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Observation of phase transformations in cement during hydration

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HIGHLIGHTS

- Phase transformation in cement during hydration is studied by XRD, FTIR and Mössbauer.
- The hydration process was monitored by self consistent analysis of the XRD results.
- Alite and belite phases control the early setting time of cement.
- Mössbauer spectroscopy results suggest that brownmillerite prolongs setting time.

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ABSTRACT

We report the phase transformations in Portland cement before and after hydration. The hydration mechanism was studied in detail by using a full Rietveld refinement of the X-ray diffraction (XRD) patterns, Fourier Transformed Infra-Red (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and Mössbauer spectroscopy at room temperature. From the Rietveld refinement of XRD data, alite, belite, celite, brownmillerite and low quartz phases were detected and quantified as major phases in dry cement powder. After hydration, calcium carbonate, portlandite and ettringite phases were found to form. A large reduction in the amounts of alite and belite phases were observed suggesting the formation of amorphous C–S–H phase and emphasizing the role of alite phase in flash setting of cement, as justified by the XRD and FTIR spectroscopy. Mössbauer spectra of all the unset samples showed quadrupole split doublets corresponding to the brownmillerite phase which remains unchanged even after about one week of hydration, suggesting that brownmillerite did not transform to other phases during initial stage of hydration process.

1. Introduction

Portland cement is widely used as a hydraulic binder in concrete. It is a heterogeneous fine grained material with four different major phases: alite ($3CaO{\cdot}SiO_2$, C_3S), belite ($2CaO{\cdot}SiO_2$, C_2S), celite ($3CaO{\cdot}Al_2O_3$, C_3A) and brownmillerite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, C_4AF). It is known that belite and alite are mainly responsible for giving the mechanical strength to cement during hydration process. Alite gives short term strength development, whereas belite contributes to better long term strength development [1]. By varying the alite to belite ratio, the setting time and the early strength of cement can be varied [2]. During cement manufacturing, fine powders of lime-stone ($CaCO_3$), clay, bauxite and hematite are mixed and exposed to high temperatures (~1450 °C) in a kiln, which form clinkers. The clinkers are then ground to fine powder and a certain amount of fly ash is mixed to it. Fly ash is basically pozzolans which are "siliceous" or "siliceous and aluminous" materials. The resultant mixture is Portland cement which sets quickly. A small amount of gypsum ($CaSO_4{\cdot}2H_2O$) is often added to reduce the flash setting of cement. Water to cement ratio of about 3–5:10 by weight is generally mixed to initiate the hydration process [3]. This process of hydration is also known as setting of cement. The cement then forms new phases such as calcium–silicate–hydrate (C–S–H) gel (the hyphens represent variable proportions of the three components; CaO, SiO_2 and H_2O), portlandite ($Ca(OH)_2$), ettringite ($3Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$) and calcium monosulfate (AFm) [4,5]. However, another important reaction which takes place during the hydration is the interaction of calcium hydroxide (portlandite) with atmospheric carbon dioxide to form calcium carbonate. The process of absorbing CO_2 is called carbonation of cement. It is often important to take the early carbonation of

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cement into account during the cement hydration process. The expected major reactions involving alite, belite, celite and brownmillerite, during hydration of cement are given below [6].

Alite + water

$$\underset{\text{(Alite)}}{2(3CaO\cdot SiO_2)}+\underset{\text{(Water)}}{6H_2O}\rightarrow \underset{\text{(C–S–H)}}{3CaO\cdot 2SiO_2\cdot 3H_2O}+\underset{\text{(Portlandite)}}{3Ca(OH)_2} \quad (1)$$

Belite + water

$$\underset{\text{(Belite)}}{2(2CaO\cdot SiO_2)}+\underset{\text{(Water)}}{4H_2O}\rightarrow \underset{\text{(C–S–H)}}{3CaO\cdot 2SiO_2\cdot 3H_2O}+\underset{\text{(Portlandite)}}{Ca(OH)_2} \quad (2)$$

Carbonation process

$$\underset{\text{(Portlandite)}}{Ca(OH)_2}+CO_2\rightarrow \underset{\text{(Calcium carbonate)}}{CaCO_3}+H_2O \quad (3)$$

Celite + gypsum + water

$$\underset{\text{(Celite)}}{3CaO\cdot Al_2O_3}+\underset{\text{(Gypsum)}}{3CaSO_4}+\underset{\text{(Water)}}{32H_2O}\rightarrow \underset{\text{(Ettringite)}}{3Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O} \quad (4)$$

Ettringite further transforms to calcium monosulphoaluminate

$$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O+2(3CaO\cdot Al_2O_3)+4H_2O\rightarrow \underset{\text{(Calcium monosulphoaluminate)}}{CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O} \quad (5)$$

Brownmillerite + water + portlandite

$$4CaO\cdot Al_2O_3\cdot Fe_2O_3+10H_2O+2Ca(OH)_2\rightarrow \underset{\text{(Calcium aluminoferrite hydrate)}}{6CaO\cdot Al_2O_3\cdot Fe_2O_3\cdot 12(H_2O)} \quad (6)$$

The improvement in strength and durability of cement over time is an area of continuing research. Many spectroscopic methods have been used for the study of hydration of cement [7–10]. However, the hydration process is not fully understood till now. In general, Portland cement is mixed with sand and water to obtain a homogenous mortar used for plastering of the walls. Portland cement is mixed directly with water to make slurry for floor finishing. As the mortar gets dry the cement hardens and strengthens. In this work, we have characterized and quantified the phases present before and after the hydration of cement in order to understand the aging process of cement in atmospheric condition by using simple but powerful methods like X-ray diffraction (XRD), Fourier Transformed Infra-Red (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and Mössbauer spectroscopy. According to our knowledge this is the first report demonstrating the hydration process of cement by a self-consistent analysis of the Rietveld refinement results of the XRD patterns.

