

A Study of Steel Alloys for Potential Use in CO₂ Sequestration

J. Tylczak, J. Rawers, and Daniel Blankenship
Albany Research Center, USA

Abstract

The effect of CO₂ as a greenhouse gas and its potential to affect global warming has led to studies of CO₂ sequestration as a mineral carbonate. Some of the processes of mineral sequestration involve handling large tonnages of silicate minerals and reacting them with CO₂ to form mineral carbonates. In this study the Albany Research Center evaluated the effects of wear and corrosion individually, as well as any synergetic combination of wear and corrosion on steel alloys that might be used in CO₂ sequestration. By understanding the mechanism of slurry material loss, a better selection of erosion/corrosion resistant steel alloys can be chosen which in turn help plan construction costs. Four different conventional alloys were studied. The alloys were AISI 1080 carbon steel, a 9Cr 1 Mo steel, a 316 stainless steel, and a heat treatable 440C stainless steel. These materials covered a large range of alloy composition, mechanical properties, corrosion and wear resistance, and cost.

A variety of erosion and corrosion tests were used to evaluate the steel alloys' responses to selected sequestration environments. The tests used included: (i) dry jet erosion tests, (ii) immersion corrosion tests, and (iii) slurry erosion/corrosion tests. The slurry wear tests were conducted using a 270- μ m silica abrasive in water and a solution (a mixture of sodium chloride, magnesium chloride, and sodium carbonate) saturated with CO₂ at pH levels of 4.5 and 9.4. The results of these tests were compared with the results of the dry erosion and immersion corrosion tests. The results of the various tests were then used to evaluate the mechanism of material loss and identify any synergetic wear/corrosion effects.

The corrosion test showed little loss of material on any of the four alloys. The erosion tests showed only a small difference between the specimens. The slurry tests showed a synergistic erosion/corrosion effect, which resulted in a significant additional loss of material. Tests also documented that either increasing the hardness and/or increasing amounts of substitution chromium decreased the alloy loss rate.

Introduction

The U.S. Department of Energy (DOE) Office of Fossil Energy has identified the mitigation of the effects of CO₂ emissions as a critical research issue for its Vision XXI power plant. A variety of methods are being investigated to capture or sequester the CO₂. Among the sequestration methods being investigated is mineral carbonation. Albany

Research Center is working on in-situ and ex-situ techniques of mineral carbonation. In mineral carbonation the CO₂ is chemically combined with minerals such as magnesium and calcium silicates to form magnesium and calcium carbonates. Mineral carbonation techniques are thermodynamically favorable and result in a product that is stable for long term storage.

Ex-situ carbonation would require large quantities of minerals to be handled in order to sequester the CO₂ from each power plant. For example, a 1,300 MW coal fired power plant produces roughly 24,000 metric tons of CO₂ per day. In order to sequester this CO₂ with olivine, (Mg, Fe)₂SiO₄, 55,000 metric tons of olivine would need to be ground, slurred, and reacted each day. The financial, physical and logistic challenges involved in mining, crush, and handling such immense quantities of minerals are beyond the scope of this paper.

The oil and gas industries have long known that CO₂ is a potent contributor to corrosion in handling wet natural gas^{1,2}. Research has been conducted to evaluate the effects of different conditions, including temperature and pressure, on the rates of reaction³. In combination with pressure and temperature the situation is complicated. Increasing pressure can increase the peak corrosion rate, but the more the pressure increases the sooner the point is reached where increasing temperature decreases the corrosion rate for a given pressure.

This research looks strictly at the wear/corrosion issues that may occur in a reactor or minerals handling pipeline where CO₂ reacts with olivine to form a carbonate.

Experimental

Previous research⁴ to determine the optimal sequestration reaction conditions between olivine and CO₂ was used to set the conditions used for this work. This research resulted in a carrier solution of 0.64 *M* NaHCO₃ and 1 *M* NaCl at elevated temperature and pressure.

