# CORROSION ISSUES IN BLACK LIQUOR GASIFIERS

James R. Keiser, Roberta A. Peascoe and Camden R. Hubbard
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831


J. Peter Gorog
Weyerhaeuser Company
Federal Way, Washington, 98477

## ABSTRACT

The kraft papermaking process, which is by far the predominant method used in North America, depends on recovery of the chemicals used in the digesting or pulping operation.  Currently, the black liquor recovery boiler is the heart of this recovery process, but replacement of this boiler with a gasification system is being intensively studied.  A switch to gasification can be justified based on capital investment, energy efficiency, and safety, but there are a number of significant obstacles to its successful development and implementation.  Identification of suitable materials for the containment of the reaction and the reaction products is considered one of the most critical issues.

There are currently two distinct gasification processes being actively developed; a low temperature process in which the alkali salts are kept below their melting point, and a high temperature process in which these compounds are handled in the molten state.  Each process has unique materials requirements and issues that are described in this paper.  In addition, results from recent studies of the compatibility of gasifier components with the respective environments are presented.

Keywords: corrosion, materials degradation, gasification, black liquor, alkali salts, hydrogen sulfide, fluidized bed, slagging gasifier

## INTRODUCTION AND BACKGROUND

Papermaking by the kraft process involves treatment of wood chips in the dissolver vessel with a steam-sodium sulfide-sodium hydroxide mixture to separate the cellulose fibers from the lignin that binds them together.   The streams exiting the digester vessel include a fiber-rich stream that is further treated to provide the fibers that are used to form paper or other cellulose-based product.  The other stream is identified as black liquor, which is an aqueous solution containing the waste organic material including the lignin as well as the spent pulping chemicals that are primarily sodium carbonate and sodium sulfate.  Other inorganic components include salts containing potassium and chloride.  In order to regenerate the pulping chemicals as well as recover some of the heating value contained in the organic components, the black liquor stream is burned in the black liquor recovery boiler.  Concentrated black liquor is injected into this boiler where the water is evaporated, the organic materials are burned

to produce heat and steam, and the inorganic components are recovered in the bottom of the boiler in a partially reduced state, primarily as sodium carbonate and sodium sulfide. After an additional processing step, the sodium sulfide-sodium hydroxide white liquor is completely regenerated and is ready for reuse in the pulping process. A diagram highlighting the steps in papermaking and chemical recovery is shown in Fig. 1.

Recovery boilers have been used very successfully for many years, but there are a number of shortcomings. First, as the most expensive component in a paper mill, the boiler is very capital intensive. In addition, the boiler is relatively inefficient in producing electric power from black liquor. Besides these economic issues, there is a safety issue because of the potential for recovery boiler explosions if the pressurized water contained in the tubes that form a boiler's walls, floor and ceiling escapes through a leak and contacts the bed of molten salt (referred to as smelt in the paper industry) that is present on the floor of the boiler. Contact of this hot water with the molten smelt could result in a violent explosion that can severely damage a boiler and cause serious injuries to personnel. Recovery boiler explosions in the U.S. have been fairly infrequent, but during the first eight months of 2002, there were two boiler explosions in the U.S. with one fatality and several injuries.

The U.S. Department of Energy (DOE) is providing support for a number of projects that have the objective of developing black liquor gasification as an alternative to recovery boilers. One justification for this support is that gasification, if used in a combined cycle mode, offers the potential for significantly greater recovery of the energy contained in the black liquor [1]. In addition, some of the safety issues associated with recovery boilers, notably explosions, would not be present in most of the gasification processes being developed. A significant number of organizations have worked to develop black liquor gasification processes, but only two processes that have been demonstrated at a reasonable scale are still being pursued [2]. These processes include a low temperature process, developed by Manufacturing and Technology Conversion International and marketed worldwide by their ThermoChem Recovery International subsidiary, and a high temperature process that is a product of Chemrec AB [3-5].

Low Temperature Black Liquor Gasification

The low temperature gasification process involves steam reforming of the black liquor. In this process, the temperature is kept low enough such that the smelt does not become molten or even reach the point where it becomes "sticky". A schematic of a typical reformer/gasifier system is shown in Fig. 2. This system utilizes a fluidized bed of sodium carbonate particles. Steam introduced through the bottom of the vessel serves as the fluidizing gas as well as the source of water for the reforming operation. The black liquor is introduced through a nozzle system, also located on the bottom of the vessel. Heat is transferred to the bed through several tube modules that carry hot combustion gas. The hot gas is produced in the refractory lined combustion chambers where the fuel, either recycled product gas or an auxiliary fuel, is burned in a pulsed combustion mode. Heat from the combustion gases is transferred through the walls of the pulsed heater bed tubes to the bed material where the reforming operation occurs.

A demonstration scale gasifier utilizing the low temperature process was installed in 1994 at a mill in New Bern, North Carolina. This unit successfully completed a continuous 500 h run on black liquor during August, 1995. Researchers at Oak Ridge National Laboratory provided assistance to this facility by examining various tube samples from the heater modules; this work will be described later in this paper. Currently, full-scale reformer/gasifier facilities are under construction at two mills, one in Big Island, Virginia, and one in Trenton, Ontario. Neither of these mills operates on the kraft process; they utilize a semi-chemical sodium carbonate cook of the wood, so the absence of significant sulfur compounds is expected to make the environments less hostile for the structural materials. Nevertheless, these installations will provide an opportunity for a more thorough evaluation of this process.

Materials concerns. In this system, the alkali salts are kept below their melting point. Consequently, no component is exposed to molten salts and most are utilized at a temperature below those encountered in the higher temperature process. However, the inside of the tubes in heater modules

of a reformer/gasifier will be exposed to fairly high temperature combustion gases, and there will be some pressure cycling due to the pulsed firing. The outer surface of the bed tubes will be exposed to a gas mixture that will include hydrogen, hydrogen sulfide, steam and carbon monoxide, and the tubes will also be subjected to the movement of the particles in the fluidized bed. The combustion gases that pass through the tubes originate in the combustion chamber, which is a refractory lined vessel. Most of the combustion occurs in this chamber, but a small amount of unburned gas leaves this chamber and enters the tubes where combustion is completed. In order to protect the bed tubes from this high temperature gas and to keep from locally overheating the bed material, a short length of smaller diameter tubing is located inside the first portion of the bed tubes. These shield tubes are exposed to higher temperature gases on both sides, but particularly on the inner diameter. The gases exiting the bed tubes are directed into another chamber that is connected by a bellows to a heat recovery system. The hot combustion gases as well as the thermal and mechanical cycling are concerns for this portion of the gasifier. The reformer/gasifier vessel is lined with refractory. The erosive action of the bed particles is a concern in the bed area, while above the bed, degradation of the refractory by the aggressive gases, as well as mechanical damage from material condensing on the refractory lining, are concerns.

Table 1 identifies the critical components, their environments, and the issues associated with each. Not listed are components in the balance of the plant including scrubbers, heat exchangers, venturis, and heat recovery steam generators.

High Temperature Black Liquor Gasification

The high temperature gasification process can be operated near atmospheric pressure or at significantly elevated pressure. The lower pressure version of this system is envisioned as a supplement to recovery boilers while the high-pressure version is expected to totally replace recovery boilers for processing of the black liquor.

