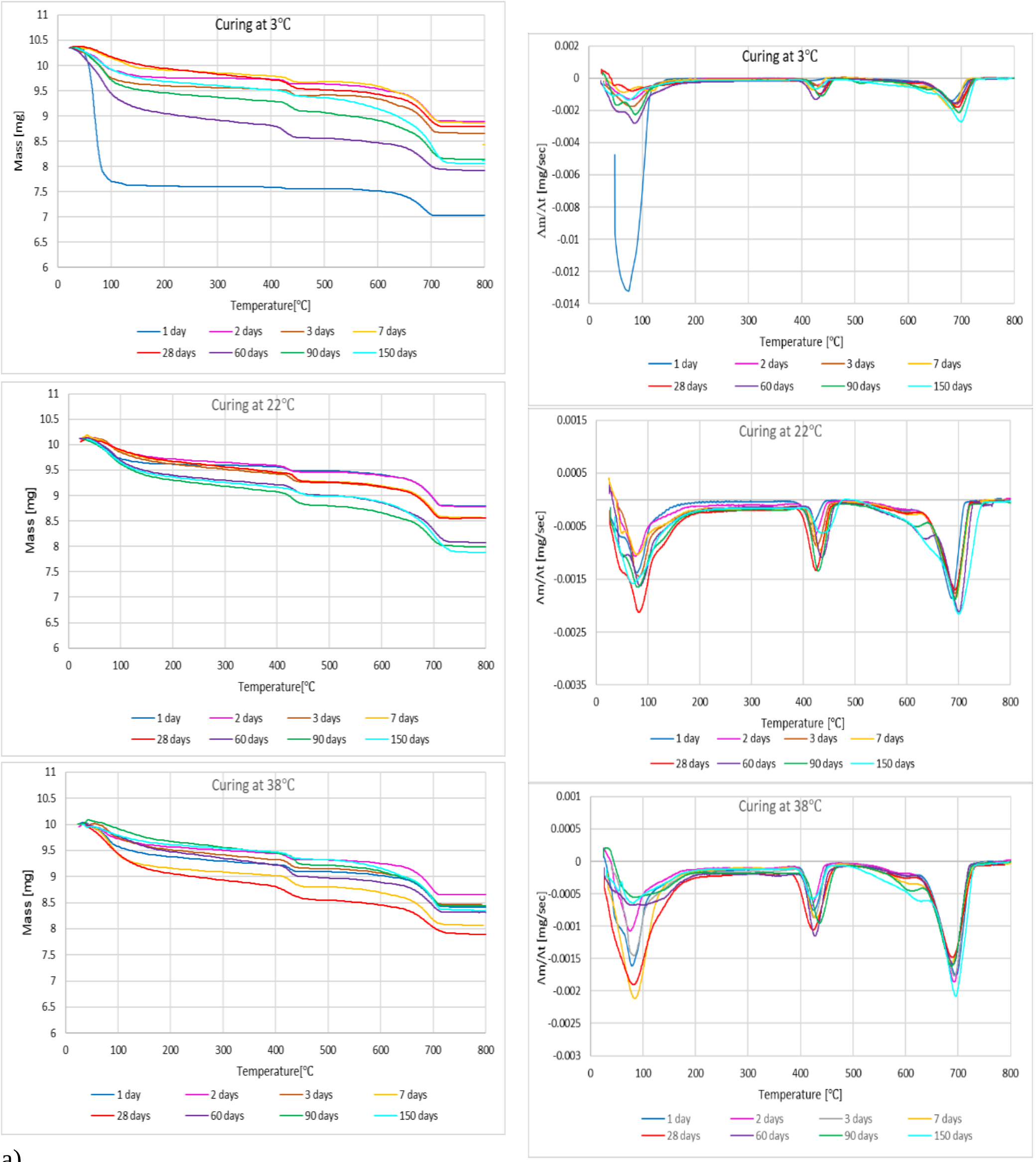
3.1 Experimental and software modelling results

Fig. 1 shows the typical TG/DTG histograms obtained as a result of thermogravimetric analyses (TGA).

