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Effect of different types of calcium sulfate on the reactivity of cement/Fe(II) system in dechlorination of trichloroethylene

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ABSTRACT

Several studies have been carried out to find out the reactive species in cement/Fe(II) system for the treatment of ground water contaminated with a number of chlorinated organic pollutants such as trichloroethylene (TCE). The previous studies suggest that cement hydration minerals associated with sulfate (SO_4^{2-}) could be one of the reactive species responsible for dechlorination reaction. Calcium sulfate which is a primary source of sulfate in cement has not been studied in detail. Present study deals with the effect of different types of calcium sulfate on the reactivity of cement/Fe(II) system in dechlorination of TCE. To evaluate the effect of different types of calcium sulfate on reactivity of cement/Fe (II) system, different types of calcium sulfate were mixed with clinker powder to get three different types of cements. TCE reduction experiments were carried out in the presence of Fe(II) using these cements. The results showed that cement with anhydrate and hemihydrate forms of calcium sulfate showed improved TCE reduction kinetics compared to cement with calcium sulfate dihydrate. Different analytical tools such as thermogravimetric analysis, X-ray diffraction, and scanning electron microscopy were used to differentiate between the types of calcium sulfate and understand the minerals generated at the end of TCE reduction experiments. Further studies revealed that the dissolution behavior of calcium sulfate in individual cement was different and had an influence on the formation of ettringite, which was suspected as a reactive mineral.

Keywords: Cement; Solidification; Calcium sulfate; Trichloroethylene

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1. Introduction

Cement/Fe(II)-based solidification is a well-established technology for the treatment of ground water contaminated with chlorinated organics such as trichloroethylene [1–4]. Different minerals associated with sulfate (SO_4^{2-}) have been suspected to play a significant role in dechlorination reaction [4].

Cement clinker consists of four major phases, namely alite ($C_3S{=}Ca_3SiO_5$) which constitutes 50–70%, belite ($C_2S{=}Ca_2SiO_4$) constitutes 15–30%, aluminate which is tricalcium aluminate ($C_3A{=}Ca_3Al_2O_6$)

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constitutes 5–10%, and tetracalciumaluminoferrite ($C_4AF{=}Ca_2AlFeO_5$) constitutes 5–15% of normal Portland cement clinker [5]. Among them, the reaction of tricalcium aluminate is of interest. C_3A reacts very quickly with water leading to uncontrolled quick setting if it is not controlled by gypsum addition. To overcome this problem, the clinker formed after calcination is subsequently ground with a small percentage of calcium sulfate (3.5–5%) to delay the initial setting time. The hydration reaction of tricalcium aluminate in the presence of gypsum leads to the formation of ettringite ($Ca_6Al_3(SO_4)_3(OH)_{12}{\cdot}26H_2O$) in which Al^{+3} could be replaced by Fe^{+3} [5–6]. Since this reaction can influence the workability of cement paste, the reaction mechanism of C_3A and gypsum has been studied by many researchers. Several research findings have contributed to explaining the reaction of C_3A and gypsum; however, the reaction mechanisms are not fully elucidated [7–8].

Gypsum exists in three different forms, namely natural gypsum ($CaSO_4{\cdot}2H_2O$), hemihydrate ($CaSO_4{\cdot}0.5H_2O$), and soluble anhydrite ($CaSO_4{\cdot}0.001H_2O$). Gypsum is added in cement during the grinding of clinker in a ball mill. During this process, the heat is generated in ball mill. The heat generated during this process is known to affect the gypsum hydration state. If more heat is generated, gypsum dehydration will be more [9–13].

Natural gypsum ($CaSO_4{\cdot}2H_2O$) is commonly added in the ball mill during clinker grinding. It has been shown that if the gypsum-grinding temperature is 90˚C then the grinds contain the residual gypsum and hemihydrate ($CaSO_4{\cdot}0.5H_2O$), 130˚C of the temperature gives only hemihydrate and 170˚C gives soluble anhydrite [14–15].

When hydration reaction of cement takes place, the form of sulfate plays a very important role in the formation of minerals like ettringite and monosulfate. The faster the sulfate dissolves, faster the minerals such as ettringite and monosulfate will form. Chemical Eqs. (1) and (2) show the reaction of C_3A and C_4AF with gypsum to generate ettringite, respectively.

$$Ca_3Al_2O_6 + 3Ca^{2+} + 3SO_4^{2-} + 32H_2O \rightarrow Ca_6\left[Al(OH)_6\right]_2(SO_4)_3{\cdot}26H_2O \tag{1}$$

$$Ca_2AlFeO_5 + Ca(OH)_2 + 3Ca^{2+} + 3SO_4^{2-} + 31H_2O \rightarrow Ca_6\left[(Al, Fe)(OH)_6\right]_2(SO_4)_3{\cdot}26H_2O \tag{2}$$

From the chemical reactions, it is clear that both aqueous solubility and dissolution behavior of the particular form of calcium sulfate are very important. Once the calcium sulfate gets dissolved in water, the SO_4^{2-} and Ca^{2+} ions available in the solution will be available to react with C_3A and ferrite phase (Ca_2AlFeO_5) [15]. The faster calcium sulfate dissolves the faster minerals, such as ettringite will form. Hence, it is important to understand the dissolution behavior of different types of gypsum.

