Corrosion of Well Casings in Compressed Air Energy Storage Environments

**R. P. Elmore
J. A. Stottlemire**

October 1980

**Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

The Compressed Air Energy Storage (CAES) Technology Program at the Pacific Northwest Laboratory (PNL) is sponsored by the Department of Energy (DOE), Divisions of Energy Storage Systems and Electric Energy Systems. The program scope includes a group of studies directed at developing a new energy storage technology to improve the cost and efficiency of electrical power utilization and to reduce the dependence on petroleum fuels such as oil and natural gas. The program has two major thrusts with the following objectives:

- Reservoir Stability Criteria - Develop design and stability criteria for long-term operation of underground reservoirs used for CAES to accelerate commercialization of the concept.
- Advanced Concepts Studies - Develop and assess advanced CAES concepts that require little or no supplementary firing by petroleum fuels to eliminate CAES dependence on petroleum fuels.

The ultimate objective of this program is to reduce the consumption of natural gas and oil used for peak power generation plants by about 100 million barrels per year. This objective could be accomplished by replacing conventional gas turbine-peaking plants currently in use with CAES plants.

A bibliography listing pertinent documents that have been published (or are to be published) has been provided.

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SUMMARY

The goal of this study is to determine corrosive effects of compressed air energy storage (CAES) environments on several well casing materials to aid in material selections. Initially a literature search was conducted to obtain information on corrosion behavior of well casing materials in similar environments, and it was found that corrosion rates of 0.02-0.25 millimeters per year (mm/y) might be expected. This information was employed in designing the laboratory study. Unstressed electrically isolated samples of various carbon steels (A120, H40 series, and A53B) were autoclaved at varying humidities, temperatures, and exposure durations to simulate anticipated environments in the well bore during CAES operation. All compressed air tests were run at 12.1 MPa. Temperatures varied between tests from a minimum of 323K to a maximum of 573K, and humidity varied from 100% to completely dry air. The effects of salts in the humidified air were also studied.

Results of autoclave testing indicated that typical well casings of carbon steel as used in oil (H40 series), gas (A120), and water (A53B) production wells adequately withstand the anticipated CAES reservoir environment. An acceptable corrosion rate arrived at by these laboratory simulations was between 0.0015 and 0.15 mm/y. Corrosion was caused by metal oxidation that formed a protective scale of iron oxide. Higher temperatures, humidity rates, or salinity content of the humid air increased corrosion. Corrosion also increased on a metal coupon in contact with a sandstone sample, possibly due to crevice corrosion. For each of these factors either singularly or collectively, the increased corrosion rates were still acceptable with the maximum measured at 0.15 mm/y.

When coupons were reused in an identical test, the corrosion rates increased (up to 0.20 mm/y) beyond the anticipated values that had been determined by extrapolation from "one-time" runs. Fine cracking of the protective scale probably occurred due to thermal variations, resulting in increased corrosion rates and a greater potential for particulates, which could plug the reservoir. Other conditions that could increase well casing corrosion rates are flow rates in the well, metal-metal electrochemical interactions, and the presence of organics; however, these conditions were not investigated in this study.

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INTRODUCTION

In this study typical well casings as used in the water, oil, and gas industries were exposed to anticipated compressed air energy storage (CAES) environments to determine their acceptability. Since CAES is a new technology, the performance of well casings in contact with CAES production environments is not yet known. It was hoped that this study would verify that inexpensive carbon steel well casings that are used in other industries would also be sufficient for this environment.

The initial phase of this program was a literature study on casing corrosion in environments similar to CAES. Laboratory tests were then designed from this information. The final results of this study were measurements of corrosion for three casing metals as a function of exposure time, temperature, humidity, vapor salinity, and cycling.

CONCLUSIONS

Typical well casings of carbon steel as used in oil, gas, and water production wells appear to withstand anticipated CAES reservoir environments adequately. An estimated acceptable corrosion rate of between 0.0015 and 0.20 mm/y was arrived at by laboratory simulations. The corrosion, caused by metal oxidation, formed a protective scale of iron oxide that at first appeared to be beneficial. However, it was discovered that the scale is a potential source of particulates.

During cycling tests it was noted that corrosion rates increased beyond anticipated values that had been determined by extrapolation of corrosion rates from one-time runs. Fine cracking of the protective scale probably occurred during thermal expansion and contraction, which would allow air and water easier access to the metal. In addition, cracking of the scale would greatly increase the potential for particulates.

The corrosion rate was primarily controlled by the formation of the protective scale, thus the corrosion rate decreased with time. Of the other parameters that were varied, temperature had the most dramatic effect on increasing corrosion rates. Increasing humidity or salinity produced minor increases in corrosion rates, and corrosion rates were also higher at the sandstone-metal interface.

