REFRACTORY TESTING AND EVALUATION AT OAK RIDGE NATIONAL LABORATORY FOR BLACK LIQUOR GASIFIER APPLICATIONS

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ABSTRACT

Work is on-going at Oak Ridge National Laboratory to evaluate refractory containment and smelt contact materials for black liquor gasification applications. Materials have been evaluated and selected for low temperature gasification processes, with a number of materials being installed in commercial units currently under construction. For high temperature low pressure gasification processes, efforts have focused on screening candidate lining materials through immersion testing, improving existing refractory performance through the application of surface treatments, and the installation and evaluation of samples in an operating gasifier in New Bern, NC. Efforts concerning high temperature high pressure gasification have involved the identification and testing of suitable refractory materials for the coating of a helical carbon steel cooling coil arrangement.

INTRODUCTION

Chemical recovery in kraft paper mills is used to regenerate the pulping chemicals (sodium sulfide and sodium hydroxide) used for separation of wood fibers for papermaking. Traditionally, this recovery has been performed using Thompson recovery boilers. However, these boilers suffer from many shortcomings including their relative inefficiency with respect to production of steam and power, their relatively high pollutant emission levels, and the inherent danger of boiler explosions due to leakage of pressurized water through breached tubes which then comes in contact with the molten salt bed (known as smelt) on the boiler floor. Black liquor gasification offers an attractive alternative technology to the Thompson recovery boiler with possible energy, environmental, and financial benefits; with energy benefits being substantially increased by operating the gasifier in a combined cycle mode [1, 2].

Current efforts to develop and industrially implement black liquor gasification have been limited by the lack of sufficient refractory and metallic containment materials which are in contact with smelt and exposed to the gasifier environment. Therefore, efforts have been undertaken at Oak Ridge National Laboratory (ORNL) to evaluate both refractory ceramic and metallic materials currently being used for black liquor gasification applications as part of the U.S. Department of Energy (DOE) support of projects to develop black liquor gasification technology. Additionally, work has been performed to identify new materials for use in this application, which may show improved lifetimes in the smelt environment. This article will concentrate on the refractory efforts at ORNL. Previous publications should be consulted regarding work at ORNL regarding metallic materials [3, 4].

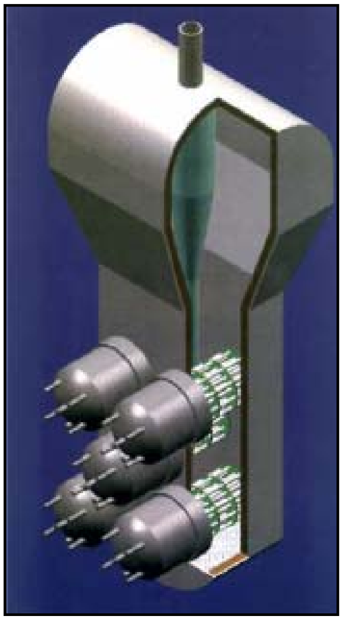

Figure 1. Schematic Drawing of Low-Temperature Black Liquor Steam Reformer/Gasifier (provide by MTCI).

GASIFICATION TYPES AND ISSUES

Black liquor gasification can be performed at either low (below the melting temperature of the smelt) or high (above the melting temperature of the smelt) temperatures. The refractory issues will differ depending on the temperature regime of operation. Yet, while each process has favorable attributes, development and implementation is limited by deterioration of the containment refractory leading to reduced refractory lifetimes for both processes.

Low temperature black liquor gasification (temperatures in the regime of 605°C) has been primarily developed by Manufacturing and Technology Conversion International, (MTCI), Baltimore, MD with commercial-scale units being constructed at mills in Big Island, Virginia and Trenton, Ontario. A schematic of a low-temperature black liquor steam reformer/gasifier is shown in Figure 1. In this process, steam reforming occurs in a fluidized bed of sodium carbonate particles with the steam introduced through the bottom of the vessel serving as the fluidizing gas and water source for the reforming operation. Heat transfer to the bed is performed through a group of tube bundles (consisting of hundreds of tubes)

