THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
345 E. 47 St., New York, N.Y. 10017

86-GT-83

Acid Corrosion in a CAES Recuperator

HOLGER LUKAS
Encotech, Inc.

BHUPEN MEHTA
Electric Power Research Institute

ABSTRACT

Cold end corrosion and deposit formation due to sulfuric acid is a phenomenon not uncommon in boilers and waste heat boilers. Normally, the operating conditions can be changed to reduce or eliminate the corrosion and deposition problem. In a Compressed Air Energy Storage (CAES) recuperator, changing the operating conditions is not a practical solution. This paper presents the results of three different test periods using various materials at different operating temperatures.

INTRODUCTION

It is economical to operate large electric generating systems as near constant power output as possible. Matching this objective to a fluctuating demand leads to the need for effective storage systems, and a variety of schemes have been proposed. One scheme is to store compressed air during off-peak hours and then use it in a gas turbine to satisfy peak demand power requirements.

During off-peak hours, a generator/motor drives the compressor train charging up the underground cavern. During the on-peak hours, compressed air is bled out of the cavern, fuel is added and the generator/motor is driven as a generator supplying power to the electrical grid.

The plant layout and cycle design parameters are described in References (1 to 7).

The Optimization of this Compressed Air Energy Storage (CAES) cycle requires a recuperator to recover exhaust waste heat and use it to preheat the incoming combustion air. Using a recuperator improves the heat rate of the plant by approximately 25 percent. A recuperator with an 82 percent effectiveness used 2000 hours per year in the generating mode will give a payback of less than two years.

Recuperators, or regenerators as they are also called, have been used with gas turbines in peaking service for many years. The duty cycle of those recuperators though is not as severe as that expected of the one for the CAES plant. The CAES recuperator is subjected to rapid temperature cycling, high internal pressures, and metal temperatures below the sulfuric acid dewpoint.

The first operational CAES plant at Huntorf in the Federal Republic of Germany was not provided with a recuperator to recover the exhaust waste heat, but the three CAES plant studies included a recuperator in their design (3) (4) (5). The lack of operational experience with recuperators in a CAES plant coupled with the high economic benefit of its use prompted the Electric Power Research Institute (EPRI) to commission a study to assist in determining the requirements necessary for satisfactory operation in the CAES environment.

The study was divided into three areas:

- o Review of recuperator experience in gas turbines
- o Thermal stress analysis using finite element modeling.
- o Low temperature corrosion problems.

The results of the first two areas are presented in Reference (7).

Presented at the International Gas Turbine Conference and Exhibit
Dusseldorf, West Germany—June 8-12, 1986

The low temperature corrosion problems is being investigated through rig testing. Three separate tests have been performed to date. The results of the first two tests have been previously published (8). This paper will concentrate on test 3.

TEST DESCRIPTION

In the test facility design, the exhaust gas conditions and metal temperatures of the low temperature section of a proposed recuperator were modeled. Gas turbines normally operate with approximately 400% of theoretical air providing an exhaust gas rich in oxygen. The impact of the high oxygen content on the corrosion rate was one of the primary questions in the testing.

The exhaust gases entering the test section therefore have to be diluted with fresh air to obtain the correct oxygen content. Water was used to control the metal temperature of the tubing used as test samples. Figure 1 is the schematic of the test facility. The test section allowed the installation of fourteen tubes for testing. Metal temperatures were monitored directly by thermocouples welded to the tubes and indirectly by the cooling water. Heat flux probes and thermocouples were installed on the inside of the tubes to determine the effect of the corrosion deposit on the heat transfer rate.

The tubes were 1 inch O.D. (25.4 mm) tubes with a 0.065 inch (1.65 mm) wall thickness spaced on 1.25 inch (31.75 mm) centers within each row. The rows were spaced 3 inches (76.2 mm) apart and were staggered. Borescope ports were provided to view each row of tubes and to take photographs of the tubes during operation.

