Optical evaluation on the setting of cement paste

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Abstract. In the construction area, one of the most widely used cement is the CPC 30R, it is a hydraulic binder consisting of CaO, SiO_2, Al_2O_3 and Fe_2O_3, when mixed with water forms cement pastes and its four crystallographic phases start to hydrate. The diffuse reflection on cement paste can give an indication of the behaviour on optical properties on the hydration of the cement and early formation products. In this study, Portland cement (CPC) pastes were prepared with 0.45 a water to cement ratio (w/c). This work is aimed to evaluate the optical properties of cement pastes on the hydration reaction during the first 24 hours by measuring the intensity of diffuse reflection changes.

1. Introduction

Portland cement is a hydraulic binder [1, 2], composed mainly of CaO, SiO_2, Al_2O_3 and Fe_2O_3, which is called clinker, after mixing with water form cement pastes and its four crystallographic phases start to hydrate: alite (C_3S), belite (C_2S), aluminate (C_3A) and the ferrite (C_4AF) [3, 4, 5, 6]. The reaction of C_3A and C_4AF phases predominate in the stages 1 and 2 of the hydration [6, 7, 8, 9] and the reaction of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) phases predominate in the third and fourth cement hydration stages, forming hydrates of calcium (CH) and calcium hydrosilicate (CSH) [6, 10].

To predict the behavior of concrete, it is important to model the hydration of cement pastes incorporating their properties. Powers-Brunauer model describes cement paste as a low-crystalline gel layer [11]; in this model, the behavior during hydration is explained in four stages. In the first stage, immediately after the cement has contact with water, there is a rapid evolution of heat, the space occupied by water between the particles of cement begins to fill whit hydration products, forming a C-S-H film around cement particles; this phase ceases in about 15 minutes [7, 12, 6]. In the second stage (15 min-4 hrs), the reaction rate slows [18], temperature decreases and there is less formation of hydrates but CH crystals grow and make pressure on the C-S-H film until they break it, leaving newly exposed to water the unhydrated cement particles. In the third stage (4-8 hrs) the reaction rate increases and the cement temperature rises [13, 11, 14]; the initial setting occurs in the early stage, when the reaction rate increase and accelerates over time; final set occurs at the end of it. In the fourth stage (8-24 hrs) there is a slow but continuous formation of hydration products [11, 12] and the temperature of the cement begins to stabilize.

Currently, the techniques that exists to monitor setting of cement are conventional, discrete and their outcomes are influenced due to the human factor [15, 16]; so, it is necessary to develop more reliable techniques; in this regard, laser technology has reached an important role due to the ability to make measurements and accurate image reproduction, besides a surface analysis of the cement [17, 18].

The Kubelka-Munk model is used to monitor the optical properties of the materials, as it establishes that the color of any turbid medium results in the absorption and scattering of light [19] and is expressed by the absorption (K) and dispersion (S) coefficient of the light reflected

from an inhomogeneous medium according to Eq. 1 [20, 21].These coefficients describe the amount of radiation that a material absorbs or reflects according to wavelength of light emitted by the source, which is reflected by the material to be measured; these coefficients vary for each material and specifically for cement pastes vary with the changes in its microstructure.

$$f(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{K}{S}, \tag{1}$$

where R_∞, is the diffuse reflection

The diffuse reflection of cement pastes can give us information about the behavior of the microstructure; so, the changes in the cement paste are monitored to obtain the initial an final setting time. In this paper, the diffuse reflection was used to continuously monitor the micro-structural changes in a cement paste sample during hydration; initial and final setting time were obtained with this technique. The temperature of the cement paste was measured in order to compare the behavior of it with diffuse reflection.

2. Materials and Methods

2.1 Materials
A cylinder of 20 mm diameter by 40 mm in height were prepared with cement CPC 30R, with w/c = 0.45 according to ASTM-C187-04 [23] standard, at an ambient temperature of 25 ° C and a relative humidity of 70%; in Table 1 the composition of the cement is shown.

Table 1. Phase composition of portland cement clinker [6].

Phase Composition	Mass (%)
C_3S	55
C_2S	20
C_3A	6
C_4AF	9

2.2 Temperature measurements
Measurement of temperature during the hydration process of Portland cement samples was performed using an infrared thermometer FLUKE model 63.

2.3 Optical arrangement
In the optical arrangement, a He-Ne laser (633nm) was used as a radiation source with an output of 5mW, it was used a beam splitter in order to obtain two beams and we use the 30% as a reference one, using a 22.2% filter to attenuate the beam and prevent the OPT sensor is saturated; The 70% beam was impinge on the sample for diffuse reflection.

