



*How do you tell which product has better thermal shock resistance? See page 4 for how refractories are tested for thermal shock.*

*Where does all that slag come from? In Pittsburgh, malls are built on it, houses are built on it, and it is probably under every road in town. See slag on page 3.*

## THE BUZZ

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**Kyanite** is a refractory mineral used to control shrinkage and expansion of many high alumina refractory products. It is also a very economical source of alumina. Pictured above in a larger crystalline state it can be a gem stone. See article on page 2 on how kyanite is used in the refractories you buy.

## STEEL WARS

Will Obi-Wan Kenobi rush to the defense of the American Steel and Refractory Industries? See page 2 for our take on the subject.

## **STEEL WARS**

On March 5, 2010, the US Commerce Department fired the first refractory missile into the belly of the Chinese export machine and placed preliminary duties of up to 349% on magnesite-carbon brick from China. The suit, brought on by several domestic refractory brick manufacturers, was deemed a success in the ongoing trade battle with the country that is now the largest exporter in the world, surpassing Germany in 2009. The initial reaction was one of joy on behalf of the refractory producers and one of dread by steel producers, caught in their own battles in international trade, and now faced with higher refractory costs. The immediate effect was to stop magnesite carbon shipments from China and cause, at least short term, shortages of magnesite and graphite, materials the U.S largely gets, you guessed it, from China.

In 2009, China produced 570 million metric tons of steel, more than the U.S., Japan, and the European Union combined! Most of this production was to feed the huge infrastructure build up in this very fast growing economy. Though China has some raw materials to feed this huge beast, it imports much of its raw materials from overseas. One raw material used in the production of steel is iron ore. China gets much of its iron ore from Australia, where the mines are largely controlled by a huge international mining corporation, Rio Tinto. In July of 2009, several Rio Tinto employees including one executive, were arrested in China for spying, bribery and price fixing. In March of 2010, 4 of the employees were convicted and sentenced to jail for up to 11 years. If people didn't know that China was serious about protecting its iron ore supply before, they know it now.

As it takes over 2 tons of raw materials to produce 1 ton of steel, that means that over a billion tons of raw materials are flooding into Chinese steel mills. Coal, limestone, and iron ore are flooding the ports of China, the same ports exporting Spiderman dolls and children's clothes to the U.S. Meanwhile, most of the Western economies are suffering from recessions or very slow recoveries, and though their steel industries have bounced back from last year, they are still significantly lower than pre-recession levels. Despite this, the Chinese steel machine's appetite for raw materials has driven up their prices and steel prices in the U.S. and Europe are also going up. Hot rolled steel in March of 2010 was up to \$650 a metric ton up from \$390 the previous June. This is a sure sign that the Western economies demand no longer drives the market, the Chinese economy does.

Mt. Savage Specialty Refractories is mostly an observer in these steel wars that other refractory companies have decided to join into. MSSR does get calcined bauxite from China, and the raw material shortages have spilled over somewhat to some domestic materials, but in the scheme of things, only in a minor way..

Though the Chinese refractory, raw material, and steel markets are not a single entity, they are closely enough related that a shot into one aspect of them will likely relate to another. The Chinese government does set export policy to promote chosen industries. For example, there used to be tax advantages for exporting refractory raw materials, these were removed and given to manufactured refractories. This is what largely spurred the anti-dumping action by the U.S. refractory manufacturers. When the Chinese economy slows, and it will, some of the 600 million tons or so of steel production will likely be turned loose on the Western economies. Before this is over, there will be many more shots fired in the steel wars.



**Taconite pellets refined from iron ore in Northern Minnesota are unloaded at Gary, Indiana for processing into iron and steel. U.S. Steel and other domestic companies, have their own mines and processing plants, reducing their dependence on outside sources.**

## **KYANITE**

Kyanite is a very important raw material for the ceramic industry in general and the refractory industry in particular. The neat thing about kyanite is when you heat it to very high temperatures, it expands. This can be very useful. Large deposits of kyanite can be found along the Appalachian foot hills in Virginia, the Carolinas and Georgia. The largest commercial mine is near Dillwyn, Virginia run by Kyanite Mining Corporation, also known as Virginia Kyanite.

