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Artificial Weathering as a Function of CO₂ Injection in Pahang Sandstone Malaysia: Investigation of Dissolution Rate in Surficial Condition

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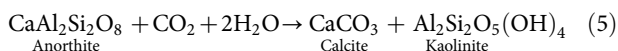
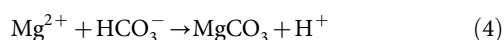
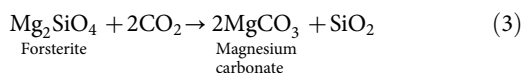
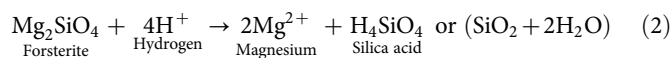
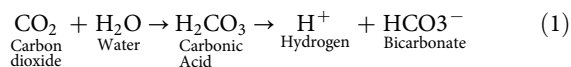
Formation of carbonate minerals by CO₂ sequestration is a potential means to reduce atmospheric CO₂ emissions. Vast amount of alkaline and alkali earth metals exist in silicate minerals that may be carbonated. Laboratory experiments carried out to study the dissolution rate in Pahang Sandstone, Malaysia, by CO₂ injection at different flow rate in surficial condition. X-ray Powder Diffraction (XRD), Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDX), Atomic Absorption Spectroscopy (AAS) and weight losses measurement were performed to analyze the solid and liquid phase before and after the reaction process. The weight changes and mineral dissolution caused by CO₂ injection for two hours CO₂ bubbling and one week' aging were 0.28% and 18.74%, respectively. The average variation of concentrations of alkaline earth metals in solution varied from 22.62% for Ca²⁺ to 17.42% for Mg²⁺, with in between 16.18% observed for the alkali earth metal, potassium. Analysis of variance (ANOVA) test is performed to determine significant differences of the element concentration, including Ca, Mg, and K, before and after the reaction experiment. Such changes show that the deposition of alkali and alkaline earth metals and the dissolution of required elements in sandstone samples are enhanced by CO₂ injection.

Carbon dioxide (CO₂) emissions from fossil fuels are estimated at 6 GtC/year¹. Fifty percent of the increased concentration of CO₂ has occurred during the last 40 years and is mainly due to human activities². Means to reduce the atmospheric carbon emissions from the energy and/or process industries has become increasingly emphasized as a primary environmental concern, because it increases the global warming and rise in sea level. In nature, the formation of carbonate minerals from atmospheric CO₂ is one of the major processes in the long-term global carbon cycle³. Gaillardet et al.⁴ stated that about 0.1 Gt of carbon per year is bound by silicate-mineral weathering throughout the world; at this rate, the consumption of global atmospheric CO₂ inventory would be after 8000 years. To accelerate this process, transformation of atmospheric CO₂ into carbonate minerals can be done via two effective ways; ex-situ and in-situ approaches. The former is performed via the industrial processes⁵ and the later by injection into subsurface geological formations where the required elements are available for creation of carbonate minerals⁶. CO₂ mineralization or mineral carbonation, as an artificial rock weathering, mimics the natural rock weathering, was first proposed by Seifritz in 1990⁷. It provides a permanent and leakage-free CO₂ disposal method such that the carbonate production is environmentally benign and stable⁸. However, mechanisms controlling mineral stabilities in contact with injected supercritical fluids containing water are relatively unknown⁹. Chemical reaction of CO₂ with minerals to form stable, solid compounds like carbonates considered as the main target of CO₂ mineralization in surface and subsurface rocks.

Formation of carbonate minerals such as calcite (CaCO₃), dolomite (Ca_{0.5}Mg_{0.5}CO₃) and magnesite (MgCO₃) is the most stable, long-term storage tool for atmospheric carbon dioxide₃. The fixation of CO₂ into divalent cations, such as Ca²⁺, Mg²⁺, Fe²⁺ is known as mineral carbonation¹⁰. Magnesium and calcium are proven to be the most suitable alkaline earth metals due to their stability¹¹, abundance¹² (they comprise ~2.0 and 2.1 mol% of the earth's crust, respectively), and solubility¹³. Alkaline earth metals, such as calcium and magnesium oxides, readily react with carbon dioxide to produce stable carbonate minerals, and this reaction in sandstone will cause precipitation and dissolution of minerals¹⁴. CO₂ is dissolved in water to form carbonic acid (H₂CO₃) as depicted in Eq. 1, which dissociates to H⁺ and HCO₃⁻. Dissolved CO₂ is expected to acidify the system and to deliver a



source for carbon for the precipitation of carbonate minerals¹⁵. As shown in Eq. 2, the hydrogen ion hydrolyzes the mineral, liberating Mg^{2+} cations and forming silicic acid or free silica and water (Eq.2). The free Mg^{2+} cations react with the bicarbonate ions to form the solid carbonate as shown in Eqs. 3 and 4. Carbonate phases and dissolution of the minerals are energetically favored to form from interaction of CO_2 with silicate phases as Forsterite and Anorthite in accordance with the theorized reaction equations shown in Eqs. 3 and 5, respectively^{16–18}.



