

# TRI CELEBRATES 50 YEARS: A LOOK AT THE PAST AND THE FUTURE

Laurel M. Sheppard, Contributing Editor

Half a century ago, five companies got together to establish The Refractories Institute (TRI). By the end of the first membership meeting, TRI had 37 members. TRI was established with one goal in mind: to promote the interests of the refractories industry by providing critical service and support to its members. To achieve this goal, through the years TRI has conducted research to develop and improve methods for testing refractories, compiled and distributed relevant information, and worked with government agencies and other official bodies in matters of interest to both the public and the industry.

However, as TRI enters the 21<sup>st</sup> century, the emphasis has changed. "Government relations, particularly work with regulatory agencies like EPA and OSHA, has become a major focus of TRI activity," explains Robert Crolius, TRI President. "Conversely, TRI support for R&D and testing has been reduced significantly as member companies have become more competitive and less inclined to fund joint research and testing efforts."

## THE VOICE OF THE INDUSTRY

Crolius believes that TRI's most significant accomplishment has been to establish itself as the "mechanism of choice" for the refractories industry to pursue joint initiatives for mutual benefit. In addition to being the industry liaison with government, TRI is the primary place for industry networking and for taking the pulse of the industry. "For many, TRI is the first call a company makes to seek information," adds Crolius. "We are often considered as a

very cost-effective extra staff person not seen on the company's organization chart that can be relied on to help."

TRI also addresses important issues facing the industry. For instance, an Institute working group is currently working with EPA as the agency develops regulations to limit emissions of hazardous air pollutants from refractory operations. Another committee is coordinating the industry's response to OSHA's pending rulemaking on workplace crystalline silica exposures.

And the Institute is looking to the future. According to Crolius, TRI members are raising concerns about the availability of trained engineers and a skilled workforce. "Ceramic schools are not teaching refractories anymore," says Crolius, "and the competition for good hourly employees is also tough." With consolidations and retirements, much expertise is being lost. Crolius envisions a role for TRI in helping members train and retain good employees. "TRI used to be much more active in this area," says Crolius. "It may be time to take a look at it again."

## MAJOR CONSOLIDATION

As mergers and acquisitions have continued, especially in the last decade, TRI's membership has shrunk. Currently, this consists of 40 manufacturers, 35 supplier or associate members, and two refractory contractors. In the 50s, TRI had more than double the number of refractory producers than it has now. Because of this consolidation, the current 40 members represent about 90% of refractory sales in the U.S.

Crolius believes that there will be more mergers but at a much slower pace. Some companies will not be able to compete and will be absorbed. "This means TRI will have to be more focused, more efficient and try to do more with less," says Crolius. "We will do more partnering to leverage resources." TRI plans to work with a number of existing refractory-related organizations to do this.

Even though some companies may disappear, there will always be areas that can be most effectively addressed in a cooperative effort, according to Crolius. However, TRI will only survive if it stays attuned to its membership's needs. Therefore, TRI is currently conducting an industry needs assessment that will continue into next year. As Crolius puts it, "...the three challenges facing TRI is to be relevant, to continue to pursue relevance, and to at all times assure that we stay relevant to industry needs."

## THE 21<sup>ST</sup> CENTURY

There is no doubt that the refractories industry will continue to operate in a global economy during the next century. Raw materials may be mined in one country, manufactured into refractory products in another country, which are sold in still another country. TRI's three largest members (RHI, Vesuvius, and Thermal Ceramics) are already foreign owned. This means that more than 50% of the membership, based on sales volume, is foreign owned. The emerging international character of the industry means TRI members must reevaluate some of their traditional thinking, like,

for example, in the area of imports and trade.

The Internet will also have an impact on the industry. Crolius believes that the Internet will have both pluses and minuses, as with other industries. "Increased availability of information and instant communication will provide easy access to research and tools to help us in our jobs, as well as help make better products," he explains. "However, the Internet will likely drive down the price of these products as e-commerce grows, reducing profit margins. Beware the salesman who has a quota to meet or an inventory surplus who gets into a bidding war on the net!"

Despite these challenges, the refractories industry is here to stay. "As long as modern society needs to heat and melt materials, we will have refractories," says Crolius. "Some may be very similar to today's, whereas others will be more exotic and certainly more durable and easier to use. They probably will be cheaper as well, which will keep up the pressure on an already-strapped industry."

Concludes Crolius, "We all have a lot invested in this industry. We want it to thrive, we want it to be interesting and fun, and we want it to succeed. We have to work to make that happen." It is clear that TRI will continue to support the refractories industry and evolve with it as it changes.

Author's Note: Special thanks to Robert Crolius for his input to this article.