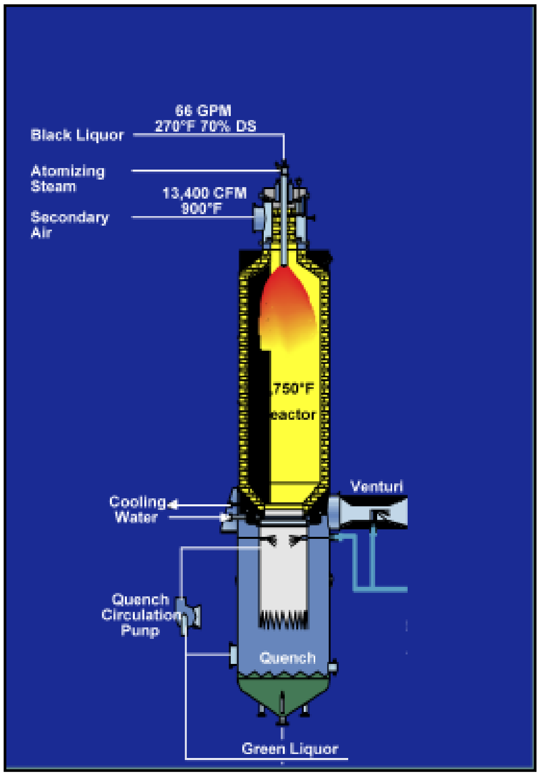

Figure 2. Typical Design for the HTLP Process.

that carry hot combustion gas produced in the refractory lined combustion chambers. Due to the lower temperatures (below the melting point of the smelt), the alkali salts in the smelt remain solid, rather than molten and do not form more aggressive liquid phases that can attack refractory and metallic components of the vessel lining. However, the refractory material is still subjected to thermal, chemical, and mechanical effects. Therefore, there is a need to identify refractory materials which have sufficient corrosion resistance and thermomechanical stability to be used in this application.

High temperature black liquor gasification (temperatures in the range of 900-1000°C) has primarily been developed by Chemrec AB, Stockholm, Sweden. Two methods have been proposed, one performed at low pressures (near atmospheric pressure) referred to as High Temperature/Low Pressure (HTLP) and one at high pressures (significantly above atmospheric pressure) referred to as High Temperature/High Pressure (HTHP). Due to the higher temperature of these processes (above the melting temperature of the smelt) gasification occurs at a much higher rate, with the rate also increasing with increasing pressure. The negative effect is that the higher temperatures will lead to the presence of molten smelt which must now be contained. Again, thermal insulation and long-term stability must also be achieved.

A typical design for the HTLP process is shown in Figure 2. It consists of a refractory lined metallic vessel with black liquor fuel, steam, and air injected at the top of the vessel. Organic material in the black liquor is gasified, while the inorganic salts are left in the liquid state along the gasifier wall. Both the liquid and gaseous products are then removed at the bottom of the vessel following a quench cycle. Several refractory materials have been proposed and tried as lining materials, with less than desired results. These include the originally proposed bonded alumina-silica brick and two brands of fusion-cast α/β alumina refractories. Current refractory materials used in this application have been seen to have a limited lifetime of 12 months or less, making them unacceptable both in terms of plant maintenance schedule and cost. Additionally, refractory degradation adversely affects the quality of the liquor produced and impacts the process downstream.

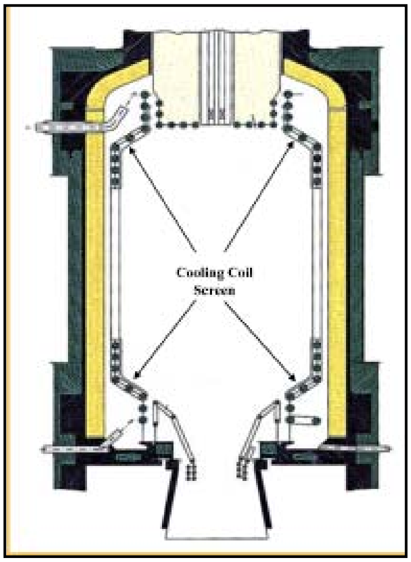

Figure 3a. Schematic of HTHP Cooling Screen DesignConcept.

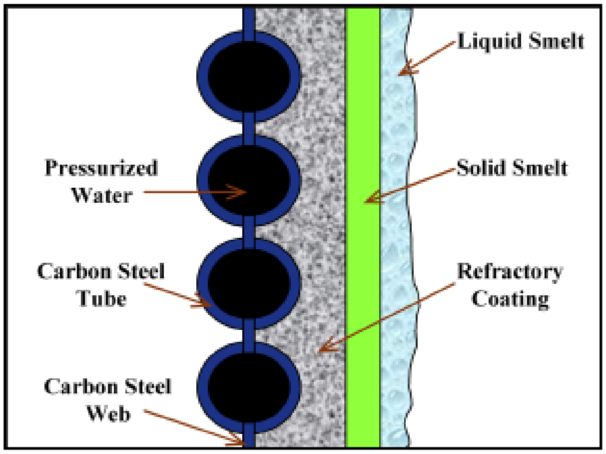

Figure 3b. Schematic of Helical Cooling-Coil Design.

