Processing Methods of Low-Clinker Multi-Component Cementitious Materials

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The wide use of multi-component cement of highly reduced Portland clinker factor is largely impeded by detrimental changes in the rheological properties of concrete mixes, a substantial reduction in the early rate of cement hardening, and sometimes the insufficient strength of mature concrete. Therefore, major changes are needed in traditional concrete-production technologies if low-clinker cement is to gain wider acceptance.

Keywords: concrete mixing technology ; early-age properties ; low-clinker multi-component cement ; magnetized water ; microwave treatment ; non-clinker constituents ; ultrasound treatment

1. Introduction

Current developments in construction material technologies are associated with a widespread trend to reduce harmful environmental impacts during the production of materials and their use in buildings and structures. The life cycle analysis of materials in construction elements also covers the issues of the durability of materials—by extending the durability and the service life of structures, the desired effect of reducing the consumption of primary mineral resources can be achieved. Due to the massive use of Portland cement (PC) concrete in construction, the issue of the emissivity of PC cement production has become of great importance. With a simple reduction in the Portland clinker content in cement, whose carbon footprint is estimated at 0.98 kg CO_2/kg clinker (the sum of process, fuel and electricity-related emissions), Gawlicki ^[1] allows for a substantial reduction in its carbon footprint. Therefore, technologies for the use of cement binders with a highly reduced clinker factor are being developed, using a variety of mineral components or industrial by-products as non-clinker cement constituents ^{[2][3][4][5]}. In accordance with the European standard EN 197-5 ^[6], the family of general-purpose cement has recently been expanded to include CEM II/C-M and CEM VI multi-component cement, allowing for an increased proportion of non-clinker main constituents, 36–50% and 51–65%, respectively. In many countries, the range of applicability of new types of cement has not been established yet, and their use is marginal ^{[2][8]}. Proske et al. ^[9] and Chen et al. ^[10] separately suggested more extreme proposals to limit the content of Portland clinker in cement to 20–35% or even 5%.

The main challenges preventing the greater use of multi-component cement with a low proportion of Portland clinker are related to detrimental changes in the rheological characteristics of concrete mix, a considerable decline in the early rate of cement hardening, and occasionally insufficient strength of mature concrete. The vulnerability of concrete to variations in ambient temperature and humidity, plastic shrinkage, the phenomenon of bleeding, and increased pressure of the concrete mix on the formwork are all increased by a delayed setting and very slow early hardening of the cement $\frac{12|2||3||4|}{|5||11||12|}$.

Moreover, a too-slow increase in concrete strength during the first day following casting restricts, if not outright prevents, the use of the slip-form construction technique; slows the removal and replacement of formwork at the construction site; extends the curing time; and delays other construction tasks that are carried out on already at least partially hardened concrete. Chemical admixtures are a very effective approach to adjusting the workability of the mix and expediting concrete's hardening when used with conventional cement. However, new multi-component cement formulations require the development of specific admixtures for efficient control of the rheological properties of innovative concrete mixtures and their rate of early hardening ^{[1][2][3][4][5][11][12]}.

Non-clinker constituents of multi-component cement basically consist of supplementary cementitious materials (SCMs) ^[13] ^[14] that need to be selected and processed properly for their optimal efficiency. The SCMs' fineness, level of clinker replacement, water-to-cementitious-materials ratio, and cement and SCM chemistry (the pozzolanic or hydraulic activity) are only a few of the variables that affect how reactive SCMs are in the cementitious system ^{[13][14][15]}. By modifying the rheological characteristics for a specific application, SCMs, such as granulated blast furnace slag (GGBFS) ^{[16][17][18][19]}. Silica Fume (SF) ^{[16][17][19][20]}, fly ash (FA) ^{[16][17][21][22]}, bottom ash ^{[21][23]}, copper slag ^[24], volcanic ash (VA) ^[18], and pulverized fuel ash (PFA) ^[18], can also increase rheological properties in addition to the mechanical properties and durability of concrete. SCMs may improve concrete characteristics primarily in two ways: by reacting with cement hydration products in the first instance and by improving particle packing efficiency in the second ^{[13][14][15][25]}. Nonetheless, the search for alternative SCMs has significantly intensified in recent years.

In order to use low-clinker cement more widely, significant changes are needed in traditional concrete-production technologies. For the objective of accelerating the early hardening of concrete in precast settings, there are further options to apply hygro-thermal treatment and even gamma irradiation ^{[26][27]} (only within radiation-controlled areas). When it comes to multi-component cement with a low clinker content, transmitting heat energy or gamma-ray energy to hardening concrete can also be a method to drive the hardening processes.

Interactions with non-ionizing radiation, such as magnetic interactions, microwaves, and ultrasonic waves, offer exciting possibilities for adding extra energy to concrete mixtures ^[28]. The potential of ultrasonic waves to carry out detailed diagnostics on the features of hardened concrete and even to demolish concrete is well recognized. Research on concrete constituents and mixtures has occasionally focused on the effects of microwaves, ultrasonic waves, and magnetic interactions.

