UPDATE ON THE COAL ASH CORROSION RESISTANT MATERIALS TESTING
PROGRAM EVALUATION OF THE FIRST TWO SECTIONS AND STATUS OF THE THIRD

Dennis K. McDonald
Babcock & Wilcox, 20 S. Van Buren Ave., P.O. Box 351, Barberton, Ohio 44203-0351
Email: dkmcdonald@babcock.com; Telephone (330) 860-6175
Edward S. Robitz
Babcock & Wilcox Research Center, 1562 Beeson St., Alliance, Ohio 44601
Email: esrobitz@babcock.com; Telephone (330) 860-6636

ABSTRACT

The "Coal Ash Corrosion Resistant Materials Testing Program" is being conducted by The Babcock & Wilcox Company (B&W), the U.S. Department of Energy (DOE) and the Ohio Coal Development Office (OCDO) at Reliant Energy's Niles plant in Niles, Ohio to provide full-scale, in-situ testing of recently developed boiler superheater materials. Fireside corrosion is a key issue for improving efficiency of new coal fired power plants and improving service life in existing plants.

In November 1998, B&W began development of a system to permit testing of advanced tube materials at metal temperatures typical of advanced supercritical steam temperatures (1100°F and higher) in a boiler exhibiting coal ash corrosive conditions. Several materials producers including Oak Ridge National Laboratory (ORNL) contributed advanced materials to the project.

In the spring of 1999 a system consisting of three identical sections, each containing multiple segments of twelve different materials, was installed. The sections are cooled by reheat steam, and are located just above the furnace entrance in Niles' Unit #1, a 110 MWe unit firing high sulfur Ohio coal. In November 2001, the first section was removed for thorough metallurgical evaluation after 29 months of operation, 15.5 at full temperature. The second section was removed in August of 2003 after 43 months of operation, 28.5 at full temperature. The final section was removed in April of 2005 and is in the process of being evaluated. This paper briefly describes the program; its importance, the design, fabrication, installation and operation of the test system, materials utilized, experience to date, presents the results of the evaluations of the first and second sections, and a status of the third and final section.

INTRODUCTION

The benefits of cycle efficiency in terms of fuel cost savings and emissions reductions are well documented and, as more recent programs are demonstrating, more than offset the added equipment costs. It has also been widely recognized, that the most effective way to improve plant efficiency is by raising steam temperature. Work by several organizations, including DOE, have demonstrated that raising steam pressure is not nearly as beneficial to efficiency as raising temperature and its impact on cost is much greater since all pressure parts must be thicker.

The greatest obstacle to raising steam temperature is the availability of materials suitable for service in superheaters and reheaters that are not only be capable of providing sufficient strength at surface metal temperatures exceeding the delivered steam temperature by 100ºF or more, but also provide corrosion resistance against the sulfur compounds formed by many U.S. coals. This corrosion issue has not been addressed by European or Asian development programs since most of their coals are very low in sulfur.

To begin to address corrosion at higher steam temperatures, Babcock & Wilcox (B&W) began conducting the "Coal Ash Corrosion Resistant Materials Testing Program" in 1999 at Reliant Energy's Niles plant in Niles, Ohio. The total estimated cost of $1,864,603 is co-funded by DOE who is contributing 37.5%. OCDO is providing 33.3%. B&W is providing 17% with the remaining 12% being in-kind contributions by Reliant Energy and suppliers of tubing for the tests. As a result of this program B&W is now also participating in a much larger follow-on program called "Boiler Materials for Ultra-supercritical Power Plants" that has been initiated by a government-industry based consortium.