High-temperature, low-pressure gasification. A schematic of the high-temperature, low-pressure (HTLP) gasifier is shown in Fig. 3. In this refractory lined vessel, the black liquor fuel and the air for partial combustion are injected at the top of the vessel. The organic material contained in the black liquor is gasified, and the inorganic salts are left in the liquid state, primarily on the gasifier wall. The liquid and gaseous products are carried out the bottom of the gasifier vessel. The product gas is routed through a gas clean-up system and the inorganic salts are directed to the green liquor tank. A 75 tons dry solids (tds)/day demonstration system was operated in Sweden in the early 1990s. A 330 tds/day gasifier of this type is located at the mill in New Bern, North Carolina, but it currently is not operating because of problems with structural materials. Plans call for refurbishing of the gasifier's structural components with a resumption of operation planned for spring 2004. Failure analysis of gasifier components will be described later.

High-temperature, high-pressure gasification. There is some limited experience with high-temperature, high-pressure (HTHP) gasification. A 10 tds/day pilot scale unit was operated in Sweden from 1994 through 2000. The unit operated continuously for an extended period, but only daytime operation was on black liquor; the system was switched to fuel oil when it was unattended. A total of only about 1000 hours operating time was accumulated on black liquor feed while the system operated for considerably longer on fuel oil. Refractory from this system has been examined. A limited amount of refractory degradation was observed, and details of the examination will be presented.

There are two competing designs being considered for the HTHP gasifier. One design utilizes a thick refractory lining within a metal pressure vessel. This design was used in the Swedish gasifier and has a refractory lining similar to that shown in Fig. 3 for the HTLP gasifier. The alternative design, called a cooling screen, utilizes a helically coiled metal tube that has a refractory surface coating (see Fig. 4) and contains pressurized cooling water. A similar design has been used successfully with the slag produced during coal gasification, but it has not yet been proven with the molten smelt produced during the high temperature gasification of black liquor. Currently, a high-temperature, high-pressure demonstration scale unit is under construction in the town of Piteå in northern Sweden. Operation is

expected to begin in mid to late 2003, and both the thick refractory lining and the cooling screen design will be tested.

    <u>Materials Concerns</u>.  In the high-temperature systems, the units operate above the melting point of the inorganic salts at an estimated upper temperature of 950°C.  The gaseous atmosphere in the gasifier includes hydrogen, hydrogen sulfide, carbon monoxide, carbon dioxide and steam.  In addition, most of the interior surface of the gasifier vessel is exposed to molten salt in a reducing environment.  There are three basic high-temperature gasifier designs, low-pressure refractory lined, high-pressure refractory lined and high-pressure refractory coated coiled tube.  For all three designs, the interior surface is primarily a refractory material.  There are metallic components that are generally exposed to less aggressive environments; these include the liquor injection system, some thermowells, the refractory support rings and the green liquor handling system.  Table 2 identifies critical components, their environments, and the issues associated with each.

    The molten inorganic alkali compounds create a very severe environment for both metals and refractories.  As will be described later, the reactions with several refractories have been characterized.

    All of the gasification systems have their advantages and disadvantages, and it is likely that the marketplace will ultimately determine which of these systems will actually be deployed commercially.  More details on each of these systems, including a description of some of the advantages and disadvantages, have been described in a number of publications [3-7].  It is important to note that containment materials are considered one of the "critical" issues that must be addressed for successful implementation of these gasification systems.

RESULTS

Component Examinations

    Analysis of components from the low-temperature gasifier has been limited to characterization of various tube metallurgies from the pulsed heater bundles, including tubes that were found to be cracked after removal from service.  Several refractory and metallic materials from the New Bern HTLP gasifier have been characterized and degradation modes have been identified.  Additionally, refractory from the HTHP pilot plant has been examined.

    In addition to the analysis of degraded components, laboratory test systems have been constructed to simulate certain gasifier environments.  These include the molten salt environment of the HT gasifiers; refractories exposed in these test systems have been characterized.  Studies have also been conducted in an environment simulating that predicted for a reformer/gasifier serving a sulfite mill.

    <u>Examination of New Bern LTLP gasifier components</u>.  Several alloys were used for the tubes in the pulsed heater tube bundles of the New Bern reformer/gasifier.  These alloys appeared to perform well during reformer/gasifier operation, but inspection a few weeks after the bundles were cooled to room temperature revealed cracking in the 253MA (UNS S30815) tubes in one of the bundles.  This tube bundle is shown in Fig. 5.  As revealed in Fig. 6, metallographic examination of cross sections of the cracked tubes showed that the cracking was intergranular.  Further examination showed that the tube material had become sensitized during operation.  It was concluded that the cracking was most likely due to polythionic acid stress corrosion cracking (PASCC).  Examination of type 310 stainless steel tubes from another tube bundle showed some evidence of sensitization, but not to an extent that the tubes were susceptible to PASCC.  As a result of these studies, it was recommended that a stabilized stainless steel (types 321 or 347) or a low carbon grade be used in future applications when sulfidizing gases were expected to be present.

    <u>Examination of New Bern HTLP Gasifier Components</u>.  The primary characterization work for the New Bern HTLP gasifier has concentrated on the refractory materials.  Samples of the original mullite-based refractory were examined, as were samples of the fused cast alumina refractory that was installed after significant degradation was observed on the original refractory.  In addition, pieces of several metallic components have been examined.  These components include one of the original

refractory support rings, the water-cooled support ring located at the transition between the gasifier and the smelt quench tank, and sections of the stainless steel gasifier vessel.

A dense high alumina, silica-bonded refractory brick was the first material used on the hot face as a heat insulating layer and as a barrier to chemical attack of the remaining insulating layers. The brick composition was 58% $Al_2O_3$, 37% $SiO_2$, 0.9% $Fe_2O_3$ with minor amounts of $P_2O_5$ in the bonding phase. Initially, the bricks were almost 23 cm high, and x-ray diffraction (XRD) identified four phases; mullite ($Al_6Si_2O_{13}$), opal ($SiO_2xH_2O$), cristobalite ($SiO_2$) and andalusite ($Al_2SiO_5$). Figure 7 shows a severely degraded refractory brick that has a reaction layer about 2.5 cm thick. XRD analysis of the reaction layer (see Fig. 8) showed a Carnegieite-like phase ($Na_2O-Al_2O_3-SiO_2$) had developed on the surface while the silicate phases had completely vanished. Based on the apparently poor chemical resistance of the bonding phase to sodium salts, as well as the tendency for the silica phases to react at operating temperature, this refractory was deemed inappropriate for use in the HTLP gasifier environment.

Because of the excessive reaction of the alumina-silica brick observed during the early operation of the gasifier, a test panel of " /$-alumina fused cast refractory bricks was installed in the alumina-silica brick lining, and subsequently, the entire lining was replaced with the " /$-alumina fused cast refractory bricks. This replacement brick was reported to have a composition of 45% " -alumina and 53% $-alumina. Analyses were performed on core-drilled samples removed from the test panel after a few weeks of operation and on brick samples removed from the lining after many months. An example of " /$-alumina fused cast refractory that appeared to be coming loose from the lining in the dome of the New Bern gasifier is shown in Fig. 9. Analysis of this material showed that a new phase, $NaAlO_2$, had formed on the surface (see Fig. 10), presumably as a result of reaction of the alumina refractory phases with the sodium compounds. The significant volume expansion associated with the formation of the compounds leading to $NaAlO_2$ would be expected to generate significant stresses in the surface of the refractory bricks.

The original design of the gasifier had several circumferential metal rings that were attached to the shell at various levels and were intended to support the refractory bricks. The 16 mm thick rings were fabricated of a Ni-Co-Cr-Si alloy, HR160 (UNS N12160), that, as shown in Fig. 11, was severely corroded during exposure. The edge of the support ring facing the gasifier interior was, in places, corroded completely through its thickness. A cross section of the ring, shown in Fig. 12, indicates that the alloy suffered very rapid general corrosion.