There is currently limited experience in HTHP technology. One design utilizes a thick refractory lining within a metal pressure vessel similar to the HTLP lining. Efforts on HTLP linings are expected to be applicable to this HTHP design as well. An alternate design utilizes a refractory-coated helically-coiled metal tube known as a "cooling coil" shown in Figure 3. Pressurized cooling water is circulated through the tube, similar to a design proven for coal gasification, removing enough heat to cool the refractory surface below the melting point of the smelt causing liquid smelt to solidify. Identification of suitable refractories is needed for both designs. For the cooling coil design specifically, materials are needed which have appropriate thermal conductivity, smelt corrosion resistance, and thermal shock resistance to serve as thermal and chemical protective layers under temperature and pressure.

Figure 4. Triangular Prismatic Refractory Sample for Installation in MTCI Fluidized Bed.

Figure 5. Refractory Coated Manway Plug for Installation at Big Island Commercial-Scale Unit.

REFRACTORY SELECTION, TESTING, AND EVALUATION

For low temperature gasification, efforts have concentrated on evaluation of currently used refractory materials and the recommendation of alternative materials. Several possible materials for consideration have been identified based on chemical composition, temperature rating, and microstructure. Samples were prepared from several of these alternative materials for installation in currently being constructed units.

For the MTCI Process Development Unit (PDU) in Baltimore, MD, an initial analysis was performed on the candidate refractory system intended for use. This system consisted of an ultra low-cement high alumina castable backed by a refractory board material; however, additional castable compositions and board materials were suggested as possible alternate materials. Later, samples were prepared for installation in the corner areas of the reactor bed. These samples were triangular prismatic refractory samples cast in carbon steel holders utilizing a carbon steel anchor system. An example of these samples is shown in Figure 4. Samples were prepared using the originally suggested material (high-alumina extra-low cement pumpable castable containing silica and calcia) along with alternate candidate refractory materials including alumina containing castable, magnesia castable, and spinel castable materials. Refractory performance will be evaluated during subsequent shutdowns. At the time of the writing of this article, these samples have been installed, but no samples have been removed and returned for inspection.

For the gasifier being constructed by Georgia-Pacific Corp. (Big Island, VA), current and candidate refractory materials were installed on 30" diameter carbon steel manway plugs for use in both the bed and freeboard areas of the unit. A total of six refractories were installed (3 1/2" thick layer) on refractory anchors on four plugs, with two being installed in each area of the unit. A pictures of the refractory coated cover is shown in Figure 5. The current refractories used in both areas were nominally 44-45% Al_2O_3, 38% SiO_2, 13-14% CaO, and 0.2-0.4% MgO. Alternate candidate refractory materials for the bed area included magnesia castable and spinel castable. Alternate candidate materials for the freeboard area included spinel castable and high alumina/low cement castable. Similar to the samples installed in the MTCI unit, refractory performance will be evaluated during subsequent shutdowns. At the time of the writing of this article, these samples have been installed, but no samples have been removed and returned for inspection.

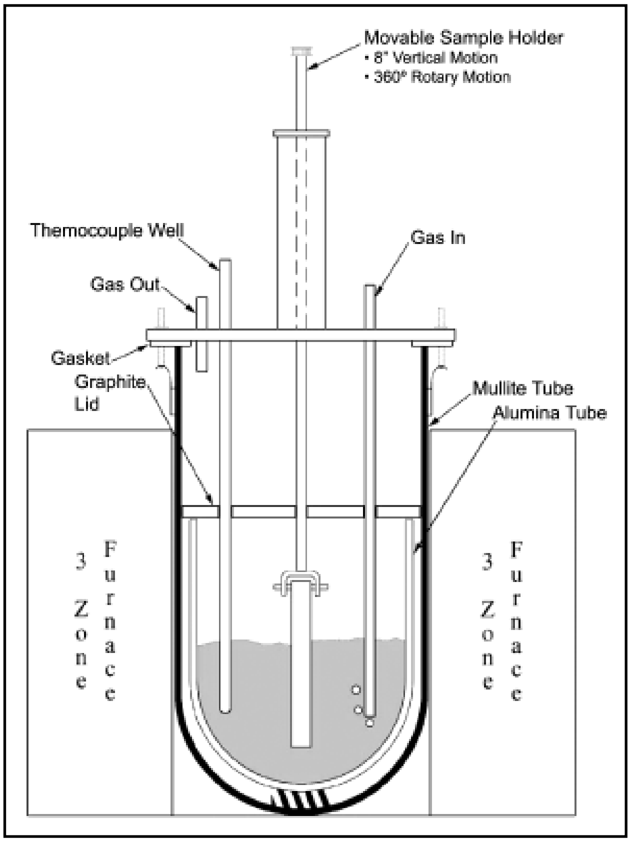

Figure 6. ORNL Immersion Test System.

