Effect of Temperature *vis-à-vis* curing time on the hydration products of OPC paste

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ABSTRACT

The curing temperature and time are the basic fundamental factors that contribute to the hydration of Ordinary Portland Cement (OPC) paste. The purpose of this work is to investigate the effect of temperature *vis-à-vis* curing time on the hydration products: Portlandite (CH), calcium silicate hydrate (C-S-H), ettringite (AFt) and monosulfoaluminate (AFm) of Japan OPC paste using the water-cement ratio (w/c) of 0.40 and following intensive procedures in sample preparation and testing. Results showed that the proportion of CH and C-S-H phases dominated the hydration products at higher curing temperature and longer time as revealed in BEI/SEM analysis. The XRD/Rietveld analysis showed that the CH had the highest peaks intensity compared to other crystalline phases cured at 40°C for 28 days. It has a mineralogical composition equivalent to 20.06% compared to 17.80% as OPC cured at room temperature. There was no C-S-H phase detected since it is non-crystalline/amorphous in nature with composition equivalent to 61.75%. The conversion of AFt to AFm phase from 0.12% to 3.10% was also detected at higher curing temperature and longer time. The CH is the major crystalline phase identified in this study.

1. Introduction

Calcite, silicates and aluminates are the major mineralogical compounds of Ordinary Portland Cement (OPC). These undergo hydration reaction when water is added and form into newly hydrated compounds such as calcium hydroxide, calcium silicate hydrate, hydro ferrite and calcium hydro aluminate (Jumate and Manea, 2011; Klug and Alexander, 1954).

The curing temperature and time are the basic fundamental factors that contribute to the hydration. The increase in temperature enhances the acceleration of hydration reaction and hardening of cement paste and concrete. To quantify the hydration products, the powder X-ray diffraction (XRD)/Rietveld analysis has been employed as a technique for the direct identification of crystalline and mineral phases of cement such as Portlandite, ettringite and other phases present during the hydration of OPC paste (Rietveld, 1969; Klug and Alexander, 1954). However, the identification of these crystalline phases is more complicated due to the presence of amorphous substance which results in a weak diffraction peak.

The major cement compounds that are easily affected by heat are the following: (a) Alite (C_3S) - colorless equi-sized grain mineralogical compound in cement. It has the highest hydration product and reacts easily with water and gives cement its high initial and final mechanical strengths. (b) Belite (C_2S) - a mineralogical compound known to take three even four polymorphous forms, which reacts with water and transforms into hydrated dicalcium silicate. The C_2S slowly contributes to the strengths of cement paste in at most seven days. After 28 days, the mechanical strength is very close to that of C_3S. (c) Aluminate (C_3A) - a mineralogical compound present as crystals in cement clinker. Pure C_3A react quickly with water that leads to the instantaneous setting of the cement paste. (d) Ferrite (C_4AF) - acts as a flux during cement manufacturing and contributes very slightly to strength gain.

Gypsum ($CaSO_4 2H_2O$) is added in a controlled amount when grinding the cement clinker. This material acts as a flux and lowers the burning

temperature of the clinker. Too much amount of gypsum leads to expansion and damage the setting of the cement paste and concrete (Young et al., 1998; Jumate and Manea, 2011).

During hydration, the ferrite reacts with gypsum, and forms into ettringite (AFt) phase and monosulfoaluminate (AFm) phase whose presence can accelerate the hydration of calcium silicates. The mineralogical component begins to lose hydrates and crystallize. Consequently, the cement paste transforms into a rigid material with very high strength (Young et al., 1998; Jumate and Manea, 2011).

In this study, the effect of temperature vis-à-vis curing time on the hydration products of Japan OPC paste was investigated.

2. Materials and methodology

2.1. The materials and sample preparation

The composition and properties of Japan ordinary Portland cement used in making cement paste is shown in Table 1. The cement was mixed with deionized water using the rotary mixer at a constant speed for at least 3mins in water/cement ratio (w/c) of 0.40, cast in 50mm diameter x 100mm height cylindrical stainless steel mold and covered with Para film to avoid water evaporation for 24hrs at room temperature. After the cement paste hardened, this was removed from the mold and cured at 20 and 40 °C temperatures in water

bath for three and 28 days curing period (Dejeto and Kurumisawa, 2015).