Studies have shown that the rate of formation of ettringite is more in the case of anhydrate and hemihydrate compared to dihydrate, suggesting that the dissolution rate of dihydrate is less compared to anhydrate and hemihydrate, respectively [15–16].

Our previous research finding showed that when different types of cements were used for TCE reduction experiments, the reactive cements namely ordinary Portland cement (OPC), calcium sulfoaluminate cement (CSA), and combination of CSA and OPC all showed the presence of ettringite crystals. The finding also showed that sulfate present in the cement during manufacturing of cement played a significant role in generating crystals like ettringite [17].

The primary objective of this work was to study the effect of different types of calcium sulfate on the reactivity of cement/Fe(II) system in the dechlorination of TCE. To achieve this objective, three different types of calcium sulfate hydrate, dihydrate, hemihydrate, and anhydrate, were selected. Thermogravimetric (TGA) analysis was performed to confirm the form of calcium sulfate. Further three different types of cements were prepared by mixing 5% (w/w) of different calcium sulfate with clinker powder. TCE reduction experiments were carried out using these cements in the presence of Fe(II). X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to find out the solids generated at the end of the reaction.

2. Materials and methods

2.1. Materials

The chemicals used were TCE (99.5%, Aldrich Chemical), methanol (99.9%, HPLC grade, Fisher Scientific), hexane (99%, HPLC grade, Fisher Scientific), acetone (99.5%, Aldrich Chemicals), ferrous sulfate (99.5%, heptahydrate, Acros Organics), potassium hydroxide (Duksan pure chemicals), clinker powder (Ssangyong Cement, South Korea), calcium sulfatedihydrate (≥99%, Aldrich Chemical), calcium sulfate hemihydrate (≥97%, Aldrich Chemical), calcium sulfate anhydrate (−325 mesh, 99%, Aldrich Chemical), and methanolic stock solutions of TCE were prepared daily. Stock solutions of Fe(II) were prepared daily by dissolving the appropriate amount of ferrous sulfate in Milli-Q water.

2.2. Synthesis of cement containing different types of gypsum

Initially, TGA analysis was performed on three types of gypsum, which are calcium sulfate dihydrate, hemihydrate, and anhydrate, to ensure the amount of chemically bound water associated with them.

Figs 1–3 show the TGA analysis of three different types of gypsum. Fig. 1 shows TGA analysis of calcium sulfate dihydrate, and the weight loss of around 20% was observed. Fig. 2 shows TGA analysis of calcium sulfate hemihydrate, and the weight loss of around 5% was observed, indicating that the chemically bound water was four times greater in calcium dihydrate than hemihydrate. On the other hand, Fig. 3 shows very negligible loss of weight of 0.3% for calcium sulfate anhydrate; this 0.3% error could be due to atmospheric humidity. Three different types of cements were prepared by mixing appropriate quantities of clinker powder (supplied by Ssangyong Cement) and different types of gypsum, namely calcium sulfate dihydrate, hemihydrate, and anhydrate in individual glass bottles. Powders were mixed by placing the bottle on a tumbler at 30 rpm for 12 h to ensure uniform mixing. Thus prepared three different cements having calcium sulfate dihydrate, hemihydrate, and anhydrate, respectively were used for TCE reduction experiment. During the experimentation, the atmospheric humidity is not taken into consideration.

2.3. Experimental procedure for TCE reduction reaction with cement/Fe(II) containing different types of gypsum

All experiments were conducted in clear borosilicate glass vials (24.3 ± 0.13 mL) with triple seals (Teflon-coated rubber septa, lead foil, and Teflon film) designed to minimize the intrusion of oxygen and the volatilization of TCE. All samples were prepared in an atmospheric environment at ambient temperature (22 ± 0.5˚C). The reactive samples were prepared either in duplicate or in triplicate and average values were taken during each sampling event. Controls contained deionized water and TCE. Slurry samples were prepared by adding appropriate solids (cements containing different types of gypsum) and appropriate

