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# Refractories Applications and News

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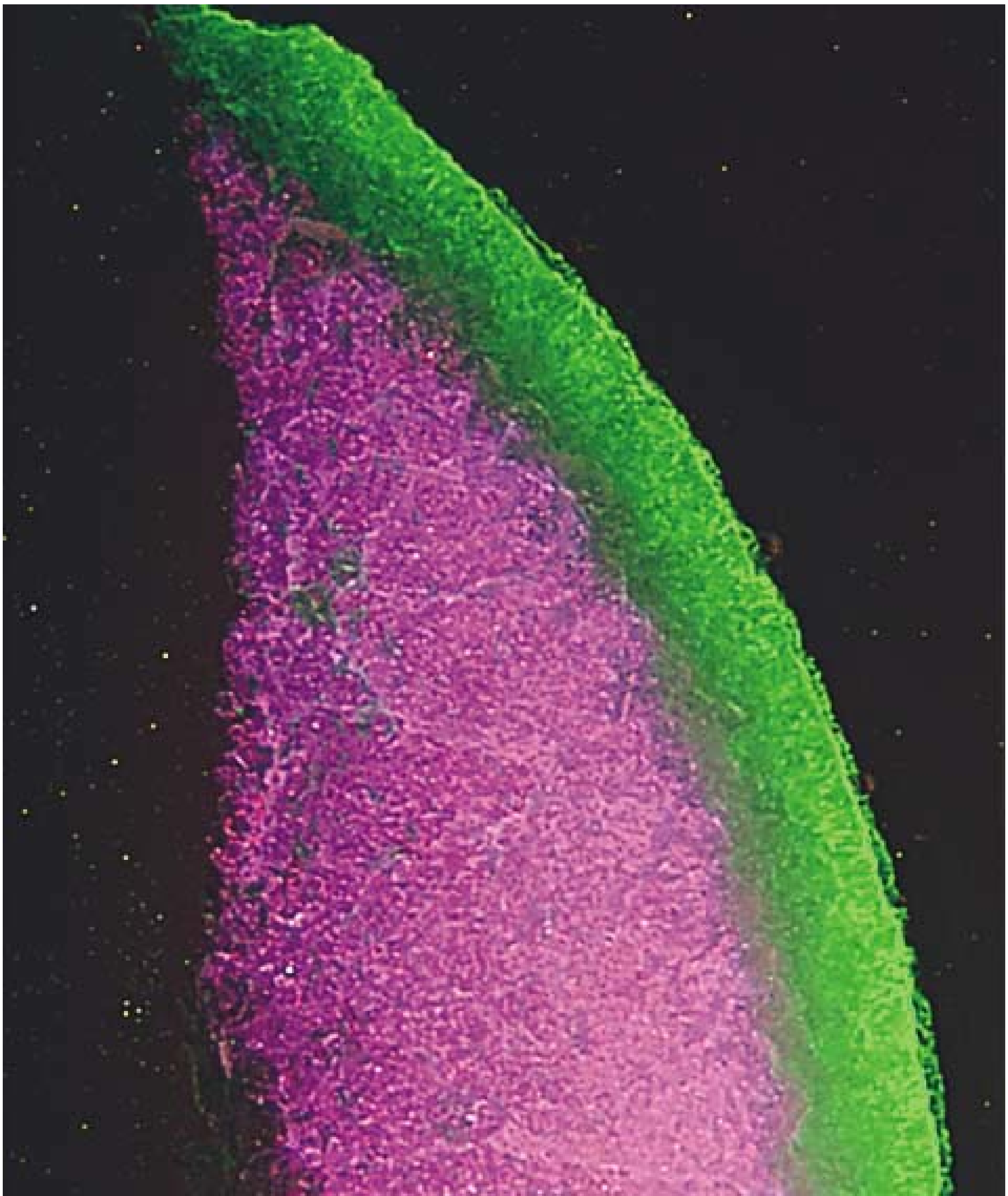

# Refractories Applications

## *and News*

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**Technology Bimonthly for the Global Refractories Industries**

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# REFRACTORIES FOR GASIFICATION

**Wade A. Taber, Application Engineer, Saint-Gobain Ceramics / Energy Systems**

***(Reprinted from The Refractories Engineer, September 2002)***

Gasification is a well-established process, used throughout the world for over fifty years. Recent environmental legislations, economics and process improvements have bolstered its commercial popularity and public recognition, creating rapid growth in the gasification industry. The refractory technology used in gasification is similar to that of other applications, however the unique combination of the process characteristics involved present challenges in refractory selection and design.

