

Iron Calcium Carbonate Formation in CO₂ Environments – Effects of A/V Ratio in Autoclave Experiments

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ABSTRACT

In aqueous carbon dioxide (CO₂) corrosion of carbon steels, the presence of calcium ions influences the kinetics of corrosion product formation and can affect both general and localized forms of attack. When conducting laboratory experiments, understanding the transient solution chemistry due to the corrosion process is critical when evaluating the effects of calcium on corrosion behavior. Autoclave experiments were conducted at 80°C and 5 barg with 3 brines containing 0, 1000 and 5000 mg/l of Ca²⁺. Iron flux into the brine was varied using high and low area to volume (A/V) ratios. Results from mass loss and electrochemical measurement techniques show that the presence of calcium reduces initial corrosion rates but slows down the formation of more protective corrosion product layers. A higher A/V ratio led to much faster corrosion product formation and altered the composition of the resulting corrosion products in the presence of calcium ions. The results demonstrate how conflicting views on the role of calcium can be observed depending on the A/V ratio and test duration.

Key words: CO₂ Corrosion, carbon steel, calcium, CaCO₃, FeCO₃, electrochemistry, autoclaves, LPR.

INTRODUCTION

Carbon dioxide (CO₂) saturated brines containing high levels of calcium are commonly encountered across the energy sector: from hydrocarbon recovery to the harvesting of geothermal energy and re-deposition of CO₂ for permanent storage. These brines originate in deep underground reservoirs at elevated pressures and temperatures.¹ Despite susceptibility to corrosive attack under these conditions, carbon steels are the preferred choice of pipeline materials for such processes, attributable to their low cost, availability and ease of manufacture.²

When carbon steels are exposed to calcium rich brines, the combination of an electrolyte rich in calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}), with the flux of Fe^{2+} from the actively corroding carbon steel, can quickly create conditions for scale and/or corrosion product precipitation and build up. The rate of accumulation, morphology and tenacity of these precipitates on the steel surface is pertinent to pipeline integrity and maintenance planning. The right environment can enable formation of compact layers that provide sustained protection to the steel substrate. Conversely, lower coverage can promote localized attack while excessive precipitation can lead to pipe clogging.^{3,4}

Multiple studies investigating CO_2 corrosion in complex brines have shown that Ca^{2+} has a particularly strong affinity towards forming a solid solution with Fe^{2+} as a mixed carbonate precipitate of the form $\text{Fe}_x\text{Ca}_y\text{CO}_3$ (where $x+y=1$).⁵⁻⁷ Differences in $\text{Fe}_x\text{Ca}_y\text{CO}_3$ stoichiometry lead to notable morphological changes, altering its effectiveness as a barrier on the steel surface. It is generally agreed from mineral growth studies that the key factor in determining $\text{Fe}_x\text{Ca}_y\text{CO}_3$ composition and formation kinetics is the relative saturation in the brine of its pure end members FeCO_3 and CaCO_3 .⁸⁻¹⁰ This in turn is dependent on the chemical activity of reactants, CO_2 fugacity and system temperature.¹¹⁻¹³ For many mineralogy studies in this area, the focus is on tightly controlled or constant solution chemistry in an attempt to build an exact understanding of its effect on crystal nucleation, growth, morphology and composition. These studies are typically conducted at low temperature and ambient pressure.^{9,14} In the context of a corrosion process, the exact composition of mixed carbonates, hereby referred to as a corrosion scale, is incredibly difficult to predict and has been shown to vary over time as system conditions change at the surface.¹⁵ The scenario of evolving chemistry due to iron flux from the carbon steel, concurrent with ion consumption through carbonate precipitation, is much more difficult to emulate.

The current study uses a combination of ex-situ analysis: mass loss, Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Energy Dispersive X-Ray (EDX) and in-situ electrochemistry (Linear Polarization Resistance (LPR)) to investigate how calcium affects the build-up of protective corrosion scales. By varying the exposed surface area of carbon steel for a fixed volume of brine solution, known as the area to volume (A/V) ratio, experiments have also been conducted to illustrate the effects of iron flux on system chemistry and corrosion-scale formation kinetics. The latter results feed in to a wider discussion on the importance of realistic chemistry control when conducting laboratory-scale corrosion experiments with more complex geothermal brines.

EXPERIMENTAL PROCEDURE

Experiments were conducted in two phases, the first being a series of 3 day mass loss tests and the second a series of electrochemical tests of varying duration to elaborate on the findings from the first phase. All experiments featured the same basic setup and experimental conditions listed in Table 1.