For HTLP gasification, initial work was conducted using a laboratory immersion test system shown schematically in Figure 6. This system has been demonstrated to successfully reproduce the corrosion products observed to form on refractories exposed in

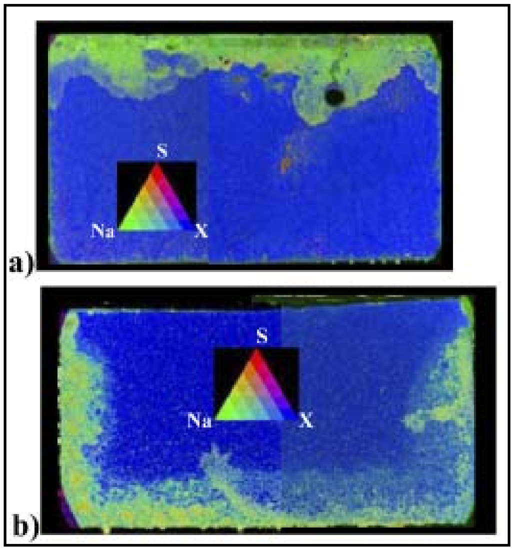

Figure 7. Electron Microprobe Images for Immersion Test Specimens (a) fusion-cast alumina, (b) fusion-cast spinel (samples are 1” x 0.5”).

operating gasifiers [5]. Various refractories have been tested in this system using smelt generated at a commercial facility (nominal composition: 60-75% Na_2CO_3, 20-38% Na_2SO_4, 1-4% Na_2S, and 1-4% $Na_2S_2O_3$). It was found that the best corrosion resistance was seen in selected fusion-cast and bonded materials. Specifically, laboratory immersion testing results led to a desire to further investigate the properties of fusion-cast α/β alumina and fusion-cast spinel materials. Examples of electron microprobe images of immersion test samples for these two materials are shown in Figure 7. These images show the relative penetration of the smelt into the cross-section of samples. Based on immersion testing results, the fusion-cast material is expected to have longer life time in the molten smelt environment than previously used non-fusion-cast materials. Bonded spinel materials were also tested. Although these materials showed less corrosion resistance to molten smelt than the fusion-cast materials, they did exhibit significantly improved corrosion resistance as compared to that seen in previous lining materials used for this application. These materials may also offer significant cost savings compared to the use of the fusion-cast material.

Another area of research has been improvement of existing refractory performance through the application of surface treatments which close off open porosity on the refractory surface or create a passive layer which would interact with the smelt. The use of a high density infra-red lamp to seal the surface porosity of refractories and to apply surface coatings has also been investigated (Figure 8a). Results of this technology have been mixed [3, 4]. The use of additional candidate coatings has been attempted by using Li_2CO_3 to form a surface layer on alumina, spinel, and mullite refractories (Figure 8b). Reaction products of the lithium treatment varied with refractory composition, with improvement in corrosion resistance to molten smelt seen in many cases [3, 4, 5]. Further investigation into the application of such coatings on the industrial scale is ongoing.

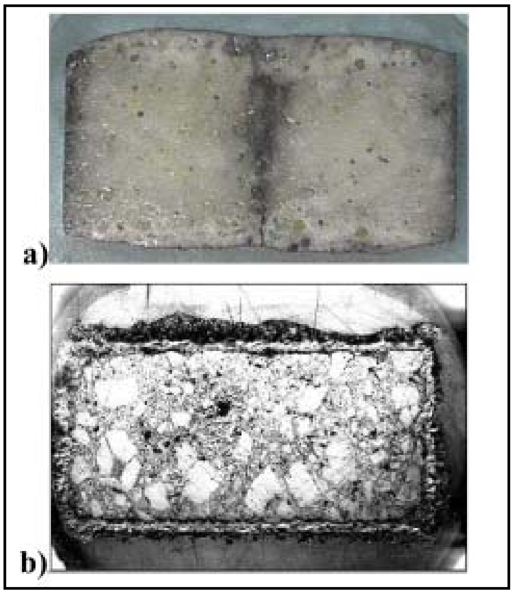

Figure 8. Examples of Surface Coated Specimens Using (a) High Density Infrared Plasma Arc Lamp and (b) Lithium Surface Treatment (samples are 1” x 0.5”).

