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Effect of sulfate containing admixture on C3A hydration

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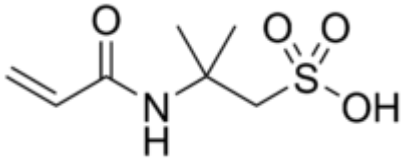
The aim of this study is to investigate the possibility for application of sulfate containing water soluble polymer in hydration process of C_3A (Tricalcium aluminate). XRD was employed to investigate hydrated C_3A and it was confirmed that some part of the macromolecules of applied admixture were included in hydrated inorganic crystals.

Key words: XRD, sulfate containing polymer, C_3A.

INTRODUCTION

The cement admixtures with sulfate group (-SO_3H) are one of the biggest groups of superplasticizers for cement. Many producers of cement admixtures use materials from this group. The application of supfonated polystyrene (SPS) for superplasticizer of cement was studied in [1] and it was confirmed by XRD, that some part of the SPS macromolecules was included in inorganic crystals of hydrated C_3A (Tricalcium aluminate). It is well known, that C_3A was part of cement and reacted with gypsum. It was also reported in the literature, that the admixtures were adsorbed and consumed to form an organo-mineral phase [2]. Nawa Toyharu investigated different copolymers and the obtained results demonstrated that the polymers with longer graft chains showed better dispersing stability with small amount of adsorption [3]. Kazuo Yamada et al. studied polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase [4]. The maxima in XRD data of this additive were given in many articles [5]. It is well known that the inclusion of some atoms in the unit cell of the materials leads to shift of their maxima and change of the values of 2Θ [6]. In this way, with XRD was possible to confirm the inclusion of parts of the macromolecules of the applied admixture in the unit cells of inorganic crystals. The application of polymers of 2-Acrylamido-2-methylpropane sulfonic acid:



(CAS Number 15214-89-8) (PAAMPSA) for superplasticizer of cements was described in the literature [7,8]. With this investigation we like to have better understanding for the interaction of hydrated C_3A with this compound. This material was with known structure and chemical composition for the difference of cement, which composition depended from applied row materials.to analyze key morphological features, to record the distribution patterns and to examine the current state of habitat quality and population–threatening changes in the environment [17]. In order to record the present status and to provide the base for the further comparison of possible changes in the ecosystem, the content of the selected metals was determined in sponge tissue, as well as in water and sediment samples collected from habitat.

EXPERIMENTAL

The laboratory made sample of C_3A was prepared according method described in [9] from raw materials: $CaCO_3$ and $Al(OH)_3$, GR for analysis (Merck). After analyses were made, samples: reference - C_3A: distilled water = 1:1 and mixtures with 0.3 and 0.5% PAAMPSA like 2% water solutions, mixed with applied distilled water. 20% TiO_2 technical grade (Cristal Global) was added in the investigated samples. XRD were made by apparatus TuR – M 62 (CuK_α, λ= 1.54056 nm),

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speed 1^0/min. The hydratation of all samples lasted 24 h. The free water was separated by filtration and the dry materials were obtained in oven at 60^0C, grinded in agate mortar and kept in sealed ampoules. The values of all maxima: the position of the maxima - 2Θ, grad, the shift of maxima in a presence of PAAMPSA - ΔΘ, grad, the intensity I,% and the values of the width at half maxima $\Delta h_{1/2}$ were calculated from the XRD patterns.

RESULTS AND DISCUSSION

Water soluble polymer with sulfate group – poly acrylamidopropionic sulfonic acid (PAAMPSA) was used in this investigation. The application of PAAMSA like superplasticizer was studded by several methods, described in BSS EN 934-2 by cement, produced from Holcim Bulgaria, but the obtained results take place in other our manuscript. This polymer has no free sulfuric acid, applied for production of SPS and thus it is not necessary to eliminate H_2SO_4 with $BaCl_2$ like in the study of this admixture. For better accuracy of XRD measurements, it was used 20% additive TiO_2 which has well known XRD pattern.

The results from XRD investigations are given in tables 1,2,3 and 4. The results in table 2 are similar with those given in the literature [10]. In fact, there are small differences in the values of some maxima, but this may be due to the differences in the investigated materials. The results from the XRD investigation of hydrated C_3A with 20% TiO_2 and 0.5% PAAMPSA are given in in table 3.

