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Physics-chemical study of hydration process of three calcium aluminate phase and Metakaolin

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Abstract: This research based on X-Ray Diffraction, SEM and chemical analyses were revealed that decreasing of $\text{Ca}(\text{OH})_2$ phase content and increasing of C_3AH_6 and trisulfate aluminate calcium-3 as the stable phases for the hydration period of first 30 to 60 minutes when comparing K-crent doping to the phase to without any doping. Also results have been proposed in case of doping metakaoline to draw structural analogies as formation of stable hydrated phases and the decrease of new formed unstable crystalline metaphases in the early stage of $3\text{CAO}\cdot\text{Al}_2\text{O}_3$ hydration process.

Introduction

Tricalcium aluminate (C_3A), which could compose up to 15% of the Portland cement, reacts very quickly with water to form calcium hydro aluminates that induces the stiffening of cement paste. To avoid this phenomenon, calcium sulphate is usually added which leads to the formation of calcium three sulfoaluminate with a slow hydration [1-2]. In last 5-6 years research for obtaining of a new crystallizing component such as crent from kaoline, basalts and zeolites has been successfully going on at the Centre for Chemistry and Technology of New Materials, National University of Mongolia. Such research also have conducted in high developed countries since ninety years. It was established that cement compressive strength increased by $100\text{-}250\text{ kg/cm}^2$ when doped 5-10% of Crent to the cement weight [3-6].

However, there were a lot of complicated situation with crystal structure formation and crystal growth mechanisms during the cement hydration processes [8-10, 16].

In recent years many researchers have interested in the study of crystallizing a substance which can serve as crystal nuclei centre and accelerate their crystal growth process [11-15].

Portland cement is a fine-dispersial system consisting of multiple phases, therefore, understanding its hydration process means studying of its each phase hydration processes [17].

Theoretical and practical consequences of this work were considered the possibility to decrease $\text{Ca}(\text{OH})_2$ phase formation and increase C_3AH_6 and trisulfate aluminate calcium as the stable phases of cement hydrated compounds by using the K-crent doping. These stable phases' formation would increase of cement paste compressive strenght by $100\text{-}250\text{ kg/cm}^2$ when doping this Crent to the C_3A as cement interphases.

Experimental

Making mineral additives

Kaolin from Khongor-Ovoo deposit of Dornogovi province's was employed in this

study. The chemical composition of kaolin is shown in table 1.

Table 1. Chemical analysis results of kaolin, %

Samples	SiO ₂	Al ₂ O ₃	TiO ₂	Fe _{total}	CaO	MgO	L.O. I
Kaolin	50.18	28.13	0.05	0.32	3.93	0.3	4.23

Samples were grinded to 80 μm by ball mill and then sieved to similar size. Metakaolin samples prepared for heat treatment and were heated at 500, 600, 700°C for 2-12 hour in laboratory furnace, then activated them by 20% sulphuric acid for 2 hour by mixing at room temperature. These activated products were grinded until size of 80 μm.

Sample preparation

C₃A standard samples and gypsum were sieved through 80μm sieves and their mixtures with a stoichiometric ratio homogenized in ball mill for 2 hour.

X-Ray diffraction (XRD), Thermal analysis (TG/DTA) and tunnelling electron microscope XRD measurements were carried out with DRON-2, Russia, using Co-filtered Kα, step size 0.001°. TG/DTA were undertaken with DERIVATOGRAPH, Hungary, thermo analyzer at a heating rate of 10°C/min using α-Al₂O₃ as a reference material.

results and discussion

XRD study on influence of metakaolin for the early hydration of 3CAO·Al₂O₃

The sample of C₃A and the mixture of C₃A and metakaolin as we've abbreviated it K-cment were prepared and were hydrated for 30 minutes and for an hour. The X-ray fluorescence analysis of those hydrated samples was done (see Figures 1-4 and Table 2-5).

