# Zeolite and fly ash in the composition of oil well cement: Evaluation of degradation by $CO_2$ under geological storage condition

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## ABSTRACT

The performance of cement class G used in cementation of oilfield wellbores with addition of pozzolans was evaluated under geological carbon storage conditions. Two commercial synthetic zeolites types (4A-1 and 4A-2) and fly ash from a coal-fired plant were used as pozzolanic materials in amounts of 5 and 10% in weight replacing the cement. After curing, the cement samples were submitted to degradation tests in $CO_2$-saturated water at 15 MPa and 90 °C for 7 and 14 days. The cement chemical degradation by $CO_2$ was investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) and compressive strength tests. The chemically altered layer thickness was averaged 3.46 mm for standard cement after 14 days of exposure to $CO_2$. On the other hand, cement systems with 10% wt. of pozzolanic material varied from 1.70 to 5.50 mm depending on the type of pozzolan and level of cementitious matrix porosity related to pozzolanic particle clustering. In general, 4A-1 zeolite presented better performance in terms of resistance to $CO_2$ attack and higher compressive strength after 14 days when compared to 4A-2 zeolite. The results showed that the addition of fly ash improved the compressive strength of the samples but increased the chemically altered layer due to $CO_2$ diffusion. SEM and XRD analyses showed that the portlandite was consumed and carbonation occurred in the chemical modified layer due to cement reaction with aqueous $CO_2$. Most cement systems with and without pozzolanic material exhibited no expressive loss on compressive strength after being exposed to $CO_2$-rich environment up to 14 days. On the contrary, some cement systems with 4-A1 zeolite and fly ash exhibited a mechanical resistance increase due to the carbonation process.

## 1. Introduction

One of the alternative ways to reduce $CO_2$ emissions to the atmosphere is the capture and geological storage of carbon dioxide (CCS) in depleted reservoirs, arousing great interest from both economic and environmental points of view. This technology consists in capturing and separating the $CO_2$ at the emitting source and afterwards the $CO_2$ is transported and injected into depleted oil wells. Saline aquifers and deep coal beds are also important geological storage options (Bachu, 2008; Bachu and Adams, 2003; Cailly et al., 2005; van der Meer, 2005). CCS has the advantage of being associated to enhanced oil recovery (EOR) or enhanced coal bed methane (ECBM), contributing for low carbon energy system and at the same time increasing oil and gas production (Aspelund

and Gundersen, 2009; White et al., 2005). However, in order to achieve the expected objectives with this $CO_2$ mitigation technology, it is necessary to guarantee the chemical integrity and mechanical resistance of the materials used in the wellbore construction, since one of the most important pathways for $CO_2$ leakage is through the wells. Cement pastes, class G or class H, usually used in the insulation between well drilling and steel casing should ensure complete sealing and maintain the integrity of the well structure for long periods of time to avoid $CO_2$ escape routes (Bai et al., 2016; Cailly et al., 2005; Scherer et al., 2005). However, class G or class H cements are chemically unstable in $CO_2$-rich environments due to the occurrence of chemical reactions in which some components of the hardened cement paste react with carbonic acid causing degradation at a quite accelerated level (Abid et al., 2015;

Bagheri et al., 2018; Bai et al., 2016; Barlet-Gouédard et al., 2007; Bertos et al., 2004; Bjørge et al., 2019; Carey et al., 2010; Huet et al., 2011; Kutchko et al., 2008, 2009; Lesti et al., 2013; Matteo et al., 2018; Omosebi et al., 2016; Yang et al., 2016; Zhang and Talman, 2014). Several factors influence the degradation of cement paste, such as pressure and temperature, which change with well depth. According to geological conditions, the oil well temperature and pressure can reach 175 °C and up to 75 MPa, respectively (van der Meer, 2005).

The degradation process of hardened cement paste in the presence of $CO_2$ occurs in three stages. In the first stage, the $CO_2$ dissolved in the formation fluids reacts with the calcium hydroxide ($Ca(OH)_2$, portlandite) and the hydrated calcium silicate (C-S-H) of the cement paste, firstly consuming the portlandite and producing a region of high porosity. In the second stage, the reaction of the calcium ions originates from the dissolution of $Ca(OH)_2$ with the $CO_2$ dissolved in water, leading to the precipitation of calcium carbonate ($CaCO_3$) in the cement paste pores, resulting in low porosity and high hardness material (carbonated zone). However, as $Ca(OH)_2$ and other alkaline phases are being consumed, the pore solution pH decreases and the dissolution of the previously precipitated calcium carbonate begins, creating a zone of high porosity. This is the third stage of the hardened cement paste degradation process known as bicarbonation (Bagheri et al., 2018; Barlet-Gouédard et al., 2007; Huet et al., 2011; Kutchko et al., 2009, 2008). Thus, the degradation process increases porosity and permeability and decreases the cement compressive strength. Chemical reactions involved in this degradation process are summarized in Table 1.

Some studies have been carried out to find solutions to minimize cement paste degradation in wells for geological carbon storage (Abid et al., 2015, 2019; Barlet-Gouédard et al., 2007; Zhang et al., 2013, 2014). Among the alternatives, the inclusion of pozzolanic material has been indicated as a possible solution, since it can decrease both the permeability and quantity of the portlandite (Abid et al., 2015; Marshdi, 2018). Predominantly composed by $SiO_2$ and $Al_2O_3$, the pozzolanic material reacts with the portlandite to form secondary C-S-H, further reducing the water content in the cement paste and decreasing the Ca/Si ratio, forming a longer C-S-H chain, and thus increasing the mechanical strength and decreasing the permeability of the hardened paste (Abid et al., 2019, 2015; Ahdaya and Imqam, 2019; Bai et al., 2016; Jupe et al., 2008; Kocak et al., 2013; Luke, 2004; Marshdi, 2018; Mehta and Monteiro, 2013; Oltulu and Şahin, 2013; Soares et al., 2015). Fly ash, finely-ground slag, silica fume and natural pozzolans are commonly used in blended cements and concrete mixtures. Use of these supplementary cementing materials has been demonstrated to provide several benefits to the fresh and hardened cement properties, such as improved workability, reduced heat of hydration, increased ultimate strength and enhanced durability (Baldino et al., 2014; Boháč et al., 2016; Kocak et al., 2013; Marshdi, 2018).

In oil-gas fields, pozzolans, such as fly ash, are already added to the cement to minimize the effects of cement thermal retrogression that occurs when well temperature is over 110 °C and for well sealing (cement plug) (Bjørge et al., 2019; Jupe et al., 2008; Kutchko et al., 2008; Luke, 2004; Nelson and Guillot, 2006; Pernites and Santra, 2016; Zhang et al., 2013). Furthermore, some pozzolans can also reduce the slurry density being beneficial for application in low fracture pressure formations (Marshdi, 2018; Onan, 1984). However, there is relatively a small number of studies reporting the interactions between $CO_2$ and cement with addition of pozzolanic material under conditions of geological carbon storage. Kutchko et al. (2009) observed that despite the $CO_2$ penetration layer for cement with the addition of fly ash being superior when compared to cement without addition of pozzolan, the alteration of the cement properties was unexpressive. Zhang and Talman (2014) also studied the carbonation reaction of cement class G with pozzolanic material using two mixtures of cement/fly ash in saline solution with 0.5 M NaCl at 53 °C and 10 MPa, with reaction periods of 3, 7, 14, 28 and 84 days. The results of the degradation tests indicated that pozzolanic material could be useful in cement reinforcement, improving

resistance to $CO_2$ acid attack. These authors pointed out that additional study is necessary to confirm this effect though. However, Bjørge et al. (2019) observed that the carbonation rate of silica-cement was much higher than the ordinary cement and the carbonation process also failed in following the three stages reported on literature (portlandite dissolution, precipitation of calcium carbonate, and bicarbonation).

Zeolites are pozzolanic materials consisting of microporous crystalline hydrated aluminosilicates with a structural arrangement composed of a skeleton formed by the three-dimensional combination $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedral linked to each other by sharing all the oxygen atoms. Its structure presents channels and cavities where water molecules and exchangeable cations are found. The most common commercial zeolite is 4A, presenting Linde type A (LTA) framework, synthesized in the sodium form ($Na_2O.Al_2O_3.2SiO_2.4.5H_2O$). The zeolites are present in a wide range of applications, such as adsorbents for the removal of ions and molecules in solutions and gaseous mixtures, dehydrators, support of catalysts, geotextiles, and fertilizer and detergent softening agents, among others (Dehghan and Anbia, 2017; Lima et al., 2019; Sedić et al., 2015; Silva et al., 2018; Weckhuysen and Yu, 2015). In

**Table 1**
Chemical reactions involved on the cement degradation process in the presence of $CO_2$.

| | |
|---|---|
| **CO₂ dissociation** | |
| Reaction 1 | $CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$ |
| **Cement carbonation** | |
| Reaction 2 | $Ca(OH)_{2(s)} + 2H^+ + CO_3^{2-} \rightarrow CaCO_{3(s)} + 2H_2O$ |
| Reaction 3 | $C\text{-}S\text{-}H_{(s)} + 2H^+ + CO_3^{2-} \rightarrow CaCO_{3(s)} + SiO_xOH_x$ |
| Reaction 4 | $Ca(OH)_{2(s)} + H^+ + HCO_3^- \rightarrow CaCO_{3(s)} + 2H_2O$ |
| Reaction 5 | $C\text{-}S\text{-}H_{(s)} + H^+ + HCO_3^- \rightarrow CaCO_{3(s)} + SiO_xOH_{x\,(s)}$ |
| **Calcium carbonate dissolution (Bicarbonation)** | |
| Reaction 6 | $CO_2 + H_2O + CaCO_{3(s)} \leftrightarrow Ca^{2+} + 2\,HCO_3^-$ |
| Reaction 7 | $2H^+ + CaCO_{3(s)} \leftrightarrow CO_2 + Ca^{2+} + H_2O$ |

