About the author

Ruth Engel has been involved in the Steel industry solving refractory problems and spending some time as a process metallurgist for over 30 years. She started out working for Armco, later to become AK Steel, where she spent 25 years in their Research center. She then worked briefly for North American Refractories, covering mainly melt shop issues. Subsequently she became an independent Consultant and has expanded her areas of expertise to include other metals and industries as they also have many challenging refractory problems.

Ruth has published extensively and has taught training seminars for highly varied audiences. Over time, Ruth has been active in several professional societies like ASTM C-8 and ISS/AIST. The latter resulted in her organizing the first refractory session to be held during the Electric Furnace Conference.

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Chrome Bearing Refractories: Is There a Future?

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Chrome bearing refractories have had a checkered history. Although they have been around for a long time and used to be a high tonne material, they currently comprise a small fraction of all refractories sold. In their heyday they were used extensively throughout the steel industry, and in many other areas. Today they can be found mainly in alloy and specialty steels converters, steel degassers, melting/refining vessels for copper and lead, some coal gasifiers and cyclones. Their change in fortune can be attributed to several reasons which will be discussed in this paper, but their demise has been greatly exaggerated.

The Past

The largest consumer of refractories has always been the steel industry, so it is not surprising that many advances have taken place to accommodate their requirements. The first documented experimentation of chrome as a refractory material was in 1879 in the open hearth furnaces at Terre Noire, France (Gargers-Craig, 2008). In the 1880s, chrome refractories were already in use in large scale in the Petersburg- Alexandrofsky steelworks (Chesters, 1973). By 1886 several European open hearths had installed them and, around 1896 they could be found in use in the USA (Garbers-Craig , 2008).

These early chrome refractories consisted of molded and fired chrome ore which is a mixture of different minerals, in particular of spinels. Its predominant phase is chromite (Cr_2O_3), but it also contains alumina (Al_2O_3), magnesia (MgO), silica (SiO_2), iron oxide (Fe_xO_{x+1}), etc. Several problems with chrome refractories lead to them being replaced by other systems, not the least of which was their bursting when in contact with iron oxide, their crumbling as a result of alternatively exposing them to oxidizing and reducing atmospheres or their continuous shrinkage and softening as a function of high operating temperatures. The addition of magnesia "solved" many of these problems and lead to the development of magnesia chrome ($MgO > 50\%$) and chrome magnesia ($Cr_2O_3 > 50\%$) refractories.

Commercially available chrome magnesia brick was reported in the 1930s (Garbers-Craig, 2008, Chesters, 1973), but patents describing these type of refractories can be found as early as 1915. Chrome magnesia brick were manufactured for many years although they sometimes presented the same problems than when using chrome brick. One of the biggest consumers of refractories were the open hearth furnaces. A 1957 article in The Making, Shaping and Treating of Steel read "the supremacy of

A Listing of Major Panel Trials during 1971-1974

1. Sea-water periclase, Transvaal chrome ore direct-bonded 60% MgO brick.
2. Sea-water periclase, Phillipine chrome ore direct-bonded 60% MgO brick (4 varieties).
3. Imported 60% MgO direct-bonded brick – Austrian magnesia, Transvaal chrome ore brick.
4. Sea-water periclase, Transvaal chrome ore direct-bonded 80% MgO brick.
5. Sea-water periclase, Phillipine chrome ore direct-bonded 50% MgO brick (2 varieties).
6. Pre-reacted magnesia-chrome direct-bonded 60% MgO brick.
7. Pre-reacted magnesia-chrome direct-bonded 50% MgO brick.
8. Fused grain magnesia-chrome 60% MgO brick.
9. Grecian periclase, Transvaal chrome ore 60% MgO brick (2 varieties).
10. 94% Al_2O_3 burned brick.
11. A silicate bonded chrome ore brick with chromic oxide addition.
12. Direct-bonded, low silica, chromic oxide fortified 60% MgO magnesia chrome brick (2 varieties).

FIGURE 1 Converter Refractory Trials

silica brick for open hearth roofs has not seriously been threatened by basic brick, although a few experimental all basic (referring to chrome magnesia) roofs have shown promise". These trials had started to take place in Europe in the 1930s (Garbers-Craig, 2008), but the switch to magnesia chrome brick for this application did not take place until much later because the refractories failed frequently and the problem of bursting or peeling had to be solved.

The big push to switch to magnesia chrome brick for many applications started in the 1960s as a result of their superior slag resistance and stability to higher temperatures. New steelmaking processes were demanding refractories which could withstand higher temperatures and different slags and the more established processes were also evolving by taking less time to melt and refine a tonne of steel. The refractory manufacturers responded to the challenge by developing many different types of magnesia chrome brick. Baker in his 1975 paper alone mentioned at least 12 different refractory trials, carried out between 1971 and 1974. Brick panels with different compositions, chemistries, raw material bases or, a combination of all of these were installed to address specific wear areas with the aim to increase converter life and decrease overall lining cost (Figure 1). In addition, the availability of magnesia chrome refractory in a castable or ramming mix form further expanded their use.