Table 1
Experimental Conditions

Experimental Parameter	Units	Value
Specimen Material	-	X65 Carbon Steel
Temperature	°C	80
Total Pressure	barg	5
Liquid Volume	ml	750
Cl^- Concentration	mg/l	18200
Ca^{2+} Concentration	mg/l	0, 1000, 5000
A/V Ratio	cm^2/l	10.53, 41.39

Material Preparation

All specimens were machined from American Petroleum Institute (API) 5L X65 grade carbon steel bar comprising a ferritic-pearlitic microstructure and elemental composition provided in Table 2. All exposed surfaces were wet ground up to P600 silicon carbide (SiC) grit paper. Each specimen was then rinsed with acetone and distilled water before drying. For gravimetric analysis, the mass of each specimen was recorded using an electronic mass balance with an accuracy of 0.1 mg. Corrosion products were later removed using Clarke's solution.

Table 2
Elemental composition of X65 carbon steel samples

C	Mn	Ni	Nb	Mo	Si	V	P	S	Cr	Cu	Fe
0.15	1.422	0.09	0.054	0.17	0.22	0.06	0.025	0.002	0.11	0.12	Bal.

Sample Configurations

The area-to-volume (A/V) ratio was varied using two different mass loss samples depicted in Figure 1. High A/V experiments contained two cylindrical specimens of 25 mm diameter and 6 mm thickness. For low A/V the samples were cut into thirds to produce cylindrical-sector specimens of 25 mm diameter, 6 mm thickness and sector angle of 120°. One sector was used per low A/V experiment. Each mass loss sample had one 3 mm diameter hole drilled through for fixing within the autoclave. A working electrode was also included in each experiment fabricated from 12 mm diameter X65 bar. The sides of the electrode were coated with high temperature lacquer and protected with Fluorinated Ethylene Propylene (FEP) shrink wrap while the back face was soldered to Kapton coated copper wire before being sealed with high temperature silicone. This left a single exposed face of 1.13 cm². The same method was used to fabricate a Hastelloy C-276 counter electrode also of 12 mm diameter. Total exposed surface area of carbon steel was 7.9 cm² for low A/V and 31 cm² for high A/V equating to A/V ratios of 10.53 and 41.39 cm²/l respectively.

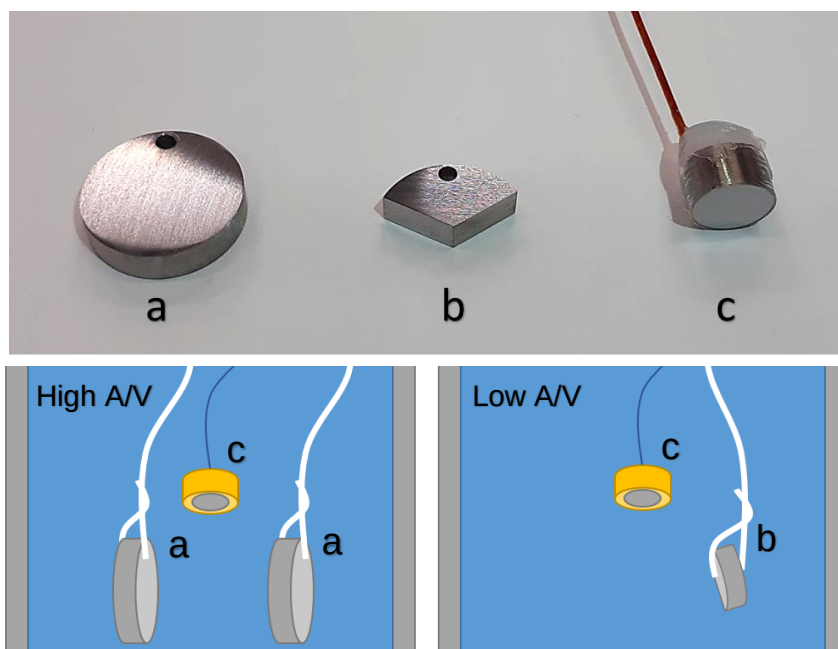


Figure 1: Types of X65 carbon steel specimens used in experiments: a) 25mm diameter mass loss coupon (x2) for high A/V tests. b) 1/3 sector of 25mm diameter mass loss coupon (x1) for low A/V tests. c) 12mm diameter WE/surface analysis specimen (x1) for all tests.

Solution Preparation

Solutions containing 0, 1000 and 5000 mg/l of Ca^{2+} were prepared by addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaCl to deionized water. For tests without Ca^{2+} , a baseline 30 g/l NaCl solution was prepared. For subsequent tests NaCl quantities were adjusted to maintain a Cl^- content of 18.2 g/l. Each solution was prepared in a 1 liter glass beaker and continuously sparged with CO_2 on a stirred hotplate at ambient pressure and temperature for at least 2 hours prior to each test.