Indeed, one of the major challenges in the mineral sequestration of CO_2 is to obtain the appropriate cations such as calcium and Magnesium. The most abundant cation source is silicate minerals, and sandstone rocks are dominant in Earth surface and subsurface geological formations. It is well documented that the reaction of CO_2 with sandstone triggering precipitation and dissolution of minerals³⁶. A number of studies have been published to assess the degree to which in situ CO_2 mineralization is possible within sandstones rocks^{14,15,21}. Nonetheless, only a few reports have focused on the dissolution of silicate minerals and precipitation of carbonate through numerical modeling^{22,23}, and experimental works^{24,25}. Other researchers were conducted mineral carbonation in other rocks such as basalt or ultramafic rocks^{10,26}, fly ash²⁷, Olivine and Serpentine¹³, Wollastonite²⁸. However, carbonates precipitation is depending on the composition of the host rock. Actually, enormous volumes of sandstone rocks with different compositions are present on the Earth's surface, which are rich of alkaline earth metals. So, these widespread volumes of feedstock may have a correspondingly large CO_2 -sequestration capacity providing vast means of ex-situ carbon-mineralization sites throughout the world. Moreover, despite of the enormous CO_2 -EOR projects that are injecting millions of tons CO_2 per year in sandstone rocks²⁹, there are limited studies of injection of CO_2 for the sake of disposal in the literature and consequently little data about the effect of CO_2 injection on dissolution rate are currently available³⁸. Moreover, due to the slow extraction rate of alkaline earth metals (e.g., Ca) in direct reaction with CO_2 ²⁰, one might speed up the reaction to make the weathering process feasible for CO_2 sequestration. Lackner et al.¹⁷, Kakizawa et al.¹⁹ and Ba³dyga et al.⁴⁰ used hydrochloric acid, acetic acid, and succinic acid, respectively as acceleration medium. However, the major disadvantage of those acids is corrosiveness. In order to accelerate the reaction, injection of different CO_2 flow rates into the acid-free carbonated water filled with sieved sandstone rocks, would be a new exploration option in this field. This mineral carbonation scenario should have contributes to large potential capacity of CO_2 sequestration, reduction of CO_2 emission, and minimal environmental impact.

This experimental analysis has been developed to assess the suitability of Pahang Sandstone for mineral carbonation. Accordingly, this paper concentrated on understanding of the impacts in weathering process and/or mineral carbonation by injection of CO_2 at different flow rates (0.5 L/min, 1 L/min, and 1.5 L/min) at 80°C and 1 bar in a carbonated water filled with 4.0 mm size Pahang

Sandstone Malaysia, which constitutes the optimum temperature and injection time as recommended by Bob et al.³⁰, to reach the steady state pH, or the steady state CO_2 concentration. In this paper, after XRD analysis and determination of the major cations of Pahang Sandstone, a complete study with the purpose of analyzing the solid and liquid phase before and after the reaction process, has been carried out. The approximate changes in weight and composition before and after the experiment and the effect of CO_2 bubbling with different flow rates on the dissolution rate of Pahang Sandstone are presented. Investigation of dissolution effects of bubbling of different CO_2 flow rates in rich carbonated waters on sandstone rocks is of great importance to increase the potential capacity of CO_2 carbonation in such abandoned rocks.

Results

XRD analysis of the Pahang Sandstone showed quartz is the major mineral, with minor amounts of K-feldspar. Figure 1 shows XRD pattern of the main mineral components [silica (SiO_2) and K-feldspar ($CaAl_2Si_2O_8$)] before and after the reaction experiment. XRD analyses before and after experiments did detect contamination by clay minerals or the presence of secondary phases^{15,36}. Illitization of smectite minerals has been widely documented by XRD studies^{15,31}. The X-ray diffraction spectra of the Pahang Sandstone showed more or less amorphous nature with very little crystalline areas between 2θ 20–22°, 26–28°, and 42–44°. Such peaks were less visible in 20–22° and 26–28° after the reaction experiment indicating the dissolution of quartz and K-feldspar minerals. The tracer presence of smectite, kaolinite, illite and calcite is verified by XRD patterns.

As the important earth metals; K, Mg and Ca are utilized for carbon mineralization. Therefore, it is necessary to determine the dissolution concentration of them in the host rock after reaction experiment. The chemical composition of the solution after the interaction of sandstone/water/ CO_2 in 300 mL with different CO_2 flow rates was analyzed and depicted in Figure 2. Pretreatment of the sandstone samples by size reduction will result in major improvements of the reaction rate. As shown in Figure 2, dissolved Ca and Mg show decreasing trend in concentration to 6.84 mg/L and 0.435 mg/L, respectively after increasing the flow rates to 1.5 L/min and reached to their equilibrium state after two weeks to 7.59 mg/L and 0.457 mg/L, respectively. In contrast, dissolved K was rapidly increased from 5.05 mg/L in 0.5 L/min CO_2 flow rate to 5.31 mg/L and 5.98 mg/L, for 1 L/min and 1.5 L/min, respectively and reached its equilibrium state to 6.2 mg/L after two weeks. As illustrated in Figure 2, dissolved K concentrations were lower than dissolved Ca by 1–2 orders of magnitude.

To further study the precipitation of secondary minerals, SEM-EDS investigation was conducted on the surface textures of the Pahang Sandstone sample. SEM microphotographs and EDS charts are shown in Figures 3a, 3b and 3b, 3c, respectively. Figures 3a and 3b show SEM microphotographs of sandstone surface textures after the reaction experiment with obvious surface abnormality and clear softening of the middle of the marked rectangular, which indicates the fluid-rock interaction^{25,37}. Figures 3c and 3d show EDS charts that detect chemicals surrounding the section being scanned.

Figure 4 shows the result for pH variation of the reactant solution as a function of different CO_2 flow rates. The pH of the solution for each injection flow rate was measured after two weeks' aging. At zero flow rate of CO_2 the figure indicates the solution will be slightly alkaline. As CO_2 flow rate injection is increased, the solution becomes more and more acidic. As CO_2 flow rate increases to 1.5 L/min, pH drops, and much of the carbonate ion is converted to bicarbonate ion, which results in higher solubility of Ca^{2+} , Mg, and K. The effect of the latter is especially evident in AAS results. Increasing the flow rate injection from 0 to 0.5 L/min, 0.5 to 1 L/