At the bottom of the cylindrical gasifier vessel, there is a transition from the very high temperature gasification environment to the lower temperature environment where the molten smelt is dissolved in water to form green liquor. A water-cooled metal ring provides the transition between the refractory and the uncooled metal components. The original support ring was constructed of heavy-wall stainless steel. Considerable problems were encountered with cracking of the stainless steel; examples are shown in Fig. 13. The problem was resolved by using treated water and thinner sections of carbon steel to promote cooling of the surface of the ring.

During the first years of operation, the stainless steel gasifier shell did not appear to be encountering any problems. However, observation of the shell was somewhat difficult since its inside surface was behind the refractory lining and the outside surface was covered by a shroud intended to promote convective flow of air over the outer surface of the gasifier shell. Some limited checks of the inside surface were made when the refractory was changed, but no careful records of any observations were kept. In December 1999, shortly before the gasifier was scheduled to restart, a short crack was noticed on the outside of the shell near the bottom of the cylindrical section. A fairly small piece was removed from the shell (shown in Fig. 14), and analysis showed that the cracking had originated on the shell's ID. To determine the extent of the cracking, several other fairly large pieces were removed from the shell, and it was determined that cracking was quite extensive. An indication of the extent of cracking can be found in Fig. 15, which shows the inside surface of the shell section after a dye penetrant check for cracking. Several cross sections were examined metallographically, and chemical analyses were performed on the insulating board that had been in contact with the stainless steel shell. The results showed that the transgranular cracking was likely caused by chloride stress corrosion. Furthermore, as shown in Fig. 16, the crack configuration suggested that the cracking proceeded more

rapidly during selected time periods.  As a result of the discovery of this cracking and some subsequent analyses of the integrity of the gasifier shell, it was decided not to restart the gasifier at that time.  After much consideration and discussion, the decision has been made to completely rebuild the gasifier; it is expected that operation will be resumed sometime in the year 2003.

Examination of HTHP Gasifier Components.  As already noted, the total operating time on black liquor of the Skoghall HTHP gasifier was about 1000 hours.  After the gasifier was taken out of service in 2000, several samples of the fused cast alumina refractory were made available for characterization under the DOE-funded refractory project.  One of the bricks received from Sweden is shown in Fig. 17.  Sections were cut from each of these refractory bricks, and the changes in composition as a function of distance from the surface were determined.  As shown in Fig. 18, the $NaAlO_2$ phase was found on the surface of these bricks, indicating that even though exposure time was limited, the reaction products found on fused cast alumina bricks from the New Bern gasifier were also present on the Skoghall bricks.

Laboratory Corrosion Studies

In an effort to reproduce the conditions of the HTLP gasifier, a laboratory test system has been constructed to permit exposure of samples in molten smelt.  This system, which is shown schematically in Fig. 19, permits immersion of refractory or metallic samples in molten smelt at controlled temperatures and in a controlled gaseous environment.  Exposure times of 50-250 hours have been used, but exposures were generally 100 hours.  This test system has been described in more extensive detail elsewhere [6,7].

Samples exposed in this system have shown degradation that is similar in appearance and in corrosion product composition to that seen in operating HT gasifiers.  For example, Fig. 8 shows a cross section of a sample of the original alumina-silica refractory after exposure for 50 hours in the immersion test system.  Both the sample exposed in the test system and the one exposed in the gasifier show the mullite, cristobalite, and opal phases in their interior, and both show sodium aluminum silicate (NAS) on the surface.  These results demonstrate that the immersion test system produces the same corrosion reactions as occur in the HTLP gasifier.

Samples of the "/$-alumina fused cast refractory were exposed in the immersion test system for 100 h, and the compositions of reaction products on the sample surfaces were determined using XRD.  The results shown in Fig. 20 indicate that only " and $-alumina phases are present on the unexposed sample and in the interior of the exposed sample, but the surface of the exposed sample has $NaAlO_2$ phase in addition to the two alumina phases.  This pattern is consistent with the phases seen on the fused cast alumina samples exposed in the HT gasifiers in New Bern and Skoghall.

In addition to the materials utilized in gasifiers, a significant number of other materials have been exposed in the immersion system.  A summary showing the range of materials tested is given in Table 3, but this list does not include the large variety of surface modifications that have been examined.  Several of these surface treatments appear to be capable of reducing or preventing penetration of the sodium salts into the refractory.  However, much more extensive testing is needed to obtain a better understanding of the mechanism of sodium penetration.

Fairly recently, a series of 100-h microbalance tests has been conducted in an $H_2$-$H_2S$-$H_2O$ gas mixture to help evaluate potential bed tube materials for use in a LTLP reformer/gasifier for a mill operating on the sulfite pulping process.  A plot showing weight change versus exposure time is presented in Fig. 21.  It is clear that the standard stainless steels and many of the conventional chromia-forming alloys have initial rates of weight gain that suggest these alloys may not be suitable for application in such a system.  Relatively small weight changes were seen for the alumina forming alloys that were tested, but cost, fabricability and weldability could be issues for these materials.  Two recently funded DOE projects will be generating more extensive information on the performance of materials in soda, kraft and sulfite mills.

## CONCLUSIONS

Black liquor gasification offers an alternative to recovery boilers. There are some clear advantages to gasification, but there are some significant difficulties that must be overcome. The two black liquor gasification systems currently being commercialized have significantly different materials issues, but both have materials problems that need to be addressed in order for the systems to be able to operate reliably for sufficient times to be economically justifiable. Analyses of degraded samples are providing some guidance for the identification of appropriate materials, but considerable laboratory testing of candidate materials and evaluation of exposed components are needed. Comparisons have shown that the immersion test system produces degradation similar to that observed on materials exposed in high temperature gasifiers, and tests are being developed to simulate the environment of the low temperature reformer/gasifiers.

## ACKNOWLEDGMENT

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TABLE 1
MATERIALS ISSUES IN LOW TEMPERATURE FLUIDIZED BED REFORMER/GASIFIERS

| Component | Material | Environment | Degradation mode |
|---|---|---|---|
| Pulse combustion chamber | Carbon steel lined with high density and insulating refractories | Kraft process – 1300-1500°C, ~5psi amplitude 50-60 Hz oscillations, trace alkali and $H_2S$<br>Sulfite process – 1300-1500°C, ~5psi amplitude 50-60 Hz oscillations, up to 9% $H_2S$<br>Biomass – 1350-1550°C, ~5psi amplitude 50-60 Hz oscillations | Corrosion, thermal shock |
| Heater tubes | 1½" Sch 40 austenitic stainless steel or super-austenitic alloy | <u>Inside of tubes</u><br>50-60 Hz pressure pulses, 4-9% $O_2$, low levels $H_2S$, HCl, ppm levels Na<br><u>Outside of tubes</u><br>Kraft process – up to 621°C, $Na_2CO_3$ bed<br>Sulfite process – up to 621°C, up to 9% $H_2S$<br>Biomass – 750-850°C, $Al_2O_3$ bed particles, low levels $NH_3$, K, $Cl_2$, Si | Corrosion, fatigue, erosion-corrosion |
| Shield tubes | Austenitic stainless steel or super-austenitic alloy | Exposed to 1300-1550°C gases, metal temperatures 900-1150°C | Corrosion |
| Reformer/gasifier vessel | Gunned refractory lining | <u>Below bed</u><br>Kraft process – up to 621°C, 350Fm dia $Na_2CO_3$ bed particles moving between 2 and 3 ft/sec<br>Sulfite process – up to 621°C, 350Fm dia $Na_2CO_3$ bed particles moving between 2 and 3 ft/sec<br>Biomass – up to 843°C, larger diameter, harder bed particles moving between 2 and 3 ft/sec<br><u>Free-board</u><br>Less than 621 or 843°C (depending on process), low boiling point volatiles condensing on refractory | Corrosion, erosion, mechanical damage from condensed material or sticky particles that might pull refractory off wall or fall and damage bed tubes |

