Lower furnace corrosion in kraft recovery boilers

Part 2: a plan for future research

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This detailed review identifies techniques that can best be applied to the study of lower furnace fireside corrosion in kraft recovery boilers.

In Part 1, the fireside environment in kraft recovery boilers was reviewed with respect to its effect on corrosion of lower furnace water-wall tubes (*1*). Laboratory research to date was also summarized, with a view towards identifying gaps in current knowledge. Although progress has been made towards understanding the nature of fireside corrosion in kraft recovery boilers, much remains to be learned. Not enough is known, for example, to predict the corrosion consequences of evolutionary changes in boiler operation like high-solids firing, new methods of sulfidity makeup, and the return of corrosive effluent streams to the boiler. Moreover, there still does not exist a simple, cost-effective means of evaluating new corrosion resistant materials and coatings before they are used in a boiler.

Experience in other industries with coal-fired boilers, oil refineries, and coal gasifiers has shown that laboratory-based research can identify durable construction materials with a high degree of confidence (*2, 3*). Appropriate operating practices for preventing corrosion and new understanding of high-temperature corrosion problems also have come from laboratory-based research. In our project, test methods for high-temperature corrosion research were evaluated for their ability to assess materials of construction in kraft recovery furnaces and ranked according to test duration, turnaround time, safety, cost, and practicality. Results were used to evaluate the current state of knowledge of recovery boiler fireside corrosion and to make suggestions for future research.

We conducted a comprehensive literature survey in the field of high-temperature corrosion research, primarily in industries other than pulp and paper. Interviews with leading experts in the field of high-temperature and molten-salt corrosion were also conducted, and their advice sought as to how our industry could best use its research efforts to solve recovery boiler corrosion problems.

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Test methods for lower furnace corrosion

Test methods to study high-temperature corrosion phenomena range from simple visual observations of the effects of the corrosive environment on the material being investigated to sophisticated studies on *in-situ* corrosion kinetics using laser Raman or UV-visible spectroscopy (*4–6*). Not all techniques are appropriate to investigate recovery boiler fireside corrosion, and only those thought useful for characterizing materials of construction of the lower water wall of recovery boilers were assessed. A complete summary of these techniques can be found elsewhere (*7*); what follows is a synopsis of our findings as they relate to recovery boiler corrosion.

No matter what the technique, certain factors must be carefully considered before a test method is used to evaluate materials for corrosion resistance in a kraft recovery boiler. These include:

- The necessity of establishing a mechanistic connection between laboratory results and corrosion in boilers
- Selection of a test duration suitable for extrapolation of materials performance to typical boiler lifetimes
- Ensuring that the test environment is characteristic of the environment causing corrosion in the boiler
- The ability to predict materials performance as a function of boiler operation.

Making a mechanistic connection

Without a well-established link between laboratory tests and corrosion in the boiler, little confidence can be placed in the extrapolation of test results to long-term performance. It has yet to be conclusively established, for example, whether the primary corrosion mechanism in the lower furnace is due to attack from hot gases, or liquid phases in the smelt deposits adhering to the walls. In addition, since chemical equilibria, gas compositions, and corrosion rates in boilers are strongly temperature dependent, different corrosion mechanisms may well be operative in low-pressure boilers than in high-pressure boilers.

The approach to high-temperature corrosion taken by other industries has been to combine short- and long-term

laboratory investigations with detailed characterization of deposits, scales, corrosion products, and metal attack from field exposure (*3, 8*).

Such an approach has never been part of investigations of high-temperature corrosion in kraft recovery boilers. Detailed, microscopic analyses of corrosion products, scales, and other deposits from field equipment and comparison to similar features in laboratory-tested specimens is the only means by which this vital mechanistic connection can be established.

Close examination of components removed from boilers can also help identify whether a single corrosion mechanism is operative in recovery boilers, or whether corrosion is being caused by a number of different mechanisms (sulfidation at lower temperatures and liquid fluxing at higher temperatures, for example). Once the predominant mechanism has been established, then experience from industries such as coal and gas, oil, and utility can also be translated with more confidence to recovery boiler operations.

Choice of test duration

Most investigations of fireside recovery boiler corrosion have limited the test duration to less than 200 h, and many tests have been as short as 4–6 h (*9–19*). Such short test durations are unsuitable for predicting long-term (100,000 h or more) boiler performance, and contrast sharply with experiments performed to find suitable materials for use in syngas coolers for the coal gasification industry (*2*) or for utility boilers (*20*), where experiment durations of between 1000 and 4500 h are most common.