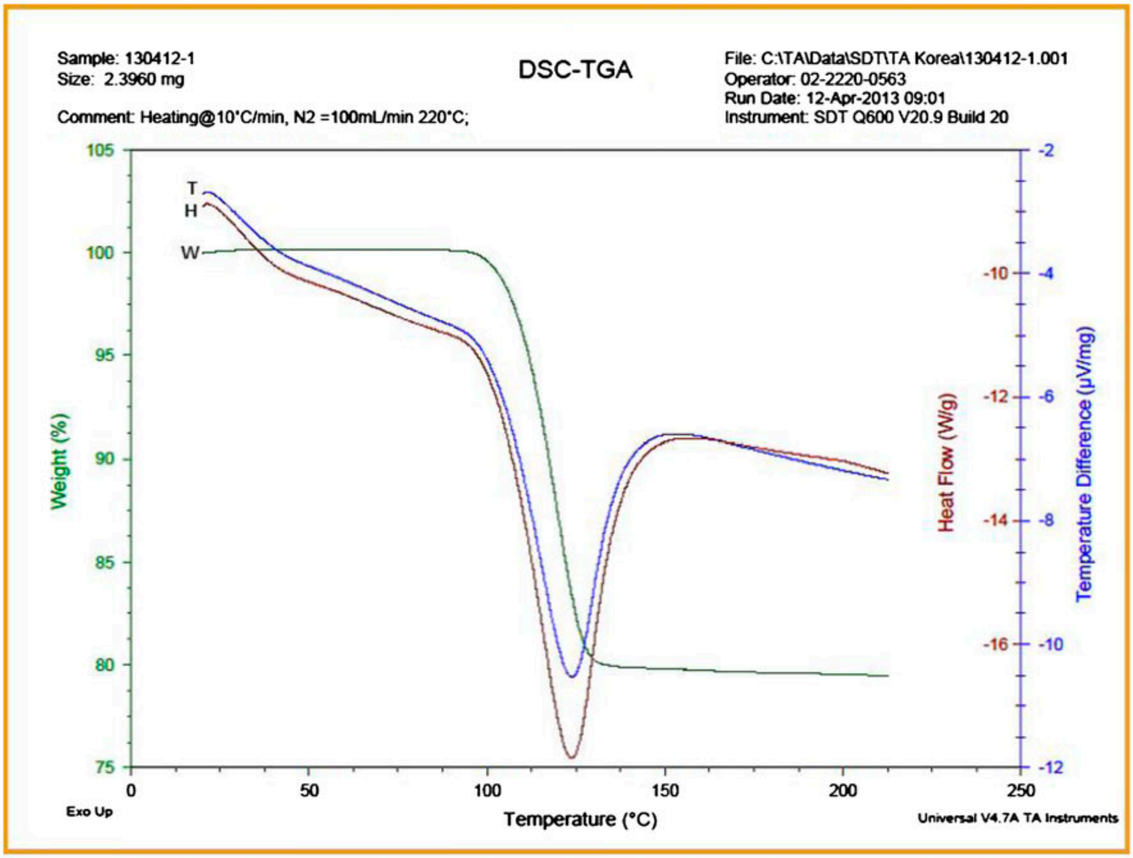

Fig. 1. TGA analysis of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$).

