PERFORMANCE OF MATERIALS IN BLACK LIQUOR GASIFICATION ENVIRONMENTS

James R. Keiser, Roberta A. Peascoe, James G. Hemrick,
Camden R. Hubbard, Peter F. Tortorelli and Bruce A. Pint
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6156
keiserjr@ornl.gov

ABSTRACT

Black liquor gasification systems have the potential to replace black liquor recovery boilers because of their increased energy efficiency, reduced emission of pollutants and inherently safer designs. However, there are significant problems that must be addressed, not the least of which is the selection of suitable materials for containment of the processes associated with gasification. There are two systems that are considerably ahead of all others in terms of development efforts and commercialization: a low-temperature process that operates below the melting point of the salts and one that operates well above it. Descriptions of both systems and the operating environments are presented, as well as a summary of the performance of materials in these systems. Laboratory studies that simulate the gasifier environments are currently underway, and initial results of these studies indicate there are significant materials issues to be resolved. Predictions of corrosion rate have also been made using proprietary software, and results of these projections are summarized.

Keywords: Black liquor, black liquor gasification, low temperature black liquor gasification, high temperature black liquor gasification, oxidation, sulfidation

INTRODUCTION AND BACKGROUND

In North America, the kraft process is the predominant chemical method used to separate the wood fibers in the pulping stage of papermaking. Black liquor, which is a by-product of this pulping process, is an aqueous solution containing both organic and inorganic material. The organic material is derived from the unused portion of the wood and is generally recovered and burned in the recovery boiler to produce heat and steam. The inorganic material is a result of the reaction between the pulping chemicals (sodium sulfide and sodium hydroxide) and the wood. The goal of the chemical recovery process in kraft mills is to regenerate these pulping chemicals. The combustion of the organic material and recovery of the chemicals are accomplished in a black liquor recovery boiler, but there are many shortcomings to this approach. These boilers are relatively inefficient with respect to production of steam and power, have relatively high pollutant emission levels and present safety issues associated with the molten salt produced in the boiler. Black liquor gasification offers an alternative to recovery boilers, and a recent publication indicated that there are energy and financial benefits to be gained by switching to gasification of black liquor.[1] In addition to the kraft process, two less frequently used pulping processes, known as the "semi-chem process" and the "sulfite process", produce waste streams that can be gasified in the same fashion as the kraft black liquor. The most significant difference is the sulfur content of the liquor: that from the semi-chem process has small or negligible amounts while liquor from the sulfite process contains about twice the sulfur of kraft liquor.

Two black liquor gasification processes have been developed to the extent that a number of pilot and/or demonstration scale units have been or are being built. These two processes are fundamentally different. In the low temperature process developed by Manufacturing and Technology Conversion International, Inc. of Baltimore, MD,[2] steam reforming occurs in a fluidized bed where the temperature is currently limited to about 605°C. By keeping the temperature at or below this point, the alkali salts remain as solids rather than melting and forming a liquid phase that can attack the structural components as well as form dense plugs in the reformer/gasifier vessel. In the high temperature gasification process developed by Chemrec AB, Stockholm, Sweden,[3] the temperature of the process is maintained well above the melting point of the salt. As a result of the higher temperature operation, gasification reactions occur at a much higher rate, but a molten salt phase is formed and has to be contained.

One issue that affects both gasification processes is an increase in the amount of sodium carbonate that must be processed. When sulfur is removed from the gasifiers as hydrogen sulfide, the sodium that had been associated with the sulfur as sodium sulfide or sulfate is converted into sodium carbonate. This significantly increases the load on the lime kiln and associated process equipment. There are chemical processes currently being investigated that would address this causticization issue.[4] At least one of these processes would increase the melting point of the salts so that the low temperature reformer/gasifier could operate about 100 C° hotter, thus significantly improving the reaction kinetics.[5]

Both gasification processes have some very favorable attributes, but further development and implementation could be limited because of a common problem: containment materials. In a previous paper, the material issues of each process were described, and some examples of the active degradation mechanisms were given.[6] Since that paper was written, a number of laboratory studies have been initiated and some degraded gasifier components have been examined. This paper will provide a brief description of the two processes and it will review some of these recent studies.

Low-Temperature Black Liquor Gasification

Steam reforming of the black liquor is key to the low temperature process. In this process, the temperature is kept low enough that the alkali salts, commonly referred to as smelt, does not become molten or even reach the point where it becomes "sticky". A typical reformer/gasifier system is shown in Fig. 1. 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 (each containing hundreds of tubes) that carry hot combustion gas. The hot gas is produced in the refractory lined combustion chambers where the fuel, either "clean" 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 paper mill in New Bern, North Carolina. This unit successfully completed a continuous 500 h run on black liquor during August, 1995.[2] Currently, full-scale reformer/gasifier facilities are under construction at mills in Big Island, Virginia, and in Trenton, Ontario. Neither of these mills operates on the kraft process; they utilize the semi-chemical sodium carbonate cooking process for treating the wood chips, so the absence of significant amounts of 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.

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 generally 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 diagram of the high-temperature, low-pressure (HTLP) gasifier is shown in Fig. 2. In this refractory-lined vessel, the black liquor fuel, steam and air for partial combustion of the liquor 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 removed through 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.[7] A 330 tds/day gasifier of this type was put into service in 1996 at the mill in New Bern, North Carolina;[8] it was taken out of operation in December, 1999 because of problems with the structural materials. Operation of the New Bern gasifier resumed near the end of June, 2003.