# MILESTONES OF THE REFRACTORIES INDUSTRY

1836 First firebrick plant established in the United States  
1860 First refractories company established in Pittsburgh  
1865 Star Fire Brick Co. established (predecessor of Harbison-Walker)  
1889 J.E. Baker Co. established  
1895 Carborundum Co. established  
1902 14 companies merge to form Harbison-Walker  
1906 American Refractories Co. established  
1910 A.P. Green Co., General Refractories Co. established  
1912 Refractories Manufacturers Association established by 20 companies  
1914 ASTM C-8 committee organizes; Plibrico Co. established  
1916 Whitacre-Greer Fireproofing Co., Vesuvius Crucible Co. established  
1917 Superior Graphite Co. established; RMA establishes Refractories Fellowship at Mellon Institute  
1921 Wahl Refractories established; General Refractories acquires American Refractories  
1924 11th Annual Meeting of Refractories Manufacturers Association; Cedar Heights Clay Co. established (now a division of Resco Products, Inc.)  
1925 American Refractories Institute is formed consisting of 150 members and holds first technical session  
1926 Six companies merge into North American Refractories Co.; Fire brick production reaches peak at over 1 billion brick

1927 Harbison Walker merges with Walsh Fire Clay Products  
1928 Massillon Stone & Fire Brick Co. changes name to Corundite Refractories Inc.; Corhart Refractories established  
1929 Johns-Manville acquires Celite Products Co.; Mexico Refractories Co. established; Harbison-Walker acquires Fulton Fire Brick Co.  
1930 >90% of steel made by open hearth process  
1931 Carborundum enters glass refractories market  
1933 ARI adopts Code of Fair Competition under National Industrial Recovery Act  
1936 Spalling test standard adopted by ASTM; Industrial Ceramic Products established  
1941 Anti-trust action taken against ARI; Kaiser Refractories established  
1946 Resco Products established; Carborundum's Refractories Division becomes the largest supplier of fired refractories in the world  
1951 A group of manufacturers organize The Refractories Institute  
1952 Carborundum expands into fused cast refractories field  
1954 Corning Glass acquires Corhart Refractories  
1957 86% of refractories industry's total capital expenditures made by four largest firms; Maryland Refractories Co. established  
1959 Research on high-fired direct bonded MgO-Cr<sub>2</sub>O<sub>3</sub> bricks in UK

1960 North American Refractories enters basic refractories market; Monolithic refractories represent 30% of total value of refractories in U.S.  
1961 Allied Mineral Products established  
1963 Introduction of direct bonded bricks  
1967 Harbison-Walker merges with Dresser Industries; AP Green Co. merges with U.S. Gypsum Corp.  
1978 Basic Inc. acquired by Combustion Engineering  
1982 Value of refractories shipments drops by 27%  
1984 Charles A. Taylor & Sons becomes division of Didier Taylor Refractories Co.; Exolon merges with ESK Co.  
1985 National Refractories and Minerals Corp. forms from Kaiser Refractories; Corhart Refractories becomes independent  
1986 North American Refractories Co. becomes independent  
1989 First Unified International Technical Conference on Refractories (UNITECR) held in California with over 900 attendees  
1990 Compagnie de Saint-Gobain acquires Norton Co.  
1992 Several Ferro plants acquired by Vesuvius Group  
1993 The Refractory Ceramic Fiber Coalition and EPA establish cooperative program for monitoring workplace exposure to refractory ceramic fibers; Plibrico (Canada) Ltd. purchased by the Didier Group's Canada Div.; H.C. Starck GmbH & Co. acquires the

fused alumina and ceramic businesses of Lonza-Werke GmbH  
1994 A. P. Green Industries Inc. acquires General Refractories  
1995 Hewitt Group plc acquires Keith Ceramic Materials Ltd.  
1996 Carborundum North American Fibers becomes Unifrax; St. Gobain acquires Carborundum; A.P. Green acquires Lanxide Thermocomposites  
1997 Shenango Refractories acquires Kentucky Technological Products; Flare Group plc acquires Gibbons Refractories; Alpine Group Inc. acquires Hepworth Refractories Ltd.  
1998 Fosbel acquires Hotwork; Alpine Group Inc. purchases American Premier's refractories business; Harbison-Walker purchases A.P. Green Industries; Reno Refractories buys Refractory Technology Inc.; Thermatex Corporation acquires Wahl Refractories  
1999 Cookson Group purchases Premier Refractories International; National Refractories and Minerals acquires Chicago/Wellsville Fire Brick Cos.  
2000 Radex-Heraklith (RHI) completes purchase of Harbison-Walker Refractories, operating as RHI Refractories America; Resco Products, Inc. purchases selected former Harbison-Walker plants from RHI; TRI celebrates 50<sup>th</sup> anniversary  
Source: *Ceramic Industry*, February 1998 and selected issues 1998-2000. All dates are approximate.