## INTRODUCTION TO GASIFICATION

Simply stated, gasification is used to produce synthesis gas from carbon-containing feedstocks that may be in liquid or solid form. The synthesis gas, or syngas, may be used to generate electricity or to produce chemical components for a variety of applications. Gasification is environmentally friendly, due to the severe reduction or absence of many pollutants produced in competing processes such as coal fired power plants, incinerators, refineries, etc.

It should also be mentioned that the term “feedstock” is used, rather than “fuel”, since the reactant materials are not consumed in the normal sense. Typical feedstocks include fossil fuels (i.e. natural gas, heavy sulfur fuel oils, coal and petcoke), carbonaceous waste and by-products, or other low-value carbon-based materials. Feedstocks are categorized as being solid or liquid (non-solid) for the necessity of gasifier vessel design and refractory selection, since the behavior of the process (i.e. slagging, temperature, etc.) is greatly dependent on the starting conditions.

The process reactions that define gasification of the various feedstocks are similar. The feedstock is combined with a stoichiometrically limited amount of oxygen, and perhaps other controlling constituents such as steam or fluxants. A series of partial oxidation (combustion) and reforming reactions then occur to produce syngas, which is primarily composed of carbon monoxide and hydrogen. The reactions may be exothermic or endothermic, and occur at different time intervals in the process, based on the specific kinetics of each reaction. Dozens of other reactions also occur within the unit, although the primary reactions are as follows:

$C_nH_m + (n + m/4)\ O_2 \leftrightarrow n\ CO_2 + m/2\ H_2O$ (combustion, exothermic)

$CnHm + n/2\ O_2 \leftrightarrow n\ CO + m/2\ H_2$ (combustion, exothermic)

$CnHm + n\ H_2O \leftrightarrow n\ CO + (m/2 + n)\ H_2$ (reforming, endothermic)

$CnHm + n\ CO_2 \leftrightarrow 2n\ CO + m/2\ H_2$ (reforming, endothermic)

$CO + H_2O \leftrightarrow CO_2 + H_2$ (shift conversion, exothermic)

A general overview of a gasification facility is shown in Figure 1. The product syngas may require additional process steps such as particulate removal, gas cleanup or further refining depending on the end-user’s desired result. In addition to producing chemicals, the gasification process can be used to generate electricity. Electricity can be produced by the direct burning of syngas in a combustion (gas) turbine or by heat recovery methods in a steam turbine. Some gasifiers may be used in a combined cycle operation, in which heat is produced as a by-product and converted into electricity, while the cooled syngas is used to make other chemicals or commodities. With the increasing demand for energy worldwide, the focus of gasification technology has shifted from chemical production to power generation in recent years. This shift is further aided by a reduction in feedstock and startup costs.

There are currently over 160 gasification facilities either running or planned in 28 countries throughout the world. When all of these units are in operation, they will have a total daily capacity of 430 million cubic meters of syngas, which is equivalent to more than 770,000 barrels of oil per day. Numerous OEM (Original Equipment Manufacturer) designers and licensors are responsible for the varied processes, such as ChevronTexaco (formerly Texaco), Shell and Lurgi, to name only a few. The historical and projected future increase in gasification activity is evident in Figure 2.