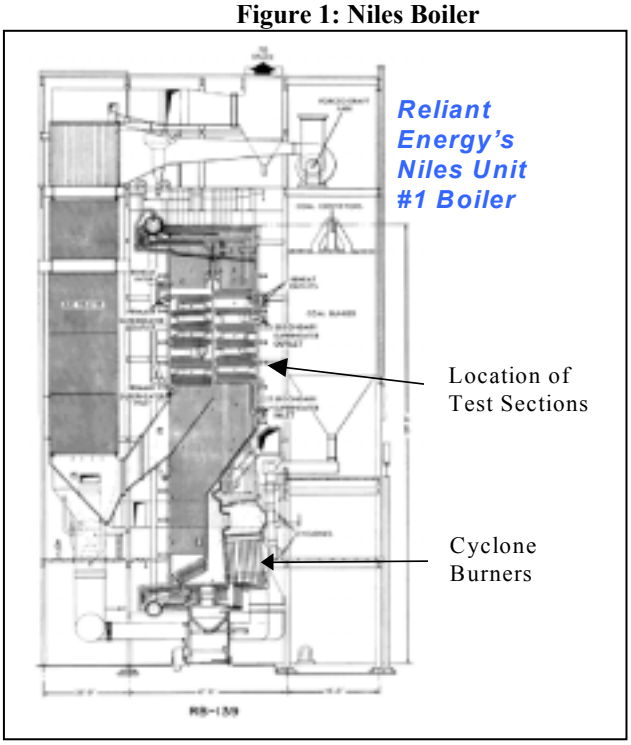
THE PROGRAM

The program was developed to 1) evaluate the corrosion performance of newer materials for coal-fired boilers at surface temperatures expected with 1100ºF (593ºC) steam temperature, 2) select materials resistant to fireside corrosion, and 3) generate long-term corrosion field data.

Section design began in November 1998. The sections are cooled by 600ºF, 315 psi reheat steam but are located within the superheater bank of the B&W 110 MWe cyclone-fired Niles boiler, a 1950s vintage subcritical unit burning a 3-3.5% sulfur Ohio coal. Figure 1 shows the location of the test sections and Figure 2 shows the system arrangement.

Three identical four-row sections contain specimens of the twelve alloys tested; most are included three times within the top two rows to expose them to three temperature regimes. The only difference between sections is that the first section was scheduled for removal and evaluation after one year of operation, the second after three years and the third after five years.

Figure 1: Niles Boiler



Surface metal temperatures are continuously calculated by the data acquisition system and correlated to the internal steam temperature, measured by thermocouples at the inlet, intermediate bend and outlet tubes, and controlled by varying the steam flow by inlet valves. Each of the test sections contains ten primary and two secondary advanced material samples. The primary samples are placed in three different locations within the section (see Figure 3 and Table 1). The sections extend through the furnace front wall for the full depth of the furnace up-pass and are supported from the baffle wall at their rear and the furnace front wall at their front. They were fabricated at B&W's research facility in Alliance, Ohio. All but one of the 6 in. long specimens are 2.5 in. diameter by 0.400 wall joined using alloy 625 filler metal in a tungsten-arc orbital welder.

Installation was completed in May 1999, followed by shakedown and controls tuning. During this period the steam temperature was controlled first to 1000ºF and then to 1050ºF before being raised to the current temperature of 1075ºF, which produced surface metal temperatures in the top row that would accelerate corrosion.

The system was plagued from startup with valve controller overheat failures as a result of unexpectedly high ambient temperatures that caused the inlet valve to open, cooling the section to around 800ºF at the outlet. This condition has seldom lasted more than a day or two, thanks to the rapid response of the operators at the Niles plant. To eliminate this

problem, a cooling fan and ductwork were installed to blow cool air across each of the valves. This resulted in significant improvement but occasional problems continued. The electronic controllers were eventually replaced with mechanical devices.