A variety of test methods were used to elucidate the possible erosion/corrosion that would be taking place in handling and reacting the CO₂ with sequestration mineral. Immersion corrosion tests were used to measure just the corrosion component of the loss process. A dry jet erosion test was used to evaluate the steel material resistance to erosion. A slurry erosion/corrosion test was used to measure the loss rate with both erosion and corrosion, and any synergistic effect. In all tests involving corrosion, identical solutions and temperatures were used.

Procedure

Immersion Corrosion tests

The immersion corrosion tests were conducted in water at both room and elevated temperatures (63°C). Using the solution shown in Table 1 tests were conducted at room

temperature, 23°C, and 63°C. Tests were also conducted at both temperature levels in basic and acidified conditions (pH 9.4 and 4.5). It was important to test in both pH environments. Tests were conducted in an acid pH because CO₂ forms carbonic acid and creates a low pH in solution. Tests were conducted in a basic solution because 1) the mineral sequestration process is enhanced with the addition of NaHCO₃ and the resulting equilibrium tends to raise the pH⁵ and 2) under high pressures CO₂ solutions tend to move toward becoming basic. In all cases the solutions were saturated, by bubbling with CO₂, before and during the immersion corrosion tests. The immersion tests used the same samples used in the other tests. In the case of immersion tests the entire surface was exposed to the test solutions. The total area of contact was 26.2cm². Samples were cleaned, dried, and weighed before testing. The samples were immersed in the stirred solution for four hrs, which matched the test time for the slurry erosion/corrosion tests. After the test the samples were again cleaned, dried, and weighed.

Component	Concentration
NaHCO ₃	0.64 <i>M</i>
NaCl	1.0 <i>M</i>
MgCl ₂	0.003 <i>M</i>

Table 1, solution test chemistry for corrosion tests.

Dry Jet Erosion

The dry jet erosion tests were performed in accordance with ASTM G76-83 “Standard Practice for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets”⁶. The apparatus consisted of a gas supply, gas-particle mixing system that delivered the abrasive flux through a WC nozzle, which in turn was aimed at a specimen stand. Figure 1 shows a dry jet erosion test taking place on a test sample. The carrier gas used for these studies was dry air. The abrasive used was 270µm silica sand particles. Particle velocity was 20mC s⁻¹, and the particle flux, or particle flow rate in the gas stream, was 2 gCmin⁻¹. A 1.5 mm diameter by 50 mm length nozzle was used to direct the dry gas-abrasive slurry at the specimen. The working distance between the end of the nozzle and the surface of the test specimens was 10 mm. The impingement angle of the gas-particle stream to the target was 90°. These room temperature tests were performed using a test duration of 20 min (giving a total amount of abrasive impacting at the target surface of 40g).

Prior to testing the specimens were prepared by surface polishing, cleaning, and weighing. The specimens were polished with a 400 grit abrasive paper, cleaned and dried. Before each test the specimens were weighed to an accuracy of 0.1mg. The samples were then eroded, sample cleaned and reweighed. Each test was repeated at least three times and the erosion rate was calculated from the average mass loss.

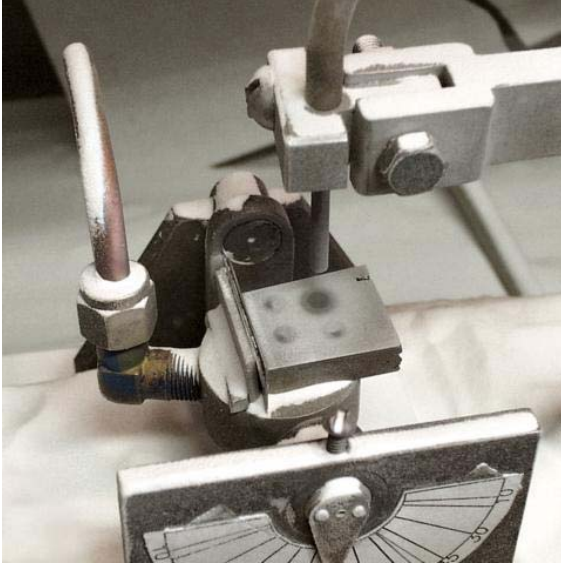


Figure 1. Dry jet erosion test at 90 deg impingement angle.