In conclusion, well casings composed of metals A120, H40 series, and A53B appear to corrode at acceptable rates in anticipated CAES reservoir environments. Factors that increase corrosion are: temperature, humidity, salinity of the humid air, sandstone-metal interactions, and any cracking or partial removal of the protective scale.

Other conditions that could increase corrosion rates are flow rates in the well, metal-metal electrochemical interactions, and the presence of organics; these factors were not investigated in this study. It is suggested that coupons be placed in accessible locations in the wells for actual field measurements of corrosion or alternately that in-line corrosion probes be installed.

LITERATURE SEARCH

The literature was examined for data on well casing corrosion under environments similar to that during CAES production; corrosion data for potential materials are presented in Table 1. Air temperature applicable to CAES may be in the range of 325-573K, and medium storage pressures of 3.5 to 12.1 MPa are being contemplated. During the initial phase of air bubble development extraction, 100% humidity conditions can be expected. Subsequent reservoir dewatering with hot undersaturated air will result in humidity decreases with time, but a finite amount of water vapor will be present in the air stream for several years and possibly for the lifetime of the plant (Stottlemire et al. 1979). Corrosion data for aerated steam represent the high-humidity phase, and data for separated (undersaturated) steam simulate the low-humidity stages of CAES plant operation. It appears that high corrosion rates--up to 0.51 mm/y or 20 mils per year (mpy)--might be expected under high-humidity conditions (Marshall and Hugill 1957). Electrochemical attack is moisture dependent; and, therefore, as the humidity decreases, the corrosion rates should also decrease. Corrosion rates between 0.02-0.25 mm/y might be expected.

In all literature cases, corrosion is characterized as general corrosion that produces an uneven surface. Stressed samples have been tested in aerated steam and separated steam (Marshall and Hugill 1957; Foster, Marshall, and Tombs 1964), and as expected the samples did not produce cracks. Thus, it appears that the form of casing deterioration expected in the CAES environment can also be characterized as a general corrosion attack.

TABLE 1. Corrosion Under Environments Similar to CAES

Metal	Condition	Corrosion Rate, mpy	Reference
Carbon Steel ASTM-A285	Aerated steam, 150 days 100°C, 1 atm, velocity <10 m/sec	4	Tolivia, Hoaski, and Miyazaki 1975
Carbon Steel	Aerated steam, 144 days, 30-lb steam to 2-lb air	20	Marshall and Hugill 1957
Carbon Steel	Separated steam, 144 days, 140°C	6	Marshall and Hugill 1957
Bore Casings API-355	Aerated steam, 144 days, 98-108°C, 0-5 psig	<10	Foster, Marshall, and Tombs 1964
API-H40	Aerated steam, 144 days, 98-108°C, 0-5 psig	<10	Foster, Marshall, and Tombs 1964
API-355	Separated steam, 144 days, 142-162°C, 10% moisture, 8-40 psig	1-10	Foster, Marshall, and Tombs 1964
API-H40	Separated steam, 144 days, 142-162°C, 10% moisture, 8-40 psig	1-10	Foster, Marshall, and Tombs 1964
Carbon Steel AISI 1060	Separated demisted steam, 171°C, 110 psig, 150 days plus 10 days air/moisture	1.3	Toney, Cohen, and and Cron 1977

EXPERIMENTAL APPROACH

For this preliminary study on the corrosive effects of CAES environments on well casings, three typical well casing alloys were chosen for testing. The specimens were cut from 3-in. A120 (gas well casing), 4-in. H40 series (oil well casing), and 6-in. A53B (water well casing) pipes and were approximately $2.54 \times 2.54 \times 0.65$ cm, with a surface area averaging 19.25 cm^2 . The surfaces of the specimens were first cleaned in CP-9 (500-ml HCl, 500-ml H_2O , plus 12.5-ml formaldehyde) to remove any initial rust as well as the protective zinc coating on A120 coupons. The specimens were hung on Teflon[®]-insulated hangers and then placed in titanium autoclaves. Due to the highly oxidizing environment associated with CAES experiments all valves and piping were fabricated from titanium. Figure 1 shows the experimental facility; the recorder, which is located a short distance from the autoclaves, is not shown.