**Table 2**
Semi-quantitative chemical composition of 4A-1 zeolite obtained by energy dispersive X-ray spectrometry.

| Element | Weight (%) | Atomic (%) |
|---|---|---|
| O | 38.7 | 45.5 |
| Na | 9.8 | 8.0 |
| Al | 18.9 | 13.2 |
| Si | 19.4 | 13.0 |

**Table 3**
Chemical composition of 4A-2 zeolite according to the manufacturer.

| Compound | Weight (%) |
|---|---|
| $Al_2O_3$ | 28 |
| $SiO_2$ | 33 |
| $Na_2O$ | 17 |

**Table 4**
Chemical composition of coal fly ash obtained by X-ray fluorescence spectrometry.

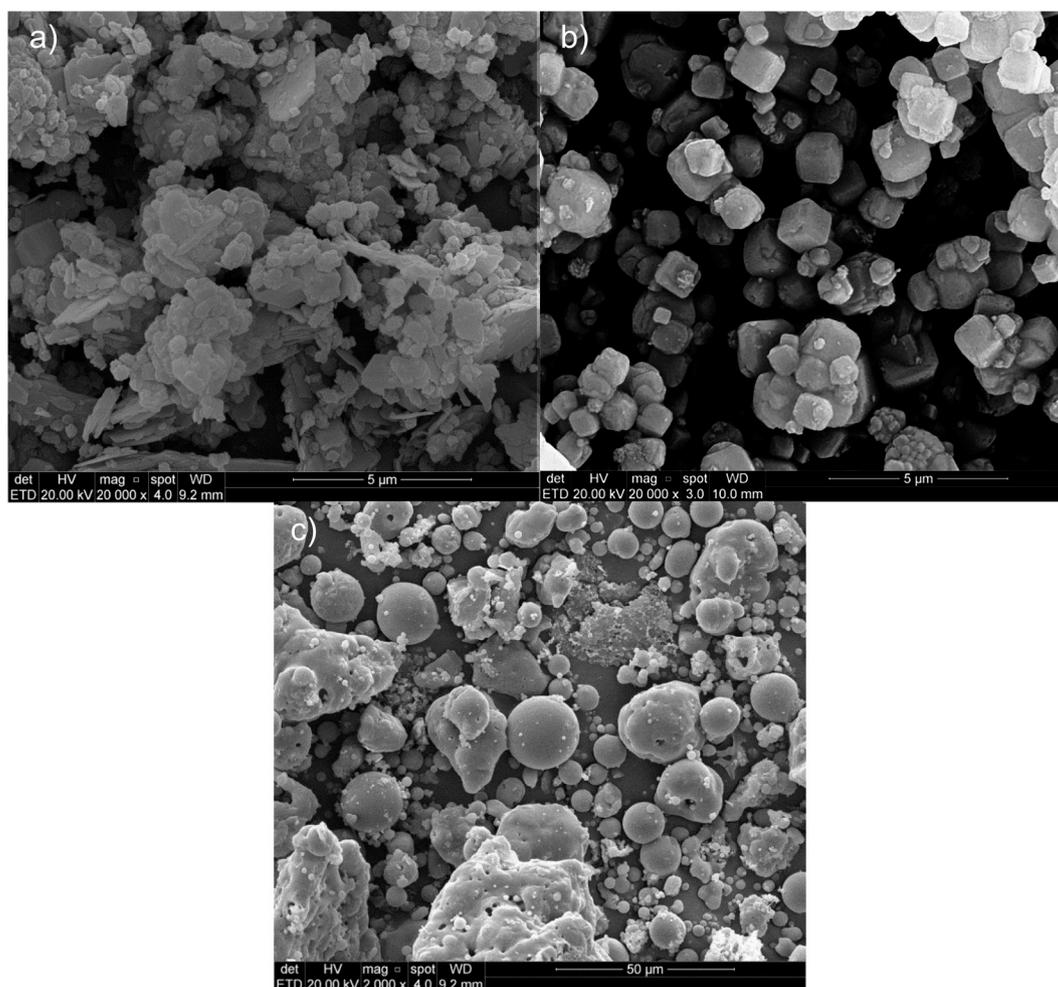| Oxide | Weight (%) |
|---|---|
| $Al_2O_3$ | 21.94 |
| CaO | 1.38 |
| $Fe_2O_3$ | 4.49 |
| $K_2O$ | 1.95 |
| MgO | 0.86 |
| MnO | 0.02 |
| $Na_2O$ | <DL |
| $P_2O_5$ | 0.05 |
| $SiO_2$ | 67.89 |
| $SO_4$ | 0.10 |
| $TiO_2$ | 0.78 |
| Si/Al | 2.70 |

**Fig. 1.** SEM images of pozzolanic materials. (a) 4A-1 zeolite, (b) 4A-2 zeolite, (c) coal fly ash.

addition, the zeolites can be synthesized from coal ash because this solid residue has high silica and aluminum contents (Cardoso et al., 2015a; Querol et al., 2002). Although there are various studies involving the addition of zeolite in cement pastes (Baldino et al., 2014; Boháč et al., 2016; Kocak et al., 2013; Perraki et al., 2010; Poon et al., 1999), they have scarcely been conducted using oil well cement (Sedić et al., 2015) and no reported investigations about the performance of zeolite cement systems in $CO_2$-rich environment were found. The addition of pozzolanic materials is also interesting for light-weight oil-well cement, and the main advantage of using zeolite is its high-porous structure allowing to absorb water and avoiding water separation from the mixture (Marshdi, 2018).

In this work zeolite or fly ash are added in substitution to cement class G to investigate the extension of cement alteration by $CO_2$ penetration and its effects on mechanical properties, simulating conditions similar to geological carbon storage.

**Table 5**
Specific surface area, particle size and pores size of pozzolanic materials as obtained by BET nitrogen adsorption technique.

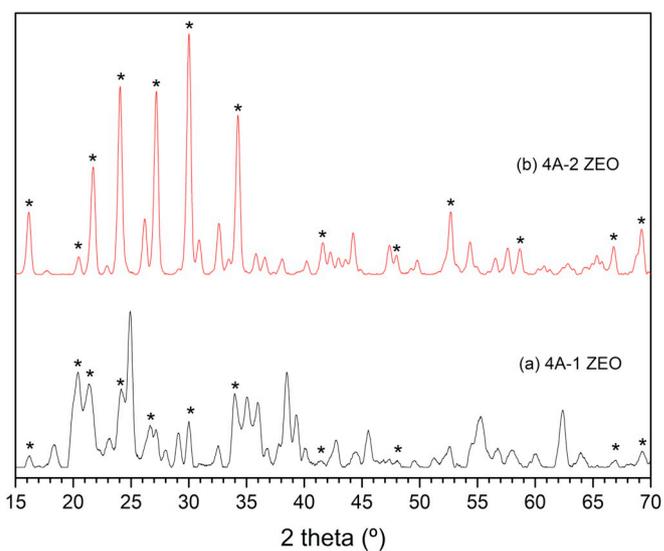|  | 4A-1 zeolite | 4A-2 zeolite | Coal fly ash |
|---|---|---|---|
| Specific surface area ($m^2.g^{-1}$) | $11.47 \pm 0.94$ | $2.54 \pm 0.10$ | $0.78 \pm 0.00$ |
| Particle size average (μm) | $0.53 \pm 0.05$ | $2.36 \pm 0.10$ | $7.67 \pm 0.03$ |
| Pore size average (Å) | $114.97 \pm 8.63$ | $93.3 \pm 3.56$ | $147.09 \pm 13.44$ |