Slurry Erosion/Corrosion tests

The Slurry Erosion/Corrosion tests were conducted in a custom designed test apparatus⁷. This apparatus holds an impeller that rotates, or pumps, a slurry past an array of specimens located in the inside of a jacked pot (See Figure 2). This arrangement provides for a low impingement angle similar to that found in most pipeline environments.

The impeller, made from wear resistant ultrahigh-molecular-weight polyethylene. This impeller turned, by an electric motor, to drive the solution past eight alloy steel specimens. In these tests the impeller turned at 2250 rpm, giving an erosion impact velocity of about $16 \text{ m}\cdot\text{sec}^{-1}$. The abrasive for the slurry, dry $370\mu\text{m}$ silica sand, was fed at $150 \text{ g}\cdot\text{min}^{-1}$ through a nozzle into the slurry hopper where the sand mixed with a liquid to form the test slurry.

To conduct a test, 1 cm thick rectangular specimens with a contact face of approximately $2.5 \times 2.5 \text{ cm}$, or an area of 6.25 cm^2 , were polished, cleaned, dried, and weighed to the nearest 0.1 mg. The specimens were then mounted in the slurry pot. The tests consisted of eight different isolated specimens. Four different alloys were tested at time, with two duplicates of each specimen. After mounting the specimens and closing up the slurry pot the slurry was pumped through the pot. To start the test the drive motor on the impeller was started and the mixture of solution and sand was allowed to erode and corrode the samples. Like the immersion tests each slurry erosion/corrosion test ran for four hrs.

After the test was completed the specimens were removed from the slurry pot. They were cleaned, dried, and reweighed to the nearest 0.1 mg. The mass change was used to evaluate the rate of erosion/corrosion.



Figure 2. Open slurry erosion/corrosion test apparatus

Slurry tests were conducted in water, acidic and basic solutions at room and elevated temperature (63°C). In order to simulate the olivine sequestration 0.003 *M* MgCl₂ was added to duplicate the Mg⁺ ion found in the solution. Silica sand, which is chemically inert and more stable than olivine, was used to simulate the abrasive component found in the process slurry. After the test solution was mixed with the abrasive sand it was injected into the slurry pot. After the slurry left the apparatus the worn sand was separated from the solution, the solution was mixed with fresh abrasive, and the process was repeated. This mixing of fresh abrasive prevents the slurry from “wearing out,” and allows for the erosion rate to be linear with respect to test time.

Materials

A variety of steels was chosen for evaluation. The high chrome alloys were chosen for their general resistance to corrosion. The high carbon steels were chosen for their ability to be heat treated and increase their hardness and strength.

The steels, as shown in table 2, included i) 440C, a high chrome high cost martensitic stainless steel, ii) 316, a high chrome high cost austenitic stainless steel, iii) 9Cr 1Mo steel, a medium cost medium alloy steel, and iv) AISI 1080 carbon steel, an inexpensive steel. All of the steels were used in their as-received, soft, condition. Two of the materials, the 440C SS and the AISI 1080 steel, are commonly heat treated to improve their strength and/or abrasion resistance. In this case the alloys were not heat treated because an alloy’s resistance to dry erosion is not generally affected by heat treatment,

and because, industrially, they would be less expensive to use if heat treatment was not needed.

Sample	440C SS	316 SS	9Cr 1Mo steel	AISI 1080 steel
Hardness, HRA	84.2	56.0	70.1	76.8
Phase	bcc/bct	fcc	bcc/bct	bcc
Cr, wt %	17	19	9	0
C, wt%	1	0.1	0.2	0.8

Table 2. Test alloys and their hardness, Cr and C content.

The materials were fabricated into test specimens measuring 2.54 x 2.54 cm on the test face (See Figure 3). The tapered sides allow the specimen to be locked into the slurry erosion/corrosion test apparatus with the surface fully exposed.