Please refer to the Gasification Technologies Council (GTC) website at www.gasification.org for a better understanding of the gasification process. More

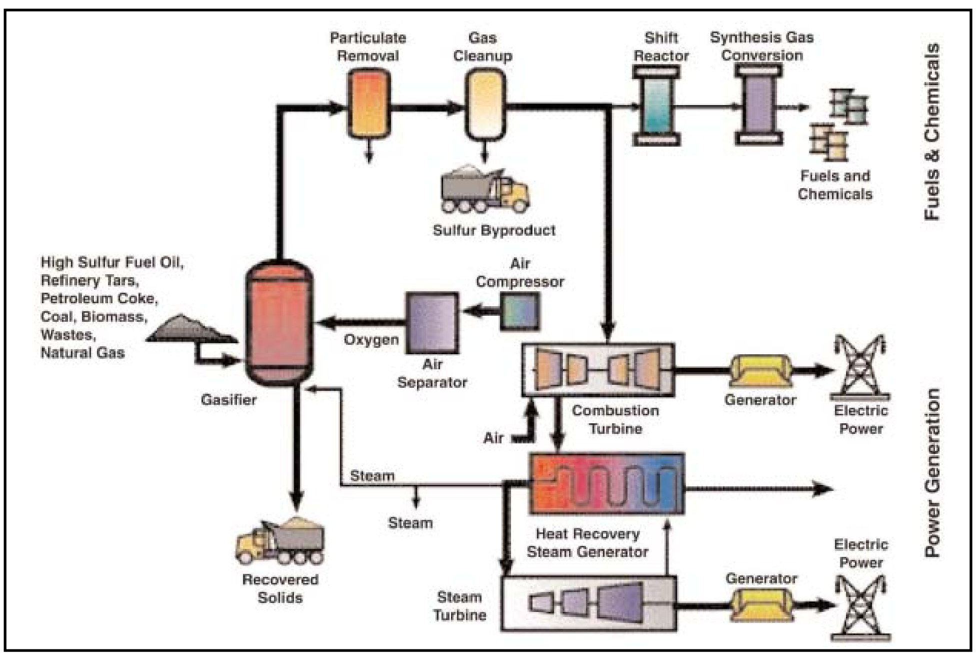


**Figure 1. Overview of the gasification process, used with permission from the Gasification Technologies Council.**

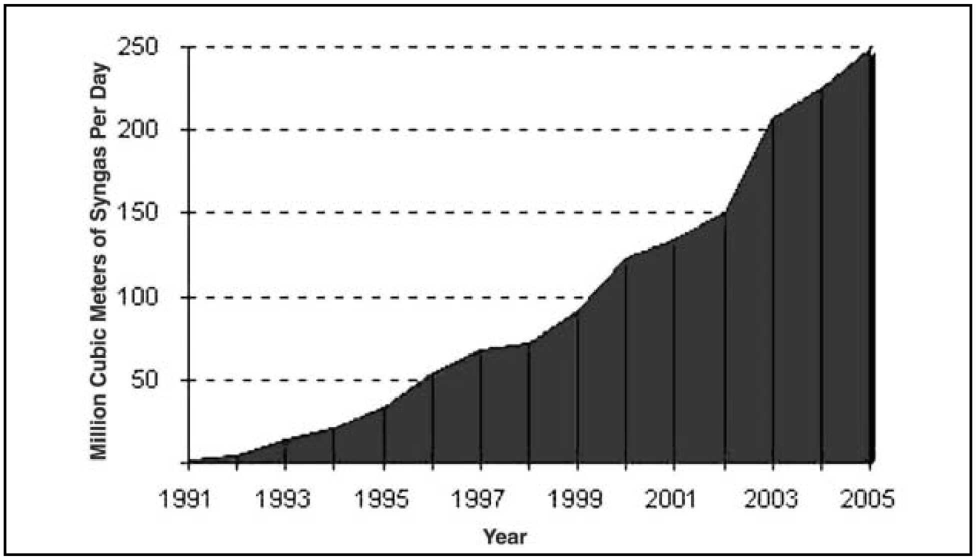


**Figure 2. Cumulative additions to world gasification capacity, from a SFA Pacific study for the U. S. Department of Energy, used with permission from the Gasification Technologies Council.**

**Figure 3. A rendered gasifier assembly. The inner (darker) layer depicts the hot face and the safety layer is white. The following shapes and monolithics represent low duty materials used primarily for insulation. The generalized steel shell is shown in gray, with expansion joint details removed.**

information, plus current news and related resources are made available to the public through the GTC organization.