**Fig. 2.** X-ray diffractograms of zeolites used in this study. (a) 4A-1 zeolite, (b) 4A-2 zeolite. Main zeolite peaks were identified in the spectrum.
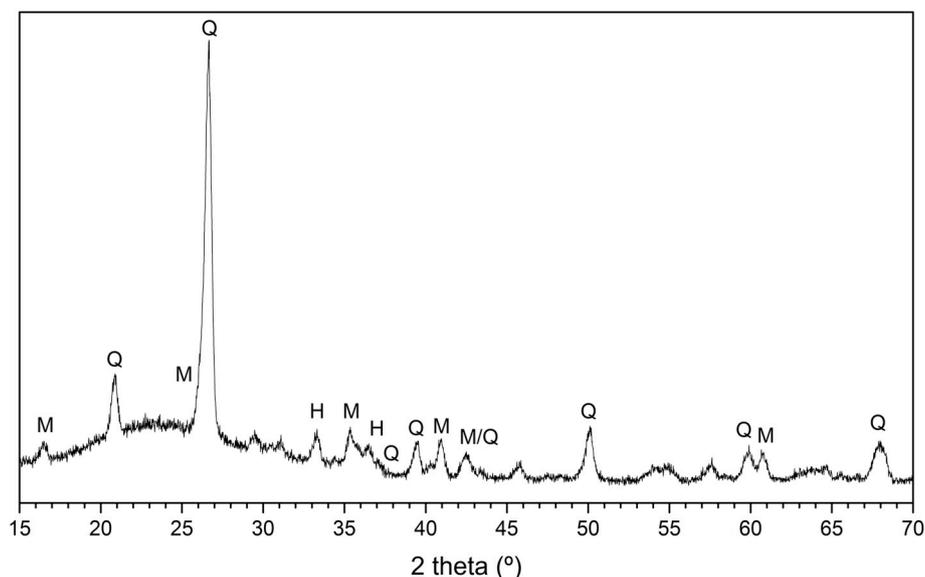
**Fig. 3.** X-ray diffractogram of coal fly ash used in this study. M = mullite; Q = quartz; H = hematite.
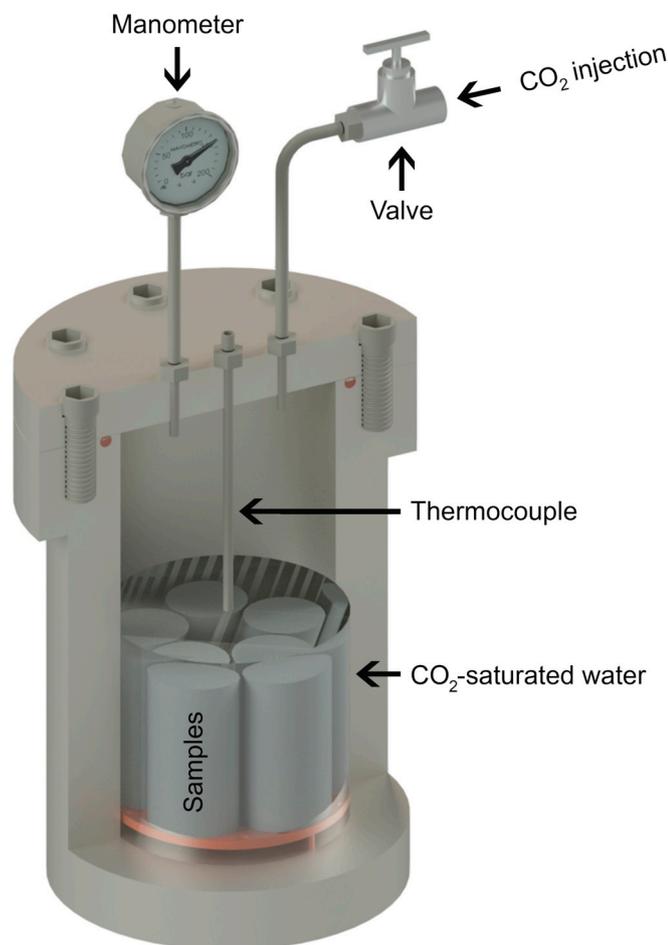


**Fig. 4.** Experimental arrangement for cement degradation tests in $CO_2$-saturated water at 15 MPa and 90 °C.

## 2. Materials and methods

### 2.1. Materials

The Portland cement used was the cement class G supplied by LafargeHolcim-Brazil. Three pozzolanic materials were used, being two types of commercial synthetic zeolites, 4A-1 zeolite (Oxanyl Raos Chemicals, Brazil) and 4A-2 zeolite (IQE- Indústrias Químicas del Ebro, Spain), and fly ash, a mineral coal combustion byproduct from the Candiota Thermoelectric Plant (RS, Brazil). Tables 2–4 show the chemical composition of 4A-1 zeolite, 4A-2 zeolite and coal fly ash, respectively, being $SiO_2$ and $Al_2O_3$ main oxides present in these pozzolanic materials.

The coal fly ash and zeolites underwent no previous heating or washing processes. Slurry was also prepared using neat cement to compare the properties with those mixtures with pozzolanic materials.

The pozzolanic materials were previously characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and surface analysis by BET (Brunauer-Emmett-Teller) nitrogen adsorption technique. For BET analysis, the samples in duplicate were previously dried with nitrogen purging at 80 °C for 24 h. Additional information about the properties of fly ash can be found in Cardoso et al. (2015b).

Fig. 1 shows SEM images of 4A-1 and 4A-2 zeolites, and coal fly ash. 4A-1 zeolite presents a multifaceted morphology, whereas the particle morphology is cubic for 4A-2 zeolite. The fly ash consists mainly of siliceous spherical particles presenting relatively low porosity and some unevenly shaped particles characteristic of unburned coal. Table 5 illustrates the BET nitrogen adsorption results, showing that 4A-1 zeolite presents larger specific surface area and lower particle size than both 4A-1 zeolite and fly ash.

Fig. 2 shows X-ray diffractograms for 4A-1 and 4A-2 zeolites where the X-ray spectrums show 4A zeolites peak characteristics demonstrating that both types are crystalline. The small number of peaks, most of them of low intensity and unindexed in the diffraction pattern could be related to the presence of crystalline impurity, other zeolitic phases or even remaining unreacted raw material. Fig. 3 shows characteristic peaks of quartz, mullite and hematite, and some amount of amorphous material are present in X-ray spectrum for coal fly ash.
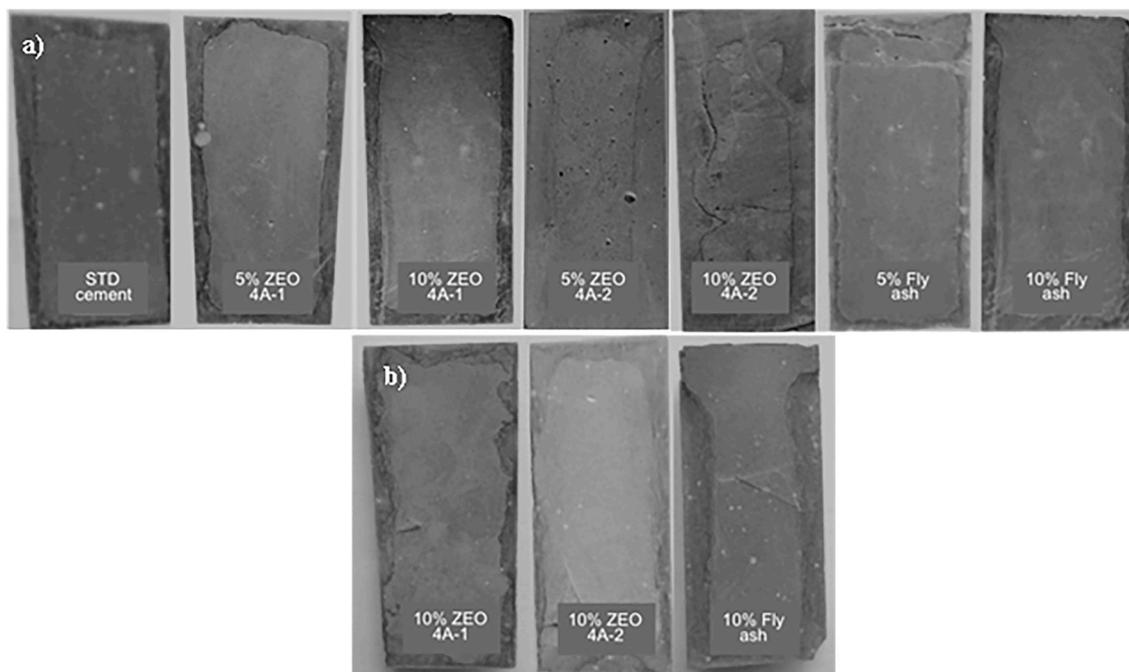
**Fig. 5.** Cement systems after degradation tests in $CO_2$-saturated water at 15 MPa and 90 °C. (a) 7 days and (b) 14 days.

## 2.2. Preparation of cement slurries and test specimens

Preparation of the cement slurries was based on the specification 10A of the API-American Petroleum Institute, published by the Committee on Standardization of Well Cements (Committee 10). Since high cement replacement by zeolite (>25% wt.) induces an increase on porosity (Poon et al., 1999), for comparative purpose the amount of zeolite or coal fly ash used in each cement system was 5% and 10% in weight. A water/solids ratio of 0.44 was used for all systems and no additives added to improve the slurry properties. The pozzolan and cement were previously mixed in solid state for about 1 h. The cement slurry was produced by adding the cement/pozzolan material to distilled water, and stirring during 15 s at a rotation of 4,000 rpm and after an additional 35 s to complete the stirring at 12,000 rpm. New cement slurry was made for each degradation test.

The slurry was poured into polymeric cylindrical molds producing specimens of 46 mm high and 23 mm of diameter. The cure of oil well cement was performed prior to the $CO_2$ degradation experiments, and cure parameters (temperature, pressure, time) used were chosen based on the study of Pang et al. (2013). For curing, the molds with slurries were sealed and arranged in a water-filled high-pressure vessel, and the curing performed under nitrogen ($N_2$) pressure of 6 MPa and 60 °C temperature for 8 h, representing a wellbore before $CO_2$ injection. At this cure condition more than 70% of hydrate products is already formed and further hydration is slow (Pang et al, 2013).