Experimental Setup

Apparatus

Experiments were conducted in a 1.3 liter 316SS-Ti LBBC Baskerville autoclave[†]. Freshly prepared mass loss coupons were suspended within the vessel using a Polytetrafluoroethylene (PTFE) holder while working and counter electrodes were installed through a high pressure Conax[†] cable gland.

Solution Transfer and CO_2 Charging

After installation of test specimens the autoclave was sealed and purged with CO_2 for 15 minutes. Solution was transferred to the vessel from the glass beaker using an external gear pump. The pump was connected to the autoclave inlet and purged with CO_2 prior to solution transfer as depicted in Figure 2. Once 750 ml of solution was transferred to the autoclave the vessel was transferred to a high pressure CO_2 supply tank. The vessel was charged up to 8 bar gauge pressure and left to settle for 10 minutes at room temperature to expedite the saturation process. After this period the autoclave was placed on a hotplate and heated to 80°C. Simultaneously pressure was regulated down to 5 bar gauge and maintained during heat-up using a back-pressure regulator fitted to the outlet. On reaching target temperature the outlet was shut off and electrochemical measurements were initiated.

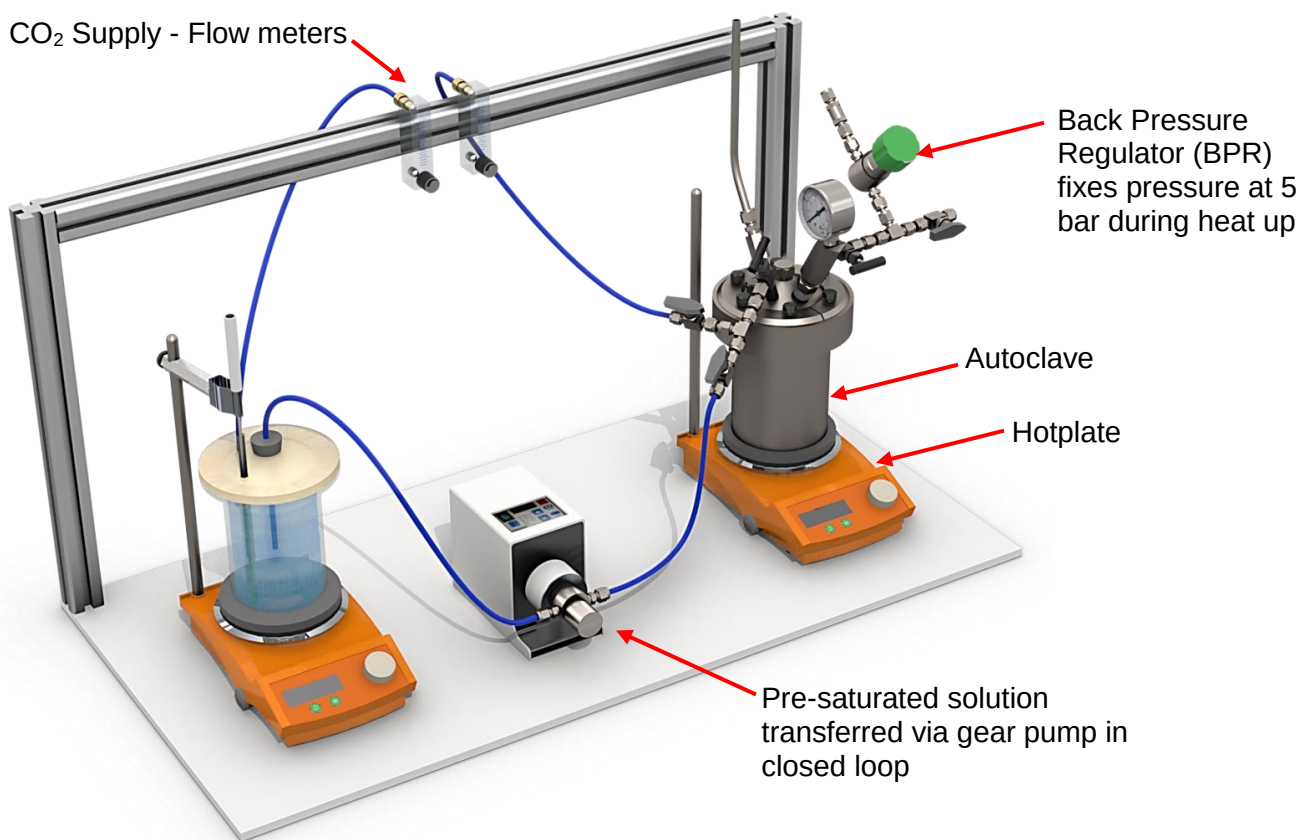


Figure 2: Apparatus for solution transfer to autoclave

[†] Trade name.