## REFRACTORY LININGS

The refractory lining is an integral part in the majority of entrained flow gasifiers. Proper material selection and well-executed lining designs are necessary to insure the longest possible service life, as even a minor lining failure could cause a shutdown of the gasifier and dependent processes. The downtime of a gasifier can result in a penalty of hundreds of thousands of dollars per day, incurred from lost production and maintenance expenses. Therefore, refractory reliability is essential. Other non-refractory related problems might frequently cause these units to go offline as well. However, refractory outages generally require the most time to resume production and operators have been successful in limiting the other shutdown causes, focusing increased attention on refractory performance.

A generalized refractory lining for a gasifier is depicted in Figure 3, taking care not to disclose some features that OEM providers consider proprietary. As with other refractory applications, a component lining is used and may contain anywhere from 2 - 6 concentric layers. All gasifiers are generally cylindrical, ranging in height from 1.5 – 25 meters and 0.5 – 5 meters in diameter for production-sized units. More complex gasifier linings may have additional cylindrical chambers to accommodate specialized reaction kinetics or syngas temperature manipulations. Feedstocks are typically introduced through the top of the vessel, using a burner or feed injector. The feedstocks then react at high temperatures and pressures to form the syngas, which is removed in the lower chambers or attached zones.

## REFRACTORIES FOR LIQUID AND GAS FEEDS

Refractory linings for liquid feedstocks are expected to last long periods of time, since there is minimal slagging and erosion induced from the non-solid feeds. Oil gasifiers may employ linings that are expected to last 4-5 years, while cleaner gaseous feedstocks can be used for 6-10 years or more, with only minor repairs required every few years. Every design detail is important to make the service life transition from months to years. A refractory engineer must also take into account the chemical stability, thermal and mechanical properties of the overall configuration. The major refractory issues may be discussed in detail, however the interdependence of all features is important to realize when designing a successful lining.

The first step in refractory design involves information gathering from the process developer. The general size and shape of a vessel are typically specified, based on the syngas capacity required by the end-customer. Process chemistry is also confirmed to make sure the lining materials will remain inert during operating conditions. A dense material is chosen for the hot face, where the exposure to the gasification reactions is most severe. The second "safety" layer is usually formed with a similar material, although lower densities may be used to yield lower thermal conductivities. Subsequent layers are used to provide insulation and expansion characteristics, as needed.

Operating temperatures can be very high in a gasifier. Depending on the type of unit, temperatures can generally range from 1200ºC - 1500ºC. Many refractory materials can not offer the mechanical strength and creep resistance (plastic deformation under load) required for linings of this size to operate at these temperatures. Lower molecular weight feedstocks, such as natural gas, are also highly reactive to changes in the mix proportions of the reactants. Temperatures may elevate very quickly if excess oxygen is supplied to the gasifier. Therefore, the thermal shock resistance of the materials can be a critical factor.

High alumina refractories are a common choice when utilizing liquid feedstocks, even though the cost may be higher than lower-grade conventional materials. These alumina materials can be used at temperatures up to 1800ºC, while offering moderate thermal shock resistance, if the purity level is greater that 99%. Alumina is also very non-reactive to the chemical components found within the gasifier.

## CHEMICAL COMPATIBILITY

Chemical stability of the refractories at high temperatures is necessary. Since syngas is rich in hydrogen, materials with very low silica content (less than 0.5%) are required. The internal atmosphere of a gasifier is highly reducing. Oxygen is a key reactant in the process, however all of the oxygen is entirely consumed near the inlet. The reduction of silica within the refractory materials is likely at temperatures over 1200ºC. By-products of this reaction are steam and gaseous silicon oxide, which has a tendency to condense out of the syngas when it cools and forms a hard, white “ash” material that may clog process lines and necessitate removal. The mechanical properties of the remaining refractories are compromised when the silica is removed from the system, since silica usually forms a glassy phase that affects the bonding characteristics of the ceramic. The silica reduction reaction appears as follows:

$SiO_{2\ (solid)} + H_{2\ (gas)} \leftrightarrow SiO_{\ (gas)} + H_2O_{\ (gas)}$

Other impurities in the high alumina materials must also be minimized. Iron oxide, soda, and other heavy metals may have negative effects on the refractories’ high temperature properties. Several fluxants, such as vanadium pentoxide, can decrease the melting temperature of alumina to a level found within the operating environment. Soda (sodium oxide) may promote a change in the crystal structure, from alpha alumina (most refractories) to beta alumina. The resulting crystalline change, or its reversal with temperature fluctuation, will cause excess expansion of the lining. Iron oxide can act as a catalyst for several deleterious reactions, such as the decomposition of carbon monoxide to form carbon, known as the “Bouduard” reaction. When carbon is deposited in the porosity of the refractory lining (in the temperature range between 400ºC - 700ºC), a volumetric expansion occurs and results in the destruction of surrounding materials. The Bouduard reaction appears as follows:

$2CO \rightarrow CO_2 + C$ (in the presence of iron oxide, and resultant iron carbides)

It’s important to note that these chemical reactions may be among the most common, but not the only ones that may cause problems with the refractory materials. The impurities that can cause these reactions may be inherent to the alumina refractories (i.e. contained in the raw materials), unintentionally added during installation, or predominantly found in the gasifier feedstock. In severe cases, vibro-cast alumina shapes may be used in place of conventionally pressed bricks, since these materials offer a higher density and resulting resistance to the diffusion of impurities.

## THERMAL AND MECHANICAL CONCERNS

Thermal and structural features of the refractory lining design are completed using an iterative method. Using the OEM-specified dimensions that constrain process volume and shape, the refractory ceramics must have adequate strength to support their structure within the steel shell. Compressive strength is typically of more concern than modulus of rupture (MOR), since few cases of tensile loading occur. During refractory manufacturing, MOR tests are still considered a valuable measure of process consistency. Creep resistance needs to be considered if periodic support is not available from the outer steel shell. The vessel fabricator may include additional supports in cases where creep is of concern or refractory strength may be inadequate for the expected mechanical loading.

The backup materials are selected based on the thermal characteristics of the design. Insulating firebricks, castables, or superduty materials may be used behind the hot face and safety layers. A thermal analysis is performed to ensure the use temperature limit of each refractory layer is not surpassed in any area of the gasifier. Perhaps more importantly, the mean temperature of each layer is determined so subsequent expansion calculations may be completed in the final design stages. Thermal analysis software is available that uses finite element methods to find the temperatures of 2D and 3D refractory systems. In a gasification unit with domes, cones and other geometries, the ability to view the thermal interaction between complex layers is extremely helpful. In addition, heat loss and thermal gradient results may be viewed to measure efficiency or corresponding areas of high thermal stress. Figure 4 shows the axisymmetric thermal analysis for the example gasifier.