# HIGHLIGHTS OF TECHNOLOGICAL DEVELOPMENTS


Technology changes have had a major impact on the market for refractories. Advances in users' processing equipment, such as the development of the electric arc furnace in steelmaking and precalciner technology in cement manufacturer, have resulted in major changes in the types and quantities of refractories produced.

When TRI was established, fireclay brick accounted for almost half the sales of refractories. In 1950, silica refractories represented about 25% of the market, and basic refractories less than 8%. Since then there has been a major shift to other types, including magnesite, high alumina, fused cast, silicon carbide, and zircon. The increase in easy-to-place monolithics has also been very significant. In general, refractories have made great strides in both quality and durability. Some of the other developments, including those before 1950, are highlighted below.

- 1886 Silica brick introduced
- 1896 First chrome refractories made
- 1899 Germany's Degussa patents the manufacture of dense MgO by melting
- 1900 "Stiff mud process" developed
- 1901 Burned dolomite introduced
- 1903 High alumina refractories introduced
- 1906 Fused alumina brick introduced
- 1908 Missouri diaspore for alumina brick discovered; Dry press method for brick introduced
- 1909 Magnesite linings introduced for copper converters
- 1910 First commercial use of SiC as refractory
- 1911 Norton Co. introduces Crystalon
- 1913 First production of unfired magnesite refractories; Discovery of the metalcase principle in basic refractories

- 1914 Monolithic refractories are introduced
- 1919 First use of SiC bricks
- 1920 First SiC muffle for porcelain enameling developed
- 1922 First mullite block successfully cast at Corning
- 1923 Glass tank linings reach 10-14 months service life; First chemically-bonded magnesite-chrome brick introduced; First production of calcium alumina cement
- 1924 First use of refractory concrete in the U.S.
- 1925 Super-duty firebrick based on mullite and alumina developed; Kaolin firebrick developed
- 1926 Insulfrax brick introduced by Carborundum; SiC tile used in carboradiant kiln; Mullite refractories replace clay brick as furnace linings
- 1928 First commercial production of proprietary castable products
- 1931 Pneumatic ramming devices advocated for the installation of proprietary castable products
- 1932 Fiber-based refractories introduced; Super duty fire brick developed; First commercial use of magnesite brick
- 1933 Carborundum patents Monofrax H (fused alumina for glass refractories)
- 1936 Spalling test standard adopted by ASTM
- 1937 First synthetic magnesia made from seawater
- 1940 First fused-cast alumina/chrome-alumina refractories patented; First commercial application of super duty silica brick
- 1942 Fiberfrax (alumina/silica) ceramic fiber invented
- 1945 High magnesia ramming mixes become popular
- 1946 First synthetic ceramic fibers patented; AZS containing 33% zirconia introduced
- 1947 Rotary kilns introduced for calcining; 99% alumina introduced for furnaces; Thermal conductivity

- test accepted by ASTM; Manufacture of MgO with larger crystal size, based on Cr<sub>2</sub>O<sub>3</sub> addition, is patented
- 1951 First commercial phosphate-bonded plastic; Tabular alumina first used as aggregate in monolithic ramming mixes
- 1952 Pitch-bonded dolomite refractories developed
- 1953 Synthetic materials introduced to meet demands of basic oxygen furnace
- 1954 Phosphate-bonded plastics and ramming mixes become available
- 1955 High alumina brick replaces fireclay/silica brick; High-purity calcium aluminate cement available on a commercial basis in U.S.
- 1956 Tar-bonded magnesite brick introduced; SiC used in rocket tail throats
- 1960 Monolithic refractories represent 30% of total value of refractories in U.S.
- 1961 98% magnesia developed; Commercial bonded AZS brick introduced
- 1962 First use of large precast refractory concrete blocks in soaking pit walls
- 1963 Direct bonded brick introduced
- 1964 Monolithic refractories resistant to CO disintegration developed
- 1965 Continuous casting of steel-making introduced
- 1970 Castables manufactured with stainless steel wires; Synthetic calcined aggregates containing 47, 60, or 70% alumina become available
- 1972 Alumina-chromia monolithics introduced
- 1973 High strength castable developed for Minuteman missile antennae
- 1974 Freeze molding (the Blasch process) developed

- 1975 Gun-casting of refractory concretes developed
  - 1976 Development of phosphate-bonded, erosion- and abrasion-resistant castables
  - 1977 Development of vibratable plastic refractories
  - 1979 Initial use of low-cement-content castables in the U.S.
  - 1980 Gunning of plastic refractories introduced in Europe
  - 1983 Development of resin bonded magnesia-graphite
  - 1987 High-purity magnesia and graphite brick introduced to North America
  - 1988 Introduction of self-flow castables
  - 1991 Increased availability and use of large crystal MgO
  - 1992 Panel spalling test eliminated as a standard thermal shock test and replaced by ribbon and prism spalling tests
  - 1993 Increased usage of Chinese raw materials, including fused types
  - 1994 Increased usage of spinel-forming and spinel-containing refractories
  - 1997 Ceramic microspheres improve insulating properties of brick
  - 1998 Method patented for relining vessel by thermal spraying refractory material onto the surface of magnesia-based refractory lining
  - 1999 Composite refractory pour tube with wear resistant plate developed that requires minimal machining
  - 2000 Unburned carbon-containing refractory material patented that contains 30 wt% or less of carbon containing graphite; Low cement castable system developed for wet process pumping or spraying based on >95% alumina and 0.5-0.15% calcium chloride
- Source: *Ceramic Industry*, February 1998 and selected issues 1998-2000. All dates are approximate. 

