Behavior of Chromate ions in CaO-Al_2 $(SO_4)_3$ Suspensio

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AbstractBehavior of the chromate ions and their removal efficiency in CaO + $Al_2(SO_4)$ suspensions with molar ratio 4:1 was studied. The suspension prepared by agitating the reactants with a magnetic stirrer for constant time intervals at room temperature. Run products were collected by filtration, washing and air-dry and evaluated by XRD, SEM and DTA. According to XRD and SEM results the major product in this suspension was ettringite with minor amounts of gypsum and calcite. DTA results showed that, the presence of the chromate ions in the suspension retard the formation of the products and decrease the degree of their crystallinity. However there is a high removal of the chromate ions by the formed suspension products. This is related to the substitution of the chromate ions by sulfate ions in the ettingite crystals. [khulood A.A.Abualola, **Behavior of Chromate ions in CaO-Al_2 $(SO_4)_3$ Suspension,** *J Am Sci* 2013;9(3):28-33] (ISSN: 1545-1003) http://www.jofamericanscience.org**.** 5

Key words: CaO-$Al_2(SO_4)_3$ suspensions, Chromate ions, Removal.

1. Introduction

The presence of heavy metals in the environment has been of great concern because of their growing discharge, toxicity and other adverse effects on receiving waters. Heavy metals contaminants in soils originate in the spreading of inorganic fertilizers, sewage sludge, and industrial wastes. One of those toxic species is chromium and its chromate derivatives which if they present in the levels greater than the permissible limit become long-term hazardous contaminants because of their high toxicity causing severe damage to the kidney and nervous system. In alkaline solutions, Cr (VI) primarily occurs as CrO_4^{2-} and $Cr_2O_7^{2-}$ (1). CrO_4^{2-} and $Cr_2O_7^{2-}$ ions are somewhat soluble and can escape into aqueous leaching solutions. The problems of determination and reduction of soluble chromates are of great interest, and this can be verified looking at the several technical papers and patents that have been presented on this topic during the last years (2, 3).

Suspensions of saturated solutions of calcium oxide with aluminum sulfate will result in different products depends on many factor like the molar ratio of calcium oxide to aluminum sulfate, initial pH of the solution and concentration of sulfate ions (4) in the suspensions. If the calcium oxide: aluminium sulfate molar ratio is more than 4 a product called ettringite, ($3CaO.Al_2O_3$. $3CaSO_4$. $32H_2O$), is formed. Ettringite, is a naturally occurring mineral found in Germany for the first time (5,6). This mineral is characterized by the very high content of water molecules and is very important to cement technology, since it appears as an early hydration product for the first stage of hydration of Portland cement. Recently, ettringite attracted a special attention in view of environmental issues, specifically in sub-surface geology concerning SO3-comprising waste dumping and fluorine sorption from contaminated waste waters as well as underground waters (7-9). Chromate ions which may present as contaminates in the waste water can substitute sulfate ions in the crystal structure of ettringite and for this ettringite represents a good reagent for their removal (10-12).

In the present study, removal behavior of chromate ions by CaO-$Al_2(SO_4)_3$ suspension with molar ratio 4:1 were studied. The characteristics of the products after various time intervals was studied using X-ray diffraction (XRD), Scanning electron microscope (SEM) and Differential thermal analysis (DTA).

