PULP AND PAPER PLANT MATERIALS ISSUES ADDRESSED BY X-RAY AND NEUTRON DIFFRACTION METHODS

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ABSTRACT

A kraft paper mill produces a steady waste stream of reacted inorganic chemicals and organic wastes called black liquor. Both monetary and environmental concerns demand that the inorganic chemicals and the organic byproducts are recycled. Currently recovery boilers are the standard means to recycle the inorganic chemicals and organic waste to produce a large fraction of the energy needed to operate a large pulp and paper mill. Energy research has indicated that gasification of the black liquor would recover the inorganic chemicals and meet a mills heat / steam requirements. In addition, gasification would produce fuel gas that can then be used to generate electricity that will meet or exceed the needs of a pulp and paper mill. Unfortunately, regeneration of the inorganic chemicals produces a highly corrosive Na₂CO₃ and Na₂S smelt. This smelt melts at about 700°C and can produce an environment conducive to stress corrosion cracking in the composite tubes lining the recovery boiler, or can cause rapid degradation of the refractory liners in gasifiers. Numerous studies have addressed various aspects of these problems. This paper summarizes the contributions of X-ray and neutron diffraction to the materials issues in recovery boilers and black liquor gasifiers.

INTRODUCTION

The heart of the pulp and paper industry is the kraft pulping process and the digestion of wood chips to separate wood fibers from the lignin that holds them together. During digestion, white liquor composed of NaOH and Na₂S is used to release the wood fibers. The fiber for paper production is separated out from a continuous waste stream called black liquor consisting of various sodium-sulfur compounds, Na₂CO₃ and lignin. Since 60% of the organic material of the original logs is in the black liquor, releasing the energy stored in the organic material has significant economic benefits.

The first step in the chemical recovery process is to evaporate the waste and burn off the organic compounds. In the process, the sodium-sulfur compounds found in the black liquor reduce to Na₂S as seen in figure 1. The smelt of Na₂CO₃ and Na₂S is then dissolved in water to form green liquor. The green liquor is then reacted with CaO forming CaCO₃, NaOH and Na₂S. The CaCO₃
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precipitates out of solution leaving NaOH and Na₂S dissolved in water or white liquor. The white liquor returns to the digester and the CaCO₃ is heated in the lime kiln to regenerate CaO.

Recovery boilers are currently used to recover the starting chemicals and to produce some of the steam and heat needed in the mill. Gasification, a process currently being developed, has the potential to convert pulp and paper mills from energy consumers to energy producers by producing fuel gas that can be used in gas fired turbines. Because of the caustic nature of the Na₂CO₃ and Na₂S molten smelt, both of these processes have unique materials issues. Material failures can cause unscheduled plant shutdown that can cost usually 1/4 to 1/3 million dollars a day in lost production and repairs.

While recovery boiler floor tubes are usually protected from direct exposure to molten smelt by a layer of solidified smelt there is the potential for water smelt explosion that can cause unscheduled plant shutdowns and possibly injuries or death. Gasifiers, on the other hand, have refractory liners and very few metal components exposed directly to the molten smelt. Current materials experience rapid degradation and limit the effective lifetime of the gasifier. The material issues encountered by the pulp and paper industry have led to DOE sponsored collaborations between numerous paper companies, industrial supplier and research organizations [1]. X-ray and neutron diffraction have been a vital component in understanding materials failures encountered during the chemical recovery process in kraft paper mills and has contributed to recommendations for replacement materials in recovery boilers.

**RECOVERY BOILERS**

Co-extruded boiler tubes with 304L a standard austenitic stainless steel cladding on SA210 carbon steel (304L/SA210), commonly called composite tubes, were developed more than thirty years ago. These tubes were found to be more resistant to sulfidizing recovery boiler smelt and gases than carbon steel [2]. Once it was established that composite tubes performed better than carbon steel tubes in boiler walls, it was logical to extend their use to recovery boiler floors since carbon steel floor tubes had occasional corrosion-caused failures. Use of composite tubes on recovery boiler floors was first implemented around 1978 in Scandinavia, but waited until the mid-1980s in North America [3,4]. Recovery boilers are now composed of panels of composite tubes welded to either a composite or sometimes a solid stainless steel membrane. The panels lining the floor and walls have water circulating through the tubes to remove heat. A protective layer of solidified smelt forms on the exposed metal surface of the floor tubes.

A few years after composite tubes were adopted for use in recovery boilers, cracking was found in the stainless steel outer layer of tubes that formed smelt spout openings and subsequently, in composite floor tubes. By 1992, it was apparent that cracking of the 304L layer in composite floor tubes was a widespread problem across the pulp and paper industry. Research studies have identified that the most likely mechanism for crack initiation in composite floor tubes as stress corrosion cracking (SCC) [5], and have found little evidence for the alternative mechanism of crack initiation by thermal fatigue [6,7]. SCC requires that tensile stresses be present on the tube surface while it is exposed to a specific corrosive environment, within a specific temperature range. In order to determine the stresses at the surface of composite tubes as well as through the tube wall, X-ray and neutron diffraction methods were utilized.
Unless otherwise stated, all x-ray residual stress measurements were conducted at ORNL on a TEC Stress Analyzer and surfaces were electrolytically polished in preparation for x-ray measurements. Neutron residual stress measurements unless otherwise stated, were conducted at the High Flux Isotope Reactor (HFIR) at ORNL. A Be (110) reflection was used as the monochromator. The take-off angle was 84° and the incident wavelength was 1.513 Å. Though gage volumes varied between experiments, all measurement volumes were located below the surface.