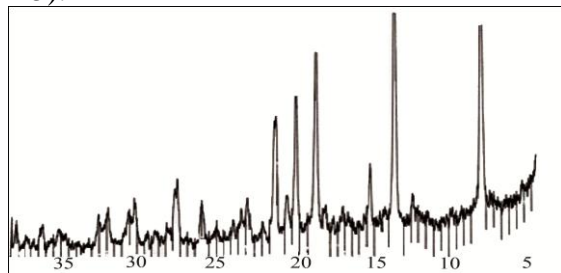


Figure 1. XRDA results for 30 min hydrated C₃A phase

Table 2. XRDA results for 30 min hydrated C₃A phase

№	d, Å	2θ, grade	Intensity, %	Phases
1.	7.16	7.9	90	CAH ₁₀
2.	3.80	14.75	100	C ₂ AH ₈
3.	3.63	15.25	20	C ₄ AH ₁₃
4.	3.26	17.2	10	CAH ₁₀
5.	2.78	20.27	50	C ₂ AH ₈
6.	2.628	21.7	40	Ca(OH) ₂
7.	2.11	27.3	20	CAH ₁₀
8.	1.90	30.5	10	C ₃ A
9.	1.817	31.96	15	C ₃ AH ₆

The X-ray diffraction analysis results for C₃A phase hydrated for 30 min show high intensity diffraction lines of CAH₁₀ at d=7.16Å, d=2.88Å, and of C₂AH₈ at d=3.80Å, d=2.78Å and medium size peaks of Ca(OH)₂ at d=2.628Å, d=1.92Å, respectively.

Also there were some low intensity peaks of calcium aluminate's phase hydration product such as C₃AH₆ at d=1.817Å, d=1.574Å and d=2.226Å. Moreover, C₃A peak shown at d=1.90Å for uncompletely hydrated phases

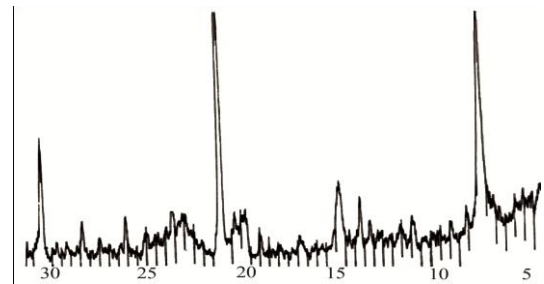


Figure 2. XRD results for 1 hour hydrated C₃A phase

Table 3. XRDA results for 1 hour hydrated C₃A phase

№	d, Å	2θ, degree	Intensity, %	Phases
1.	7.16	7.9	80	CAH ₁₀
2.	5.14	10.95	8	C ₃ AH ₆
3.	4.25	13.2	12	C ₂ AH ₈
4.	4.08	13.72	10	C ₃ A
5.	3.80	14.75	25	C ₂ AH ₈
6.	3.366	16.81	25	C ₃ AH ₆
7.	2.69	21.05	100	C ₄ AH ₁₃
8.	2.45	23.63	18	C ₂ AH ₈
9.	1.817	30.65	30	C ₃ AH ₆

The X-ray diffraction analysis results for C₃A phase hydrated for an hour show diffraction lines of CAH₁₀ at d=7.16Å, d=5.39 Å, d=2.88Å, C₂AH₈ at d=10.7Å, d=2.39Å,

$d=4.25\text{\AA}$, $d=3.80\text{\AA}$, $d=2.86\text{\AA}$, $d=2.78\text{\AA}$, $d=2.49\text{\AA}$, $d=2.45\text{\AA}$ and of C_4AH_{13} at $d=2.69\text{\AA}$ and $d=2.04\text{\AA}$, respectively.

The presence of diffraction lines of C_3AH_6 at $d=5.14\text{\AA}$, $d=3.366\text{\AA}$, $d=2.469\text{\AA}$, $d=2.30\text{\AA}$, $d=1.817\text{\AA}$ and that of C_3A at $d=4.08\text{\AA}$ shows increase in calcium hydro aluminates compounds content in comparison to the samples hydrated for 30 minutes. But the existence of spectral line of C_3A phase shows that the reaction wasn't even completed for the given time.

