Advanced Construction Materials.

HW#3.

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95/100

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박 지 슬

1. $100cm^3$ cement was mixed with w/c of 0.5. Determine porosity of cement hydrates with 0%, 25%, 50%, and 100% degrees of hydration, respectively. Assume density of cement as $3.14 g/cm^3$. (20pt)

1) volume of water V_w.

$$w/c = 0.5 = \frac{1g/cm^3 \times V_w}{3.14 g/cm^3 \times 100 cm^3}$$

$$V_w = 0.5 \times 3.14 g/cm^3 \times 100 cm^3 / (1g/cm^3) = 157 cm^3$$

2) porosity.

① DoH = 0%.

[w | c]

$$porosity = \frac{157}{100+157} = 61.1\%$$ ✓

② DoH = 25%.

[w | cp | c]

$cp = 50 cm^3$

$w = 157 - 25 = 132$

$$porosity = \frac{132}{257} = 51.4\%$$ ✓

③ DoH = 50%.

[w | cp | c]

$cp = 100 cm^3$

$w = 157 - 50 = 107$

$$porosity = \frac{107}{257} = 41.6\%$$ ✓

④ DoH = 100%.

[w | cp]

$cp = 200 cm^3$

$w = 157 - 100 = 57$

$$porosity = \frac{57}{257} = 22.2\%$$ ✓

2. High temperature XRD experiment was performed on portlandite. Based on the obtained peak positions (d-space, Å) at different temperatures, calculate thermal expansion coefficient (α_v) of portlandite. ($\Delta V / V_0 = \alpha_v \Delta T$.) where ΔV is volume variation, V_0 is initial volume at ambient temperature of 30°C, and ΔT is temperature variation. Discuss thermal expansion behavior of different lattice parameters of a and c. (30pt).

1) crystal system of portlandite : Trigonal

2) (hkl) & d relation : $\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$

3) ① Temp = 30°C.

$(h,k,l) = (0,0,1)$, $\frac{1}{4.9115^2} = \frac{1}{c^2}$, $c = 4.9115$

$(h,k,l) = (1,0,0)$, $\frac{1}{3.6005^2} = \frac{4}{3} \cdot \frac{1}{a^2}$, $a = 4.1575$

$(h,k,l) = (0,0,2)$, $\frac{1}{2.456^2} = \frac{4}{c^2}$, $c = 4.912$

⇒ $a = 4.1575$. $c_{avg} = 4.9118$. ✓

$\therefore V_{cell} = \frac{\sqrt{3}}{2} a^2 c = 73.5251$.

② Temp = 100°C

(h,k,l) = (0,0,1) $c = 4.9312$

(h,k,l) = (1,0,0) $\frac{1}{3.6031^2} = \frac{4}{3} \cdot \frac{1}{a^2}$, $a = 4.1605$

(h,k,l) = (0,0,2) $c = 2 \times 2.4657 = 4.9314$

⇒ $a = 4.1605$, $c_{avg} = 4.9313$

$\therefore V_{cell} = \frac{\sqrt{3}}{2} a^2 c = 73.9236$

③ Temp = 200°C.

Calculate a, c, and Vcell in the same way as above,

$a = \frac{2 \times 3.6071}{\sqrt{3}} = 4.1651$, $c = 4.9615$, $2 \times 2.4806 = 4.9612$, $c_{avg} = 4.9614$

$\therefore V_{cell} = \frac{\sqrt{3}}{2} a^2 c = 74.5394$

④ Temp = 300°C.