The results of measurements of the axial and tangential residual stresses due to composite tube fabrication have been reported [8]. These results showed that compressive stresses were present on the outer surface of 304L/SA210 tubing from two tube manufacturers. These compressive stresses almost certainly develop during the straightening process, which is the final manufacturing step. Stress measurements have also been made on tube panels, both in the as fabricated condition and after exposure. The results for the exposed panel show that both axial and tangential stresses on the fireside surface of the tubes are tensile [9]. These results indicate that the necessary tensile stresses for SCC to occur are present on the outer surface of the 304L/SA210 composite tubes after service in a recovery boiler at room temperature. Modeling has shown that due to differences in linear expansion between the carbon steel and the 304L, the clad layer will undergo plastic deformation at operating temperatures, and will experience tensile stresses on cooling.

X-ray and neutron residual stress measurements have been made on the composite tubes with different cladding materials and weld overlays. Results show that as-fabricated composite tubes made with a modification of Alloy 825, a nickel-based alloy, on carbon steel have compressive axial stresses and tensile tangential stresses [8]. Measurement of stresses in tubes made with an Alloy 625, a nickel-based alloy, weld overlay on carbon steel revealed very large stresses in the as-fabricated condition [10]. These stresses were very effectively reduced by heat treatment at a temperature high enough to anneal both the carbon steel and alloy 625 weld overlay as seen in figure 2.

The thermal expansion behavior of a material can be substantially modified by the presence of residual stresses when composite tubes are heated [11]. Because of the thermal expansion mismatch between the carbon steel core and the clad layer, thermal residual stresses change from room temperature values to those associated with the boiler at operating temperature. The residual stresses values change again as the boiler cools after shut down. The temperature-dependent residual stress causes the effective coefficients of thermal expansion to be different along the different specimen directions and from the
unconstrained condition. Measurement of residual stresses as a function of temperature have been presented and used to adjust properties for finite element modeling of stresses in recovery boiler floor panels [6,12].

Air ports incorporated in the recovery boiler walls have recently been identified as another potential cracking site [5]. To form air ports, two composite tubes are bent backwards out of plane and sideways, and then welded at the top and bottom of the bends forming a hole through which air is forced into the recovery boiler. To determine the stresses along the bend, X-ray and neutron diffraction studies were undertaken on a 304L/SA210 bent composite tube manufactured for an operating recovery boiler [13,14]. Neutron diffraction strain mapping was undertaken using the SMARTS beam line at Los Alamos Neutron Science Center. Axial and radial strain components were determined at selected locations in both the carbon steel core and stainless steel cladding. It was found that, at the locations examined, the SA210 core and 304L cladding layers had opposite strains (i.e., tension versus compression) of significant magnitude and that these strains changed sign going through the bend as seen in figure 3. These preliminary results suggest that the initial forming (bending) of the tubes prior to welding may contribute significantly to the residual stresses that are responsible for the weakened resistance to stress corrosion cracking. The residual stresses observed in bent composite tubes vary significantly from the residual stresses observed in single composition bent tubes.

![Figure 3](image-url)

**Figure 3.** Axial and radial strains were measured along an as manufactured bent composite tube by neutron diffraction using the SMARTS beam line at Los Alamos Neutron Science Center in the stainless steel cladding (a) and the carbon steel core (b). The gap in the center results from excessive attenuation of the beam due to the bent tube geometry.

**BLACK LIQUOR GASIFICATION**

An alternative to the recovery boiler involves the gasification of black liquor. A high pressure, high temperature gasifier (HPHT) that incorporates combined cycle has the potential to produce more energy than the pulp and paper mill uses and is a long-term goal of the industry. This process operates in a reducing environment at higher temperatures (to 1000°C) and requires refractory liners in the gasifier vessel. In addition, low pressure, high temperature (LPHT) and low pressure, low temperature (LPLT) gasifier designs are also being considered. Each of these potentially commercial gasification processes requires refractory liners or coatings that potentially have significant materials compatibility issues.
To date, a demonstration HPHT and pilot HPHT plant have been operational in Sweden at Frövi and Skoghall, respectively. In the US, Weyerhaeuser and Kvaerner Chemrec built the first commercial scale LPHT black liquor gasifier at the Weyerhaeuser Company’s paper mill in New Bern, NC. This gasifier was constructed with a cylindrical stainless steel shell lined with refractory bricks. During operation, the gasifier’s atmosphere is a highly reactive, reducing environment with high sodium carbonate and sodium sulfide contents. The unit operates at an estimated temperature of 950°C. Due to the harsh environment, numerous materials issues have surfaced. The experiences at the New Bern and Skoghall gasifiers clearly demonstrate that serious material problems exist with the refractory lining.