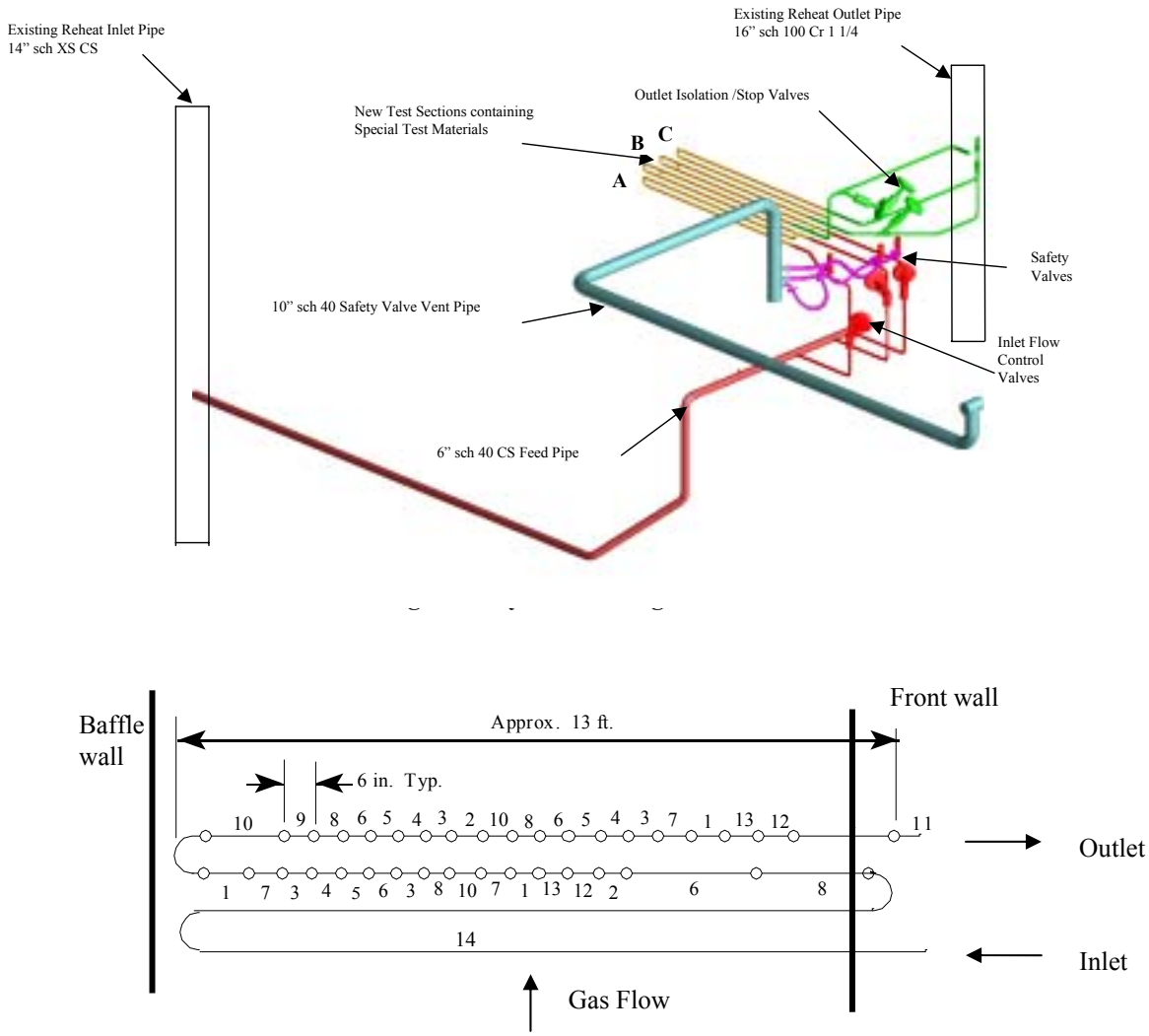


Figure 3: Location of Specimens within the Section

Due to outage scheduling, Section A was removed in November 2001 after 29 months of operation, equivalent to 15.5 months at temperatures conducive to corrosion rather than the intended 12. Varying corrosion was exhibited among the specimens with extreme corrosion experienced in the SAVE25 piece. The SAVE25 specimen actually developed a pinhole leak just prior to removal and in order to ensure operability of the remaining two sections, a six-segment length containing the SAVE 25 specimens was removed from both Sections B and C and replaced by Incoclad tubing "dutchmen."

Between startup and removal, inspections have been made on about 6-month intervals to monitor the extent of corrosion to avoid a failure. Following removal of Section A and repair of Sections B and C, Sections B and C were returned to service. Sections B and C next were examined again in situ, in June 2002, after about seven additional months of service. This inspection also raised concerns, and two additional tube lengths were removed from both sections and replaced by "dutchmen." The sections then continued in service until May 2003, which marked the end of the next planned section removal and assessment period. At that time, for practical reasons, it was decided to remove and evaluate Section C rather than Section B. After replacement of some corroded segments to ensure Section B could operate for another 12 to 18 months, Section B was returned to service in December 2003.

