

DYNAMIC CORROSION TESTS IN A CO₂-RICH ENVIRONMENT

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Abstract

The Allam Cycle is a transcritical CO₂ power cycle that shows great potential to generate low-cost electricity from fossil fuels while producing near-zero air emissions, including CO₂. NET Power is currently demonstrating the core cycle by building and commissioning a 50 MW_{th} natural gas-fired power plant in La Porte, Texas. In parallel, a team consisting of the University of North Dakota Energy and Environmental Research Center (EERC), 8 Rivers Capital, the U.S. Department of Energy National Energy Technology Laboratory, ALLETE, Inc., Basin Electric Power Cooperative, and the Lignite Energy Council is working to develop lignite-based Allam Cycle technology. Material corrosion is one of the major issues being studied. A high temperature (up to 750°C), high pressure (up to 300 bar) dynamic corrosion test rig was built at the EERC for testing alloys under various conditions relevant to a lignite-fired Allam Cycle system. In this paper we describe tests of several high nickel alloys to determine their relative performance under conditions representing the low-pressure and high-pressure passages of the primary heat recuperator in conditions similar to those that would be experienced in a lignite fired Allam Cycle power plant. All nickel-based alloys displayed good resistance to oxidation and sulfidation in tests lasting up to 1500 hours. Based on the information obtained to date, none of the nickel-based alloys tested can be rejected for use in this type of system.

Introduction

North Dakota has an opportunity created by the state's oil and gas successes to grow the use of lignite coal for dependable, low-cost electric power production while addressing future CO₂ regulations. Projections for electricity demand growth are estimated to be between 2.5 and 5 GWe in order to address the needs created by development of the Bakken oil field. The objective of this project is to support the increased power need by continued evaluation and development of a low-carbon pathway to lignite utilization for electric power generation. The technology to achieve this objective, termed the Allam Cycle, is a direct-fired, transcritical CO₂ power cycle with the potential for significant efficiency advantages over conventional steam-based Rankine systems. In addition, the Allam Cycle also allows for inherent CO₂ separation and pressurization to comply with carbon capture regulations now facing the lignite industry and potentially provides a valuable CO₂ feedstock for enhanced oil recovery, further enhancing North Dakota's oil production. Successful development of this technology can enable the cost-effective and sustainable use of lignite into the future, even in a carbon-constrained economy.

The Coal Allam Cycle system is based upon the Allam Cycle platform: a transcritical carbon dioxide power cycle with a low-pressure-ratio turbine (between approximately 300 bara [4350 psia] and 30 bara [435 psia]) employing high recirculation, inventive high- and low-grade

heat recuperation, and the ability to utilize various hydrocarbon and hydrogen-based gaseous, liquid, and solid fuels. The natural gas variant of the Allam Cycle is currently in the demonstration phase of a 50-MW_{th} plant with NET Power LLC, carrying significant industry support from 8 Rivers Capital, McDermott, Exelon Generation, and Toshiba [1]. Since 2012, Toshiba has been developing a first-of-a-kind turbine and combustor specific to the Allam Cycle [2]. The core cycle of the Coal Allam Cycle is based significantly on this natural gas version in development, with the addition of syngas generation and cleanup, as well as system integration between coal gasification and the core Allam Cycle power generation. A more rigorous description of the core process is outside the scope of this paper and is available elsewhere [1, 3].

The core Allam Cycle requires several additional operations in order to utilize a solid fuel input such as coal. Figure 1 depicts the general arrangement. These include the addition of 1) a coal gasifier and ancillary systems for production of a clean syngas, 2A) syngas precombustion cleanup of sulfur, chlorine, heavy metal and other species, 2B) postcombustion impurity removal, and 3) unique