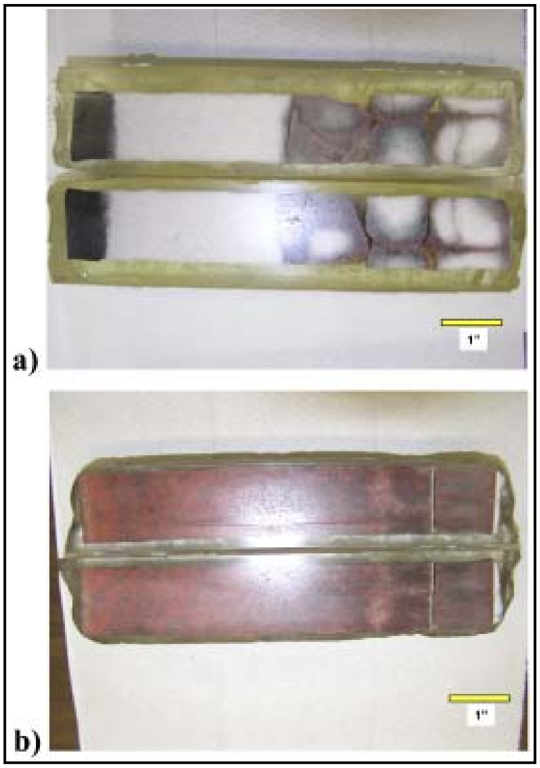

Figure 9. Core-drilled Samples from New Bern Gasifier (a) fusion cast alumina, b) fusion cast spinel)

Finally, based on immersion testing and other laboratory results, candidate refractory materials have been installed in a commercial HTLP gasifier constructed by Weyerhaeuser Inc. in New Bern, NC. These materials were subjected to service for about six months prior to a maintenance shut-down of the unit. At that time, core-drilled samples (as shown in Figure 9) of the candidate materials and currently used fusion-cast alumina material were removed from the unit and analyzed at ORNL by optical microscopy, SEM/EDS, X-ray diffraction, and electron microprobe. Performance of the materials was found to agree well with laboratory results and predictions [6]. Comparisons will be made between the relative performance of the various materials.