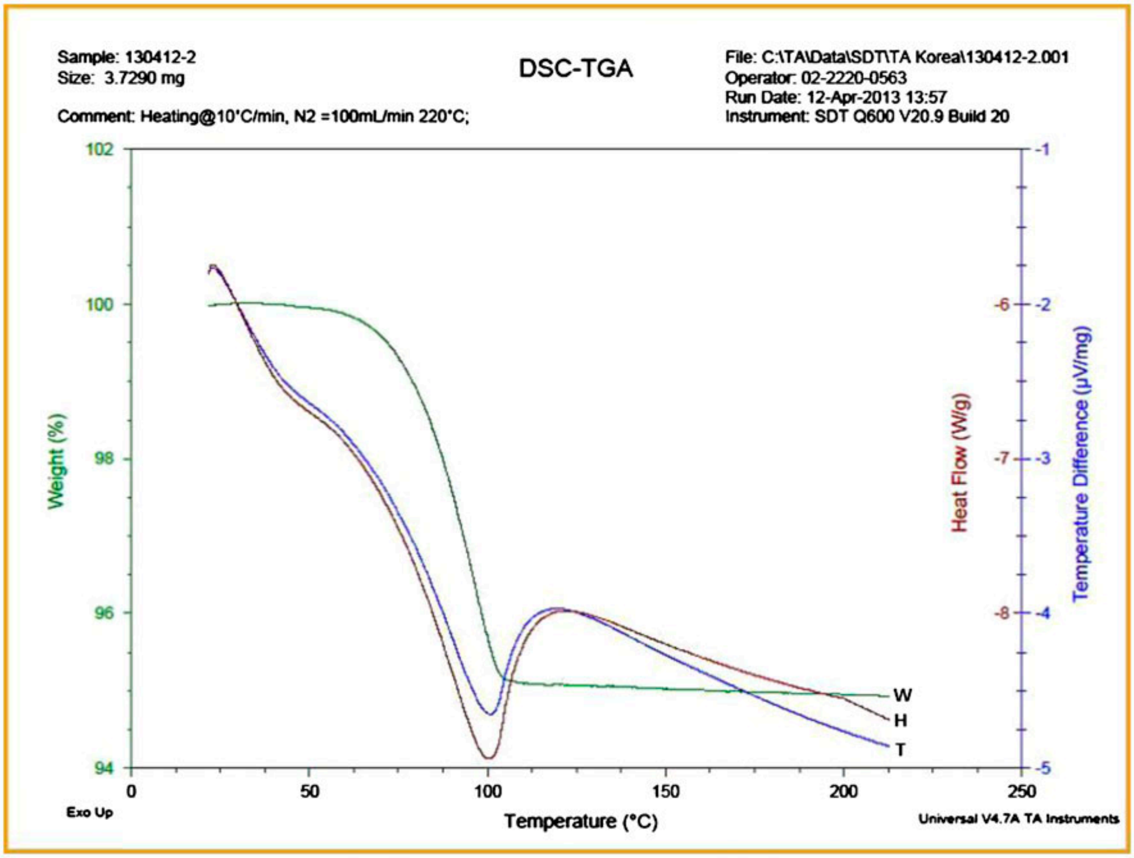

Fig. 2. TGA analysis of calcium sulfate hemihydrate ($CaSO_4{\cdot}0.5H_2O$).

aliquots of water and Fe(II) stock solution of 100 mM. The mass ratio of solids to solution was 0.10. The vials were completely filled with the aqueous solution so as to minimize gas phase partitioning of the chlorinated solvents. 1 M KOH was used to control the pH. As soon as the slurry reactors were made, 10 μL of methanolic stock solution of TCE was spiked so as to get 0.25 mM (32.8 ppm) of initial concentration of TCE in the reactor. After TCE was spiked, the reactors were rapidly capped with closures and were placed on a rotary motion with end over end rotation of 8 rpm. At specified intervals, the duplicate or triplicate samples were retrieved from the rotator and centrifuged at 112 × *g* for 3 min to separate the solid and aqueous phases. For TCE, 50 μL aliquot was extracted with 1,000 μL of hexane in a 2 mL GC vial. The vials were shaken for 5 min on an orbital shaker. After equilibrating at room temperature, the samples were analyzed using gas chromatography (GC). For XRD and SEM analysis of the surfaces, the solid portion of the slurries was dried in an anaerobic nitrogen chamber. Acetone was added to stop the hydration reaction. However, the samples were exposed briefly to atmospheric conditions during XRD and SEM analysis.

2.4. Analytical methods

TCE, was analyzed on a gas chromatograph (GC, Shimadzu GC-17A) equipped with an electron capture detector and a HP-5 column (30 m × 0.250 mm i.d × 0.25 μm film thickness; Agilent tech). Hexane extractant was injected in a split mode (50:1) using an auto sampler at 250˚C. Extra pure nitrogen was used as a carrier gas at a flow rate of 1.5 mL min^{-1}. The oven temperature was isothermal at 60˚C for 3 min, ramped to 150˚C at a rate of 15˚C min^{-1} and held for 5 min. The temperature of the detector was 280˚C.

The three different types of calcium sulfate used in the study were analyzed using simultaneous differential scanning calorimetry (DSC)/TGA analysis with the heating rate of 10˚C min^{-1}, up to 220˚C under nitrogen atmosphere (N_2 = 100 mL min^{-1}), to understand the amount of bound water associated with it. The different cement samples at the end of TCE

