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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 $Ca(OH)_2$ 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 $3CAO \cdot Al_2O_3$ 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 100-250 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 formationing 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 $Ca(OH)_2$ phase formation and increase C_3AH_6 and trisulfate aluminate calcium as the stable phases of cement hydrated compoundsby using the K-crent doping. These stable phases' formation would increase of cement paste compressive strenght by 100-250 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_2O_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

C_3A standard samples and gypsum were sieved through 80μm sieves and their mixtures with a stoichiometric ratio homogenized in bal 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-Al_2O_3 as a reference material.

results and discussion

XRD study on influence of metakaolin for the early hydration of $3CAO \cdot Al_2O_3$

The sample of C_3A and the mixture of C_3A and metakaolin as we've abbreviated it K-crent 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).

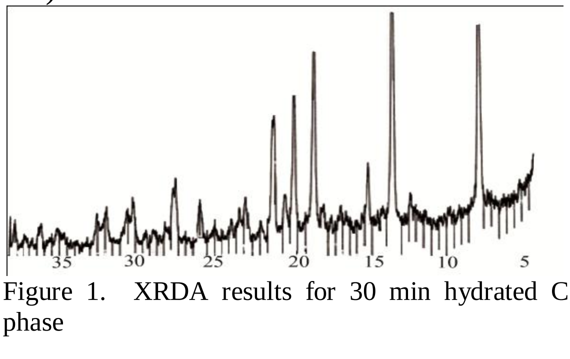

Figure 1. XRDA results for 30 min hydrated C_3A phase

Table 2. XRDA results for 30 min hydrated C_3A phase

№	d, Å	2Θ, grade	Intensity, %	Phases
1.	7.16	7.9	90	CAH_{10}
2.	3.80	14.75	100	C_2AH_8
3.	3.63	15.25	20	C_4AH_{13}
4.	3.26	17.2	10	CAH_{10}
5.	2.78	20.27	50	C_2AH_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_3A
9.	1.817	31.96	15	C_3AH_6

The X-ray diffraction analysis results for C_3A phase hydrated for 30 min show high intensity diffraction lines of CAH_{10} at d=7.16Å, d=2.88Å, and of C_2AH_8 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 C_3AH_6 at d=1.817Å, d=1.574Å and d=2.226Å. Moreover, C_3A peak shown at d=1.90Å for uncompletely hydrated phases

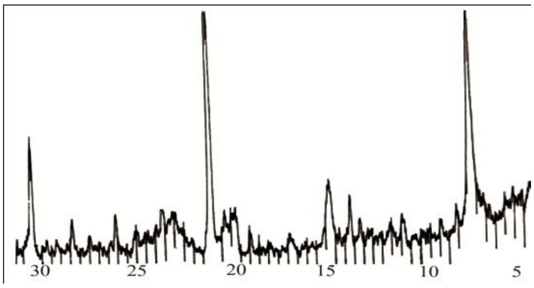

Figure 2. XRD results for 1 hour hydrated C_3A phase

Table 3. XRDA results for 1 hour hydrated C_3A phase

№	d, Å	2Θ, degree	Intensity, %	Phases
1.	7.16	7.9	80	CAH_{10}
2.	5.14	10.95	8	C_3AH_6
3.	4.25	13.2	12	C_2AH_8
4.	4.08	13.72	10	C_3A
5.	3.80	14.75	25	C_2AH_8
6.	3.366	16.81	25	C_3AH_6
7.	2.69	21.05	100	C_4AH_{13}
8.	2.45	23.63	18	C_2AH_8
9.	1.817	30.65	30	C_3AH_6

The X-ray diffraction analysis results for C_3A phase hydrated for an hour show diffraction lines of CAH_{10} at d=7.16Å, d=5.39 Å, d=2.88Å, C_2AH_8 at d=10.7Å, d=2.39Å, d=4.25Å, d=3.80Å, d=2.86Å, d=2.78Å, d=2.49Å, d=2.45Å and of C_4AH_{13} at d=2.69Å and d=2.04Å, respectively.

The presence of diffraction lines of C_3AH_6 at d=5.14Å, d=3.366Å, d=2.469Å, d=2.30Å, d=1.817Å and that of C_3A at d=4.08Å 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.