The experimental test matrix is presented in Table 2. Unstressed electrically isolated samples of various carbon steels were autoclaved in varying humidities, temperatures, and exposure durations. Initially the tests ran between 168 and 366 hours, but a few tests were extended to 700 hours. All compressed air tests were run at 12.1 MPa. The temperatures varied between tests from a minimum of 323K to a maximum of 573K. Humidity varied from 100% (the initial field condition) to completely dry air (a potential final field condition) and was controlled by the amount of water initially added to the vessel. The compressed air was mixed from water-free components (dew point 200K), and the autoclaves were preheated to bake out any moisture in them prior to the test. After the specimens were sealed in the autoclaves, dry compressed air was flushed through the system to sweep out any moisture to insure that the 0% humidity tests were totally water-free. For the 100% humidity tests excess water was added to each autoclave to insure saturation throughout the test even though slight leaks often occurred. The tests at 50% humidity had a controlled water-to-air ratio; therefore, no leaks were permissible, which was not easy to attain. The results of one successful 50%

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FIGURE 1. Experimental CAES Corrosion Facility

TABLE 2. Test Matrix

<u>Trial</u>	<u>Run</u>	<u>Temperature, K</u>	<u>Humidity, %</u>	<u>Duration, h</u>
1	9	323	0	168
2	15	323	0	336
3	5	323	50	168
4	17	323	50	336
5	1	323	100	168
6	4	323	100	336
7	10	448	0	168
8	16	448	0	336
9	2	448	50	168
10	8	448	50	336
11	13	448	100	168
12	3	448	100	336
13	14	573	0	168
14	11	573	0	336
15	18	573	50	168
16	7	573	50	336
17	6	573	100	168
18	12	573	100	336
19 ^(a)	19	573	100	336
20 ^(b)	20	448	100	336
21 ^(b)	21	573	100	336

(a) Standstone core in contact with metal specimen.

(b) Additional tests using a salt solution as the reservoir for producing humidity.

humidity test (no leaks) were similar to those of the 100% humidity test, qualitatively implying that there were no significant differences between 50 and 100% humidity conditions. Thus, the cost/benefit of the 50% humidity tests was deemed questionable and these experiments were eliminated. As a substitute, 100% humidity tests were conducted using a salt solution as the reservoir water to measure the effects of salts upon corrosion rates in humidified air.

At the completion of each test the specimens were placed in a desiccator to dry and then reweighed. In all cases the weight of the specimen either remained constant or increased, which was due to the formation of scale--a corrosion product. The scale coverage varied, ranging from patchy to complete. The scale was mostly a reddish color, but after some tests the coupons were black with reddish patches. X-ray diffraction analyses of the red scale identified it as hematite, and Figure 2 shows the typical patchy hematite scale. To determine the weight loss for the specimens the scale had to be removed without removing significant quantities of the metal, which was accomplished successfully with the cleaning solution CP-9. After treatment with CP-9 the coupons were rinsed in water, rinsed with acetone, and then placed in a desiccator. For each of the three pipe metals tested, three blanks of each metal were treated with the cleaning solution in the same manner as during descaling to determine the metal lost during this procedure.

FIGURE 2. Hematite Scale on Casing Material
(Test Conditions: 323K, 100%
Humidity, 504 Hours)

An average of 0.0008 g was lost for A53B pipe specimens; 0.0006 g, for H40 series; and 0.0009 g, for A120. Weight loss was determined by the difference between the initial sample weight and the weight after descaling (post weight) plus the weight correction. Some samples were not descaled; instead these were reused in a test with the same conditions to extend the coupon exposure time.

Due to their irregular shape the surface area of each specimen was calculated using a computer program. Since the specimens were actual pipe sections, they had a curvature that complicated surface area calculations. For each specimen, eight measurements were taken to within 0.00025 cm for area calculations. The area for the hole was subtracted from the total surface area.

From the weight loss data and the surface area calculations the corrosion rate in millimeters per year was determined by the following equation:

$$\text{mm/y} = \text{mpy} (0.0254) = \frac{(526,800) (\text{weight loss, grams})}{(\text{area, in.}^2) (\text{density, g/cc}) (\text{time, h})}$$

RESULTS AND DISCUSSION

Corrosion rates for various test conditions for the three metals are summarized in Table 3. The rates are mean values in mils per year ± 1 standard deviation, and the number of samples in each averaged data point is given in parentheses. The metal corrosion rates were averaged and are listed for each test. The averaged corrosion rates ranged from a low of 0.0015 mm/y (0.06 mpy, 323K, 0% humidity) to a maximum of 0.14 mm/y (5.65 mpy, 573K, 100% humidity). Initial corrosion rates start as high as 0.08 mm/y (3 mpy) for 0% humidity cases but rapidly decrease to around 0.025 mm/y (1 mpy) after 300 hours. Most of the 100% humidity cases do not decrease to 0.025 mm/y (1 mpy) until after almost 500 hours. For both 0 and 100% humidity the 573K cases display the highest corrosion rates. The three types of casing material--A120, H40 series, and A53B--behave in a similar manner in all environments with corrosion rates increasing with higher temperatures and humidity rates. In most instances, corrosion rates decrease with exposure time.