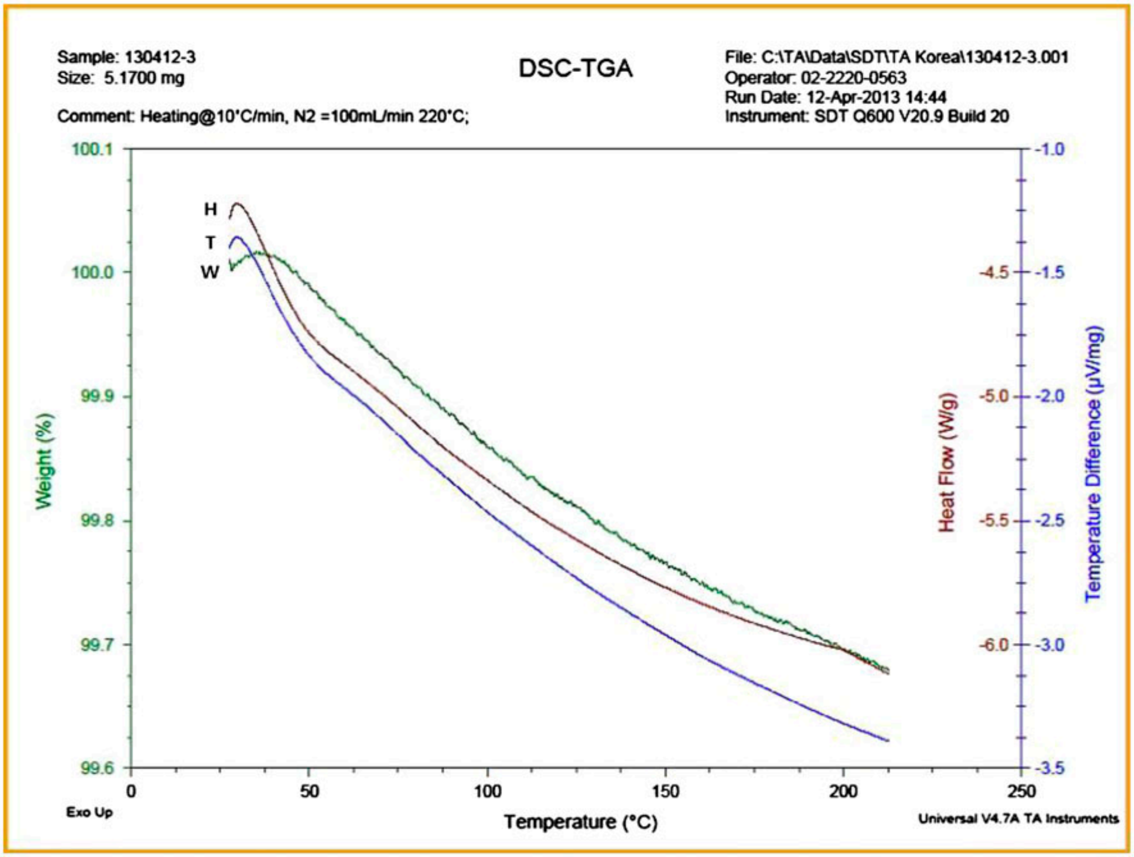

Fig. 3. TGA analysis of calcium sulfate anhydrate ($CaSO_4 \cdot 0.001H_2O$).

reduction experiment were analyzed using XRD analysis. Powder XRD with 2θ values ranging from 4° to 90° using a Bruker AXS D5005 goniometer was collected at a constant scanning rate of 1 min^{-1} with CuKα radiation (λ = 1.540 nm). The resultant peaks of individual minerals were compared with JCPDS cards. The detection of surface morphologies of the solid minerals was carried out using field-emission scanning electron microscope (Carl Zeiss SUPRA 55VP) with platinum (Pt) coating by sputter coater (BAL-TEC/SCD 005). The pH was measured with a pH meter (Orion 720A+) and electrode (9157BN).

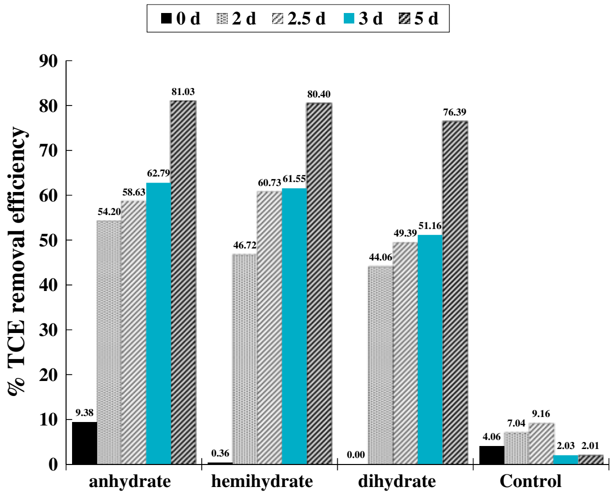

Fig. 4. TCE reduction in the presence of cements/Fe(II) containing different types of gypsum.

3. Results and discussion

3.1. Reactivity of cement/Fe(II) containing different types of gypsum for TCE dechlorination

Individual batch experiments were conducted simultaneously to find the TCE reduction rate of cement/Fe(II) containing different forms of gypsum. TCE reduction with different cements on a time scale is shown in Fig. 4. The TCE reduction rate was fastest in a cement containing gypsum in the form of anhydrate, followed by cement containing hemihydrate and dihydrate. The rate of reduction was faster up to 2 d, and then after 2 d TCE reduction rates of cement with anhydrate and hemihydrate were almost the same. However, the cement with dihydrate form of gypsum always shows less reactivity compared to both cement with anhydrate and hemihydrate. TCE reduction was observed at a faster rate initially and reached equilibrium towards the end. This is because reactive minerals responsible for TCE reduction were probably generated as soon as the Fe(II) solution was added in the cement.

In present study, the gypsum added in the clinker powder was slightly higher (5%) compared to conventionally added (3.5–5%) gypsum during the manufacture of OPC. Additionally, we added a specific form of gypsum that could differ from OPC composition, which has combination of three forms of gypsum in varying percentages. The form of gypsum and percentage depend on the operating conditions of ball mill and various other factors, such as moisture content and temperature of ball mill and form of gypsum added at the time of grinding.