As mined, kyanite is a very refractory material that consists of approximately 55% alumina and 41% silica. It is very low in alkalis, iron, and other impurities. When heated to high temperatures (above 2300°F), the kyanite converts to mullite and glass, both of which are less dense than the kyanite itself. This leads to an expansion of the grain. Coincidentally, this occurs at a temperature where many ceramic bodies are starting to develop a ceramic bond which usually leads to some shrinkage. By balancing the amount of kyanite you put in the mix to the amount of shrinkage that would otherwise occur, the refractory engineer can develop a volume stable product that doesn't shrink or expand.

In other cases, it is desirable to have a little bit of expansion, and higher amounts of kyanite can be added to the product to produce this. Regardless, the next time you use a fireclay or high alumina product, it is likely to contain some kyanite.

## Slag

Living in Pittsburgh, people see mountains of slag. Some people actually live on piles of slag while others have businesses built on it. How did all that slag get there and what is slag anyway?

Slag is the waste oxide components of metal ores. During smelting, these oxides will melt and float to the top of the metal and must be disposed of. The two most common components in the Earth's crust, and thus in slags, are silica and alumina. These components sometimes need a little help melting so lime is often added to flux them. Add too much lime and you attack refractories, don't add enough and the slag is too thick to skim off. Knowing the chemistry of the slag is important to both the metallurgist running a furnace and to the refractory engineer making lining recommendations.

Mt. Savage offers a variety of products designed to prevent slag attack. One is to add neutral and non-wetting additives to the products such as silicon carbide or graphite. Slag tends to not wet these minerals and thus not penetrate into the refractory body (picture water on a freshly waxed car hood). Neutral oxides like chromic oxide are resistant to both acid and basic slags, but can cause disposal problems in some cases. As alumina is more neutral than silica, higher alumina products will tend to have better resistance against alkaline slags than lower alumina products.

When dealing with a slag issue, consider your choices starting with what has worked before. Get the chemistry of the slag and if increasing service is the goal, move the chemistry of your next choice toward the chemistry of the slag. Neutral products like alumina and chrome are often good choices for a variety of slag conditions. For very alkaline conditions, such as in steel mill BOF's, basic products may be necessary to prevent rapid slag attack.



Blast furnace slag being dumped into a pit. Much of this is allowed to cool and is processed into aggregate for bedding for roads.

## Ask Dr. Dirt

**Dear Dr. Dirt,** Do I really need to spend all this money on these expensive stainless steel anchors? What is the difference between stainless and carbon steel anyway? **Fred in Houston**

**Dear Fred,** The short answer is you only need to use the stainless steel anchors if you want your refractory to stay on the wall. The main difference between stainless and carbon steels is that stainless contains chromium and other alloys including nickel and molybdenum to resist corrosion. At higher temperatures, even the lime from the refractory can corrode plain old carbon steel. So rarely are carbon steel anchors a good choice. Three common stainless anchors that are used are 410, which has about 12% chrome (Cr) and no nickel (Ni), 304 which is 18% Cr and 8% Ni, and for very high temperatures, 310 which is 25% Cr and 20% Ni. Lists of proper anchors for a given temperature and environment are available by calling your local MSSR agent. **Dr. Dirt**

**Dear Dr. Dirt,** If something is a no cement castable or gun mix, how in the heck does it get hard? **Clueless in Seattle**

**Dear Clueless,** Excellent question. Mt. Savage has several no cement products. One definition is that cement is a lime containing material that has a chemical reaction with water to form a hydration phase which hardens a concrete. By that definition, the calcium aluminate refractory cements and Portland cement both fall into that category. There are other materials, such as reactive alumina bonds, that also hydrate, but since are lime free are not considered a cement. Mt. Savage "NC" mixes are based on this hydratable alumina.

The more interesting cement free mixes, however, do not hydrate. They form a gel where water acts as a catalyst. Colloidal silica is a product that can form a gel, and once the water is driven out, the bond gets stronger and stronger as the temperature goes up. Other forms of silica and other compounds can also be made to gel and form the same type of high strength, high temperature bond that can be formed with colloidal silica. The main advantage of these gel bonds is that the water is not chemically combined with the particles and is driven off at around the boiling point of water. Cement water of hydration is driven off at much higher temperatures, increasing the chance of pressure build up and a steam spalling incident. Thus, no cement mixes can generally be dried out faster than cement containing mixes. Mt. Savage will be introducing a new line of cement free gunning mixes under the trade name **SAVAGE PDQ** (for you can dry it out "pretty darn quick") in the very near future.