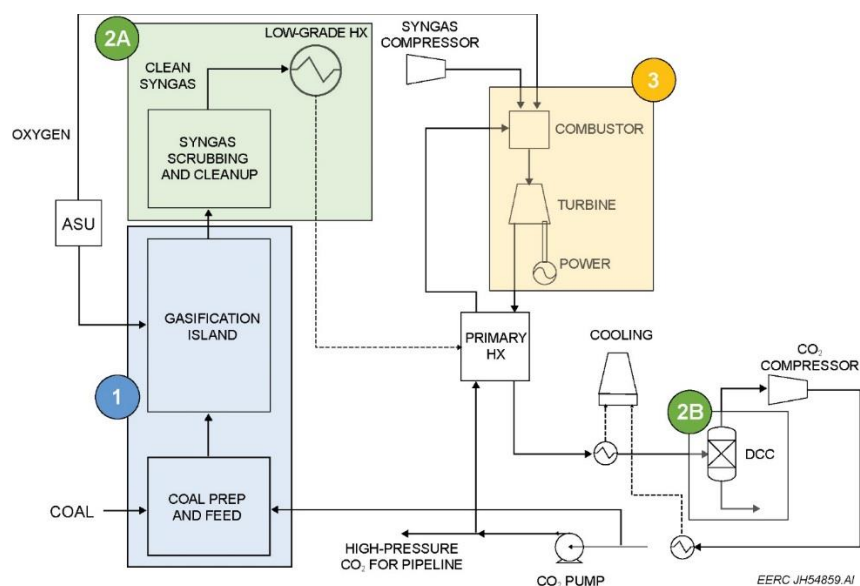


Figure 1. The general arrangement of the coal Allam cycle.

considerations for a syngas combustion system. Modeling that encompasses a variety of coal feedstock and gasification schemes has shown that the full-carbon-capture Allam Cycle can utilize a syngas fuel at power production efficiencies substantially higher than current integrated gasification combined-cycle (IGCC) baselines which do not employ carbon capture. In addition, the cycle efficiency remains relatively consistent to changes in feedstock selection, gasifier type, and produced syngas composition. The particular operational points of the cycle allow for inventive pre- and postcombustion sulfur removal processes, resulting in considerable energy savings in addition to significantly lower water usage. However, the Allam Cycle requires additional unique considerations regarding gasification processes that differ from those of a typical combined cycle such as IGCC. These include selection of coal gasifiers with high cold-gas efficiency, syngas cooling, particulate removal, heat recovery, syngas cleanup, and modified turbine combustor and turbine.

An integral part of the development of these systems is the choice of materials of construction based on their ability to resist corrosion in the impurities that could exist with a coal-fired system. With current interest in exploring the use of sCO₂ as a working fluid for both direct-fired and indirect-fired power generation cycles, using fossil fuels, nuclear power, concentrated solar power (CSP), and waste heat recovery applications, many studies focus on the metal corrosion at different conditions in a CO₂-rich environment. Pint et al. investigated the effect of temperature and pressure on sCO₂ compatibility of conventional structural alloys at 400°–750°C (750°–1380°F) in 12–30 MPa (1800–4350 psi) CO₂ and found that many of the higher-alloyed materials exhibited low mass changes and thin reaction products at all conditions. Little effect of pressure on the mass change or reaction products was observed at 750°C [4]. Walker et al. investigated corrosion performance of carbon steels in industrial grade sCO₂ at 260°C and 17.6 MPa. Their results indicate that these alloys experience breakaway oxidation after an exposure period of 1500 hr. The post-breakaway corrosion rate was measured to be 0.032 mm/year. Corresponding to the onset of breakaway oxidation are cracks in the surface oxide along with oxide growth dominated by the magnetite inner oxide layer of the two-layer (hematite + magnetite) corrosion products [5]. Holcomb et al. conducted experiments at 730°C/207 bar (sCO₂) and 726°C/208 bar (sH₂O) to compare the oxidation behavior of austenitic stainless steel and Ni-base alloys. The results show that Ni-base alloys in sCO₂ did not exhibit much change in corrosion rate with pressure. Ni-base alloys in sH₂O had an increase in corrosion rate, and the log of the parabolic rate constant was proportional to pressure. Austenitic stainless steels in sCO₂ and sH₂O were less protective with pressure as the dense protective chromia scales were replaced with faster growing iron oxide-rich scales [6]. Mahaffey et al. investigated the effect of oxygen impurity on corrosion in sCO₂ environment at 750°C and 200 bar. Nickel alloys Haynes 230 and Haynes 625 were tested in research-grade (99.999%) carbon dioxide and research-grade carbon dioxide with 100 ppm O₂ added. They found that samples exposed to higher temperatures showed increases in oxide thickness. Scanning electron microscopy (SEM) also showed preferential carburization along grain boundaries, along with uniform carbon deposits throughout the oxide for samples exposed to all conditions. As a result of these findings, it was advised that O₂ should be limited in the CO₂ environment to reduce oxide growth [7].

