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ABSTRACT

The University of Missouri-Rolla will identify materials that will permit the safe, reliable and economical operation of combined cycle gasifiers by the pulp and paper industry. The primary emphasis of this project will be to resolve the material problems encountered during the operation of low-pressure high-temperature (LPHT) and low-pressure low-temperature (LPLT) gasifiers while simultaneously understanding the materials barriers to the successful demonstration of high-pressure high-temperature (HPHT) black liquor gasifiers. This study will define the chemical, thermal and physical conditions in current and proposed gasifier designs and then modify existing materials and develop new materials to successfully meet the formidable material challenges.

Resolving the material challenges of black liquor gasification combined cycle technology will provide energy, environmental, and economic benefits that include higher thermal efficiencies, up to three times greater electrical output per unit of fuel, and lower emissions. In the near term, adoption of this technology will allow the pulp and paper industry greater capital effectiveness and flexibility, as gasifiers are added to increase mill capacity. In the long term, combined-cycle gasification will lessen the industry's environmental impact while increasing its potential for energy production, allowing the production of all the mill's heat and power needs along with surplus electricity being returned to the grid. An added benefit will be the potential elimination of the possibility of smelt-water explosions, which constitute an important safety concern wherever conventional Tomlinson recovery boilers are operated.

Developing cost-effective materials with improved performance in gasifier environments may be the best answer to the material challenges presented by black liquor gasification. Refractory materials may be selected/developed that either react with the gasifier environment to form protective surfaces in-situ; are functionally-graded to give the best combination of thermal, mechanical, and physical properties and chemical stability; or are relatively inexpensive, reliable repair materials. This report covers Task 1.3, Simulative corrosion of candidate materials developed by refractory producers and in the laboratory based on the results of Task 1.1 and Task 1.2.

Refractories provided by in-kind sponsors were tested by cup testing, density/porosity determinations, chemical analysis and microscopy. The best performing materials in the cup testing were fused cast materials. However, 2 castables appear to outperforming any of the previously tested materials and may perform better than the fused cast materials in operation. The basis of the high performance of these materials is the low open porosity and permeability to black liquor smelt.

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INTRODUCTION

The Tomlinson recovery boiler is the conventional technology for recovering cooking chemicals and energy from black liquor. As a potential replacement for the Tomlinson recovery boiler, black liquor gasification (BLG) technology has garnered much interest over the last two decades in the papermaking industry. The BLG technology has higher energy efficiency and generates far more power with overall lower cost than conventional technology. It improves safety by reducing the risk associated with smelt-water explosions. It reduces the wastewater discharges and harmful emissions into the environment. BLG systems recover sodium and sulfur as separate streams that can be blended to produce a wide range of pulping liquor compositions [Stigsson (1998)]. As a technique that is still under development, it has problems including refractory failure during operation due to a combined effect of chemical reaction and thermomechanical stress [Brown and Hunter (1998), Dickinson, Verrill and Kitto (1998)]. The objective of this study is to investigate refractory materials for the lining of the gasifier.

High temperature black liquor gasifiers are generally cylindrical in shape as shown in Figure 1. The height ranges from 1.5 m to 25 m and diameter ranges from 0.5 m to 5 m. In the gasifier reactor vessels, there are usually 2-6 coaxial layers of component lining [Taber (2003)]. Refractory lining is used to protect the exterior metallic part of the gasifier vessel. A dense refractory material layer is designed to be exposed to the highest temperature environment. The second “safety” layer is usually made of a similar material. Subsequent layers are used to provide insulation and allow for expansion. The steel shell is used to provide reaction space and confinement. The gasifier generally operates at temperature ranging from 950 to 1000°C.

Figure 1 Schematic construction of a typical high temperature gasifier

The commercial high temperature black liquor gasifier was developed by Kvaerner Chemrec. A pilot plant first started running in 1994 at a pulp mill near Karlstad, Sweden [Larson, Consonni and Katofsky (2003)]. The first commercial size Chemrec system (75-100 tons of dry solids/day) was built in 1991. This air blown gasifier has performed well and been proven to be easy to operate and maintain. The first commercial Chemrec system in North America started operation in 1996 at Weyerhaeuser's New Bern, SC, USA [Brown and Hunter (1998)]. It was an atmospheric, air-blown, entrained bed gasifier operating between 950-1000 °C with a capacity of 350 ton black liquor solids per day. However, this system was shutdown in January 2000 due to failure of the stainless steel shell [Brown and Landalv (2001)].