## TRI: Celebrating 50 Years of Service!



USX Chairman and CEO Tom Usher addresses TRI fiftieth Anniversary Membership Meeting in Ponte Vedra Beach, Florida, May 2000.



Current TRI Chairman George Taylor presents safety award to long time TRI member Charlie Nock.



James L. Crawford, Walsh Refractories Corp., first elected president of The Refractories Institute who served from April 1951 to June 1953.

## A LOOK AT THE PAST AND THE FUTURE



Fred H. Atwood, TRI President 1953-55, poses with H.T. Murray, W.T. Tredennick (TRI President 1971-73), H.P. Barrand, and L.Y. Greene at 1954 TRI Membership Meeting held at the Homestead. After 1977, the title of the chief volunteer executive of the Institute was changed from President to Chairman.



1951 Fall Meeting of the Refractories Institute Grand Hotel, Point Clear, AL.

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Continued from Page 1

drill (corrosion due to metal components), are a common problem when using recycled materials. Recycling for this industry is considered to be very high risk. A realistic option should include recycling only of the TV-panel glass (not funnel glass), absolute cleaning (no stones, dirt, etc.), complete separation of lead glass, assure reliable compositions, and appropriate color components (which are very expensive).

4. J. Alexander of BOC on Electrostatic Batch Preheating Technology. A practical example was given from a pilot unit tested for E-type batch as a "one box" solution, which includes batch and cullet, preheat. The system is integrated with oxyfuel and compared with results under air/gas firing. The concept includes the heat transfer from hot gases directly to the batch, under counter flow of gas and capturing the pollutants, and recirculating the cold gases to the incoming gases. The unit (Gallo) runs 6 to 14.4 tons/day with a cullet ratio of 0 to 100%. The next unit is scheduled for installation of a furnace that can produce 50 to 200 tons/day.

5. Bill Snyder of Praxair on the Economic Aspects of Preheating Batch in an Oxyfuel Furnace. A review of benefits and costs was made which includes energy savings, production rate increases, and emissions reduction. This in turn is due to lower furnace temperatures, longer furnace life, foreign cullet cleaned (which infers on redox stability), recycling of particulates, and potential batch sulfate reduction. Savings are estimated from \$132,000/year at the low end (furnace size 100 ton/day, no electric boost) to 2,244,000/year at the high end (furnace size 600 ton/day and 15% electric boost).

### REFRACTORIES

6. Michael Dunkl of Vesuvius-VGT-DYKO on Cr<sub>2</sub>O<sub>3</sub>-based Refractories for the Glass Industry. Two refractories -- CR95WB (isostatically-pressed, 95% Cr<sub>2</sub>O<sub>3</sub>, 4% TiO<sub>2</sub>, no glassy phase) and CR80AA (ceramic bonded, contains 3% SiO<sub>2</sub>)-- were reviewed for glass tank applications, including their use in critical areas, corrosion behavior, and coloration potential. These refractories show high thermal shock resistance and low glass defect potential (from dynamic finger tests) make them good candidates when compared to AZS-based refractories.

7. M. Velez of UMR on Corrosion of Commercial Silica Refractories Using an Oxyfuel Furnace Simulator. The furnace is designed to simulate selected conditions of industrial melters, mainly temperature and NaOH concentration in the combustion chamber. A variety of parameters are measured, including combustion chamber temperature and pressure, combustion gases, and vapor concentration of NaOH and KOH. Six runs have been performed so far, whose results have supported other predictions that corrosion occurs when there is a high NaOH concentration (estimated above 200 ppm by volume). Microstructural studies have identified what phases are present at the cold face, middle section and hot face. This type of information will be used to develop corrosion models.

8. Amul Gupta of Monofrax on Field Experiences with Fused Alumina Crowns. Fused alpha-beta alumina is preferred over beta-alumina, for crown and superstructure applications in service up to 1700 C (higher density, higher strength, and higher resistance to batch dust). Physical stability of the alpha-beta-alumina refractory has been demonstrated in the field and also in

laboratory tests at ORNL -- however, experimental creep data goes as high as 1450 C. The information from industrial furnaces suggests that fused alumina offers superior performance compared to refractories with significant silicate phase content. Advantages include longer campaign life, multiple campaign potential, high throughputs, and increased glass quality.