Short- to medium-term tests can be used to rank potential materials for resistance to the environment or to establish the initial kinetics of high-temperature corrosion in recovery boilers, but only if a common mechanism can first be demonstrated by means of detailed metallographic analysis. Such mechanistic connections have not been made in recovery boiler tests to date, making materials selection based on short-term test results highly speculative. For example, it was concluded from long-term testing of prospective materials for use in syngas coolers (where the environment closely resembles that found in recovery boilers) that low-chromium steels (17–19% by weight) like American Iron and Steel Institute 304 stainless steel are not suitable for use in high-sulfur-activity gases at temperatures greater than 350°C (660°F), and that plasma spray coatings of the type now being used in recovery boilers are only suitable for use as short-term repair coatings (*21*). These conclusions differ markedly from current state-of-the-art practice in kraft recovery boilers, which is based primarily on short-term laboratory tests and ad-hoc testing in boilers.

Characterization of the corrosive environment

The ideal corrosion test, particularly one used for screening purposes, will incorporate only those elements of the environment critical to service life. There is no need, for example, to incorporate the use of molten salts into a test program if the primary corrosion mechanism in the boiler is gas-phase attack. In addition, the range of composition and concentration of corrosive components in the test program should reflect those found in the boiler. To date, however, the environmental factors causing corrosion in the lower furnace of kraft recovery boilers have not been clearly identified.

The approach taken by most recovery boiler corrosion research has been to use temperature as the accelerant in tests, and to fix gas compositions close to the average bulk values found in the lower furnace (*9–19*). However, even for boilers operating at high pressures and correspondingly high water-wall surface temperatures, it is not clear that the test conditions have been appropriately selected to represent the worst-case conditions in a boiler. A concentration of 0.1% by volume H_2S was chosen for early gas-phase laboratory tests (*11*), and subsequently adopted by later workers (*16, 18*), even though analyses of boiler gases showed average bulk concentrations as high as 0.8% by volume, and maximum bulk lower furnace concentrations of 5.0% by volume (*11*).

The composition of gases exposed to the water-wall surface may also not be those of the bulk gas composition measured in the furnace. In particular, pyrolysis of lignin trapped in the smelt layer covering the water-wall tubes may produce significantly different gas mixtures than found in the bulk composition of the lower furnace (*22*). A much more satisfactory and realistic approach to recovery boiler fireside corrosion testing would be to fix the test temperature at typical tube temperatures for each class of boiler (low and high pressure) and modify corrosive gas compositions until the detailed metallographic appearance of the test sample matches that of samples from the field.

Predicting materials performance as a function of boiler operation

Predicting the influence of changes in boiler operation on corrosion is extremely difficult, primarily because of the need to know how operating changes affect the environment next to the water-wall tubes. In particular, the role on corrosion played by the layer of frozen smelt covering the water-wall tubes is still relatively unknown. The smelt definitely inhibits diffusion of reactive species to the metal surface, but it is also widely accepted that the smelt layer reacts with, and modifies, these species (*13–16*). One means of improving the understanding of this process would be to construct thermodynamic stability diagrams for the phases present in the lower furnace environment. These diagrams provide an excellent starting point for anticipating the consequences of changing the composition of the gas-fired liquor or operating practices in the boiler (*23*). Limited applications have already been made of thermodynamic stability diagrams to operation and corrosion in kraft recovery boilers (*24, 25*).

A technical problem related to understanding how the molten smelt layer affects corrosion is depletion of reactive salts during laboratory tests. Burner rig tests have demonstrated the importance of the contaminant flux rate on corrosion in turbines (*26*), and the same is likely to be true in recovery boilers. Even in short-term tests, it has proven difficult to control the composition of powders and frozen smelt layers applied to specimens (*11, 14, 16*). Depletion of reactive species occurs rapidly at the smelt-metal interface or corrosion does not occur until reactions within the deposit produces species more corrosive than those originally included in the melt. Homogeneity of the frozen smelt or powder is also often difficult to guarantee.