2. Methodology

2.1. Preparation of the suspensions

Reagents of Ca Oxide, CaO, special grade of Sigma Aldrich, BET specific surface area 13.37 m^2/g, and Al-sulfate hydrate, $Al_2(SO_4)_3$.(14–18)H_2O were used. Primarily, Al-sulfate solution was prepared by diluting with deionized water to obtain 0.01mol/L solution as $Al_2(SO_4)_3$ which mixed with 100 ml water containing 0.04 mol/l CaO in presence of various concentrations of chromate ions. Different mixes was prepared which designated as, E0, E1, E2, E3 and E4 with concentrations of CrO_4^{2-} ions were 0, 0.01, 0.02, 0.03 and 0.05 molar/l respectively**.** Each suspension was agitating by a magnetic stirrer for constant 3 h at room temperature. After 1, 2, 4, 6 and 24 hrs of the mixing process, filtration was carried out and the filtrate was stored for determination the remains of CrO_4^{2-} ions. The precipitation remained in the filter paper was washed out by distilled water and dried in air for 24 hours in dry-air. After drying, it stored in a dessiccator containing dry calcium chloride to decrease the carbonation effect. The precipitated was evaluated by XRD, SEM and DTA.

2.2 Evaluation of the Products

The products produced from the calcium oxide + aluminum sulfate suspension in presence and absence of chromate ions were evaluated by using X-ray diffraction analysis (XRD), Scanning electron microscope (SEM) and Differential thermal analysis (DTA). X-ray examination was carried out by employing Mac Science MXP3 diffractometer under 40kV–20mA Cu*K*α radiation. The growth of the products crystals was studied by SEM examination. A JEOL-JSM-5400 high resolution scanning electron microscopy was used (Shimadzu Co., Japan). For DTA test, Differential thermal analyzer was used at heating rate of 20°C/min. The measurements were made in N_2 atmosphere using Shimadzu DTA – 50H.The sample chamber was purged with nitrogen at a flow of 30 ml/min.

2.3. Behavior of the removal of chromates ions

The remains of CrO_4^{2-} ions in the filtrate were measured by colorimetric techniques. This done using colorimeter at 370 nm corresponding to the maximum absorbency of CrO_4^{2-} ions. The uptake of chromate ions by the suspension products (molar/l) was calculated by subtraction the remained concentration in the solution after various time intervals from the initial concentration of chromate ions presents in CaO+ $Al_2(SO_4)_3$ suspensions.

3. Results and Discussion

3.1. X -Ray Diffraction

XRD patterns of E0, E1, E3 and E4 mixes after 6 hrs of mixing are shown in Fig.1. According to the identified XRD peaks the products of E0 suspension after 6 hours of mixing were ettringite , gypsum ($CaSO_4$) and gibbsite ($Al(OH)_3$) phases. Ettrinigte was the main phase produced in the suspension products as indicated by the increase in the intensity of the peaks characterized to ettringite compared to those of the other products. Calcite, $CaCO_3$ was also identified in X-ray patterns. Minor calcite formation was also reported by some authors during synthesis of ettringite in suspension solutions [8, 13, 14, 15]. Peaks of unreacted CaO and $Al_2(SO_4)$ were also identified in E0 patterns.

For E1, E3 and E4 suspensions, similar products were obtained as in E0 mix. There is a slight decrease intensities of the peaks characterized to the obtained products (ettringite, gypsum and Calcite) beside an increase in the intensities of the peaks of the reactants (CaO and $Al_2(SO_4)_3$). The decrease in the intensities of the peaks characterized to ettrringite has the order E4> E3> E1. This indicates a retardation to the reaction between CaO and $Al_2(SO_4)$ as a results of presence of chromate ions. This retardation to the suspension reaction increases with increasing the molar ratio of chromate ions present in CaO+ $Al_2(SO_4)_3$ suspension. This retardation can be related to absorbance of the chromate ions on the surface of the reactants which retard their interaction.