9. Mike Nelson of Corhart on new Fused Refractories for Glass Furnace Superstructures. Tests at 1500 C, 72 h, and up to 700 ppm of NaOH indicates the following trend regarding corrosion resistance: beta-alumina > alpha-beta-alumina > low glassy phase AZS > conventional AZS >> silica. The microstructural information was reviewed, mainly by using SEM assisted with EDS for chemical analysis.

10. R. E. Davis of Thomson Consumer Electronics on High Zirconia Fused Cast Applications in CTV Panel Glass Melters.

11. Larry Kotacska of Corning on Applications of Zirconia Fusion Cast in Various Glasses. A summary was presented on the benefits of ZFC such as high corrosion resistance and high thermal shock resistance.

### FOURTH INDUSTRIAL ENERGY EFFICIENCY SYMPOSIUM AND EXHIBITION: February 19-22, 2001, Washington, D.C.

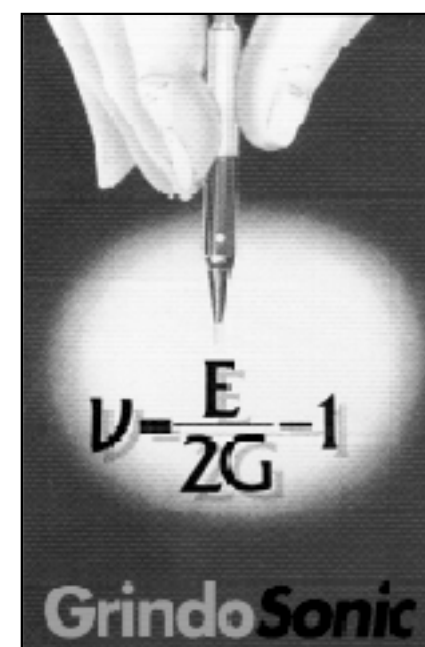
This Exhibition is being organized by the Department of Energy's Office of Industrial technology with the theme: Challenges and Solutions. The GMIC (Glass Manufacturing Industry Council) will host a technical workshop during this event, being the main topic New Melting Techniques for the Glass Industry.

### CATHODOLUMINENCE (CL) APPLICATIONS IN REFRACTORIES

Dr. Musa Karakus

Fluidized Bed Refractories from Titanium Chlorinating Plants: Typical feed material may contain rutile ore, synthetic rutile, leucocoxene, and ilmenite as well as slag for TiO<sub>2</sub> chlorinating process. In this process, the oxide ores are reacted with chlorine in a fluidized bed with petroleum coke. As a result, oxygen combines with the coke to form CO and CO<sub>2</sub> while titanium and chlorine combine to form TiCl<sub>4</sub>. Typical operating temperature varies from 800°C to 1000°C. Fireclay refractories are commonly used in the fluidization zone while high alumina castable refractories are preferred at the burner.

Figure 1 is a CL micrographs showing corrosion of mullite brick from titanium chlorinating plant. (A.) RL (reflected light) micrographs of heavily corroded



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brick showing precipitation of rutile (rt), (B) CL micrograph of the same area as in A, showing corrosion of mullite by chloride phases and formation of porous cristobalite (blue CL) and Na-Mn-Mg-chloride hydrate phases (cl, yellow CL).

Spinel Based Castable: Spinel added or spinel forming high alumina castables are used commonly in steel ladles. The case example illustrated in Figures 2 and 3 are spinel forming high alumina castables after service. It is clearly shown that a fully dense, well-sintered spinel ceramic bond has been formed in the hot face or hot zone of the castable (Figure 2). The fillers and grains are highly impure and defective fused brown alumina grains are observed.

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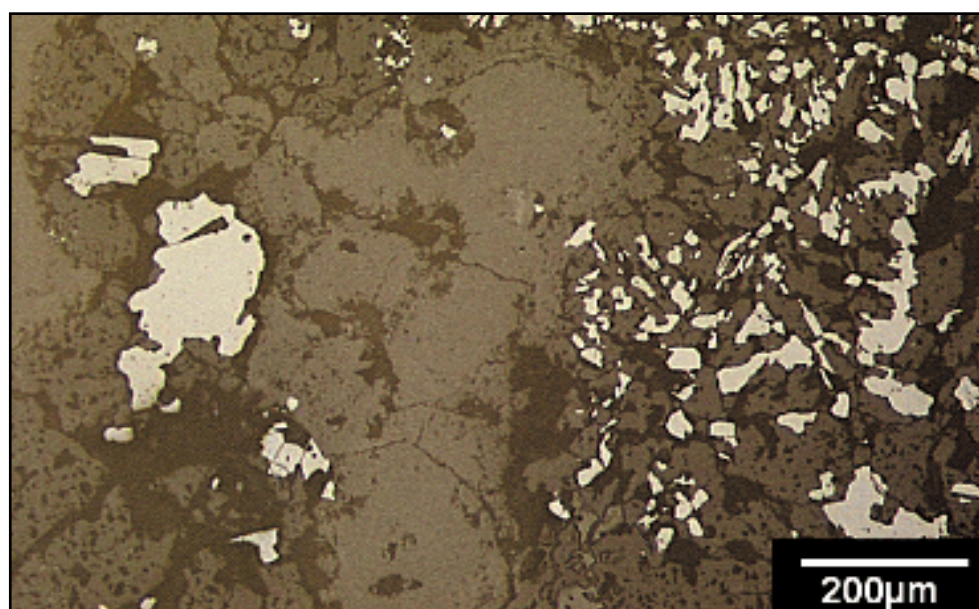