The curves exhibit three significant weight loss steps. Two out of three steps are relevant for our study, representing two different kinds of reaction: dihydroxylation and decarbonation. Weight loss step range between 400÷520°C is important for $Ca(OH)_2$ quantification and weight loss step range between 600÷780°C for quantification of lost CO_2 derived from the decarbonation process of calcite ($CaCO_3$).

Based on these considerations and using Equation (2) the $Ca(OH)_2$ content of cement pastes was quantified. Considering that we did not avoid the contact with the environmental CO_2 the carbonation of $Ca(OH)_2$ took place, so when we quantified its content we took this into consideration and made the necessary corrections.

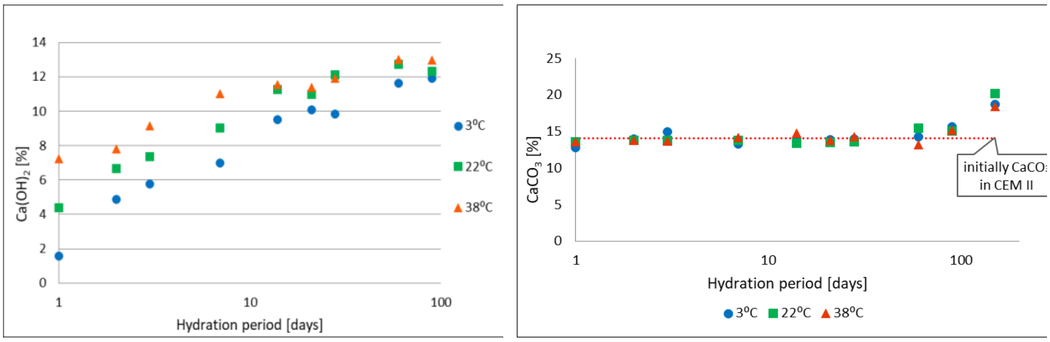
Fig. 2 shows the logarithmic representation of kinetic evolution of the content of Portlandite and Calcite during 150 days of hydration.



a) b)

Fig. 1. Thermogravimetric (TG), column (a), and first derivative (DTG), column (b), curves of cement paste hydrated for 150 days at three different curing temperature

It can be seen that the $Ca(OH)_2$ amount is directly proportional with the hydration degree and curing temperature. Regarding the amount of $CaCO_3$, until 60 days it has slight variations around the concentration in which it was added. After that, it is clear that its amount increased as a result of $Ca(OH)_2$ carbonation. This phenomenon has also been observed in other studies such as that of Soja *at al* [17] even earlier than 60 days. After $Ca(OH)_2$ quantification, the values of the hydration degree $a_{(t)}$ were obtained by using Equation (1). The effect of curing temperature on the degree of hydration of hardened cement pastes after 150 days from the start of the hydration process are shown in Fig. 3.



a) $Ca(OH)2$ evolution

b) $CaCO_3$ evolution

Fig. 2. Kinetic evolution of the content of $Ca(OH)_2$ and $CaCO_3$ estimated trough TGA

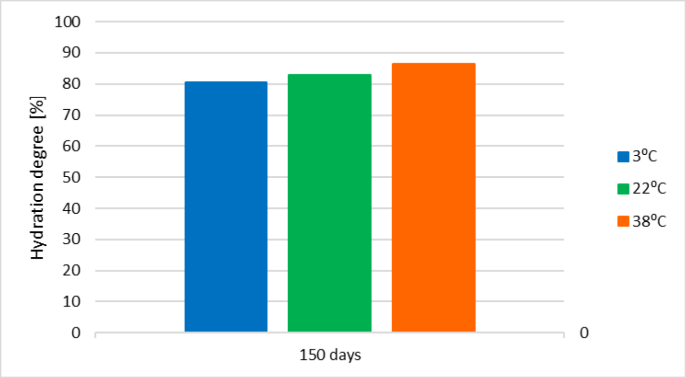


Fig. 3. Degree of hydration of hardened pastes.