$a = \frac{2 \times 3.6111}{\sqrt{3}} = 4.1697$, $c = 4.9911$, $2 \times 2.4956 = 4.9912$, $c_{avg} = 4.9912$

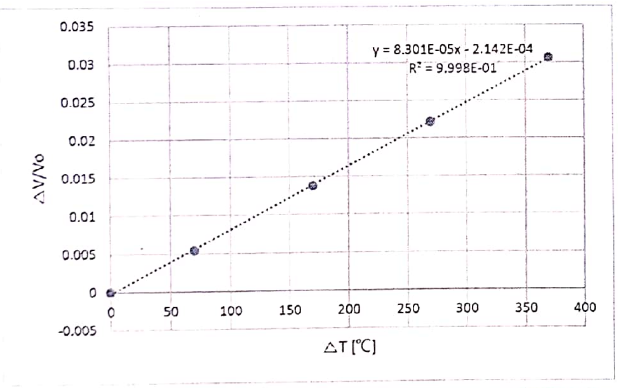
$\therefore V_{cell} = \frac{\sqrt{3}}{2} \times a^2 c = 75.1528$

⑤ Temp = 400°C

$a = \frac{2 \times 3.6151}{\sqrt{3}} = 4.1744$, $c = 5.0212$, $2 \times 2.5107 = 5.0214$, $c_{avg} = 5.0213$

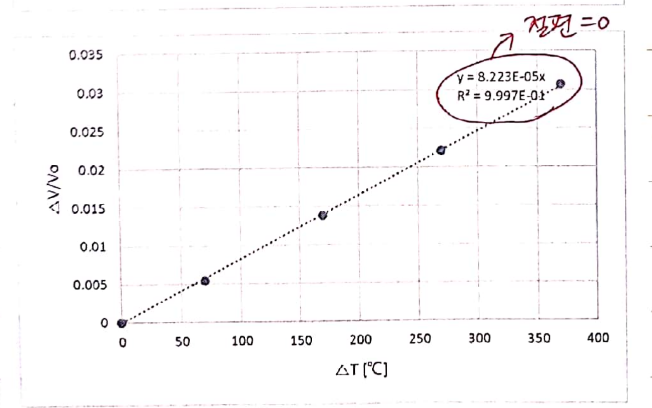
$\therefore V_{cell} = \frac{\sqrt{3}}{2} a^2 c = 75.7766$.

4) From the result, we obtain the plot representing the relation between $\Delta V / V_0$ & ΔT.



T [°C]	ΔT [°C]	V [Å^3]	ΔV [Å^3]	ΔV/Vo
30	0	73.5251	0	0
100	70	73.9236	0.3985	0.00542
200	170	74.5394	1.0143	0.013795
300	270	75.1528	1.6277	0.022138
400	370	75.7766	2.2515	0.030622

$\therefore \alpha_V = 8.223 \times 10^{-5} / K$



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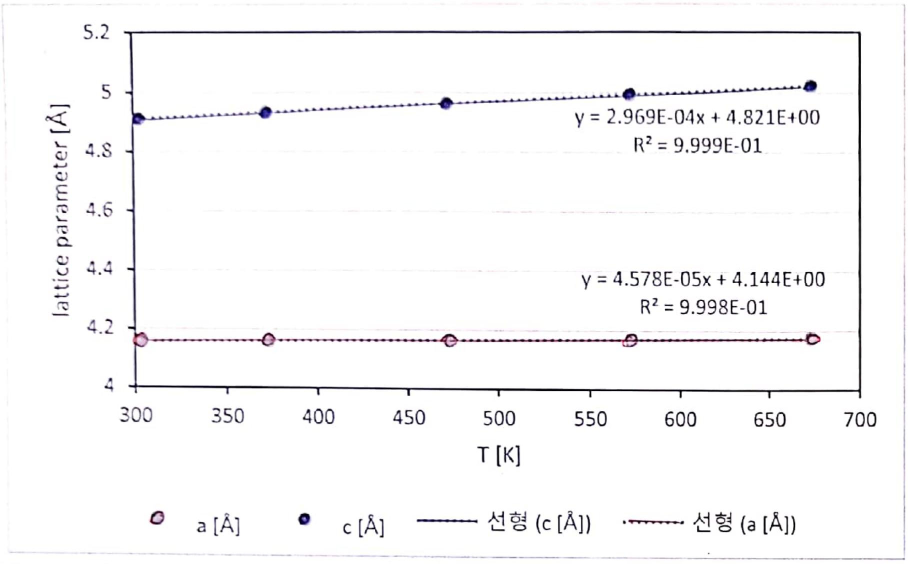
5) Thermal expansion behavior of lattice parameters a and c.