## 3. Results and Discussion

3.1 Temperature measurement
At the beginning of the first stage there is a fast generation of hydration heat as shown in Figures 1a and 1b, according to Carmel Jolicoeur [12]; this hydration heat is produced due to the initial hydrolysis reaction with the aluminate and ferrite phases [12, 24]; hydration process generates heat and increases the temperature inside and outside of the cement paste, so that the temperature rises in the first stage to 28.3 ° C [25]. Hydration products formation occurs, creating a protective layer around the cement particles in the final part of the stage.

After two hours the temperature drops, recording the minimum of the curve due to a slow hydration reaction due to cement particles are coated by a layer of hydration products, this layer hinders diffusion of water with the cement, reducing the rate of reaction of the components [12];

so that, less heat is released; furthermore, the formation of calcium hydrosilicate (C-S-H) in the second stage is lower than in the first stage and the temperature depends on the formation of the C-S-H [11]. At the end of the second stage CH crystals grow causing a breakdown of the protective film, exposing the unhydrating cement particles to water.
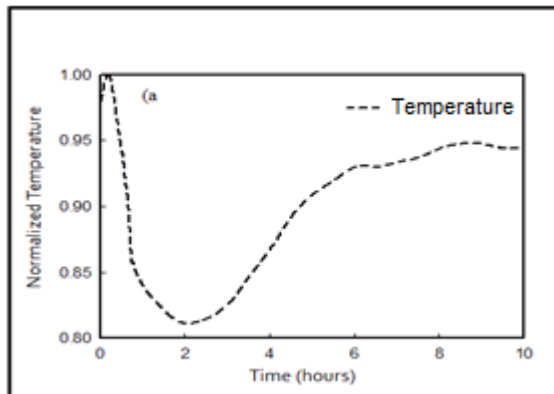
Figure 1a. Temperature behavior during hydration of cement paste.
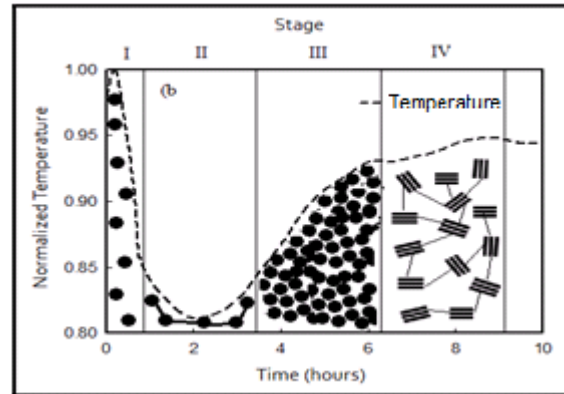
Figure 1b. Temperature behavior during hydration correlated with the stages of Powers-Brunauer model.

At the start of the third stage the initial setting is given. After the breakdown of the protective layer, the unhydrated cement is exposed to water, so that, the hydration reactions generate greater heat release; the silicate phases predominates from this stage forward and hydration products continue to form until the system has resistance to deformation, giving place to the final set [12]. In the fourth stage, there is a lower reaction rate and a slow but continuous formation of hydration products [8, 13]; besides, concrete temperature starts to stabilize, so changes in the temperature of the cement paste are small [14].

3.2 Diffuse reflection
At the first stage, the cement particles are more exposed to the incident light since the cement paste is an agglomerate of small particles, interlaced and intertwined; so, it forms a porous mass [26] in which the incident light may penetrate due to the separation of cement particles; monomeric silicates are unified reaching an amorphous C-S-H gel form and the film formed around the cement particles is small at the beginning and grow with time. The diffuse reflection has a maximum at this stage, before the film grows.

At the second stage, hydrates layer becomes larger, coating the cement particles, in addition, the cement paste is agglomerated and the light cannot penetrate the cement grains; thus, there is a greater absorption of incident light, causing decreasing of the diffuse reflection; the hydration rate is very slow and the loss of water determines the agglomeration of C-S-H in sheets [11] and, this effect is manifested in the contraction of the material; This stage can last several hours [11], and finally crystallization processes of hydration products will be accelerated.