It was observed that zeolite accelerates the hydration process and consequently changes the rheology of the fresh paste, hindering the molding as its percentage in the blend increased. The acceleration role of zeolite on the hydration of $C_3S$ and early C-S-H formation was studied by Boháč et al. (2016) and Perraki et al. (2010). The increase of water demand is mainly attributed to a low particle size of zeolite. In the case of using fly ash, it retarded the hydration process, which can be also
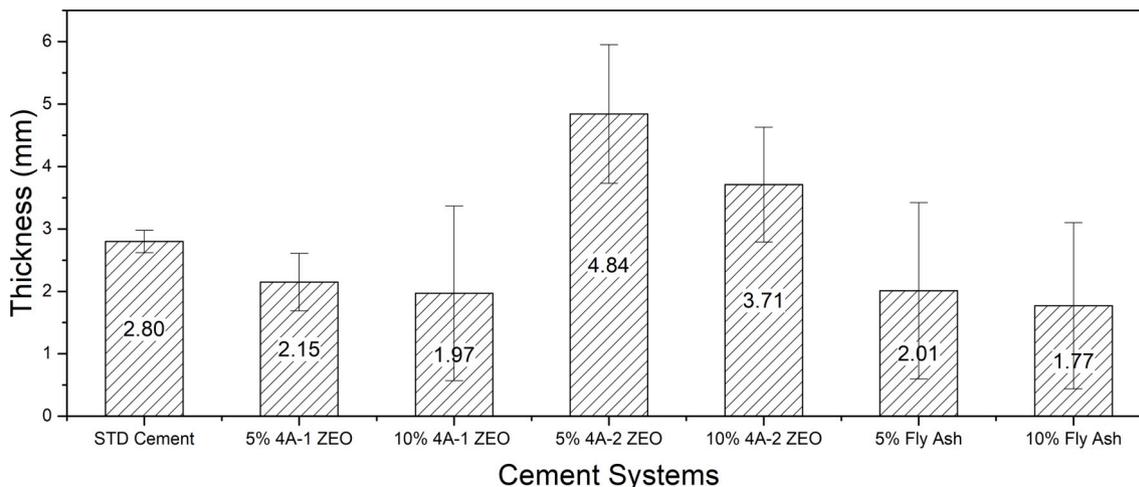


**Fig. 6.** Thickness of chemically altered layer of cement systems after 7 days of immersion in $CO_2$-saturated water at 15 MPa and 90 °C.
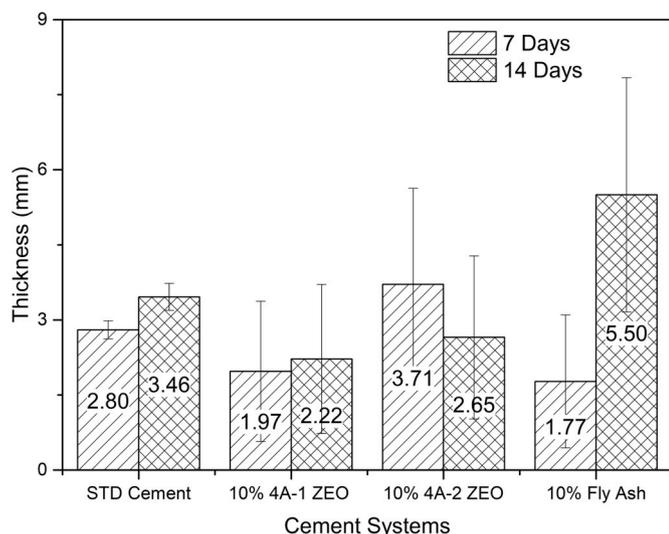
**Fig. 7.** Comparison of chemically altered layer thickness of cement systems after 7 days and 14 days of immersion in $CO_2$-saturated water at 15 MPa and 90 °C.

interesting for use in active wells repairing.

### 2.3. Degradation tests in $CO_2$ environment

Following curing, the five hardened cement test specimens for each type of pozzolan/cement system were placed in a 1L volume stainless steel high-pressure vessel (AISI 316), and filled with deionized water until covering all samples, as illustrated in Fig. 4.

The pressure and temperature to perform the degradation tests were chosen to be above the critical point of $CO_2$ (7.38 MPa and 31.1 °C), suitable for geological storage of carbon. The $CO_2$ degradation tests were performed under 15 MPa and 90 °C corresponding to an approximately 1,500 m deep wellbore considering that a wellbore pressure varies according to a gradient of about 10 MPa $km^{-1}$. Besides, 90 °C temperature produces a high carbonation depth (Barlet-Gouédard et al., 2007). Pressurizing was performed with 99.9% pure $CO_2$.

The thermodynamic model of Duan and Sun (2003) was used to calculate the $CO_2$ solubility in water and the pH as well. Considering the degradation test parameters, the values are 1.02 mol $kg^{-1}$ and 3.2, respectively.

The test specimens were kept immersed in $CO_2$-saturated water for 7 and 14 days to evaluate samples degradation with time. The experiments were carried out under static conditions (no flow) simulating geological conditions at a well distant from the injector or when the $CO_2$ injection period is ended. Once the degradation period was completed, the pressure was slowly released.

The cement microstructural changes were analyzed by field emission scanning electron microscopy (FE-SEM) and by X-ray diffraction (XRD). Additionally, the mechanical strength was determined by uniaxial compression.

For SEM analyses, the samples were cut in approximately 5 mm thick discs using a diamond precision saw, afterwards they were mechanically ground with SiC paper (#320 up to #1200) and then polished with alumina 1 μm and 0.3 μm, respectively. The cement samples were covered with a thin film of gold to become conductive and the images were acquired in secondary electron mode. Powder material was removed from the chemically altered layer and from the core (unreacted cement) for XRD analyses using a Cu Kα X-ray source, 40 kV and 30 mA, 0.1542 nm wavelength diffractometer. The compression tests were carried out in triplicate for each cement system, before and after being exposed to $CO_2$.

## 3. Results and discussion

### 3.1. Carbonation behavior

Fig. 5 shows images obtained from the specimens after being exposed
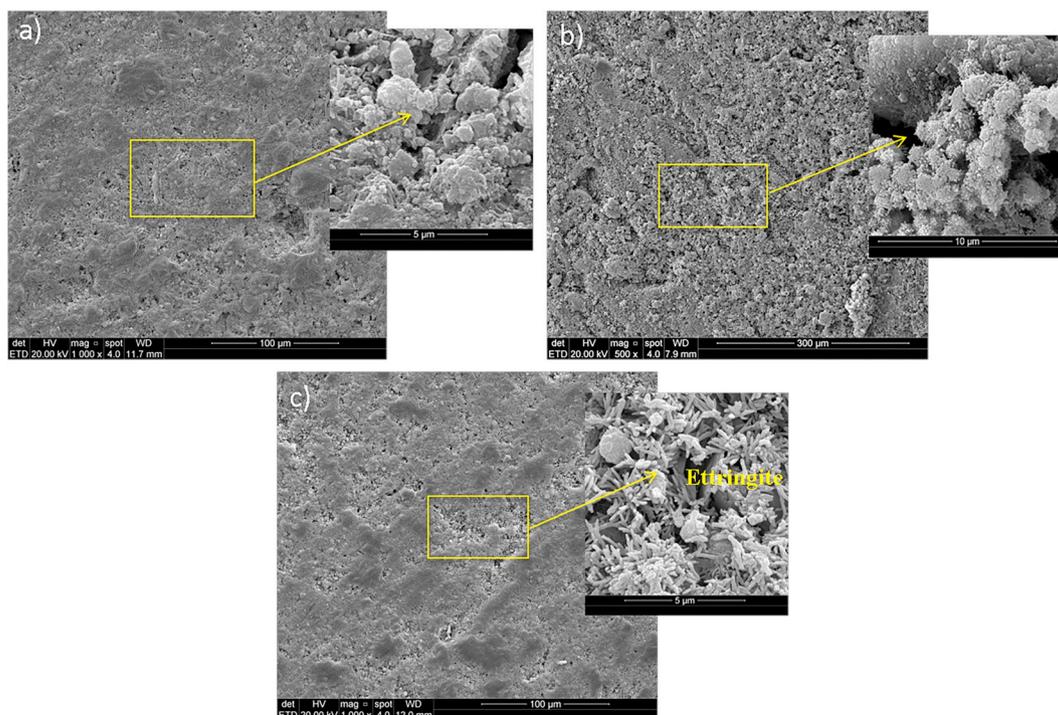


**Fig. 8.** SEM images of the cross section of unaltered cement with addition of zeolites. (a) 5% 4A-1 zeolite, (b) 10% 4A-1 zeolite and (c) 10% 4A-2 zeolite.
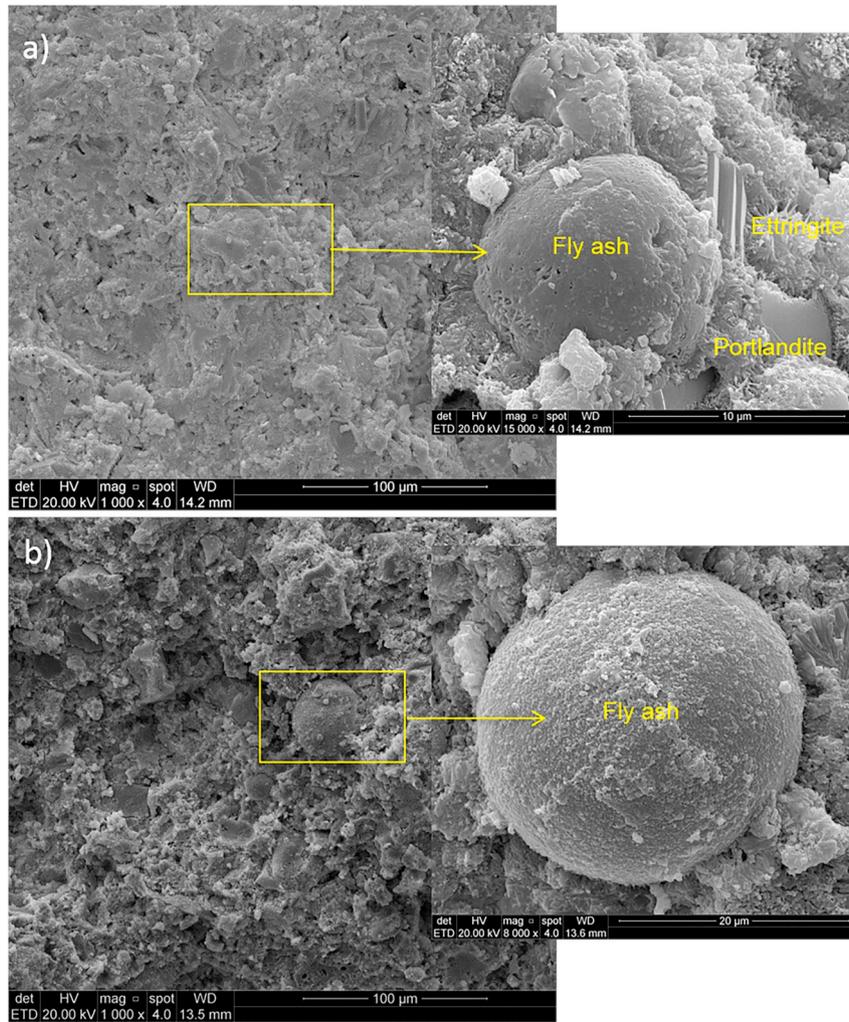
**Fig. 9.** SEM images of cross sections of unaltered cement with addition of coal fly ash showing high adhesion of the ash particles in the cementitious matrix. (a) 5% Coal fly ash and (b) 10% coal fly ash.

to $CO_2$-saturated water at 15 MPa and 90 °C for 7 and 14 days, illustrating the depth of the chemically altered layer.