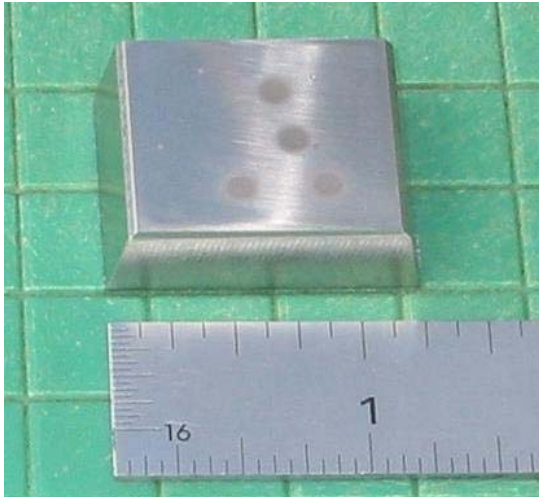


Figure 3. Picture of a 440C test sample with four dry jet erosion scars on the surface. Sample has a 2.54 x 2.54cm test surface and is 1.cm thick.

Results and Discussion

In all cases the worn specimens were compared on a basis of mass change. While most alloys lost mass, some alloys gained mass during the immersion corrosion test due to a protective oxide layer forming on the surface of the specimens.

Immersion Corrosion

The results of the immersion corrosion tests are shown in Table 3. In all cases the sandblasted surfaces showed more mass loss than the polished surfaces. It is thought that the sandblasted surfaces corroded faster because 1) they have more surface area due to the roughing of the surface and 2) the sandblasting put localized work into the surface that corrodes preferentially to the areas without the work.

The specimens in the acid solution corroded faster than the samples tested in either the water or basic environments. The specimens in 63°C water corroded at a faster rate than the samples tested at room temperature. Conversely, the specimens tested in 63°C basic solution gained mass. This mass gain was a function of a fairly thick corrosion layer adhering to the specimen surface. It is not clear whether this thick corrosion layer would be protective over a long test period. In general the high chrome stainless steels showed only small mass changes due to corrosion. The steels with the lower chrome content, the AISI 1080 and the 9Cr 1Mo steel corroded rapidly in most conditions. These low alloy steels corroded particularly rapidly in both warm water and the warm acidic solution.

Solution	Temp	Surface	440 SS	316 SS	9Cr 1Mo	AISI 1080
			wt loss in mg for 4 hr test			
water	room	polished	-0.20	-0.10	-0.80	-1.10
		sandblasted	0.20	0.10	1.30	-1.70
water	63°C	polished	0.40	0.50	-0.30	7.00
		sandblasted	1.00	0.80	5.10	8.40
basic	room	polished	1.20	0.10	2.90	2.60
		sandblasted	1.70	2.80	2.90	7.70
basic	63°C	polished	-0.60	-0.80	0.40	-2.00
		sandblasted	1.00	-0.60	3.00	-4.30
acidic	63°C	polished	0.20	-1.00	5.00	21.50
		sandblasted	2.40	0.80	10.30	25.90

Note: a negative mass indicates a mass gain for the sample, due to corrosion film on surface.

Table 3. Immersion corrosion mass loss results for the different alloys in the variety of solutions.

Dry Jet Erosion

The dry jet erosion tests showed a relatively high erosion rate for the 440C stainless steel. The rest of the alloys performed nearly identically. It has been previously shown that most steel alloys perform nearly the same in dry erosion⁸.

	440C SS	316 SS	AISI 1080	9Cr 1Mo
wt loss in mg for test				
20 m/sec	0.30	0.27	0.26	0.26

Table 4. Dry jet erosion results for the different alloys using a velocity of 20 mCsec⁻¹ and a 90 deg impingement angle.

Slurry Erosion/Corrosion

Table 5 shows the results of the slurry erosion/corrosion testing. The tests in water were duplicated after a new impeller was installed. The measurable difference between the two tests is believed to be a function of using two different impellers. The water slurry at room temperature produced the lowest mass loss, with the hard corrosion resistant 440C

performing the best. In the other slurry conditions different alloys showed different responses. For both the 440C and 316 stainless steels the warm acidic slurry had the second lowest loss rate, followed by the warm basic slurry, warm water slurry, and highest lost was for the basic slurry at room temperature. The 316 had a slightly higher chrome level, which in the case of immersion corrosion resulted in a lower corrosion rate for the 316. With the addition of erosion to the corrosion the harder 440C had a lower loss rate than the 316. The 9Cr 1Mo steel had the second least wear loss for the warm water, followed by the warm acidic slurry, then the warm basic slurry, and the highest loss was with the room temperature basic slurry. The AISI 1080 alloy the warm water had the second best resistance to loss, followed closely by the warm basic slurry, then the basic slurry at room temperature, the highest loss was with the warm acidic slurry.