At the third stage, the cement has a more homogeneous but rough arrangement, breakage of the film leaves the particles exposed to the incident beam, increasing the diffuse reflection. At the end of this stage the cement begins to lose plasticity and hydration products begin to crystallize [27, 28]. At fourth stage, the formation of hydration products continue to grow and the cement paste is crystallized [11], causing diffuse reflection decreases slightly. After this stage, the diffuse reflection decreases. During hardening of the cement paste, the diffuse reflection begins to decrease; this may be due to crystallization of the elements, so that, the reflections are more specular. The diffuse reflection changes when the micro-structure changes; besides, it is possible to infer the time of initial and final setting from it.
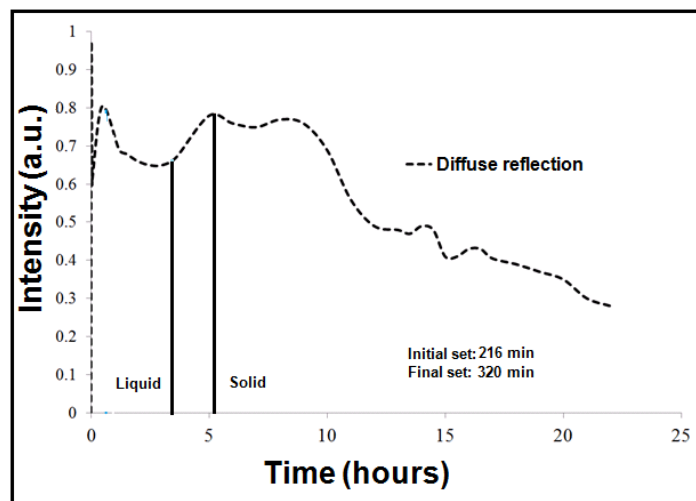
Figure 2. Diffuse reflection of cement paste for 24 hours.

During the cement setting process, the behavior of the diffuse reflection and the temperature is similar, see Figure 3; therefore, from the diffuse reflection it is possible to infer the initial and final setting time; 216 minutes and 320 minutes, respectively, the results obtained by the diffuse reflection are within the range marked in norms C 150-02 and ASTM C 191-01 and our results can be compared with those obtained by D. Mikulić *et al.,*2005 and Yimen *et al*., 2009. With these results, it is possible to distinguish the stages of hydration and define the start and end of each stage. Therefore it is possible to eliminate human error in the measurement for obtaining the setting times. These results are only from one cylinder and in future work we contemplate more cylinders.
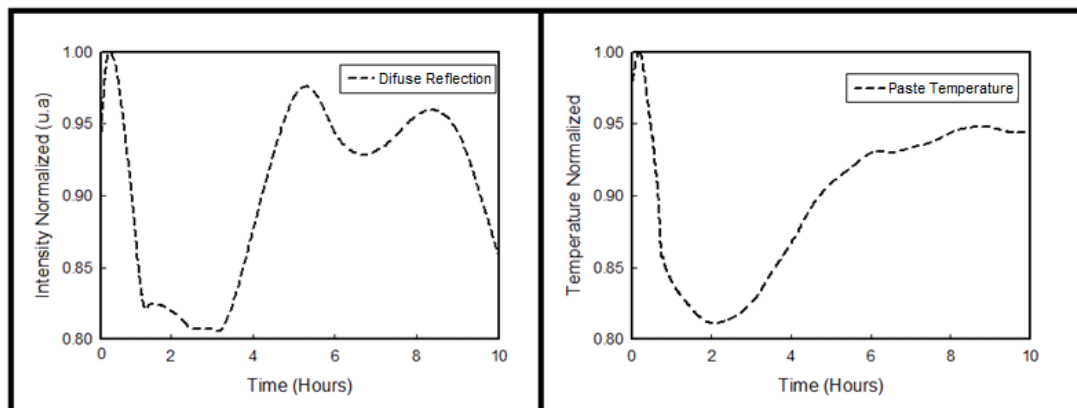
Figure 3. Comparison between diffuse reflectance and temperature behavior

4. Conclusions

During the setting process of the cement paste, the behavior of the diffuse reflection changes as the microstructure changes; as a result, it can be inferred the initial and final setting time of the cement paste by means of diffuse reflection. The setting times obtained by the diffuse reflection are: 216 minutes for initial and 320 minutes for the final setting time, respectively.

By optical monitoring with laser technology, the dynamic behavior of cement pastes was measured, and therefore, it can be seen in real time the changes in the behavior of cement pastes at different ages and at different stages. The behavior of the diffuse reflection curve is similar to the behavior of the temperature curve, so one can infer the setting times from diffuse reflection, due to one of the techniques to measure the properties of cement, is the temperature.

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