Black liquor gasification converts the organic components into combustible fuel gas and leaves inorganic components as smelt to generate high-quality green liquor for regenerating pulping chemicals [Kelleher and Kohl (1986)]. The combustible gas contains carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄), nitrogen (N₂), water vapor (H₂O) and hydrogen sulfide (H₂S). The smelt drops are mainly sodium carbonate (Na₂CO₃) and sodium sulfide (Na₂S). Some of the smelt drops form a thin layer of smelt flowing along the reactor wall.

The current refractory materials for the BLG reactor vessel lining are not deemed adequate. The combination of high temperature and alkalinity produces an aggressive environment for

the reactor lining. Chemrec has used several refractory materials in the pilot units and the commercial atmospheric units. The refractories last from 1 to 18 months, with a replacement cost of up to 1 million dollars and several weeks of downtime. Severe refractory thinning occurred and several bricks were found lost from the upper part of the gasifier vessel during operation. The refractory lining is subjected to the penetration of sodium and subsequent reactions with alkali-rich molten smelt, such that the refractory undergoes significant volume change and strength degradation. Several refractory samples have been studied after immersion in molten smelt by Peascoe, Keiser, Hubbard, Brady and Gorog (2001). The results of their study are summarized below. For mullite based refractories, molten smelt first attacks mullite and forms sodium aluminum silicates. This reaction is accompanied by a volume change. A significant surface expansion occurs during immersion testing in smelt. Furthermore, a liquid phase can develop in the mullite refractory as Na_2O concentration increases. Surface expansion coupled with the loss of structural integrity lead to the spalling of the lining. MgAl_2O_4 spinel based refractories react with the smelt to form NaAlO_2 and MgO , with an associated expansion of 2.1% to 13%. For α/β -alumina refractories, expansion was accommodated partly through spalling and a significant radial expansion of the gasifier's lining. The alumina refractories show the least corrosion, the chemical expansion of alumina samples is from 0 to 0.7%. Due to this reason, fused cast alumina which is expansive and sensitive to thermal shock is being used in the most recent commercial high temperature black liquor gasifier at New Burn, SC, USA, [Brown, Leary, Gorog and Abdullah (2004)].

During Task 1.1 of this study candidate refractory materials suitable black liquor smelt containment were determined through a combination of thermodynamic calculations and phase diagrams. During Task 1.2 samples were made of the candidate materials for property measurements including density, porosity, smelt contact angles and reaction products. Task 1.3 involves testing refractory materials developed by the in-kind cost share partners in a cup test with a simulative environment to determine the resistance of refractory materials that can be produced commercially to black liquor smelt. Refractories provided by in-kind sponsors were tested by cup testing, density/porosity determinations, chemical analysis and microscopy. The best performing materials in the cup testing were fused cast materials. However, 2 castables appear to outperforming any of the previously tested materials and may perform better than the fused cast materials in operation. The basis of the high performance of these materials is the low open porosity and permeability to black liquor smelt.

EXECUTIVE SUMMARY

Black liquor gasification is a high potential technology for production of energy which allows substitution for other sources of energy. This process uses a waste of the pulp and paper industry as black liquor to produce synthetic gas and steam for production of electricity; therefore development of this technology not only recovers the waste of the paper industry but also decreases dependency on fossil fuel.

Today one of the main obstacles in the development of this technology is the development of refractory materials for protective lining of the gasifier. So far the materials used for this application have been based on alumino-silicate refractories but, thermodynamics and experience shows that these materials are not sufficiently resistant to black liquor under the harsh working conditions of Black liquor gasifiers. Consequently development of cost-effective materials with improved performance in gasifier environments to answer the material challenges presented by black liquor gasification (HTHP, HTLP) is the objective of this project. Refractories provided by in-kind sponsors were tested by cup testing, density/porosity determinations, chemical analysis and microscopy. The best performing materials in the cup testing were fused cast materials. However, 2 castables appear to outperforming any of the previously tested materials and may perform better than the fused cast materials in operation. The basis of the high performance of these materials is the low open porosity and permeability to black liquor smelt.

EXPERIMENTAL

Cup testing has been used for the preliminary determinations of smelt refractory reactions for Task 1.3. Cup test processing was performed at UMR. Cups were prepared from monolithic materials according to the manufacturers directions as a 9" long by 4.5" wide by 3" deep sample with 2 of 1.5" diameter by 1.5" deep holes formed during casting as shown in Figure 1. Brick samples were cut from a 9 inch straight into 2 of 4.5 inch by 4.5 inch by 2.5 inch specimens. A diamond core drill cored a 1.5" diameter by 1.5" deep core. The core was removed with a chisel.