In a dynamic environment, simulated flue gas continuously flowed over the metals. Therefore, in the laboratory corrosion testing of candidate construction alloys described here, we used a dynamic flowing environment that closely simulates the modeled process conditions on the low-pressure and high-pressure passages of the primary heat recuperator in a coal-fired Allam system where the atmosphere contained low levels of acid gases, reflecting a system in which acid gases were largely, but not completely, removed from the syngas before firing in the turbine.

Experimental

The EERC dynamic corrosion test system is capable of operating at 750°C and pressures up to 280 bar with flowing gas. The reactor body is made of Inconel 625 and is 1.9-cm ID, 4.1-cm OD, and 366 cm long. It was constructed by Autoclave Engineers. The reactor has five heating zones, with the middle three zones at steady-state conditions. The system is designed to allow for the testing of flat coupons with dimensions of 0.32 cm × 1.3 cm × 17.7 cm, which are stacked vertically in the reactor and spaced 1.3 cm apart. This allows for 18 test coupons to be tested at a time. The test coupons are supported within the reactor on a strip of Inconel 625 measuring 0.32 cm thick by 1.3 cm wide by 188 cm long. Coupons are secured to the Inconel

625 support using alumina screws, nuts, and washers. A washer is used to provide space between the support and coupon. The alumina nut is tightened loosely to accommodate differential expansion between the metal coupon and screw.

Gaseous reactants used in the corrosion testing consisted of CO₂, H₂O, O₂, NO, and SO₂. The blended gases were preheated before injection into the reactor. A flow rate of 3.0 standard liters/min was used for both tests. The high consumption rate of the carbon dioxide, relative to the other reactants, required the parallel manifolding of three cylinders to provide reasonable processing time between change-outs.

A consensus of the project sponsors determined the final selection of the alloys to be tested. Alloy selection was also constrained by the availability of the alloys in the required shapes and dimensions (coupons or tubes). The sponsors also determined that the initial test would simulate conditions on the turbine exhaust stream in a scenario in which the acid gases were largely removed from the coal syngas prior to combustion in the turbine. The modeling indicated that temperature and pressure would be 750°C at 30 bar and a molar gas composition of 97% CO₂, 2% H₂O, 1% O₂, along with trace amounts of NO and SO₂. Three coupons of each of the high-nickel alloy candidates for the construction of the heat recuperator were evaluated. The alloys were G130, 740H, 617, 230, 625, and 282. Their compositions are given in Table I. The positions of the coupons in the dynamic test reactor were randomly distributed. This test was run for 1500 hr in two increments of 750 hr. After the first 750 hr, the reactor was cooled and depressurized, and the coupons were removed and weighed. Two of the three coupons were then put back into the reactor for an additional 750 hr of exposure. However, at the end of the test, the 1500-hr coupons were contaminated by limestone-rich slurry which was used to neutralize the acid gases when the pressure in the reactor dropped below that in the neutralizing bath. Therefore, weight gains for the 1500-hr test at 30 bar are not reported.