2.2. The morphological analysis

Samples were cut into cubes of 5x5x5 mm using a diamond saw. Initial weights were measured. The samples were oven dried at 105 °C for 24 hrs, then immersed in acetone to interrupt hydration reaction and subsequently placed in a vacuum desiccator for 24 hrs. These were molded into epoxy resin and hardened for at least 48hrs. The surfaces were polished using the course to fine abrasive paper.

Finally, a 0.25 μm diamond paste was used for final polishing. These were then freeze-dried using Eyela Freeze Dryer model FD-1000 for 24hrs.

Prior to Backscattering Electron Images (BEI)/ Scanning Electron Microscope (SEM) analysis, the samples were coated with Platinum (Pt) ions using Jeol Auto fine coater model JFC-1600. The BEI were obtained using Shimadzu model SSX-550 super scan SEM to separate each phase namely: unhydrated cement particle (UH), Portlandite (CH), calcium silicate hydrate (C-S-H) and pores. Each phase has different density; therefore the brightness of each phase was different. White appearance is identified as UH, bright gray is CH, dark gray is C-S-H and the black spots are pores (Dejeto and Kurumisawa, 2015; Kurumisawa and Nawa, 2016).

Table 1: Composition and properties of Japan OPC (Dejeto and Kurumisawa, 2015)

Chemical analysis (%)		Normative phase composition	Bogue Eqn. (%)	Rietveld Method (%)	Density (g/cm³)	Surface area (cm²/g)
SiO_2	21.56	C_3S	70.76	65.60	3.16	3310
Al_2O_3	4.68	C_2S	8.83	12.40		
Fe_2O_3	2.98	C_3A	7.37	7.20		
CaO	65.63	C_4AF	9.06	12.50		
MgO	1.30	$CaSO_4.2H_2O$		0.00		
SO_3	1.90	$CaSO_4.1/2H_2O$		2.20		
Na_2O	0.33	MgO		0.00		
K_2O	0.39	$CaSO_4$		0.10		
TiO_2	0.23	CaO		0.00		
P_2O_3	0.27					
MnO	0.14					
Cl	0.005					

2.3. The mineralogical analysis

The samples used in BEI/SEM analysis were crushed and screened to 2.5-5 mm sized aggregates using a hammer, and then ground using Fritsch pulverisette 5 ball mills at 300 rpm for 3mins. The powdered samples were mixed with 10% Al_2O_3, an ultra-pure agglomerate-free precision aluminum oxide by Baikalox, Baikowski International Corporation as standard reference material for XRD/Rietveld analysis. Siroquant software ver. 3 was employed to interpret the Rigaku X-ray Diffractometer (XRD) data (Dejeto and Kurumisawa, 2015).

3. Results and discussion

The comparative BEI/SEM images of Japan OPC paste with a water/cement ratio (w/c) of 0.40

cured at different temperature and time is shown in Fig. 1.

It can be seen that there are UH: unhydrated cement particle (white color), CH: Portlandite (light gray), C-S-H: calcium silicate hydrate (dark gray), and P: pores (black), as revealed in Figs. 1a-1d. The main characteristic features observed are the presence of Aft (Fig. 1b) and AFm (Fig. 1d), reduction of pores and unhydrated cement particles despite curing at higher temperature and longer time.