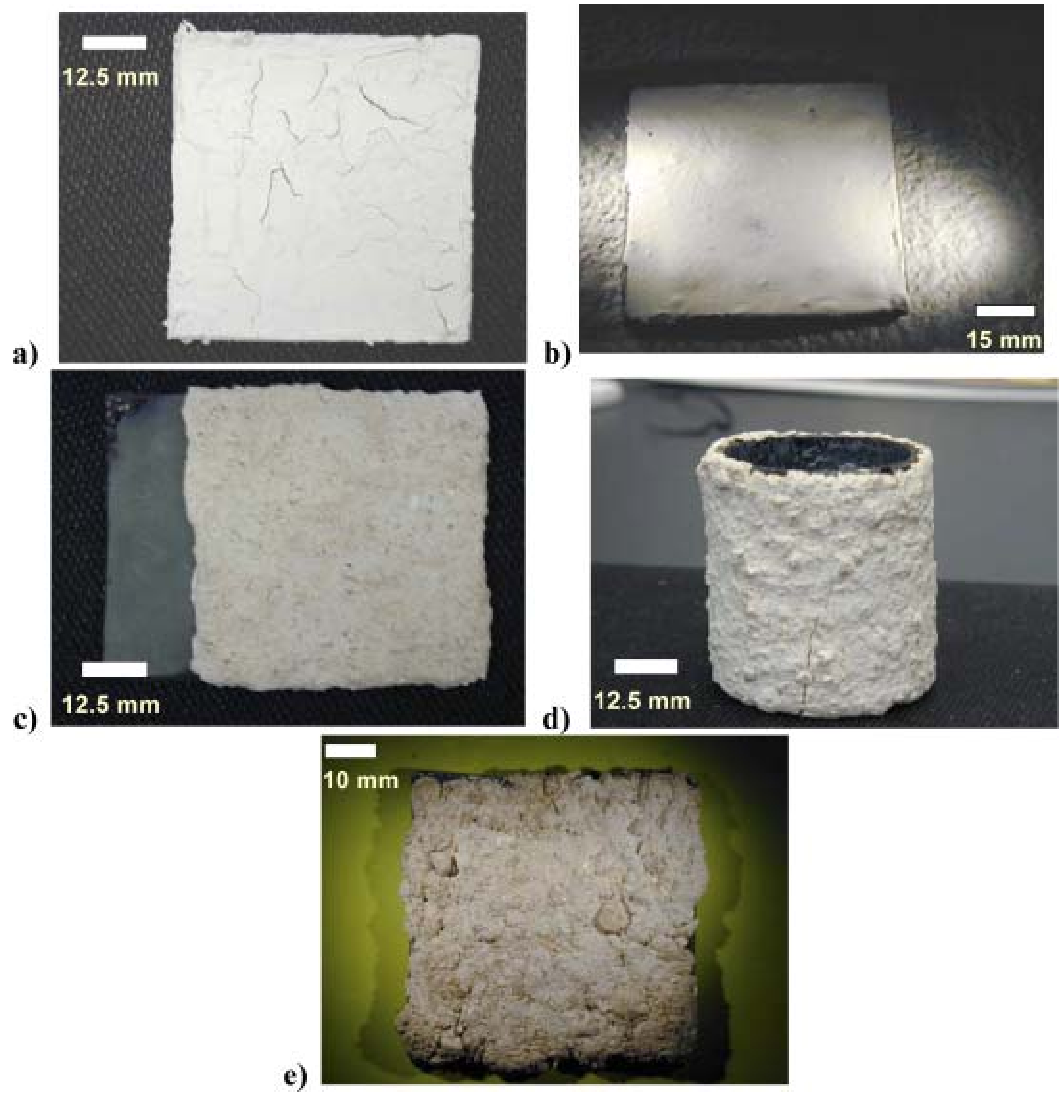

Figure 10. Refractory Coatings on Carbon Steel (a) alumina cement, b) magnesia cement, c) alumina ram mix on plate, d) alumina ram mix on cylinder, e) magnesia castable).

For HTHP gasification, efforts have focused on identifying suitable candidate refractories for coating of the carbon steel cooling coil arrangement. These refractory materials will act as a chemical and thermal barrier to protect the metallic tubes beneath them and therefore must have appropriate thermal conductivity, thickness, corrosion resistance to molten smelt, and thermal expansion response to match that of the base metal. Efforts concentrated on identifying ceramic systems which possessed these properties by evaluating the adhesion and thermomechanical properties of candidate materials (thermal conductivity, thermal expansion, spall resistance). Subsequent efforts focused on the corrosion resistance of candidate materials.

Alumina and magnesia materials were initially evaluated due to previous success experienced with alumina materials used in contact with molten smelt and the favorable coefficient of thermal expansion of magnesia (closer to that of the carbon steel substrate material than that of alumina). Materials with low-cement phases and phosphate binder systems in place of calcium cement binders were also considered, as it is expected that the cement phase will be the less corrosion-resistant phase and thus more prone to attack in the molten smelt environment.

Initial testing was performed to evaluate the adhesion and surface quality of coatings applied to both plate and cylindrical carbon steel substrate geometries. Alumina-based material was found to show poor surface quality after drying with substantial cracking in the coating due to thermal expansion mismatch between the base metal and the ceramic coating and drying effects as shown in Figure 10a. Magnesia-based coatings, in contrast, showed higher surface quality with no cracking observed (Figure 10b). This is thought to be due to the higher thermal expansion coefficient of this material. An alumina ram mix was next tested. This material was found to show poor adhesion to the carbon steel in the plate geometry, but better adhesion to carbon steel in the cylindrical geometry (Figure 10c and 10d). Cracking was prevalent in both coatings, but surface quality was improved by using an intermediate layer of alumina or magnesia cement between the carbon steel and the refractory coating. Finally, a magnesia castable was tested. This material showed good adhesion to both the plate and cylindrical geometries and good surface quality (Figure 10e).