3.2. Mineralogical characterization

The SEM and XRD analyses were performed on the cement/Fe(II) samples containing different types of gypsum to understand the types of hydration minerals generated during the TCE reduction reaction. Initially, all three types of cement samples were collected immediately after TCE was spiked. The samples were dried in anaerobic chamber under nitrogen atmosphere. The dried samples were further analyzed using SEM and XRD analysis. Fig. 5 shows the SEM analysis of three different types of cements. All the images show the presence of lumps of amorphous solids. However, when the cement samples were analyzed at the end of 5 d of TCE reduction experiment, all the samples showed the presence of rod-like ettringite structure. Fig. 6(a) shows the presence of abundant ettringite rods in cement sample containing gypsum in the form of anhydrate. Cement containing gypsum in the form of hemihydrate showed less abundant ettringite rods in Fig. 6(b) compared to Fig. 6(a). And, the least ettringite rods were seen in cement samples containing gypsum in the form of dihydrate as shown in Fig. 6(c). The cement with dihydrate form of gypsum showed a significant amount of irregular-shaped amorphous solids, which were less in other two types of cements. The SEM images clearly showed that ettringite rods with rod-like morphology were abundant in cement samples

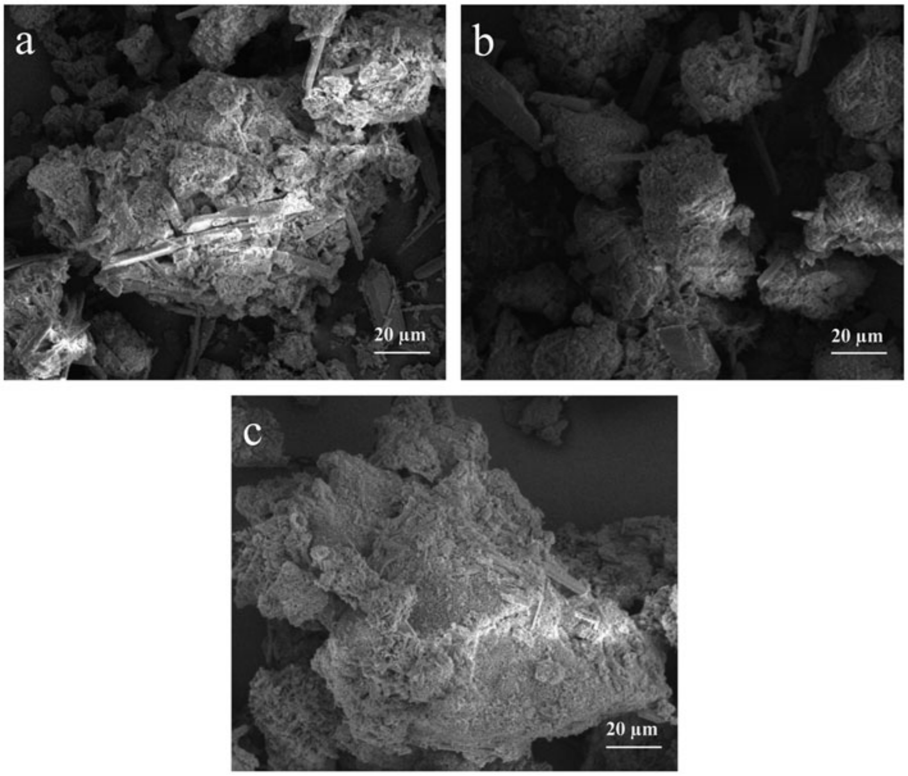

Fig. 5. SEM images of cement samples taken just after the start of TCE reduction experiment. (a) Cement sample with anhydrate gypsum, (b) Cement with hemihydrate gypsum, and (c) Cement with dihydrate gypsum.

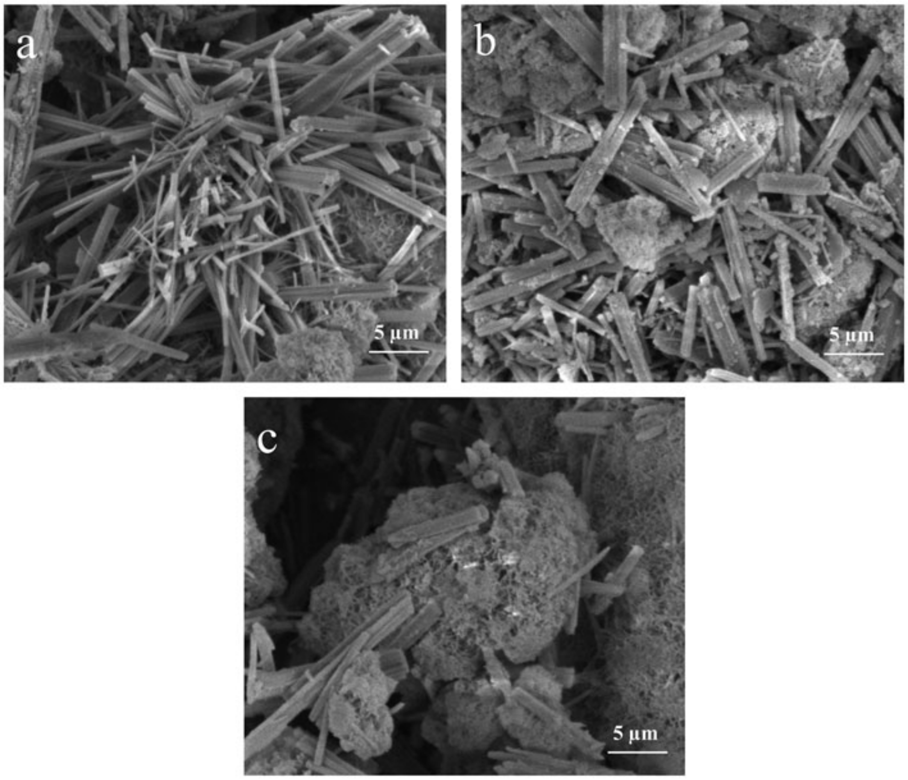

Fig. 6. SEM images of cement samples taken after 5 d of TCE reduction experiment. (a) Cement sample with anhydrate gypsum, (b) Cement with hemihydrate gypsum, and (c) Cement with dihydrate gypsum.

having gypsum in the form of anhydrate, and comparatively fewer ettringite rods were seen in cement samples having gypsum in the form of hemihydrate and dihydrate, respectively.