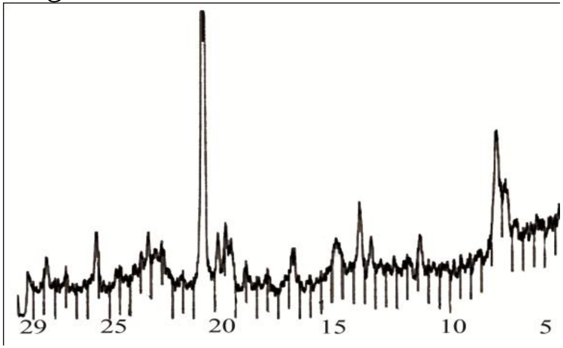

Figure 3. XRD results for 30 min hydrated C_3A phase with metakaolin

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

№	d, Å	2Θ, degree	Intensity, %	Phases
1.	5.14	11	15	C_3AH_6
2.	**4.05**	**13.75**	**30**	$\mathbf{C_4AH_{13}}$
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**	$\mathbf{C_4AH_{13}}$
8.	2.226	25.67	15	C_3AH_6
9.	**2.17**	**26.15**	**20**	$\mathbf{C_4AH_{13}}$
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=14.30Å, d=2.88Å and of C_4AH_{13} at d=8.05Å and its high intensity peaks at d=4.05Å, d=2.17Å etc, respectively

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

But there were C_3AH_6 hydrated compound's medium intensity d=5.14Å, d=3.366Å, d=2.816Å, d=2.226Å, d=2.043Å peaks and low intensity d=3.149Å and very low intensityC_3A phase peak at d=3.34Å, respecively.

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.

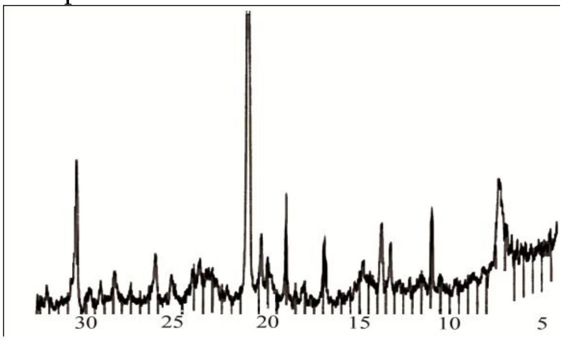

Figure 4. XRD results for 1 hour hydrated C_3A phase with K-crent

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

№	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=2.88Å, C_2AH_8 at d=4.25Å, d=3.80Å, d=2.45Å, d=2.39Å and of C_4AH_{13} at d=4.05Å, d=2.69Å, =2.36Å, d=2.17Å , respectively.

The existence of diffraction lines of C_3AH_6, which is a final product of C_3A phase at d=5.14Å, d=3.366Å, d=3.149Å and d=2.226Å 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}

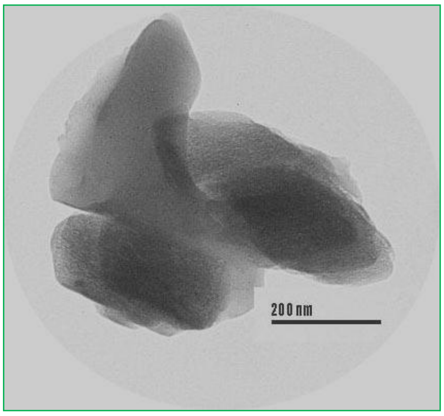

Figure 5. TEM results for 30 min hydrated C_3A phase

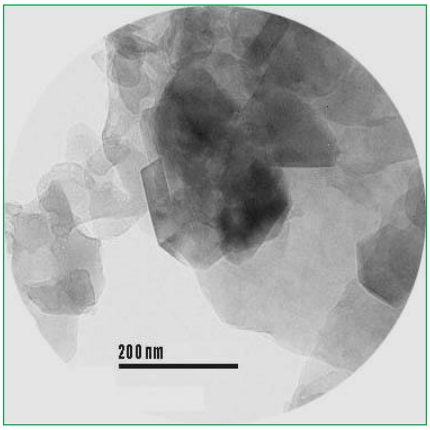

Figure 6. TEM results for 30min hydrated C_3A phase with K-crent

From the TEM analysis results of these hydrated $3CaO·Al_2O_3$ and $3CaO·Al_2O_3$ + K-crent systems can be concluded that the following reactions take place:

$3CaO·Al_2O_3 + Al_2O_3 ·2SiO_2 + H_2O \rightarrow 4CaO·Al_2O_3·13H_2O$ *(hexagonal)*