The comparative composition and mineralogical analysis of OPC before and after hydration are shown in Table 2. The residual unhydrated cement refers to the sum of C_3S, C_2S, C_3A, C_4AF, and gypsum product (Bassanite and Anhydrite). The CH and AFt denote the proportions of respective hydration products; AFm denotes the sum of AFm, Ms, and H hydrates (Table 2).
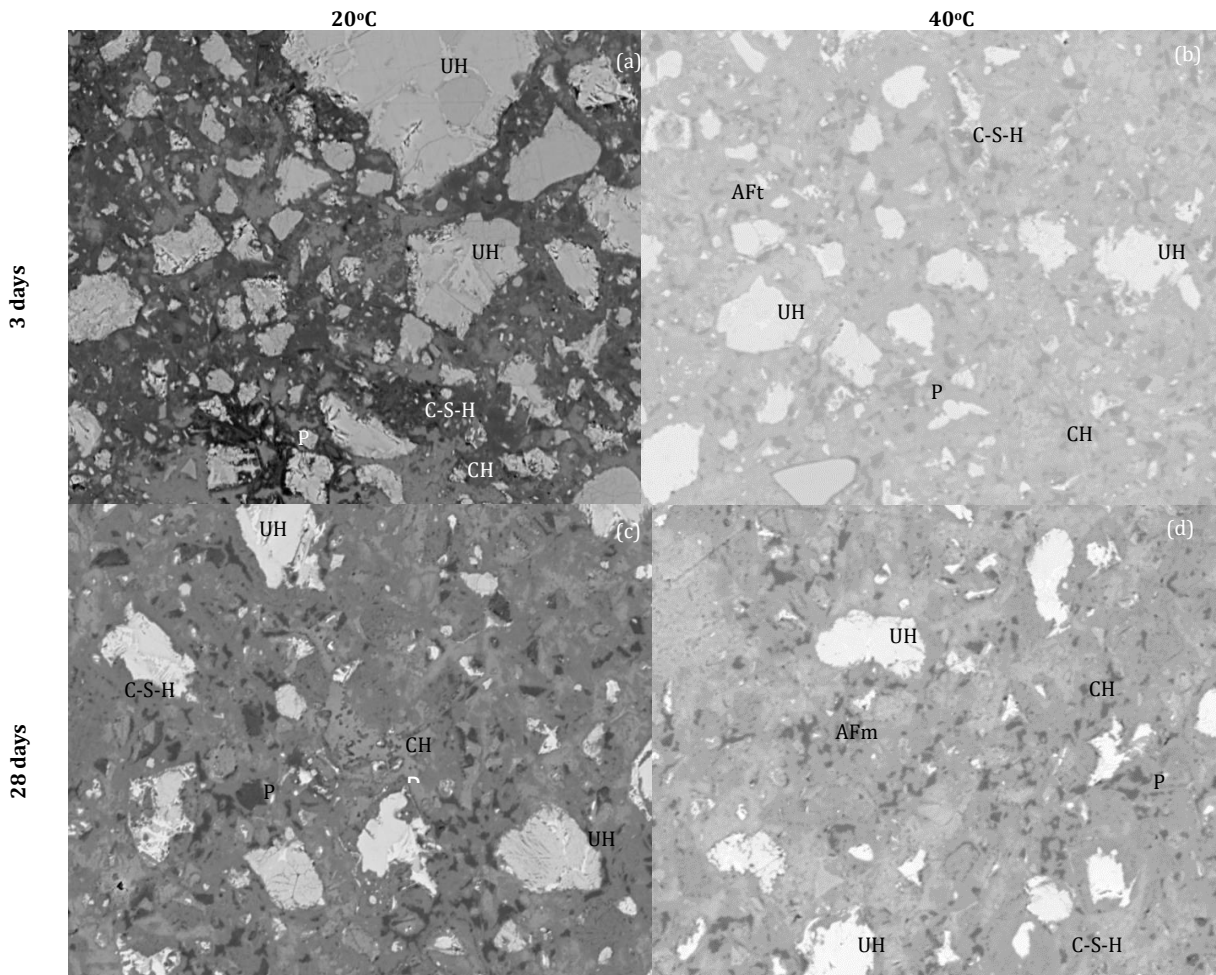
Fig. 1: The BEI/SEM images (150x200μm) of Japan OPC paste with a water/cement ratio (w/c) of 0.40 cured at different temperature and time: three days (a) 20°C, (b) 40°C and 28 days (c) 20°C, (d) 40°C. *Note*: UH: unhydrated cement particle (white color), CH: Portlandite (light gray), C-S-H: calcium silicate hydrate (dark gray), P: pores (black), Aft: Ettringite, and AFm: monosulfoaluminate

Table 2: The comparative composition of Japan OPC before and after hydration at the different curing temperature and time