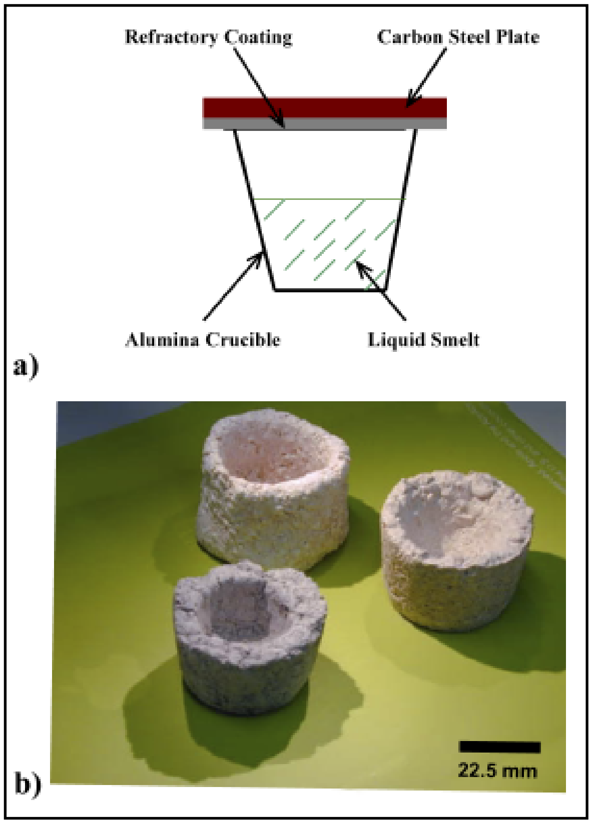

Figure 11. Samples of Refractory Coating Corrosion Testing (a) Modified Lid Test, b) Modified Cup Test.

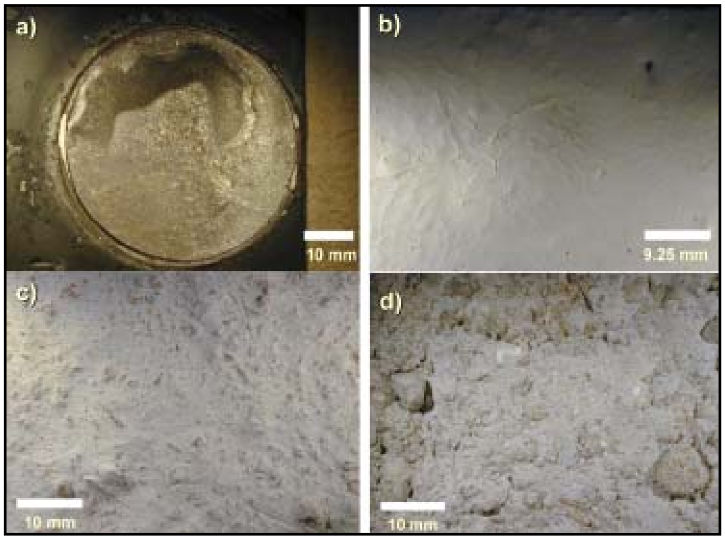

Figure 12. Lid Corrosion Test Results (a) bare carbon, b) magnesia cement coating, c) alumina ram mix coating, d) magnesia castable coating).

Resistance to molten smelt in both vapor and liquid forms was also evaluated through a modified lid and modified cup corrosion test, respectively. These tests consisted of exposing either refractory coated plates to vapor from molten smelt or exposing refractory crucibles to molten smelt for controlled periods of time at a temperature (900-1000°C) well above the melting point of the smelt. A schematic and examples for the two corrosion tests are shown in Figure 11. The smelt used for testing was taken from production smelt generated at a commercial facility (nominal composition: 60-75% Na_2CO_3, 20-38% Na_2SO_4, 1-4% Na_2S, and 1-4% $Na_2S_2O_3$). Lid corrosion tests indicated that the refractory cements (alumina and magnesia) have relatively poor resistance to smelt vapor, while the alumina ram mix and magnesia castable material exhibited good resistance in 20 hour exposure test as shown in Figure 12. Liquid smelt was also found to be contained by the alumina ram and magnesia castable mixes through cup tests performed for 50 hours in the temperature range of 800-1000°C.

Additional testing of refractory coating materials for HTHP gasification should include evaluation of the effects of anticipated thermal gradients between the cooled carbon steel tubes and the solidified smelt on the refractory hot face. To accomplish this, a rotary cold finger immersion test system similar to that used for HTLP material evaluation (Figure 13) is planned for construction for further evaluation of candidate coating materials.

SUMMARY

Work has been performed to evaluate and select new candidate materials for both low temperature (below the melting point of the smelt) gasification and high temperature (well above the melting point of the smelt) gasification applications. For high temperature gasification, both low pressure (near atmospheric) and high pressure (significantly above atmospheric pressure) systems have been considered.