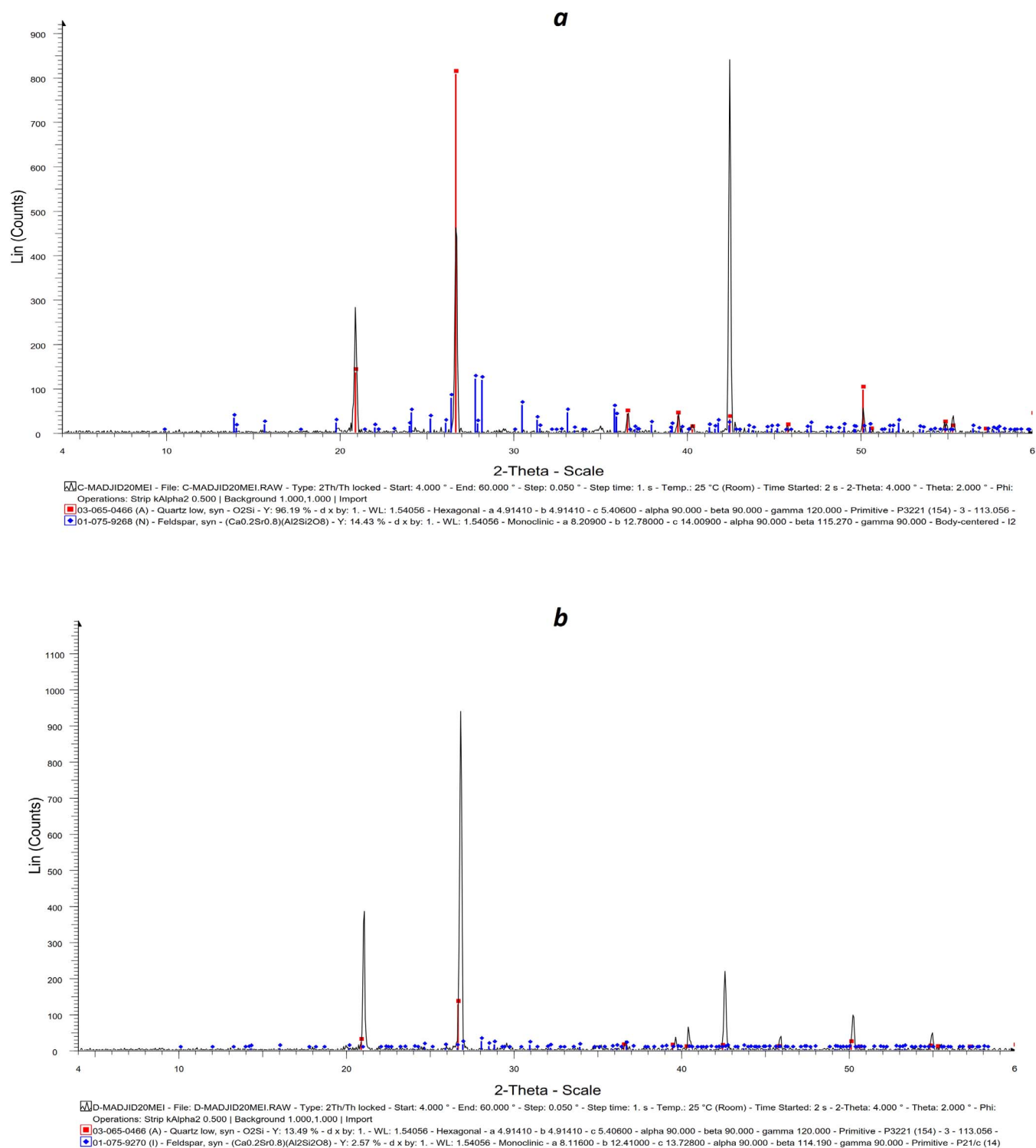


Figure 1 | XRD for mineralogical analysis of Pahang Sandstone before (a) and after (b) the reaction experiment with water/CO₂. It showed less noise in (b) indicating reduced amorphous content.

min, and 1 to 1.5 L/min increase the pH by the factor of 2.29, 5.41, and 16.69, respectively.

Figure 4 depicts the pH of element concentration in residual solution (Ca, K, and Mg) measured at surficial condition as a function of CO₂ flow rate. The initial pH was about 7.0. At a CO₂ flowrate of 0.5 L/min, a pH of 6.84 was reached in 2 hours. The measured pH for 1 L/min and 1.5 L/min were reached the values of 6.47 and 5.39 respectively. Figure 4 shows the solution to be more acidic by increasing the injection flow rate of CO₂. Increasing CO₂ flowrate and

addition of alkali and alkaline earth metals affect the dissolution rates of Pahang Sandstone (Figure 2).

Figure 5 shows formation of secondary minerals on quartz surface through SEM microphotographs. As shown in Figure 5, the identification of some clay minerals was confirmed by SEM microphotographs. Figures 5d, 5e and 5f illustrate enlargement of one of the etch spots of quartz outlined by the white box in 5d, showing dissolution features and presence of kaolinite platelets. Enlarged view of the kaolinite coating is shown in Figure 5f that do not form a continuous

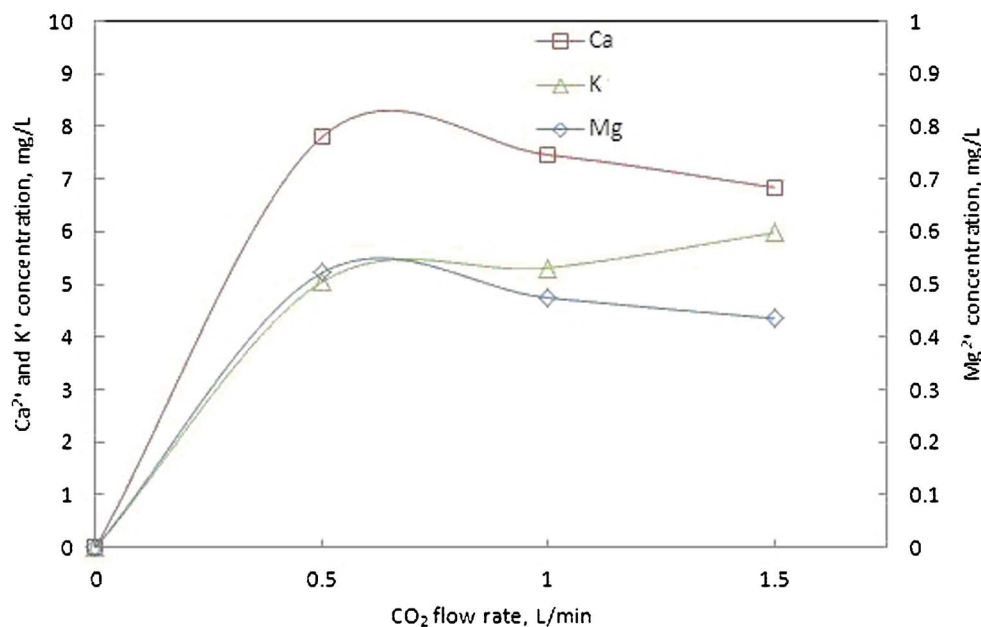


Figure 2 | Element concentration in residual solution as a function of CO₂ flow rate for Ca, K, and Mg.

