

# Refractories Applications *and News*



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Technology Bimonthly for the Global Refractories Industries

## Theodore J. Planje Award recipients at the 46<sup>th</sup> St. Louis Refractories Symposium



From left to right, Louis J. Trostel, 1996, Michelle A. Rigaud, 2004, Dalip Jain, 2007, Roy J. Bottjer, 2002, James L. Hill, 2010, George Taylor, 2005, Mark A. Stett, 2001, Orvil Hunter Jr., 1998, Kent Weisenstein, 2000, Charles E. Semler, 1995.

# THE REFRACTORIES INSTITUTE



**congratulates**  
**Miguel A. Pereyo**



**Recipient of the 2010  
WILLIAM T. TREDENNICK AWARD**

The Tredennick Award is named for long-time TRI Board Member Bill Tredennick and recognizes a career of significant and lasting service to the refractories community.

***For membership information  
contact:***

The Refractories Institute  
P.O. Box 8439  
325 Maple Avenue  
Pittsburgh, PA 15218  
Phone: (412) 244-1880 Fax: (412) 244-1881  
[rob@refractoriesinstitute.org](mailto:rob@refractoriesinstitute.org)

***A NATIONAL ASSOCIATION PROMOTING THE INTERESTS OF THE REFRACTORIES INDUSTRY***

## From the Editor . . .

Jeffrey D. Smith, Editor, [jsmith@mst.edu](mailto:jsmith@mst.edu)




Jeffrey D. Smith

I am keeping this editorial very short for effect. I have made the difficult decision that we must move Refractories Applications and News to an electronic-only publication. This decision does not come lightly as I have struggled with it for many months and I during that time I have had many discussions with many people throughout our industry. My conclusion is that given the current economic realities, this is the only responsible action.

During the upcoming weeks we will be contacting all of our advertisers to determine ways to provide, if at all possible, a significant benefit for their continued support of *RAN*. The advertising fees will obviously be adjusted accordingly.

I want to be clear that we appreciate everything that our sponsors have done for *RAN* over the years and as such the switch to an "online only" format WILL NOT begin until all of their concerns have been satisfactorily addressed.

This decision will be revisited as the industries we serve, and care about, climb out of these tough times.

Many view *RAN* as a significant benefit to these industries and I pledge that we will continue to provide the best possible technical content for our readers. Thanks to all of you for supporting *RAN* over the years. I very much hope that you will continue to provide technical content and support *RAN* in the same ways you always have. 

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*Photos from the St. Louis Refractories Symposium provided by Dan Snyder, MS& T graduate student.*

# Refractories Applications and News



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Editorial offices at Missouri S&T

Materials Science and Engineering Department, 223 McNutt Hall, 1870 Miner Circle Drive, Rolla, MO 65409-0330

Phone: (573) 341-6561 Fax: (573) 341-6934 Website: www.ranews.info

Editor, Jeffrey D. Smith  
Assistant Editor/Webmaster, Mary Lee  
RAN Advisor, Mariano Velez (MO-SCi Corporation)  
Contributing Editor, Charles E. Semler (Semler Materials Services)

jsmith@mst.edu  
leemj@mst.edu  
mvelez83@alum.mit.edu  
CESemler@aol.com

Phone: (573) 341-4447  
Phone: (573) 341-6561  
Phone: (573) 341-6561  
Phone: (480) 895-9830

Lou Trostel, Councilor, Refractories Ceramics Division, ACerS  
Rob Crolius, President, TRI

## Corresponding Editors:

**Esteban Aglietti**, (CETMIC, Buenos Aires, AR)  
E-mail: eaglietti@cetmic.unlp.edu.ar  
**Carmen Baudin**, (Institute for Ceramics and Glass, Madrid, Spain)  
E-mail: cbaudin@icv.csic.es  
**Richard C. Bradt**, (University of Alabama)  
E-mail: rcbardt@coe.eng.ua.edu  
**Elena Brandaleze**, (Universidad Tecnológica Nacional, San Nicolás, Argentina)  
E-mail: ebrandaleze@frsn.utn.edu.ar  
**Geraldo E. Gonçalves**, (Magnesita, Brazil)  
E-mail: ggoncalves@magnesita.com.br  
**Delia Gutierrez-Campos**, (Universidad Simon Bolivar, VE)  
E-mail: dgutierr@usb.ve  
**Bill Lee**, (Imperial College London)  
E-mail: w.e.lee@imperial.ac.uk

**Jose L. Mendoza-Bedolla**, (Technical Consultant, Saltillo, MX)  
E-mail: jlmendozaab@prodigy.net.mx  
**Li Nan**, (Wuhan University of Science and Technology, P.R. China)  
E-mail: linan@mail.wust.edu.cn  
**George Oprea**, (University of British Columbia, CA)  
E-mail: oprea@interchange.ubc.ca  
**Victor C. Pandolfelli**, (UFSCar, Brazil)  
E-mail: vicpando@power.ufscar.br  
**Michel A. Rigaud**, (École Polytechnique, Montreal, CA)  
E-mail: michel.rigaud@polymtl.ca  
**Analia G. Tomba Martinez**, (INTEMA, Mar del Plata, AR)  
E-mail: agtomba@fi.mdp.edu.ar  
**Raul Topolevsky**, (Siderar, Buenos Aires, AR)  
E-mail: yaptky@siderar.com

Subscription is free upon request in the U.S. only.

Please e-mail address changes to *Refractories Applications and News*, Missouri S&T, 223 McNutt Hall, 1870 Miner Circle Dr., Rolla, MO 65409-0330. Allow six weeks for address change. Foreign readers may receive a hard copy by sending \$40.00/yr. in U.S. currency or view the current issue (free) on our website: www.ranews.info. Foreign institutes, research centers and libraries will continue to receive a free printed copy upon request.

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Instructions for the preparation of articles to be submitted for possible publication in this magazine are available from the Assistant Editor, Mary Lee, leemj@mst.edu, (573)341-6561, Missouri S&T, 223 McNutt Hall, Rolla, MO 65409.

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**U.S. readers who would like to subscribe or unsubscribe to this magazine should e-mail their name and address to Mary Lee at: leemj@mst.edu**

## REFRACTORIES RELATED MEETINGS

2010

June 2-4, **TRI Spring Membership Meeting**, Silverado Resort, Napa, CA.

June 6-18, **12<sup>th</sup> International Ceramics Congress CIMTEC 2010**, Florence Italy, [www.cimtec-congress.org/2010/](http://www.cimtec-congress.org/2010/).

September 6-10, **The 25<sup>th</sup> International Mineral Processing Congress 2010 (IMPC)**, Brisbane Convention Ctr., Australia; IMPC 2010 Event Management – The AusIMM, Tel: +61 3 9658 6123, Fax: +61 3 9662 3662, [impc2010@ausimm.com.au](mailto:impc2010@ausimm.com.au), [www.impc210.org](http://www.impc210.org), PO Box 660, Carlton South, Victoria 3053, Australia.

September 8-9, **Colloquium on Refractories**, Aachen, Germany.

October 3-6, **COM 2010-Conference of Metallurgists, 5<sup>th</sup> International Symposium on Advances in Refractories**, Vancouver, BC, Canada, George Oprea: [oprea@interchange.ubc.ca](mailto:oprea@interchange.ubc.ca), [www.metsoc.org](http://www.metsoc.org).

October 3-6, **The Michel Rigaud International Symposium on Advances in Refractories for Metallurgical Industries V** (in conjunction with Conference of Metallurgists-COM2010), Vancouver, British Columbia, Canada.

October 17-21, **Materials Science & Technology 2010 Conference and Exhibition - MS&T '10 combined with the ACerS 112<sup>th</sup> Annual Meeting**, George R. Brown Convention Center, Houston, TX.

Nov. 14-18, **3<sup>rd</sup> International Congress on Ceramics**, Osaka International Convention Center, Osaka, Japan.

December 6-9, **35<sup>th</sup> ALAFAR Congress**, Lima, Peru.

### Refractories Course To Be Offered June 14, 15 & 16, 2010

In response to industry demand, Orton has scheduled its "Introduction to Refractories" course for June 14, 15 & 16 in Columbus, Ohio. In addition to the classroom lectures and demonstrations the course will include a "hands-on" lab session each day. Visit <http://www.orton-ceramic.com/> for additional details and registration information. Do not delay, class size is limited so that the labs are truly "hands-on".

Who Should Attend? Engineers, managers, installation contractors, purchasing agents, furnace operators, maintenance supervisors, and technicians who are involved in the manufacturing, marketing, installation, research and product development, or consumption of refractory materials will find this course beneficial.

#### Course Objectives

- The objectives of this course are to introduce the participants to the material fundamentals of all classes of refractories, their basic formulation, their applications, and some of their degradation and failure processes.
- The laboratory sessions are designed to provide direct experience in test specimen preparation and hands on application of standard ASTM test methods.
- Each participant will receive course notes and reference material for future reference.