Both current and alternative materials have been evaluated and selected for low temperature gasification processes, with a number of materials being installed in commercial units currently under construction. At the time of the writing of this article, samples had been installed, but no samples have been removed and returned for inspection. For high temperature low pressure gasification processes, efforts have focused on screening candidate lining materials through immersion testing, improving existing refractory performance through the application of surface treatments, and the installation and evaluation of samples in an operating gasifier in New Bern, NC. Efforts concerning high temperature high pressure gasification have involved the identification and testing of suitable refractory materials for the coating of a helical carbon steel cooling coil arrangement.

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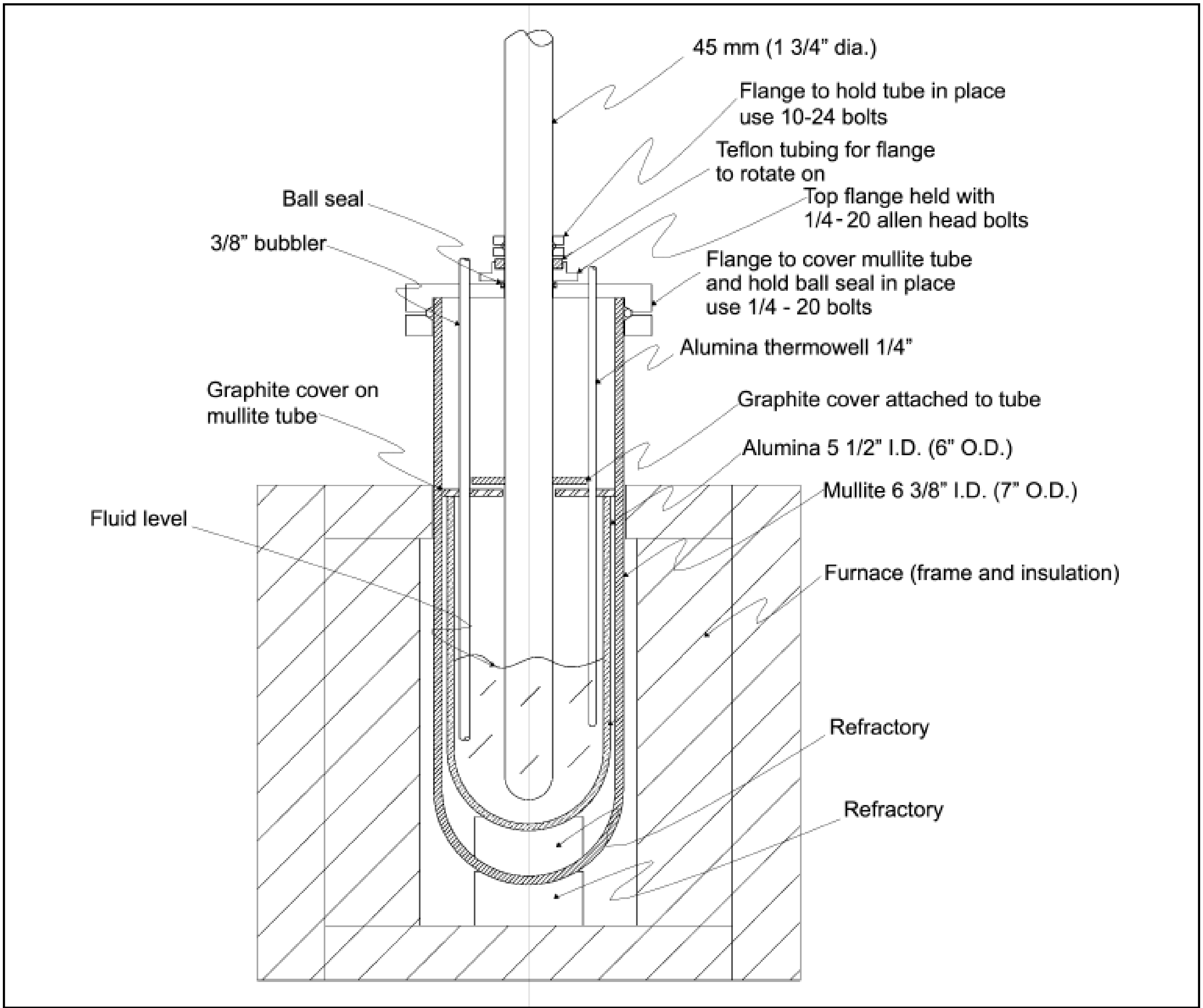

Figure 13. Schematic of Rotary Cold Finger Immersion Test System.

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