AN UPDATE ON THE DEVELOPMENT OF AN IMPROVED PERFORMANCE REFRACTORY MATERIAL FOR SLAGGING COAL GASIFIERS

Cynthia A. Powell, Kyei-Sing Kwong, James P. Bennett,
Richard E. Chinn, and Rick Krabbe

U.S. Department of Energy/Office of Fossil Energy
Albany Research Center
Albany, OR 97321

ABSTRACT

Severe slag attack of high temperature materials that line coal gasifiers used in the production of chemicals, liquid fuels, and/or electricity result in their unacceptably short lifetimes, lasting anywhere from 3 months to 24 months. Lengthening of this short service life to increase gasifier reliability and increase on-line availability of a gasifier is viewed as critical for greater technology acceptance and utilization. A phosphate-containing high chrome oxide refractory has been developed by the Albany Research Center of DOE and scaled up by an industrial producer of refractories for plant trials. An update of this material and its properties will be presented.

INTRODUCTION

Gasification is expected to be at the heart of many of the Advanced Fossil Fuel Power Systems planned for the future; however, while the technology has proven itself to be an efficient and relatively clean way to produce electricity, liquid fuels, and chemicals, it has not yet reached the level of reliability, availability, and maintainability that will lead to widespread market acceptance. For slagging gasifier systems, the lack of reliable and affordable structural materials that can effectively contain the gasification reaction for long periods of operation is a contributing reason for this lack of market acceptance. The harshest operating conditions within the gasifier island occur inside the gasifier itself, where the environment includes elevated temperature and pressure, as well as the presence of corrosive slags and gases. Attempts to enhance gasifier output and economics by operating at higher temperatures, with higher throughputs, and/or with variable feedstocks, put additional stress on the materials exposed to the operating environment, and typically result in a corresponding decrease in their useful service life. Because of the extreme operating conditions, refractory ceramic materials, consisting primarily of chromium oxide, are the only workable option for lining a slagging coal gasifier [1-7]. Current generation high chromium-oxide refractories typically last between three and 18 months inside a gasifier, depending on the operating conditions of the specific system. As gasification technology matures, the need for new and improved refractory materials will increase as the time between required maintenance shutdowns, and hence the economics and reliability of operation, are defined more and more by the service life of the materials from which the system is built. To address this need for improved materials, the U.S. Department of Energy's Office of Fossil Energy and the Albany Research Center have developed a phosphate-modified chromium oxide refractory designed specifically for longer service life in slagging coal gasifiers In this paper, we present the properties of this new material and discuss the results of laboratory exposure tests. Based on test results, this new refractory is predicted to significantly enhance gasifier reliability and availability through increased service life.

REFRACTORY LIFE IN SLAGGING GASIFIERS

Refractory service life in a slagging gasifier system is typically defined by the inherent ability of the material to withstand the physical conditions of the operating environment, combined with the specific stresses imposed on the material by the design and operation of the gasifier, as illustrated in Figure 1. In terms of materials performance, extensive *post-mortem* studies of refractories removed from commercial slagging gasifiers indicate that while all of the mechanisms outlined on the left path in Figure 1 can contribute to material loss, physical wear caused by slag penetration of the refractory and subsequent spalling is the primary mechanism of material failure [8,9]. Thus, the key to improved refractory performance is to design a material that can more effectively resist slag penetration in the gasifier environment.

Several factors promote slag penetration of refractories in the slagging coal gasifier. One is the operating temperature, which by necessity is much higher than the fusion temperature of the coal slag in order to ensure the slag flows easily. Unfortunately a less viscous slag can easily penetrate the pores and grain boundaries of the refractory material, especially if the refractory is easily wet by the slag, as is the case for most coal slags. In addition, the refractory lining the gasifier is multi-layered, with the purpose of the inner-most, hot face refractory primarily to resist the severe environment created by the gasification process. As a result, the hot face refractory has a relatively low thermal conductivity, which results in a small temperature drop across the brick and allows the slag to remain molten (and penetrating) inside the refractory much longer. Finally, the chemistry and the microstructure of most commercially-available chromium oxide refractories are not designed to resist coal slag penetration and attack. The first two of these factors are related primarily to the effective production of syngas and to the selection of feedstock, and any modifications to these in an attempt to extend refractory life can be expected lower the efficiency and economy of gasifier operation. However,