Table I. Alloys Tested at 30 bar and 750°C for 750 hr

Alloy	Chromium, wt%	Nickel, wt%	Iron, wt%	Molybdenum, wt%	Cobalt, wt%
G130	24.0–26.0	Balance	1.5 max.	0.5 max.	18.0–22.0
740H	23.5–25.5	Balance	3.0 max.	2.0 max.	15.0–22.0
617	20.0–24.0	Balance	3.0 max.	8.0–10.0	10.0–15.0
230	20.0–24.0	Balance	3.0 max.	1.0–3.0	5.0 max.
625	20.0–23.0	Balance	5.0 max.	8.0–10.0	1.0 max.
282	18.5–20.5	Balance	1.5 max.	8.0–9.0	9.0–11.0

In the second test, conditions were chosen to approximate the oxidant stream in the heat recuperator which was modeled to be 750°C and 269 bar. The molar gas composition used was lower in CO₂ and H₂O and higher in O₂, with trace amounts of NO and SO₂. This test was run for 1500 hr total, but after 750 hr, the system was cooled and depressurized, and the coupons were weighed. For the final 750 hr, one coupon of each alloy was kept out for additional analyses so only two coupons of each alloy were returned to the reactor for the additional 750 hr of exposure. Four of the same alloys tested at 30 bar were also tested at 269 bar: 740H, 617, 625 and 282.

Results and Discussion

Low-Pressure 30-bar Test

Figure 2 shows the average weight gain per unit area of the three coupons for each alloy after 750 hr of exposure. The highest weight gain was found in the 282 coupons which also had the lowest Cr content. However, the second highest weight gain was in the G130 coupons which

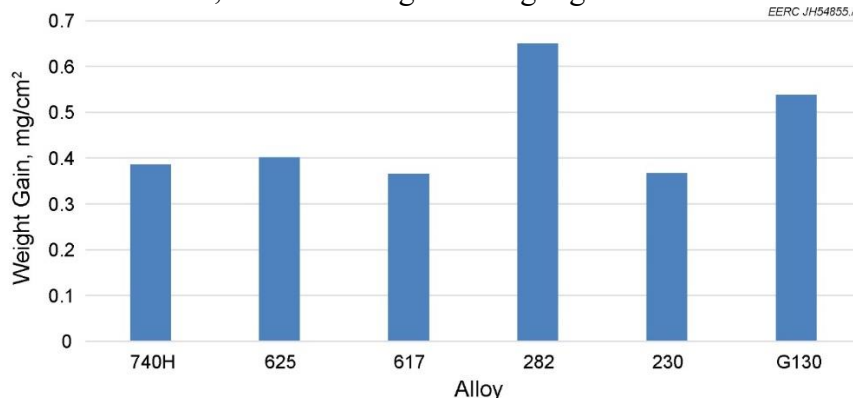


Figure 2. Average weight gain per unit area after 750 hr at 750°C and 30 bar.

has the highest Cr content. The other four alloys showed similar weight gains. Higher Cr content had been shown in other studies to significantly reduce the oxidation of alloys in high CO₂-rich atmospheres, but the relatively high concentrations of chromium in all of the alloys in these tests were at or above suggested levels presented in those studies for good oxidation resistance [4].

Figure 3 shows a cross section of a 282 coupon and its scale after 1500 hr in the 30-bar test. Initial sample preparation with epoxy mounts polished with grinding wheels yielded poor cross sections at the scale–metal and scale–epoxy interfaces. Therefore, coupons were concentrated beam of argon ions under vacuum, which removes the surface evenly. This process “polishes” the surface without the need for epoxy and grinding wheels, thereby eliminating smearing of the surface to be examined, giving a clear SEM image of the coupon edge.

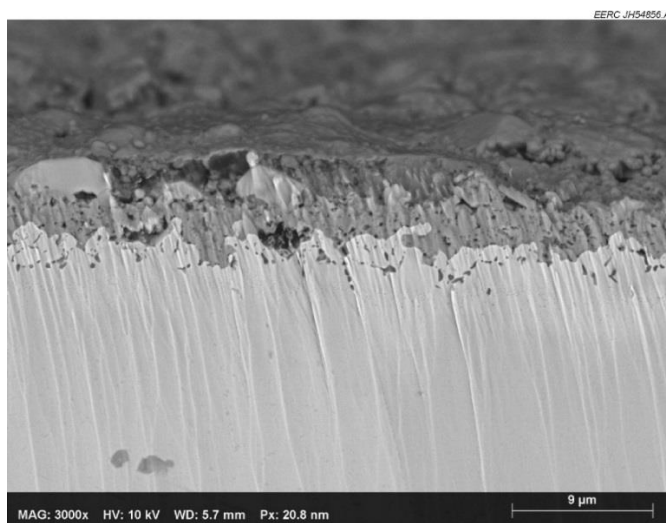


Figure 3. Cross section at the surface of Alloy 282 after 1500 hr at 750°C and 30 bar.