For additional questions contact: Dr. Joseph Homeny, Tel: 614-818-1323, [homeny@ortonceramic.com](mailto:homeny@ortonceramic.com)



**Rob Crollius**

## **INTERNATIONAL TRADE ADMINISTRATION RULES ON CHINESE, MEXICAN MAG CARBON BRICK**

Responding to a petition filed by Resco Products, on March 4, the International Trade Administration of the U.S. Department of Commerce announced its preliminary determinations in the antidumping investigations on imports of magnesia carbon brick

from the People's Republic of China and Mexico. For purposes of antidumping investigations, dumping occurs when a foreign company sells a product in the United States at less than fair value. Commerce preliminarily determined that Chinese and Mexican producers/exporters have sold magnesia carbon brick in the United States between 132.74 and 349.00 percent and 54.73 percent less than normal value, respectively.

## **IN MEMORIAM: FRITZ HENRY**

Francis (Fritz) Walter Henry, Jr. died January 10, 2010 at home. TRI members and staff express our condolences to his wife Charlotte, his family, and friends.

Mr. Henry attended the State University of New York (SUNY) College of Ceramics at Alfred University in Alfred, NY. In 1970, he was awarded the Raymond Q. Hitchcock Award for Undergraduate Research in 1970 and received a Bachelor of Science degree in Ceramic Engineering, graduating Cum Laude.

After being discharged from the U.S. Army as a First Lieutenant in 1974, Mr. Henry was employed with General Refractories Research Center from 1974 to 1989. He received the W.S. Treffner Award from the General Refractories Company in 1981.

Employed with Martin-Marietta from 1989-2001, Mr. Henry designed many highly technical ceramic products used in critical areas in steel making and power plant operations which are still in worldwide use today.

Fritz joined Minteq International, Inc. in 2001 as a Senior Research and Development Engineer in refractories and high temperature ceramic materials for various industrial applications. Throughout his career in the refractory industry, Fritz was highly regarded as a leading researcher with seven patents registered in the U.S. and two registered in the U.K.

Memorial gifts may be made to the Hospice of the Chesapeake, 445 Defense Highway, Annapolis, MD 21401.

## **IN MEMORIAM: RICHARD LEE "DICK" WUSKE**

TRI has learned of the passing of Richard "Dick" Wuske. A ceramic engineering graduate from Ohio State University, Dick Wuske spent thirty-three years working in manufacturing for Harbison-Walker. He was retired in South Carolina at the time of his death.

## **RATH INCORPORATED ANNOUNCES ISO 9001:2008 CERTIFICATION**

Rath Incorporated has announced that it has successfully achieved ISO 9001:2008 certification for Rath USA, which includes its Newark, Delaware and Milledgeville, Georgia plants. In addition to the U.S. plants, Rath is ISO certified in Austria, Germany, and Hungary. Rath USA is the North American subsidiary of the Rath Group headquartered in Vienna, Austria.

## **MEIER NAMED CHAIRMAN OF H.C. STARCK**

Andreas Meier, Ph.D., has been named chairman of the board of H.C. Starck GmbH and CEO of the international H.C. Starck Group. H.C. Starck is a producer of metal and ceramic chemicals, electronic chemicals, and advanced ceramics, headquartered in Goslar, Germany. Dr. Meier had served in many roles at RHI-AG in Vienna, Austria, beginning his career in 1985, and rising to Chairman of the Board in 2007. Mr. Meier left RHI in 2009.

## **REGULATORY**

### **EPA Greenhouse Gas Rule Expected**

While Congress debates cap and trade and other supposed fixes to address global climate change, the Environmental Protection Agency is moving ahead with its plan to require permits for large industrial sources of greenhouse gases through Clean Air Act Title V procedures. Under a proposed rule which as of this writing was expected to be finalized by the end of March, the agency will require facilities which emit more than 25,000 tons of carbon dioxide equivalents to obtain permits which would demonstrate they are using best practices and technologies to minimize greenhouse gas emissions.

The EPA rule will address emissions of six greenhouse gases—carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulfur hexafluoride. Facilities emitting these gases in excess of 25,000 tons measured in "carbon dioxide equivalents" would be subject to new source review procedures and also existing source permitting requirements as permits come up for review and renewal. In addition, sources emitting a "significance" level from 10,000 to 25,000 tons of carbon dioxide equivalents would be subject to prevention of significant deterioration (PSD) review.

The new requirements will go into effect immediately upon publication of the final rule. EPA will operate this new program for five years, at which time it will conduct a review as to its effectiveness and either continue it or make revisions based on the experience regulators have had and the effect on emission levels.

### **TSCA INVENTORY; CLARIFICATION FOR CHEMICAL IDENTIFICATION DESCRIBING STATUTORY MIXTURES, INCLUDING CERAMIC MATERIALS, CEMENTS, AND FRITS FOR TSCA INVENTORY PURPOSES**

The Environmental Protection Agency has announced plans to review when certain materials such as ceramics, cements, and frits might be considered as new chemicals subject to the agency's review

*Continued on Page 17*

## GLOBAL CEMENT DEMAND TO REACH 3.5 BILLION METRIC TONS IN 2013

Global demand for hydraulic cement is forecast to rise 4.1 percent per year to 3.5 billion metric tons in 2013, valued at \$246 billion. Gains will be fueled by rising investments in infrastructure among the developing countries of the world, driven by economic growth and increasing per capita income levels. Additionally, an improvement in the market for cement in developed areas, particularly the United States but also Western Europe and Japan, will also benefit world cement demand. However, gains in demand through 2013 will lag the robust advances seen from 2003 to 2008. Many of the fastest-growing markets for cement during this period, including China, Russia, Brazil and other large consumers, will experience a substantial deceleration in cement demand going forward. The global economic recession which began in 2008 led to a notable slowdown in construction activity, and increases in construction spending and cement sales will rise at a more moderate pace through 2013. These and other trends are presented in *World Cement*, a new study from The Freedonia Group, Inc., a Cleveland-based industry research firm.

Nonetheless, a number of countries will continue to see strong gains in demand for cement, particularly in the Asia/Pacific region. China, which accounts for nearly half of world cement demand, will see a slowing rate of growth through 2013 as construction spending decelerates, but gains will remain above the global average. India, the world's second largest cement market, will see some of the most rapid advances of any country in the world. Other fast-growing markets for cement in the region will include the Philippines, Taiwan and Vietnam, all with growth rates exceeding six percent per year. In the developing nations of Latin America, Eastern Europe and the Africa/Mideast region, however, advances in cement demand will slow considerably from the robust gains seen during the 2003-2008 period.

Increases in cement demand in the developed areas of the US, Western Europe and Japan will lag the average global pace of growth, although improving substantially from their 2003-2008 performance. In the US, cement demand plummeted in the wake of a residential building slump and economic recession from 2006 to 2008, but a solid rebound is expected through 2013. In Western Europe, improvement in construction activity will fuel a turnaround in the region's three largest cement markets, Spain, Italy and Germany. Similarly, a modest rise in construction spending in Japan

will drive increases in cement consumption after a long period of decline.

## CONSTRUCTION CHEMICALS DEMAND TO REACH \$9.1 BILLION IN 2013

Demand for construction chemicals used in on-site applications is forecast to increase 3.4 percent per year in the US to \$9.1 billion in 2013. A rebound in the housing market will promote growth, as the residential segment is a key outlet for construction chemicals. Demand will also benefit from a shift to higher value products and solid levels of residential improvement and repair spending. A significant deceleration in nonresidential building activity will limit aggregate gains. These and other trends are presented in *Construction Chemicals*, a new study from The Freedonia Group, Inc., a Cleveland-based industry research firm.

The large protective coatings and sealers product category is expected to register subpar growth, partially due to their heavy use in industrial settings, which achieved big gains between 2003 and 2008 but are expected to experience outright declines over the next five year period. Caulks and adhesives, the second largest product type, find use in a wider variety of construction contexts, providing opportunities. Grout and mortar demand is expected to lead construction chemical gains through 2013. Polymer flooring, also most heavily used by the industrial construction segment, is forecast to post sluggish gains through 2013.

The residential building market will offer the strongest opportunities for on-site construction chemical growth. Gains will be promoted as new residential construction expenditures rise from a depressed base and completions of new single-family homes rebound. Improvement and repair applications will also provide opportunities, supported by favorable growth in the residential improvement and repair market, the gradual aging of the housing stock and the fact that many homeowners enjoy remodeling older homes.

Demand gains in nonresidential building applications will be checked by declining construction spending in the industrial sector and the lodging and commercial sector. Advances will be further restrained by below-average spending in the office sector. Slightly offsetting this sluggishness will be rising construction spending in the institutional sector, as more hospitals, nursing homes, schools and university dormitories are built. In the nonbuilding market, gains will be driven by an increasing focus on better performing

WORLD CEMENT DEMAND (million metric tons)					
Item	2003	2008	2013	% Annual Growth	
				2003-2008	2008-2013
Cement Demand by Region	2006	2839	3465	7.2	4.1
North America	151.4	142.4	162.0	-1.2	2.6
Western Europe	202.6	199.9	213.0	-0.3	1.3
Asia/Pacific	1268.0	1895.0	2400.0	8.4	4.8
Other Regions	384.0	601.7	690.0	9.4	2.8

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US ON-SITE CONSTRUCTION CHEMICALS DEMAND (million dollars)					
Item	2003	2008	2013	% Annual Growth	
				2003-2008	2008-2013
Construction Chemicals Demand	5828	7690	9085	5.7	3.4
Protective Coatings & Sealers	1927	2504	2740	5.4	1.8
Caulks & Adhesives	1728	2402	2950	6.8	4.2
Cement & Asphalt Additives	954	1169	1385	4.1	3.4
Grout & Mortar	569	680	965	3.6	7.3
Polymer Flooring	370	556	560	8.5	0.1
Sprayed PU Foam & Other	280	379	485	6.2	5.1

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materials in road and bridge construction, commonly achieved through the use of cement and asphalt additives.