High-temperature, high-pressure gasification. There is limited experience with high-temperature, high-pressure (HTHP) black liquor gasification. A 10 tds/day pilot scale unit was operated in Sweden from 1994 through 2000.[9] 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 about 1000 h of operation was accumulated on black liquor feed while the system operated for a considerably longer time on fuel oil. Samples of refractory liner from this system have been examined.[6] A limited amount of refractory degradation was observed and this was consistent with that subsequently seen in refractory removed from the New Bern gasifier.[6]

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. 2 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. 3) and circulates 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 HTHP demonstration scale unit is under construction in the town of Piteå in northern Sweden. Operation is not expected to begin before summer 2004. Both the thick refractory lining and the cooling screen designs will be tested.

OPERATING CONDITIONS AND MATERIAL CHOICES

Low-Temperature, Black Liquor Gasification

The low-temperature black liquor steam reformer/gasifier presents a range of conditions for which materials have to be selected. The highest temperature region is the pulse-combustion chamber where temperatures are expected to reach 1300-1500°C. The carbon steel chamber is lined with refractory insulation in order to contain the hot combustion gases. The refractory being used in at least one of the systems under construction is a high-alumina extra-low cement pumpable castable that contains 60% Al_2O_3, 36.3% SiO_2, 0.6% CaO and 1.6% TiO_2. If the product gas is used as fuel for the combustor and if problems were to develop in the gas clean-up system, contaminants in the fuel could be detrimental to the refractory. Designers of future systems will have to determine whether to consider the possibility of fuel contaminants when the refractory material is being selected for systems processing black liquor containing a significant amount of sulfur compounds.

It is expected that about 90% of the combustion will occur in the combustion chamber, while the remaining fuel is burned in the first section of the bed tubes. In order to prevent heat generated during this last stage of combustion from raising the bed tube temperature above the sodium carbonate melting point, a short length of tube, called a shield tube, is used inside the first portion of each bed tube. This shield tube should be fabricated from a material with sufficient corrosion resistance to survive in the hot combustion gas that includes oxygen, moisture, and possibly contaminants from the fuel. Materials being utilized in the systems under construction include high-chromium content stainless steels or more highly-alloyed “super” stainless steels like N08330 and N08810.

The pulsed-heater tubes that provide heat to the bed are exposed to hot combustion gases on the inside and the product gas and bed material on the outside. As with the shield tubes, the insides of the bed tubes are exposed to an atmosphere containing oxygen, moisture and possible contaminants, but at a lower temperature than experienced by the shield tubes. The outside of the bed tubes is exposed to an atmosphere that contains hydrogen, moisture, carbon monoxide and carbon dioxide at a temperature of about 605°C. If the liquor being processed is from a kraft or sulfite mill, significant amounts of hydrogen sulfide will also be present in the reformer atmosphere, and this will appreciably increase the aggressiveness of the environment. For a gasifier/reformer processing liquor from a semi-chem process mill, the bed atmosphere is expected to be sufficiently benign that a stabilized stainless steel like types S32100 or S34700 should provide adequate corrosion resistance. Because the operating temperature is in the range where sensitization could occur, it is essential to use an alloy that will not become susceptible to intergranular attack. When liquor from a kraft or sulfite mill is processed, the hydrogen sulfide in the environment will require the bed tubes to have significantly greater corrosion resistance. Thermodynamic calculations suggest that alloys exposed to this environment should have no more than a limited amount of nickel (probably <15%) and sufficient chromium and/or aluminum to form a surface oxide that provides adequate resistance to sulfur penetration. The mechanical motion of the sodium carbonate bed particles on the bed tubes could accelerate degradation by damaging or removing protective scales, but no data exist on the effects of long-term exposures on tubes to this environment.

The carbon steel or low-alloy reformer/gasifier vessel is lined with refractory to provide protection from thermal, chemical, and mechanical effects of the bed environment. Different refractories are used in the bed area and the freeboard area. In one of the systems currently under construction, refractories for both areas are nominally 44-45% Al_2O_3, 38% SiO_2, 13-14%

CaO and 0.2-0.4% MgO. However, the bed refractory has a crush strength at 815°C that is about six times that used in the freeboard area [56.9 vs 8.3 MPa (8,250 vs 1,200 psi)].

High-Temperature Black Liquor Gasification

As noted previously, the high-temperature gasification process can be operated near atmospheric pressure or at significantly elevated pressure. Furthermore, there are two designs being considered for the elevated-pressure version. Consequently, there are several environments that have to be considered in identifying suitable materials for high-temperature black liquor gasifiers.

High-temperature, low-pressure gasification. The design currently used for the single existing gasifier of this type, as well as that expected to be used in any future gasifiers of this kind, has a thick refractory brick lining inside a metal shell. As shown in Fig. 2, this is a cylindrical vessel and the refractory bricks have to be fabricated to form the conical shape at the bottom, the cylindrical section in the midsection, and the dome at the top of the gasifier vessel. The refractory initially used for the lining was a bonded alumina-silica brick.[10] This material showed unacceptably rapid degradation, so a replacement of fusion-cast alpha/beta alumina was installed. This material degraded less rapidly, but the rate was still unacceptably high. The shell of the gasifier was originally constructed of 316L stainless steel, but extensive cracking developed because of chloride stress corrosion. Carbon steel was used for the replacement shell that is currently in use. When the gasifier was restarted in late June, fusion-cast alpha/beta alumina from an alternate manufacturer was installed.

High-temperature, high-pressure gasification. As noted previously, there are two designs being evaluated for the high-pressure gasifier; a solid refractory brick lining and the cooling screen design. There is very limited experience with high-pressure gasification; the Swedish pilot-scale system utilized a refractory brick lining made of fusion-cast, alpha/beta alumina. The cumulative operating time on black liquor was limited to about six weeks, but chemical phases were identified on the refractory surface that were the same as the degradation products found on the fusion cast alpha/beta alumina exposed in the New Bern low pressure gasifier. As with the low pressure gasifier, less expensive and/or longer life refractories will be required if this gasifier design is to be successfully commercialized.