Statistically, the most significant relationship between the loss of material in the slurry tests was the material's hardness: higher hardness resulted in lower slurry material loss.

Solution	Temp	440 SS	316 SS	9Cr 1Mo	AISI 1080
wt loss in mg for 4 hr test					
water	room	23.5	38.4	43.6	40.3
water	room	30.6	47.6	53.3	48.3
water	63°C	78.3	89.7	106.6	109.6
basic	room	87.9	133.3	175.3	122.2
basic	63°C	65.7	96.5	133.3	114.5
acidic	63°C	59.7	74.8	127.3	179.1

Table 5. Slurry erosion/corrosion results for the different alloys in the variety of solutions with abrasive traveling at $\sim 16\text{mCsec}^{-1}$.

Discussion

An effort was made to determine if and how much synergism was occurring between the erosion and the corrosion.

Certain assumptions were made about the process. It was assumed that dry jet erosion was comparable to slurry wear of a corrosion resistant alloy, 316, at room temperature. With these assumptions the loss for the dry jet test and the slurry erosion/corrosion test can be compared.

Any difference between the sandblasted and polished samples in the immersion corrosion test would indicate that cold-working the surface activates the surface to stimulate or enhance corrosion.

Because the three tests used for the alloy evaluation all have somewhat different characteristics there are limitations to the comparison that can be made, this lead to some uncertainty in the resultant calculations. The limitations included the actual angle(s) of impacts in the slurry test are not known, so the impacting velocity was approximated to be the tangential velocity the particle would acquire at the edge of the slurry impellor.

Table 6 shows the results of converting the results to common units. The slurry erosion/corrosion results were chosen to be the base “SEC” units. To convert the immersion corrosion test results to SEC units the immersion test results were divided by a ratio of the exposed surfaces, 6.25cm² for the slurry erosion/corrosion and 26.2cm² for the immersion tests. For the dry jet erosion conversion to SEC units the results of the 316’s dry jet erosion tests were compared to the slurry erosion/corrosion tests. All of the dry jet erosion tests were multiplied by this same factor to make dry jet erosion SEC units. In general this makes all the dry jet erosion test results comparable to the water room temperature slurry erosion/corrosion tests. It is also apparent that the slurry erosion/corrosion tests in more aggressive conditions had much higher loss rates.

Solution	Temp	Surface	440C SS	316 SS	9Cr 1Mo	AISI 1080
Jet erosion	room	polished	42.30	38.07	36.66	36.66
water	room	polished	-0.05	-0.02	-0.19	-0.26
		sandblast	0.05	0.02	0.31	-0.41
		slurry	23.50	38.40	43.60	40.30
water	63°C	polished	0.10	0.12	-0.07	1.67
		sandblast	0.24	0.19	1.22	2.00
		slurry	78.30	89.70	106.60	109.60
basic	room	polished	0.29	0.02	0.69	0.62
		sandblast	0.41	0.67	0.69	1.84
		slurry	87.90	133.70	173.30	122.20
basic	63°C	polished	-0.14	-0.19	0.10	-0.48
		sandblast	0.24	-0.14	0.72	-1.02
		slurry	65.70	96.50	133.30	114.50
acidic	63°C	polished	0.05	-0.24	1.19	5.12
		sandblast	0.57	0.19	2.46	6.17
		slurry	59.70	74.80	127.30	179.00

Table 6. Results of three tests converted to common “slurry erosion/corrosion” (SEC) units.