2. Materials and methods

Three cement samples were collected from three different firms located around Gulbarga/Kalaburagi region of Karnataka, India. The samples were labeled as CB, CJ and CU. The dry powder was characterized by XRD, FTIR spectroscopy, TGA and Mössbauer spectroscopy. To study the hydration process, each of the dry cement powders was mixed with distilled water (water to cement ratio of 4:10) separately to obtain a paste. This paste was then used to make small pellets of (diameter of ~1 cm, thickness of ~3 mm) by using a hollow cylindrical plastic mold. The plastic mold was then removed and pellets were kept on a plastic plate in ambient atmosphere to set. The pellets were then cured by pouring distilled water on it every day for about 7 weeks. The pellets were then ground to fine powder after the selected number of days for XRD, FTIR, TGA and Mössbauer spectroscopy measurements.

2.1. X-ray diffraction and Rietveld analysis

The XRD patterns of all the analyzed samples were recorded by using "PANalytical" X-ray diffractometer in the detector angle (2θ) range of 10–90° (Cu Kα radiation, Ni filter). The step size for the scans was 0.0263°. The phases present in the samples were identified by referring to the Bragg positions of the assumed phases. Rietveld refinement of the XRD patterns were carried out in order to quantify the amount of various phases present in the sample. The crystallographic information required for Rietveld refinement was taken from Crystallographic Information Files (CIF) of Inorganic Crystal Structure Database (ICSD) for all the samples. Rietveld refinement is the least square fit to the experimental diffraction data using generated patterns based on crystal structure information. The fit quality was assessed by the Rietveld agreement factors R_p, R_{wp} and χ^2 [11]. The computer Program "FullProf" was used for this purpose [12].

During the Rietveld refinement of our measured XRD data, we had taken into account a maximum number of seven phases (additional phases caused FullProf program to halt). However, there was clear evidence of the presence of a few more phases in small quantities in the samples. In order to quantify all the phases present in the samples, we manually calculated all the possible crystalline phases, with the minimum accuracy of ~2 wt.%, based on the relative intensity of major peaks from each phase. The value of the Rietveld agreement factors (R_p, R_{wp}) were 30–50 and χ^2 was (2–5), which are high. This can be attributed to the fact that we could not consider all constituent phases during Rietveld refinement.

The Rietveld refined XRD patterns for the CB, CJ and CU samples are shown in Figs. 1–3, respectively. Tables 1–3 list the amount of the crystalline phases (in wt. %) of the cement samples with different hydration times as observed from Rietveld refinement. The Rietveld agreement factors (30) and χ^2 (~3) after the fit were found to be satisfactory. In Figs. 1–3, dots in red[1] are the experimental data, black lines are the calculated intensities by the FullProf program, while blue lines below each plot, are the difference between observed and calculated intensities.

2.2. Fourier Transformed Infra-Red (FTIR) spectroscopy and Thermogravimetric Analysis

FTIR transmission spectra were measured by Agilent 610 spectrometer by Attenuated Total Reflection (ATR) technique in the scan range of 500–4000 cm^{-1} for all the cement samples before and after hydration. The samples absorb light of wavelength that is characteristic of its chemical nature. FTIR can be used to study the vibrational properties of amorphous as well as crystalline samples. In this study, the hydration process of cement was monitored. As in Fig. 4, all the an-hydrated Portland cement (as received) samples, CB, CJ and CU, showed absorption peaks at around 655, 844, 875, 916, 1084, 1400–1500 and 2352 cm^{-1}.

In Fig. 5, the FTIR spectra of the three cement samples CB, CJ and CU after different hydration durations are shown. The figure compares the unset cement samples with sample hydrated for 3, 5, 6, 7 and 50 days.

Thermogravimetric Analysis (Fig. 6) is performed for dry and hydrated cement sample in N_2 atmosphere at a heating rate of 20 °C/min by using TA Q50 instrument.

2.3. Mössbauer spectroscopy

The Mössbauer spectra of all the cement samples were recorded at room temperature in transmission geometry by using ^{57}Co source in Rh-matrix. The data were collected by using a Kr-gas proportional counter. The velocity calibration of the doppler-velocity-drive was performed by using α-Fe foil. For the typical measurement, about 25 mg of cement powder was sandwiched in a PMMA holder to record Mössbauer spectra. To evaluate the Mössbauer spectral parameters, NORMOS program was used [13,14]. ^{57}Fe Mössbauer spectroscopy is an established tool to study the structural, electrical and magnetic properties of iron containing phases. Hence, the Mössbauer spectra can be used to understand the role of brownmillerite phase alone in the hydration process of cement. Fig. 7(a and b) shows the Mössbauer spectra of all the as received dry cement powder and all the cement samples after one week of hydration, respectively.

3. Results and discussion

3.1. Rietveld refinement of XRD data

From the XRD patterns, different crystalline phases present in the dry cement samples were quantified by performing Rietveld refinement. The weight fractions of identified phases (in wt.%) along with their space groups are given in Tables 1–3 for the samples CB, CJ and CU, respectively. The alite (C_3S), belite (C_2S), celite (C_3A) and brownmillerite (C_4AF) phases were present in all the analyzed samples along with low quartz, a low symmetry form of quartz.

Presence of the alite (C_3S), belite (C_2S), celite (C_3A) and brownmillerite (C_4AF) phases were also observed along with low quartz in all the analyzed samples, after one week and seven weeks of hydration. The presence of portlandite (calcium hydroxide) phase

[1] Please note that Figs. 1–3 will appear in B/W in print and color in the web version. Based on this, please approve the footnote 1 which explains this.