Fig. 6 shows the chemically altered layer thickness of cement systems after 7 days of immersion in $CO_2$-saturated water and Fig. 7

comparatively presents the chemically altered layer thickness in function of immersion periods.

The thickness of the chemically altered layers observed for all cement systems, with and without addition of zeolites or fly ash, are of
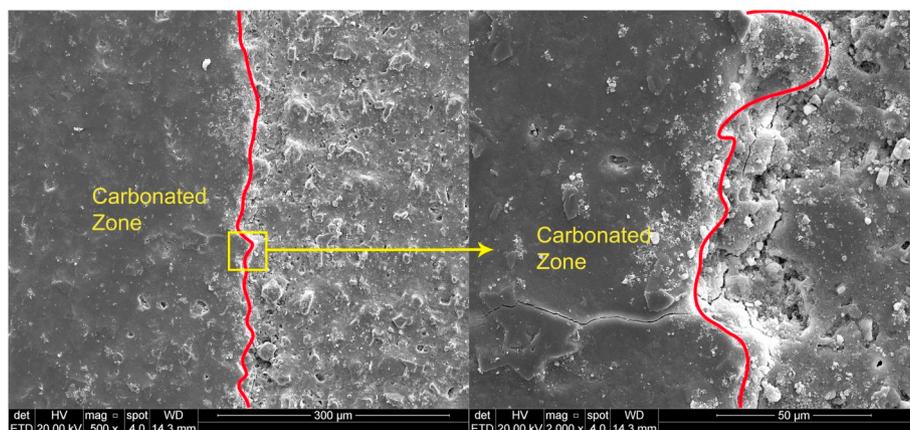


**Fig. 10.** SEM images of the cross section of standard cement at the interface of carbonated zone with portlandite depleted zone after being exposed for 7 days to CO2-saturated water at 15 MPa and 90 °C.
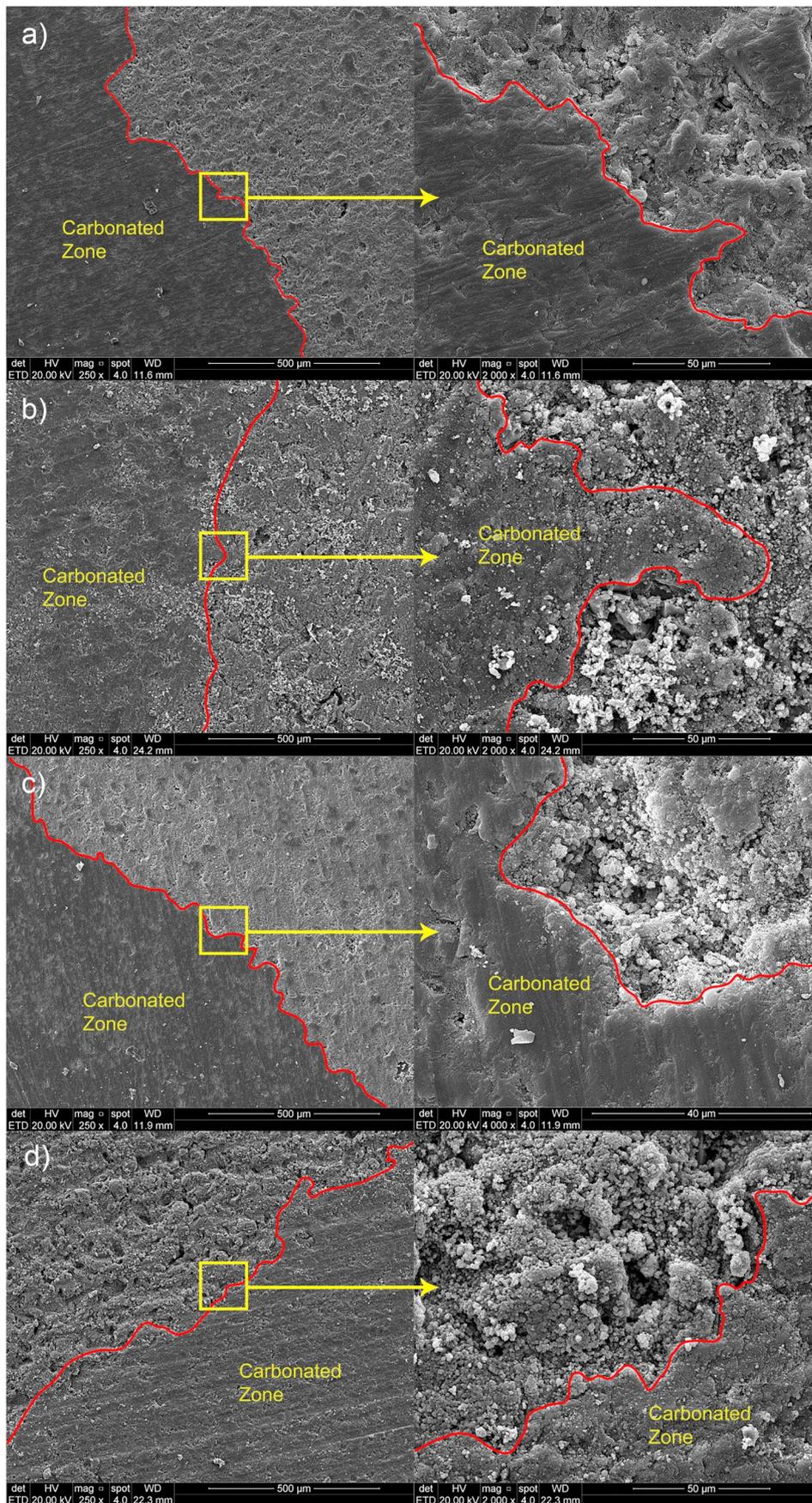
**Fig. 11.** SEM images of the cross section of cement with addition of zeolites at the interface of carbonated zone with portlandite depleted zone after being exposed to $CO_2$-saturated water at 15 MPa and 90 °C. a) 5% 4A-1 zeolite; 7 days. b) 10% 4A-1 zeolite; 7 days. c) 10% 4A-1 zeolite; 14 days. d) 10% 4A-2 zeolite; 14 days.
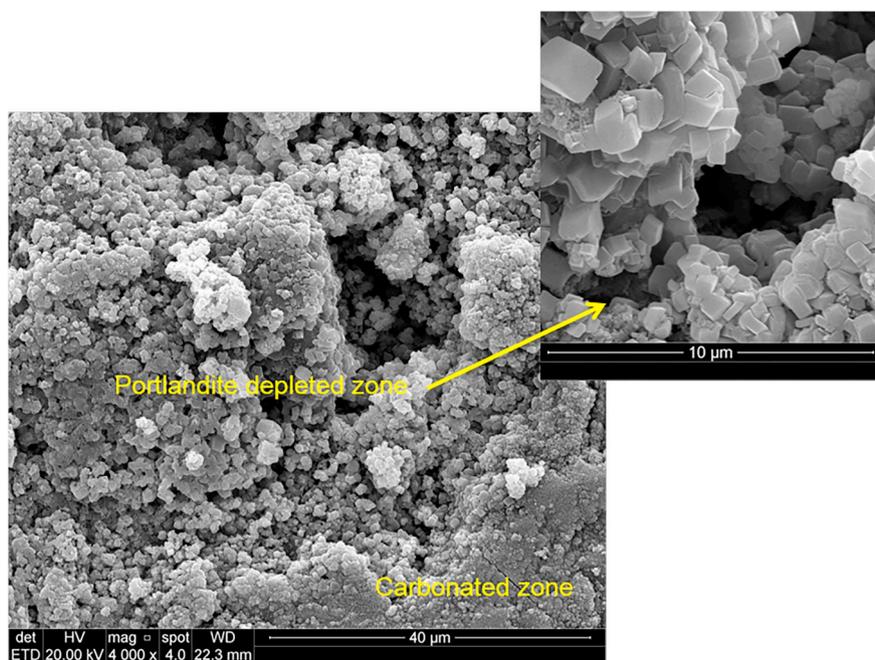
**Fig. 12.** SEM image of the cross section of cement with addition of 4A-2 zeolite at the portlandite depleted zone after being exposed for 7 days to $CO_2$-saturated water at 15 MPa and 90 °C.

the same order of magnitude as reported in the literature (Abid et al., 2015; Barlet-Gouédard et al., 2007; Huet et al., 2011; Kutchko et al., 2009; Zhang et al., 2014, 2013).