The conclusion is that the hydration degree is directly proportional with the curing temperature. This is expected since $Ca(OH)_2$, the element based on which the degree of hydration is determined, is in the same dependence relationship with curing temperature.

Comparisons between the degrees of hydration function of the curing temperature led to the observation that the degree of hydration for cement pastes cured at 22°C and 38°C is higher than those cured at 3°C by 2.8% and 6.6% respectively and by 3.9% for those cured at 38°C compared to those at 22°C. Cement dissolution and Portlandite formation predicted by Parrot and Killoh model calculations and GEMS software modeling as a function of time and temperature are shown in Fig. 4. Thus, the dissolution of cement is directly proportional to the curing temperature and Portlandite is directly proportional to dissolution hence to curing temperature.

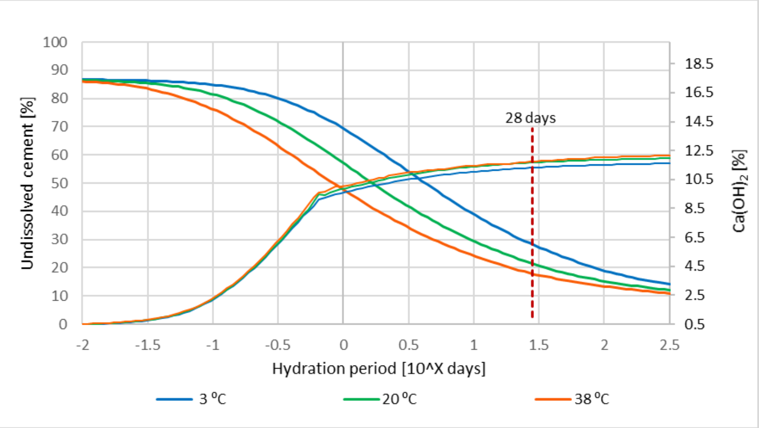


Fig. 4. Dissolution kinetics of cement and formation and evolution of Portlandite.

3.2 Comparative studies between experimental data and software-generated models

Comparative analyses were carried out between the modeling results using the Parrot and Killoh model, GEMS software and experimental data. The results are plotted in Fig. 5 and Fig. 6.

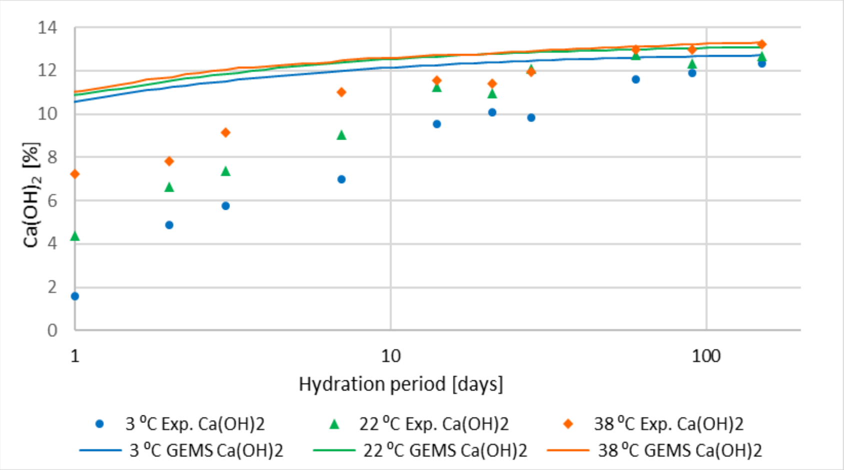


Fig. 5. $Ca(OH)_2$ kinetic evolution by both method approaches (software modeling and experimental determination).

Fig. 5 shows the comparative kinetic evolution of $Ca(OH)_2$, where in the first part a greater difference between the two approaches can be observed, difference that reduces considerably as the hydration period increases. This difference can be attributed to the errors in the quantification of the amount of $Ca(OH)_2$ in the early stage of hydration. Moreover, there are studies such as that of Panea and Hansenb [14] confirming that the thermogravimetric analyses are not very accurate in estimating the amount $Ca(OH)_2$ in the early stages of hydration, but it seems they refer to hours not days as in this case. However, both approaches show the same dependence on the curing temperature.