TABLE 1: Advanced Materials			
#	MATERIAL	SUPPLIER	ASME RECOGNIZED
1	Incoclad – Core is Incoloy 800H	INCO	Yes - Code Case 1325
2	Thermie	ORNL	No
3	HR3C – SA213TP310HCbN	Sumitomo	Yes
4	Ta Modified 310	ORNL	No
5	800 Modified	ORNL	No
6	Save25	Sumitomo	No
7	HR120	Haynes	No
8	NF709	Nippon Steel	No
9	Fe3Al-2Cr/304H	ORNL	Yes
10	TP347HFG – SA213TP347HFG	Sumitomo	Yes
11	Transition Piece (not a test sample)	SA312TP304 H	Yes
12	690 clad 800HT weld metal INCO 52	INCO	Yes
13	671 clad 800HT weld metal INCO 72	INCO	Yes
14	SA213TP310H (not a test sample)	NA	Yes

The results of the evaluation of Section A were reported in a paper presented in 2003 (see references) and will not be repeated in detail. However, after presenting the results from Section C, a brief comparison is presented.

SECTION C RESULTS

Total Exposure Time

After operating for 49 months, the total time at temperature Section C was 28.5 months. Figure 4 shows the locations of the segments in Section C that were removed early. These segments were set aside and included in the overall evaluation of Section C performance. The segments removed in June 2002 experienced 21.6 months of exposure while those removed in November 2001 experienced 18.6 months at temperature, differing from the exposure time for Section A due to operational differences.

Surface Metal Temperature

The daily average surface metal temperature for Section C was monitored and controlled in the same manner as was done for Section A. Calculations based on the Section C data showed that, in general, the tube segments in Section C ran approximately 10°F hotter than those at the same positions in Section A.

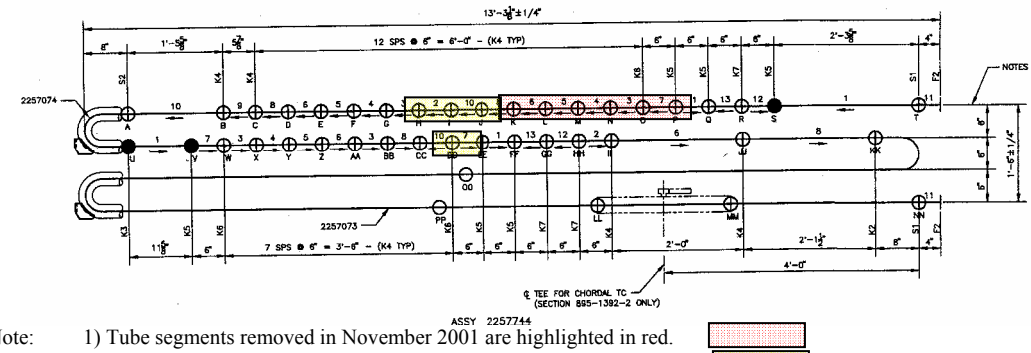
Evaluation

The evaluation of Section C proceeded much as it had for Section A with only a few exceptions. The most significant of these stemmed from the fact that examination of the INCO 72 weld overlay revealed that it was experiencing degradation due to a cracking mechanism that appeared to be unrelated to coal ash corrosion wastage. Additional work was performed to further characterize and understand this phenomenon.

Summary of Results

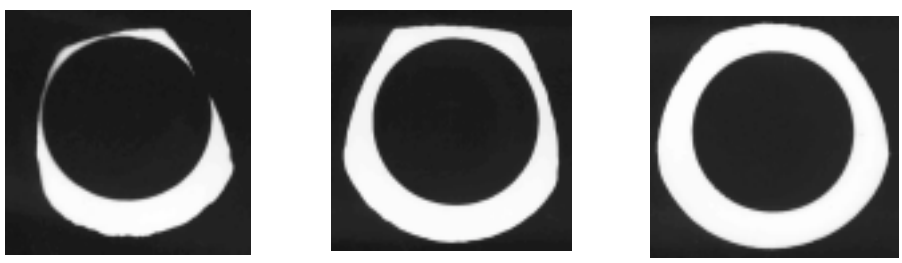
Analysis of deposits from the surface of Section C revealed the presence of constituents of the alkali-iron-trisulfates. This and the loss of wall thickness confirm that the test environment challenged the ability of the candidate materials to resist wastage over the critical temperature range of 1000°F to 1300°F. Dimension rings provided the primary means of measuring the resistance of the candidate materials under these conditions.

Figure 5 shows the appearance of three Save 25 dimension rings demonstrating that, for Save 25, the wastage rate was a strong function of temperature. For these, and all of the other Section C segments, wall thickness measurements were taken at eight evenly spaced locations around the circumference of the dimension rings. These data were used to calculate wastage rates. Figure 6 shows the maximum wastage rate for the tube segments as a function of position within Section C and Figure 7 plots the maximum wastage rate data as a function of temperature.