No. 2 fuel oil doped to 1.0 to 1.1% sulfur content was used as the test fuel. Gas turbines have a higher SO_2 to SO_3 conversion rate (9) than furnaces and this fuel is therefore equivalent to using fuel with 0.5% sulfur in a gas turbine. The measured acid dewpoint was 240°F (115.6C) to 245°F (18.3C) which is approximately 10 PPM (by volume) of sulfuric acid in the gas stream.

Tests 1 and 2 were steady state tests at temperatures of 190°F (87.8C) and 130°F (54.4C) respectively while Test 3 was a cyclic test at 190°F (87.8C).

The cyclic testing consisted of firing the facility for 8 hours and then force cooling the tubes using the furnace blower. When the metal temperature dropped below 100°F (37.8C) the unit was automatically restarted.

The test rig was operated for a total of 2100 fired hours with a shutdown for inspection at 1049 hours. During the inspection, the tubes were washed with water to remove all deposits.

Table 1 shows the corrosion rates of the three tests.

DEPOSITS

Heavy deposits formed on all of the tubes during each of the tests. The 0.250 inch (6.4 mm) gap between tubes plugged in less than 1000 hours in some cases. The deposits were loose enough that some spalling occurred in operation. The deposits appear hygoscopic and are water soluble therefore rising with water removed most of them.