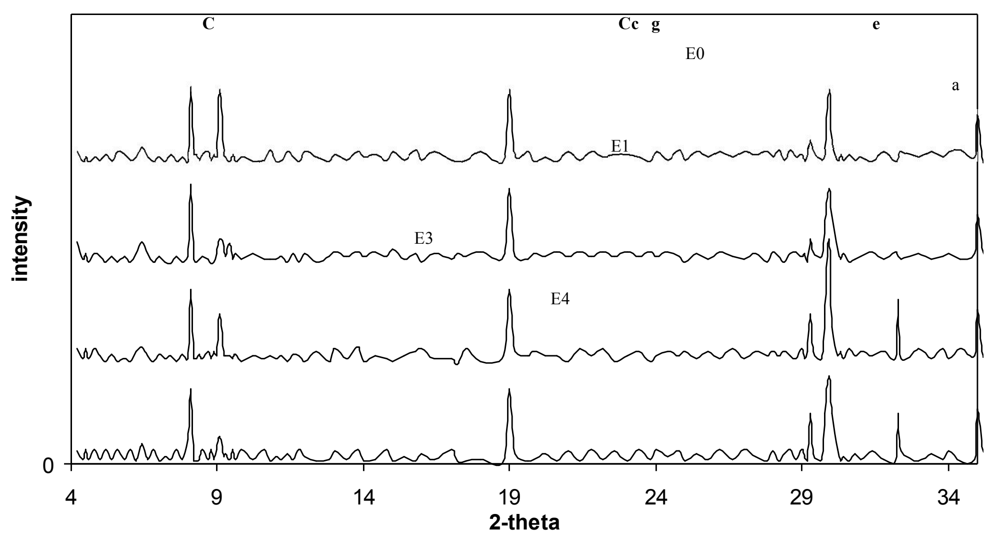


Figure (1) : X-ray after 6 hours, g-gypsum , e- ettringite, C –Ca O , a- $Al_2(SO4)_3$ Cc – $CaCO_3$

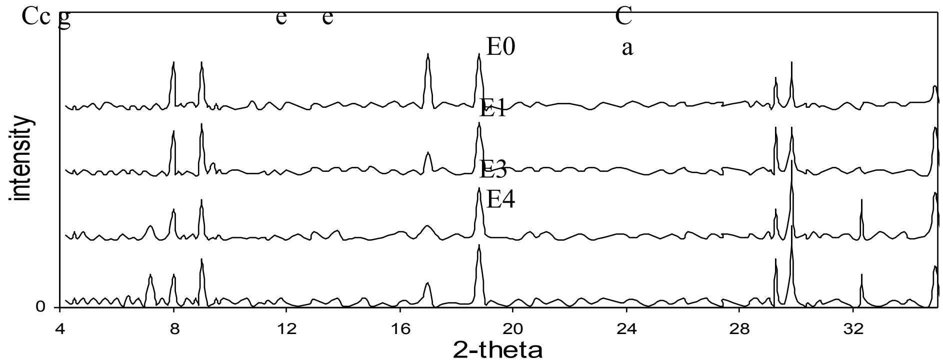


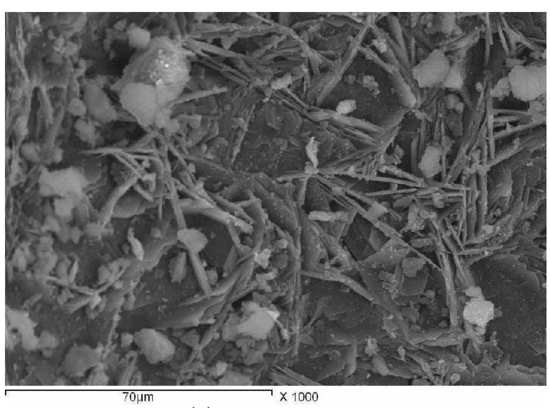
Figure (2): X-ray after 24 hours, g- gypsum, e- ettringite, C –CaO

After 24 hrs of mixing process, XRD patterns of the different mixes were represented in Fig. 2. From the obtained pattern of E0 suspension we can notice that the intensity of the ettringite and the other reaction products were increased while as the intensity of CaO and $Al_2(SO_4)$ decreased indicating a progress of the reaction. Besides there are an increase in the intensities of the peak characterized to gypsum phase in that suspension. For CaO+ $Al_2(SO_4)_3$ suspensions which containing chromate ions, E1, E3 and E4, a similar observation was also noted. Besides there is no significant difference between the intensities of the peaks identified for the reaction products (gypsum and ettringite) for E0 and the other suspensions.