The cooling screen concept has been successfully employed in coal gasification, but there is essentially no experience with this design in black liquor gasification. In addition to finding a refractory that has the appropriate thermal conductivity and corrosion resistance, the refractory will need to have a coefficient of thermal expansion such that it will remain in good thermal contact with the helically-coiled, metallic tube to which it is applied.

EXPERIMENTAL STUDIES

Low-Temperature Black Liquor Gasification

Studies are underway to assess the corrosion resistance of selected alloys in environments characteristic of those in low temperature gasifiers. Specifically, laboratory tests are being conducted at temperatures and in oxygen and sulfur partial pressures expected for 1) the bed tubes in a reformer/gasifier that is processing kraft black liquor, 2) the bed tubes in a reformer/gasifier processing sulfite black liquor, 3) the shield tubes in a reformer/gasifier operating in a mill where fuel contaminants are minimal and 4) the bed tubes in a reformer/gasifier processing kraft black liquor where the temperature is 100 C° higher as a result of the switch to one of the alternate processes involving the use of titanates.[4] Identification and composition of alloys used in corrosion studies and in corrosion rate calculations are given in Table 1.

Results of the first 200 h of corrosion tests of alternate bed tube materials in the gas expected in a reformer/gasifier processing kraft black liquor are summarized in Table 2 and shown graphically in Fig. 4, and they reveal that some of the commonly used alloys experience significant rates of degradation. Another test providing important results is evaluating potential shield tube materials at 1000 and 1100°C in oxidizing environments that are cooled to room temperature every 100 or 500 h. The results, presented in Fig. 5, suggest that most chromia-forming alloys, like those being used in the systems under construction, may experience considerable corrosion if the tests with some thermal cycling give a representative indication of the corrosion that will be experienced in the actual systems.

High-Temperature Black Liquor Gasification

High-temperature, low-pressure black liquor gasification. A laboratory test system has been constructed that successfully reproduces the corrosion products observed to form on refractories that were exposed in operating gasifiers.[6,11] Using this system, extensive laboratory studies have been conducted to evaluate the resistance of a large number of refractories to degradation by the molten salt collected from a black liquor recovery boiler. These studies have shown that certain surface treatments can be used to improve the resistance of a number of refractories to molten smelt. Improved corrosion resistance can result from creation of a surface layer by reaction with an added material to form a new phase, or it can be the result of chemical or microstructural modifications of the surface, made before exposure. An example of the improvement in corrosion resistance as a result of modifications that form a new phase are shown in Fig. 6. The photo on the left side shows a cross-section of a mullite-based refractory after immersion in molten smelt at 1000°C for 50 h.[12] The dark material around the outside of the sample is the corrosion product from reaction of the refractory with the smelt. The photo on the right shows a cross-section of the same refractory that had been treated with Li_2O_3 followed by a heat treatment prior to exposure in molten smelt under the same conditions. The reaction of the lithium compound with the alumina and/or silica in the refractory formed a glassy surface layer that improved the resistance of the refractory to smelt penetration.

Studies of fusion-cast refractories have shown that the as-cast surface can promote or inhibit penetration of smelt.[12] Figure 7 shows a cross-section of such a refractory where the surface along the upper side of the photo is as-cast, while the other three sides have been ground to fabricate the sample. The image on the right gives an indication of the composition of the refractory after exposure at 1000°C for 100 h in molten smelt. It is clear that in this case, penetration of smelt components proceeds more rapidly through the as-cast surface than through the ground surfaces. The fusion-cast refractory shown in Fig. 8 which also has the as-cast surface along the upper side of the photo, showed the opposite effect. As indicated by the darkening in the photo on the left and by the elemental maps in the image on the right, in this refractory smelt components penetrated much more rapidly through the ground surfaces than through the as-cast surface. Studies have shown there are significant compositional and microstructural differences between the as-cast surfaces and the bulk material in each of these two refractory samples, and work is in progress to reproduce these phenomena in a controlled way.

In addition to the examples just described, characterization studies are underway on samples of a bonded refractory that has an intercrystalline phase that appears to have unusually good resistance to molten smelt and on samples of several refractories that have had their surfaces treated with a high-intensity plasma-arc lamp. In both cases, improved resistance to penetration by sodium and sulfur has been observed in laboratory immersion tests.

To complement the refractory corrosion tests, studies in molten salts have been conducted on a series of high-chromium alloys being developed specifically for their resistance to the sodium salts. Studies show that these alloys have resistance to smelt degradation that is significantly better than that of a nominal 50% Cr-50% Ni alloy that is similar to materials that have been used in molten smelt service.[13] Currently, a sample of one of the high-chromium content alloys is being exposed in the New Bern gasifier.

High-temperature, high-pressure black liquor gasifier. There is an apparent absence of experimental data on the stability of refractory and metallic materials in molten smelt at high pressures. It is expected that the refractory studies being conducted for the HTLP gasifier will have some relevance to HTHP gasifiers. However, since the effect of pressure on the thermodynamic equilibrium and reaction kinetics is not known for the reaction of smelt with refractory and metallic materials, some caution has to be used in applying the results of near-atmospheric pressure corrosion studies to elevated pressure.

CORROSION RATE PREDICTIONS

Low-Temperature Black Liquor Gasification

As another means to provide some guidance in the selection of metallic materials for the new gasifier systems, software designed for alloy selection for service at elevated temperature (ASSET)[14] has been used. This software utilizes an extensive data base that was compiled from a large number of corrosion studies of commercial alloys. The software can predict corrosion rates as a function of temperature as well as the partial pressures of oxygen and sulfur in gaseous environments considered to be oxidizing or oxidizing-sulfidizing. This has been particularly useful for the low-temperature reformer/gasifier where the primary corrodents are gaseous species rather than liquid as is the case for the high-temperature systems. Unfortunately not all alloys that should be considered for this application are included in the data base, so that alloys of similar composition are used to get an estimate for the corrosion rate of some alloys.