cover. The dissolution of feldspar and precipitation of kaolinite (Figures 5d, 5e, 5f), is a weathering reaction that accelerated by CO₂ bubbling. The secondary minerals are likely to be illite (ribbons or fibrous) intergrown with smectite, which suggests the progressive illitization of smectite (Figures 5g, 5h, 5i). As indicated by Lu et al.¹⁵, removal of cations such as Na⁺, K⁺ and silica by fluid flow is the requirement of illitization process. Those cations, such as Mg²⁺, were detected by AAS analysis after the experiment and their concentration in residual solution as a function of CO₂ flow rate is shown in Figure 2.

Figure 6 shows the rock sample weight loss before and after the interaction procedure. The initial weight before the experiment was 32.70 gram and started to decrease from 32.50 gram in 0.5 L/min to 32.47 gram and 32.43 gram in 1 L/min and 1.5 L/min, respectively. The decrease for 0.5 L/min flow rate was 0.612% and 0.094% for 1 L/min, and this trend increased to 0.123% for the flow rate of 1.5 L/min.

Discussion

Rock weathering reaction plays an important role in global carbon cycle, and has been previously used by a few scenarios^{20,21}, which is principally the reaction of calcium silicates or magnesium silicates, as shown in Eqs. 4 and 5, with the atmospheric CO₂ to form carbonates. Calcium and Magnesium are capable of being carbonated because carbonic acid is a stronger acid than silicic acid¹⁹, and alkaline earth metals can be found in sandstone rocks that are dominant in Earth surface. It is well documented that the reaction of CO₂ with sandstone triggering precipitation and dissolution of such minerals³⁶. Consequently, in this paper, the focus of the artificial weathering effort by injection of CO₂ at different flow rates (0.5 L/min, 1 L/min, and 1.5 L/min) at 80°C and 1 bar in a carbonated water filled with 4.0 mm size Pahang Sandstone Malaysia has thus far been mainly on the sandstone dissolution rates, addressing mineral carbonation of alkali as well as alkaline earth metals.

Our observation on K-feldspar precipitation show that carbonation process occurred on Pahang Sandstone sample. The percentage change in SiO₂ and CaAl₂Si₂O₈ showed a decrease in those minerals over the flooding period from 96.16% to 13.49% and 14.43% to 2.57%, respectively. These minerals are predicted by many researchers (e.g., Lu et al.¹⁵) to play active role in geochemical interaction of sandstone with aqueous CO₂. As indicated by Lu et al.¹⁵, usually some

clay minerals, such as smectite and kaolinite persists on K-feldspar surfaces, which can cause pore throat clogging and reduction of permeability and result in significant decline in productivity³². In Pahang Sandstone, a noticeable decrease in the K-feldspar content is commonly observed suggesting that it has been dissolved in the process of illitization of kaolinite and possibly also smectite³⁶. As confirmed by AAS analysis, K shows increasing trend from 5.05 mg/L in 0.5 L/min CO₂ flow rate to 5.31 mg/L and 5.98 mg/L, for 1 L/min and 1.5 L/min, respectively and reached its equilibrium state to 6.2 mg/L after two weeks. SEM observations confirmed the illitization of smectite. Dissolution of K-feldspars and conversion of smectite to illite are likely to be the two reactions that contribute to the release of SiO₂.

Consistent with the XRD results, SEM-EDS analyses indicates that Si and C are the major components of sandstone, while Al, and K, (~6 atoms %) are minor components (Tables 1 and 2).

AAS analysis also shows that K and Ca concentrations are present in the solution of sandstone/water/CO₂ reaction system, whereas the concentration of Mg is less than 0.522 mg/l after the first injection flow rate of CO₂ as illustrated in Figure 2. Dissolved Ca and Mg show increasing trend by increasing the CO₂ flow rate and reach equilibrium state after two weeks. The K concentrations measured at 0.5 L/min, 1 L/min, and 1.5 L/min were 5.04 mg/L, 5.31 mg/L, and 5.98 mg/L, respectively. By increasing the CO₂ flow rate, dissolved K concentration increased gradually to above 5.97 mg/L. Approximately 12% and 17% lower concentrations of dissolved Ca and Mg were observed in the experiments, respectively. Whereas dissolved concentrations of K was increase 16% by in the slurry created by the interaction of sandstone/water/CO₂. Experimental results showed that CO₂ flow rate has a significant influence on the interactions between sandstone and synthetic water/CO₂ system. The lower amount of carbonate mineral precipitation is due to the solubility trapping in aqueous phase that is the dominant CO₂ sink^{15,23,33}.

ANOVA test is performed to determine significant differences of the element concentration (Ca, Mg, K) before and after the reaction experiment and the results were tabulated in Table 3. The *F* critical value (*F* crit) is the number that the test statistic (*F*) must exceed to reject the test. As shown in Table 3, *F*crit at $\alpha = 0.05$ for Ca, Mg, and K equal to 5.98, 5.99, and 5.97, respectively. Since *F* for Ca, Mg, and K equal to 61.80, 652.37, and 343.62, respectively, and they are higher