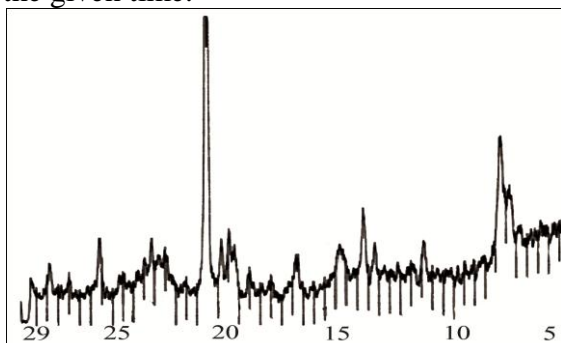


Figure 3. XRD results for 30 min hydrated C_3A phase with metakaolin

Table 4. XRD results for 30 min hydrated C_3A phase with metakaolin

No	d, Å	2θ, degree	Intensity, %	Phases
1.	5.14	11	15	C_3AH_6
2.	4.05	13.75	30	C_4AH_{13}
3.	3.80	14.75	20	C_2AH_8
4.	3.366	16.75	15	C_3AH_6
5.	2.816	20	20	C_3AH_6
6.	2.78	20.4	18	C_2AH_8
7.	2.69	21	100	C_4AH_{13}
8.	2.226	25.67	15	C_3AH_6
9.	2.17	26.15	20	C_4AH_{13}
10.	2.043	28.85	14	C_3AH_6

The X-ray diffraction analysis results for C_3A phase with metakaolin as we've abbreviated it as K-crent addition hydrated for 30 min show low intensity spectral lines of CAH_{10} at $d=14.30\text{\AA}$, $d=2.88\text{\AA}$ and of C_4AH_{13} at $d=8.05\text{\AA}$ and its high intensity peaks at $d=4.05\text{\AA}$, $d=2.17\text{\AA}$ etc, respectively

Also there were some low intensity peaks of calcium aluminate's phase hydration product formed as C_2AH_8 at $d=4.25\text{\AA}$, $d=2.45\text{\AA}$ and medium intensity peaks at $d=3.80\text{\AA}$, $d=2.86\text{\AA}$, $d=2.78\text{\AA}$ which show hydration was rapid for this system.

But there were C_3AH_6 hydrated compound's medium intensity $d=5.14\text{\AA}$, $d=3.366\text{\AA}$, $d=2.816\text{\AA}$, $d=2.226\text{\AA}$, $d=2.043\text{\AA}$ peaks and low intensity $d=3.149\text{\AA}$ and very low intensity C_3A phase peak at $d=3.34\text{\AA}$, respectively.

From these C_3A with K-crent addition XRDA results can be suggested that there were increased the content of calcium hydroaluminate phase if compared them to the XRD patterns of C_3A phase for 30 min time period.

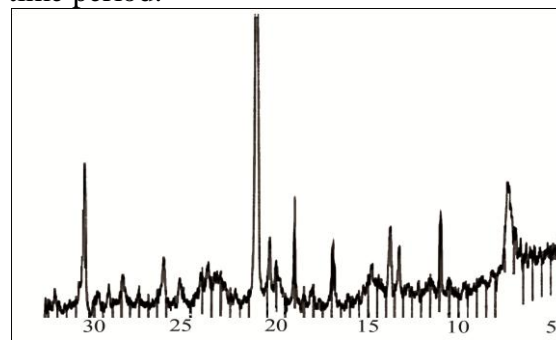


Figure 4. XRD results for 1 hour hydrated C_3A phase with K-crent

Table 5. XRD results for 1 hour hydrated C_3A phase with K-crent

No	d, Å	2θ, degree	Intensity, %	Phases
1.	7.5665	7.35	35	
2.	5.14	11	30	C_3AH_6
3.	3.366	16.75	25	C_3AH_6
4.	3.149	18	35	C_3AH_6
5.	2.816	20	10	C_3AH_6
6.	2.78	20.4	15	C_2AH_8
7.	2.69	21	100	C_4AH_{13}
8.	2.226	25.67	5	C_3AH_6
9.	1.817	30.65	50	C_3AH_6

The X-ray diffraction analysis results of C_3A phase with the addition of K-crent hydrated for an hour show diffraction lines of CAH_{10} at $d=2.88\text{\AA}$, C_2AH_8 at $d=4.25\text{\AA}$, $d=3.80\text{\AA}$, $d=2.45\text{\AA}$, $d=2.39\text{\AA}$ and of C_4AH_{13} at $d=4.05\text{\AA}$, $d=2.69\text{\AA}$, $d=2.36\text{\AA}$, $d=2.17\text{\AA}$, respectively.

