Abstract

The effect of dolomite on alite hydration was investigated in order to elucidate the effect of dolomite addition in cement hydration. The rate of heat evolution both in cement–dolomite and alite–dolomite system was taken as a starting point. Subsequently the chemical shrinkage, conductivity of liquid phase and rheological parameters of pastes were characterized. The observations of microstructure were carried out under SEM and the hydration degree of alite was determined by XRD. The accelerating effect of additive was proved. At low percentage dolomite plays a role of cement replacement; at higher dosage the „dilution” effect can be observed. However, increasing dolomite content is accompanied by higher amount of hydration products, as a results of crystallization on the fine dolomite grains and better absorption of water. The hydration degree of alite increases as well.

Keywords: Cement hydration; alite; dolomite; calorimetry; chemical shrinkage; conductivity; microstructure

1. Introduction

The CEM I type cements are the most frequently replaced by the CEM II type materials, with the other main compounds, apart from the Portland cement clinker. The limestone supplementary material when used for this purpose allows to get some specific properties. First of all, the early strength of cement is similar to the reference CEM I, at additive content \( \leq 10\% \) by weight of cement. The water demand is reduced and therefore the
workability becomes better. The lowering of carbon dioxide and nitrogen oxides emission, due to the partial clinker replacement and the reduction of electric energy consumption, resulting from the better grindability of soft limestone component should be discussed as ecological reasons. The possibility of waste materials/by-products disposal as additives to cement (or cement components) has been an important challenge improving the sustainable development of cement and concrete technology, as it has been pointed out by many researches, e.g. by Lothenbach et al. [1], Giergiczny et al. [2], Nocuń-Wczelik and Łoj [3].

The idea of dolomitized limestone application in common cements is not quite new; the results of research projects held in Germany were reported recently by Zając et al. [4] and Schöne et al. [5]. The authors relate to the elder works and patents. There are the two reasons that the dolomites are not taken into account in the production of common cements. There is no standards and recommendations as the use of dolomite (calcium–magnesium carbonate) is concerned, though the limestone (CaCO₃) is a component of Portland limestone cements and blended, multicomponent cements. Further, there are some doubts dealing with potential durability of dolomite additive because in highly alkaline environment of cement paste the so-called dedolomitization process can occur, leading to the formation of brucite (magnesium hydroxide) with no binding properties and possible risk of destruction. This phenomenon is observed in the concretes with dolomite aggregate on the paste–aggregate interface. It has been found however that the action of dolomite as a component of binder is very similar to the effect of limestone according to Zając et al. [4] and Schöne et al. [5].

The studies of hydration process in the mixtures of cement with limestone powder, dolomite powder and limestone–dolomite additive were reported by Nocuń-Wczelik et al. [6]. In the pastes hydrating with fine grained dolomite powder the crystallization of products is accelerated and as a consequence the strength development is improved. Because of the modification of microstructure the relative strength decrease is much lower that the percentage of inert carbonate in cement [5, 6]. It seems that dolomite will be used in future as an additive to cement; there are many limestone deposits with significant inclusions of dolomite and some amount of dolomitized by-products as well. In this work the effect of dolomite meal on the kinetics of heat evolution accompanying cement and alite hydration. The other studies of hydrating alite (simplified model of cement) – dolomite systems were performed to find the way of dolomite interaction with dominating silicate phases from cement.

2. Experimental

2.1. Materials and methods

The commercial Portland cement CEM I 42.5R was used in the experiments; chemical composition of clinker used in cement production is given in table 1. The synthetic alite was produced in the laboratory by repeated heating of analytically pure limestone and silica gel stoichiometric mixture at temperature 1450°C. The pure dolomite powder was added in amount from 5 to 30% by mass of cement.

Table 1. Chemical composition of Portland cement clinker.

| Component | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | Cl⁻ | L.o.i. |
|-----------|------|-------|-------|-----|-----|-----|------|-----|-----|-------|
| [%]       | 21.25| 5.15  | 2.44  | 65.14| 4.15| 0.13| 0.18 | 1.25| 0.013| 1.4   |

Phase composition approximately is as follows: C₃S=65.6; C₂S=11.5; C₃A=9.5; C₄AF=7.4

The microcalorimetry was applied as a basic method for the estimation of hydration progress. Heat evolution measurements were carried out by use of so-called differential microcalorimeter on the pastes produced at w/c ratio 0.5 using 5g cement specimen. The starting temperature was kept constant at 25°C. The samples were prepared as pastes at w/c 0.35, 0.4 and 0.5 respectively. The conductivity of liquid phase was measured with help of installation composed of sample container, magnetic stirrer, conductometric sensor and computer aided registration system. The measurements were performed on suspensions produced at w/c 100. The chemical shrinkage was determined according to the ASTM C 1608-07 standard. This method is based upon the observation of upper level of water in the capillary placed above the hydrating paste (w/c=0.4) sealed in a polystyrene container (the heights and diameter of containers differed slightly from those recommended in the standard). The “chemical shrinkage”
means the volume of water consumed as a result of hydration reaction. The flow curves of cement–dolomite pastes were plotted as $\tau = f(D_r)$ basing on the data from rheometer at increasing and decreasing shear stress. The rheological parameters, such as plastic viscosity ($\eta$), yield stress $\tau_y$ and maximum shear stress $\tau_{\text{max}}$ (a measure of rigidity of structure) were determined from these curves. Some cement–dolomite hydrated samples were examined under the scanning electron microscope with EDS microanalyzer. The degree of alite hydration in the alite–dolomite hydrated pastes was estimated by quantitative X-ray diffraction.