World Cement (published 01/2010, 453 pages) is available for \$6,100 from The Freedonia Group, Inc., 767 Beta Drive, Cleveland, OH 44143-2326. For further details, please contact Corinne Gangloff by Tel: 440-684-9600, Fax: 440-646-0484 or e-mail: [pr@freedoniagroup.com](mailto:pr@freedoniagroup.com). Information may also be obtained through [www.freedoniagroup.com](http://www.freedoniagroup.com).

#### CERAM STRENGTHENS ITS TEAM OF REFRACTORY CONSULTANTS

Expert materials testing, analysis and consultancy firm CERAM is very pleased to announce the appointment of Paul Myers to the post of Principal Consultant for Refractories. Paul will lead the growing team of expert consultants for this important area, responsible for both business direction and capability development.

Having studied at CERAM during his PhD, Paul has subsequently worked as a senior scientist with CERAM, working with many clients in the refractory sector, and has, since then, gained significant industry experience with leading refractories producers, Parkinson Spencer Refractories and Dyson Thermal Technologies, as their group Technical Manager. He has worked on refractories for a myriad of applications and has a detailed knowledge of both traditional and advanced ceramic-forming technologies. His first degree was a B. Eng. in Industrial Mineral Engineering from the University of Leeds and his master's degree was in Chemistry with New Materials from Aberdeen University (specializing areas of ceramic science).

Speaking about his appointment, Paul commented: "I am excited to be returning to CERAM at a key point in its business development. This is a significant centre of expertise in refractory technology, recognized globally and highly valued by many clients. I'm proud to be part of that and to lead the team forward."

John Hines, CERAM's Director of Consultancy, added: "The demand from our clients for expert guidance regarding sourcing, designing, installing and maintaining refractories is increasing in this current economic climate. Paul is a significant addition to our team, bringing not only world-class technical ability but also highly relevant industrial and commercial experience."

For further information please contact: Mandy Rymill, CERAM Marketing Communications Manager, Tel: +44 (0)1782 764 326, [www.ceram.com](http://www.ceram.com) or e-mail [mandy.rymill@ceram.com](mailto:mandy.rymill@ceram.com).

#### ALLEN REFRACTORIES COMPANY'S 40<sup>th</sup> ANNIVERSARY

Allen Refractories is proud to mark 2010 as its 40<sup>th</sup> anniversary. Jim and Peig Shackelford started the company February 19, 1970 from an office in their home in Canal Winchester, OH. From those beginnings, the company has grown to employ approximately 50 full time personnel, including skilled craftsmen and office personnel. The company sells and installs heat resistant materials, called refractories, to nearly every industry and every type of heat enclosure throughout the United States. Just a few of the industries served are the power generating, aluminum, foundries, and mineral processes. Every industry that uses heat in its processes requires refractories. Our refractory construction experience is extensive and inclusive: we perform original installations and repair work, sometimes ranging from one-day emergency jobs to major turn-key installations.

In 1987, the company moved to its new facilities in Pataskala, Ohio to increase its capacity and allow for ancillary services such as large-scale castings and other in-house work.

The surviving co-founder, Peig Shackelford, was asked to what she would credit the company's growth and success. "We have the finest customers, for starters. Our greatest asset, for sure, is our employees. We have a very low turnover rate, and point with pride to those who have been with us since the early years. (We affectionately refer to these as our 'old timers'.) John Fry, VP of Construction, 40 years; Jim Gibson, VP of Sales, 38 years, Gary Lott, Chief Estimator, 38 years, and Nancy Richards, Office Manager, 35 years. Our Sales Reps have been with us more than 20 years, as have been many of our Construction Supervisors. As an aside, to reminisce just a bit—in the earliest days of our company, we used to say to one another that we were the 'white hats' referring to the old 1970's cliché about good guys always wore white hats, as in the westerns. This came to mean we did the right thing because it is the right thing, and not just what is expedient. May sound a little 'corny' but in today's business climate, this value is not so common. How gratifying to see the younger management espousing this same attitude and value."

Joe Schaeufele, Operations Manager, Allen Refractories Company, Tel: 740-927-8000, Fax: 740-927-9404, e-mail: [Joe.Schaeufele@AllenRefractories.com](mailto:Joe.Schaeufele@AllenRefractories.com). 

# 46<sup>th</sup> ANNUAL SYMPOSIUM ON REFRACTORIES

Dan Snyder, Missouri S&T, Materials Science and Engineering, [das89b@mst.edu](mailto:das89b@mst.edu)



Attendees at the 2010 symposium meeting.

The 46<sup>th</sup> annual Symposium on Refractories was held at the Hilton St. Louis Hotel on the 24<sup>th</sup> and 25<sup>th</sup> of March. The program for this year was “Innovative Materials for Energy Efficiency”. I have attended this meeting in the past and found the experience to be very educational. This year I have had the additional pleasure to give a short presentation on the second day. I would like to thank the St. Louis Section and the Refractories Division for inviting the student presentations and also to thank the attendees for their comments and advice afterwards.

The first paper of the symposium was presented by Steve Chernack (Thermal Ceramics). His presentation focused on refractory lining design in fired units. Designs for each of the sections of a unit were discussed then analyzed for heat loss. New designs were then shown with new materials that would yield heat loss savings. The next presentation was by John Peterson (ExxonMobil) on the difficulties of

end users comparing refractory solutions. The API STD 930 was presented as a solution to this difficulty.

After an extended coffee break the morning session continued. John Hellmen from Penn State gave the invited paper presentation. This talk explained the use of proppants in the oil and gas wells as well as similarities between their design and that of refractories. He presented some results of his research group in the modification of currently used materials as well as promising results for the development of proppants from lower cost materials such as mixed glass cullet or mine tailings.

Orville Hunter presented James L. Hill (ANH Refractories) with the T.J. Planje St. Louis Refractories Award after the luncheon. Mr. Hill then showed us some pictures from his business travels around the world highlighting the changes in refractories over time. We were then shown the Adrain County Firebrick Museum which covers some of the history of refractories in Missouri.



Section officers: Back row: Dilip Jain and Dennis Hageman. Front row: Roger Smith, Mary Reidmeyer, Kent Weisenstein and Patty Smith.



Division officers: Bill Headrick, James Hemrick and Paul Ormond.



James Hill being presented the 2010 T. J. Planje Refractories Award by Orville Hunter.



Two images from the table top exhibition and cocktail hour prior to the symposium banquet.




Attendees gathering for the symposium luncheon.

The afternoon session started with Mahesh Jha (U.S. Department of Energy) walking us through the selection process for government funding and awards. He stressed the benefits of co-operation between the university and industry in these applications. In addition, the non-solicited governmental program available for industry partners for energy efficiency assistance. Next Rob Crolius (The Refractories Institute) covered some of the legislative and regulatory changes that will be enacted in the near future. Of particular interest to the refractory field were the potential changes in the OSHA regulation of silica and EPA review of new materials for entry into the TSCA inventory. Then Dale Zacherl (Almatis) presented on the energy savings that could be achieved by using a bonite based castable rather than other high alumina materials such as andalusite and bauxite as a backup lining in steel ladles. The final presenter of the afternoon was Steve Libby (Vesuvius) who showed us a new formulation of gunite that appears to combine the properties of shotcrete with lowered capital and maintenance cost and faster turnaround. The day ended with the traditional combination expo and cocktail hour followed by a banquet dinner.

The second day started with Andrew Hall giving his presentation on reduced oxygen drying for accelerated drying. Michel Rigaud (FIRE) then presented on the benefits to be gained by supporting the efforts of FIRE. A competitive yet cooperating

organization will allow for the spread of ideas and results among the members while still maintaining the benefits of a competitive market. Participation in FIRE and utilization of the research provided may be necessary to survive in the refractory market in North America. The next presenter, Chris Parr (Kerneos), presented on some opportunities that SecarPelenium provides as a replacement for other high alumina cements. Rudy Olson (Selec Corporation) presented on the properties of their changed ceramic filters. This new product has on-par or improved properties in comparison to old products with reduced environmental impact due to changed bonding methods.

After the final break Karl Schmidt presented on the broad spectrum of products provided by SGL Group and their ability to modify properties of carbon to meet a variety of needs. The last two presenters were Kelley O'Hara and I. We are both graduate students advised by Dr. Jeff Smith at Missouri S&T. Kelley presented on the effect of solid solution on thermal conductivity. I presented on the investigation on the viability of high alumina cement as an investment mold. The topic of student interest in refractories was brought up both days of the meeting with great emphasis in the FIRE presentation. The comments expressed a concern about the number and availability of students trained in refractories. This year in addition to the two student presenters there were four other students in attendance. I believe that this meeting is one of the best opportunities for members of the refractory industry to interact with students and attract their interest in the field. I look forward to attending next year and hope to see you there. 

