SILICA REFRACTORY: SOMETHING OLD THAT IS NEW

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When I started working in the refractory field, about 30 years ago, the brick qualities were completely different from what is currently available. Many of these changes have been driven by raw material availability and cost, and have resulted in a continuous improvement of properties. Additionally, demands for longer campaigns have also pushed for the use of new raw materials. For illustration purposes a loosely constructed and highly abbreviated time line for alumina brick used in steel ladles, based mainly on personal experience, follows. In the late 70s and early 80s most steel ladles in the US were lined with bloating fireclay brick which had about 30% Al_2O_3 (Schamotte is the European equivalent) and lasted for 12 to 15 heats before having to be replaced. The heats had minimal residence time in these ladles as this was before ladle treatment stations. In order to improve ladle life in the US, the brick quality was changed, first to 50% Al_2O_3 and subsequently to 70% Al_2O_3. The raw materials went from fireclays to SEUS grain (South Eastern US bauxite, no longer available) and Guyanese bauxites (mine flooded, and this product was not available for many years; the mine has since been reopened). Because of availability and cost issues, these bauxites were supplanted by Chinese ones which led to major changes in properties and therefore ladle life. Subsequent changes have seen an increase in the overall purity of the raw materials, higher alumina levels, use of fused aluminas, additions of MgO and carbon to the brick. At the same time the residence time of each heat in the ladle increased anywhere from 60 to 180 minutes with the concurrent increase in temperature loading and stressing of the refractory as a result of ladle refining. Nevertheless, ladle life has increased manyfold. A similar progression has not been observed with silica brick.

Silica brick are one of the older refractories still in use and their expected properties have not changed over, at least, the last 50 years. Depending on whose summary is used the first silica brick are believed to have been made in ~1842 from Dinas rock in South Wales [1] or even earlier, in 1820 [2]. In the US the first such brick were produced around 1866, although a patent for the manufacture of lime bonded silica brick was already granted in 1858 [1]. The 1957 edition of The Making, Shaping and Treating of Steel [3] reflects the easy availability of raw material and the ubiquitous use of silica refractories in the US. It also states that "massive rock forms analyzing over 98% SiO_2 are the chief raw materials for silica brick manufacture and are mined in Pennsylvania, Wisconsin, etc." [3]. But 1957 also seems to have been a water shed year as shown by the next few quotes. In Steelplant Refractories [4], the author states that "although silica continues to meet severe competition from basic refractories ....it still maintains its position as the No 1 steelplant refractory..." and "In 1957 silica was still the number one steel plant refractory, even though it was meeting severe competition from basic Refractories" [1]. The eminent position of silica brick in steel making was about to change. Over the period 1947–1965 the US production of silica brick dropped to a third, as a result of the shutting down of the open hearth furnaces [1] and the use of other types of refractories. It is of note that although the steel industry is the major consumer of refractories, silica brick is also used in the glass industry which has made up for some of these loses.

The properties of silica brick were well established early on. In the early 1900 it was already known that silica (SiO_2) is found in nature in one of three major forms: quartz, cristobalite and tridymite, nevertheless, much more work needed to be carried out to be able to elucidate the different relationships between them and how they affected the brick's properties. By the 1950's the technology for making silica brick was mature. In general, the expectation was that during manufacture of the brick the firing temperature would be sufficiently high to convert most quartz to either cristobalite or tridymite so the final product would have a consistent and small amount of permanent reheat expansion. Although a great amount of work can be found on the effects of different mineralizers on the rate of transformation of quartz to cristobalite and tridymite, most brick use only the originally determined small amount of lime for their bond. Silica brick are classified as KN (112 pcf or 1.79 gr/cm^3) or KD (116 pcf or 1.85 gr/cm^3) under the DIN 1089 standards [5]. ASTM C416 [6] presents another classification scheme, this one is based on a "flux factor" which is equal to the percent alumina plus twice the percent of total alkalies.

Silica brick's physical properties are unique making them the optimum material for many installations. Camerucci, et al. (2008) [7] showed that the properties of the brick have not changed significantly over time even though different raw materials were used for their manufacture. Camerucci, et al. (2008) [7] compared the properties of unused 25 year old brick with newly manufactured ones and determined that they were equivalent and therefore could be used interchangeably.

Silica brick have good thermal shock resistance once they exceed 600°C . Generally, high purity silica brick form only a small amount of low melting point phases up to 1650°C after which they can fail rather quickly. Tests carried out to simulate use conditions should prevent catastrophic failures. Although the properties required have not changed, silica refractory manufacturing technology has evolved over time. Originally all that was available were small, often intricately shaped brick which required very careful installation which took a long time to carry out. Currently, silica refractories can be obtained in brick or castable form. The latter has led to brick installations being replaced with precast shapes or even to be cast in place. The successful use of big precast shapes in place of the small and numerous brick which had to be painstakingly fitted together (example: part of a coke oven wall) has led to faster installations. In some cases whole walls are built out of a few precast pieces accomplishing a total replacement in hours instead of days [8]. In addition, changes in castable technology have also lead to the possibility of cast in place installations.

In summary, major changes have taken place in the alumina silica refractory system because of the use of new raw materials and the demands for improved life. Over the same time frame, the chemistry and properties of silica refractories have remained constant although new raw materials have had to be found. The reason is that their properties are optimized for the application. The changes that have occurred can be found in the "manufacturing" processes in that developments in castable technology have expanded the brick size and installation choices available.

If you have comments about this column or suggestions for future topics please visit me at www.refractoryexpert.com and I will try to address them.

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www.ceramics.org, Refractories World Forum, www.refractories-worldforum.com, Interceram (including the Refractories Manual issue), www.interceram.info, and Taikabutsu Overseas (Japan), www.tarj.org. The website for the next large international refractories meeting (Unified International Technical Conference on Refractories), in Salvador, Brazil, October 13-16, 2009, is www.unitecr2009.org; the program will include 240 papers, with attendees from around the world.

SUMMARY

What a huge change since the days of dial phones, manual typewriters, carbon paper, onion-skin copies, snail mail, no overnight mail, lab-developed photos, hand-drawn graphs, and the many other standard operating practices (SOP) that we utilized in past decades. Now there are countless sources for obtaining information and making business contacts worldwide which have provided incredible increases in productivity and efficiency.

Given the space limitations, this article just skims the surface of the countless Internet options for doing business, obtaining information, and many other tasks. Clearly there are numerous other good and useful sites and sources in addition to those mentioned herein. The content of this article is not intended to promote or endorse any company or website. The author welcomes any comments from readers regarding use of the Internet for work, and favorite refractory-related websites, and if enough responses are received, a follow-up article will be considered.

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