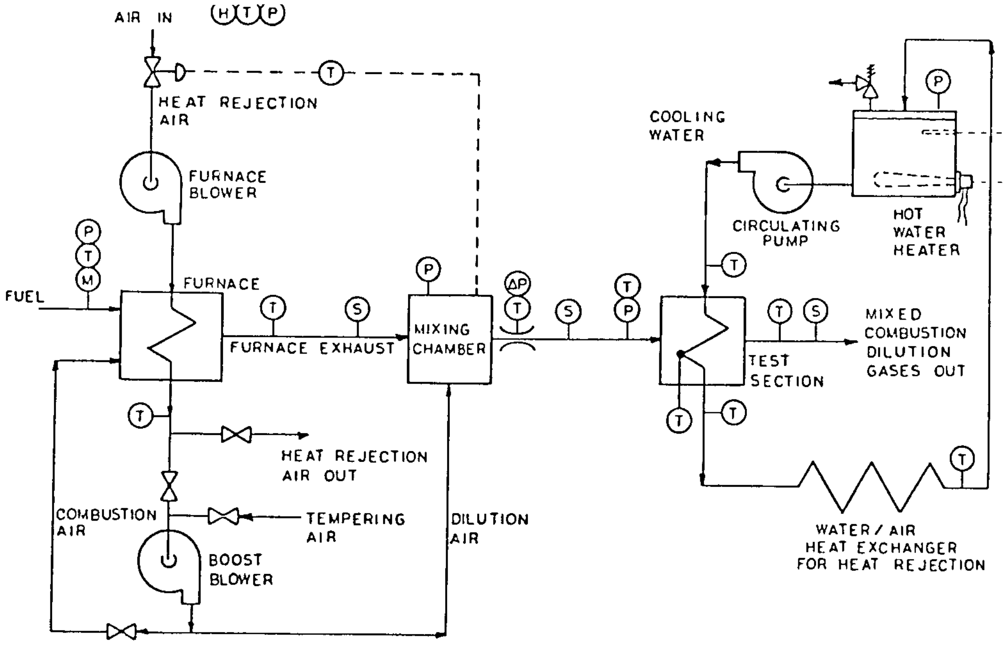

FIGURE 1 TEST FACILITY SCHEMATIC

TABLE 2

CHANGES IN HEAT FLUX

TUBE	PERIOD 1 INITIAL 40 HOURS	PERIOD 1 BEFORE WASH 1049 HOURS	PERIOD 2 AFTER WASH 1060 HOURS	PERIOD 2 AT SHUTDOWN 2100 HOURS	HEAT FLUX RATIO PERIOD 1	HEAT FLUX RATIO PERIOD 2	HEAT FLUX RESTORED RATIO	OVERALL HEAT FLUX RATIO
625	2632.4	1149.4	1303.2	1068.5	0.437	0.820	0.495	0.406
179	321.3	756.3	548.7	680.1	2.354	1.239	1.708	2.117
304	1196.9	961.1	1235.6	982.3	0.803	0.795	1.032	0.821
825	1604.5	1178.3	1870.3	1234.4	0.734	0.660	1.166	0.769
C20	1586.9	1136.9	1644.2	876.4	0.716	0.533	1.036	0.552
825	755.1	396.2	990.7	385.6	0.525	0.389	1.312	0.511
316	1525.4	871.5	1544.7	881.6	0.571	0.571	1.013	0.578
C20	2079.4	1410.9	2417.0	1637.0	0.679	0.677	1.162	0.787
MONIT	1590.9	1569.3	2073.9	1977.9	0.986	0.954	1.304	1.243
825	1131.8	1234.3	1257.2	1037.6	1.091	0.825	1.111	0.917
625	2101.0	1533.5	2210.4	1806.5	0.730	0.817	1.052	0.860
316	1377.4	844.0	1541.0	1053.0	0.613	0.683	1.119	0.764
179	422.5	322.0	511.0	395.1	0.762	0.773	1.209	0.935
825	1157.9	762.7	980.7	611.3	0.659	0.623	0.847	0.528

TABLE 1

COMPARISON OF THREE TESTS

MATERIAL	TEST 1 RATE MDY	TEST 1 RATE (MM/YR)	TEST 2 RATE MPY	TEST 2 RATE (MM/YR)	TEST 3 RATE MPY	TEST 3 RATE (MM/YR)
A179	26	(0.66)	107	(2.71)	29	(0.71)
A179*			79	(1.99)		
304SS	53	(1.34)	31	(0.78)	44	(1.11)
316SS	67	(1.70)	NT		36	(0.90)
410SS	55	(1.40)	NT		NT	
CORTEN	5	(0.13)	27	(0.69)	NT	
20CB3	29	(0.74)	2	(0.05)	8	(0.21)
825	24	(0.61)	5	(0.14)	8	(0.21)
625	38	(0.97)	16	(0.41)	5	(0.13)
4130	NT		47	(1.19)	NT	
825SMLS	NT		3	(0.08)	8	(0.21)

* SPECIMEN PREVIOUSLY EXPOSED TO 920 HOURS AT 190°F - VALUE IS TEST 2 ONLY CORROSION

NT - NOT TESTED

The literature, as well as the experience recorded in reference (7), indicates that a high level of corrosion occurs during shutdown. One possible explanation for this phenomena is that the deposits are acid soaked and that during shutdown, ambient moisture dilutes the acid making it more aggressive. Removal of all of the deposits therefore is important.

The deposits caused a dramatic loss in heat flux. Although the data is not consistent, it appears that in approximately 400 hours of operation, the heat flux has been halved. Some of the inconsistencies in heat flux can be attributed to the weight loss and deposit spalling. Table 2 shows the heat flux at the start of the test; just before the wash; just after the wash; and at the end of the test for each of the tubes.

Figure 2 shows the variations in heat flux for Carpenter 20Cb3 tubes. Each of the data points is the average of approximately 450 readings taken over each fired cycle. Figure 3 is for 316 stainless steel tubes and is representative of a tube with relatively high material loss.