# SPINELS AND REFRACTORIES

Ruth Engel, Refractories Consultant, 121 Olde Farm Rd., Oxford, OH 45056

ruthengel@refractoryexpert.com



Ruth Engel

Although alumina-magnesia spinel containing brick and monolithics are currently in wide use, they are by no means the first nor the only spinel bearing refractories available. Over time, chrome, magnesia-chrome, alumina-chrome and now alumina-magnesia spinels have all been used to impart important high temperature properties to refractories.

## SPINEL, DEFINITION

There is some confusion as to what constitutes a spinel. The source of the problem is that spinel, the mineral ( $MgAl_2O_4$ ), is part of the spinel group, general formula  $R_8^{+2}R_{16}^{+3}O_{32}$ , and there is seldom a distinction made between these two entities. The spinel group consists of many minerals amongst them: spinel, chromite, magnetite, etc. Deer, Howie and Zussman [1] list 13 end members, which can be sub-divided into three series depending if the trivalent ion is Al, Fe or Cr. Pure end member minerals are rare in nature and, they exhibit extensive solid solution between Mg, Fe, Cr, Al, Zn and other cations.

Even though I just clarified the term spinel, I will use it the way it is common practice in the refractory world; i.e. without distinguishing between the mineral and the group.

## CHROME

The first documented experimentation of chrome as a refractory material was in 1879 in the open-hearth furnaces at Terre Noire, France [2]. In the 1880s, chrome refractories were already in use in large scale in the Petersburg- Alexandrofsky steelworks [3]. By 1886 several European open hearths had installed them and, around 1896 they could be found in use in the USA [2].

The 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. Chromite is a so-called mixed spinel of the type  $R^{+2}OR^{+3}O_3$  [3]. It readily reacts with iron oxides forming a solid solution, which, in service, leads to an increase in porosity and the subsequent expansion of the brick, the phenomenon called bursting. Additional challenges when using these brick consisted of crumbling because of exposure to alternating oxidizing and reducing atmospheres while at temperature and, continuous shrinking and softening as a function of high temperatures, which limited their applicability. To address these problems, magnesia was added to improve their refractoriness and to create a composition with better slag and thermal shock resistance. Poirier and Bouchetou's [4] contrasted the ter-

nary  $MgO-FeO-Fe_2O_3$  phase diagram with a slice through the 40%  $Cr_2O_3$  level quaternary showing how the presence of chrome oxide extends the spinel region of the  $MgO-FeO-Fe_2O_3$  field thereby improving the refractory's corrosion resistance in the presence of iron oxide.

## MAGNESIA CHROME

Magnesia chrome, also called periclase-chrome, refractories date from the early 1930s when they were simultaneously developed in several countries [2, 3]. By about 1935, chemically bonded and fired brick had become available. In the late 1950s and 1960s work on firing temperatures and their effect on the brick microstructure elucidated the mechanism behind direct bonding (DB) which was defined as "...direct periclase-spinel and periclase-periclase bonds" [3]. By developing a ceramic bond between these high melting point minerals, improved slag resistance and high hot strengths could be achieved. In 1952, the first fusion cast magnesia chrome blocks became a reality. The use of fused grain obtained through this process greatly improved the high temperature properties of the refractories made with it and it is still one of their major components.

When I started working for the steel industry, magnesia chrome refractories were the go to type of refractory for demanding environments. They could be found in all areas, from open-hearth furnaces, which had a never-ending appetite for all sorts of brick, to reheat furnace hearths to many other applications in between. They were also used extensively in other industries. Today, many of these processes are no longer and magnesia chrome refractories are found only in select applications: alloy and specialty steels converters, steel degassers, melting/refining vessels for copper and lead, some coal gasifiers and cyclones and, a few others.

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. This 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 because of magnesia-chrome refractories and the danger of formation of Chrome (VI) at high temperature and in the presence of alkalis, in particular, lime. The problem is 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 the disposal of chrome bearing refractories resulting "...from the recognition of hexavalent chromium as a known human carcinogen ..." [7]. Lee and Nassaralla, published several studies [8, 9] 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 environments and were compared to as received samples to determine the fundamentals of Chrome (VI) formation. Because of this and the work of many others in academia and in the refractory's industry, the use and disposal of chrome bearing refractories, no longer present a problem.

### ALUMINA CHROME

Other chrome bearing refractories have been manufactured, but only alumina chrome is routinely used. In the late 1970s alumina chrome brick were developed [10] 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. The refractory color change from green to a deep red signals the completion of the spinel forming reaction. If the spinel so formed would be of gem quality, it would be called a ruby. Prior to firing, these refractories present the same disposal challenges as the magnesia containing ones.

### ALUMINA MAGNESIA

The impetus for the development of the  $Al_2O_3$ -MgO spinel refractories was as a replacement for the magnesia-chrome due to their possible disposal issues.  $Al_2O_3$ -MgO spinel refractories have been available for over 30 years. Initially, they were used mainly in Japan and the early formulations had poor properties. Many advances have taken place over time and today the availability of refractories with added spinels and/or magnesia for in-situ spinel formation are numerous and they can be found in many applications.

Although  $Al_2O_3$ -MgO spinel refractories were originally developed as a replacement for magnesia chrome, you will seldom find them used as a substitute. Process changes leading to higher temperatures and different slag compositions have changed the environment necessitating the application of more basic refractories.

### OTHER

Other spinel compositions are available. Some are undergoing trials and may be considered for use in future refractories, others have been


found to be unsuitable for this application and some are not economically worth pursuing.

### CONCLUSION

Refractory technology development is a continuous process where one kind of material is replaced by another due to the ever increasing demands of processes, environmental legislation or, raw material availability and cost. In this paper, I briefly reviewed the differing refractory spinel compositions easily available and the changes over time in their usage because of new challenges.

If you have comments about this column or suggestions for future topics please visit me at [www.refractoryexpert.com](http://www.refractoryexpert.com) and I will try to address them.

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# 2010 REFRACTORIES CONGRESS IN INDIA

Charles E. Semler, Refractories Consultant, Semler Materials Services, Chandler, AZ, [CESemler@aol.com](mailto:CESemler@aol.com)



Charles E. Semler

## INTRODUCTION

The 8<sup>th</sup> India International Refractories Congress (IREFCON'10) was held, February 4-6, 2010, at the Taj Bengal Hotel in Kolkata (Calcutta), India. The meeting was organized by the Indian Refractory Makers Assn. (IRMA), which was founded in 1958 by four leading Indian refractory companies – IRMA celebrated their Golden Jubilee in 2008, and currently they have 72 member companies. The theme of

IREFCON'10 was **“Future of Refractories: Challenges & Opportunities”**. There were 454 registered delegates, including 84 from foreign countries; only two of the attendees were from the United States. Most of the foreign delegates came from the following five countries:

Germany	21
China	20
France	12
UK	5
Japan	4

The technical program included 11 sessions, with 65 papers. About half of the papers (32) dealt with iron- and steel-making applications (blast furnace, BOF, EAF, ladles, tundish, continuous casting, etc.). There were fourteen (14) papers on monolithics/castables. Other topics included raw materials, nano-materials, cement/lime/glass/non-ferrous applications, refractory installation, and energy management. Concurrent with the technical program was an exposition with 20 participating companies.

## INAUGURAL SESSION AND KEYNOTE

The Inaugural Session was attended by 480 people, including media and press. Dr. A.K. Chattopadhyay, Tata Refractories, and Chairman of IRMA, gave a welcoming address in which he discussed globalization of the refractories industry, noting that new players are emerging which are intensifying the level of competition. Globalization is a reality, so no time should be wasted considering whether the situation is good or bad, rather it is necessary to be proactive and do whatever is needed to meet and surpass the ever-increasing competition. It will be very difficult for weak and inefficient companies to succeed. In addition, he reminded us that Mahatma Ghandi said, “The future depends on the work we are doing now”.

Prof. William E. Lee, Imperial College, UK delivered the Keynote Address (see **Figure 1**). Lee reviewed the recent downturn and recovery of the steel industry, which is evidenced by the increasing capacity utilization since December 2008. The performance of the steel industry is vital to the refractories industry - the steel and economic downturn had a direct and negative impact on the refractories industry. But recovery is in progress, with world refractory demand



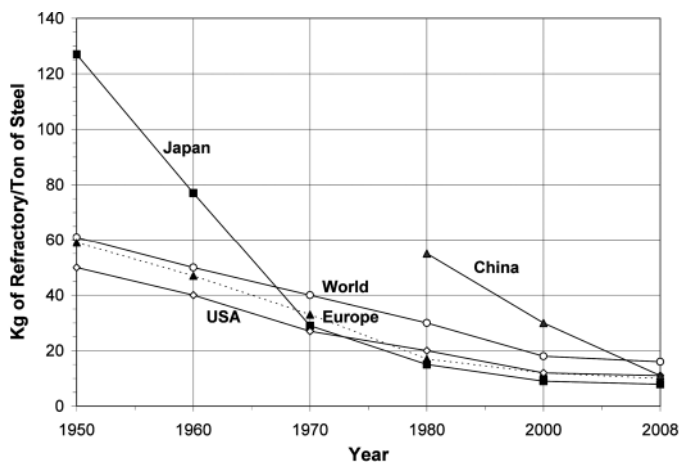
**Figure 1.** Prof. W. E. Lee, Imperial College, UK, presenting the Keynote lecture at IREFCON'10 in Calcutta, India, February 4, 2010.

expected to increase 3.5% annually through 2012, to reach 45.2 million metric tons (mmt). China is by far the leading refractory producer in the world (25 mmt in 2008), with the U.S. a distant second. Historically the refractories industry has continually provided new and improved products to the user industries, contributing to the ongoing decrease in the rate of consumption of refractories, as illustrated by the data for the steel industry since 1950, shown in **Figure 2**.