TABLE 2
MATERIALS ISSUES IN HIGH TEMPERATURE BLACK LIQUOR GASIFIERS

| Component | Material | Environment | Degradation mode |
|---|---|---|---|
| Black liquor injection system | 316L stainless steel | Oxidizing environment (preheated air or oxygen), black liquor is 100-125°C with 70-80% solids content | Erosion, oxidation |
| Gasifier vessel | A36 carbon steel | Max 260°C, avg 121°C, $H_2S$, $H_2$, CO, reducing when operating, oxidizing during start-up and shut-down, condensate may be present | Sulfidation, creep |
| Gasification vessel lining | Refractory materials including mullite based, fused cast alumina, magnesia-alumina spinels, etc. | Molten or solidified smelt, as high as 1000°C on wall, $H_2S$, $H_2$, CO | Corrosion, erosion-corrosion, thermal shock |
| Refractory support ring | Water-cooled carbon steel or stainless steel | Hot bricks on top surface, water quench occurs just below ring | Corrosion |
| Green liquor quench system | 316L and 304L stainless steels | 220°C, 30 atm pressure, caustic environment | Corrosion |

TABLE 3
SUMMARY OF REFRACTORY MATERIALS TESTED IN MOLTEN SMELT IMMERSION TESTS

| Number of Different Commercial Refractory Samples | Major Phase Present | Range of % of Expansion | Reaction Products Observed |
|---|---|---|---|
| 6 | Mullite | 8% - 30% | Sodium aluminum silicates |
| 12 | $MgAl_2O_4$ Spinel | 1% - 14% | $NaAlO_2$ + MgO |
| 3 | $Al_2O_3$ | None - .7% | $NaAlO_2$ |
| 2 | $(Cr,Al)_2O_3$ | Not measured | $NaAlO_2$, $NaCrO_2$ |
| 1 | $Si_3N_4$ | Not applicable | Decomposed in smelt |
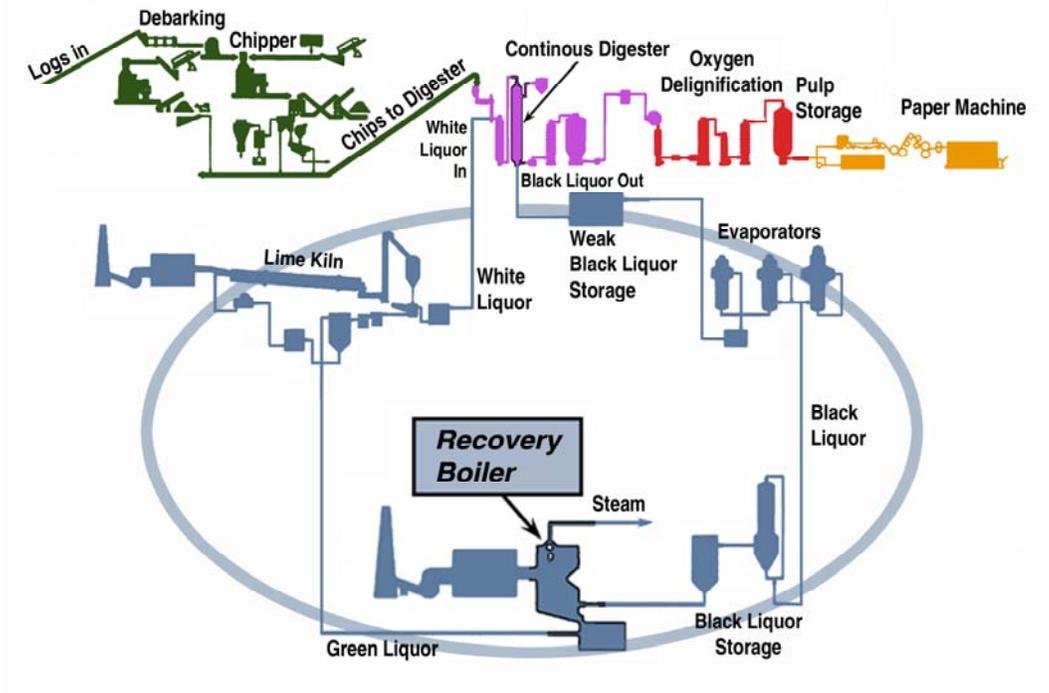
Figure 1. Schematic of a paper mill with emphasis on the chemical recovery area
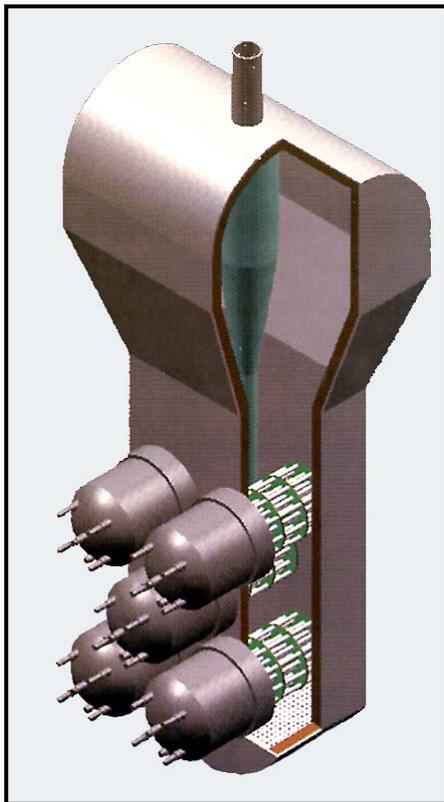


Figure 2. Schematic of steam reformer/gasifier vessel.
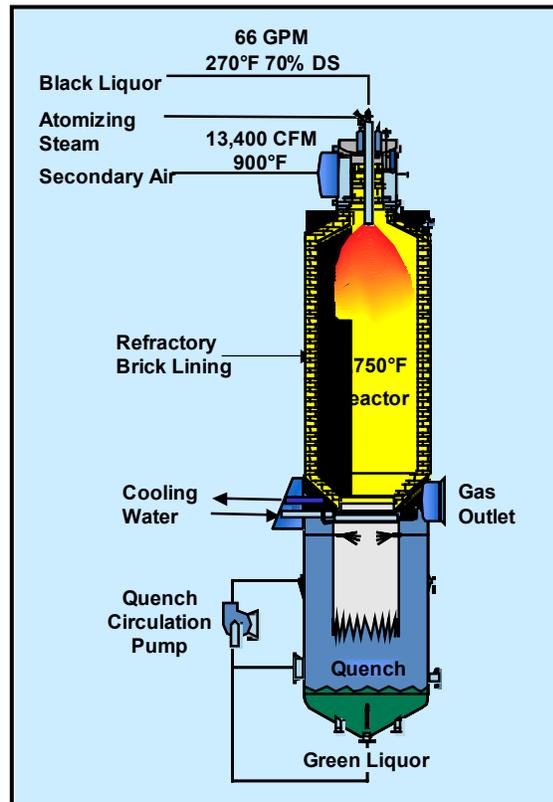