$3CaO·Al_2O_3 + Al_2O_3 ·2SiO_2 + H_2O \rightarrow 3CaO·Al_2O_3·6H_2O$ *(cubic)*

$3CaO·Al_2O_3 + Al_2O_3 ·2SiO_2 + H_2O \rightarrow 4CaO·Al_2O_3·11H_2O$ *(hexagonal)*

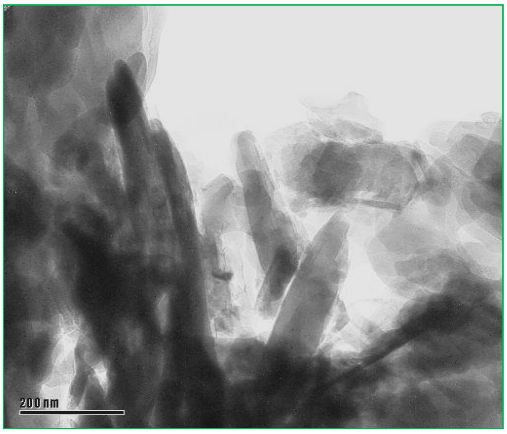

Figure 7. TEM results for 1 hour hydrated C_3A phase

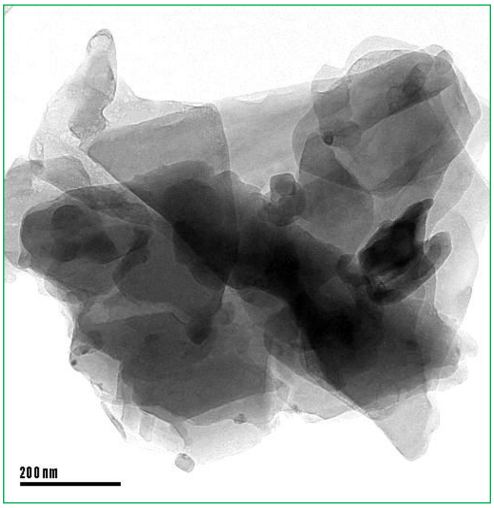

Figure 8. TEM results for 1 hour hydrated C_3A phase with K crent

From the TEM analysis results of 1 hour hydrated $3CaO·Al_2O_3$ and $3CaO·Al_2O_3$+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 C_3A phase

Russian standard sample of C_3A 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 $CaCO_3$ and Al_2O_3 reagents from China were mixed in stoichometric ratio and were calcined at 1000-1200^0C 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 C_3A, the same standard sample with K-crent addition and the C_3A 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, ^{0}C	$CaO_{free,}$ %
1.	1000	17,528
2.	1050	9,215
3.	1100	4,226
4.	**1150**	**0,256**
5.	1200	0,112

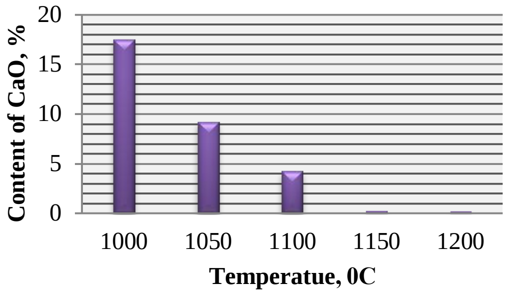

Figure 9. Free CaO content dependence on calcining temperature

Table 7. Study on compressive strength for C_3A with K-crent

Phase composition	COMPRESSIVE STRENTH, (KG/CM^2)		
	30 min	1hour	1 day
C_3A	54	62	71
C_3A+K-crent	77	83	90
C_3A(sintering)+K-crent	50	74	82

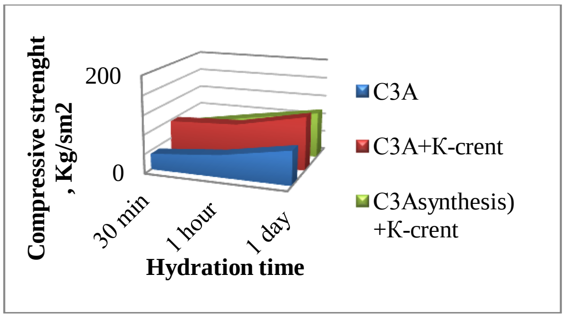

Figure 10. Study on K-crent influence on compressive strength of C_3A phase

The results of above mentioned analysis show that the optimal preparation temperature of C3A phase is 1150^{0}C.

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 $3CaO\cdot Al_2O_3$ phase.
- TEM analysis results show that compared to $3CaO\cdot Al_2O_3$ 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 "$3CaO\cdot Al_2O_3$+gypsum" system at the beginning of hydration.

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