The existence of diffraction lines of C_3AH_6 , which is a final product of C_3A phase at $d=5.14\text{\AA}$, $d=3.366\text{\AA}$, $d=3.149\text{\AA}$ and $d=2.226\text{\AA}$ and the absence of diffraction lines of C_3A demonstrate that the addition of K-crent had a positive effect on C_3A phase hydration and the final reaction product C_3AH_6 formed from the intermediate phases, C_2AH_8 , C_4AH_{13}

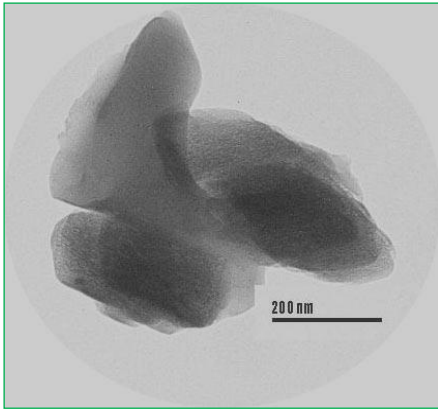


Figure 5. TEM results for 30 min hydrated C₃A phase

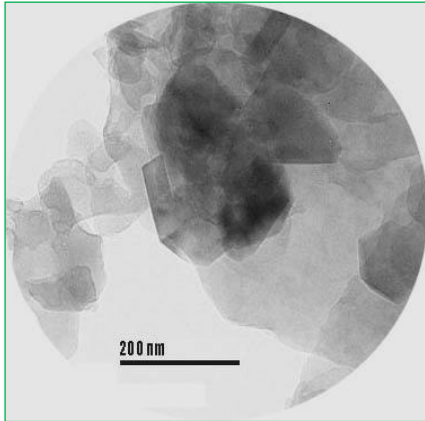


Figure 6. TEM results for 30min hydrated C₃A phase with K-crent

From the TEM analysis results of these hydrated 3CaO·Al₂O₃ and 3CaO·Al₂O₃ + K-crent systems can be concluded that the following reactions take place:

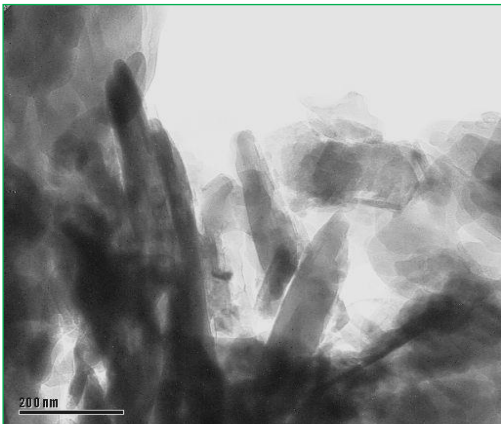
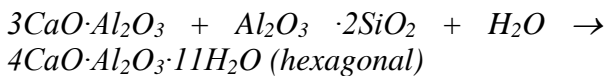
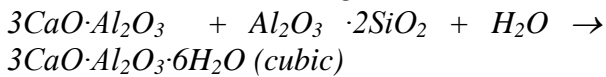
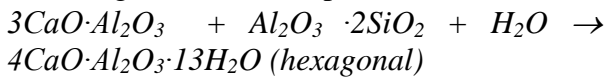