There are some considerations that have to be addressed when using these calculated corrosion rates to make an alloy recommendation. First, where the equilibrium calculations made by ASSET indicate the formation of a molten phase, any predicted corrosion rages are flagged as not valid. This is particularly relevant for exposure of some of the high-nickel content alloys in a sulfidizing environment above about 660°C. Other issues that have to be considered in making an alloy selection are the properties (particularly strength) at service temperature, the alloy's fabricability, the capability of the alloy to be welded and the availability of the alloy in the desired product form.

Corrosion rate predictions have been made for 1) the screen tubes in the high temperature combustion gas environment, 2) bed tubes in the product gas from reforming of kraft black liquor at 605°C (tube temperature assumed to be 675°C), 3) bed tubes in the product gas from reforming of kraft black liquor at 705°C (tube temperature assumed to be 775°C), and 4) bed tubes in the product gas from reforming of sulfite mill black liquor.

Examples of the corrosion rates predicted for the high-temperature, oxidizing, combustion gas environment are shown in Table 3. It should be noted that the large error bars associated with some of these predicted corrosion rates result from the fact that the corrosion database considers the maximum depth of corrosion penetration, which can vary considerably among alloys. These results indicate that an alumina-former or a fairly highly alloyed chromia-forming material should be considered for the shield tubes, particularly since corrosion will occur on both sides of the tubes. In fact, the volatility of chromia at the anticipated combustion gas temperatures could make use of chromia-forming alloys questionable.

The calculated corrosion rates for bed tubes in a reformer operating on kraft liquor (sulfidizing/oxidizing environment) at a nominal temperature of 605°C are given in Table 4. These results suggest that S32100 stainless steel that is appropriate for a semi-chem process liquor may also have adequate corrosion resistance for kraft liquor at 675°C. However, the issue of strength at operating conditions would be a major concern. It is important to note that the predicted corrosion rates for higher nickel-content alloys were high.

Table 5 lists the predicted corrosion rates for bed tubes in a reformer operating on kraft liquor (sulfidizing/oxidizing environment) but at a temperature of 775°C. For this application, an alloy that forms an alumina scale, or more highly-alloyed materials, will be required than for the similar conditions at a lower temperature. Many of the nickel-base alloys that might normally be suggested for a harsh environment at this temperature are not suitable because they would form a liquid sulfide product under these conditions. The alloys that would be expected to form a low-melting nickel sulfide are indicated by an asterisk in the table.

The corrosion rates calculated for the environment that would be present in a reformer processing sulfite liquor (sulfidizing/oxidizing environment) are shown in Table 6. These results show the higher-sulfur concentration makes this a very harsh environment. Because the tube temperature will be very near the melting point of nickel sulfide, the higher nickel-content alloys shown in Tables 4 and 6 could be susceptible to rapid degradation. As the results indicate, there will be some problems in finding an affordable alloy that has sufficient corrosion resistance and can be welded and fabricated into the required forms.

High-Temperature Black Liquor Gasification

Corrosion rate calculations have not been made for the high-temperature gasifier systems since there would be very few metallic components exposed to the molten smelt, and data bases for corrosion by molten salts are not very extensive for these environmental conditions.

SUMMARY AND CONCLUSIONS

There are two significantly different processes being developed for the gasification of black liquor. One process operates below the melting point of the inorganic constituents, while the second process operates well above it. Both processes share the common problem of finding suitable containment materials.

For the low-temperature reformer/gasifier systems currently under construction at the mills operating on the semi-chem process, the bed tubes are constructed of S32100 stainless steel, while N08810 and N08330 stainless steel are being used for the shield tubes. Laboratory studies suggest that the combustion gas temperature experienced by the shield tubes could severely degrade the alloys being used, and alloys designed for higher temperature service, such as the alumina-forming alloys, may be required in subsequent installations. For the bed tubes, the environment developed during processing of liquor from a semi-chem mill will be relatively benign, while the sulfur contained in the liquor from kraft and sulfite mills will require consideration of alloys more corrosion resistant than S32100 stainless steel.

Refractories are the major structural component in a high-temperature, low-pressure gasifier and there are serious compatibility issues between the molten inorganic salts and the refractory bricks. The fusion-cast alumina bricks currently in use provide improved performance over the bonded mullite bricks initially used, but further improvements in the refractories are needed in order to improve the economics of the gasifier. Refractories that are more corrosion resistant have been identified in laboratory tests, but further studies will be needed to show their resistance in an operating gasifier, as well as to establish if they can be produced commercially.

The high-temperature, high-pressure gasifier will place severe demands on the refractory materials whether the refractories are in the form of monolithic bricks or as a coating on the helically coiled metal tube that forms the gasifier screen.

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TABLE 1

Identification and composition of alloys used in corrosion studies.