Prof. Lee cited the following main challenges and opportunities for the refractories industry:

- a. Consolidation in the industry. The two largest refractory groups, RHI and Vesuvius, each share 10-12% of the world-wide market.
- b. Static markets – the downward trend in refractory consumption is expected to continue, never to increase again.
- c. Raw materials issues.
- d. Energy issues.
- e. Recycling used refractories.
- f. The need to attract the best young talent to maintain and improve the industry’s skill base. To help gain the interest of students, Lee uses a modern definition of refractories as “high temperature, nano-bonded composite materials which have critical thermochemical and thermomechanical properties”.

And he concluded with a review of some recent R&D activities, to illustrate the kind of work being done to further advance refractories technology, such as:



**Figure 2.** Data showing the continuing decrease in refractory consumption by the steel industry since 1950, according to Lee, and updated by Semler.

- Use novel processing technology to reduce the synthesis/sintering temperature of refractory oxides such as  $\text{CaZrO}_3$ , mullite, and spinel.
- Synthesis of refractory materials from industrial wastes (e.g., Al dross, red mud).
- Prepare hydration-resistant MgO-CaO aggregates
- Synthesis of oxide – nonoxide composite materials.
- Make complex carbide antioxidants ( $\text{Al}_4\text{SiC}_4$ ,  $\text{Al}_4\text{O}_4\text{C}$ , and  $\text{Al}_2\text{Si}_2\text{C}_5$ ) for carbon-containing refractories.
- Use  $\text{Mg}_2\text{SiO}_4$  to make MgO-SiC-C.
- Study in-situ phase development in refractories.
- Study nano-structure refractories with nano-fibrous phases such as carbon nanotubes or oxide/carbide nano-whiskers.

## REFRACTORIES INDUSTRY OVERVIEW

The program included other invited/special lectures, ranging from general reviews to specific topics. S. Das Gupta, Dastur & Co., spoke about the development and status of the steel industry in India. He noted that the refractories industry is knowledge-based, and depends upon development of multi-tier technological capabilities and R&D activities to create a range of value-added products and services. But, except for a few leading refractory manufacturers, he considers that the refractories industry in India has failed to attract the talent needed to fulfill the tasks. He noted that the long-term prospect for the global steel market is strong, and that India will likely achieve a steel capacity of 200 mmt by 2020.

Dr. A.K. Chattopadhyay reviewed the business situation of the refractories industry, given the fact that half of the global GDP may soon come from developing countries, whereby it is important to shed the traditional mindset and understand the paradigms of global business, recognizing that the U.S. dollar could weaken and may not remain the sole international currency. He noted the special importance of research to address the raw materials situation, and the need to attract the best minds to refractories. He showed the comparative annual returns (profits) for the steel and refractories industries as 25-34% and 10-14%, respectively, and expressed concern about the disparity, because the poor return on investment has negative effects on the refractories industry. He concluded with the advice that “the best way to predict the future is to create it”.

Dr. Claude Dumazeau, Vesuvius Group, discussed the challenges and opportunities for refractories in the future. He noted that the cur-

rent world demand for refractories is about 40 mmt; the growth rate is expected to continue at a rate of 3-4% per year, once the economy has recovered. The industrializing regions of the world, led by China, will drive the growth, while growth will remain essentially flat in the industrialized countries. He discussed four main areas where attention should be focused for the future:

- Health, safety, and environmental.
- Lower energy costs and increase productivity for refractory producers and users.
- Increase technical sophistication, including the lab equipment used to characterize and model the products and processes.
- Increase the understanding and overall impact of refractories on user’s processes and equipment.

And he concluded that the biggest challenge for the refractory industry will be to attract talented material scientists to allow closer collaboration with the refractory users.

Dr. C.E. Semler, U.S. Consultant., discussed the ongoing advancement of refractories technology. Included was a historical review of selected examples of refractory development and know-how from the 1500’s to now. Current information was cited to illustrate a few examples of actual refractory service improvements which have significantly benefited steel companies, as follows:

Slide gates (Japan)	+30%
BOF converter lining life (Japan)	+65%
Iron ladle lining life (U.S.)	+100%
Steel ladle lining life (U.S.)	+136%
Torpedo car lining life (Japan)	+490%

He also suggested a few topics where R&D is needed, which could contribute to the further advancement of refractory technology:

- The refractories industry has received a “wake-up call” in recent years regarding raw materials, so research is essential to minimize/eliminate future problems. Several examples are more recycling of used refractories, novel treatment/processing, upgrading lower grade materials and industrial waste products, effect of additives and nano-materials, etc. Materials are limited, but creativity is unlimited.
- More use of spinels, especially of prescription type for specific environments.
- High temperature simulative (dynamic) testing coupled with advanced modeling, thermodynamic/thermochemical analysis, and other sophisticated methodology.
- Consideration of composition/structure changes that can result in the modification of fundamental property relationships, e.g., MOR vs. MOE.

## REFRACTORIES FOR THE STEEL INDUSTRY

Because numerous representatives of the steel industry attended IREFCON’10, there was good discussion and exchange of information in the technical sessions, and at the breaks. This situation was reminiscent of past years in the U.S. when the refractory meetings were well-attended by people from the steel and other user industries, and discussion was lively and beneficial.

As noted above, papers about steel industry applications dominated the program, and the most popular steel industry topic was ladles (9). Selected information from some of the steel papers is highlighted below:

- Using computational fluid dynamics, RHI determined that a cylindrical tap nozzle on an EAF had a flow rate of 270

kg/sec, whereas a conical tap nozzle had a flow rate of 342.3 kg/sec.

- b. Krosaki-Harima discussed the improvement/optimization of submerged entry nozzles (SEN). The life of the  $ZrO_2$ -C slagline is a key factor, and nano-technology is used to achieve optimum corrosion resistance. To improve the thermal shock resistance of the alumina-graphite (AG) body of the SEN, nano-technology was applied; thermal shock testing of the conventional AG material showed cracking after two cycles, but the nano AG material endured 10 cycles without cracking.
- c. Almatris reported a change in ladle wear linings at 10-12 European steel works. In 2000, eight used bauxite- or andalusite-based wear linings, but in 2008 there were none. The ladle wear linings used in Europe for the increased steel-making demands are synthetic alumina castables, alumina-magnesia-carbon (AMC) bricks, or basic bricks (MgO-C, doloma).
- d. Corus IJmuiden implemented a ladle refractory management program, which has resulted in an increase of ladle sidewall life from 77 heats in 1998 to 174 heats in 2007 (+126%). They evaluate refractories on a “value in use” basis in which not only the refractory cost, but also the availability/capability of the installations, are considered.
- e. Based on the development of AMC bricks for the bottom impact area (ladles) and a modified zoned lining with improved MgO-C bricks, the Steel Authority of India Ltd. (SAIL) achieved an increase in lining life of 150 ton ladles from 60-90 heats to an average of 116 heats (130 max.).
- f. Refratechnik noted that the target of refractory users to lower their refractory costs has reduced their use of cheap and low performance refractories, with a change to lining designs based on high quality and high performance refractories. The example of an EAF shop showed a 120% increase in lining life with higher grade/quality refractory, coupled with improved steelmaking and maintenance processes.
- g. Essar Steel has reduced their refractory consumption rate from 9.3 kg/ton of steel in 1999 to 3.9 kg/ton of steel in 2009. During that period, the wall life has increased from 140 to 260 heats (+86%) and the delta life has increased from 100 to 520 heats (+420%).

## DEVELOPMENT AND USE OF MONOLITHICS

With monolithic refractories being roughly only 22% of the annual refractory production in India, they lag behind the world leaders (e.g., Japan, 68% and U.S., 52%). So with the many opportunities for progress, there was active interest in the papers by Indian and foreign speakers on monolithics technology and use. Highlights from several of the monolithics papers are presented below:

- a. Central Glass & Ceramic Research Inst. (CGCRI - Calcutta) reported the development of various high alumina aggregates (58% to 80%  $Al_2O_3$ ) by reaction sintering of Indian sillimanite sand, with and without alumina.
- b. A poster by CGCRI described their beneficiation of lower grade Indian bauxite, which is available in large quantity. Prior efforts to reduce the impurities, and develop useful aggregate, were not successful. But using a novel approach, the Indian bauxite was blended with other materials (not specified) to convert the impurities into phases that are not low melting and detrimental, which resulted in an improved aggregate.