Figure 3. Schematic of high-temperature, low pressure gasifier.
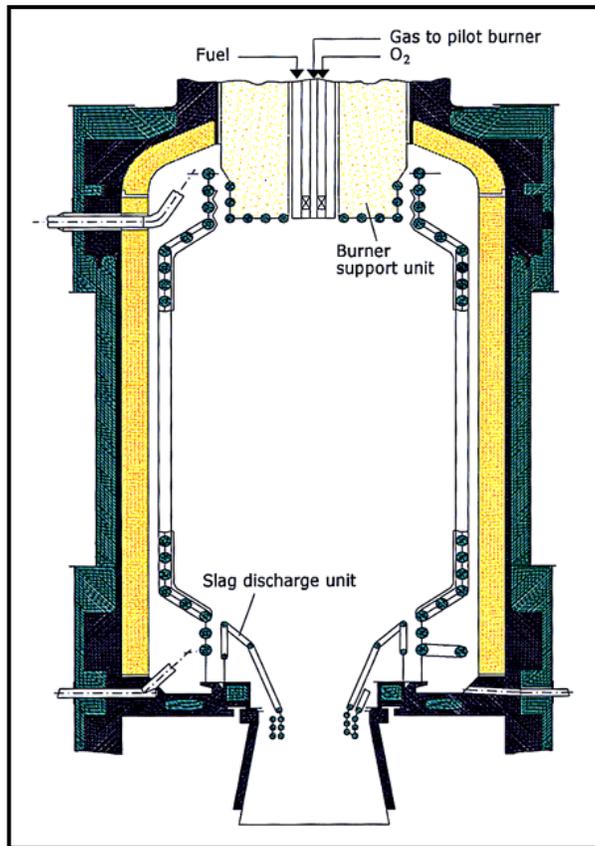
Figure 4. Schematic of high-temperature, high-pressure gasifier with cooling screen.
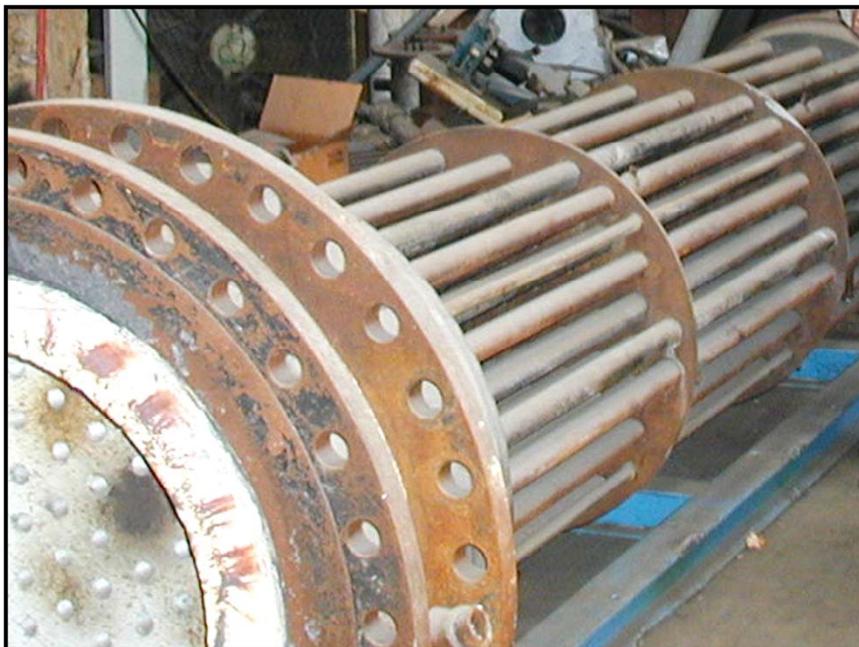


Figure 5. Tube bundle used in PulseHeater steam reformer/gasifier.
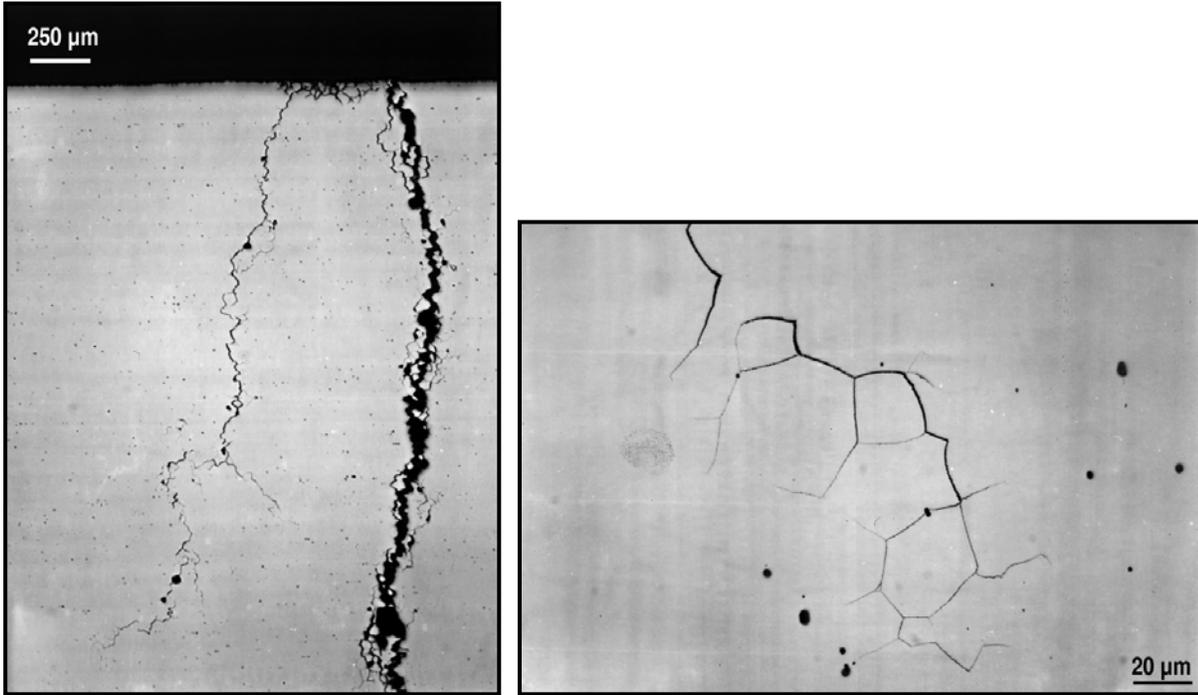
Figure 6.  Cross section of cracked tube showing cracking is intergranular.
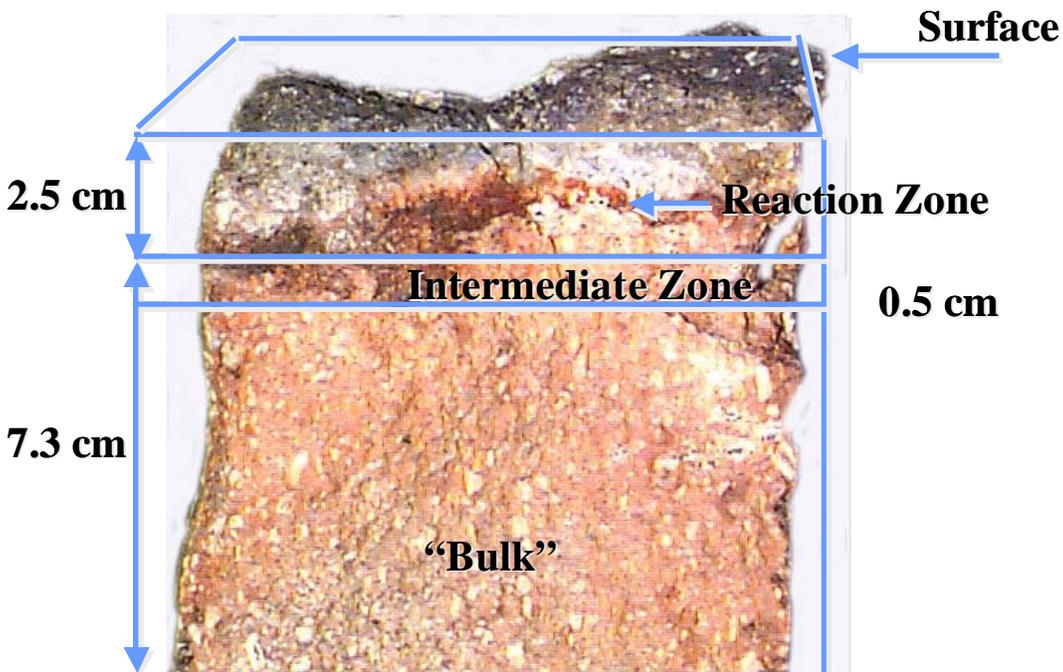