Figure 1A. Fireclay refractory-reflected light

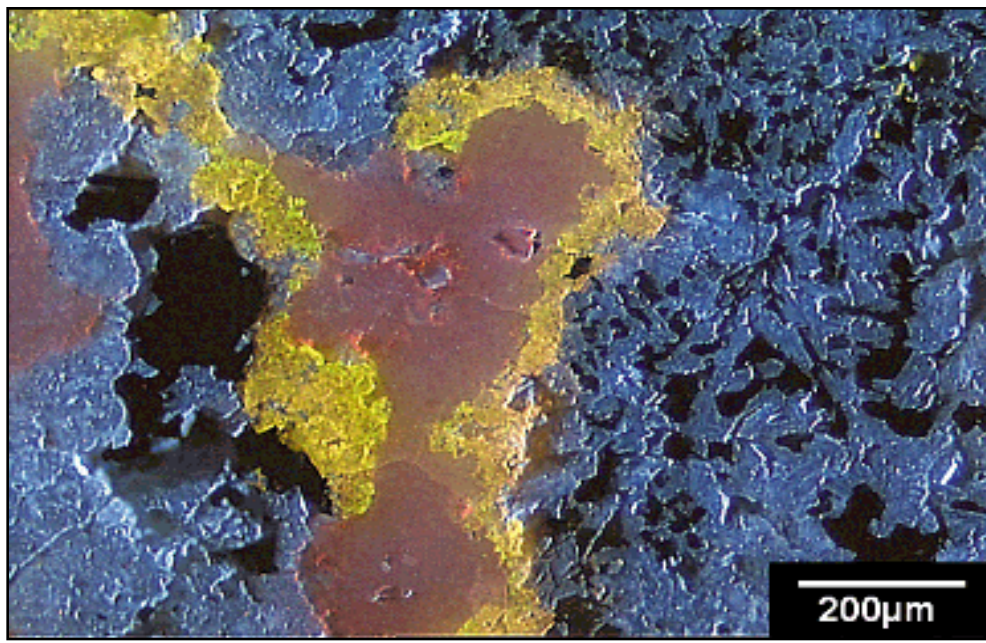


Figure 1B Fireclay refractory - catholuminescence light

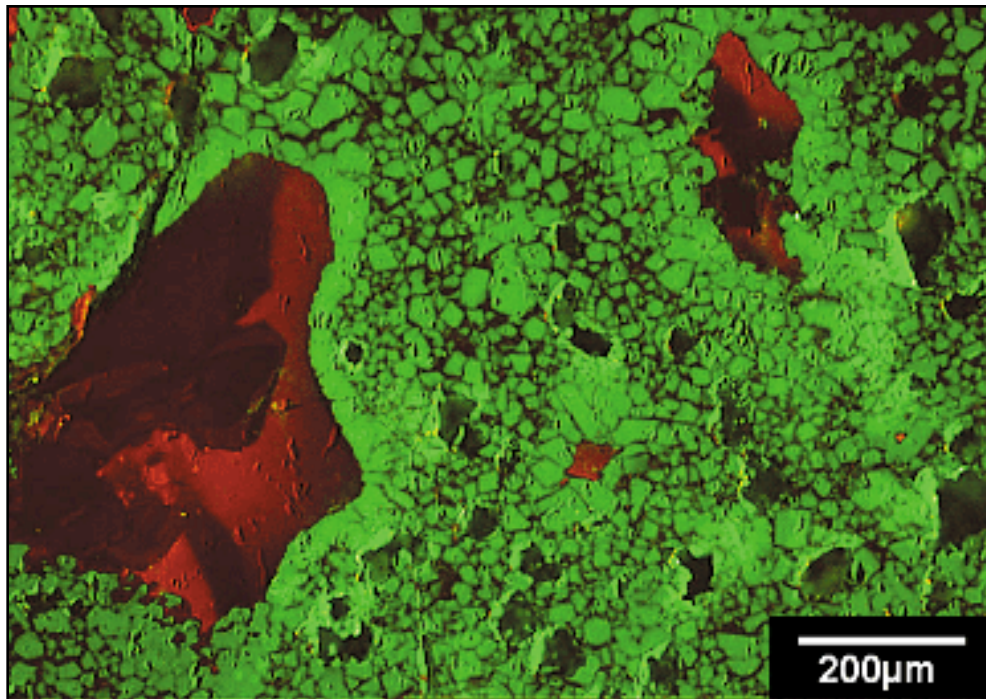


Figure 2 CL of spinel forming castable

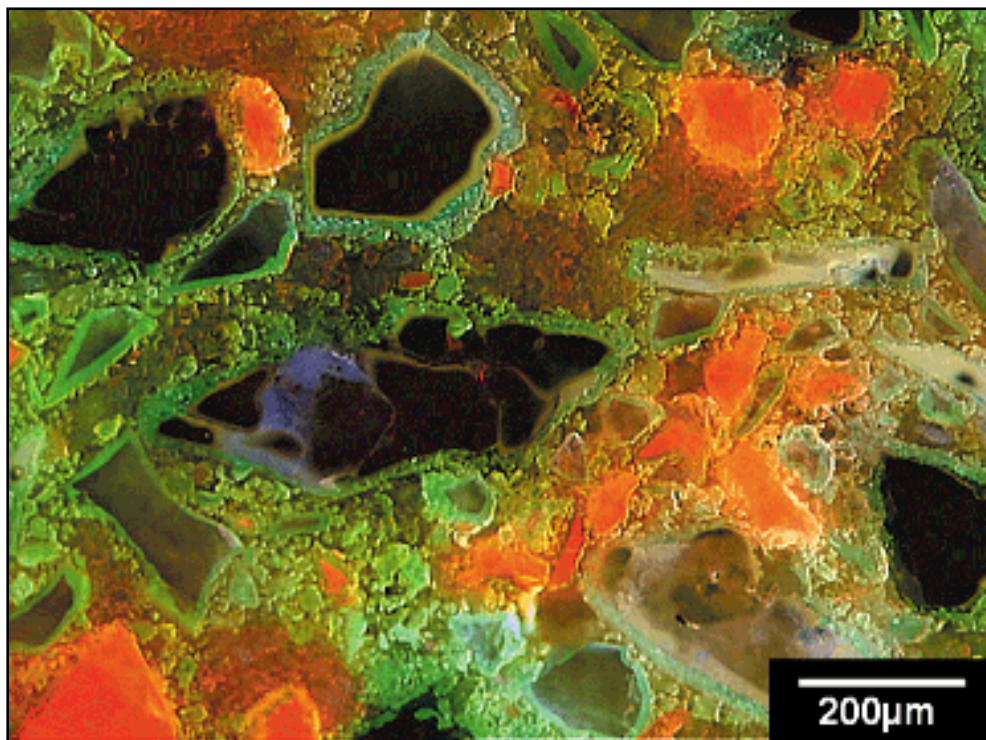


Figure 3 CL of spinel forming castable

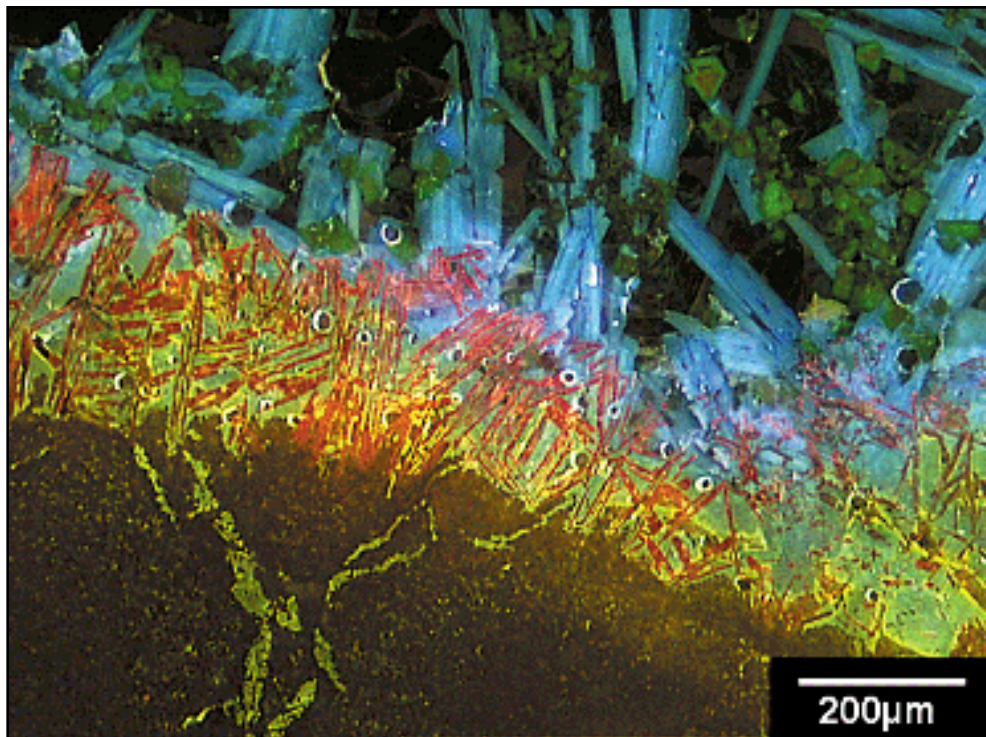



Figure 4 CL of high alumina brick

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They have a high content of FeO and TiO<sub>2</sub> therefore many of them exhibit various CL colors (Figure 3). This example shows that the spinel based castable refractories are perfectly suited to study by the cathodoluminescence technique.

Laboratory Test Samples: Slag-cup test samples exposed to synthetic steel slags or CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) slags can be best studied by CLM in order to determine