- c. Kerneos discussed new aluminate binders for refractory castables, which offer the opportunity for more predictable behavior and improved properties. Examples of regular and low cement castables were reviewed.
- d. Tata Refractories reported the study of  $MgO-Al_2O_3-Cr_2O_3$  (MAC), no-cement, self-flow basic castables with added spinel and hydratable alumina binder. The spinel addition was optimized at 10 wt%. These MAC castables showed excellent corrosion/penetration resistance to copper slag.


## PANEL DISCUSSION

The meeting concluded with a panel discussion. Six panel members (Spreij, Han, Chattopadhyay, Semler, Parr, Chakraborty) spoke about various current topics such as raw materials, total refractories management, fundamental research, etc., followed by questions and comments from the audience. **Figure 3** shows a view of the 250 attendees. A few of the discussion points are mentioned below:

- a. Although some people say that refractory research doesn't pay, it was noted that there is evidence contrary to that view. In India the investment in research is low (0.8%-3%). R&D is definitely needed to make it possible to use the large quantity of bauxite and magnesite in India.
- b. It is expected that the price of Chinese bauxite, magnesite, and BFA will increase in the short term.



**Figure 3.** View of the audience (250) at the Panel Discussion, IREFCON'10.

- c. The refractories industry is moving in a vicious circle. The profit difference with the steel industry is due to the refractories industry itself. It is important to not misguide the customers. It is important to know and understand the refractory problems/needs of the users, and then to provide solutions for them. Wherever possible, create markets and add value.
- d. The urgent need and importance of attracting good people to the refractories industry was re-emphasized, having been mentioned by several speakers during the course of the meeting. The salary issue doesn't have to be a problem because it is a good and interesting industry, and people don't work only for money. It is very important to hire people that are creative, and good at interaction/collaboration. 

# COLLOIDAL SILICA SELECTION FOR NANOBONDED REFRACTORY CASTABLES

M.V.M. Magliano, E. Prestes, J. Medeiros\*, J.L.B.C. Veiga\*, V.C. Pandolfelli

Materials Engineering Department - Federal University of São Carlos, 13565-905, São Carlos - SP, Brazil

\*Petrobras - CENPES/EB-AB-G&E/EEQ, Rio de Janeiro – RJ, Brasil

epres@uol.com.br or vicpando@power.ufscar.br

## ABSTRACT

Commercial silica sols have different particle sizes and solid contents. The reactivity of colloidal suspension strongly influences the sol stability and the bonding strength. Highly reactivity suspensions increase the mechanical strength, but induce shrinkage and internal stresses that can result in crack formation during the drying stage. The effect of sols with different solid content/particle size ratios in the properties of refractory castables was analyzed for a system based on tabular alumina, calcined alumina and fume silica. The results pointed out that the high reactive silica sols reduce the workability, decrease the fluidity and deteriorate the cold and hot mechanical properties of refractory castables due to the significant microstructure cracking during the drying stage. Therefore, the results attained help to make a better selection of the colloidal silica when nanobonded refractory castables are produced.

## INTRODUCTION

Recent publications suggested the use of silica sol as a promising alternative to calcium aluminate cements [1-8]. This nanostructured colloidal suspension can substitute the hydraulic binders and hydratable aluminas leading to a new category of refractory named nanobonded castables. The commercial silica sols have different particle sizes and solid contents. The particle size affects the maximum attained solid content, because small particles can only be stabilized in more diluted suspensions. Colloidal silica sol stabilization can be carried out in acid or basic pH and is typically ammonium-stabilized in a pH range between 9 and 10 [9-10]. The gelation mechanism of colloidal silica is carried out when the hydroxyl groups (Si-OH) present on the surface of the particles generate siloxane bonds (Si-O-Si), resulting in a three-dimensional network [11]. The mechanical strength in colloidal silica containing refractory castables is provided by a gel formation that keeps the matrix particles bonded and, after drying, generates a solid film. The suspension reactivity strongly influences the stability of the colloidal silica sols and bond strength. More reactive suspensions (higher specific surface area) present shorter gelling time

and increase the castable mechanical strength. However, these suspensions induce drying shrinkage, generating internal stresses that can result in the crack formation. Two factors are responsible for the solution reactivity: the average particle size and the silica content, where, suspensions with smaller particle sizes and a higher solid content are more reactive [9]. In this work, the effect of colloidal silica sols with different characteristics in the properties of refractory castables comprising tabular alumina, calcined alumina and microsilica, was analyzed. The mixing behavior, free and vibrated flow, mechanical strength after drying and firing, hot modulus of rupture and sinterability under load were evaluated.

## EXPERIMENTAL PROCEDURE

High-alumina refractory castables containing tabular alumina, calcined alumina and microsilica were adjusted to a particle size distribution based on the Andreasen's packing model [12], with a distribution coefficient (q) equal to 0.21 and maximum particle size diameter of 4.75mm. Five commercial silica sols were evaluated as binder agents of the same refractory composition. **Tables 1** and **2** show the colloidal silica sols characteristics and castable formulations, respectively.

Castable compositions were dispersed with citric acid (Labsynth Brazil). Due to the distinct solid content of the silica sols used, different water amounts were added to the castables to keep the total water at 4.8 wt%. The mixing step was carried out in a castable rheometer [13] and the free and vibrated-flow was measured according to the ASTM C-860 standard. Castable compositions were cast into molds for the mechanical strength, apparent porosity, elastic modulus, hot modulus of rupture and sinterability under load measurements. A gelling agent was not used for the colloidal silica. The samples were cured at 110°C in an acclimatized chamber (Vötsch 2020) for 12 hours to promote the gelling by the drying process. The mechanical strength of cured samples was measured according to the ASTM C496-90 standard in a MTS System (Model 810) at a constant load rate of 42N/s. The rupture stress ( $\sigma_f$ ) was calculated based on equation A.

**Table 1. Silica sols characteristics.**

Colloidal silica	30%-8	30%-14	40%-14	40%-80	50%-80
Average particle size (nm)	8	14	14	80	80
Solid content (wt%)	30	30	40	40	50
Specific surface area (m <sup>2</sup> /g)	300	220	250	-	-
Stabilizing agent	Na	Na	Na	NH <sub>3</sub>	Na

**Table 2. Castable formulations.**

Aggregate (wt%)	Tabular alumina (Almatis)	(6-3)mm; (3-1)mm; (1-0.5)mm; (0.6-0.2)mm; (-0.2)mm				66.5
Matrix (wt%)	Calcined alumina (Almatis)	A1000SG and CL370C				28.5
	Microsilica (Elkem)	MS 971 U				5.0
Colloidal silica (wt%) - (Nalco or Eka)						5.0
Colloidal silica	30%-8	30%-14	40%-14	40%-80	50%-80	
Additional water (wt%)	1.3	1.3	1.8	1.8	2.3	

$$\sigma_f = 2 \cdot \left( \frac{P_{max}}{\pi \cdot l \cdot d} \right) \quad (A)$$

where,  $P_{max}$  is the maximum load,  $l$  and  $d$  are the height and diameter of the sample, respectively. After firing the samples at 1500°C for 10 hours, the mechanical strength was inferred by means of elastic modulus measurements using 150 mm x 25 mm x 25 mm samples. The elastic modulus determination was based on resonance frequency measurements obtained by Escanelastic equipment (ATCP Brazil). The elastic modulus ( $E$ ) was calculated according to equation B.

$$E = \frac{\rho}{K_n} \cdot \left( \frac{2 \cdot l \cdot f_n}{n} \right)^2 \quad (B)$$

where,  $\rho$  is the sample density,  $f_n$  is the bar flexural resonance frequencies (of  $n$  order),  $l$  is the sample length and  $K_n$  the correction factor. Apparent porosity of cured and fired samples was obtained by the Archimedes immersion method according to the ASTM C 830-88 standard. The hot modulus of rupture ( $\sigma_F$ ) of fired samples was determined in a three-point bending strength testing machine (Netzsch - model HBST 422) at a constant load rate of 12.5N/s, according to the ASTM C 583-8 standard. The following equation was used to calculate the hot modulus of rupture.

$$\sigma_F = \frac{3}{2} \cdot \frac{P_{max} \cdot L}{b \cdot h^2} \quad (C)$$

where,  $P_{max}$  is the rupture strength,  $L$  is the distance between the rods (125 mm);  $b$  and  $h$  are the width and height of the sample, respectively. The sinterability under load in 50 mm x 50 mm cylindrical samples (with a passing hole of 12.4 mm at the center) fired at 600°C for 2 hours, was conducted under compressive stress of 0.02 MPa up to 1500°C and 5 hours of dwell time at this temperature, (Netzsch-421 equipment).