Chemical Analysis (%)		Phases (%)	Unhydrated cement (UH)	3 days		28 days	
				20°C	40°C	20°C	40°C
SiO$_2$	21.56	Amorphous phase (C-S-H)		54.91	52.89	61.75	61.75
Al$_2$O$_3$	4.68	Alite (C$_3$S)	65.60	16.28	17.66	2.70	4.72
Fe$_2$O$_3$	2.98	Belite (C$_2$S)	12.40	9.34	9.35	8.60	6.05
CaO	65.63	Aluminate (C$_3$A)	7.20	0.90	0.76	1.97	1.62
MgO	1.30	Ferrite (C$_4$AF)	12.50	2.18	1.22	0.98	1.18
SO$_3$	1.90	Bassanite	2.20				
Na$_2$O	0.33	Anhydrite	0.10				
K$_2$O	0.39	Periclase (α-Al$_2$O$_3$)	0.22				
TiO$_2$	0.23	Portlandite (CH)		13.48	16.15	17.80	20.06
P$_2$O$_3$	0.27	Ettringite (AFt)		1.17	0.12		
MnO	0.14	Monosulfoaluminate (AFm)		0.39	0.06	2.65	3.10
Cl	0.005	Calcium Aluminum hyd. (Ms)				1.96	
		Calcite 1		1.12		1.03	0.59
		Hemicarbonate			1.51	0.54	0.93

The CH is one of the major hydration product develop at 40°C for 28 days curing period. It has a mineralogical composition equivalent to 20.06% compared to 17.80% as OPC cured at room temperature (Table 2). The C-S-H denotes the proportion of amorphous substances determined by α-Al$_2$O$_3$ in the internal standard (Kumar et al., 2014). There was no substantial difference in C-S-H composition which is equal to 61.75% at 20°C

and 40°C curing temperature in 28 days curing period.

The conversion of ettringite (AFt) to monosulfoaluminate (AFm) phase from 0.12% to 3.10% was also detected at higher curing temperature and longer time. This was due to low concentration of sulfate present that resulted to less stable ettringite at early hydration period and converted to monosulfoaluminate as shown in Table 2.

The AFt phase is stable as long as there is sufficient amount of gypsum available (Young et al., 1998). Once gypsum is depleted, the AFt and C_3A react further to form the AFm phase. The AFm is the stable phase in mature cement paste and concrete. The proportion of AFt and AFm formed during hydration at lower curing temperature are smaller than those cured at higher temperature due to stagnation in the reaction of C_3A and C_4AF in the early hardening of cement paste (Young et al., 1998).

The Portlandite is the major crystalline phase identified all throughout the study at different magnitudes (Fig. 2). Detection of C-S-H phase is not possible since it is non-crystalline/amorphous in nature. Both CH and C-S-H shows greater proportion of hydration product at higher curing temperatures and time.

The unhydrated cement compounds (alite, belite, and calcite), traces of calcium aluminum hydrate and hemicarbonate were detected in the XRD/Rietveld analysis. These have trends similar with the reaction rates of CaO/SiO_2 mole ratio of C-S-H from the mass balance of CaO and SiO_2 which was determined from the proportion of CH and the reaction rate of C_3S and C_2S at longer curing period (Young et al., 1998; Feng et al., 2004).