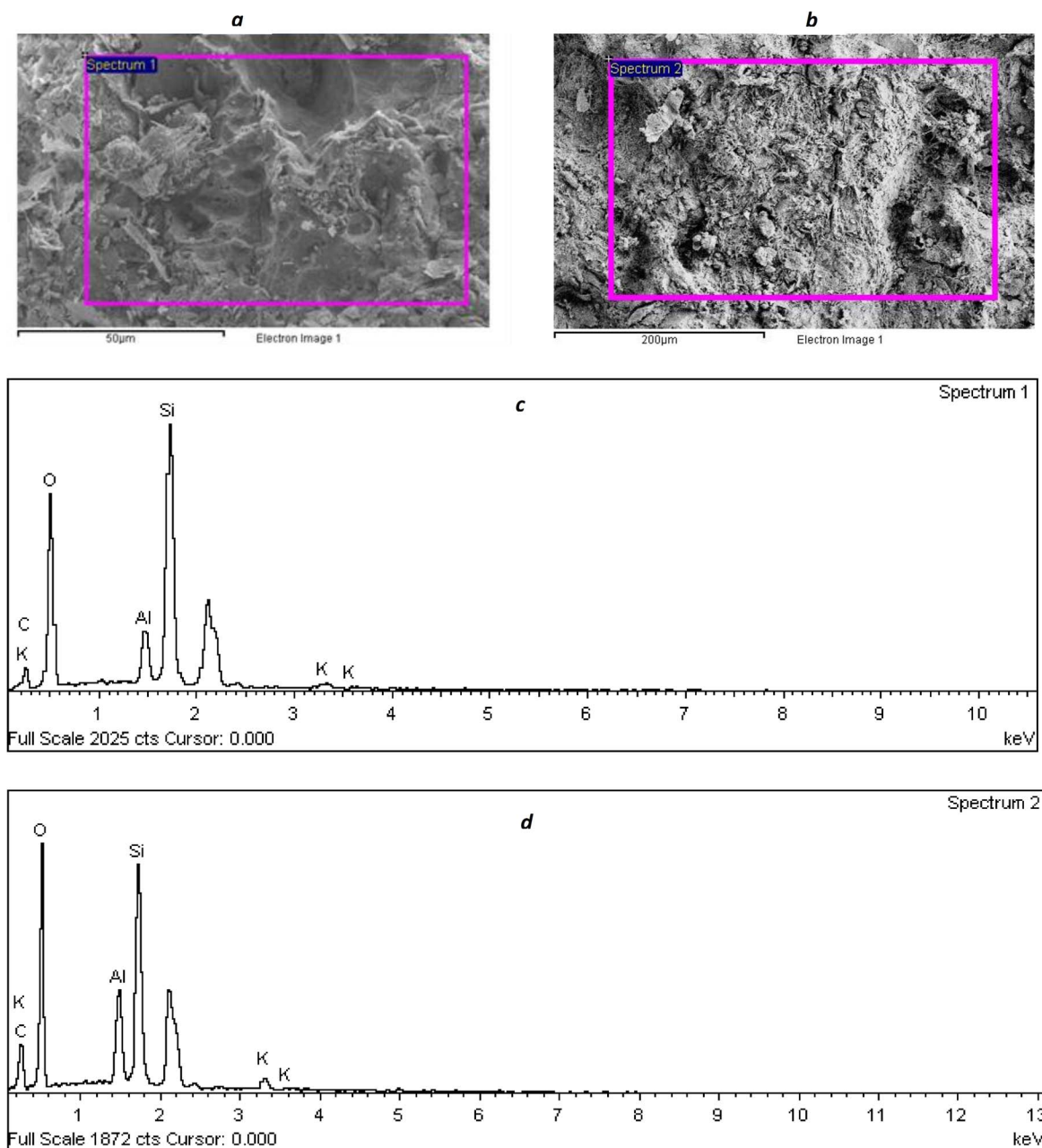


Figure 3 | (a) and (b) ESM of the sandstone surface; (c) and (d) EDS that detects chemicals surrounding the section being scanned.

than their F_{crit} , the results are significant at the 5% significance level. One would reject the null hypothesis, concluding that there is strong evidence that the expected values in the two groups, before and after the reaction experiment for the elements, considerably differ. The p -value for these tests are tabulated in Table 3 that are 0.0002, 2.37E-07, and 1.59E-06 for Ca, Mg, and K, respectively, which are smaller than α and considered an extra evidence to reject that the null hypothesis. Therefore, high confidence is present about the difference between the mean of the first group (before experiment) and the mean of the other group (after experiment). In Table 3, the divisor is called the degrees of freedom (df), the summation is called the sum of squares (SS), the result is called the mean square (MS), and they show the variations between groups. Sum, average, and variance show the three statistics of the second groups (the results after reaction experiment) of the studied elements. Bowker et al.⁴¹ confirmed the significance of the alkali and alkaline earth metals concentration before and post CO₂ breakthrough and the rate of increase of Ca, Mg, and K after CO₂ injection reported 19%, 29%, and 10%, respectively.

It's clearly shows that quartz dissolution is the major process liable for the weight loss in the sample and increasing the concentration of Si and K in the residual solution. Also, as clearly illustrated in Figure 4, the pH of the solution has an increased trend toward acidic from 0.5 L/min to 1.5 L/min CO₂ injection, indicating that there has been precipitation of secondary minerals.

The results of the weight loss (e.g., mineral-fluid interaction) show that higher flow rate (1.5 L/min) is greater than 1 L/min flow rates in 80°C, but lower than initial flow rate. The higher weight loss in 0.5 L/min flow rate may associate with loosening of the rock samples and dissolution of some clay minerals. As showed in Figure 1, the differences in silica and K-feldspar before and after the reaction/experiment procedure are noticeable and they counts were reduced after the experiment. This unusual phenomenon arises from the increase in the increase in CO₂ flowrate and removal of cations, including silica, by illitization process that well documented in the literature^{15,36,39}. The dissolution behavior of silica/feldspar minerals reveal more acidic fluid conditions in the sandstone/water/CO₂ system,