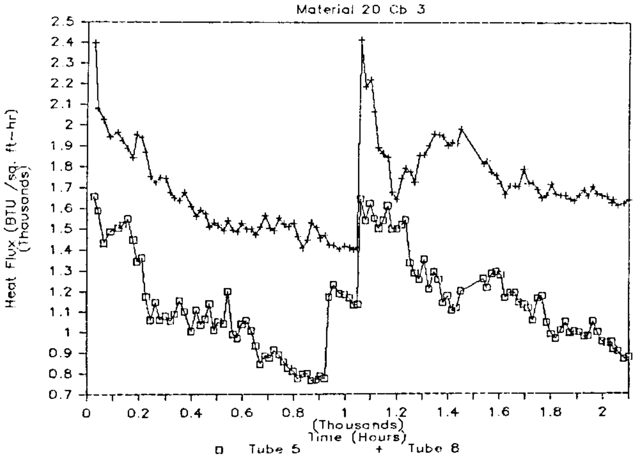

Figure 2 Heat Flux vs. Time

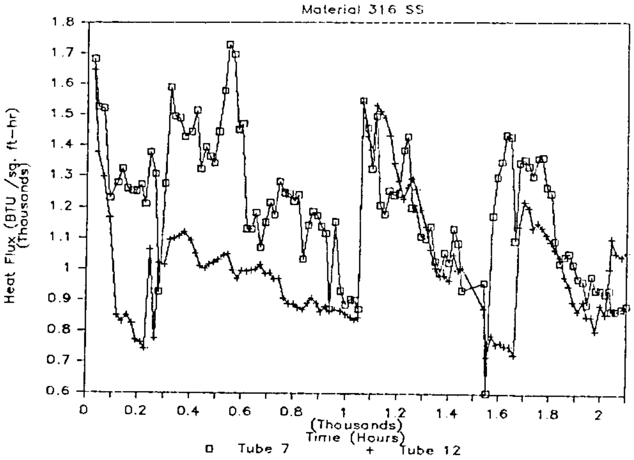

Figure 3 Heat flux vs. Time

DISCUSSION

The recuperator in the CAES plant will see material temperatures ranging from well below the water vapor dewpoint to well above the sulfuric acid dewpoint. Materials which are attacked at one concentration are not attached at another. For example carbon steel has a minimum corrosion rate point at around 70% by weight sulfuric acid while at that concentration 304 stainless steel is near its highest (10) (11) (12). As the concentration of acid is reduced the corrosion rate increases for carbon steel and decreases for stainless steel. The high nickel alloys follow corrosion curves similar to the stainless steels (13) (14) (15).

The design life goal used for these tests is a loss of material less than 15 mils per year (mpy) (0.37 mm/yr). Referring to Table 1 it can be seen that the only materials which met that criteria are the high nickel content Inconel 625, Incoloy 825, and Carpenter 20Cb3 tubes if the results of the continuous firing of test 1 are ignored. The operating cycle of the CAES plant is such that continuous operation is not possible.

The deposit formation is another problem which needs to be addressed. The results of Test 3 should give an indication of the reduction in heat transfer due to the deposits.

ECONOMICS

There are several approaches that can be used to extend the life of the tubing in the CAES environment. Sulfur restrictions can be incorporated. These restrictions will reduce the quantity of acid produced and therefore limit the areas affected. Another approach is to increase the wall thickness and therefore increase the allowable corrosion. Increasing the wall thickness from the base line of 0.065 inches (1.65 mm) to 0.072 inches (1.83 mm) increases the allowable corrosion rate to 22 mpy (0.56 mm/year) while a wall thickness of 0.109 inches (2.77 mm) increases it to 69 mpy (1.75 mm/year). Both of these approaches need to be evaluated on a site specific cost basis.

Material cost, of course, is also a major economic design consideration. Corrosion rate, allowable material loss, and material cost must all be considered. Table 3 shows the relative material costs and Table 4 the relative life cost using the material loss in Test 3 and making allowances for the allowable differences in material loss.

The need to replace tubes or tube modules must also be considered. The relative life cost of Carpenter 20Cb3 and A179 carbon steel is not to different, but the use of carbon steel allows only about 50% of the corrosion and would require more frequent replacement.

TABLE 3

RELATIVE MATERIAL COSTS

MATERIAL	COST
CARBON STEEL - A179	1.00
CARBON STEEL - 4130	1.16
CORTEN	1.79
STAINLESS STEEL - 304	2.52
STAINLESS STEEL - 316	3.10
MONIT	4.53
CARPENTER 20CB3	7.56
INCOLOY 825	7.94
INCONEL 625	13.71
HASTELLOY C-22	14.51
HASTELLOY C-276	15.24