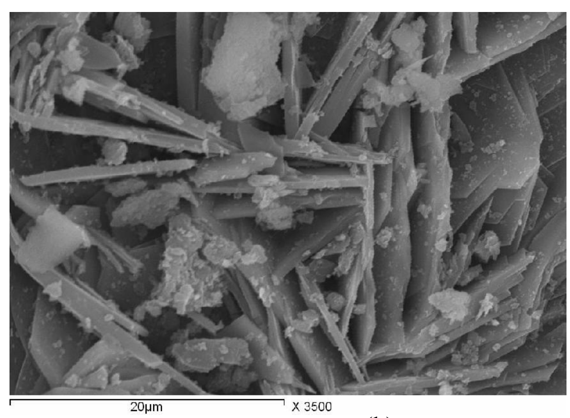
It is obvious that ettringite formation and its amounts in the suspension comparing to other products depends on the molar ratio of calcium oxide to aluminum sulfate in the starting suspensions. Also its precipitation depends on pH of the solutions [10] which is also a function of this molar ratio in suspensions. Strictly saying, ettringite precipitation may depend on the concentrations of ionic species dissolved in the suspensions. Here although the ratio of calcium oxide to aluminum sulfate used in the suspension was 4:1 but not all CaO is soluble. This permits the formation of other products beside ettringite like gypsum and calcite. However, the main reaction product is ettringite which explains the high uptake of the chromate ions noticed in the later section.

3.2. Scanning Electron Microscope

SEM micrographs of the precipitate formed from E0 and E3 mixes after 6 and 24 hours of mixing are shown in Figs 3 and 4 respectively.



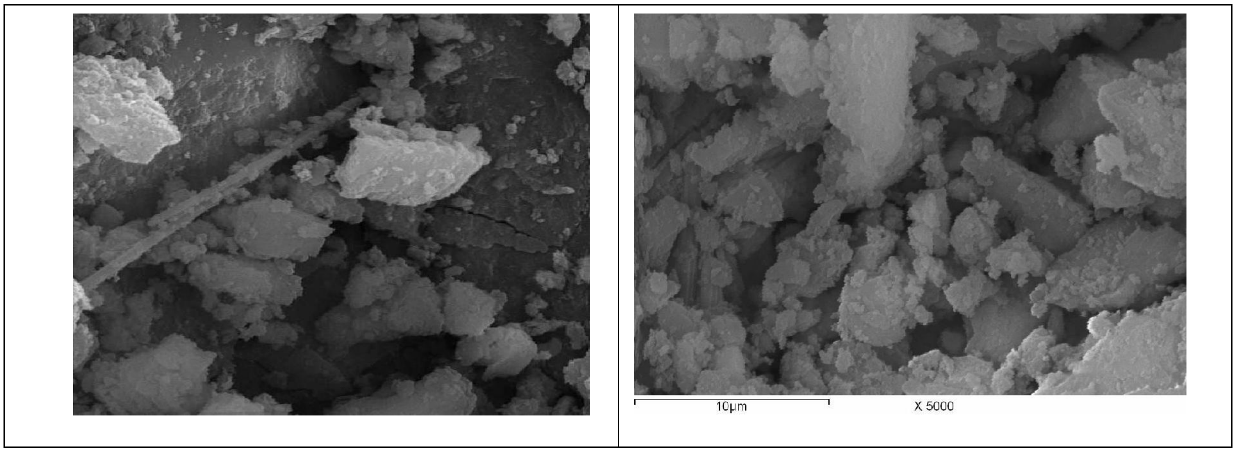
(a)



(b)

Figure (3) SEM micrographs of E0 suspensions 0a)- after 6 hours, (b)- after 24 hours.