The results of calorimetric measurements are illustrated in fig.1, 2; the calculated heat values are given in tables 2 and 3. The conductivity vs. time example plots are shown as fig. 3. The chemical shrinkage data are plotted as fig. 4. The example SEM images are shown in fig. 5.

3. Results and Discussion

![Fig. 1. Calorimetric studies – rate of heat evolution in the hydrated cement–dolomite pastes produced at w/c=0.4.](image)

![Fig. 2. Calorimetric studies – rate of heat evolution in the alite–dolomite pastes produced at w/c=0.5, calculated per 1g alite in the hydrated material.](image)
Analyzing the heat evolution data (figs 1 and 2) one can find that the induction period is not elongated in the presence of dolomite additive. It means that there is no especially retarded setting at additive up to 30% cement replacement. One can see (table 2) that the total heat related to the amount of neat cement is higher in the pastes with dolomite. It means that the hydration of cement is accelerated in the presence of additive. The same effect is observed in case of alite hydration, however the relative growth of total heat evolved is the highest. This would indicate that the hydration of silicate components is first of all modified by dolomite additive. Presumably the nucleation barrier is thus lowered. The accelerating effect depends upon the water content. It seems that the w/c=0.4 is generally the optimum value.

Table 2. Total heat evolved in the hydrated cement - dolomite pastes.

| Dolomite [%] | w/c=0.35 | w/c=0.4 | w/c=0.5 |
|--------------|----------|---------|---------|
|              | 1kg(C+D)* | 1kgC** | 1kg(C+D)* | 1kgC** | 1kg(C+D)* | 1kgC** |
| 0            | 232      | 232     | 278      | 278     | 238      | 238     |
| 5            | 239      | 252     | 267      | 281     | 245      | 258     |
| 10           | 223      | 248     | 223      | 248     | 220      | 244     |
| 15           | 227      | 267     | 203      | 239     | 240      | 282     |
| 20           | 231      | 289     | 217      | 271     | 217      | 271     |
| 30           | 180      | 257     | 200      | 286     | 173      | 247     |

* cement – dolomite mixture; ** cement as component of cement - dolomite mixture

Table 3. Total heat evolved in the hydrated alite - dolomite pastes.

| Dolomite [%] | Heat evolved in alite-dolomite mixture[kJ/kg] | Heat calculated per alite [kJ/kg] | Relative heat growth [%] |
|--------------|--------------------------------------------|---------------------------------|-------------------------|
| 0            | 256                                       | 256                             | -                       |
| 5            | 252                                       | 265                             | 3.5                     |
| 30           | 198                                       | 282                             | 10.2                    |

The processes occurring in the presence of dolomite in alite pastes are intensified as the consumption of water is concerned. This can be proved by the chemical shrinkage measurements (fig. 3).

Table 4. Rheological properties of cement – dolomite paste.

| Composition | Parameter | η [Pa·s] | τ_{max} [Pa] | τ_y [Pa] |
|-------------|-----------|---------|-------------|---------|
| CEM I 42.5 R + 0 % dolomite | η [Pa·s] | 2.0      | 101.3       | 96.6    |
| CEM I 42.5 R + 15 % dolomite | η [Pa·s] | 1.9      | 89.5        | 95.7    |
| CEM I 42.5 R + 30 % dolomite | η [Pa·s] | 1.9      | 89.5        | 86.3    |

As one can from the rheological data (table 4), some amount of dolomite (5 to 15% cement replacement) has an effect of weak plasticizer, reducing the values of rheological parameters. The conductivity after a time, it means the concentrations of ions in the liquid phase become higher in the presence of dolomite (fig. 4). Presumably the crystallization of portlandite and simultaneous precipitation of disordered, colloidal C-S-H in alite suspension contribute in this effect.
The hydration degree of alite increases in the presence of dolomite (table 5). The nucleation accelerating effect of this phase is thus proved.
4. Conclusions

- At low percentage, from 5 to 15%, dolomite additive plays the role of active component or even acts as cement replacement. At higher amount the “dilution” effect occurs.
- The heat evolution process is not significantly altered in the presence of dolomite it means that setting of paste with dolomite additive is not retarded.
- The reactions dealing with water consumption and releasing some components to the liquid phase are accelerated in the presence of dolomite.
- The hydration of alite is accelerated.
- The application of dolomite material as a component of non-standard material, for example for geotechnology should be considered.

References

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