The strength development of cement paste is entirely owed by the hydration of calcium silicates (C_3S and C_2S) in the early days of hydration. The major component responsible for the strength generation is the C-S-H (Feng et al., 2004).
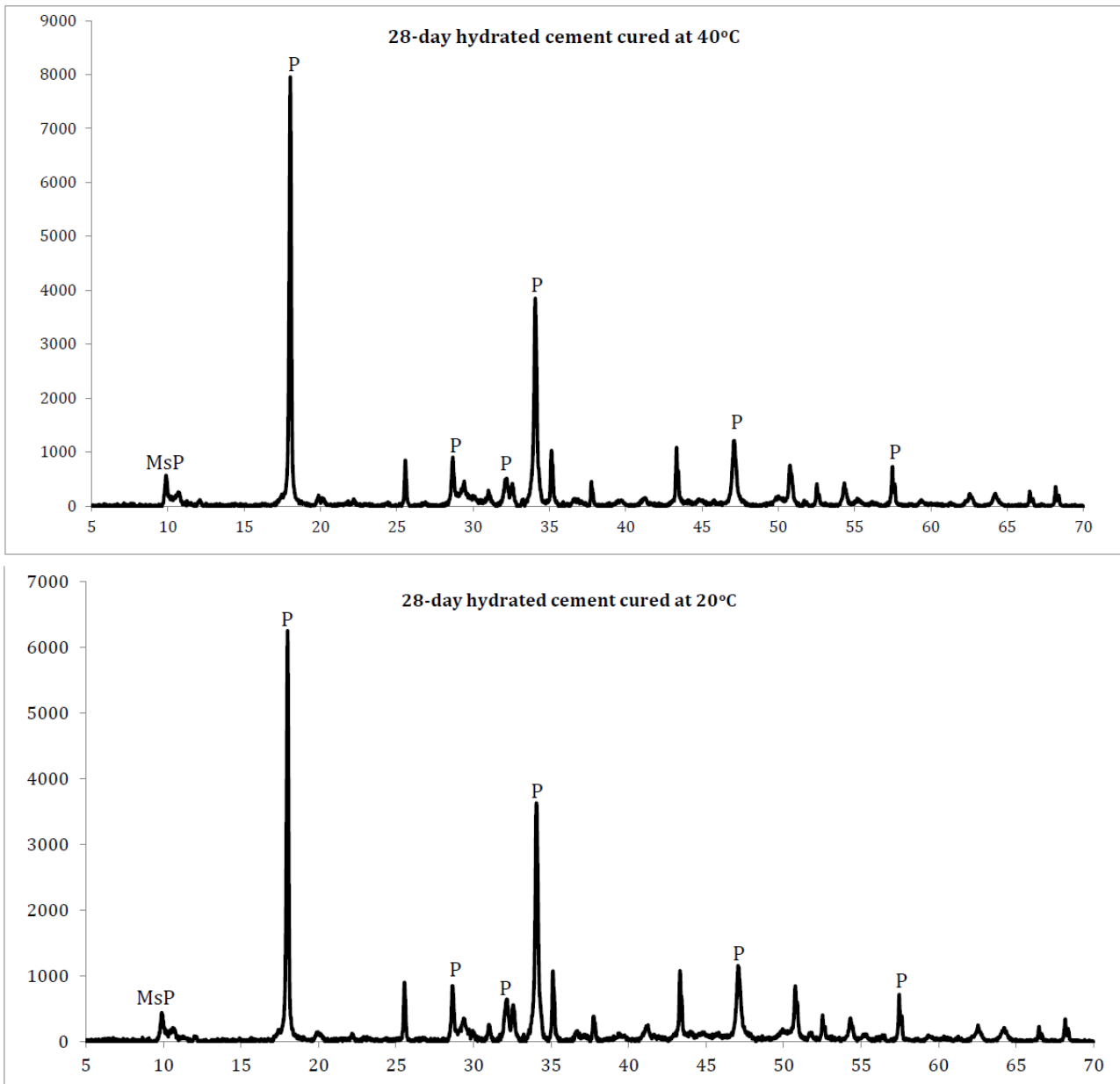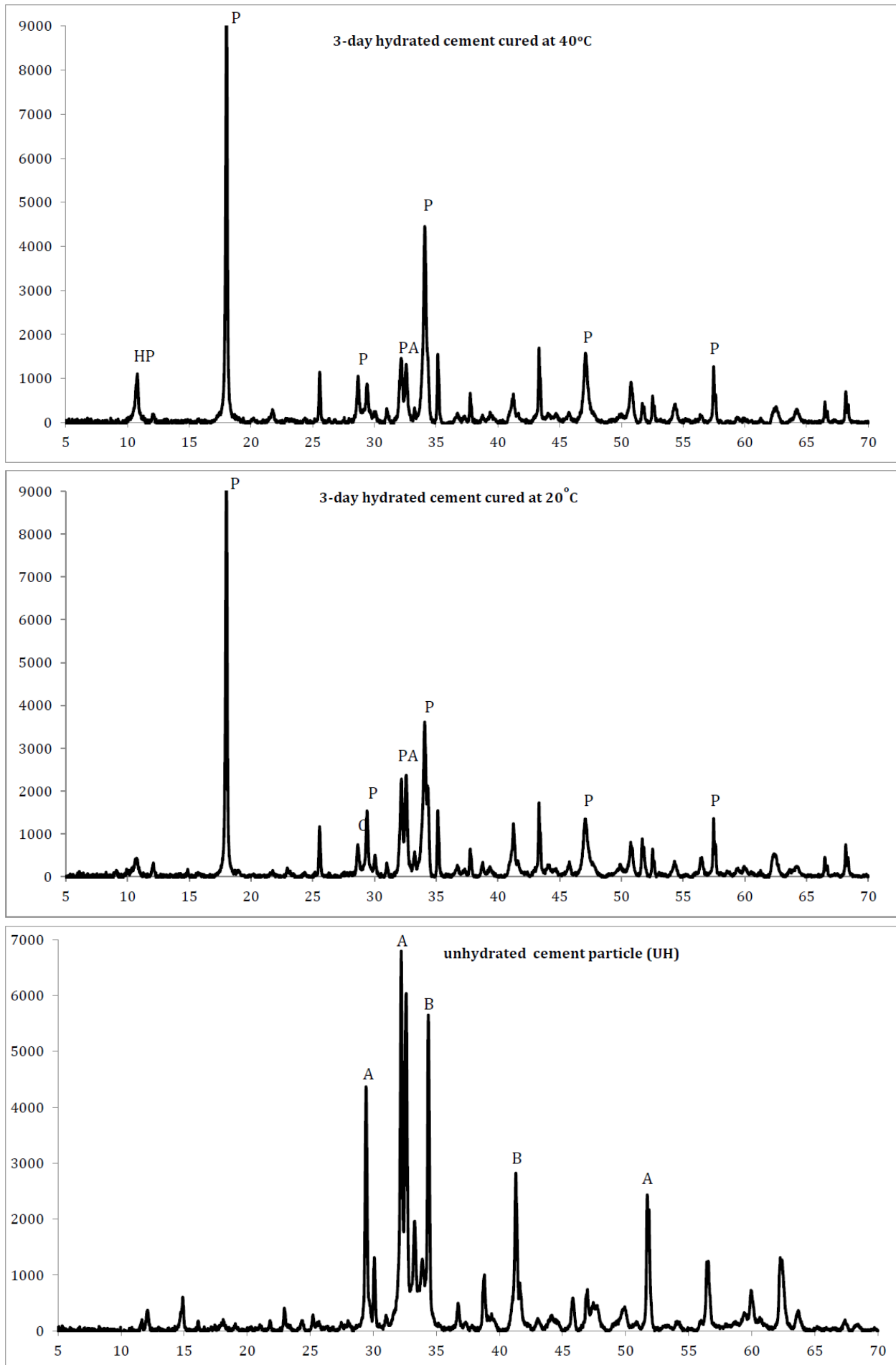
Fig. 2: The comparative XRD/Rietveld analysis of Japan OPC paste cured at different temperature and time. A: alite (C_3S), B: belite (C_2S), and C: calcite (CaO), and P: Portlandite, Ms: calcium aluminum hyd. H: Hemicarbonate

The rise in heat particularly in the early hydration reaction affects the C_3S and C_3A which are characterized by highly exothermic reactions. The fast hydration in the initial stage leads to a more heterogeneous distribution of the hydration products as the hydrated precipitate around the clinker particles and build up a dense inner shell around the clinker. At low temperature, for instance, hydration starts very slowly which allows the dissolved ions more time for diffusion before the hydrates precipitate (Lothenbach et al., 2007; Elkhadiri et al., 2009).

4. Conclusion

The hydration reaction product of ordinary Portland cement (OPC) paste cured at 40 ^{o}C produced greater amount of hydrated compounds compared to cement paste cured at room temperature (20 ^{o}C) in both three days and 28 days period. The Portlandite phase, for example, shows the greatest amount formed at higher curing temperature compared to curing at room temperature. This is due to the acceleration of hydrates which is characterized by a highly exothermic reaction. The hydration reaction starts very slowly at low temperatures that allow the dissolved ions more time for diffusion before the hydrates precipitate. For fast curing period, it is possible to work with cement paste and concrete at elevated temperatures.

Acknowledgment

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