The altered layer is more irregular (high standard deviation) for cement systems with zeolite or fly ash when compared with standard cement, which can be related to particle clustering leading to a more porous cementitious matrix. When adding 4A-1 zeolites the average values of chemically altered layer thicknesses were lower than the standard cement for both exposure times (7 and 14 days) and the percentage of zeolite (5 or 10% in wt.) has little effect on the layer thickness. However, in presence of 4A-2 zeolite the chemically altered layer thickness increased compared to the standard cement in both percentages (5 and 10% in wt.) for 7 days. The chemically altered layer for the specimen exposed for 14 days to $CO_2$ was lower than for 7 days, probably related to zeolite dispersion heterogeneity due to small particle size of 4A-2 zeolite, as shown by BET analysis (Table 5).

The addition of fly ash reduces the depth of the degraded layer for both 5% and 10% of substitution to the cement class G for exposure time of 7 days. However, for a longer exposure time (14 days), the addition of 10% fly ash promoted a considerable increase in layer thickness. Zhang et al. (2014) also observed that in the presence of a greater amount of fly ash (65% in vol.), the cement was more susceptible to degradation over time in the presence of $CO_2$ and $H_2S$ (50 °C, 15.1 MPa) than those with the lowest pozzolan content (35% in vol.). Kutchko et al. (2009) also found a carbonated layer for the cement with the addition of fly ash superior to the cement without addition of fly ash, but with different reaction mechanism in relation to standard cement.

In order to better understand the behavior of the reaction of $CO_2$ on the degraded layer thickness and reaction mechanism, cross sections of the test specimens were observed in SEM.

Figs. 8 and 9 show SEM images of unreacted cement with addition of zeolites and fly ash, respectively. The cement system with 10% 4A-1 zeolite exhibited a more porous cementitious matrix when compared to the other cement systems. Due to the morphology of 4A-1 zeolites particles, it was not possible to identify them by SEM, since they present a similar morphology to the hydrated components of the cement paste. In 10% 4A-2 of zeolite, Fig. 8(c), the formation of a large amount of

ettringite can be seen. In the SEM images of Fig. 9, corresponding to the unreacted cement with 5% and 10% fly ash, a high adhesion of the fly ash particles to the cement matrix can be observed, and also the formation of ettringite, Fig. 9(a), due to the pozzolanic effect.

Figs. 10–14 show SEM images of cross sections at the interface of carbonated and portlandite depleted zones of specimens corresponding to different cement systems after being exposed to $CO_2$-saturated water at 15 MPa and 90 °C. The presence of a high-density carbonated zone and high porosity portlandite depleted zone are clearly visible in all cement systems containing or not zeolites or fly ash (Figs. 10 and 12). Therefore, the reaction mechanism seems to follow the usual mechanism reported in literature for cement degradation in $CO_2$-rich medium (Abid et al., 2015; Barlet-Gouédard et al., 2007; Huet et al., 2011; Kutchko et al., 2007), involving the formation of a high porosity degraded zone near the carbonated zone due to the dissolution of the portlandite and consequent leaching of calcium from the matrix to the solution to form amorphous $SiO_2$. Diffusion is considered the major transport mechanism into the cement in radial direction, usually following the Fick's second law increasing the carbonation depth with the square root of reaction time (Abid et al., 2015; Bagheri et al., 2018; Bai et al., 2016; Kutchko et al., 2008). Comparing all cement systems, those systems with 4A-1 or 4A-2 zeolites immersed in $CO_2$-rich environment for 14 days were the ones that portlandite depleted zones were more porous. Fig. 11 shows a magnification of portlandite depleted zones of cement systems with 10% of 4A-2 zeolite illustrating the presence of zeolite clusters, indicating that particles dispersion was heterogeneous. On the other hand, fly ash cement systems seem to present a smoother transition from carbonation zone to portlandite depleted zone, being less porous than in the other systems. Furthermore, standard cement seems to present the carbonated zone denser than cement systems with zeolite or fly ash.

Fig. 14 shows a SEM image corresponding to the interface between carbonated zone and portlandite depleted zone of cement system with fly ash after immersion in $CO_2$-saturated aqueous solution evidencing porosity and spherical fly ash particles. Kutchko et al. (2009) found that the dissolution of portlandite is more gradual in pozzolan mixtures (fly ash), and consequently less critical to compromise the cement properties.
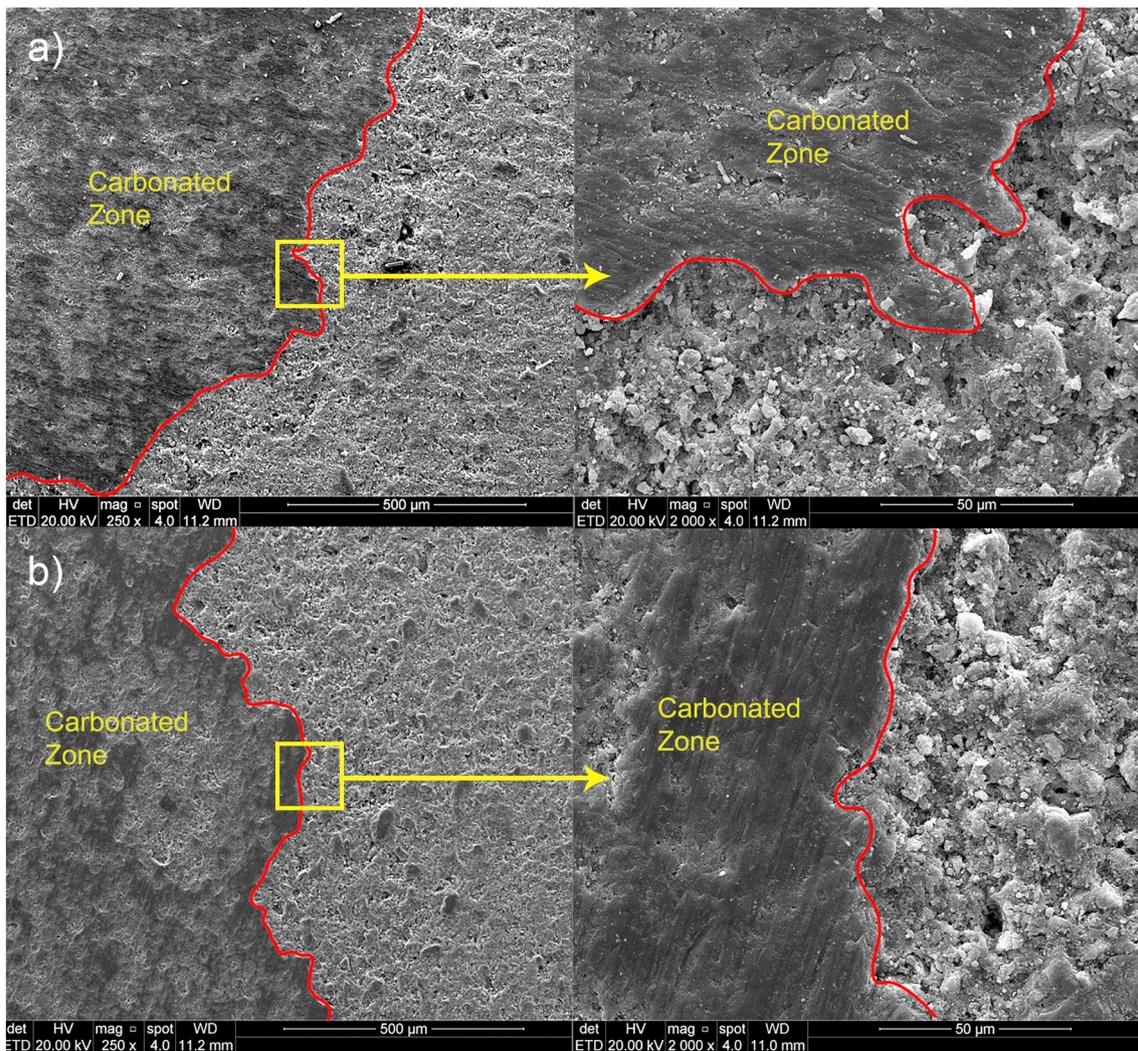
**Fig. 13.** SEM images of the cross section of cement with addition of coal fly ash at the interface of carbonated zone with portlandite depleted zone after being exposed to $CO_2$ saturated water at 15 MPa and 90 °C. a) 5% Coal fly ash after 7 days. b) 10% coal fly ash after 7 days.
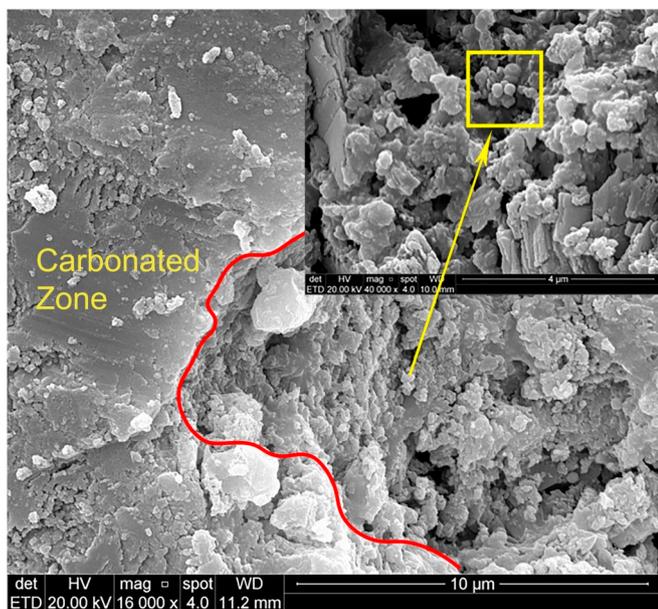
**Fig. 14.** SEM image of the cross section of cement with addition of coal fly ash at the portlandite depleted zone after being exposed to $CO_2$-saturated water 7 days at 15 MPa and 90 °C.

