Research in refractory materials

by Prof Andrie Garbers-Craig

A new research drive in refractory materials, spurred on by Prof Andrie Garbers-Craig, aims to develop South African expertise in refractory materials in the pyrometallurgical industry. Industrially relevant research has already been conducted in the department's undergraduate and postgraduate programmes.

South Africa's natural heritage is unquestionably its abundant mineral resources. A large portion of these resources are pyrometallurgically treated, whereby commodities such as iron and steel, stainless steel, ferrochrome, ferromanganese, silicomanganese, ferrosilicon, silicon, copper, platinum group metals and titania are produced. South Africa also has the largest petrochemical industry in Africa, a cement industry that supplies its civil engineering and building sectors, glass smelting and recycling operations, and a foundry industry, all of which require refractory materials for successful operation.

A drive in the field of refractory materials research was therefore started in the Department of Materials Science and Metallurgical Engineering at the University of Pretoria (UP), as research in refractory materials at tertiary academic institutions in South Africa is currently very limited. The main aim of this drive is to develop South African expertise in refractory materials in the pyrometallurgical industry. Other role-players from industry that have become involved in this drive include Exxaro, Hatch SA, Lonmin, RHI, Vereeniging Refractories and Vesuvius SA. Collaboration with the Department of Civil Engineering at UP, through the use of certain laboratory facilities, has also been established.

This research programme is divided into research on MgO-based materials and on acidic materials. Research on MgO-based refractory materials focuses on the hydration of MgO-based materials, as well as wear mechanisms associated with the iron and slag tapholes, and centre piece refractory of ilmenite smelters. The latter project ties up with previous work by the department on bricks and castables that were removed from an industrial scale and a pilot plant ilmenite smelter, during which phase relations due to chemical wear were compared with those predicted by FACTSage calculations.

Research on the hydration of MgO-based refractory materials is important, because if an MgO-based lining hydrates significantly, it has to be replaced due to the associated danger of subsequent lining failure. Costs associated with the replacement of a complete MgO-based lining amount to tens of millions of rands, depending on the size of the smelter. Downtime and loss in production when the plant waits for a new lining add substantially to these costs.

MgO-based refractory materials hydrate at temperatures below ≈270°C, whereby periclase (MgO) transforms into brucite ($Mg(OH)_2$) according to the following reaction:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

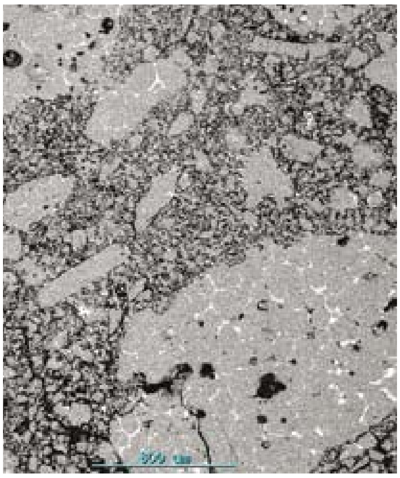
This hydration reaction is associated with a large volume expansion, which first leads to densification of the refractory material, followed by crack formation, loss in strength and eventually to the disintegration of the brick. Even if the degree of hydration of the MgO-based material is limited, the microstructure of the brick is not restored during refiring.

In the first project on the hydration of MgO-based refractory materials, the hydration of various MgO-based raw materials (sintered MgO, fused-grain MgO and fused-grain MgO-chrome) and MgO-based bricks (MgO, MgO-chrome and MgO-spinel bricks) was studied, using the humidity of a steam oven at 80°C over extended periods of time. Hydration was found to be mostly affected by the particle size of the raw material and its firing temperature, with fused grains having the highest hydration resistance. It was also found that the level of hydration of the examined MgO-based bricks increased with

1. Fused grain MgO raw material and an MgO-based brick.

the increase in CaO/SiO_2 ratio in the brick. This project was followed by another in which the relationship between the degree of hydration of MgO-based bricks and their CCS (cold crushing strength) and H-MOR (hot modulus of rupture) were evaluated.

Techniques to quantify the extent of hydration of MgO-based refractory bricks include assessing the LOI (loss on ignition), TG/DTA (thermogravimetry and differential thermal analysis) measurements and acoustic methods. The disadvantage of the LOI and TG/DTA tests is that they are destructive, while the acoustic test is dependent on the shape of the refractory product. An MEng project was therefore started in late 2009 on the development of a mobile, user-friendly hydration testing device, whereby the extent of the hydration of MgO-based refractory linings can be evaluated in a non-destructive manner.



2. Electron backscatter image of the typical microstructure of an MgO-based brick.

Research on acidic materials included a project on the evaluation of different refractory materials that can potentially be used in non-recovery coke-making ovens. This study aimed to understand why different suppliers of the non-recovery coke-making technology use different types of refractory materials. The properties of high silica (>95% SiO_2), alumina-silicate (40–85% Al_2O_3) and high alumina (85–100% Al_2O_3) refractory bricks were compared by evaluating them with respect to thermal shock resistance, CO resistance, creep resistance, RUL (refractoriness under load) and H-MOR. In general, the alumina-containing bricks showed superior behaviour when compared to silica bricks during the thermal shock, RUL and H-MOR tests. Results from the creep resistance test revealed that silica and alumina-silicate bricks have similar resistances to creep.

Research projects that cover both basic and acidic materials include a study in which the correlation (if any) between the H-MOR, CCS, abrasion resistance and micro-structure of both basic and acidic refractory materials is studied, as well as a Cr(VI) formation in Al_2O_3-Cr_2O_3-based materials, Cr_2O_3-containing materials that also contain calcium alumina cement and magnesia-chrome materials that are currently used in the South African pyrometallurgical industry. Although chromium-containing refractories have been eliminated and replaced by alternatives in certain countries and industries because of the health risk associated with hexavalent chromium, very few papers have been published on Cr(VI) formation in refractory materials. A need, however, exists for a more comprehensive study on the conditions under which, and to what extent, Cr(VI) formation is associated with Cr_2O_3- and chromite-containing refractory materials. Such data would serve as a guideline for the minimisation of Cr(VI) formation during refractory production, the development of alternative materials for specific applications, and the management of Cr(VI)-containing refractory waste.

This new research drive in the Department of Materials Science and Metallurgical Engineering on refractory materials has brought industrially relevant research in refractory materials into both the final undergraduate and the postgraduate programmes. Strong cooperation with and support from industry are highly appreciated and valued by the department.

Prof Andrie Garbers-Craig *is an associate professor in the Department of Materials Science and Metallurgical Engineering at the University of Pretoria and specialises in refractory materials. She was the 2008/09 President of the Southern African Institute of Mining and Metallurgy (SAIMM).*
(andrie.garbers-craig@up.ac.za)