Another form of cement free bonding that is used in the refractory industry is a phosphate bond, either single or two component. Mt. Savage has a long and successful history with its phosphate bonded **Q-TEK** family. This is a chemical bond between phosphate and alumina and is also very strong and refractory. This has the added advantage of bonding much better to used refractory surfaces compared to cement bonded or colloidal silica bonded mixes. **Dr. Dirt**

## Thermal Shock Testing

Thermal shock resistance is one of the most important properties in a refractory. As most ceramic products, refractories are brittle and wide swings in temperature can damage and crack the material. Some refractories are less brittle than others, so are less prone to thermal shock. Refractory design engineers have developed several laboratory tests to determine what is more and what is less thermal shock resistant.

One test, called the prism spall test, consists of taking a group of three 2" or larger cubes, heating them to a given temperature, usually 2200°F, dunking them into water, then repeating this cycle every 10 minutes until the cube breaks into two or more pieces. To differentiate further, the technician running the test will also note when cracking first appears. The more cycles that the product goes, the better the thermal shock resistance is. For instance, a high cement castable will break apart in 3 to 5 cycles in this test, a low cement castable will go 20 to 30 cycles, and a fused silica castable or brick will go 40 plus (they usually stop the test at 40).

As you can imagine, the prism spall test is pretty severe and the argument against it is that it is rare that refractories in service see such severe thermal shock. A somewhat less severe and usually faster test is the loss of strength test. This is usually run on 6x1x1" samples. Either 6 or 10 bars are prepared. If it is a specialty product, the bars are pre-fired. Half the samples are cycled from 2200°F to air every 10 minutes for five times. The cycled bars and the bars not cycled are both tested for modulus of rupture (MOR). The percent loss of strength is calculated by subtracting the MOR of the cycled bars from the MOR of the un-cycled bars then dividing by the un-cycled MOR (and multiplying by 100 for percent if you are keeping track). The higher the number, the higher the loss of strength in percentage terms, the higher the apparent thermal shock. A fireclay brick would have a loss of 50% or so of its strength in this test while a fused silica brick would be less than 10%.

Neither test is a perfect predictor of what materials will do in service, but it gives the design engineer some feel for overall thermal shock resistance. This kind of testing allowed the accurate prediction that low cement shotcrete products would work better than high cement gunite mixes in an ash hopper, a high thermal shock application. These tests, however, are fairly variable so are not accurate enough to determine small differences in thermal shock resistance. That is probably why you don't usually see these numbers on a refractory data sheet.

Thermal shock is a major wear mechanism in refractory products. Ask your Mt. Savage representative for more information if thermal shock is a problem in your application.

## Thermal Shock Guide

Below are some selected specialty product types listed from best thermal shock resistance to worst. This list can vary a little based on temperature, but is a good general guide. When looking at thermal shock applications, consider staying high on this list.

1. Fused Silica Low Cement
2. Fused Silica Conventional
3. Silicon Carbide Low Cement
4. No Cement High Alumina
5. Ultra Low Cement High Alumina
6. Low Cement High Alumina
7. Ultra Low and Low Cement Fireclay
8. Conventional High Alumina
9. Conventional Fireclay

Note that fused silica in cycling applications has a temperature limit around 2000°F, but below that is almost immune to thermal shock. Also, the lower the cement, the better the thermal shock resistance is another general rule of thumb.



**Buzzi says "when dealing with large temperature swings, make thermal shock your number one concern. If you don't keep it from cracking, high strength won't do you any good"**

**Mt. Savage, Maryland** has always been a hot bed for industry, but is also in a beautiful area to visit. Located at the base of scenic Big Savage Mountain, there are lots of wonderful tourist destinations only minutes from town. There is the Great Allegheny Passage, a rails to trail that spans from Washington, DC to Pittsburgh, the Frostburg Scenic Railroad, Wisp Ski Resort, Deep Creek and Youghiogheny Lakes, white water rafting and expert kayaking, Swallow Falls State Park (pictured below), and the Savage River Scenic Valley. Contact your travel agent or Dr. Dirt to book your vacation travel to the area soon!