The X-ray diffraction technique was used to identify the main crystalline phases present in the different test specimens before and after being exposed to $CO_2$-rich environment. The diffractograms of the standard cement and cement systems with zeolites or fly ash are shown in Figs. 15–17.

The main hydrated components present in the standard cement (Fig. 15(a)) are calcium hydroxide (P-portlandite) and hydrated calcium silicate (C-S-H).

Fig. 16(a) and (c) corresponding to unreacted cement with the addition of 5% and 10% 4A-1 zeolites, respectively, show peaks similar to the standard cement paste with presence of portlandite (P) and hydrated calcium silicate (C-S-H). When the zeolite content is increased from 5% to 10%, the main portlandite peak (at 18°) decreases in intensity indicating the pozzolanic effect of the zeolite. After being exposed to $CO_2$, the portlandite (P) was totally consumed and the peaks
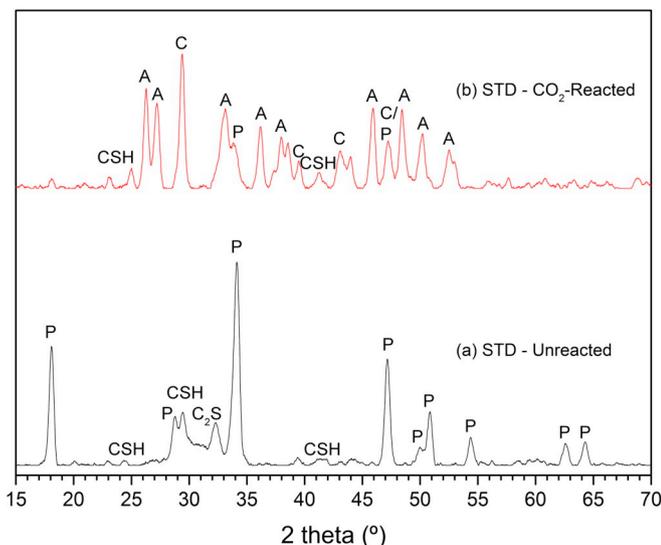
of calcite (C) and aragonite (A) appeared in the chemically altered layer. Similarly, to 4A-1 zeolite cement system, the X-ray diffractogram of 4A-2 zeolite cement system, Fig. 16(e), the portlandite (P) peak intensity decreases in the X-ray diffractogram and the calcite (C) and aragonite (A) peaks are present. In addition, a small peak of hydrated calcium silicate (C-S-H) is also present.

Fig. 17 shows the X-ray diffractograms of cement with 5 and 10% fly ash after being exposed to $CO_2$. The X-ray diffractograms of the cement with the addition of fly ash show the characteristic peaks of the other cement systems after being exposed to $CO_2$. When adding a higher amount of fly ash (10%), a halo of amorphous components at low angles appears near the peak of the C-S-H.

It is important to point out that the main property of pozzolans, such as fly ash and zeolites, is their ability to react and combine with portlandite, generating stable products (C-S-H) with agglutination characteristics. As a result, there is a decrease in the amount of calcium hydroxide (portlandite) (Mehta and Monteiro, 2013). The zeolites and fly ash used in cement systems demonstrate high pozzolanic activity. The SEM images and XRD analyses indicate that pozzolans increase porosity causing higher rate of $CO_2$ diffusion, thus reducing the portlandite content and preventing the high precipitation of carbonates. Thereby, it can positively influence the penetration of $CO_2$ bearing fluids into the cement with time as also pointed by Bagheri et al. (2018).

### 3.2. Compressive strength

Figs. 18 and 19 show the results of compressive strength tests for the standard cement and the cement without addition of pozzolans before and after being exposed to the $CO_2$ medium for 7 and 14 days, respectively. Considering the 7 days age, the standard cement reached a higher value of compressive strength when compared to the cement systems with pozzolan addition. The compressive strength average value of 51.4 MPa found for standard cement was similar with those reported in the literature (Barlet-Gouédard et al., 2007; Omosebi et al., 2016).

The addition of 4A-1 zeolites to the standard cement reduced significantly the compressive strength in the first 7 days, about 66% when compared to the standard paste at 7 days. Even at 14 days age the compressive strength values were about 41% lower than the standard cement. In addition, there was a significant difference in strength from 7 to 14 days and the higher the concentration of this zeolite, the greater the loss of resistance. This can indicate that the particle distribution was heterogeneous producing pastes with high level of porosity, thus compromising the mechanical properties. Even considering that the cement cure was performed under pressure and high temperature, allowing the obtainment of high amounts of hydrated products, there was an increase in mechanical resistance from 7 days to 14 days age. Sedić et al. (2015) optimized cement pastes for oil wells by adding zeolites. In their study, cement systems using cement class G containing 20%, 30% and 40% of clinoptilolite (natural) zeolites were used, and the results obtained in terms of compressive strength for the different blends were 15.29 MPa for 20% zeolite, 17.28 MPa for 30% zeolite and 15.27 MPa for 40% zeolite after 3 days cure. This study showed similar results, being 17.38 MPa for 7 days and 32.54 MPa for 14 days with 5% and 13.14 MPa for 7 days and 29.95 MPa for 14 days when adding 10%. It is important to mention that Kocak et al. (2013) also added zeolites in various proportions (5%, 10%, 15% and 20% by weight) but in Portland cement mortars and observed that adding zeolite decreased the mortar specific mass and delayed the development of flexural and compressive strength during the first days. They also observed that the higher the amount of zeolite, the lower the compressive strength.

Using the 4A-2 zeolites the compressive strength values were also below the standard cement and the compressive strength values did not present significant differences from 7 days to 14 days of age. The compressive strength for cement systems with 4A-2 zeolite at 14 days age was lower than for zeolite 4A-1. It is important to mention that this is the blend, which presents high porosity and formation of particle
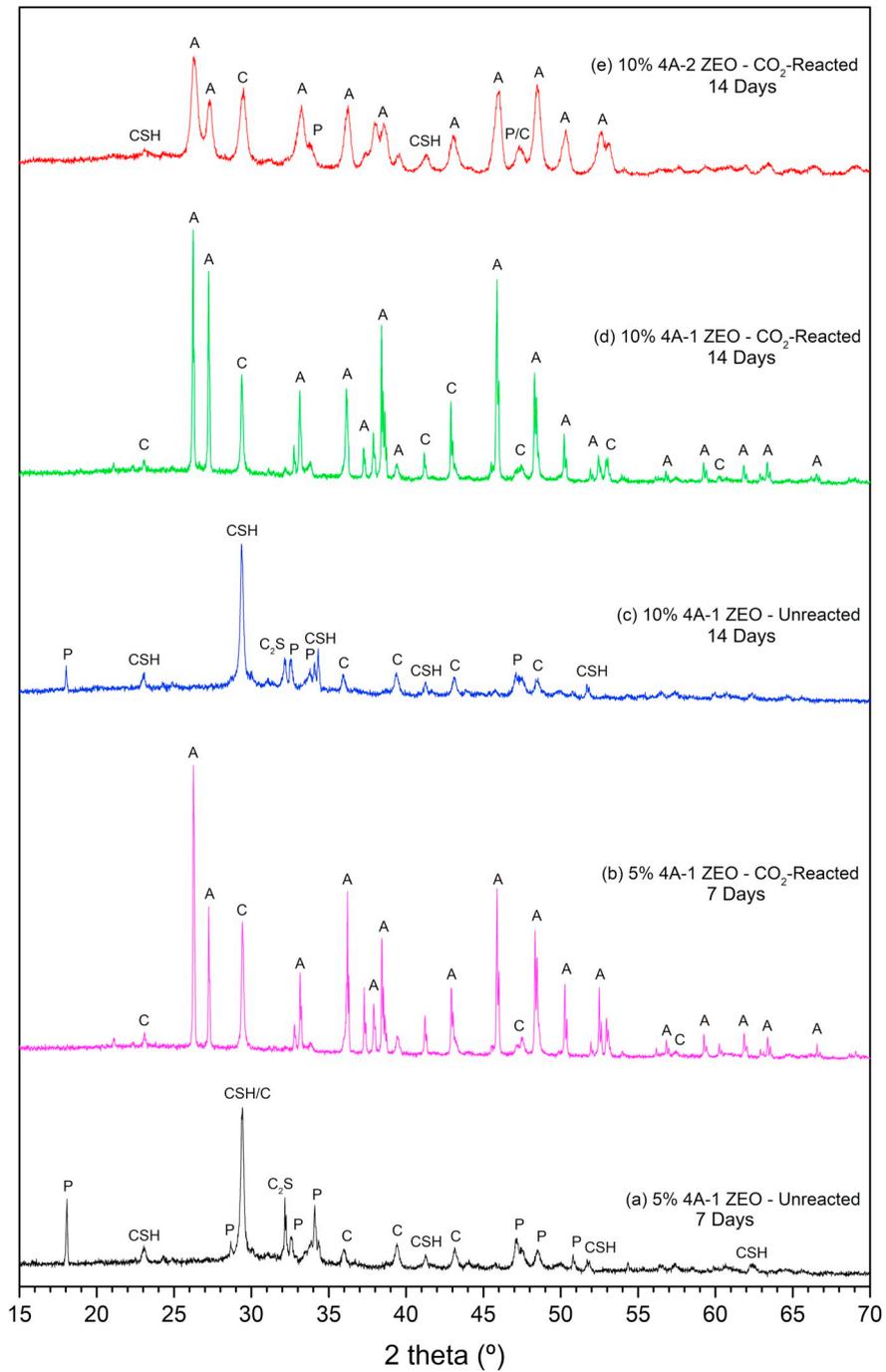


**Fig. 15.** X-ray diffractograms of standard cement before (a) and after being exposed to $CO_2$ for 7 days (b). A = Aragonite; C= Calcite; P= Portlandite.