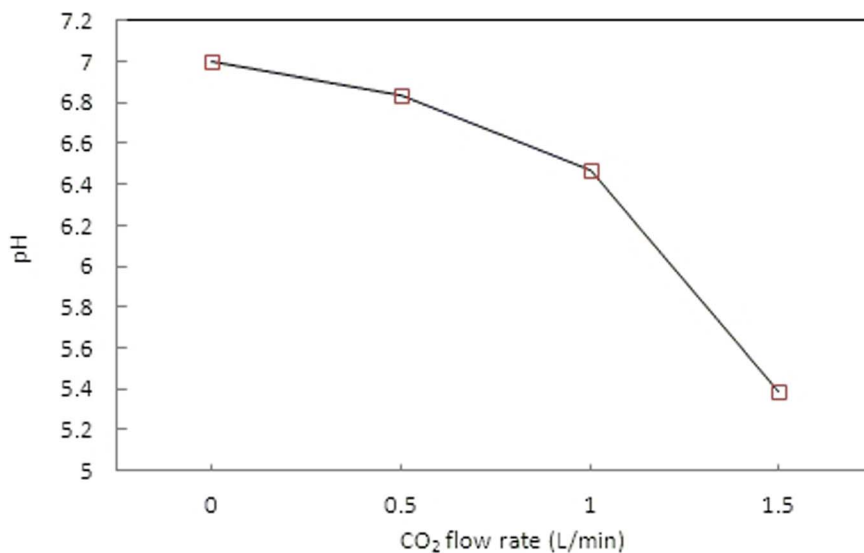


Figure 4 | pH as a function of CO₂ flow rate.

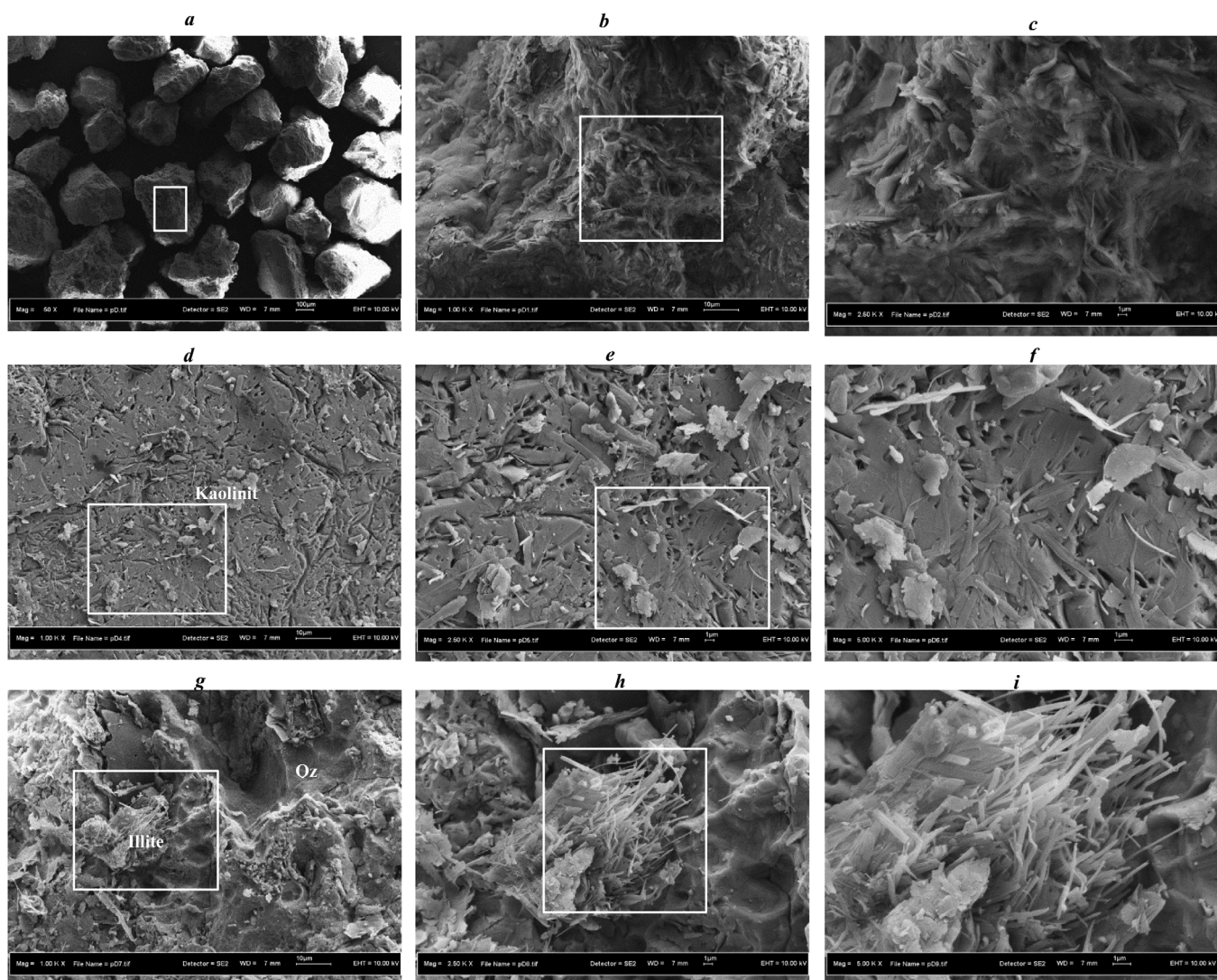


Figure 5 | SEM microphotograph of Pahang Sandstone dissolution by CO₂ bubbling.

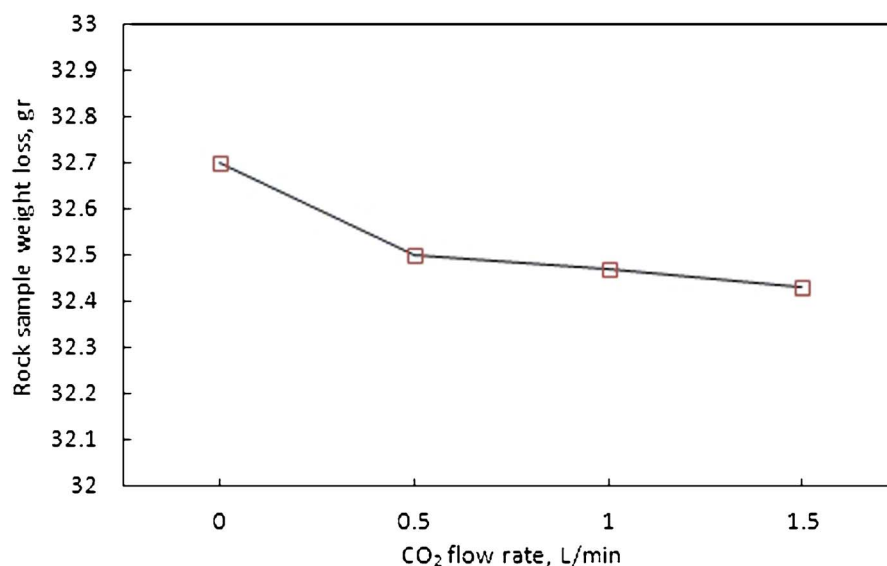


Figure 6 | Rock sample weight loss as a function of CO₂ flow rate.

greater porosity and fluid mobility and as inferred by Liu et al.³⁴, the sample weight change can be accommodate by deposition of secondary minerals and by the corresponding fixation of CO₂ in the rock sample. Also, the presence of oxygen in the solution³⁵ may be contributed to enhanced dissolution of calcite and attributed to acid generation resulting from oxidative dissolution of Pahang Sandstone.