I. Methodology for Investigating boiler tube samples

Step	*Procedure or technique*
Obtain sample	Sample location and corrosion history must be well documented. Scales and deposits on tubes must be preserved in as near their original state as possible. Under ideal circumstances, samples should be removed from the boiler before the boiler is water washed.
Initial observations, topographical examination	Visual examination of sample for general appearance, areas of localized corrosion or corrosion-free areas, relation of scale and deposits to corrosion on sample. Low-power (25-50 times) light microscopy examination of deposits and scales to determine scale adherence, whether the scale is smooth or puckered, etc. SEM examination of surface of deposits and scales as for light microscopy.
Phase identification, chemical analysis	X-ray diffraction of *in-situ* or detached scales and deposits. Chemical analysis of scales and deposits.
Cross-section analysis	Preservation of deposits and scales is essential during cross-sectioning and preparation of polished, etched metallographic specimens. Light microscopy and SEM examination of deposits, scale, and underlying metal to determine porosity and adherence of scale. Identification of distinct phases and layers in the scale is an important part of this examination. Elemental mapping by SEM or electron microprobe analysis to determine distribution of metals, oxides, sulfides, and chlorides throughout the deposit, scale and metal surface.

Suggestions for future research

The following suggestions for advancing the state-of-the-art of recovery boiler corrosion testing are based on responses from the expert consultants, a review of current high-temperature investigation techniques, and the methodology of the experimentation applied in other industries. The order of presentation corresponds to the chronological sequence in which we believe the information should be obtained.

Characterization of fireside corrosion

A thorough investigation of recovery boiler fireside corrosion should be carried out so that a mechanistic connection can be established between laboratory testing and corrosion in the field. A suggested methodology for this investigation is given in **Table I.** At a minimum, such examination should include analyses of scales, deposits, and metal surfaces by means of visual microscopy, scanning electron microscopy, and electron microprobe analyses. General appearance, scale porosity, homogeneity of the scale, and scale adherence should be assessed, along with elemental distributions throughout the deposit, scale, and metal surface. Similar analyses of laboratory samples are also required.

Calculation of thermodynamic stability diagrams

Thermodynamic stability diagrams are used to explain corrosion behavior and help predict alloy compositions resistant to specific corrosive, high-temperature environments. They can show the phases (e.g., corrosion products, scales, and metal composition) that are stable under a given set of environmental conditions (e.g., temperature, oxygen, and sulfur activities), or alternatively, they can be used to explain, or predict, the conditions that would lead to the formation of specific phases. For gas-phase attack in recovery boilers, the most useful would be those expressed in terms of sulfur (including organic sulfur-containing species) and oxygen activities. Some appropriate diagrams would be those for iron, nickel, chromium, and aluminum at temperatures of 300°C (572°F), representing low-pressure recovery boilers, and 370°C (700°F), representing high-pressure recovery boilers. Similar diagrams can also be constructed to explain corrosion caused by the presence of molten phases or liquid fluxing on the tube surface. In these specific circumstances, the stability diagrams could also be expressed in terms of electrochemical potential and the basicity of the melt.

Testing for gas-phase attack

Gas-phase attack is the most likely mechanism of corrosion of water-wall tubes in the lower furnace. Thus, thermogravimetric and cyclic oxidation testing of steel in mixed gases is the most appropriate way to bring the worst-case recovery boiler condition into the laboratory. A suggested methodology for this testing is outlined in **Table II.** Testing should determine wastage rate as a function of time for periods up to and including 4500 h; tests should include isothermal tests, as well as cyclic exposure to alternately high- and ambient-temperature gases.

Exposure of specimens to alternate reducing-oxidizing gas composition and inclusion of water wash cycles in an experimental matrix is also suggested. Tests should focus on at least two temperatures, namely 300°C (570°F) to represent low-pressure boilers, and 370°C (700°F) for high-pressure boilers. Gas compositions should be fixed in terms of total sulfur activity and total oxygen activity, rather than being expressed in terms of the concentrations of the constituent gases. It would be preferable to use gas concentrations somewhat higher than previously adopted as "standard;" a 1% H_2S plus 1% O_2 mixture might represent a good starting point. Once proven, these tests can be further used to establish the influence of operating variables such as sulfidity and chloride levels on water-wall fireside corrosion, and to qualify new materials and repair techniques. As a general principle, such testing must be validated by detailed metallographic comparison with field samples.

Testing for the influence of salts on corrosion

Past experience of high-temperature corrosion testing in the presence of salts has shown that the results are difficult to assess because of uncontrollable depletion or changes in the salt composition over the test period. Consequently, the composition of smelts or deposits are better considered in terms of their influence on the gas composition at the surface of the water-wall tubes, rather than in terms of their overall effect on corrosion. We feel, however, that

such testing is not likely to provide useful or reproducible results.