Figure 2 Cup specimen preparation, cup cut along dotted line

The removed cores were used to determine density by ASTM C-820 and sectioned for chemical analysis by ICP and microscopy. The cups are processed by drying at 110°C for 24 hours. The cup was charged with 50 grams of raw black liquor smelt. Heated at 1°C/minute to 1000 °C, held 240 hours at 1000°C and cooled at 2°C/minute to 25 °C, in an argon flooded furnace.

RESULTS AND DISCUSSION

Samples of currently used , in-house, and refractories developed based on the results provided previously were provided by in-kind sponsors. These samples were tested according to the experimental procedure given in the experimental section. Table 1 is an overview of the results.

Table 1 Cup testing results

No.	Chemistry										Density			Performance
	Al ₂ O ₃	SiO ₂	ZrO ₂	MgO	CaO	Fe ₂ O ₃	Na ₂ O	TiO ₂	P ₂ O ₅	Other	(g/cc)	Theoretical	(g/cc) (%)	Relative
5	93.29		5.07							1.64	3.43	4.06	84.37	Good
10	72.29	26.24								1.47	2.56	3.47	73.85	Good
16	59.46	34.06				1.51		2.33		2.64	2.46	3.35	73.35	Good
18	80.14	16.45			1.27					2.14	2.91	3.64	80.04	Good
20	97.23	1.17								1.6		3.94		Good
21	95.3	0.25		2.34						2.11	3.60	3.95	91.24	Good
22	92						7			1	2.75	3.96	69.39	Good
23	95	0.5					4			0.5	3.34	3.96	84.33	Good
25	78.2	18.1		0.1	0.1	1.4	0.2	1.9		0	2.69	3.16	85.02	Good
26	84	7.5		8	0.2	0.1	0.2			0	3.02	3.55	85.09	Good
4	95.61		2.67							1.71	3.07	4.01	76.60	Small Cracks
8	88.72	0.8	7.76							2.72	3.29	4.10	80.19	Small Cracks
9	89.62	0.82	7.97							1.58	3.39	4.10	82.79	Small Cracks
11	89.43	0.78	7.78							2.01	3.33	4.10	81.24	Small Cracks
12	80.21	17.31								2.48	2.54	3.64	69.75	Small Cracks
13	89.74	0.81	8.11							1.34	3.24	4.10	78.99	Small Cracks
15	2.52	36.74	57.84							2.9	3.78	4.42	85.62	Small Cracks
17	95.95	0.21			0.89					2.95	3.00	3.94	76.23	Small Cracks
19	89.37	0.17		2.35			2.32		4.47	1.3	2.79	3.84	72.75	Small Cracks
24	87.1	11.36								1.54	2.82	3.69	76.41	Small Cracks
1	79.3	18.75								1.95	2.64	3.61	73.20	Failed
2	84.84	1.17	12.27							1.72	3.31	4.15	79.85	Failed
3	73.7	24.18								2.72	2.42	3.53	68.67	Failed
6	74.74	14.72	8.91							1.63	2.91	3.86	75.40	Failed
7	73.81	9.51	15.18							1.5	3.05	4.08	74.79	Failed
14	80.34	17.48								2.18	2.52	3.63	69.54	Failed

The best performing materials in the cup testing were fused cast materials. Two new castables appear to be outperforming any of the previously tested materials. 4 new magnesia castables are being developed by a cost share partner and submitted for testing. They plan to submit one to two more during the project. The materials that performed well are shown in more detail in the following discussion.

A company provided two castable refractories materials, 25 and 26 to UMR for cup testing with black liquor smelts (high alkali content).

Sample: 25

Type: Castable

Chemistry: Al₂O₃ 78.2%, SiO₂ 18.1%, Fe₂O₃ 1.4%, TiO₂ 1.9%, CaO 0.1%,
MgO 0.1%, Alk. 0.2%, P₂O₅, SiC, ZrO₂, Other.

Density: 2.69 g/cc

Porosity: 14.98%

Sample: 26

Type: Castable

Chemistry: Al_2O_3 84.0%, SiO_2 7.5%, Fe_2O_3 0.1%, TiO_2 0.0%, CaO 0.2%,
 MgO 8.0%, Alk. 0.2%, P_2O_5 , SiC, ZrO_2 , Other.

Density: 3.02 g/cc

Porosity: 14.91%

Cup Preparation:

Casting

25: 5.8% water was used, and the mixture is easy to cast.