The figure shows that the scale is relatively uniform across the surface and typically 3–5 μm thick. Energy-dispersive spectroscopy (EDS) indicates that the scale is chromium and oxygen (Cr–O)-rich. In the metal below the scale, thin 1–3- μm -long channels were created through internal oxidation that contain high levels of aluminum and oxygen (Al–O) and sometimes carbon. No distinct sulfur-rich phases were seen in the scales or metals for any of the alloys created during the 30-bar exposure, and sulfur (S) concentrations measured were always below 1%, except in some cases where the alloys had high molybdenum contents in which high S levels showed up in spots. However, we believe that in those cases there was interference between the Mo x-ray signal and the S x-ray signal and that, in fact, the EDS detector was incorrectly attributing the signal to S when it should have been attributed to Mo. Also, no C enrichment was seen in the alloys except in some cases in submicron particles along grain boundaries, but the concentrations of these particles did not increase near the surface of the alloys.

High-Pressure 269-bar Test

Figure 4 shows the average weight gain per unit area of the three coupons for each alloy at 750 hr and two coupons each for 1500 hr.

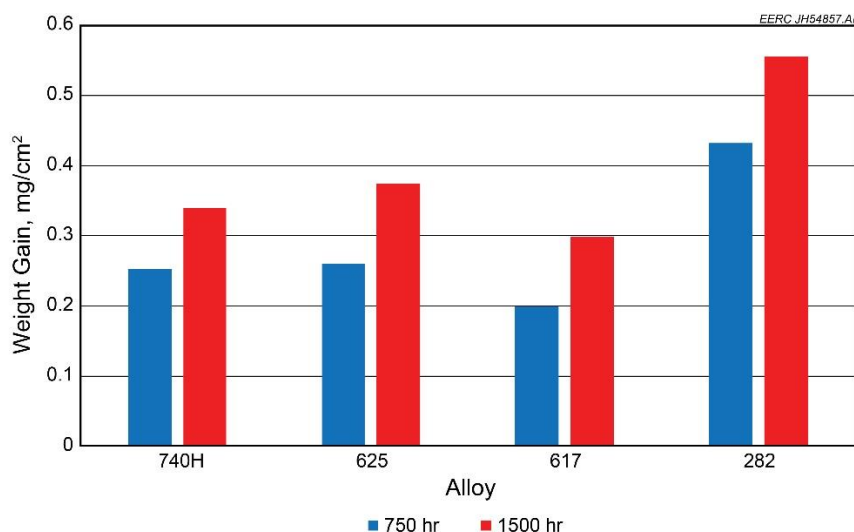


Figure 4. Average weight gain per unit area after 750 and 1500 hr in conditions reflecting the interior of the heat recuperator.

The tested four alloys had relative weight gains similar to those in the 30-bar tests, with 282 gaining the most weight and the other three having similar weight gains. However, these four alloys showed less weight gain under high pressure oxidant conditions than low pressure combustion flue gas conditions. Also, the weight gain in the second 750 hr was much less than in the first 750 hr, indicating passive (parabolic) oxidation rates.

Figure 5 shows a cross section of a 282 coupon and its scale after 1500 hr in the 269-bar test. The chromium oxide scale appears similar in thickness to that created during the 30-bar test, but it is possibly more dense in the 269-bar sample. However, not all scales appeared to be more dense in the 269-bar samples as compared to the 30-bar samples. In general, the differences in the scales are generally small between the 30- and 269-bar samples in terms of scale thickness, internal oxidation to form Al–O-rich channels, or Cr depletion in the near surface of the alloys.