Figure 7. TEM results for 1 hour hydrated C₃A phase

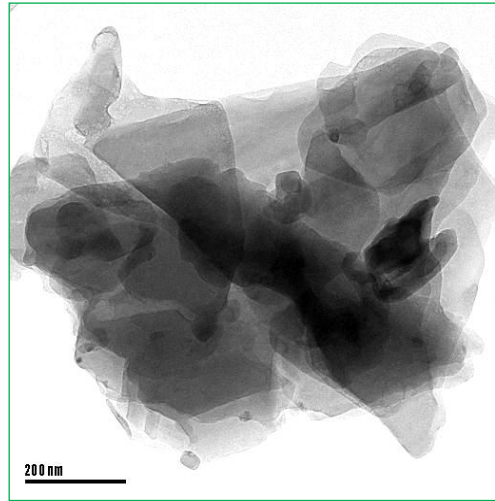


Figure 8. TEM results for 1 hour hydrated C₃A phase with K-crent

From the TEM analysis results of 1 hour hydrated 3CaO·Al₂O₃ and 3CaO·Al₂O₃+K-crent samples can be suggested that crystal hydrates with more stable structures formed as a result of hydration reactions. This was especially the case in the samples with addition of K-crent. This shows that K-crent intensifies the formation of stable crystal hydrates.

Physics-chemical study on synthesis of three calcium aluminate as C₃A phase

Russian standard sample of C₃A was used in this study. One of the main goals of this work was to prepare standard sample in our laboratory. For this, chemically pure CaCO₃ and Al₂O₃ reagents from China were mixed in stoichiometric ratio and were calcined at 1000-1200⁰C for 6 h.

Physical and chemical analyses were done in each aluminate phase prepared. The results are shown below in Table 6.

First of all, the free calcium oxide content for the samples was determined according to the methodology described in materials and methods section. The results of this analysis are shown in Table 6.

The results of compressive strength of Russian standard sample C₃A, the same standard sample with K-crent addition and the C₃A prepared sample with K-crent addition are shown in Figure 9 and in Table 7.

Table 6. Content of CaO free for varous temperature burning

№	Temperature, °C	CaO _{free} , %
1.	1000	17,528
2.	1050	9,215
3.	1100	4,226
4.	1150	0,256
5.	1200	0,112

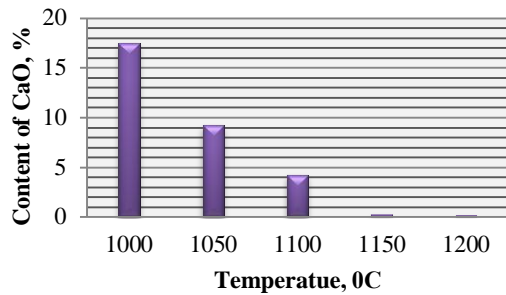


Figure 9. Free CaO content dependence on calcining temperature

Table 7. Study on compressive strength for C₃A with K-crent

Phase composition	COMPRESSIVE STRENGTH, (KG/CM ²)		
	30 min	1hour	1 day
C ₃ A	54	62	71
C ₃ A+K-crent	77	83	90
C ₃ A(sintering)+K-crent	50	74	82

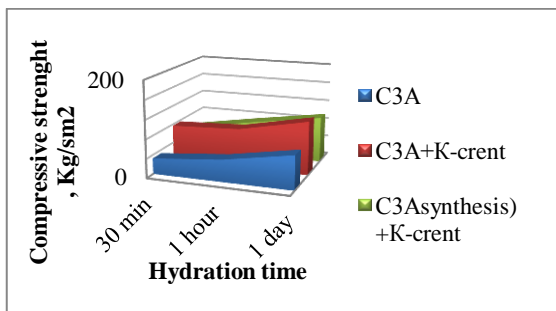


Figure 10. Study on K-crent influence on compressive strength of C₃A phase

The results of above mentioned analysis show that the optimal preparation temperature of C₃A phase is 1150⁰C.

Conclusions

- X-ray Diffraction analysis results show that the final product of hydration C₃AH₆ forms dominantly within 30 to 60 minutes after the addition of K-crent to 3CaO·Al₂O₃ phase.

- TEM analysis results show that compared to 3CaO·Al₂O₃ without the addition of K-crent the one with addition crystallizes with forming of stable crystals with right geometric forms. This supports the results of XRDA.
- X-ray analysis results show that the content of Ca(OH)₂ phase decreases and the formation of trisulfate aluminate calcium phase increases due to the addition of K-crent in “3CaO·Al₂O₃+gypsum” system at the beginning of hydration.

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