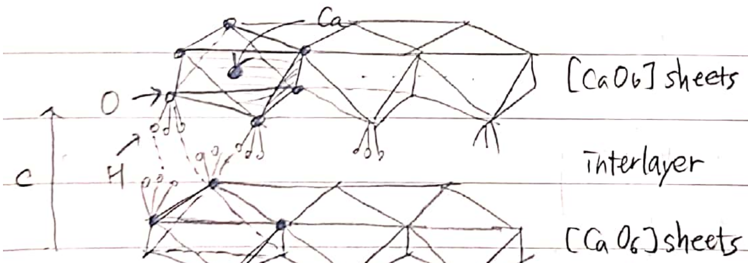


T [°C]	T [K]	a [Å]	c [Å]
30	303.15	4.1575	4.9118
100	373.15	4.1605	4.9313
200	473.15	4.1651	4.9614
300	573.15	4.1697	4.9912
400	673.15	4.1744	5.0213

$$\left(\begin{array}{l} c = 4.821 + 2.969 \times 10^{-4}\, T \\ a = 4.144 + 4.578 \times 10^{-5}\, T \end{array} \right)$$

⇒ As temperature increases, both unit-cell parameter a & c increase, thus cell volume V also increases. However, the structural expansion occurs at a much higher rate along the c-axis than along the a-axis, which is highly anisotropic.

Since the portlandite structure is composed of (001) $[CaO_6]$ octahedral sheets



that are held together via H-mediated dispersive forces. (O---H, H---H)

The cell parameter c can be treated as the sum of $[CaO_6]$ layer and of interlayer. With increasing temperature, the $[CaO_6]$ layer thickness increases slightly, whearas the interlayer spacing increases rapidly due to much weaker forces between neighboring $[CaO_6]$ sheets than within the sheets themselves.

Reference : Anisotropic thermal expansion and hydrogen bonding behavior of portlandite.
: A high temperature neutron study (April, 2007, Journal of Solid State. Chem.)

MooKeuk

3. Quantatative X-ray diffraction was performed to evaluate the chemical reactivity of new cement admixture (X). To consider the amount of amorphous material, internal standard method was adopted by mixing 20 wt% of TiO_2 in total weight of measure sample after removing free water in samples.

Anticipated chemical reaction from the admixture X is :

C + X + water → C-S-H + CH ✓

(C ← cement; C-S-H ← non-crystalline; CH ← $Ca(OH)_2$)

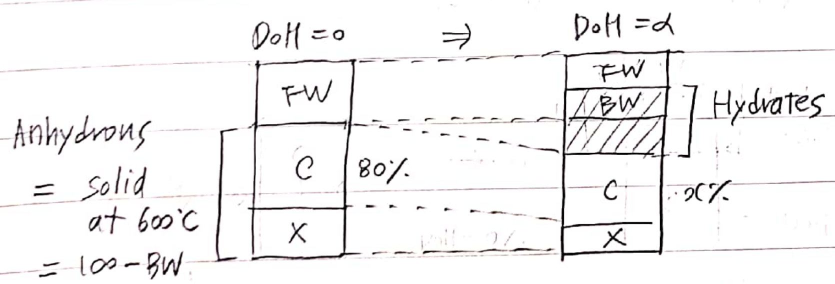
TGA was also performed for quantification of chemically bound water. Mass of bound water was determined by 100% − mass % of solid at 600°C

Draw following curves considering normolization to anhydrous materials.

1. BW versus time
2. CH content versus time
3. C-S-H content versus time

Which one do you think is the most appropriate to express the degree of hydration of this binary system? (50 pt)

- The calculation process and graphs are attached next page.
- We can define the DoH of cement as the ratio of "the amount (wt) of cement reacted with water and X" to "the initial amount of cement" both which are normalized to solid at 600°C.



$$\Rightarrow DoH = \frac{80 - x}{80} \times 100 \ (\%)$$

From the result, we found that CH content is proportional to DoH.

Therefore, CH content is the most appropriate to express the DoH of this system. ?