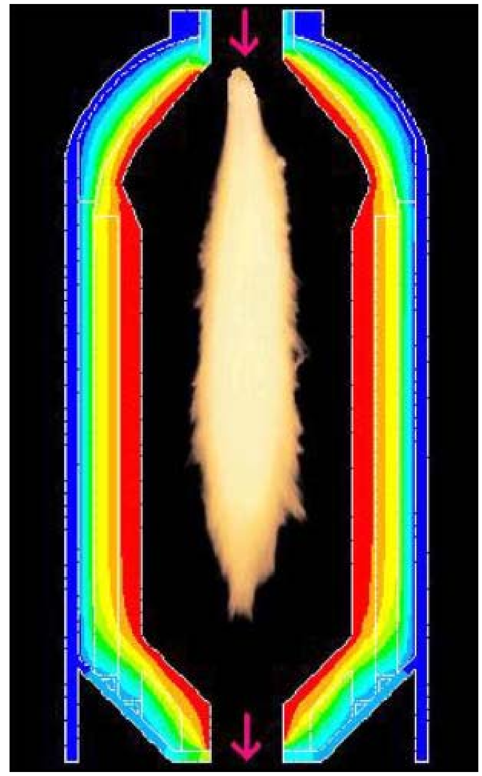

**Figure 4. Thermal analysis of a gasifier, using finite element techniques.**

Two important oversights often occur while reconciling a thermal analysis. First, the presence of hydrogen inside the gasifier must be considered. Hydrogen has a thermal conductivity nearly seven times that of air, and a density one-fourteenth that of air. Due to the consequent mobility of hydrogen through the refractory layers, the thermal conductivity of each lining material must be adjusted to compensate for the hydrogen concentration. Since the thermal conductivity of refractory materials is measured in an air environment, the refractory would have a higher conductivity in hydrogen when the air throughout the porosity is displaced. Factors to multiply the thermal conductivity of refractory materials are developed to take into account the materials’ porosity and amount of hydrogen in the syngas. A seemingly confusing example of this phenomenon would be the use of insulating firebricks versus superduty (mullite) brick. Due to their increased porosity, insulating firebricks may become more thermally conductive than their superduty (higher density) counterparts in elevated hydrogen environments.

Another mistake of many vessel designers is to strive for the lowest temperature possible against the steel shell, for safety concerns. Dew point corrosion and embrittlement issues may arise if the internal shell temperature is too low. With the presence of steam and hydrogen, the steel could react over time and cause the metal to lose strength and pressure rating. For this reason, the insulating layers are sometimes replaced by materials having higher thermal conductivity to increase the shell temperature above dew point limits (based on the climate and humidity of the geographical region).

Expansion of the individual layers is also an important consideration while designing a gasifier. The mean temperature of each layer is used to calculate the linear and radial expansion (relative to the expansion of the steel shell), using the thermal expansion coefficient. If possible, the lining should be designed in a manner such that no expansion joints are in direct contact with the operating environment, because the silica containing fiber materials used for expansion may not withstand the operating temperatures, reactions or velocities. Fibrous expansion materials are usually found at the top of vessel for vertical expansion and in the outer layer (against the steel shell) to account for radial growth of the concentric rings. Expansion should be designed precisely so that the fibers are thick enough to compress without becoming rigid (around 70% - 75% compression), but not so thick as to cause the lining to become loose or develop hot spots after the unit has cycled several times. Expansion issues become more complicated when the gasifier has attached chambers. In these cases, as seen in Figure 5, cylinder-to-cylinder transitions are designed so that the chambers expand together and align at operating temperature.