Note: 1) Tube segments removed in November 2001 are highlighted in red.
2) Tube segments removed in June 2002 are highlighted in yellow.

Figure 4: Test Section Showing Position of Welds and Location of Dutchmen (i.e. Samples Removed Early)



ASMT*	**1180 F**	**1096 F**	**1058 F**
Wastage	**>259 mils/yr**	**148 mils/yr**	**56 mils/yr**
Rate	**Nov. 2001**	**Jun. 2002**	**May 2003**

Figure 5: Save 25 Dimension Rings from Section C (* ASMT = Average Surface Metal Temperature)

The coal-ash corrosion rate was expected to increase continuously as the exposure temperature increased which was the case for Save25 and 800 Mod but some materials, such as 347 HFG and HR 120, exhibited an apparent decrease in wastage rate at an intermediate temperature, and other materials such as 310 HCbN and 310Ta exhibited an apparent increase in wastage rate at an intermediate temperature. Also, materials such as Incoclad 671, INCO 72 weld overlay and INCO 52 weld overlay appeared to demonstrate a decrease in rate as temperature increased.

The data in Figure 7 can be used to rank the relative performance of the candidate materials but for several reasons such as operational variations reasons, caution must be exercised when drawing more detailed conclusions. In spite of the anomalies, Sections C showed the same trends observed for Section A, thus, the performance was consistent from section-to-section.

Mapping of tube samples for all of the other candidate materials suggested that, in general, those samples located close to either wall experienced a lower wastage rate than that of the samples near mid-span which is an explanation for the lower wastage at the intermediate point than expected. Several factors such as differences in gas flow rate and velocity near the walls, differences in particulate density and composition, and variations in gas temperature due to the cooling effect of the furnace walls.

There are additional issues that should be taken into account in assessing the wastage data in Figures 6 and 7. First, some of the candidate materials relied on a surface coating that had been breached at some point during the Section C exposure period so at the point that the coating was breached, the remaining tube life depended on the corrosion

resistance of the underlying substrate. Analysis of Section A showed that the coating on the Fe_3Al-coated specimen was breached rapidly resulting in wastage of the underlying 304H substrate. This was also true for Section C, and in fact, no evidence could be found of the original Fe_3Al coating on these segments.