UNS Number	Alloy Identification	Ni	Cr	Fe	Al	Si	C	Other
N06025	602 CA	63	25	9	2.2		0.18	0.08 Y, 0.08 Zr
N06045	45 TM	46	27	23		2.8	0.09	
N06230	230	60	22	1	0.3	0.4	0.10	0.02 La, 0.004 B
N07214	214	76	16	3.5	4.5		0.04	0.03 Zr, 0.005 Y
N08120	HR 120	37	25	35	0.1	0.6	0.05	0.7 Nb, 0.1 Ti, 0.004 B
N08330	330 SS	35	19	43		1.2	0.05	
N08810	800H	31	21	45	0.3	0.4	0.06	0.4 Ti
N12160	HR 160	36	28	2		2.8	0.05	30 Co, 0.5 Ti, 0.5 Mn
R30556	Haynes 556	21	22	29	0.3		0.1	18 Co, 2.5 W, 0.2 N, 0.02 La, 0.6 Ta
S30815	253 MA	11	21	65		1.7	0.08	0.17 N, 0.04 Ce
S31008	310 SS	20	25	52		0.5	0.05	
S32100	321 SS	9	17	70		0.7	0.01	0.2 Ti
S34700	347 SS	9.5	17	70		0.7	0.04	0.5 Nb
S35315	353 MA	35	25	36		1.2	0.05	0.16 N, 0.05 Ce
S67956	MA956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3
--	Incoloy DS	37	17	44		2.3	0.06	

TABLE 2
Mass change after two100 h cycles of selected alloys at 675°C in a steam reformer environment during reforming/gasification of kraft black liquor

UNS Number	Ni	Cr	Fe	Al	Si	C	Other	Mass Gain (mg)
N06025	63	25	9	2.2		0.18	0.08 Y, 0.08 Zr	0.77
N06045	46	27	23		2.8	0.09		3.75
R30556	21	22	29	0.3		0.1	18 Co, 2.5 W, 0.6 Ta, 0.02 La	7.91
S35315	35	25	36		1.2	0.05	0.16 N, 0.05 Ce	4.81
N08120	37	25	35	0.1	0.6	0.05	0.7 Nb, 0.1 Ti, 0.004 B	6.42
N12160	36	28	2		2.8	0.05	30 Co, 0.5 Ti	3.72
S67956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3	2.10
N08810	31	21	45	0.3	0.4	0.06	0.4 Ti	38.4
N08330	35	19	43		1.2	0.05		14.3
S32100	9	17	70		0.7	0.01	0.2 Ti	9.65
N07214	76	16	3.5	4.5		0.04	0.03 Zr, 0.005 Y	**

** Large scale build-up; some material lost in removing sample from holder

TABLE 3
Calculated corrosion rates for alloys exposed in the combustion gas (shield tube) environment of a low-temperature reformer/gasifier at 1100°C.

Alloy UNS Number	Ni	Cr	Fe	Al	Si	C	Other	Corrosion Rate (mm/yr) 8800 h	18000 h
S67956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3	0.03 ± 0.18	0.04 ± 0.26
R30556	21	22	29	0.3		0.1	18 Co, 0.02 La	0.30 ± 0.16	0.42 ± 0.24
N07214	76	16	3.5	4.5		0.04	0.03 Zr, 0.005 Y	0.33 ± 0.31	0.47 ± 0.44
N06025	63	25	9	2.2		0.18	0.08 Y, 0.08 Zr	0.34 ± 15.7	0.48 ± 22.4
S30815	11	21	65		1.7	0.08	0.17 N, 0.04 Ce	0.34 ± 0.55	0.49 ± 0.79
N06230	60	22	1	0.3	0.4	0.10	14 W, 0.02 La	0.47 ± 0.20	0.67 ± 0.29
S31008	20	25	52		0.5	0.05		0.69 ± 0.35	0.99 ± 0.50
N12160	36	28	2		2.8	0.05	30 Co, 0.5 Ti	0.98 ± 0.52	1.41 ± 0.75
N08810	31	21	45	0.3	0.4	0.06	0.4 Ti	1.11 ± 0.69	1.59 ± 0.99
S32100	9	17	70		0.7	0.01	0.2 Ti	1.55 ± 2.07	2.21 ± 2.95
S34700	9.5	17	70		0.7	0.04	0.5 Nb	2.01 ± 8.35	2.88 ± 11.9

TABLE 4
Calculated corrosion rates for alloys exposed as bed tubes in the product gas from reforming of kraft black liquor at 605°C (tube temperature assumed to be 675°C).

Alloy UNS Number	Ni	Cr	Fe	Al	Si	C	Other	Corrosion Rate (mm/yr) 8800 h	18000 h
S67956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3	0.02 ± 0.24	0.03 ± 0.34
S34700	9.5	17	70		0.7	0.04	0.5 Nb	0.07 ± 0.30	0.10 ± 0.41
S31008	20	25	52		0.5	0.05		0.12 ± 0.12	0.18 ± 0.18
N12160	36	28	2		2.8	0.05	30 Co, o.5 Ti	0.13 ± 1.10	0.18 ± 1.59
N08120	37	25	35	0.1	0.6	0.05	0.7 Nb, 0.1 Ti	0.15 ± 0.17	0.21 ± 0.24
S30815	11	21	65		1.7	0.08	0.17 N, 0.04 Ce	0.16 ± 0.29	0.22 ± 0.42
N08810	31	21	45	0.3	0.4	0.06	0.4 Ti	0.18 ± 0.14	0.26 ± 0.19
N06025	63	25	9	2.2		0.18	0.08 Zr, 0.08 Y	0.46 ± 0.21	0.65 ± 0.30
R30556	21	22	29	0.3		0.1	18 Co, 0.02 La	0.56 ± 0.69	0.79 ± 0.98
N07214	76	16	3.5	4.5		0.04	0.03 Zr, 0.005 Y	2.70 ± 0.94	3.90 ± 1.30

TABLE 5

Calculated corrosion rates for alloys exposed as bed tubes in the product gas from reforming of kraft black liquor at 705°C (tube temperature assumed to be 775°C).