It was evident that in the presence of PAAMPSA there are some differences in the values of maxima of hydrated C_3A with and without admixtuer. The reason for these differences could be a result from including of some part of the macromolecules of applied admixture in the obtained crystals. In the Introduction is given information for this process. There are only few works in support this hypothesis. Biagini et all [11] reported the decreased fluidity of cement paste with sulfurated polystyrene-based admixture by molecular weight 50000 and explained this with adhesion of the long single polymer chain to different cement grains and formation of coagulation due to the generation of bridge effect. This effect was described also by Kim [12]. The values of maxima for TiO_2 in the table 3 have no differences, because the crystals have the same structure before and after hydration. It is evident, that only the data in table 3 for crystals of hydrated C_3A are changed in the presence of investigated admixture PAAMPSA. From the obtained XRD patterns are calculated and the values of $\Delta h_{1/2}$ of some maxima. The results are given in table 4 which are consistent with the hypothesis for the inclusion of parts of macromolecules of PAAMPSA in inorganic crystal of hydrated C_3A.

It is evident that with increasing of the quantity of the admixture from 0.3 to 0.5% in the investigated samples leads to increasing of the values of $\Delta h_{1/2}$ of some maxima which confirms that some parts of macromolecules of applied admixture are included in the crystal of hydrated C_3A.

Table 1. XRD results of hydrated C_3A

2Θ, grad	17.30	20.00	26.80	28.20	31.70	31.70
I,%	100	48.15	50.62	38.27	83.96	23.46
2Θ, grad	34.70	36.30	39.50	44.70	52.90	55.00
I,%	14.81	25.93	97.53	91.34	34.57	50.62

Table 2. XRD results of applied TiO_2

2Θ, grad	27.70	36.20	39.40	41.40	44.10	55.58	56.70
I,%	100	39.17	6.67	17.50	6.67	43.33	11.25

Table 3. XRD results of hydrated C_3A with 20% TiO_2 and 0,5% PAAMPSA

2Θ, Grad	17.40	20.05	26.90	27.70	28.30	31.90	32.20	34.90	36.20
ΔΘ,Grad	+0.1	+0.1	+0.5	-	+0.1	+0.2	-1.5	+1.6	-
I,%	100	34.29	42.86	100	40	65.71	11.43	8.57	29.12
2Θ, Grad	39.30	41.40	44.80	52.5	54.50	55.58	56.70		
ΔΘ,Grad	-0.2	+0.05	+0.1	-0.4	-0.5	-	-		
I,%	96.30	8.95	77.78	25.93	81.48	23.13	8.05		

Table 4. Results for $\Delta h_{1/2}$ of some maxima in XRD patterns of hydrated C_3A with 20% TiO_2, 0,3% and 0.5 % PAAMPSA

2Θ, Grad	17.30	28.20	34.70	39.50	44.70	52.90	55.00
$\Delta h_{1/2}$, C_3A mm.	0.6	1	0.9	0.8	0.9	0.8	0.8
$\Delta h_{1/2}$,mm.with 20%TiO_2, 0,3% PAAMPSA	0.7	1.2	1	1	1	1	1
$\Delta h_{1/2}$, mm with 20%TiO_2, 0,5% PAAMPSA	0.8	1.8	1.1	1.2	1.3	1.2	1.3

CONCLUSION

The study demonstrates that water solution of PAAMPSA, made in lab. of Chemical faculty of Sofia state university "St. Kliment Ohridsky" like admixture can be used as a superplasticizer having a profound effect on the hydration process and suggests that some parts of its macromolecules are included in the inorganic crystals of hydrated C_3A.

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ВЛИЯНИЕ НА СУЛФАТСЪДЪРЖАЩА ДОБАВКА ВЪРХУ ХИДРАТАЦИЯТА НА C3A

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(Резюме)

Целта на тази статия е да се изследва възможността за приложение на сулфатсъдържащ водоразтворим полимер в процеса на хидратация на C3A (Трикалциев алуминат). Използван е XRD за изследване на C3A и е направено заключение, че някои части от макромолекулите на използваната смес се включват в хидратираните неорганични кристали.