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0) Given data

	days	0	1	14	28	56	77
QXRD result	C	80	32	12.8	5.1	2	0.82
	X	20	15.1	12.4	10.3	9.1	8
	CH	0	17.9	31.8	36.6	38.9	40.18
	TiO2	none	35	43	48	50	51
	SUM	100	100	100	100	100	100
TGA result	BW	none	25.2	27.4	28.1	29.2	30.1

1) IS =>20%

days	0	1	14	28	56	77	
C'	80	18.29	5.95	2.13	0.80	0.32	=C*20/TiO2
X'	20	8.63	5.77	4.29	3.64	3.14	=X*20/TiO2
CH'	0	10.23	14.79	15.25	15.56	15.76	=CH*20/TiO2
TiO2'	none	20.00	20.00	20.00	20.00	20.00	=TiO2*20/TiO2
CSH'	0	42.86	53.49	58.33	60.00	60.78	=100-(C'+X'+CH'+TiO2')
sum		100	100	100	100	100	=C'+X'+CH'+TiO2'+CSH'

2) exclude IS

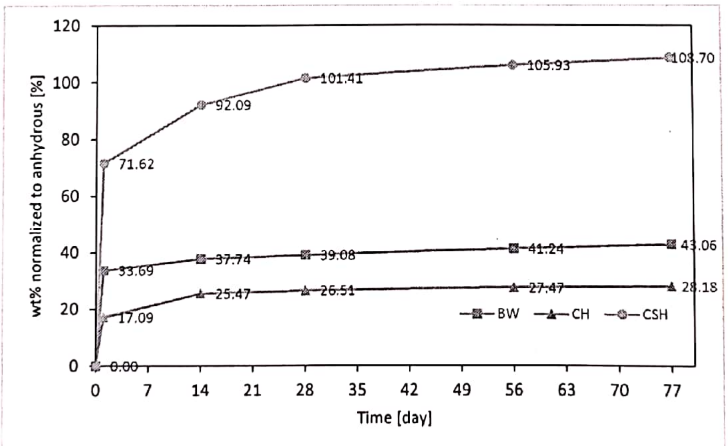
days	0	1	14	28	56	77	
C''	0	22.86	7.44	2.66	1.00	0.40	=C'*100/80
X''	80	10.79	7.21	5.36	4.55	3.92	=X'*100/80
CH''	20	12.79	18.49	19.06	19.45	19.70	=CH'*100/80
CSH''	0	53.57	66.86	72.92	75.00	75.98	=CSH'*100/80
sum		100	100	100	100	100	=C''+X''+CH''+CSH''

3) normalized to anhydrous

days	0	1	14	28	56	77	
Solid	-	74.8	72.6	71.9	70.8	69.9	=100-BW
C'''	80	30.56	10.25	3.69	1.41	0.58	=C''*100/solid
X'''	20	14.42	9.93	7.46	6.43	5.61	=X''*100/solid
CH'''	0	17.09	25.47	26.51	27.47	28.18	=CH''*100/solid
CSH'''	0	71.62	92.09	101.41	105.93	108.70	=CSH''*100/solid
BW'	-	33.69	37.74	39.08	41.24	43.06	=BW''*100/solid
sum		133.69	137.74	139.08	141.24	143.06	=C'''+X'''+CH'''+CSH'''

4) wt% normalized to anhydrous vs. time

days	0	1	14	28	56	77
BW	0.00	33.69	37.74	39.08	41.24	43.06
CH	0.00	17.09	25.47	26.51	27.47	28.18
CSH	0.00	71.62	92.09	101.41	105.93	108.70



5) DoH of cement vs. BW, CH, CSH

days	1	14	28	56	77	
C reacted with W	49.44	69.75	76.31	78.59	79.42	=80-C'''
DoH of C	61.80	87.19	95.38	98.23	99.28	=(80-C''')/80*100
BW : DoH of C	0.55	0.43	0.41	0.42	0.43	
CH ; DoH of C	0.28	0.29	0.28	0.28	0.28	
CSH : DoH of C	1.16	1.06	1.06	1.08	1.09	