**Figure 5. Cylindrical transitions are designed for high temperature lining alignment.**

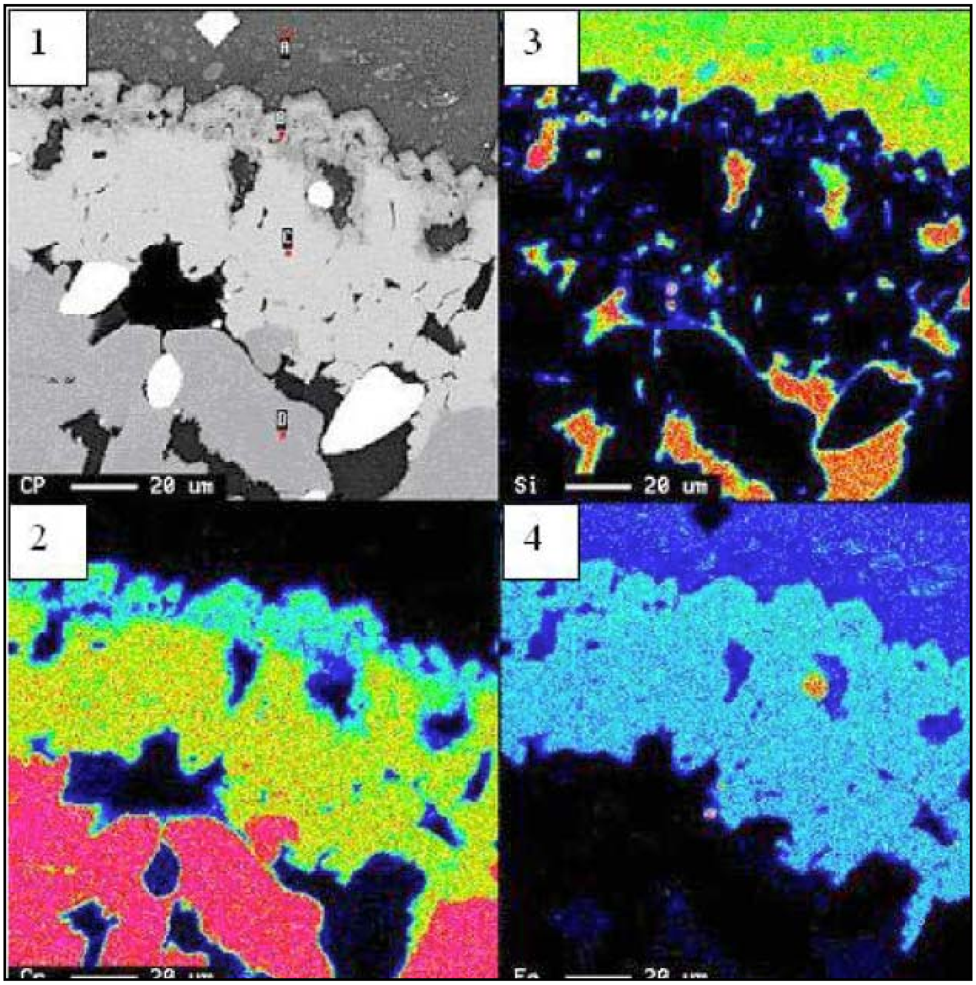


**Figure 6. (1) SEM photomicrograph of chrome oxide refractory with slag layer examined using microprobe analysis. Brightest contrasts indicate higher concentrations of slag. (2) Chrome oxide structure has become displaced where slag attack initiated. (3) Diffusion of silicon contained in the slag into the refractory structure. (4) Diffusion of iron contained in the slag into the refractory structure.**

The iterative design stages are necessary since the mechanical, thermal and expansion results are interrelated. For instance, changing the thermal properties of one layer will change the expansion of the system. Expansion joints may become too tight and impart high mechanical stresses in the lining. Many poorly designed linings have a combination of problems that can lead to failure.

## REFRACTORIES FOR SOLID FEED

Solid feedstock units have the additional problem of hot face erosion from two factors. The feedstock itself may be abrasive, causing erosion of the hot face when injected at high velocities. Also, slag produced from coal or petcoke residues may penetrate the hot face surface and weaken the refractory.

While the previously mentioned design concepts are important for all gasifiers, hot face wear is the primary concern when gasifying solid feedstocks. Refractory linings for solids gasification have a life expectancy generally ranging from 3 months to 2 years, depending on size and mass throughput. These units are primarily found in North America and Asia, where coal reserves are plentiful.

The mechanism for hot face wear in a coal or petcoke feedstock unit is related to the slag resistance of the hot face materials. Chrome oxide based refractories are used in the hot face due to their high erosion resistance and ability to withstand the other process conditions.

Slag erosion occurs by direct abrasion or through penetration of the hot fact. The biggest cause of material loss occurs when slag penetrates the porous hot face and forms a solid solution phase with the ceramic body. An example of this penetration is demonstrated in Figure 6. This new phase has differing material properties through its discrete thickness, as compared to the rest of the unaltered chrome oxide structure. The melting temperature can be decreased, causing the material to soften during operation. Also the differential thermal expansion of the penetrated zone and host refractory will cause hot face spalling when the unit is thermally cycled. Therefore, a small thickness of hot face material (typically ranging from 3 – 7 mm) is lost whenever the unit is cooled, occurring as of as every 15 – 30 days. The hot face linings for solid feedstocks are usually designed to be thicker to account for this erosive loss. Further improvements in material properties (i.e. slag resistance) and decreased operator cycling are helping to increase the life span of these linings.