Calculation of Corrosion Enhancement and Synergism

Variation in mass loss of the polished and sand blasted corrosion samples would indicate what the effect of erosion impact might have on corrosion of sample surfaces during slurry tests. The slurry erosion process results in at least two accelerators for corrosion. The first is removal of the corrosion layer, which maybe protective. The second is the continuously creation of cold-worked surfaces, which are being presented to the corrosion environment as a result of the erosion. Both of these will then result in faster corrosion in the slurry erosion/corrosion test than in the immersion test. To see if the creation of the cold-worked surface is accelerating the corrosion, the mass change of polished corrosion samples was subtracted from the mass change of the sand blasted corrosion samples. This resulting corrosion enhancement, table 7, showed for many

alloys there was substantial increase in corrosion for the cold-work (sandblasted) surfaces.

Solution	Temp	Condition	440 SS	316 SS	9Cr 1Mo	AISI 1080
water	room	polished	-0.20	-0.10	-0.80	-1.10
		enhanced	0.40	0.20	2.10	-0.60
water	63°C	polished	0.40	0.50	-0.30	7.00
		enhanced	0.60	0.30	5.40	1.40
basic	room	polished	1.20	0.10	2.90	2.60
		enhanced	0.50	2.70	0.00	5.10
basic	63°C	polished	1.20	0.10	2.90	2.60
		enhanced	-0.20	-0.70	0.10	-6.90
acidic	63°C	polished	0.20	-1.00	5.00	21.50
		enhanced	2.20	1.80	5.30	4.40

Table 7. Showing corrosion enhancement due to cold-working the surface prior to immersion corrosion tests. The highlighted results show samples that had >~50% enhanced corrosion due to cold-working.

A value for synergy was also calculated. This was defined as the excess slurry erosion/corrosion loss above the loss for dry jet erosion and the polished immersion corrosion. Table 8 shows the results for the amount of synergism versus the slurry erosion/corrosion. The results show that in most of the test solutions the synergy between the erosion and the corrosion was responsible for more than 50 pct of the specimen mass loss. The negative synergy for the 440C in water at room temperature is attributed to the higher dry jet erosion the 440C experienced versus its low room temperature water slurry loss. It is thought the chrome added extra protection to loss in the room temperature water slurry tests. The 440C was the superior alloy in all of the slurry erosion/corrosion tests and showed the least synergy in all of the conditions.

Solution	Temp	Condition	440 SS	316 SS	9Cr 1Mo	AISI 1080
water	room	slurry	23.5	38.4	43.6	40.3
		synergism	-18.8	0.4	7.2	4.0
water	63°C	slurry	78.3	89.7	106.6	109.6
		synergism	35.9	51.6	70.1	71.3
basic	room	slurry	87.9	133.3	175.3	122.2
		synergism	45.3	95.7	136.0	85.0
basic	63°C	slurry	65.7	96.5	133.3	114.5
		synergism	23.5	58.7	96.6	78.4
acidic	63°C	slurry	59.7	74.8	127.3	179.1
		synergism	17.4	37.0	89.5	137.3

Table 8. Showing alloys loss in the slurry erosion/corrosion test and loss due to the effects of synergism. The highlighted results show samples that had >~50% of their loss due to synergism.

Conclusions

A series of abrasive wear, corrosion, and slurry tests were conducted on a series of iron based alloys in neutral, basic, and acidic liquid media.

Slurry tests results show hardness can accounts for approximately +80% of the material loss in a benign neutral water/silica sand solution.

Corrosion tests results show that a cold-worked surface enhances corrosion. However, corrosion accounts for only a minor contribution to slurry material loss.

There is a large amount of synergism between wear and corrosion that needs be accounted for in the loss of material during slurry tests. Comparison of polished and cold-worked immersion corrosion results indicates that the presence of a continuously fresh, cold-worked surface resulting from abrasive wear might account for some increased corrosion.

The results show for aggressive CO₂ sequestration conditions, such as pumps and valves, the hard corrosion resistant 440C steel is the most appropriate alloy tested. For the more benign conditions, such as piping the most appropriate steel tested would depend. i) If the solution being handled is room temperature and basic, based on cost the AISI 1080 steel is better than the 316 or 9Cr 1Mo steel. ii) If the solution is acidic then the 316 or 440C is likely the better choice.

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