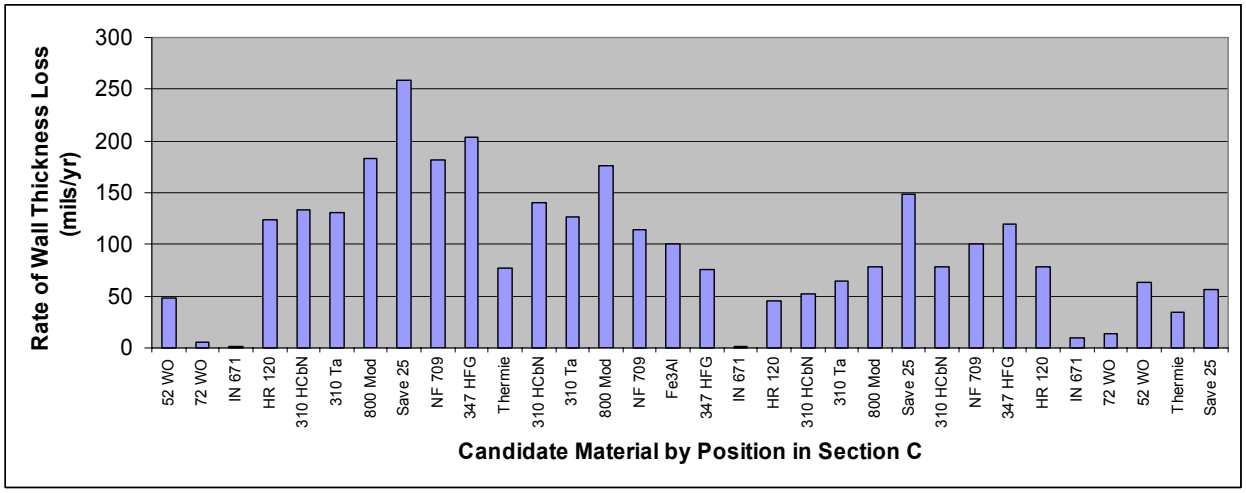


Figure 6: Maximum Wastage Rate as a Function of Position within Section C

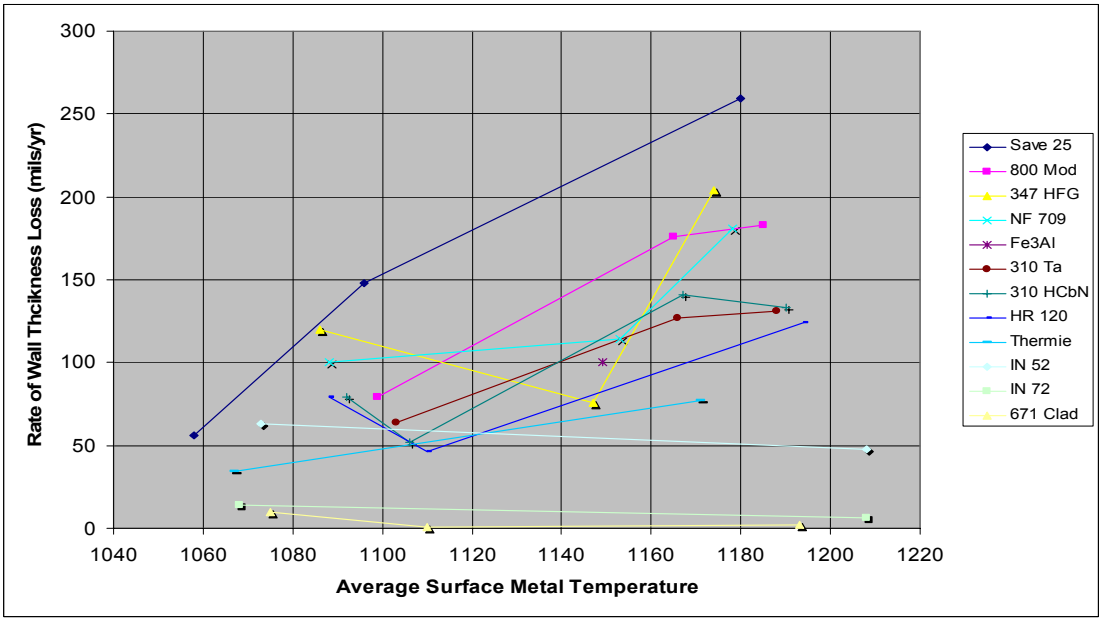


Figure 7: Maximum Wastage Rate as a Function of Temperature for Section C

Although the INCO 52 weld overlay segments appear to have performed well compared with many of the other materials, by the time Section C was removed, the original 80 mil protective cladding was completely breached leaving the 800H substrate to provide corrosion resistance. Note from Figure 6 or 7 that 800H has demonstrated one of the higher wastage rates.

Finally, while the INCO 72 weld overlay demonstrated excellent corrosion resistance, it exhibited cracking. Figure 8 shows an SEM image of an underlying crack intersecting the tube surface. Figure 9 shows evidence of cracking at other locations in this same segment. More detailed evaluation of the other INCO 72 weld overlay segments in Section C, Section A, and in archive material revealed that these grain boundary cracks existed for all of the samples evaluated. Though the implications are not clear, the fact that Incoclad 671, a very similar composition, appears to be

performing well without cracking suggesting that this may be a process related problem rather than a material chemistry issue. Additional work would be required to resolve this.

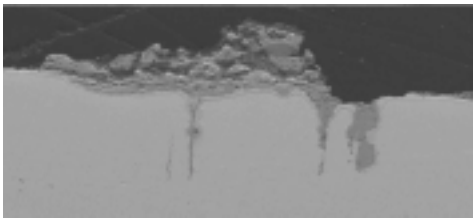


Figure 8: Weld Cracks Intersecting External Corrosion for INCO 72 Weld Overlay Test Segment