## RESULTS AND DISCUSSION

### Processing characteristics and mechanical strength after curing and firing

Figure 1 shows the mixing behavior of the refractory castables containing distinct silica sols. In the systems with 30 and 40% of solid content, the effect of different particle sizes in the mixing curve was mainly detected at the castable turning point, where smaller particle sizes provided shorter mixing times. For the sols with the same particle size, it is believed that a lower solid content allows for longer mix-

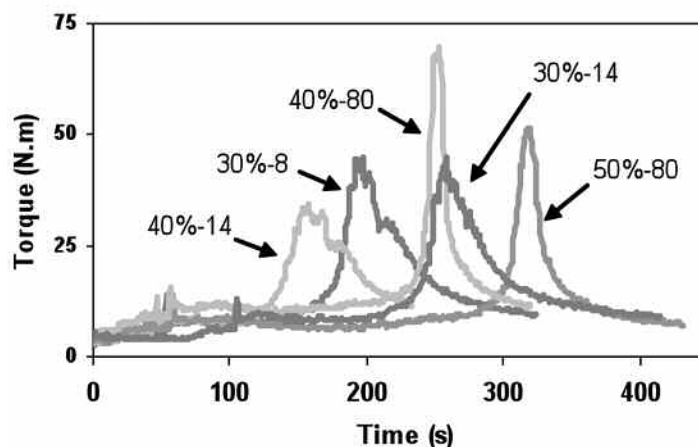


Figure 1. Mixing behavior for the distinct silica sols containing castables.

ing times to the castable, which can be shown based on the silica sols containing a particle size of 14 nm. Nevertheless, for the colloidal suspensions with a particle size of 80nm, this behavior was not observed which was most likely due to the different stabilizing agent (see Table 2). The turning point of castables was shorter for the colloidal suspensions containing a small particle size and/or high solid content. It was also noticed that higher torque levels were attained for the 80 nm particle size colloidal silica containing systems. A clear general straightforward correlation for all results is difficult considering the different silica sol suppliers, the stabilizing agents and their interaction with the dispersant, whether the silica sol is an isolated particle or an agglomerate, if the agglomerate breaks or not at the mixing stage, etc.

Free and vibrated flow results (Figure 2) show that the fluidity of the produced castables was influenced by the sol particle size and the solid content. In the systems with the same solid content, the higher free and vibrated-flow was related to sols with higher particle sizes. Considering the systems with the same particle size, the lower solid content resulted in the castable fluidity increase. The higher torque levels for the silica sols with an 80 nm particle size induced a greater agglomerate rupture, leading to a higher free-flow value for this system.

Figure 3 shows the mechanical strength and apparent porosity measurements for the cured samples. The silica sols with a higher solid content/particle size ratio, 30%-8 and 40%-14 systems, have greater reactivity due to the higher specific surface area, resulting in larger shrinkage during the drying stage and the generation of internal stress. These aspects lead to greater microstructure cracking and

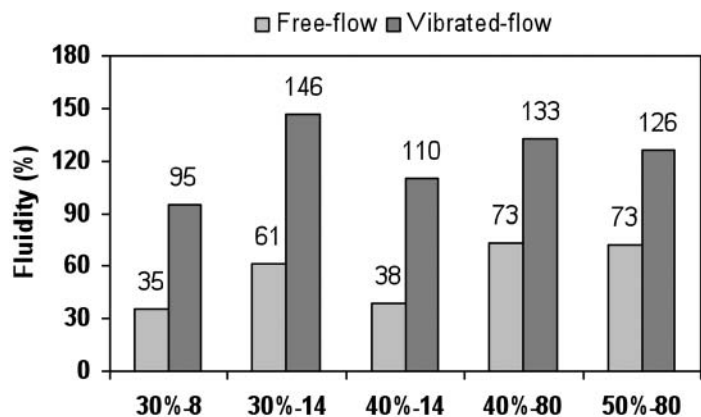


Figure 2. Free and vibrated-flow measurements of distinct silica sol containing castables.

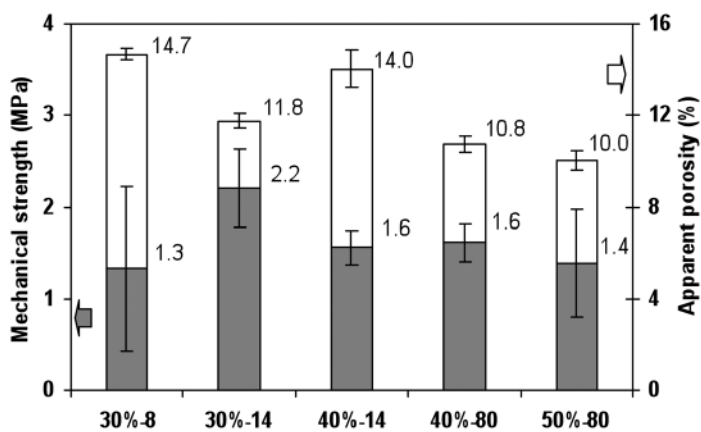


Figure 3. Mechanical strength and apparent porosity for the cured samples.

a consequent increase in the apparent porosity and decrease in the mechanical strength [9]. The best balance between solid content (directly related to particles bonding strength) and the resulting internal stress (which could affect the porosity) was attained for the 30%-14 system.

Figure 4 shows the elastic modulus, which is indicative of mechanical strength and the apparent porosity measurements for the fired samples. The inferior apparent porosity for the 80nm particle-size colloidal silica containing castables (Figure 3) resulted in higher elastic modulus after the firing stage. The effect of the cracking after curing also influenced the properties after firing for the high reactive colloidal silica containing castables. The evidence of this effect can be attested based on the higher apparent porosity value in the 40%-14 system. For the 30%-8 one, the evaluation of elastic modulus was not possible due to the severe cracking of the samples after the drying stage. Comparing the systems of the same particle size but different solid contents, the increase in the mechanical properties for the higher solid content ones was not observed due to the influence of the cracks generated.

### THERMO-MECHANICAL PROPERTIES: HOT MODULUS OF RUPTURE AND SINTERABILITY UNDER LOAD

Figure 5 shows that the higher hot modulus of rupture values at 1450°C for the fired samples were related to the lower apparent porosity levels. The lower reactivity of the 40%-80 and 50%-80 sys-

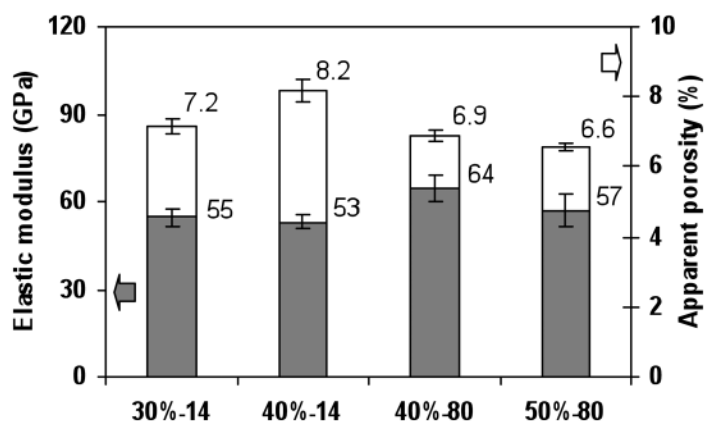


Figure 4. Elastic modulus and apparent porosity of fired samples at 1500°C for 10 hours..

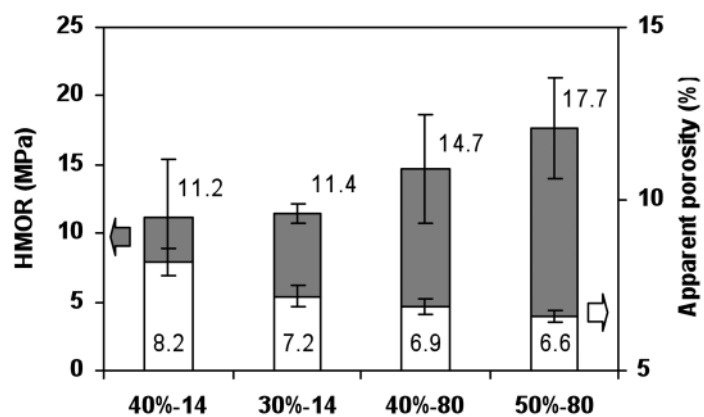


Figure 5. Hot modulus of rupture (HMOR) at 1450°C for distinct colloidal silica containing refractory castables.

tems provided the higher hot modulus of rupture and the lower apparent porosity values, whereas for the higher reactive systems, 40%-14 and 30%-14 sols, the behavior was the opposite.

Therefore, the materials which showed higher apparent porosity after the drying stage had their cold and hot mechanical properties reduced. The results of sinterability under a load for the 50%-80 (lower reactivity), 30%-8 (higher reactivity) and 40%-14 (mostly used in refractory castables) are shown in Figure 6.

For the evaluation of sintering profiles, two aspects must be considered: the higher sinterability provided by the high reactive silica sols and the defects originated during the drying stage. Thus, the 30%-8 system had a higher shrinkage when compared to the 50%-80 one of lower reactivity. The characteristic expansion peak related to the mullite formation in the 1200 - 1500°C range was also detected for all systems. The intensity of this peak cannot be directly associated with the mullite quantity formed in the system because, besides the expansive reaction, the shrinkage due to the sintering process counterbalanced it.