Fig. 3 represents SEM micrographs for E0 suspension, after 6 and 24 hours of mixing process. The micrographs showed a well definite crystal which can be related to ettringite beside to platy crystals which can be related to CaO. This confirm that the main products of the reaction of CaO and $Al_2(SO_4)$ suspensions is the etringite. After 24 hours of mixing the suspensions, Fig.3 (b), there is an increase in the size and the crystallinity of the formed ettringite.



(a) (b)

Figure (4): SEM micrographs of E4 suspensions (a)- after 6 hours,(b)- after 24 hours.

For E3 suspension, Fig 4-a, a fewer numbers and smaller ettringite crystals can be identified in the micrographs after 6 hours of preparing the suspensions. This confirm that the presence of chromate ions retard the rate of formation of ettringite and decrease its crystal size. After 24 hours, higher numbers of ettringite crystal can be observed in SEM micrographs, Fig.4-b. The reduction in the ettringite crystal noticed here in the micrographs agrees with decrease in the intensities of XRD peaks obtained at the same mixing age and have the same explanation.

3.3. Differential Thermal analysis

The DTA thermogrames of precipitates produced from suspensions E0 and E3 after 6 hours of mixing are shown in Fig.5. All DTA curves showed three main endothermic peaks located at 105, 490, and 700–780 ºC. The first endotherm located at 105ºC is mainly due to the dehydration of the ettringite which is the main suspension products. The second peaks located at 490ºC, which represents the major mass loss, is mainly related to the decomposition of CaO [16]. We can noticed the increase in the intensity of such peak in case of suspension E3 which confirm the retardation effect to the reaction of CaO and $Al_2(SO_4)_3$ as a results of the presence of chromate ions.

The third endothermic is double peak located at 718–770 ºC is due to the decomposition of calcite, $CaCO_3$ with different degrees of crystallinity [17,18]. The enthalpy of this endotherm varies as a result of change in the degree of carbonation of the specimens.

The DTA curves for E0 and E3 after 24 hours of mixing are shown in Fig. 6. The same three endothermic peaks are also observed in the DTA thermogrames for both E0 and E3. These three endothermic peaks have the same intensities for E0 and E3 suspensions. This indicates the disappearance of the retardation effect to the suspension reaction observed in the earlier ages. Also, for the two suspensions, E0 and E3, there is a notable decrease in the intensity of the second peaks characterized to CaO. Besides there is a notable increase in the intensity of the first peak characterized to ettringite, which is the major reaction products. From that we can concluded the progress of the reaction for the suspensions free from (E0) or containing chromate ions(E3).