Figure 7.  Alumina-silica refractory brick from the New Bern high temperature, low pressure gasifier that was examined for evidence of chemical attack
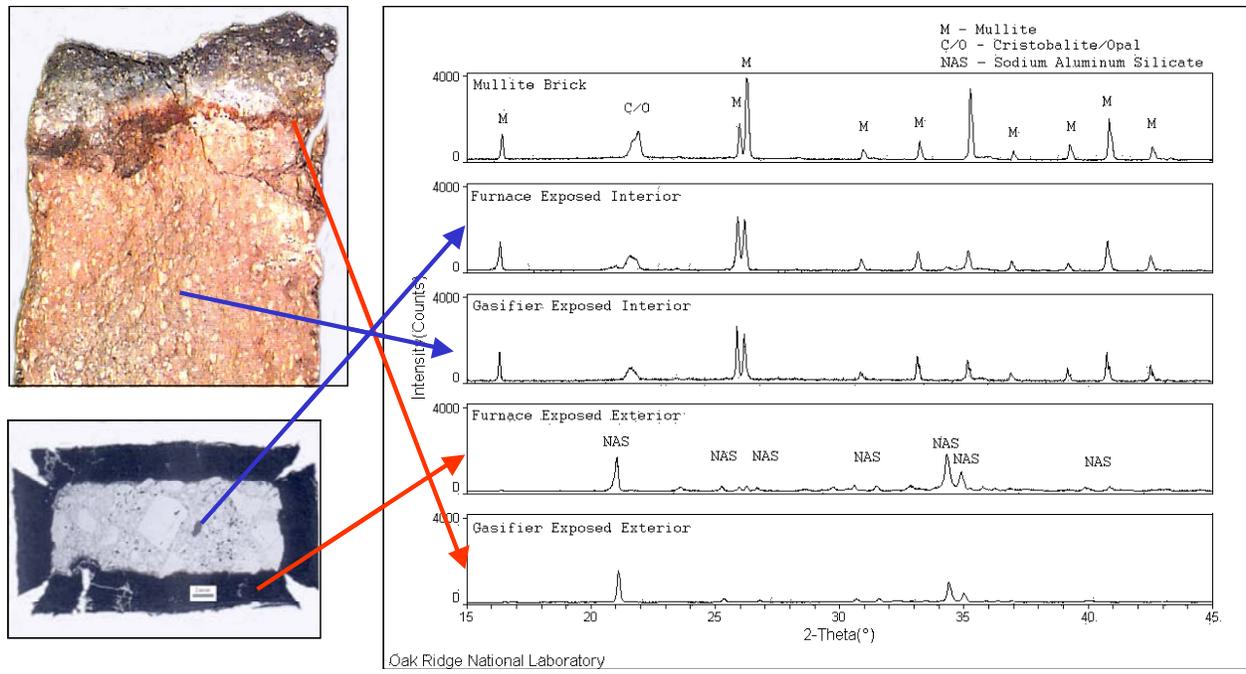
Figure 8.  Upper photo shows brick removed from New Bern gasifier.  The XRD patterns show phases present in the interior and in the degraded surface layer.  Lower photo shows sample exposed in the immersion test system.  The XRD patterns show the similarities in the phases present on the two samples.



Figure 9.  Refractory lining on the gasifier dome with a piece of loose refractory that was removed for analysis.
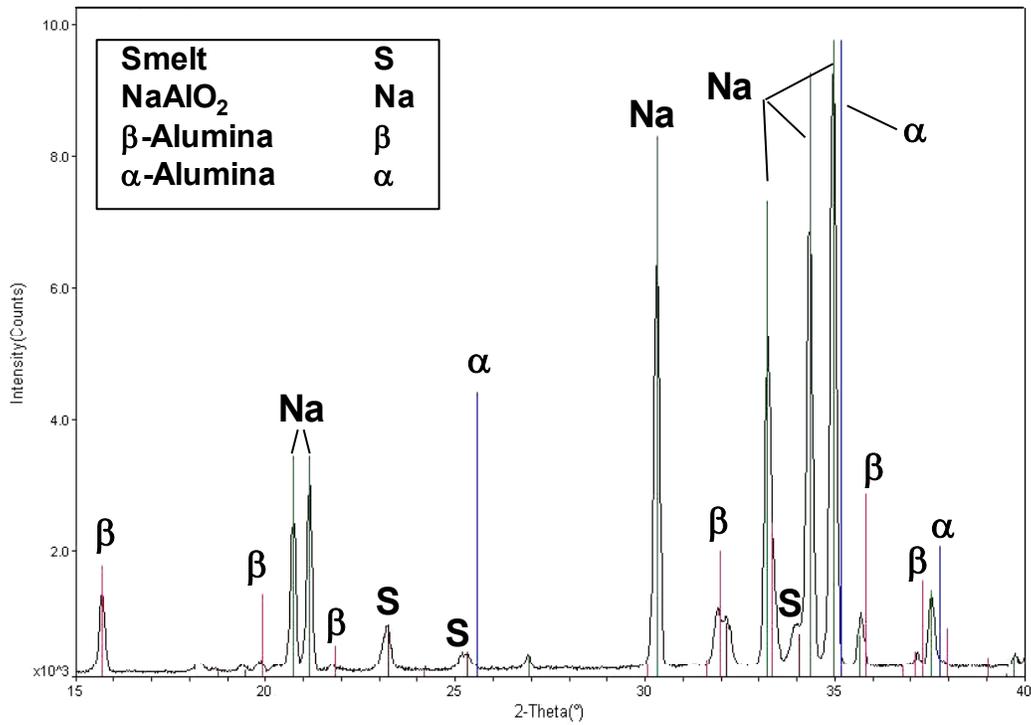
Figure 10. XRD pattern of degraded refractory removed from the gasifier dome showing that NaAlO$_2$ is one of the phases present.