Results show that the Pahang Sandstone will react with carbonated water through injection of CO₂ in 80°C and 1 atm. Also, pH decreased by 2.30%, 5.41%, and 16.70% after CO₂ flow rates of 0.5 L/min, 1 L/min, and 1.5 L/min, respectively. Lower the pH cause more severe reactions in the sandstone/water/CO₂ system. Therefore, dissolved CO₂ acidify the solution and carbon source will be provided by carbonate minerals. Based on the XRD, AAS, and ESM-EDS results, Ca and Mg were released as calcite and dolomite were dissolved by carbonic acid, while K and Si were released by cation exchange of K with Ca and dissolution³⁵. The presence of Ca, Mg, and K in considerable amounts in the solution of reaction experiment with sandstone samples is an indication that the Pahang Sandstone is the right candidate for CO₂ mineralization and utilization of CO₂ flow rate as acceleration medium shows good results, thus accelerating the mineral carbonation for CO₂ sequestration.

Clearly, increasing CO₂ flowrate accelerates the reactions between the carbonated water and Pahang Sandstone and consequently the rate of dissolution increased. As verified by XRD, SEM and AAS, mineral dissolution is the explanation of K-feldspar's loss. Also, the C signal on one EDS points on Figures 3c and 3d are the direct evidence on carbonate chartered crystal morphology. This confirmation is supported by XRD analysis and AAS results after carbonation process. Therefore, in this study, the existence of carbonate minerals is validated. However, special care must be taken because the C signal

can result from organic contamination, trace original carbonates in sandstone or C coating one the sample. Fourier transform infrared (FTIR) spectroscopy is sensitive to carbonate C-O bond, compare the FTIR signal before and after the reaction can provide useful information on carbonate existence.

For mineral carbonation the use of alkali and alkaline earth metals, K, Mg, Ca, is favoured because they are worldwide available in huge amounts. Mineral carbonation in sandstone rocks contain alkaline earth metals is potentially significant for carbon sequestration. As a technique for CO₂ storage in solid form, an aqueous process for the direct carbonation of alkaline and alkali minerals in Pahang Sandstone has been developed in this study. The abundant in the Earth's surface, make sandstone rocks as a liable candidates for the purpose. This study focuses on understanding the potential impacts of injection of different CO₂ flow rates on the sandstone/water/CO₂ system. Three CO₂ injection flow rates with the same pressure and temperature conditions in laboratory scale have been examined to assess the impact of CO₂ flow rate to sandstone/water/CO₂ systems. Si and C appear as the prevailing components in all of the samples, while Al and K are minor constituents in Pahang Sandstone. The weight changes and mineral dissolution caused by CO₂ injection for two hours were 0.28% and 18.74%, respectively. The average variation of concentrations of alkaline earth metals in solution varied from 22.62% for Ca²⁺ to 17.42% for Mg²⁺, with in between 16.18% observed for the alkali earth metal, potassium. Such changes show that the deposition of alkali and alkaline earth metals and the dissolution of required elements in sandstone samples are enhanced by CO₂ injection. Finally, injection of higher rates CO₂ showed a particularly strong effect. To the best of our knowledge, the major sequestration product appears to be calcium and potassium carbonates; however, more detailed material characterization, such as

Element	App Conc.	Intensity Corr.	Weight%	Weight% (Sigma)	Atomic%
C K	0.10	0.6308	18.79	1.60	27.86
O K	0.56	1.3863	44.02	1.14	48.99
Al K	0.09	1.1202	8.92	0.39	5.89
Si K	0.23	1.0460	24.65	0.74	15.62
K K	0.03	1.0179	3.61	0.44	1.65
Totals			100.00		

Element	App Conc.	Intensity Corr.	Weight%	Weight% (Sigma)	Atomic%
C K	0.05	0.5056	12.66	1.93	19.92
O K	0.47	1.4422	42.39	1.23	50.05
Al K	0.05	1.1450	6.03	0.37	4.22
Si K	0.30	1.0758	37.02	1.07	24.90
K K	0.01	1.0188	1.90	0.45	0.92
Totals			100.00		



Table 3 | ANOVA test result comparing element concentrations of the solution before and after the reaction experiment

Element	Sum	Average	Variance	SS	df	MS	F	P-value	F crit
Ca	29.67	7.42	0.17	58.89	1	58.89	61.80	0.0002	5.98
Mg	1.89	0.47	0.001	0.45	1	0.445	652.37	2.37E-07	5.99
K	22.54	5.63	0.98	52.72	1	52.72	343.62	1.59E-06	5.97

FTIR, may useful on pre- and post-carbonated samples to better interpret carbonation products in sandstone rocks. The undertaken assessment is generally representative for Pahang Sandstone, Malaysia.