Whereas the slag layer erodes the refractory, it is somewhat useful in the process. In some vessel designs, the slag acts to protect the lining or steel shell if it is completely insoluble in the lining materials. Also, the slag is able to vitrify many of the heavy metal impurities by covering them in a sand-like structure. This stabilized material can then be disposed of without fear of environmental contamination, or may provide extra value to the user if processed to form resalable metals or sulfurous compounds. Facilities that do not use gasification would be burdened by these impurities, in the form of regulated emissions or hazardous waste.

## IN ADDITION TO THE DESIGN ISSUES

After the design phase, additional factors such as refractory manufacturing and installation remain critical to achieve the full potential of each lining. Refractory suppliers must deliver high quality materials, free of defects and impurities that can shorten the service life. Property audits and inspections are typically done before the refractories are shipped to the job site. Once on site, proper installation techniques using competent personnel and equipment are necessary to perform the desired assembly. Tight tolerances (i.e. brick joints of less than 1.5 mm) are utilized when lining a gasifier, since syngas leaks can cause excessively high shell temperatures, forcing the unit offline for repairs. The use of proper mixing procedures for castables and mortars are also important. During most new installations or repairs, refractory inspectors are typically available to assess the condition of each lining and provide technical support to the end-user, ensuring that the lining design concepts are followed.

The dry-out or curing of the refractory lining is key to its long-term success. This step should not be skipped or accelerated by end-users, eager to resume production and profits. The curing schedule is frequently tailored to fit the particular lining design and materials. This gradual temperature increase allows the lining to expand evenly and eliminates the excess mechanically and chemically held water present in the monolithics. Many materials containing cement or calcium aluminate are able to hold water in their chemical structure to temperatures higher than 450ºC. This water, when multiplied by the volume of refractories in a given lining, is enough to completely destroy the lining if not dealt with correctly. A setback of this magnitude would be costly, both in terms of extended downtime and replacement value of the lining (which may be hundreds of thousands, if not millions of dollars). Therefore, the refractory supplier's curing recommendations need to be followed as closely as possible.

These fossil-fuel feedstocks result in nearly 94% of the worldwide syngas production capacity. Other feedstocks, such as biomass or metallurgical coke, are increasing in popularity as users search for new ways to extract riches from low-value or waste materials. The refractory materials and design technology must constantly evolve to meet the demands of tomorrow's gasification requirements. Saint-Gobain Ceramics continues to address the needs of this market. RAN

*Saint-Gobain Ceramics has provided high-grade refractory materials and technical expertise to the gasification industry for over a half century. Pressed alumina materials such as Alundum® AH199B or AL100, in addition to vibro-cast AH199H are used for liquid gasification. Chrome oxide shapes such as Zirchrom® or Chromcor® are recommended for solid feedstock gasifiers. For more information on Saint-Gobain Ceramics materials for gasification, please visit our website at www.refractories.saint-gobain.com

# The Book Shelf

## TECHNOLOGY OF MONOLITHIC REFRACTORIES, REVISED EDITION, 1999

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This book is an updated edition of the classical and comprehensive Plibrico's Technology of Monolithic Refractories (1984), with a larger format, impeccable drawings and reorganized for a more coherent reading. As in the original edition, the book includes an Appendix section listing main Plibrico Japan products, international standards relevant to monolithics (JIS, ASTM, DIN and ISO), a summary of non-standard test methods, and useful conversion tables. The revised edition covers new materials (i.e., alumina hydrates and alumina cements), new application techniques (i.e., fiber gunning installation), and an expanded section on the manufacture and properties of monolithics. The topics cover:

- History of monolithic refractories, from man's discovery of fire to recent developments and installation methods.
- Furnace descriptions indicating main monolithic refractory linings; a section with superb illustrations.
- Refractory Materials; the main section which includes:
  - Classification of monolithics
  - Raw materials used in the industry
  - Manufacture of monolithics, and
  - Properties of monolithics and wear mechanisms (abrasion, spalling, corrosion)
- Design of monolithic refractory linings
- Installation of monolithic refractory linings including methods, drying and initial heat-up, and inspection and safety instructions. RAN