Figure 11. Section of Ni-Co-Cr-Si alloy support ring that was severely corroded during use in the gasifier.
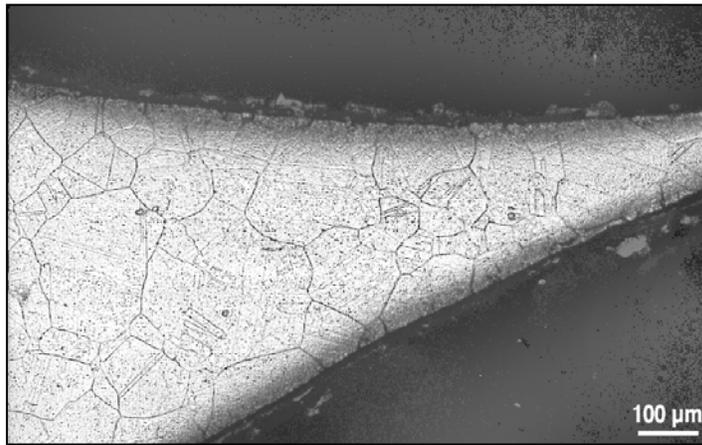
Figure 12.  Micrograph of support ring cross section showing thick corrosion product.
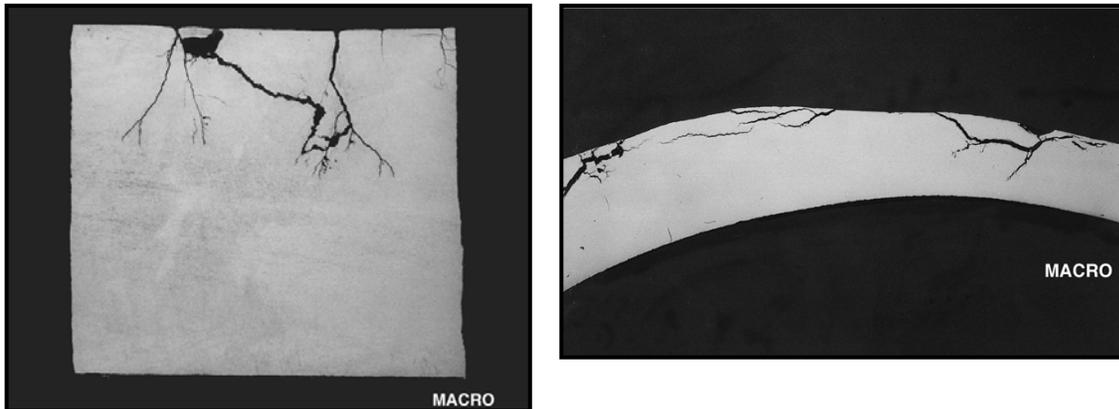


Figure 13.  Examples of cracking found on portions of the water-cooled stainless steel support ring.



Figure 14.  Cracking pattern revealed by dye penetrant examination of the inner surface of approximately 40x40 cm panel removed from the stainless steel gasifier shell.  Note that lower right corner was not inspected.
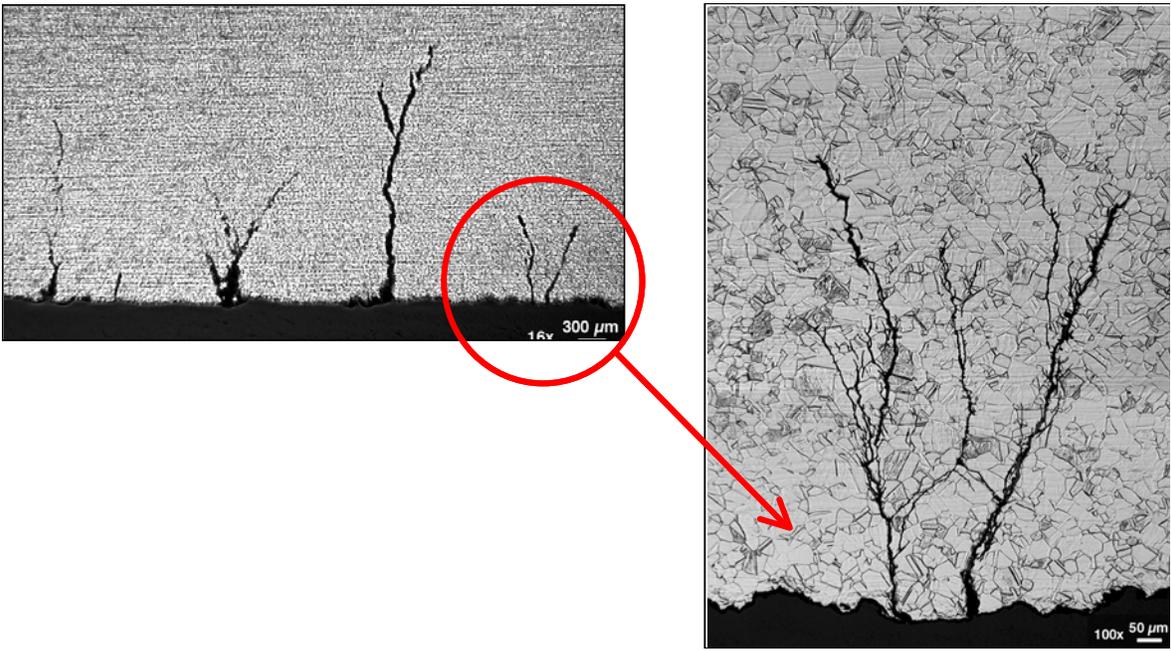
Figure 15.  Examples of the narrow, transgranular, branched cracking found on the gasifier shell.
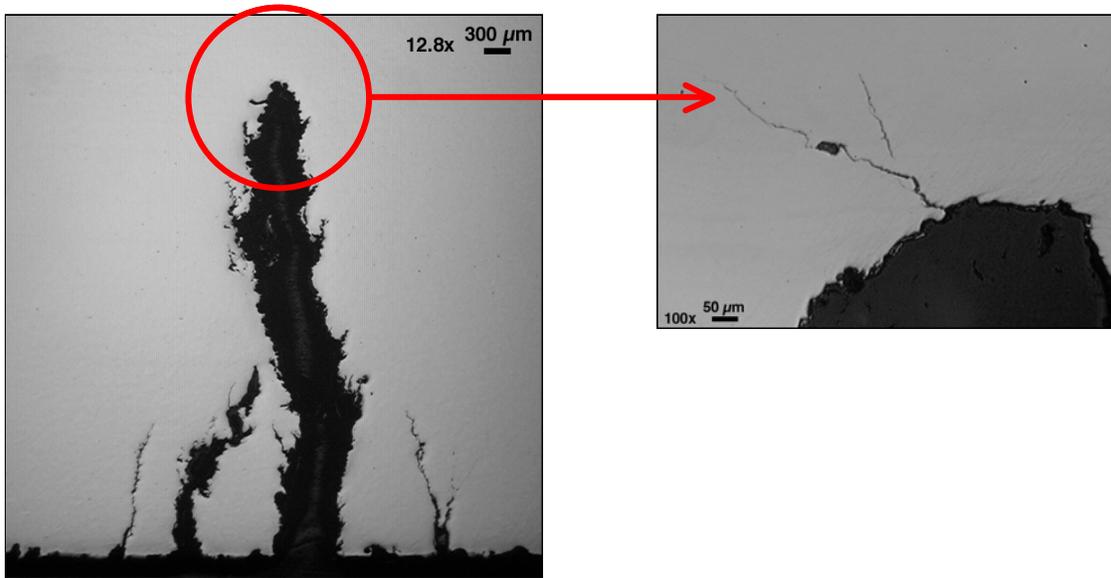