Alloy UNS Number	Ni	Cr	Fe	Al	Si	C	Other	Corrosion Rate (mm/yr) 8800 h	18000 h
S67956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3	0.02 ± 0.27	0.03 ± 0.40
S34700	9.5	17	70		0.7	0.04	0.5 Nb	0.15 ± 0.64	0.22 ± 0.92
S31008 *	20	25	52		0.5	0.05		0.26 ± 0.26	0.38 ± 0.38
N08120 *	37	25	35	0.1	0.6	0.05	0.7 Nb, 0.1 Ti	0.27 ± 0.30	0.38 ± 0.43
N12160 *	36	28	2		2.8	0.05	30 Co, 0.5 Ti	0.28 ± 2.47	0.40 ± 3.53
S30815	11	21	65		1.7	0.08	0.17 N, 0.04 Ce	0.32 ± 0.60	0.46 ± 0.86
N08810 *	31	21	45	0.3	0.4	0.06	0.4 Ti	0.33 ± 0.24	0.47 ± 0.34
R30556 *	21	22	29	0.3		0.1	18 Co, 0.02 La	0.56 ± 0.69	0.86 ± 0.99
N07214 *	76	16	3.5	4.5		0.04	0.03 Zr, 0.005 Y	2.79 ± 0.97	3.99 ± 1.38
N06025 *	63	25	9	2.2		0.18	0.08 Zr, 0.08 Y	5.78 ± 2.67	8.27 ± 3.82

* Expected to form liquid sulfide at specified conditions.

TABLE 6

Calculated corrosion rates for alloys exposed as bed tubes in the product gas from reforming of sulfite liquor at 605°C (tube temperature assumed to be 675°C).

Alloy UNS Number	Ni	Cr	Fe	Al	Si	C	Other	Corrosion Rate (mm/yr) 8800 h	18000 h
S67956		20	74	4.5	0.1	0.02	0.5 Ti, 0.5 Y_2O_3	0.02 ± 0.20	0.03 ± 0.31
S34700	9.5	17	70		0.7	0.04	0.5 Nb	0.06 ± 0.30	0.09 ± 0.37
S31008	20	25	52		0.5	0.05		0.11 ± 0.11	0.16 ± 0.16
----	37	17	44		2.3	0.06		0.12 ± 0.54	0.18 ± 0.77
N12160	36	28	2		2.8	0.05	30 Co, 0.5 Ti	0.13 ± 1.10	0.18 ± 1.60
N08120	37	25	35	0.1	0.6	0.05	0.7 Nb, 0.1 Ti	0.14 ± 0.16	0.20 ± 0.22
S30815	11	21	65		1.7	0.08	0.17 N, 0.04 Ce	0.15 ± 0.28	0.21 ± 0.39
N08810	31	21	45	0.3	0.4	0.06	0.4 Ti	0.17 ± 0.13	0.25 ± 0.18
N06025	63	25	9	2.2		0.18	0.08 Zr, 0.08 Y	0.44 ± 0.21	0.63 ± 0.29
R30556	21	22	29	0.3		0.1	18 Co, 0.02 La	0.56 ± 0.70	0.81 ± 1.00

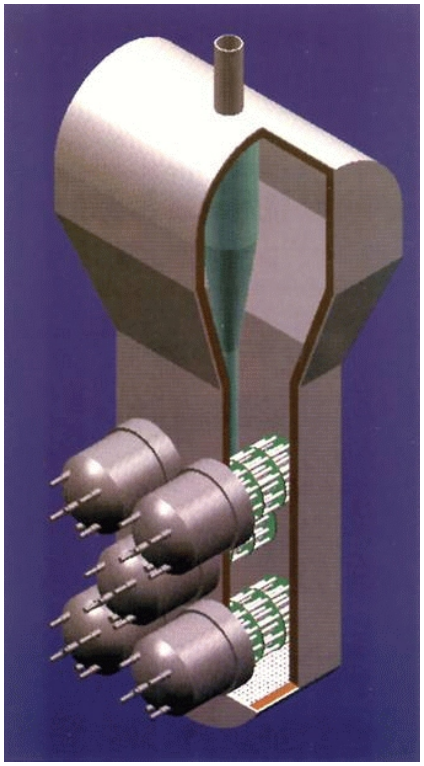

Figure 1. Schematic drawing of the low-temperature black liquor steam reformer/gasifier

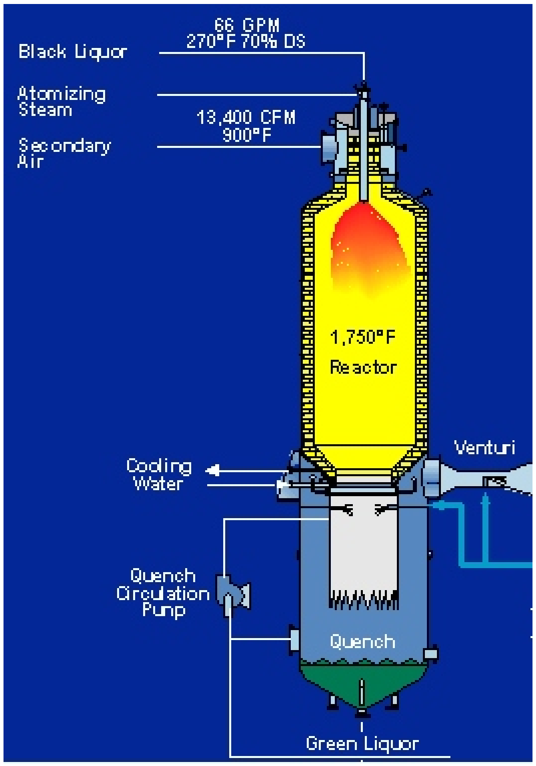

Figure 2. Schematic drawing of the reactor vessel of a high-temperature, low-pressure black liquor gasifier