Corrosion (weight loss/surface area) as a function of temperature, humidity, and exposure was plotted for A120 (Figure 3) to demonstrate graphically how these parameters affect corrosion. Since the metals behave similarly, only one metal will be detailed. Among the three variables (temperature, humidity, and exposure time) humidity had the smallest effect toward increasing corrosion, see Figure 3(b). Corrosion continually increased with temperature, Figure 3(a), and rose most rapidly between 448 and 573K. The relationship between corrosion and exposure was the most interesting: As exposure time increased, the rate at which corrosion increased leveled off, implying that a protective coating was forming on the metal surfaces.

Recycling also increased corrosion of the coupons. Corrosion rates for one-time tested coupons ranged between 0.0015-0.08 mm/y while the range for retested coupons was from 0.01 to 0.20 mm/y. For each temperature and humidity condition a coupon was retested with the corrosion scale undisturbed. In each case corrosion was higher than would be inferred from extrapolation of the original corrosion data to these times. Figure 4 illustrates these trends for A120. In the graph the disconnected points are coupons that were used in the

TABLE 3. Corrosion Rates of Casing Materials Under Simulated CAES Environment

TEMPERATURE HUMIDITY HOURS	573 K									
	312	336	100% 351	384	696	699	168	286	306	0% 336
A120	1.61±0.70 (2)	4.82 (1)*	5.99 (1)**	1.54±0.59 (2)	0.98 (1)	5.19 (1)*	3.21±1.10 (3)	1.22±0.34 (3)	0.62±0.14 (2)	1.23±0.23 (3)
H40 SERIES	1.62±0.24 (2)	7.89±0.11 (2)*	---	1.37 (1)	1.47 (1)	---	2.65±0.05 (2)	1.60±0.14 (3)	0.77±0.12	0.89±0.37 (3)
A53B	1.49±0.18 (2)	3.82±2.52 (2)*	---	2.27 (1)	1.71 (1)	2.73 (1)*	2.51±0.96 (3)	1.19±0.32 (3)	0.77±0.16	1.05±0.32 (3)
AVERAGE	(1.57±0.35 (6)	(5.65±0.24 (5)		(1.68±0.53 (4)	(1.39±0.37 (3)	(3.96±1.74 (2)	(2.81±0.85 (3)	(1.34±0.32 (9)	(0.73±0.14 (8)	(1.06±0.33 (9)

TEMPERATURE HUMIDITY HOURS	448 K						
	312	100% 504	816	50% 168	216	0% 335	551
A120	1.07±0.49 (2)	0.70 (1)	1.40 (1)*	1.39±0.15 (3)	0.73±0.04 (2)	1.10±0.08 (2)	0.77 (1)*
H40 SERIES	0.99±0.13 (2)	1.07 (1)	1.33 (1)*	1.50±0.65 (3)	1.01±0.39 (2)	0.80±0.20 (2)	0.84 (1)*
A53B	1.36±0.20 (2)	0.91±0.05 (2)	1.31 (1)*	0.47±0.14 (3)	0.80±0.37 (2)	0.34±0.00 (2)	0.94 (1)*
AVERAGE	(1.14±0.19 (6)	(0.90±0.15 (4)	(1.35±0.05 (3)	(1.12±0.059 (9)	(0.84±0.27 (6)	(0.75±0.35 (6)	(0.85±0.09 (3)

TEMPERATURE HUMIDITY HOURS	323 K					
	350	100% 504	854	169	0% 350	519
A120	0.11±0.06 (2)	0.61 (1)	0.67 (1)*	3.05±0.81 (2)	0.06±0.02 (2)	0.87 (1)*
H40 SERIES	0.26±0.08 (2)	1.47 (1)	0.56 (1)*	2.71±0.13 (2)	0.15±0.07 (2)	0.78 (1)*
A53B	0.24±0.10 (2)	0.73±0.04 (2)	0.51 (1)*	2.51±0.76 (2)	0.09±0.00 (2)	0.42 (1)*
AVERAGE	(0.20±0.10 (6)	(1.15±0.68 (5)	(0.85±0.08 (3)	(2.76±0.56 (6)	(0.10±0.05 (6)	(0.69±0.24 (3)

THE RATES ARE MEAN VALUES IN MILS PER YEAR PLUS OR MINUS ONE STANDARD DEVIATION. THE NUMBER OF SAMPLES IN EACH AVERAGED DATA IS GIVEN IN THE PARENTHESIS. FOR EACH TEST THE THREE METALS WERE AVERAGED.