Initial test methods used to evaluate refractory materials in smelt environments did not accurately predict the performance experienced in the New Bern gasifier. X-ray diffraction, electron microprobe, and SEM were the key characterization tools used in understanding the degradation mechanisms of the candidate refractories and alloys obtained from the operating gasifiers. ORNL’s involvement in the failure analysis and initial exploration of suitable replacement materials led to the realization that a simple and reliable method for screening materials needed to be developed. A smelt immersion furnace developed at ORNL can simulate the exposure of refractory or metal alloy in a black liquor gasifier. A complete description of the test furnace and operating conditions has been reported in separate papers [15,16].

To mimic the gasifier environment as well as possible, the smelt was supplied from the recovery boiler at Weyerhaeuser’s pulp and paper mill in New Bern, NC. X-ray patterns of solidified smelt reveal the presence of crystalline phases of sodium sulfide, sodium sulfate, and sodium carbonate. The furnace system loaded with smelt was ramped over 18 hours to approximately 1000°C before the sample (~102 x 26 x 13mm) was lowered into the smelt for a 100 hour exposure. The sample was raised and cooled for 24 hours before examination. Photographs and measurements of the exposed portion of the sample were taken before and after immersion in molten smelt to check for changes in dimensions and appearances. Screening of a number of commercially available and developmental refractory samples is summarized in Table 1.

<table>
<thead>
<tr>
<th>Number of Different Commercial Refractory Samples</th>
<th>Major Phase Present</th>
<th>Range of % of Expansion</th>
<th>Reaction Products Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Mullite</td>
<td>8% - 30%</td>
<td>Sodium aluminum silicates</td>
</tr>
<tr>
<td>12</td>
<td>MgAl2O4 Spinels</td>
<td>1% - 14%</td>
<td>NaAlO2 + MgO</td>
</tr>
<tr>
<td>3</td>
<td>Al2O3</td>
<td>None -.7%</td>
<td>Na2H(CO3)2·2H2O</td>
</tr>
<tr>
<td>2</td>
<td>(Cr,Al)2O3</td>
<td>Not measured</td>
<td>NaAlO2 + NaCrO2 + Na2CO3</td>
</tr>
<tr>
<td>1</td>
<td>[-Si3N4</td>
<td>Not applicable</td>
<td>Decomposed in smelt</td>
</tr>
</tbody>
</table>

XRD examinations were carried out on a Scintag PAD V powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) to identify degradation products and to address the problem of predicting material expansion or loss from the refractory lining. Care was taken in preparing the
individual test specimens because prior experience showed that exposed samples contain hygroscopic corrosion products that are very water soluble. Two exposed samples that fell off the sample holder and into the molten smelt during the test could only be extracted from the molten smelt by washing with water. These test samples were repeated. In both of these cases, the XRD of the exposed outer surface of the washed and unwashed samples were compared for completeness. NaAlO_2 is clearly absent in the exposed and washed samples, but it is easily observed in the XRD patterns of exposed and unwashed sample, see figure 4. This clearly reveals the solubility of NaAlO_2 and indicates the care needed in sample preparation.

Results of the smelt immersion tests varied widely depending on refractory composition and smelt penetration. In some cases, the molten smelt attack on the test samples was quite dramatic with the extreme case being a Si_3N_4 refractory, where the sample simply dissolved during immersion. In other cases, minimal penetration and chemical reactions occurred, such as for the dense alumina samples, a fused cast spinel and a fine grain MgAl_2O_4 spinel. In most cases, however, samples showed smelt penetration with either the observation of a chemical reaction of the starting materials or as solidified smelt within the sample.

While each refractory material behaves differently, there are a few general trends observed for each refractory type. Results of the XRD phase identification are summarized in Table 1. Mullite, Al_6Si_2O_13, reacted to form sodium aluminum silicates, Na_1.75Al_1.75Si_0.25O_4. MgAl_2O_4 spinel reaction products are NaAlO_2 plus MgO, while solid solution mixtures of (Cr,Al)_2O_3 and Al_2O_3 results primarily in the conversion of the Al_2O_3 end member to NaAlO_2. The extent of chemical reaction also depended on the density, grain size, intergranular phases and other factors.

**SUMMARY**

X-ray and neutron diffraction have played a key role in investigating material issues encountered in the chemical recovery process of kraft pulp and paper mills. Stress measurements have been used to evaluate potential for stress corrosion cracking, recommend changes in the manufacturing of composite tubes, and have led to recommendations of alternate clad materials for composite tubes. For materials issues in gasifiers, X-ray diffraction identified reaction products that form when molten smelt from black liquor gasification coats the refractory liner. Screening of refractory materials has led to the identification of characteristics that inhibit smelt refractory interactions. Temperature dependent studies have been used to study the reaction of
Na$_2$CO$_3$ on refractory material in order to understand the Na$_2$O attack on refractory material in hopes of discovering materials resistant to molten smelt.

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