Effect of Inert Nanoparticles on Cement Hydration

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Abstract:

Inert nanoparticles of titanium dioxide and ultra-fine limestone are used as fillers in Portland cement, because of their potential to reduce the amount of required cement without compromising early age properties. The effect of these fillers on early age hydration of cement was investigated using isothermal calorimetry and specific surface area analysis. Isothermal calorimetry measurements, in the presence of different concentrations of nanoparticles and at different temperatures, were used to determine the apparent activation energy of cement hydration according to the Arrhenius equation. Inert nanoparticles of titanium dioxide and limestone were shown to alter the apparent activation energy and specific surface area of the cement depending on their size and rate of use.

Filler	Crystal Size (nm)	Agglomerate Size (µm)	BET Surface Area (m^2/g)
Cement	-	-	0.98
P25	21	0.58	48.02
UFLS	-	0.7	9.47
PC105	15-25	1.2	74.65
PC50	20-30	1.5	42.20

Table 1: Size and specific surface area of raw materials.

Introduction:

Cement is one of the most common materials used throughout the world. However, cement production is energy intensive and produces significant amounts of carbon dioxide [1]. The use of fillers in cement is an effective method for reducing cement consumption. The introduction of fillers such as titanium dioxide and limestone could also improve concrete properties including increased workability, strength, or durability. Photocatalytic nanoparticulate itanium dioxide in particular is known to have self-cleaning, pollution reducing, and biocidal capabilities that make it desirable for use as a cement replacement.

The complex series of simultaneous chemical reactions that occur when cement reacts with water is known as cement hydration. Cement hydration results in the formation of calcium silicate hydrate (C-S-H), the main strength-giving phase of hydrated cement, as well as other hydration products. The presence of fine fillers acts as sites for heterogeneous nucleation for hydration that could increase the rate of product formation [2]. The cement hydration reaction follows the Arrhenius equation with the apparent activation energy of cement hydration representing the overall temperature dependence of the reactions [3]. The specific surface area can be used as an indication of the progress of hydration, as the addition of fillers could increase the surface area over time due to increased product formation.

Experimental Procedure:

In order to calculate the apparent activation energy of the cement-filler mixtures, the heat of hydration was measured using an isothermal calorimeter at 15, 25, 35, 45, and 55°C. The water to solids ratio (w/s) was kept constant at 0.5, and the fillers were added at 5 and 10% mass replacement of cement. Samples were run at least in duplicate to measure the effect of the following fillers: PC50, PC105, P25 titanium dioxide, and ultrafine limestone (UFLS). Table 1 lists the crystal and agglomerate size of the fillers compared to cement. Measurements were obtained from 44 to 84 hours depending on the sample temperature. A specific surface area analyzer was used to measure the 1-day and 3-day sample surface areas.

Results and Conclusions:

From the heat of hydration data, it was observed that the addition of fine fillers increased both the total energy released as well as the rate of heat released compared to the control. P25, the finest filler used in these experiments, exaggerated the effects the most. When comparing the cumulative heat of hydration data, it was observed that the fillers also increased the total heat released. The increase in heat release could be attributed to the fillers acting as heterogeneous nucleation sites and increasing the rate of C-S-H formation.

$$\alpha(t) = \alpha_u e^{-\left[\frac{\tau}{t}\right]^{\beta}}$$

Eq. 1: Three-parameter model for degree of hydration [3].

Heterogeneous nucleation and the increased rate of hydration in the presence of fillers also altered the degree of hydration. The degree of hydration is the fraction of cement that has reacted with the water to form hydration products. Because the cement hydration is temperature sensitive, the degree of hydration could dramatically increase at higher temperatures.

The degree of hydration curve was modeled according to Equation 1 [4] and the apparent activation energy of each sample was calculated. Table 2 lists the apparent activation energy of each sample mixture up to 50% degree of hydration. All additions of fillers increased the apparent activation energy compared to the control. Yet again, the finest filler P25 had the most prominent effect on the activation energy. The change in apparent activation energy represents the temperature sensitivity of the overall reaction with an increase in activation energy corresponding to a decrease in temperature sensitivity.

The BET surface area and corresponding degree of hydration are listed in Table 3. The specific surface area is a quantitative measure of C-S-H formation and microstructure development. As hydration proceeds, the C-S-H formation continues and the surface area increases. The specific surface area for all filler-cement samples was higher than the control after both one and three days. This data correlates well with the degree of cement hydration that increased when fillers were added.

In conclusion, it was observed that the different fine filler cement replacements increase all of the measured properties of cement paste. The increase in rate of heat release, total heat of hydration, surface area evolution, and decrease in temperature sensitivity, suggests that inert fine fillers have the potential to replace cement without compromising the early age properties.

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Apparent Activation Energy (kJ/mol)							
0%	5% P25	5% UFLS	10% UFLS	5% PC105	10% PC105	5% PC50	10% PC50
36.32	39.12	38.33	37.80	37.58	39.06	36.86	37.80

Table 2. Apparent activation energy at 50% degree of hydration.

	1 Day		3 Day	
	BET Surface Area (m^2/g)	Degree of Hydration	BET Surface Area (m^2/g)	Degree of Hydration
Control	14.92	0.46	16.18	0.63
P25	17.33	0.58	22.37	0.70
5% UFLS	5.89	0.49	15.23	0.66
10% UFLS	16.29	0.51	16.68	0.67
5% PC105	16.06	0.50	18.42	0.67
10% PC105	16.10	0.50	19.46	0.66
5% PC50	16.24	0.48	16.72	0.65
10% PC50	16.41	0.48	18.64	0.64

Table 3: Specific surface area for early age samples.