TABLE 4

RELATIVE LIFE COST - TEST 3

CONSIDERING CORROSION ALLOWANCE

MATERIAL	ALLOWABLE COROSION	RELATIVE COST	RELATIVE HOURS	RELATIVE LIFE COST
INCOLOY 825	.043	7.94	12.81	0.62
CARPENTER 20CB3	.037	7.56	8.94	0.85
INCONEL 625	.041	13.71	15.85	0.86
CARBON STEEL A-179	.015	1.00	1.00	1.00
STAINLESS STEEL 316	.028	3.10	1.50	2.07
STAINLESS STEEL 304	.027	2.52	1.19	2.12

$$\text{RELATIVE LIFE COST} = \frac{\text{RELATIVE COST}}{\text{RELATIVE HOURS}}$$

ADDITIONAL TESTING

The high rate of deposit formation requires that the deposits be removed on a periodic basis. There are indications that the deposits act as a corrosion barrier and that removal accelerates the corrosion. Testing is continuing using the cycle parameters of Test 3 with the addition of weekly water washing. Coated and finned tubes are also included in this new text. A continuous corrosion rate monitoring probe will also be used.

CONCLUSION

The metal temperature distribution of a CAES recuperator is such that it will be difficult to find one material which will exhibit a low corrosion rate throughout the low temperature section (80 to 220^{o}F) (26.7 to 104.4C). Compromises may have to be made between fuel sulfur content, material selection, and life.

High nickel alloys such as Carpenter 20CB-3, Incoloy 825, and Inconel 625 exhibit fair resistance to corrosion but cost trade-offs will have to be made.

ACKNOWLEDGEMENT

This study was performed under the auspices of the Electric Power Research Institute (EPRI) under the direction of Dr. Robert Schainker and Mr. Bhupen Mehta with valuable input by Dr. Barry Syrett. To those gentlemen and others to numerous to mention I extend my sincere thanks.

REFERENCES

1) "220 MW Sixty-Cycle Asset Plant", BBC Brown Boveri Publication No. CH-T 113 390 E.

2) Schainker, R., et al, "Turbomachinery Engineering and Optimization for 25 MW and 50 MW COmpressed Air Energy Storage Systems", ASME Paper 84-GT-17.

3) "Preliminary Design Study of Underground Pumped Hydro & Compressed Air Energy Storage in Hardrock", U.S. Department of Energy and Electric Power Research Institute Report EM-1589, April 1981.

4) "Preliminary Design Study of Compressed Air Energy Storage in a Salt Dome", U.S. Department of Energy and Electric Power Research Institute Report EM-2210, January 1982.

5) "Compressed Air Energy Storage: Preliminary Design and Site Development Program in an Aquifer", U.S. Department of Energy and Electric Power Research Institute Report EM-2351, 1982.

6) Lukas, H., Montgomery, M., and Schainker, R., "Recuperative Heat Exchangers in Compressed Air Energy Storage", AIAA/EPRI International Conference on Underground Pumped Hydro and Compressed Air Energy Storage, AIAA 82-1650-CP.

7) "Recuperative Heat Exchangers in Compressed Air Energy Storage Plants", Electric Power Research Institute Report EM-3843, January 1985.

8) Lukas, H., "Corrosion of Materials in a Simulated CAES Exhaust Gas Environment", ASME Paper 85-GT-143.

9) Hunter, S.C., "Formation of SO_3 in Gas Turbines", ASME Paper No. 81-GT-42.

10) Fontana, M.G., Greene, N.D., Corrosion Engineering 2nd Edition, McGraw Hill Book Company, NY, 1978.

11) Dean, S.W. Jr., and Grab, G.D., "Corrosion of Carbon Steel in Concentrated Sulfuric Acid", National Association of Corrosion Engineers, Corrosion 84, Paper Number 147.

12) "The Corrosion Resistance of Nickel Containing Alloys in Sulfuric Acid and Related Compounds", Corrosion Engineering Bulletin CEB-1, The International Nickel Company, Inc., 1983.

13) "Carpenter 20Cb-3 Stainless Steel", Carpenter Technology Corporation, 1980.

14) "Inconel Alloy 625", Huntington Alloys, Inc., 1966.

15) "Incoloy Alloy 825", Huntington Alloys, Inc., 1960.