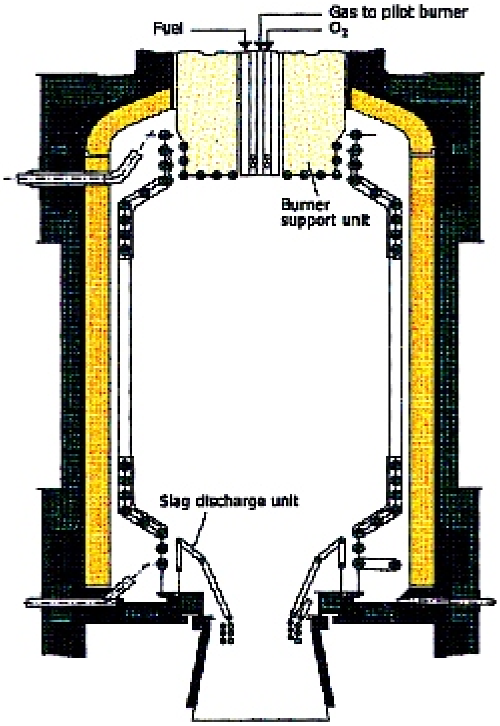

Figure 3. Schematic of cooling screen design of the high-temperature, high-pressure gasifier.

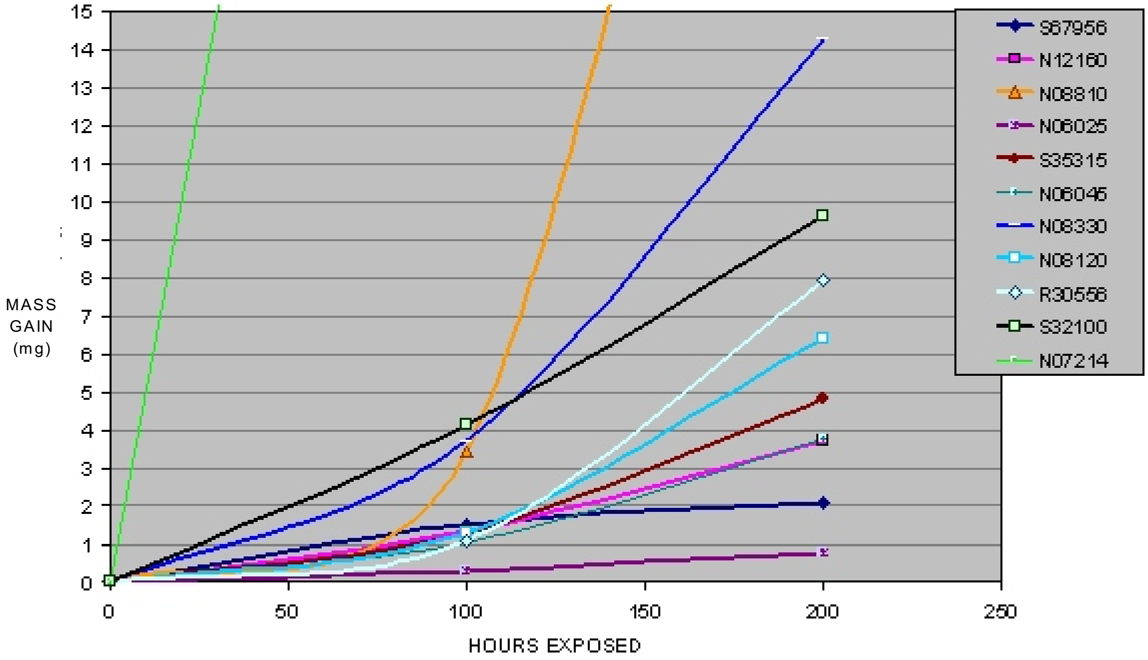

Figure 4. Mass change results for potential bed tube materials exposed at 675°C to a gaseous environment simulating the conditions of a steam reformer processing kraft liquor.

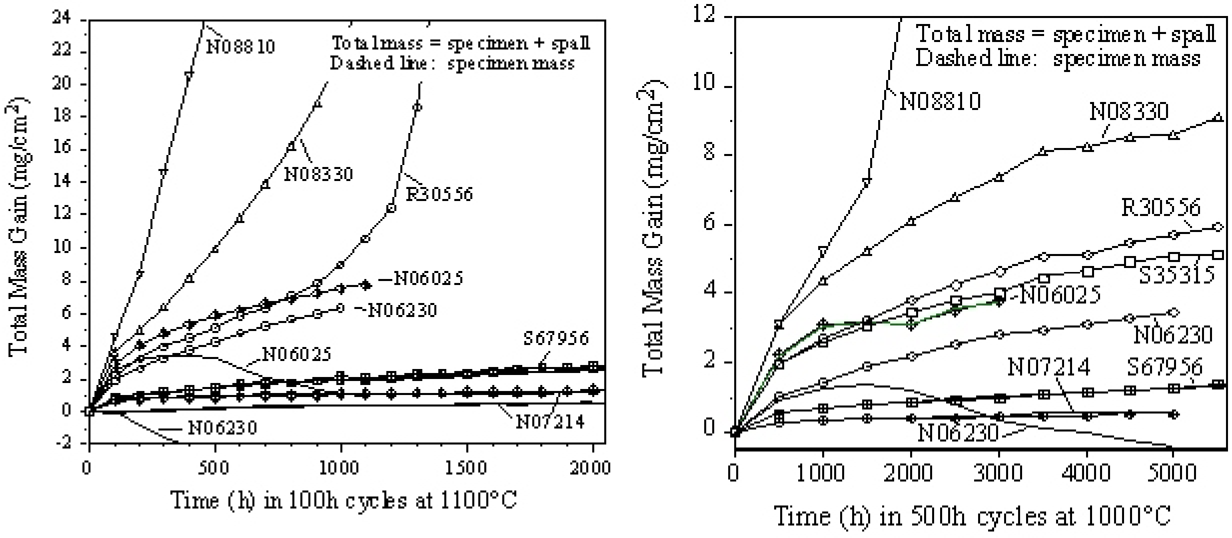

Figure 5. Weight change results for potential shield tube materials as a result of cyclic exposures to air at 1000 and 1100°C.