26: 4.6% water was used, and the mixture is easy to cast.

Firing

All two cups were fired at 1050 °C for 5 hr. The heat rate was 1 °C/min. The cooling rate was also 1 °C/min.

Charge smelt

50 g smelt was charged to each cup.

Two cups were set in the box furnace. The furnace was flooded with Argon gas. The test temperature was 1000 °C. The test time was 240 hr. the heat and cooling rate were 1 °C/min.

Both cups have good resistance against smelts attack. Figure 3 shows the top view of sample 25 after cup test with 50 g smelts at 1000 °C for 240 hr. Figure 4 shows the cross-section in which there is an average thickness of 2.3 mm corrosion ply formed.

Figure 5 shows the top view of sample 26 after cup test with 50 g smelts at 1000 °C for 240 hr. Figure 6 shows the cross-section in which there is no corrosion ply observed.

Figure 3 Top view of sample 25 after cup test.

Figure 4 Cross-section of sample 25 after cup test.

Figure 5 Top view of sample 26 after cup test.

Figure 6 Cross-section of sample 26 after cup test.

Figure 7 and Figure 8 show RL and CL microstructures of virgin sample 25 before firing. This sample is identified as cement-free high alumina castable refractory, which is made up of large alumina aggregates (AA), medium-sized fused mullite (FM) grains blended with most likely microsilica matrix. No calcium aluminate cement particle is identified. Alumina aggregates are highly impure containing Fe-Ti oxides as well as alkali matrix suggesting they are derived from clay-balls or bauxitic raw materials.

Figure 7 Pre-test microstructure for sample 25.

Figure 8 Pre-test microstructure for sample 25.

In Figure 9, RL/CL microstructures of sample 25 after BL smelt cup test showing reaction front. About 2 mm thick reaction interface is visible on the surface of this sample. BL smelt has reacted with refractory material to form mullite and alkali rich silicate glass.

Figure 9 Post-test microstructure for sample 25.

In Figure 10, these micrographs are also taken from sample 25 (adjacent to above micrographs) showing refractory-smelt interface. A dense layer is formed at the interface, which blocked further penetration of smelt. Although, this refractory altered relatively more intense compared to sample 26, the alteration is still not too intense or strong.

Figure 10 Post-test microstructure for sample 25.

Figure 11 shows RL/CL microstructure of sample 25 after cup test, showing interface between refractory and smelt. The thickness of alteration is negligible.

Figure 11 Post-test microstructure for sample 25.

Figure 12 shows RL and CL microstructure of virgin sample 26 before firing, which is identified as cement-free, spinel reinforced high alumina castable refractory, which contains large tabular alumina aggregates (TA), medium sized fused spinel (FS) grains, blended with most-likely microsilica (?). No calcium aluminate cement particles are identified.

Figure 12 Pre-test microstructure for sample 26.

Figure 13 shows the same sample under low magnification showing general structure of the refractory.

Figure 13 Pre-test microstructure for sample 26.

Figure 14 shows RL and CL micrographs taken from sample 26 after cup test, illustrating microstructure of smelt-refractory interface. Note that there is almost no smelt penetration and reaction at the interface.

Figure 14 Post-test microstructure for sample 26.

Figure 15 shows RL and CL microstructures of sample 26 taken from refractory-smelt contact surface. Micrographs show that there is no sign of refractory degradation, for example reaction of refractory grains with smelt to form intermediate phases, in this given experimental conditions.

Figure 15 Post-test microstructure for sample 26.

Both 25 and 26 refractory have good corrosion resistance against smelts attack. Results indicate the 26 material is better to against smelts attack than 25.

Sample:	5
Type:	Brick
Chemistry:	Al ₂ O ₃ – 93.29%, ZrO ₂ – 5.07%, Impurities – 1.64%
Density:	4.06 g/cc
Porosity:	15.6%
Notes:	Sample 5 performed well in the 10 day test.

Figure 16 Sample 5 cup

Figure 17 Sample 5 pre-test microstructure

Figure 18 Sample 5 post-test microstructure

Sample: 10

Type: Brick

Chemistry: Al_2O_3 : 72.29 %, SiO_2 : 26.24 %

Density: 2.56 g/cc

Porosity: 22.2 %

Notes: Sample 10 performed very well in 10 days cup test. It did not exhibit serious chemical expansion that damages most high alumina containing products. Slight corrosion happened in 10 days cup test. These were smelt remnants left after test.