The ability to fuse magnesia and chrome ore in an electric arc furnace lead to many advances in refractory technology. Once fused, the liquid can be cast into ingots for use as is (for example C-104) or can be broken up and converted into grain for brick manufacture. In 1962 a rebonded-fused grain (RFG) refractory was introduced in the USA (Garbers-Craig, 2008). The advantages of RFG type brick are their higher density than the standard product due to lower porosity of the grain, the ability to use big grains and its direct bonding between magnesia to magnesia or magnesia to spinel grains thereby greatly improving its slag resistance. Tonindustrie Zeitung und Keramische Rundschau published many basic research articles on the topic. Figure 2 comes from their July, 1967 issue and shows the improvement of open hearth roof life as a result of the use of fired instead of unfired brick.

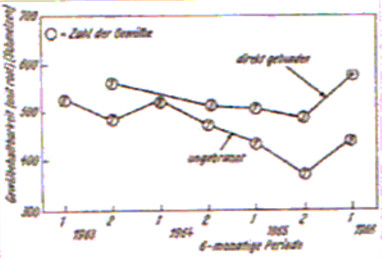

Bild 5
Vergleich der Gewölbehaltbarkeit
von ungebrannten und direkt-gebundenen Steinen
in einem Werk

FIGURE 2 Comparison of OH roof life

The 1970s and early 1980s were an exciting time in that much work was carried out in furthering the understanding and technology of magnesia chrome refractories: their wear, the required bond properties for best life in different slag environments, the slag chemistries needed for refractory compatibility, etc. Figure 3 shows the early utilization of electron microscopy to elucidate how the magnesia and chrome are found in a fused grain. This investigative enthusiasm was dampened considerably in the USA when, in 1986, the Environmental Protection Agency (EPA) released its maximum leachable chromium level mandate as the result of attempting to regulate the pollution created by the chromium used in industries such as chrome plating, leather tanning, and textile manufacturing. Refractories were not part of the original "offending" industries, but found themselves drawn in due to the use of magnesia-chrome and the consequent danger of formation of Chrome(VI) at high temperature and in the presence of alkali oxides. The issue was the recognition that Chrome (VI) is highly soluble in water and could find its way into the water systems if the used linings were simply dumped. Today, most countries have some type of regulation*5, 6 addressing this as "hexavalent chromium is widely considered to have significantly greater toxicity than the trivalent form. This results in part from the recognition of hexavalent chromium as a known human carcinogen by ..."(EPA, 1998). Lee and Nassaralla (1997, 1998), published several studies based on work carried out on used magnesia chrome refractories recovered from industrial processes. The used brick had been exposed to known temperatures and slag

Bild 38
MgO-Cr_2O_3-Schmelzprodukt

FIGURE 3 High magnification of fused Mag-chrome grain environments and were compared to as received samples to determine the fundamentals of Cr(VI) formation. As a result of this and the work of many others in academia and the refractories industry, the use and disposal of chrome bearing refractories, should not present a problem. Some of the changes made to their manufacture to avoid Cr(VI) formation were to increase the use of fused grain, control the amount of CaO in the refractory, minimize the use of fine chromite phase during manufacturing, etc.

Other chrome bearing refractories have been manufactured, but with limited commercial success. Alumina chrome though is the one that is routinely used. In the late 1970s alumina chrome brick were developed (Schacht, 2004) containing chromic oxide instead of chrome ore. This functions as a sintering aid allowing for the direct bonding at firing temperature without resorting to silica and leading to a highly refractory product which also has very good slag and thermal shock resistance. This product can also be bought as a castable, a ramming mix, plastic or a mortar. Due to the presence of chrome in these mixes they fall under the same disposal restrictions as the magnesia bearing refractories.

The Future

The past is easily discussed as all that is required is recounting established facts while predicting the future is risky and fraught with unknowns. I will speculate, on the probability of the continued use of chrome bearing refractories, but keep in mind that this is one person's educated guess and the probable timeframe is about five years.

The use of magnesia chrome refractories has declined over the time, but, for the last 10 years or so, their consumption has remained fairly stable and they continue to be used in very severe environments. In addition, alumina chrome refractories continue to be used in special applications. To completely replace them, new types of materials or combinations would need to become available. The development of alumina spinel (AMC) technology was driven as a replacement for magnesia chrome in slagging applications. Even though it achieved this goal in many areas, alumina spinel refractories have not been successful in very severe environments, where magnesia chrome is still preferred as its life is significantly longer. Alumina chrome monolithics are often found in cyclones even though alumina silicon carbide can also be used, but again its life is not as reliable.

Over time many naturally occurring oxides or silicates have been used for refractories: olivine, silica, fireclay and so on. Some have been supplanted by more refractory variations while others have been relegated to niche applications. Because of the limited number of plentiful oxides which also are refractory in nature the quest for synthetic materials with suitable properties and cost structure is actively being pursued. Non oxides are used, by themselves or in combination with oxides, in several areas, but they have restrictions as to their applicability. In the future there will probably be an expanded role for them. These technical hurdles have lead me to believe that, the use of magnesia chrome refractories will continue unless a major raw material upheaval occurs whereby fused grain is either no longer produced or its cost becomes prohibitive, the alumina chrome refractories will keep their place as their slag resistance is superb, but chrome ore refractory use will approach zero.

Thanks to the diligent efforts of peoples from many different disciplines, refractory manufacturers have successfully developed products that address public health concerns enabling the continued use of chrome bearing materials. As always, the proper disposal of these refractories should be incorporated into their life cycle considerations. The future holds many surprises as we have "limited raw materials, but unlimited creativity" (Semmler, 2010) and the development of new and novel combinations will undoubtedly expand the available choices and move some systems into the historical curiosity bracket, but chrome bearing refractories are not one of them.

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

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