**Fig. 16.** X-ray diffractograms of cement with 4A-1 and 4A-2 zeolites before and after being exposed to $CO_2$ for 7 days. A = Aragonite; C= Calcite; P= Portlandite.
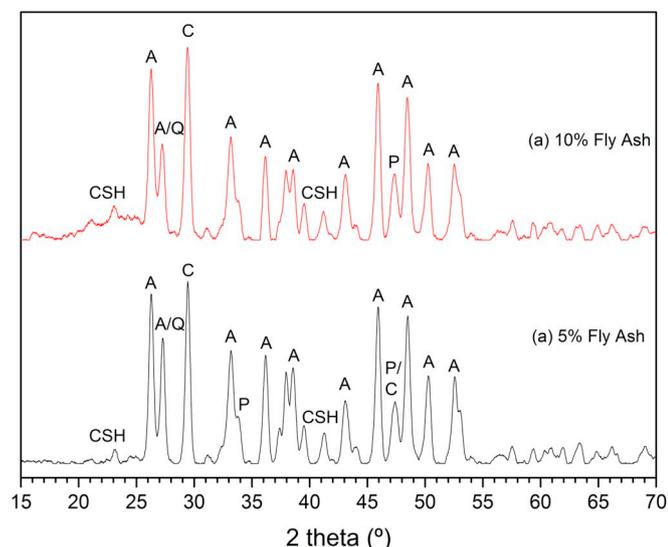
**Fig. 17.** X-ray diffractograms of cement with coal fly ash after being exposed to $CO_2$ for 7 days. A = Aragonite; C= Calcite; P= Portlandite; Q = Quartz.

clusters, as shown by SEM images in Fig. 12, contributing perhaps to the lower compressive strength as well.

The cement systems with addition of fly ash presented a compressive strength very close to the standard cement, specially at 14 days of age. Cements with fly ash in percentages of 5% and 10% develop mechanical resistance a little more slowly than reference cement.

In general, there was no expressive loss in compressive strength when exposed to $CO_2$ for all systems with and without adding pozzolans. Actually, in most cases there was an increase in resistance, which could be related to pore filling of the cement with carbonates due to carbonation process. It is interesting to note the high resistance achieved for cement system with 10% addition of fly ash after being exposed to $CO_2$ saturated water for 14 days, reaching compressive strength average value of 65.76 MPa.

The $CO_2$ chemical reaction when in contact with hydrated cement

produces calcium carbonate, calcium bicarbonate and silica gel. In the early stage of the process, the carbonation itself is beneficial to compressive strength due to clogging of cement pores with calcium carbonate. However, as the reaction process advances, the dissolution of the previously precipitated calcium carbonate takes place due to bicarbonation that is quite damaging to cement and critical for the wellbore because the physical and mechanical properties of cement become seriously compromised. However, the results indicate that 14 days was a relatively short period to reach a significant bicarbonation process for promoting a negative impact on compressive strength in all cement systems. These results indicate a further need for investigating pozzolans on $CO_2$-degradation cement behavior and the impact on mechanical properties over longer periods of exposure.

## 4. Conclusions

- SEM and XRD analyses showed that the pozzolanic cement systems containing zeolites or fly ash exhibited the same reaction mechanism reported in literature for ordinary oil well cement in $CO_2$-rich environment, involving the formation of a high porosity portlandite depleted zone, high density carbonated zone and bicarbonated zone. However, the standard cement seems to present a denser carbonated zone than cement systems with zeolite or coal fly ash.
- The pozzolans properties, such as chemical composition, particle size, morphology and specific surface area influenced cement paste properties and its resistance to $CO_2$ attack. The results indicate that if particles are homogeneously distributed on the cementitious matrix, it is possible to reach a lower carbonation depth.
- In general, 4A-1 zeolite presented better performance in terms of resistance to $CO_2$ attack when compared to 4A-2 zeolite. The addition of coal fly ash reduced the chemically altered layer thickness for both 5% and 10% of substitution to the cement class G for exposure time of 7 days. However, for a longer exposure time (14 days) the addition of 10% fly ash promoted a considerable increase in layer thickness.
- The cement systems with and without pozzolanic material in most cases exhibited no loss in compressive strength after being exposed to $CO_2$-rich environment, meaning that 14 days was a relatively short period to reach a significant dissolution of calcium carbonate for promoting a negative impact on compressive strength in all cement systems.
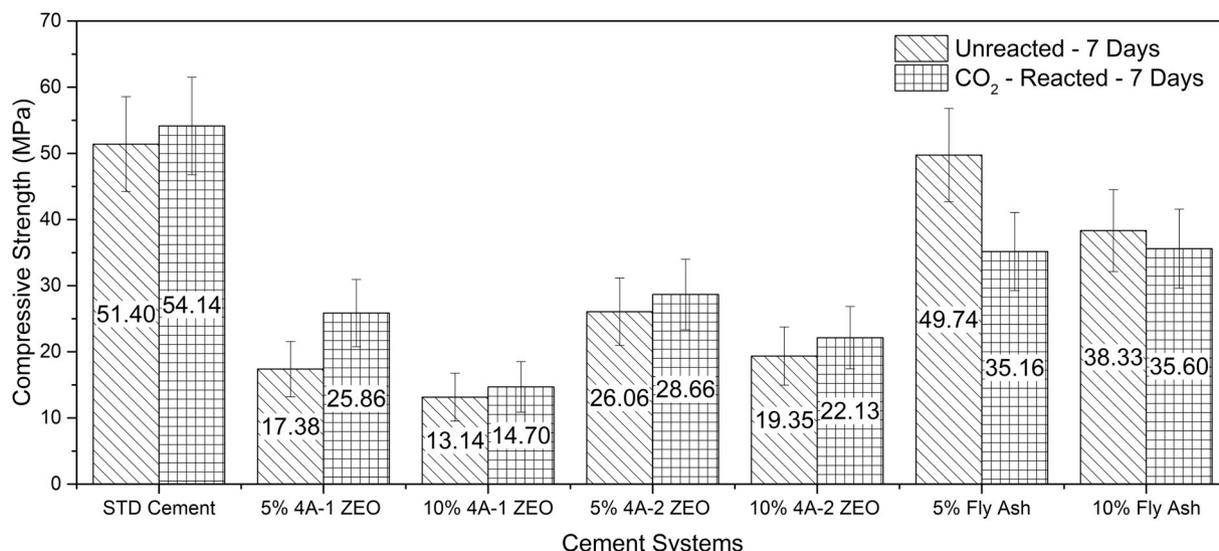


**Fig. 18.** Compressive strength for the standard cement and for cement with addition of zeolites and coal fly ash before and after being exposed to $CO_2$ for 7 days.
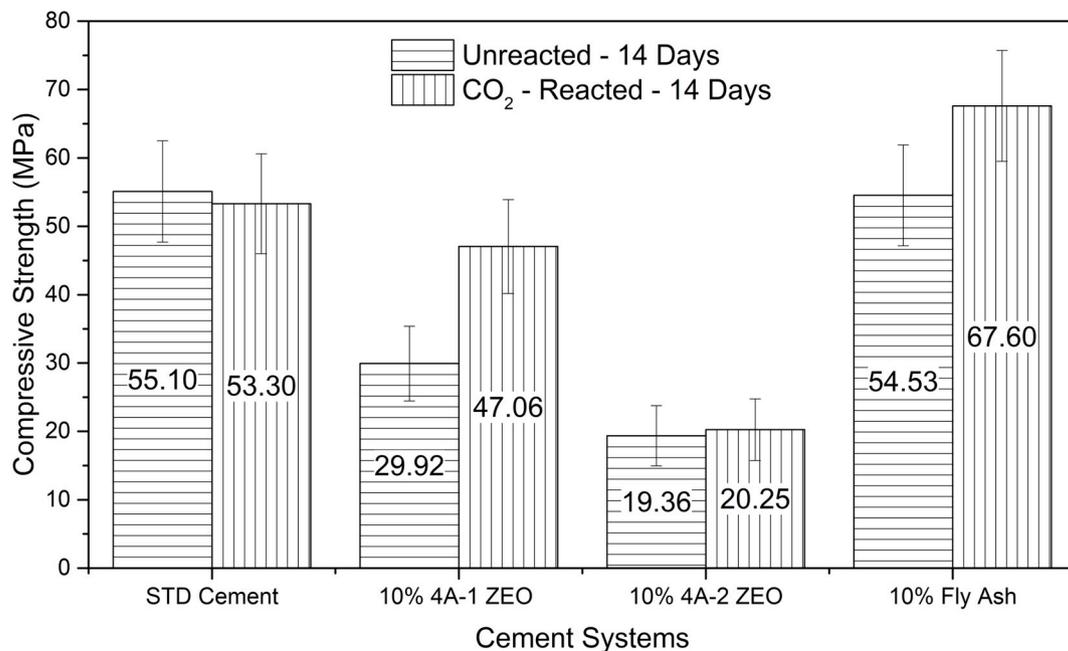
13

**Fig. 19.** Compressive strength for the standard cement and for cement with addition of zeolites and coal fly ash before and after being exposed to $CO_2$ for 14 days.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petrol.2019.106656.

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