To support this claim, XRD analysis was performed on the cement solids immediately after TCE reactions were started and after 5 d of TCE reduction experiments. The XRD plot of cement samples immediately after TCE reaction is shown in Fig. 7. The samples were taken within few minutes from the addition of Fe(II) and TCE to cement. All the three samples showed the presence of calcium sulfate hydrate at 2θ value of 11.6,

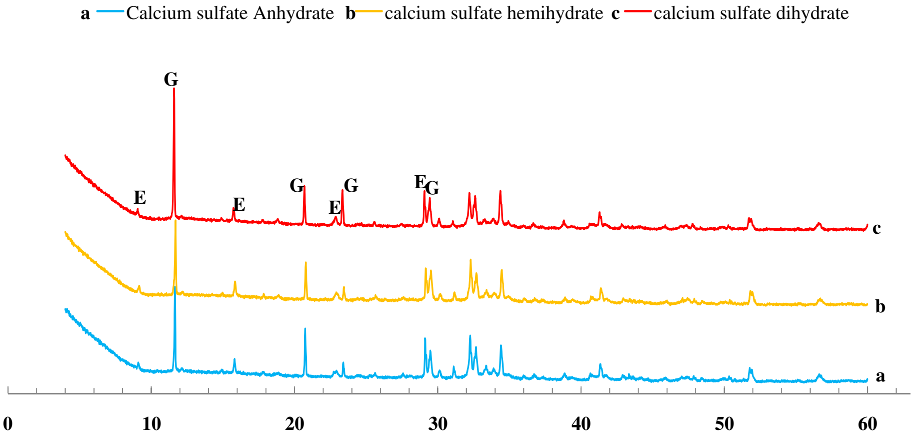

Fig. 7. XRD plot of cement samples taken just after the start of TCE reduction experiment. (a) Cement sample with anhydrate gypsum, (b) Cement with hemihydrate gypsum, and (c) Cement with dihydrate gypsum where E and G represent ettringite and calcium sulfate hydrate, respectively.

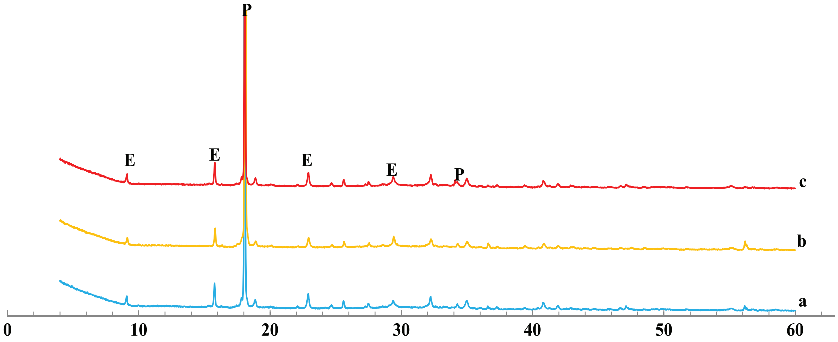

Fig. 8. XRD images of cement samples taken after 5 d of TCE reduction experiment. (a) Cement sample with anhydrate gypsum, (b) Cement with hemihydrate gypsum, and (c) Cement with dihydrate gypsum.

20.6, 23.3, and 29.1. These values matched with standard JCPDS card No. 700983. Very small peaks of ettringite at 2θ value of 9.0, 15.3, 22, and 29.4 were seen, which showed close match with JCPDS card No. 400292 of Fe-ettringite crystal. However, these peaks were of very low intensity. The major intensity peaks were of calcium sulfate hydrate. As the hydration reaction had just started, the calcium sulfate in all three cements reacted with water to give calcium sulfate hydrate irrespective of its form. It can be seen that the calcium sulfate hydrate peak is of more intensity in cement which had calcium sulfate in the form of dihydrate (Fig. 7(c)).