2. Ultrasound Treatment (US-T) Methodology

Power ultrasound with a frequency spectrum of 20 kHz–100 kHz finds numerous applications in chemistry and material processing due to its unique properties, which include cavitation, acoustic streaming, and sonochemistry ^{[29][30][31]}. US-T can initiate and accelerate chemical reactions through a phenomenon called acoustic cavitation. The rapid formation and collapse of small bubbles in a liquid create localized high temperatures and pressures, leading to enhanced reaction rates and yield. Ultrasonic waves can also disperse and de-agglomerate particles in suspensions, emulsions, and colloidal systems. The cavitation forces break down larger particles into smaller ones, leading to improved stability and homogeneity of the material ^{[29][30][31]}.

Cavitational collapse produces deeply felt local heating (5000 °C), high pressures (1000 atm), and heating/cooling rates (>10¹⁰ °C s⁻¹), thus creating individual conditions for different types of chemical and physical changes [32][33][34][35][36][37]. The acoustic power, frequency, hydrostatic pressure, the gas used, and reactor shape are only a few variables that may impact acoustic cavitation [32][33][34][35][36][37]. An intermediate-frequency ultrasound (between 100 and 1 MHz) encourages the production of hydroxyl radicals through regional hot spots caused by cavitation [32][33][34][35][36][37]. US-T can control crystal size distribution and reduce particle agglomeration due to more stable particles. It can help to direct the course of rapid crystallization processes in which the nuclei are produced due to acoustic cavitation process [33][38][39].

3. Magnetic Field Treatment (MF-T) Methodology

Magnetic Field Treatment (MF-T) can improve water's properties by causing the separation of hydrogen nuclei (protons) and water "clusters" into single or smaller molecules due to strong magnetic forces [40][41][42][43]. The effectiveness of MF-T depends on the duration of exposure to the MF-T (water flow velocity), magnetic flux density, and volume of water exposed to the field [41][42]. Magnetized water (M-Water) is formed when water passes through a permanent MF-T, leading to molecular structural changes and new characteristics [40][42]. The M-Water layer surrounding cement particles becomes thinner, reducing the need for water during mixing and modifying the physical and chemical properties of M-Water, including surface tension, conductivity, pH, density, volatility, and the ability to alter dissolved substances [41][42][43]. M-Water also exhibits a lower viscosity than tap water due to a decreased bond angle (from 104.5° to 103°) [40][42][44].

The relationship between MF-T and the surface tension coefficient (σ) of M-Water is not monotonic ^[45]. The optimal MF-T is 300 mT, and both higher and lower intensities lead to an increase in the σ of M-Water, indicating an enhanced magnetization effect. The duration of magnetization varies with the MF-T intensity; stronger MF-T requires shorter treatment times, such as 3 min at 1000 mT and 20 s at 1500 mT ^[45]. Obtaining M-Water with lower ST is challenging at very high MF-T, and excessive magnetization may even lead to an increase in σ , as reported in lino and Fujimura's research ^[46]. The σ of tap water decreases considerably as the treatment duration increases, reaching a minimum of a 9% decline at 13 min with an MF-T of 1000 mT ^[47].

4. Microwave Treatment (MW-T) Methodology

Microwave treatment (MW-T) is the term for non-ionizing electromagnetic radiation with wavelengths between 1 mm and 1 m and spatial frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm) ^{[48][49][50][51]}. By rapidly attenuating MW-T through the intense vibration of polar molecules, it can increase the temperature of the material and accelerate chemical reactions. The entire specimen becomes heated as a consequence of the movement and friction this causes between molecules ^{[51][52][53][54][55][56]}. The frequencies of 915 MHz and 2450 MHz are currently mostly used on cement and concrete for industrial and scientific objectives ^[57]. Microwaves interact with matter more sensitively than ultrasonic and electromagnetism, which can penetrate dielectric materials and convert electromagnetic energy into heat energy without needing to first warm up a heating cavity. Microwave-absorbing materials generate volumetric heat as a result of the interaction between propagating waves ^{[58][59][60]}. Short reaction times, easy control, improved reaction kinetics, reduced heat loss, clean heating processes, good energy efficiency, and environmental protection are only a few advantages of MW-T over conventional heating techniques ^{[56][61][62][63]}. These heating qualities make it possible to cure concrete in an eco-friendly way.

Precast concrete, in particular, has undergone heat curing to expedite the development of strength ^{[61][64]}. The skin effect, which is produced by conventional heating methods and is more efficient for surface heating ^[48], is the fast evaporation of water from treated materials' exterior surfaces. It is difficult to accomplish consistent heating because of the steep temperature gradient, and heated materials lose a large amount of energy through heat conduction and convection.

In contrast, MW-T may promote a temperature rise as a consequence of the polar molecules' ability to absorb heat and form localized heating spots that are independent of position, which is beneficial to generating uniform volumetric heating [51][52][53][54][65]. The utilization of MW-T is based on the internal energy loss associated with the stimulation of molecular ions and dipoles under electromagnetic fields ^[66]. The specimens' microwave heating characteristics can be varied by the secondary material's propensity to absorb, transmit, or reflect MW-T ^[67]. It has been proven that microwave-assisted heating can cut processing times and lower the expenses of additive manufacturing ^{[51][52][53][54][55][68][69]}. Combining these approaches for the best materials processing could be plausible, and it would follow the properties of power ultrasound, microwave, and magnetic processing stated in the preceding chapters.

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