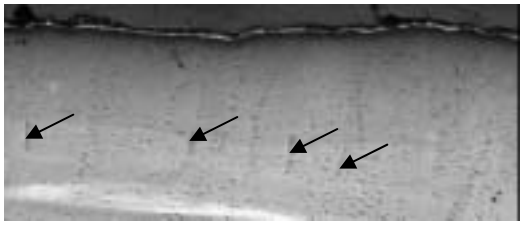


Figure 9: Internal Cracking in INCO 72 Weld Overlay Test Segment from Section C

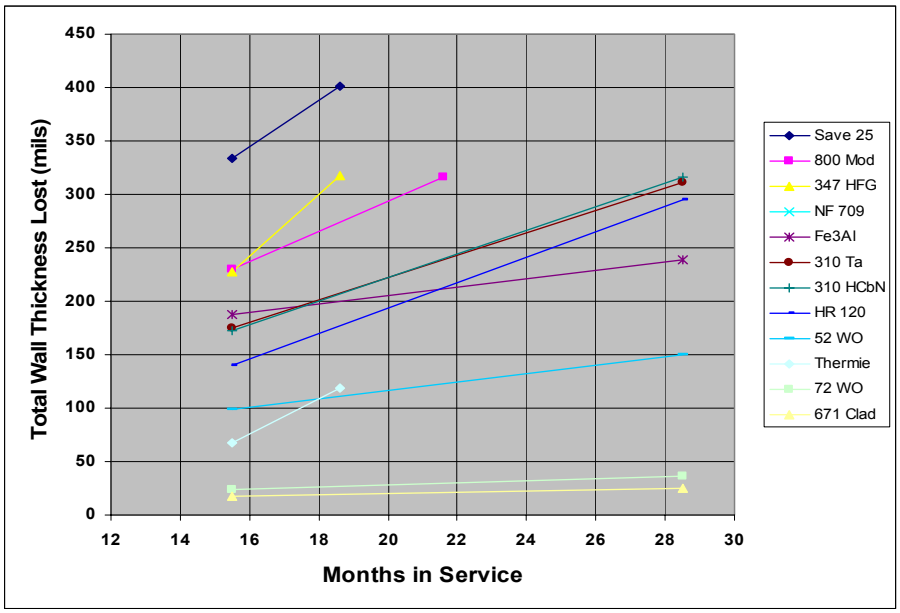


Figure 10: Wastage as a Function of Time for the Candidate Materials

Tube-to-Tube Weld Cross Sections. Due to concern that the welding heat input might have degraded the properties of the adjacent tube or cladding material, tube-to-tube weld cross sections were prepared. For ten of the twelve candidate materials, the Inconel 625 weld metal was more resistant to corrosion than the tube metal and the weld heat affected zone corroded less rapidly than candidate material. When the more corrosion resistant materials were considered, it was found that at some temperatures the Inconel 625 weld metal fared well compared to the base metal while at others the weld metal began corroding to the extent that the adjacent tube metal was affected.

Wastage as a Function of Time. The reason for evaluating multiple test sections was to characterize wastage as a function of time for each of the candidate materials. Figure 10 plots worst case wastage for the materials from Section A and Section C. The straight line fit to the data is not intended to suggest that the corrosion rate was linear for these

materials. In comparing the rates for Section A and Section C, it can be said that the Section C corrosion rates typically were lower for the tube segments that showed better corrosion resistance.

STATUS OF THIRD SECTION

From its return to service in December 2003, Section B, in the C location, has operated at temperature nearly continuously and without incident. On April 26, 2005, during a planned five-week outage, Section B was removed from the unit and transported to B&W's Research Center where it is undergoing evaluation. Results are expected in mid to late summer. Visual inspection following removal did not show any unexpected corrosion.

REFERENCES

"Coal Ash Corrosion Resistant Materials Testing Program - Evaluation of the First Section Removed in November 2001" by Dennis K. McDonald, The Babcock & Wilcox Company, presented at the 28th International Technical Conference on Coal Utilization & Fuel Systems", March 10-13 2003

"Topical Report: Removal of Section A" by Edward S. Robitz Jr., The Babcock & Wilcox Company, submitted to DOE (DE-FC26-99FT40525) and OCDO (CDO/D-97-02) October 31, 2001.

"Update on Coal Ash Corrosion Resistant Materials Testing Program" by Dennis K. McDonald, The Babcock & Wilcox Company, presented at the 16th Annual Conference on Fossil Energy Materials, Baltimore, Maryland, April 2002

"Status of Coal Ash Corrosion Resistant Materials Test Program" by Dennis K. McDonald and David K. Meisenhelter, The Babcock & Wilcox Company, and Vinod K. Sikka, Oak Ridge National Laboratory, presented at the 1999 Pittsburgh Coal Conference.

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