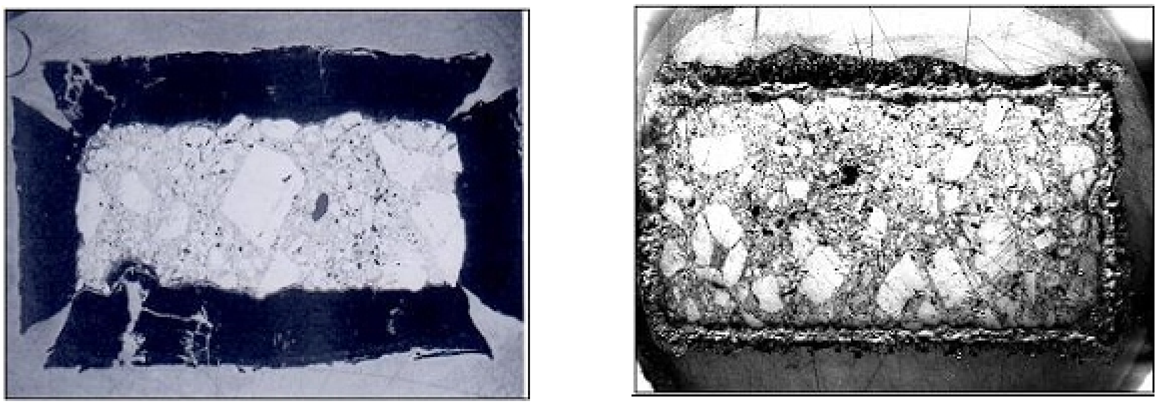

Figure 6. Cross-sections cut from a mullite based refractory after immersion testing in molten smelt for 50 h at 1000°C. The sample shown on the left was exposed in the untreated condition while the sample on the right had a Li_2CO_3 surface treatment.

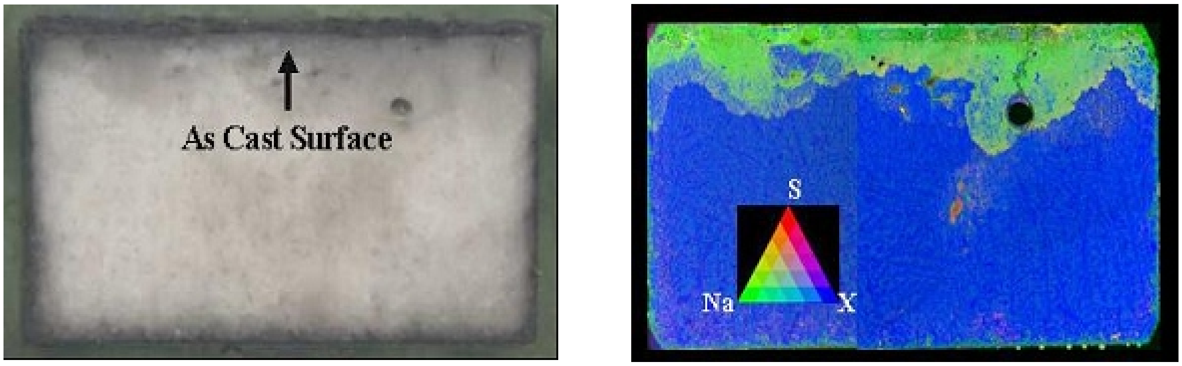

Figure 7. Cross-sections of fusion-cast refractory where the surface on the upper side is as-cast while the other three sides are ground. There is some darkening along the upper edge in the image on the left, and the EDS map on the right shows the greater amount of sodium and sulfur penetration through the as-cast side.

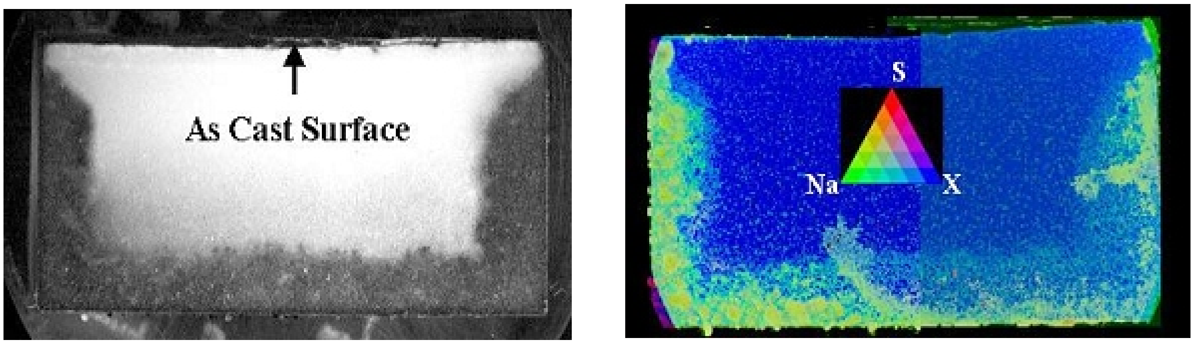

Figure 8. Cross-sections of fusion-cast refractory where the surface on the upper side is as-cast while the other three sides are ground. There is significant darkening along the three ground surfaces. The EDS map shows penetration of sulfur and sodium occurred primarily through the ground surfaces of this sample.