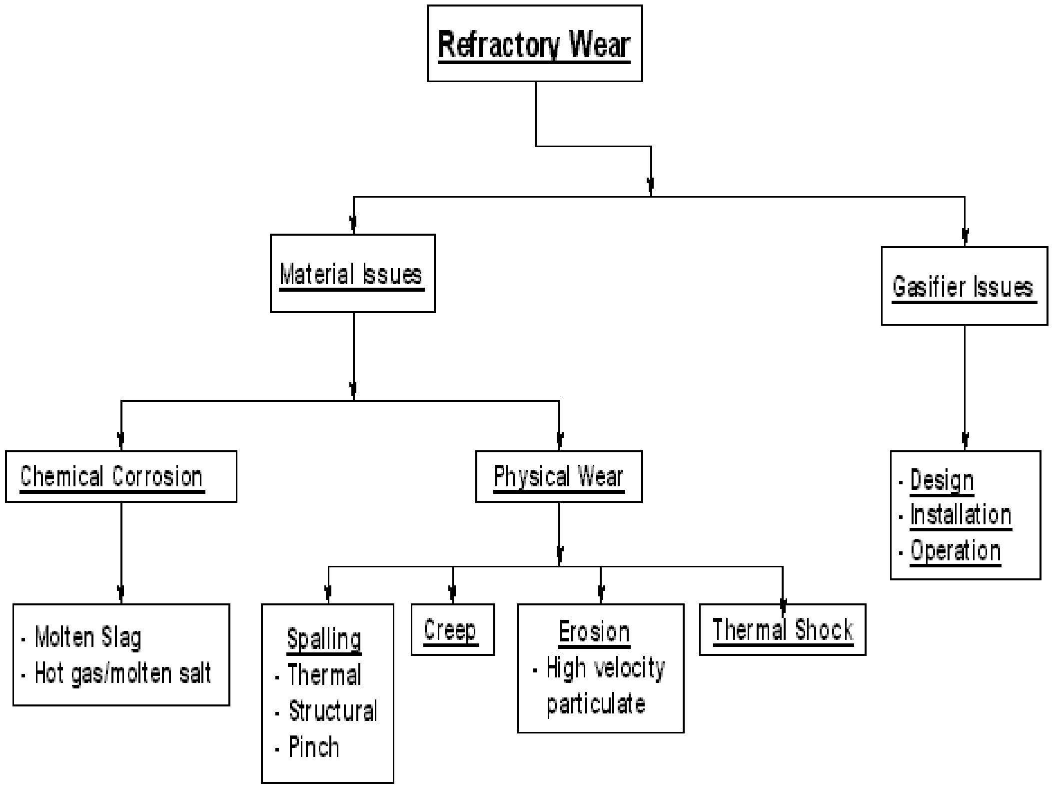

Figure 1. Possible refractory wear mechanisms in a slagging gasifier.

the third factor, the optimization of chemistry and microstructure of the refractory to better resist slag penetration, suggests a path to improved material performance without impacting overall gasifier operation.

ARC'S IMPROVED REFRACTORY MATERIAL

Again, based on information gained in *post-mortem* studies of spent refractories, the key to reducing slag penetration and attack in this particular application is to re-design the refractory chemistry so as to freeze the slag as it reacts with the matrix. The coal slag penetrates the refractory primarily in the form of calcium silicates, and so chemical reaction of the refractory with either the silicon or calcium component, causing the slag to solidify, is needed to effectively stop slag penetration. In addition, the microstructure of the matrix should be re-engineered to reduce the volume of interconnected porosity and to strengthen the bonding between particles. Adopting this approach, ARC developed a phosphate-modified high chromium oxide refractory material that was shown to significantly reduce slag penetration in initial laboratory exposure tests, when compared with refractory materials currently used by the gasifier industry[10-12]. In expanded testing, the more aggressive rotary kiln exposure tests also predicted improved performance by the ARC developed brick. In the rotary kiln test (Figure 2), a barrel lined with the test refractory materials is rotated around its horizontal axis, exposing the brick to a dynamic pool of molten coal slag. The kiln is heated by an oxy-propane torch, to a temperature in this case in excess of 1600º C. Four types of high chromium oxide

Figure 2 Rotary Kiln Exposure Test Apparatus

refractories (three commercial materials and the ARC-developed material) were exposed to this environment for a total of five hours. Post-test evaluation of the refractory materials indicates little or no cracking in the ARC material, as compared to extensive fracture in all of the commercial materials (Figures 3 and 4). Slag penetration was also minimized in the ARC material, to less than 20% that observed in the commercial refractories. Tests of the physical and thermal properties of the ARC-developed refractory (Table I) also indicate comparable, or in many cases superior, properties when compared to several commercially-available high chromium oxide refractory materials.

As a result of these laboratory test results, the ARC-developed refractory has been scaled to commercial production in collaboration with a refractory manufacturer, and a test panel produced for placement in a commercial coal gasifier. These refractories were installed in the gasifier and the field test begun in late 2003. Detailed results of that field test are pending at the writing of this paper; however, initial observations of the ARC-developed refractory indicate improved performance when compared to other high-chromium oxide refractories.