As for the hydration kinetics of cement pastes, Fig. 6 shows that the experimental results overlap quite well with those obtained by modeling. These are also supported by the values obtained for the coefficient of determination (R^2) shown in Table 2.

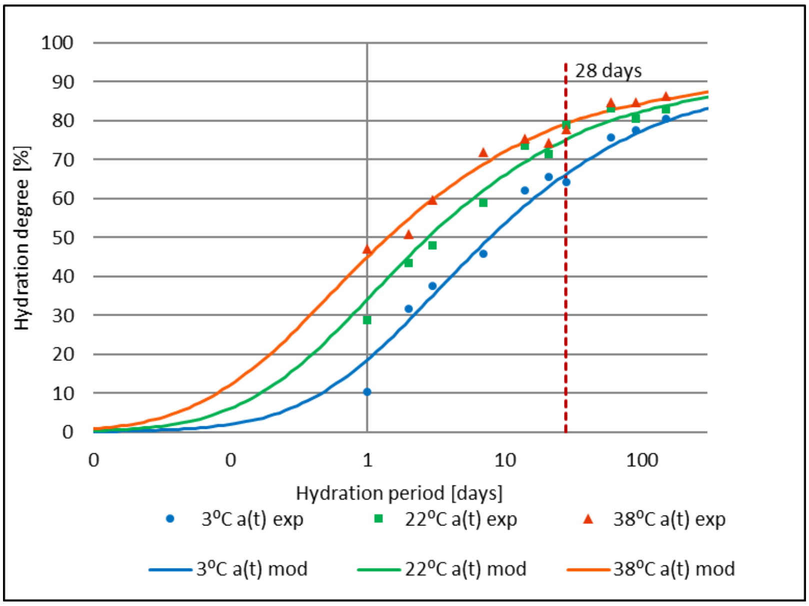


Fig. 6. Hydration degree comparative studies between experimental and modeling approach.

Table 2

The extent of how well the data obtained by modeling replicates the experimental one

Process studied	**Coefficient of determination R^2**		
	3°C	22°C	38°C
Degree of hydration	0.981	0.984	0.966
Portlandite quantification	0.969	0.966	0.964

4. Conclusion

The aim of this study was to compare the experimental data with those resulting from software modeling to assess the influences of the curing temperatures on the hydration of hardened cement paste based on CEM II/B-M (S-LL) 42.5 R cement type. The results of these two approaches are correlated and compared to understand how the modeling can be use in long time hydration evolution estimations of this complex multicomponent-multiphase system of the cement based materials. The results obtained indicate that there is a relatively good agreement between $Ca(OH)_2$ estimated by thermal analysis and $Ca(OH)_2$ predicted by the GEMS software. Even if at the beginning of the hydration period the difference in the amount of $Ca(OH)_2$ estimated by the two methods is slightly larger, it reduces considerably as the hydration period increases.

As for the hydration kinetics of cement pastes, data obtained by simulation with GEMS geochemical modelling code and an Excel file C by Lothenbach *et al* [20] overlaps quite well with the experimental results. This is also supported by the values obtained for the coefficient of determination exceeding 0.96 for all curing temperature regimes. Regarding the effect of the curing temperature, both approaches show that the amount of Portlandite depends on the rate of the hydration reaction that increases with time and temperature.

Understanding these processes and how to program and operate with these modeling codes and mathematically models can facilitate the assessment of the evolution of cement-based materials leading to the improvement of construction efficiency and increasing durability and safety, while contributing to significant energy and costs savings. The experimental and modeling activities will further study the influence of temperature on mechanical strength to show that the concrete strength increases with the cement hydration degree, and the rate of hydration reaction increases with temperature. This dependence gives us the possibility to describe the strength development as a function of the combined effects of time and temperature by using the maturity index.

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