- ** COUPON IN CONTACT WITH SANDSTONE
- * RETESTED COUPONS

FIGURE 3. Corrosion as Weight Loss (mg) per Surface Area (cm^2) Versus (a) Temperature, (b) Humidity, and (c) Hours Exposed for Metal A120

indicated conditions (i.e., $\nabla = 573\text{K}$, 100% humidity) and then reused in the same environment in a later test. It can be seen that the rate at which corrosion increased beyond the expected extrapolated value rose with temperature. Thus, temperature or humidity cycling affects the resilience of the metals to corrosion. Fine cracking of the protective scale probably occurred during the thermal expansion and contraction between tests, increasing the possibility for oxidation.

A sample from each of the test series was cross sectioned and examined by electron microscopy to determine the thickness, chemistry, and structure of the corrosion products. The results were similar among the coupons; thus, just one sample is presented: Coupon 329, 448K, 100% humidity, 504 hours. As shown in Figure 5, the corrosion product is iron that was determined to be an iron oxide, which is also implied by its smaller iron peak when compared to the metals. The more important observation is the solidity of the scale; this dense iron-oxide corrosion product apparently formed a protective cover so that corrosion rates reduced with time.

The scale was also tested for its cohesiveness to the metal, which is important because sandblasting could occur in the well during high airflow and produce loose scale fragments. Similar scale fragments have plugged pore spaces in the reservoir and/or formed sandface filter cakes, thus reducing the air injectivity of the well and surrounding zones (Barkman et al. 1972; Owen et al. 1979). The scale on the coupons exposed in 323K environments was the easiest to remove; with higher temperatures the scale was more cohesive except when it became thicker and flakier and thus easier to remove. The amount of potential particulates was quickly estimated at 42 g for 1 day (using the 448K, dry air test, which produces approximately 1 mg of scale per 20 cm^2 area) for a well 20 cm in diameter and 1200 m deep. No estimate of particle size distribution was attempted.

FIGURE 4. Corrosion as Weight Loss (mg) per Surface Area (cm²) Versus Hours Exposed for Recycled Samples of Metal A120

FIGURE 5. Cross-Sectional Electron Microscopy of Corrosion Coupon

The corrosion potential for some CAES well casing materials was measured after exposure to heated dry or humid air. Corrosion rates varied between 0.0015 and 0.15 mm/y; the literature had reported higher corrosion rates in similar environments. There are several factors that may have been present in the other studies that could increase the laboratory-determined corrosion rates:

- chemistry of the steam or water droplets
- cracking in the protective scale due to temperature or humidity changes
- sandstone-metal interactions
- higher O₂ content.

In determining the effects of varying the salinity of the liquid phase, NaCl and KCl were added to the water reservoir. The metals were then tested at 448 and 573K in this humid compressed air with salts. The results--corrosion rates of 0.0036-0.078 mm/y (1.41-3.07 mpy, see Table 4)--are not enough higher to alter the acceptability of these metals. Thus, chemistry of the steam or water droplets does not appear to be significant. Scale cracking has already been discussed, and any removal of the protective scale will increase

TABLE 4. Corrosion Rates (mm/y) for Casing Materials Exposed in a 100% Humidity Environment Produced from Salt Solution Reservoir

Pipe Casing	448K	573K
A120	0.036 $\pm$ 0.009 (3) ^(a)	0.070 $\pm$ 0.022 (2)
H40 series	0.056 $\pm$ 0.013 (3)	0.078 $\pm$ 0.015 (2)
H53B	0.064 $\pm$ 0.008 (3)	0.063 $\pm$ 0.001 (2)

Test conditions: 12.1 MPa
 336 hours exposure
 0.50 g/l NaCl + 0.14 g/l KCl

(a) Data in mean averaged mm/y $\pm$ 1 standard deviation.
 Number of samples averaged given in parentheses.

the corrosion rate of the metals. The corrosion rate of the casing in contact with the sandstone aquifer in heated compressed air was measured to be 0.15 mm/y (5.99 mpy). Thus, there is a potential for corrosion on the outside of the casing, which is most likely due to crevice corrosion that occurs between the sandstone and the metal wall. Even though these laboratory simulations were under static conditions it was calculated that there was sufficient oxygen for oxidation of the metals. Using the ideal gas law as 12.1 MPa and 573K there was at least 17-g O₂. Thus, higher O₂ content is not a viable concern.

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