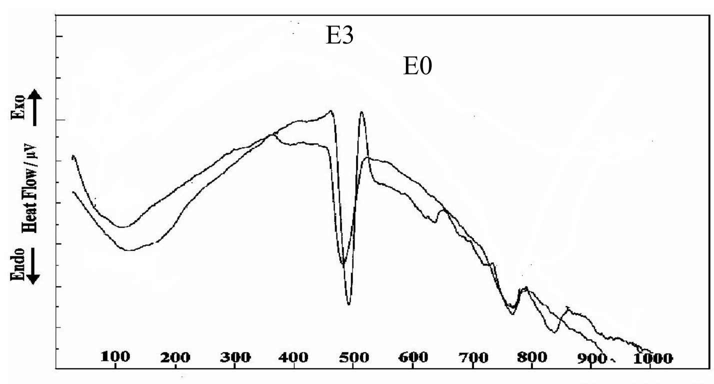


Figure 5: DTA thermgrams of E0 and E3 suspensions after 6 hours

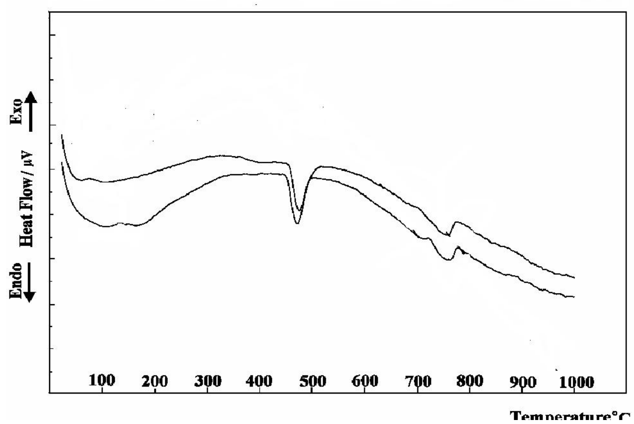


Figure 6: DTA thermgrams of E0 and E3 suspensions after 24hours

3.2. Removal Behavior of CrO_4^{-2} ions

The rate of removal of CrO_4^{2-} ions (mole/l) by CaO- $Al_2(SO_4)$ a function of the mixing time was shown in Fig.(7).

The amount of CrO_4^{2-} ions removed by all mixes increases gradually and continuously during the first 6 hours of mixing and nearly 80 % of the chromate ions were removed during this time interval. From 6-24 hours a gradual removal was noticed and an equilibrium stage was reached after 24 hours of the mixing process. The amount removed of CrO_4^{2-} ions by the suspension products increased by increasing the initial concentration of the CrO_4^{2-} ions presents in the suspensions. However not all the chromate ions are removed for mixes containing 0.03 and 0.05 molar/l of chromate ions, E3 and E4 respectively. While, for E1 and E2 suspensions (containing 0.01 and 0.02 molar/l of chromate ions), nearly all the chromate ions presents in CaO + $Al_2(SO_4)_3$ suspensions are uptaked by the suspension products. This indicates that, up to 0.02 molar/l of these anions can be removed by suspension products. By considering that the ettringite is the main suspension products (as we show in the later sections) we can related the removal of the chromate ions to the exchange of the sulfate ions by the chromate ions in the ettringite crystal. The uptake affinity of the ettringite phase toward the chromate ions is greater than other products like gypsum and calcite. This high uptake affinity of ettrigite is related to presence of three exchangeable sites in the structure of the ettrirgite.

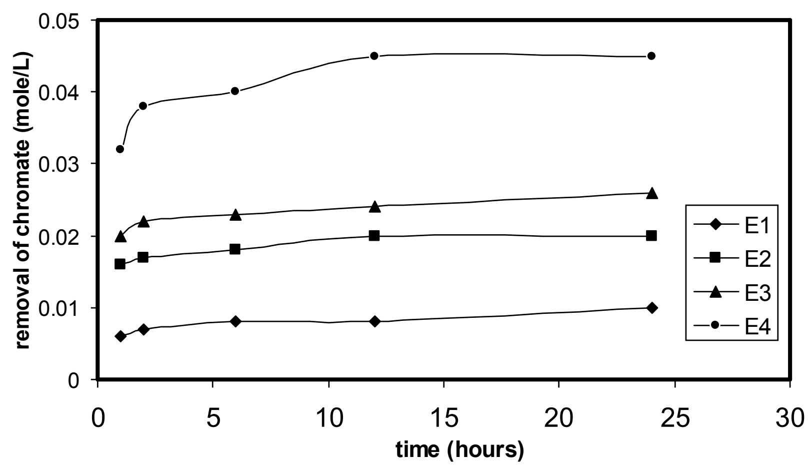


Figure (7): Removal of chromate ions of different mixes

Conclusion

1-The products of the suspension of CaO and $Al_2(SO_4)_3$ with molar ratio Ca/Al = 4 is the ettringite with an minor amounts of gypsum and calcite.

2-According to the X- ray results and SEM micrographs, presence of chromate ions in the suspension results to slight decrease in the degree of formation of ettringite and reduction the size of the formed ettringite crystals.

3- DTA results showed that the presence of chromate ions in the suspension decreases the rate of the reaction and the formation of the products.
4-There is high removal of the chromate ions by CaO-$Al_2(SO_4)_3$ suspension products which is related to substitution of chromate ions in the crystal structure of ettringite.

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