Figure 19 Sample 10 cup

Figure 20 Sample 10 post-test microstructure

Type: Brick

Chemistry: Al_2O_3 : 59.46 %, SiO_2 : 34.06 %, Fe_2O_3 : 1.51 %, TiO_2 : 2.33 %

Density: 2.46 g/cc

Porosity: 26.6 %

Notes: Sample 16 performed well in 10 days cup test. It did not exhibit chemical expansion that damages most high alumina containing products. There was smelt remnants left after test.

Figure 21 Sample 16 cup

Figure 22 Sample 16 pre-test microstructure

Figure 23 Sample 16 post-test microstructure

Sample: 18
Type: Castable
Chemistry: 80% Al_2O_3 , 16% SiO_2 , 1.3% CaO
Density: 2.91 g/cc
Porosity: 20%

Notes: Sample 18 performed well in the cup tests. Only fused cast alumina performed better.

Compositions similar to this have been panel tested in black liquor smelt gasifiers and have performed as well as 60% alumina brick and almost as well as fused cast alumina. Sample 18 does not exhibit chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as 60% alumina brick, spinel based brick and other castable systems.

Figure 24 Sample 18 cup

Figure 25 Sample 18 pre-test microstructure

Figure 26 Sample 18 post-test microstructure

Sample: 20
Type: Fusion Cast
Chemistry: 97% Al₂O₃, 1.2% SiO₂
Density: Immeasurable due to inhomogeneity
Porosity: Immeasurable due to inhomogeneity
Notes: Block had a high density zone and a very porous zone

Figure 27 Sample 20 cup

Figure 28 Sample 20 pre-test microstructure

Figure 29 Sample 20 post-test microstructure

Sample: 21
Type: Fusion Cast
Chemistry: 95% Al₂O₃, 0.2% SiO₂, 2.3% MgO
Density: 3.60 g/cc
Porosity: 9%
Notes: Fused cast alumina performed best in cup tests.

Figure 30 Sample 21 cup

Figure 31 Sample 21 pre-test microstructure

Figure 32 Sample 21 post-test microstructure

Sample: 22

Type: Fusion Cast

Chemistry: 92% Al_2O_3 , 7% Na_2O (data provided by manufacturer)

Density: 2.75 g/cc

Porosity: 31%

Notes: Fused cast alumina performed best in cup tests. Sample 21 has been used in black liquor smelt gasifiers and have performed well. Sample 21 exhibits chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as other systems.

Figure 33 Sample 22 cup

Figure 34 Sample 22 pre-test microstructure

Figure 35 Sample 22 post-test microstructure

Sample: 23

Type: Fusion Cast

Chemistry: 95% Al_2O_3 , 4% Na_2O , 0.5% SiO_2 (data provided by manufacturer)

Density: 3.34 g/cc

Porosity: 16%

Notes: Fused cast alumina performed best in cup tests. Sample 23 have been used in black liquor smelt gasifiers and have performed well. Sample 23 exhibits chemical expansion which damages most high alumina containing products and does not seem to corrode as fast as other systems.

Figure 36 Sample 23 cup

Figure 37 Sample 23 pre-test microstructure

Figure 38 Sample 23 post-test microstructure

The best performing materials in the cup testing were fused cast materials. Two new castables appear to be outperforming any of the previously tested materials. 4 new magnesia castables are being developed by a cost share partner and submitted for testing. They plan to submit one to two more during the project.

A fused cast magnesia or spinel should perform better than other fused cast materials. However, during shutdowns magnesia would be prone to hydration and thus problematic. Spinel would form a dense magnesia layer, as shown in Task 1.2, that would be prone to hydration and may slough off during shutdowns.

Low open porosity and permeability appear to be important for materials although it can not be proven by the current work. Low permeability spinel and magnesia castables should be formulated and investigated. It is also show that materials that form a viscous glass smelt refractory interface layer perform well. This has not been proven in the field and may be detrimental to green liquor quality or may be rapidly removed by scouring action of the liquid with entrained solids smelt washing down the interface layer.

CONCLUSION

Samples provided by in-kind sponsors were tested using cup testing. The best performing materials in the cup testing were fused cast materials. Recent testing of 2 castables and 1 magnesia brick were promising. Additional samples of magnesia castables have been provided. These may outperform any of the previously tested materials. It is hoped that additional testing will be performed in the future on additional spinel and magnesia based materials. Gunned materials as overlays and patches may be able to improve the lifetime of the reactor with hydration prone materials such as magnesia backing them up.

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