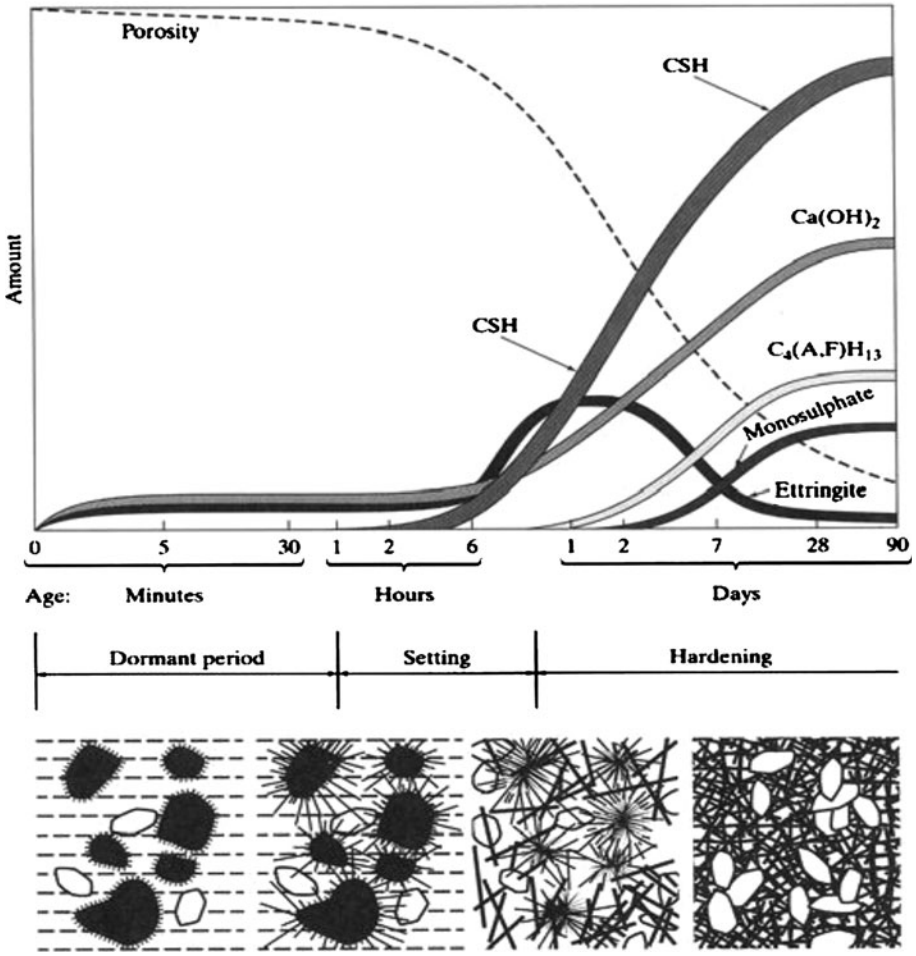

Fig. 9. Different hydration phases generated during cement hydration reaction.

Further, when the XRD analysis was done on the cement samples at the end of 5 d of TCE reaction, the XRD analysis showed that the ettringite crystals peak with more intensity in all samples (Fig. 8). Noticeably, the gypsum peaks were absent in all the three samples, indicating that gypsum in all cases got consumed. The high intensity peak at 2θ value of 18° was observed in all three samples and the intensity of this peak was more in cement containing gypsum in the form of dihydrate compared with hemihydrate and anhydrate.

Although it is difficult to conclude from XRD results which sample generated more ettringite, there is a possibility that cement with anhydrate generated most ettringite rods among all three samples as it is evident from the SEM image in Fig. 6(a). Also, the peak at 2θ value of 18° showed less intensity in the case of cement with anhydrate form of gypsum. Further, this peak at 18° was found to be of calcium hydroxide (Portlandite, $Ca(OH)_2$). The peak matched with standard JCPDS card No. 441481. It is known that gypsum that is more reactive forms more ettringite, and this leads to the delayed formation of calcium silicate hydrate (C–S–H), $Ca(OH)_2$ which are responsible for strength of the cement as shown in Fig.9 [9]. However, if gypsum is not reactive then the ettringite formation will be less and other hydration products of cements such as C–S–H and $Ca(OH)_2$ takes place at a faster rate. In the case of cement with dihydrate form of gypsum, we suspect that the formation of $Ca(OH)_2$ took place in more quantity and consequently the ettringite formation was less. From the present study, it is clear that TCE reduction takes place in a cement sample which generates more ettringite rods. It is known that TCE reduction takes place on the surface of minerals and electrons are required for the reduction reaction. Fe-ettringite generated in the cement system is suspected to give the surface for TCE molecule, and Fe(II) acts as electron donor. The combination of Fe(II) and Fe-ettringite gives a reactive composition for TCE reduction. The studies done by previous researchers also suggest that the combination of Fe(II) and Fe(III) mineral plays a significant role in TCE dechlorination [18]. The results of the our study show that Fe(III) is in the form of Fe-ettringite mineral.

4. Conclusions

The present experimental studies indicated that the form of gypsum in cement plays a very important role. From the TCE reduction experiment and mineralogical analysis it is clear that cement sample containing gypsum in the form of anhydrate generated more ettringite rods and has fastest TCE reduction rate. The hemihydrate has intermediate ettringite generation and TCE reduction rate. The cement with dihydrate form of gypsum showed least ettringite generation and TCE reduction rate among all three cements.

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