As was also true for the 30-bar samples, no distinct S-rich phases were seen in the scales or metals for any of the alloys created during the 269-bar exposure, and S contents in the scale were below 1%. Also, no C enrichment was seen in the alloys except in some cases in submicron particles along grain boundaries, but the concentrations of these particles did not increase near the surface of the alloys.

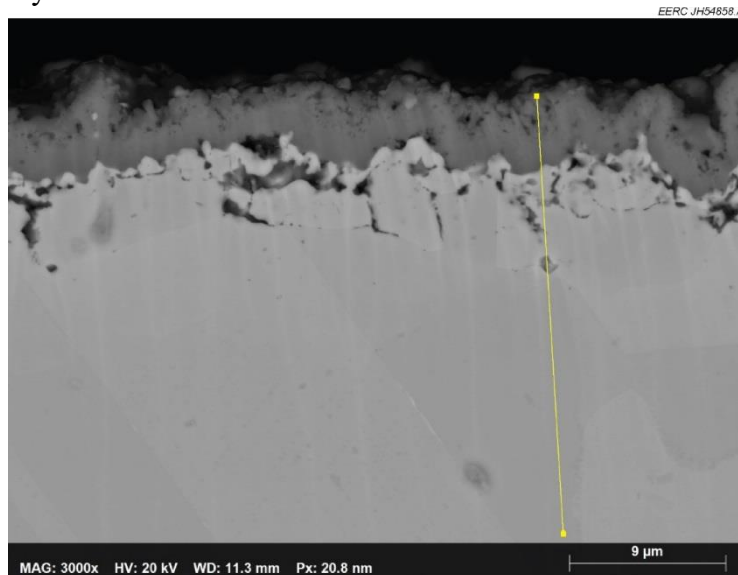


Figure 5. Cross section at the surface of Alloy 282 after 1500 hr at 750°C and 30 bar.

Conclusions

Weight gains for high Ni alloys were similar to those measured in other high CO₂ oxidation tests such as those reported by Pint et al. [4]. Haynes 282 showed somewhat higher oxidation rates than the other Ni-rich chromia-scale forming alloys. No S-rich phases were detected in the Cr–O scales or in the alloys. Slightly higher weight gains occurred in conditions reflecting the exterior of the heat recuperator than those reflecting the interior. No C enrichment was detected in the alloys except in submicron particles along grain boundaries, but these phases did not increase in concentration near the surface of the alloy.

The corrosion mechanisms and rates do not present any barriers to uses of any of the high nickel alloys in a lignite-fired Allam Cycle. However, long-term creep testing under these conditions also needs to be performed in order to determine the best alloys for demonstration testing. Pint et al. found very little effect from pressure, and the results of these tests tend to agree even though a higher concentration of O₂ was used at a higher pressure [4].

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References

1. Allam, R.J., Fetvedt, J.E., Forrest, B.A., and Freed, D.A. “The Oxy-Fuel, Supercritical CO₂

Allam Cycle: New Cycle Developments to Produce Even Lower-Cost Electricity from Fossil Fuels Without Atmospheric Emissions,” in *Proceedings of ASME Turbo Expo 2014: Turbine Technical Conference and Exposition*, Dusseldorf, Germany, June 16–20, 2014.

2. Isles, J. “Gearing Up for a New Supercritical CO₂ Power Cycle System,” *Gas Turbine World*, pp. 14–18, December 2014.

3. Allam, R.J., Palmer, M. and Brown, G.W. “System and Method for High Efficiency Power Generation Using a Carbon Dioxide Circulating Working Fluid,” United States of America Patent US 8,596,075 B2, 3 December 2013.

4. <http://sco2symposium.com/www2/sco2/papers2016/Materials/056paper.pdf> (accessed May 2018).

5. <http://sco2symposium.com/www2/sco2/papers2016/Materials/043paper.pdf> (accessed May 2018).

6. <http://sco2symposium.com/www2/sco2/papers2016/Materials/027paper.pdf> (accessed May 2018).

7. <http://sco2symposium.com/www2/sco2/papers2016/Materials/114paper.pdf> (accessed May 2018).