If laboratory corrosion testing of salts is performed, our judgment is that furnace testing of steel in contact with powdered synthetic smelt is the least unsatisfactory means to evaluate the corrosive effects of smelt components in the laboratory. Powder may be held in a boat with a half-covered coupon, or alternatively, powder-filled ceramic pots could be attached to a steel plate. Ideally, the furnace atmosphere should be controlled to a worst-case standard composition, although it may be necessary to tailor the gas composition to minimize the volatility of components of the synthetic smelt. Variables in such a test program might include smelt composition and depth of the protective smelt layer. Long-term tests could be performed by periodically replenishing the powder, but the required interruptions and handling of the specimen could have random, unquantifiable effects on test results.

Other methods of applying a smelt layer to test specimens have generally proven to be unsatisfactory. Techniques like dipping in a molten smelt pool or spraying-on a layer of smelt limit the quantity of salt contacting the metal surface and make renewal of the salt layer extremely difficult. A better approach to using a powdered bed of salts would be to dip a cooled probe into a pool of molten smelt containing the appropriate salts or to suspend a cooled probe over a bed of smelt containing the salts to allow high-vapor-pressure salts to sublime on the cool metal surface. Due to the relatively large volume of salt in these tests, depletion of reactants would be less of a problem than with dipping techniques or sprayed-on layers.

Experience to date, however, has shown that experiments incorporating heat transfer conditions do not give significantly different corrosion rates than isothermal experiments conducted with frozen layers of smelt (*1*), and the composition of sublimed salts on a cold finger is likely to be much different than the composition of salts found at the smelt-metal interface in a boiler. While these tests could appropriately be used to investigate specific circumstances of fireside corrosion, the extra level of complexity and cost they introduce into the experiment do not appear to justify their use as general screening tests for materials or for the effects on corrosion of changes in the boiler environment. Again, as a general principle, any salt-phase testing must be validated by detailed metallographic comparison with field samples.

II. Testing for gas-phase attack

Type of test	*Methodology*	*Purpose*
Cyclic oxidation	Long-term (minimum duration of up to six months). Use standard gas composition. Gas composition should be defined in terms of fixed oxygen and sulfur activities. Test temperature should be cycled between ambient and either 300°C or 370°C. Fix cycle frequency to between 2 and 10 days. Metallographic analysis of samples is essential.	Define worst-case corrosion conditions for boiler.
Isothermal	Long-term (same duration as longest cyclic oxidation test). Use standard gas composition. Other conditions identical to cyclic oxidation test. Metallographic analysis of samples is essential.	Establish corrosion envelope between worst-case and optimal (isothermal) conditions in the standard environment.
Isothermal or cyclic oxidation	Medium-term. Must be of sufficient duration (up to 400 h) to establish relationship between corrosion kinetics of this test and long-term cyclic oxidation and isothermal tests. Use to study effects of mixed oxidizing-reducing atmosphere. Use to study effects of added species to standard gas (i.e., HCl, S, etc). Use to study effects of water wash on subsequent high-temperature corrosion rates. Metallographic analysis of samples essential.	Establish effects of operating environment and procedures on corrosion of waterwall materials.

Field testing with cooled probes

Field testing is a necessary element of any development program for corrosion resistant materials. From the point of view of cost and ease of installation, cooled probes are the best means of collecting data on corrosion resistance of materials from the field. The drawbacks of nonuniform heat transfer and poorly characterized environment are offset by the expense of the only real alternative way to achieve the same end: in-boiler testing of experimental water-wall panels. Multiple specimens can be installed on probes with relatively constant, well-controlled heat transfer characteristics. In all cases, analysis of the specimens at the conclusion of field testing should parallel the methodology outlined in the first recommendation. A major advantage of using insertable probes for field testing is the ability to obtain corroded samples with smelt deposits and scales intact. Long-term testing (at least to 4500 h) may prove to be the only means of obtaining such samples.

Conclusions

A thorough review of fireside corrosion in kraft recovery boilers has revealed a number of deficiencies in the understanding of corrosion mechanisms in recovery boilers. We propose a five-part plan of action for laboratory and field research to help strengthen understanding of these corrosion mechanisms so operation and maintenance of kraft recovery boilers can be made safer and more cost-effective. □

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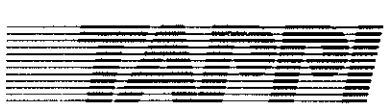

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