Methods

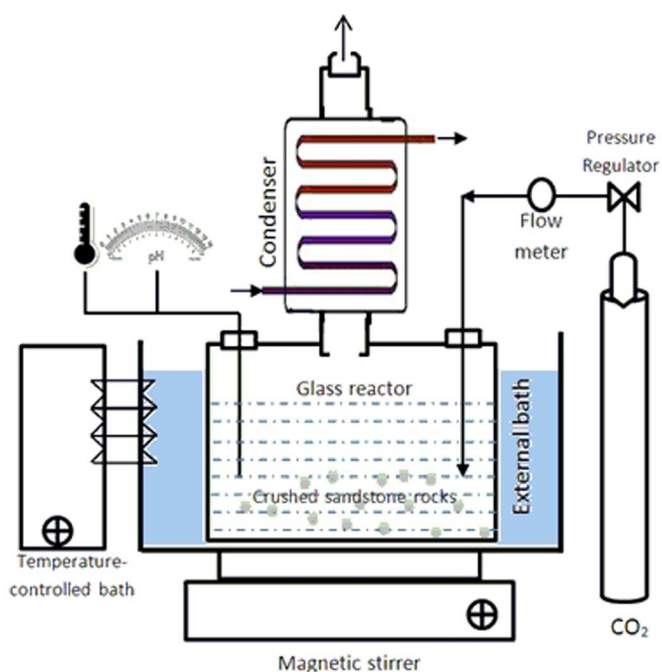
Materials. In this research, high purity CO₂, carbonate water, sandstone rock samples were used. Sandstone samples were collected from an outcrop of a local sandstone formation from Bukit Bangkong, Kuala Rompin, Pahang, which were grind into 4.0 mm in size. In order to have CO₂ equilibrated aqueous solution, CO₂ gas has been injected into deionize water and stirred accordingly to from carbonated water. The slurry and rock samples collected after each injection CO₂ flow rates (0.5 L/min, 1.0 L/min, 1.5 L/min) preserved for two weeks and then characterized by performing XRD, SEM with EDX, AAS, which were used to further analyze the mineralogy and major element concentrations of the residual solution (Ca, K, and Mg) of several selected samples. Pre-treatment of the minerals performed by size reduction of the sandstone rock samples to 4.0 mm to increase reactivity.

Experimental procedure. Three sets of experiments were conducted with analogous temperature and pressure experimental conditions, to investigate the effect of CO₂ flow rate on the dissolution of primary minerals and deposition of secondary minerals in sandstone/water/CO₂ system. The reaction experiments performed under atmospheric pressure and controlled temperature (80°C) conditions, as well as all solution preparations, were carried out using a glass reactor with a volume of 300 ml. The experimental setup is shown in Figure 7, which contained a glass reactor in which solutions were stirred by a magnetic stirrer.

The glass reactor was surrounded by an open water bath, which was heated using a separate, temperature-controlled water bath connected to the open water bath. To avoid evaporation losses, the reactor was equipped with a condenser cooled with tap water. The pH and temperature of the solution were measured allowing data to be monitored and logged in real time. CO₂ gas bottle was connected through a pressure regulator and a flow meter, allowing CO₂ to be injected through the solutions by different flow rates (0.5 L/min, 1 L/min, and 1.5 L/min). Grinded rock sieved by 4.0 mm and then weighted. 32.70 gram of sandstone rock sample was poured into glass reactor, which contained 300 ml of carbonate water. Then slurry bubbled by 0.5 l/min CO₂ flow rate. The carbon dioxide flow was switched off after two hours and the solution was immediately filtered through a Whatman 40 µm filter paper, and the

solution was sealed for two weeks. Same procedure repeated for the second and third tests, which 32.50 and 32.47 grams of rocks samples were bubbled by 1.0 L/min and 1.5 L/min CO₂, respectively. The filtered debris and rocks were washed using deionize water, dried at 120°C overnight then weighted and prepared for the second and third experiments. At the end of each experiment, the reactor glass was washed and the reacted sandstone was collected for solid phase characterization. The slurry of each experiment was analyzed for alkali and alkaline earth metals using AAS. The rock samples from the third experiment (1.5 L/min) were analyzed using XRD and SEM-EDS.

Analytical methods. Rock and fluid samples were taken from the reactor at consistent intervals, in which they remained in the solution for two weeks after two hours of CO₂ injection. Then they were analyzed for phase identification by XRD, phase relationships and surface morphology by SEM-EDX, and chemical analysis of products by AAS. XRD were used to identify crystalline mineral phases of the sandstone samples before and after the mineral carbonation experiment. The crystalline minerals of the rock samples were characterized using XRD with Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $2\theta = 4^\circ - 60^\circ$ at scanning speed of 0.05° per second and dwell time of 1.5 second to generate the XRD pattern of the material. Magnesium, potassium, and calcium concentrations in solution were assessed by Analyst 400 Perkin Elmer Atomic Absorption Spectrophotometer. Samples were filtered using Whatman 40 µm filter paper and the filtrates after suitable dilutions, were analyzed. AAS is performed to evaluate the slurry after each step of CO₂ injection. 32.70 grams of the rock sample were reacted with 300 ml of carbonated water in three injection flow rates of CO₂ at 80°C and 1 atm. The rate of CO₂ injection was kept constant at each corresponding flow rate (two hours) for the whole experiment. The dissolved concentrations of Ca, Mg, and K were measured in each CO₂ flow rate. SEM is used to visualize very small topographic details on the surface or entire or fractioned objects and provide semi-quantitative elemental analysis of the sandstone rock sample after the carbonation experiment. In this study, JSM-6701F was used to obtain the scanning images of sandstone rock sample after the experiment. The JSM-6701F is an ultra-high resolution SEM suitable for observation of fine structures such as multi-layered film and nanoparticles fabricated by the nanotechnology. High resolution at 1 nm (15 kV) and 2.2 nm (1 kV) with the maximum 2 nA probe current and without changing the objective lens aperture size. The specimen's size will be up to 200 mm diameter. In addition, an energy dispersive X-ray spectroscopy (EDS) is attached to this system that used for the elemental analysis or chemical characterization of the sandstone samples after reaction with CO₂/water.

Figure 7 | Experimental apparatus for CO₂ mineralization.

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Author contributions

M.Z. designed and directed the study. M.J. and F.A. performed the experiments as well as most of the coordination with XRD, SEM, and AAS laboratories. R.J. and R.M. took part in the supplementary materials and discussion of chemical processes, Figures 3–5 and statistical analysis. M.Z. wrote the manuscript and all authors reviewed the manuscript.

Additional information

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