Figure 16.  Cracks revealed in the stainless steel gasifier shell.  Note that the primary crack on the left appears to have been mechanically deformed causing the sides to separate.
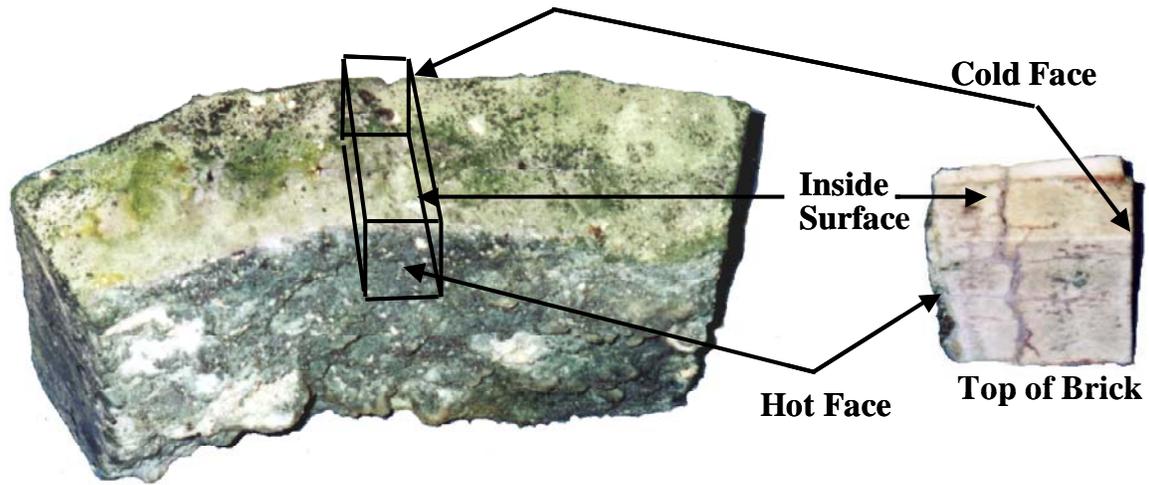
Figure 17. Refractory brick removed from the Skoghall HTHP gasifier and provided for analysis of degradation products.
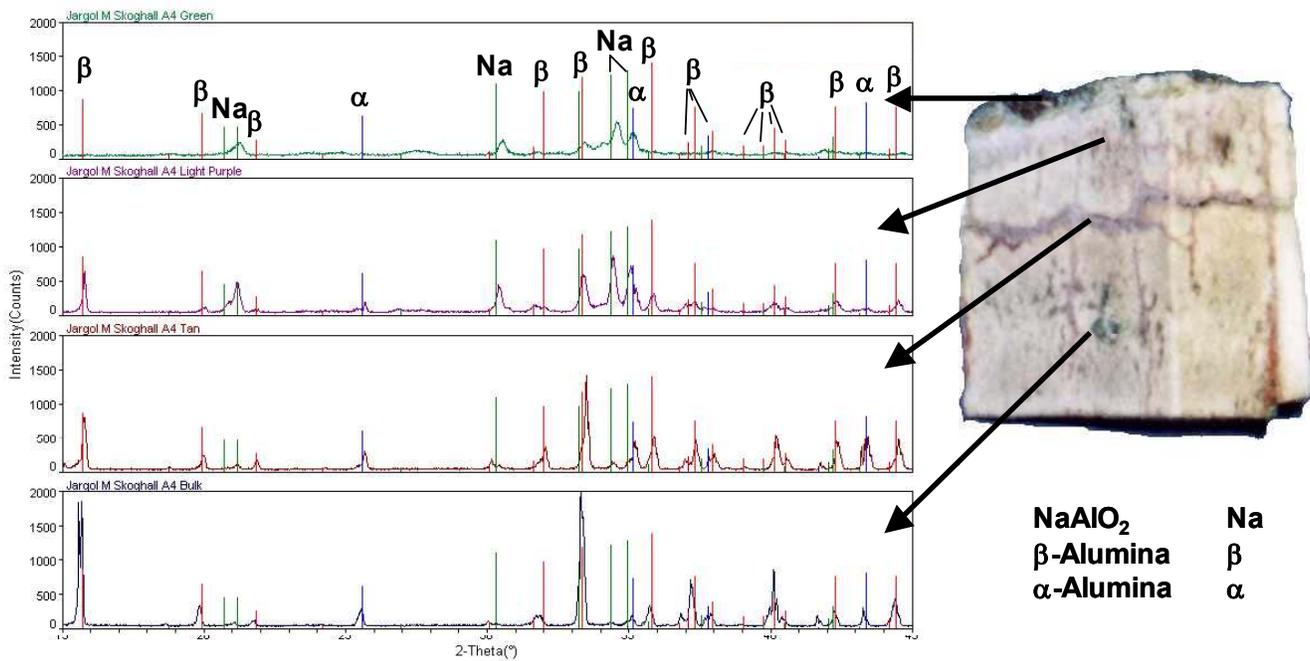


Figure 18. XRD patterns showing that NaAlO$_2$ was formed on the refractory surface.

Figure 19.  Schematic showing immersion text system.



Figure 20. XRD patterns for sample exposed in immersion test system showing $NaAlO_2$ formed on the surface (1000°C, 100 hrs).
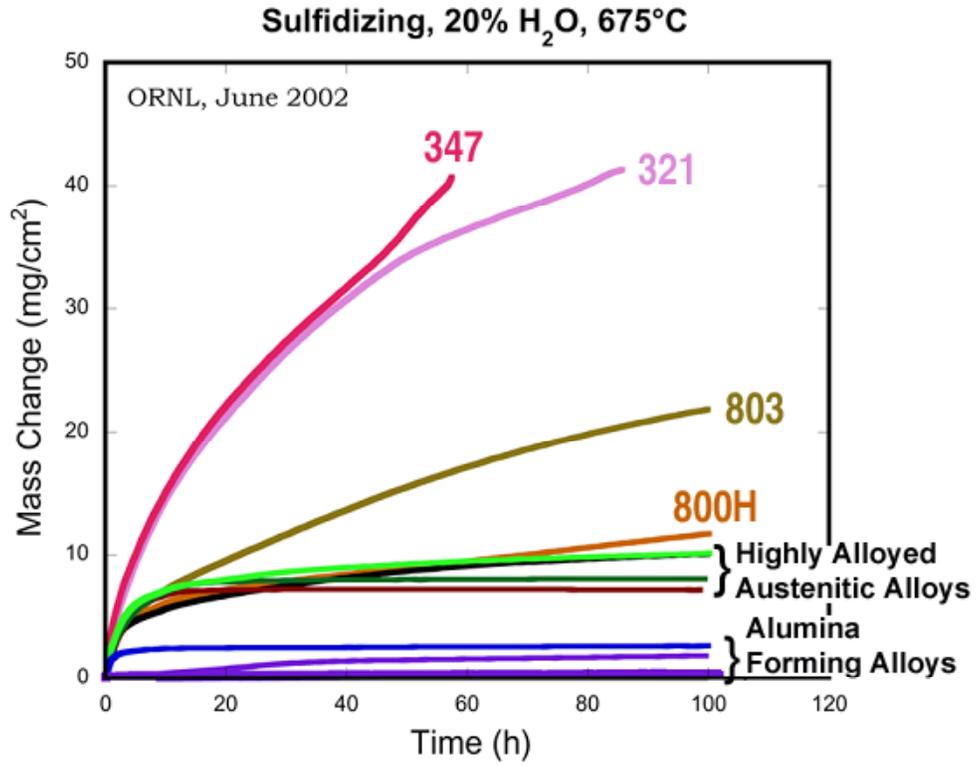
Figure 21. Mass change versus exposure time for samples tested in the simulated environment of a reformer gasifier operating at a sulfite mill.