the slag penetration and corrosion resistance of newly developed refractory test materials. Figure 4 demonstrates the corrosion of high alumina brick by a CMAS slag. Dissolution of mullite into a CMAS slag progresses by the formation of anorthite (yellow CL) and needle-like corundum (red CL) crystals on the surfaces of mullite aggregates. Reaction between tabular alumina and CMAS slag resulted in the formation of a dense spinel layer on the surfaces of the alumina grains (not shown in Figure 3). The bulk slag cooled to form mostly amorphous glass, and

large anorthite and euhedral spinel crystals. Anorthite crystals in the bulk of the slag interestingly exhibit intense blue CL color. This example shows that the CL technique is able to distinguish anorthite crystals crystallized in the bulk of the slag (blue CL) and anorthite crystals formed as a result of reaction between slag and mullite aggregates (yellow CL).

Tundish Veneer and Coatings: Tundish linings, in general, include a backup safety lining and a high alumina castable working lining. The surface of this working lining is coated with magnesia based gunning mixes to make descaling work easier after casting. Olivine based tundish veneer materials were also studied by CL microscopy (Figure 5). CL microstructures have revealed that the olivine, (Fe,Mg)<sub>2</sub>SiO<sub>4</sub>, sands do not exhibit CL, but due to the re-crystallization of olivine, one can clearly observe bright red CL crystals of forsterite. Because of interaction with the tundish cover, commonly high alumina castable covers, monticellite as well as spinel are also formed. 

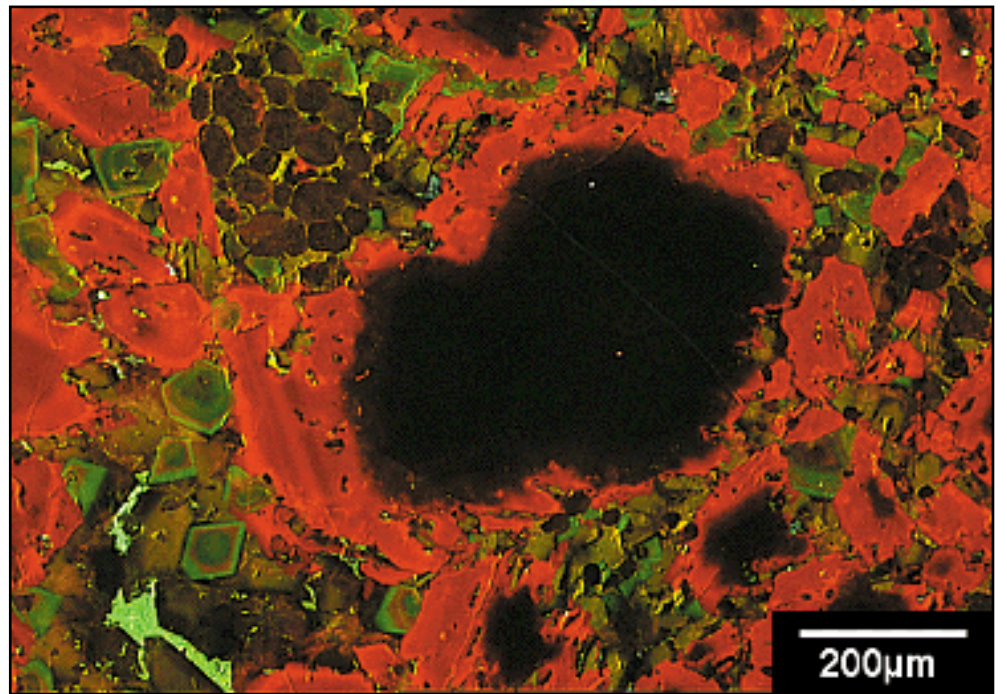


Figure 5 CL of Olivine based material

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