Table I. Physical Properties of Several High Chromium Oxide Refractories

	ARC Refractory	Commercial A	Commercial B
Porosity, %	13.4	14.5	16.9
Density, g/cc	4.3	4.2	4.1
Cold Crushing Strength, MPa	81	65	67
1550°C/50hr Creep Deformation, %	-0.24	0.18	-1.98
1550°C/50hr Reheat Expansion, %	0.18	0.64	-0.08
Rotary Slag: % area change	0.13	5.2	5.8
Rotary Slag: slag penetration, mm	1.28	4.8	5.2

Figure 3. High chromium-oxide refractory brick after rotary kiln test. The ARC-developed brick is left, a commercial brick is right.

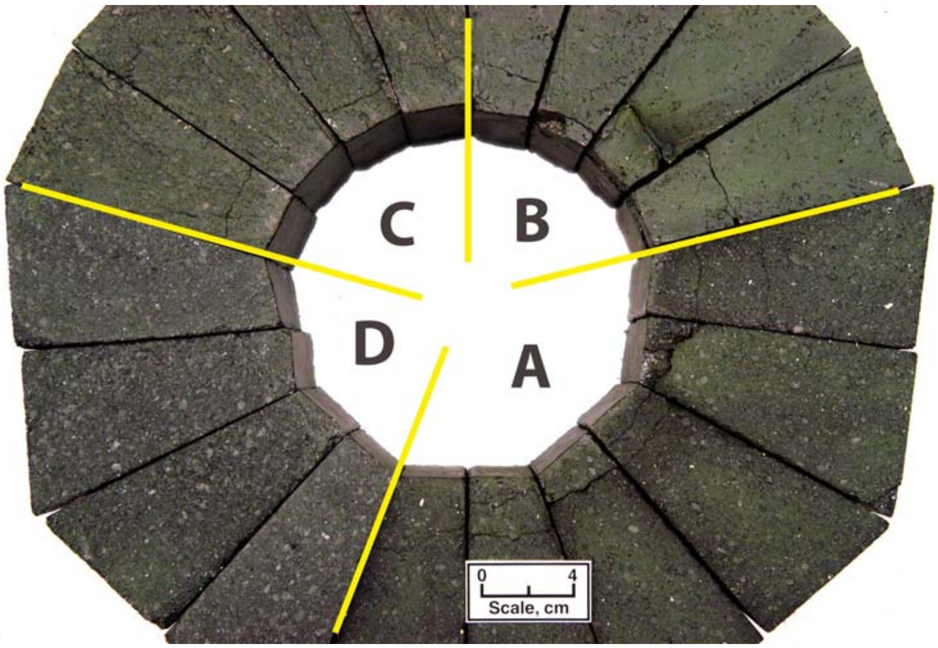

Figure 4. Side view of the refractory samples as they were oriented in the rotary kiln test. The inner surface was exposed to slag and heat. Samples A through C are commercial high-chromium oxide materials; samples D are the ARC-developed refractory. Note that there is much less cracking in D.

REFERENCES

[1] Bonar, J.A., Kennedy, C.R., and Swaroop, R.B., *Am. Ceram. Soc. Bull.* **59** 473-478 (1980).

[2] Bakker, W.T., Darling, S.L., and Coons, W.C., *Am. Ceram. Soc. Bull.* **62** 1359-1363 (1983).

[3] Bakker, W.T., *Key Engineering Materials* **88** 41-70 (1993).

[4] Fahrion, M.E., *Materials at High Temperatures* **11** 107-112 (1993).

[5] Bakker, W.T., *EPRI Report TR-110507*, Palo Alto, CA.(1999).

[6] Guo, Z-Q, Han, B-Q, and Dong, H, *Ceramics International* **23** 489-496 (1997).

[7] Guo, Z-Q and Zhang, H., *J. European Ceramic Soc.* **19** 113-117 (1999).

[8] Doğan, C.P., Bennett, J.P., Kwong, K-S., and Chinn, R.E., in *Proceedings from the 7th Bienneial Unified International Technical Conference on Refractories,* Cancun, Mexico (2001).

[9] Doğan, C.P., Kwong, K-S., Bennett, J.P., and Chinn, R.E., in *Proceedings from the 17th Annual Conference on Fossil Energy Materials*, Baltimore, MD (2003).

[10] Kwong, K-S., Doğan, C.P., Bennett, J.P., Chinn, R.E., and Petty, A.V., DOE Invention Disclosure S-97-969, "The Use of Phosphates to Stop Slag Penetration in Cr_2O_3-Based Refractories," (2001).

[11] Dogan, C.P., Kwong, K-S, Bennett, J.P., Chinn, R.E., and Krabbe, E., in *Proceedings from the 28th International Technical Conference on Coal Utilization and Fuel Systems,* Clearwater, FL (2003).

[12] Kwong, K-S, Dogan, C.P., and Bennett, J.P., in *Proceedings from the 18th International Conference on Low-Rank Fuels,* Billings, Montana (2003).