Electrochemical Setup

For electrochemical measurements, a 3 electrode configuration was used which comprised of a hastelloy counter and X65 working electrode (details of fabrication described earlier). A refillable type external pressure balanced Silver/Silver Chloride probe supplied by Corr Instruments[†] was used as the reference. Measurements were performed using an Ivium Compactstat Potentiostat[†] interfaced through IviumSoft[†] software. LPR measurements were conducted every 15 minutes from -15 mV vs Open Circuit Potential (OCP) to +15 mV vs OCP at a scan rate of 0.25 mV/s. OCP was monitored between each LPR.

Surface Characterization

Surface morphology and cross sections were imaged using a Hitachi TM3030Plus SEM[†] with accelerating voltage of 15kV and back scattered electron image signal. Elemental analysis was conducted using a Carl Zeiss EVO MA15 SEM[†] with Oxford Instruments AZtecEnergy EDX[†] system. A Bruker D8 X-ray diffractometer[†] was used for crystalline phase identification across a 2θ scan range of 20 to 70°, step size of 0.016° and scan rate of 0.02°/s. The resultant diffraction patterns were used to identify the phases present along with the molar fraction of Ca in $\text{Fe}_x\text{Ca}_y\text{CO}_3$ for experiments conducted in the presence of Ca^{2+} .

RESULTS

3 Day Experiments

Gravimetric Analysis

The average corrosion rate over the course of 3 day experiments and the mass of corrosion product are shown in Figures 3 and 4 respectively. The data plotted is the average of repeats, error bars represent the standard deviation. The observed corrosion rates were significantly higher at low A/V. This could be a result of slower pH evolution – Fe^{2+} flux into the bulk causes an increase in system pH.¹⁵ A larger A/V ratio will mean a higher Fe^{2+} flux initially causing pH to rise quickly and in turn slow down the corrosion reactions.² A consequence of faster pH evolution is also an increased rate of corrosion scale formation which would in turn reduce corrosion rates. A/V ratio also appeared to reverse the trends observed in terms of Ca^{2+} . At low A/V, corrosion rates were higher in the absence of calcium, in contrast at high A/V the corrosion rate increased almost linearly with calcium concentration. Similarly contrasting trends were also observed for corrosion product mass (CPM). At low A/V CPM was much higher in the absence of calcium and almost identical to the CPM at high A/V. Increasing calcium decreased the CPM at low A/V while increasing CPM at high A/V.

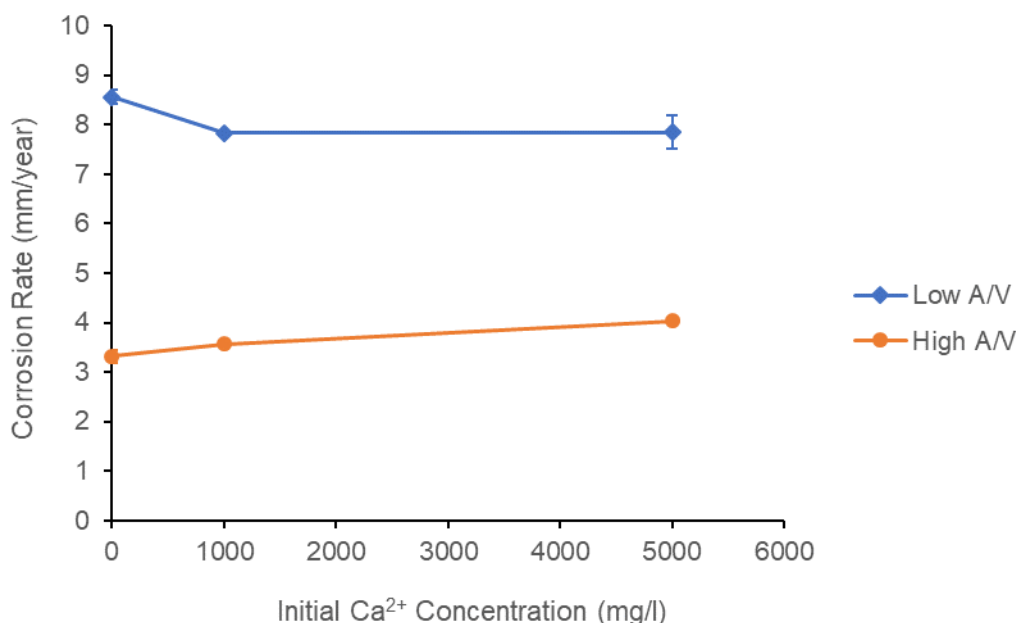


Figure 3: Average corrosion rates from 3 day mass loss experiments

[†] Trade name.