### CONCLUSIONS

The characteristics of colloidal silica sols are a key issue in the properties of nanobonded refractory castables. Higher reactivity suspensions reduce the workability, decrease the fluidity and deteriorate the cold and hot mechanical properties due to the crack formation during the drying stage. Silica sols with average particle sizes lower than 14

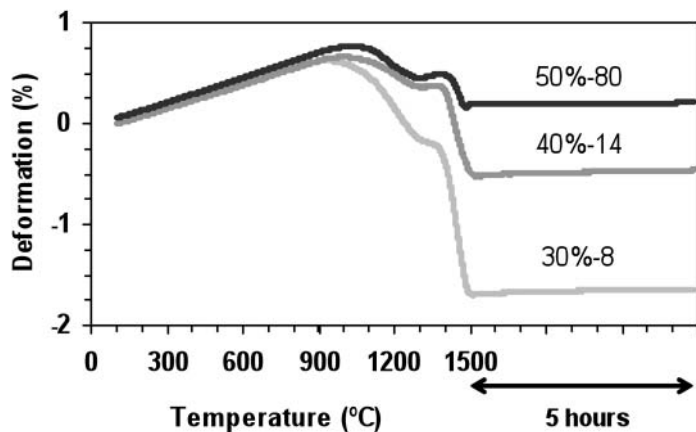


Figure 6. Sinterability under load up to 1500°C for different colloidal silica containing refractory castables.


nm are not indicated for isolated use in nanobonded refractory castables due to the negative effects associated with their high reactivity.

## ACKNOWLEDGEMENTS

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before manufacture. While the project is not as yet listed on EPA's semi-annual regulatory agenda, it was listed in the recently published December 2009 "Action Initiation List". The announcement is quoted as follows:

"EPA is clarifying the guidance on chemical identification of certain statutory mixtures for purposes of the TSCA Chemical Substance Act Inventory (TSCA Inventory). For the initial reporting period that established the TSCA Inventory, EPA developed broad listing criteria ("category listings") for the complex reaction products known as statutory mixtures. These include ceramics, cements and frits. Since that time, there has been inconsistent guidance for manufacturers of such substances with regard to whether new chemical notification under Section 5 of TSCA was required for such new substances. Under this action, EPA will clarify which chemical substances comprise complex reaction products that fall under the "category listings" and which chemical substances (not currently on the TSCA Inventory) would be considered to be "new" chemical substances under TSCA and thus be subject to new chemical notification under TSCA Section 5."

## OSHA HEARINGS ON GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELING OF CHEMICALS

OSHA held three informal hearings on its proposed rule which would align the OSHA hazard communication regulation with the Globally Harmonized System of Classification and Labeling of Chemicals. The first meeting was to be held at OSHA headquarters in Washington on March 2, followed by one in Pittsburgh on March 31 and one in Los Angeles on April 13. For details, go to: <http://edocket.access.gpo.gov/2009/E9-30713.htm>. 



# PROBABILISTIC LIFE DESIGN OF REFRACTORIES FOR STEEL CASTING<sup>1,2</sup>

A. Wereszczak, Mechanical Characterization and Analysis Group, High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6069

J.D. Smith and R.E. Moore, Department of Ceramic Engineering, Rolla, MO 65409

*The St. Louis Section of The American Ceramic Society at the University of Missouri-Rolla, (now Missouri S&T) Rolla, MO on March 19-20, 1998*

## ABSTRACT

The failure probability of magnesia-graphite components was predicted using an established probabilistic life prediction design algorithm. The described algorithm is commonly employed in the design of load bearing structural ceramics components; however, interest existed for the present study to demonstrate its use and applicability in the design (or failure probability analysis) of arbitrary refractory components. Two components were examined: [i] a 25.4 x 25.4 x 152 mm (1 x 1 x 6 in) magnesia-graphic prismatic bar subjected to three-point flexure using a 101.6 mm (4 in) span, and [ii] a vertical suspended magnesia-graphic nozzle whose dimensions were 203 O.D. x 101.6 I.D. x 1524 mm length (8 O.D. x 4 I.D. x 60 in length). Magnesia-graphite strength data were combined with finite elements analysis of the components and an appropriate multiaxial ceramic failure criterion to predict the failure probabilities of each. The latter exercise illustrated how laboratory-generated strength distributions may be used to predict the failure probability of a representative refractory component used in steel casting, while the former provided useful information of strength-dependence on size between two commonly used specimen geometries used for refractory strength tests. The results indicated an approach of probabilistic life design is applicable to refractory component design for the steel casting industry.

## I. INTRODUCTION

Magnesia-graphite (MgO-G) and alumina-graphite (Al<sub>2</sub>O<sub>3</sub>-G) refractories are used as ladle shrouds and submerged entry nozzles in continuous steel casting. These refractories are chosen because they tend to prevent reoxidation and flux entrapping of the molten steel, and because they provide a combination of good corrosion, erosion, and clogging resistance and cost effectiveness [1]. MgO-G refractories reportedly exhibit better resistance to high sulfur, oxygen, and manganese wear than Al<sub>2</sub>O<sub>3</sub>-G [2]. Ladles and nozzles are subjected to large thermal excursions during service, so the refractory comprising them must be resistant to thermal shock. To take advantage of these MgO-G and Al<sub>2</sub>O<sub>3</sub> physical property attributes and to increase the service life of components made from these refractories, the mechanical performance and thermal shock resistance of MgO-G and Al<sub>2</sub>O<sub>3</sub>-G refractories are being actively explored by both suppliers and end-users of these materials.

To achieve more predictable and longer component service lifetimes, it is recognized that the mechanical properties of MgO-G and Al<sub>2</sub>O<sub>3</sub>-G must be appropriately measured [3]. Toward this end, numerous researchers have performed mechanical tests on these refractories in an attempt to better understand their behavior when subjected to mechanical and thermal loadings. Strength and toughness tests conducted at room temperature have shown the mechanical behavior of these materials to be quite complex, in that: they can be anisotropic [1]; their porosity can vary and control the failure mechanism [4] and; there is a specific firing temperature range (which is lower than typical service temperatures) which yields maximum 20°C (70°F) strength and fracture resistance [4-5]. These materials are exceedingly difficult to mechanical test at elevated temperatures because of their propensity to react with test fixturing unless they are tested in a reducing environment. Some high temperature test results have shown the apparent elasticity of Al<sub>2</sub>O<sub>3</sub>-G to be a function of loading rate, which suggests the softening of at least one phase [6]. Additionally, the high temperature oxidation process was found to impose or affect residual stress state Al<sub>2</sub>O<sub>3</sub>-G [6], which can increase the likelihood of failure if the residual stresses become more tensile in nature. Due to the difficulty of testing these materials at elevated temperatures, many studies have circumvented these difficulties somewhat by exposing the refractories to elevated temperatures and then performing mechanical tests at room temperature [4-5, 7].

A primary driving force behind most of the mechanical testing is to understand, predict, and promote better thermal shock resistance of these materials. Several investigators have explored the thermal shock resistance [1, 4-6] and have related it to the material's fracture energy, Poisson's ratio, modulus of elasticity, and thermal expansion coefficient using a classical approach. Specifically of interest for the present study, Phillips, et al., [1] proposed that the thermal shock resistance of these refractories was achieved by avoiding crack initiation rather than inhibiting crack propagation; if true, then the utilization of a probabilistic life design algorithm (developed for load-bearing structural ceramic components) is applicable for predicting the thermomechanical failure probability of such refractory structures.

The intent of the present study was to illustrate how laboratory-generated strength distributions may be used to predict the failure probability of refractory components using a probabilistic life

1. Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials Program under Contract DE-AC05-96OR22464, managed by Lockheed Martin Energy Research Cooperation.
2. The generation of the strength results at the University of Missouri-Rolla (now Missouri S&T) was part of a project sponsored by the Refractory Collaborative Group of the American Iron and Steel Institute.

design algorithm. MgO-G strength distribution data were combined with finite element analysis (FEA) of a MgO-G prismatic bend specimen or a MgO-G nozzle and a multiaxial failure criterion to predict the failure probability of these two components. The result of failure probability prediction of three-point flexure bar geometry was a determined strength-size relationship between the diametral compression and flexure specimens. The result of the nozzle failure probability exercise was an illustration of how laboratory-generated strength distributions may be used to predict the failure probability of a representative refractory component used in steel casting. Although not examined in the present study, if FEA thermal boundary or service conditions were known for the nozzle, then the algorithm utilized in the present study could also be used to predict the failure probability under thermal shock conditions. Furthermore, the probabilistic life design algorithm could also be used to optimize the design of the nozzle to minimize the likelihood of thermal shock failure and to extend nozzle lifetime.

## II. DESIGN AND FAILURE PROBABILITY PREDICTION OF BRITTLE MATERIALS

### III. A. Strength Distribution

Strength distributions for most ceramic and brittle materials follow a “weakest-link” theory and are well represented by two-parameter Weibull distribution. The failure probability as a function of applied stress, Weibull modulus (which qualitatively is inverse to the standard deviation), and size or scale is represented by:

$$P_f = 1 - \exp[-K_v (V/V_0) (s/s_0)^m] \quad [1]$$

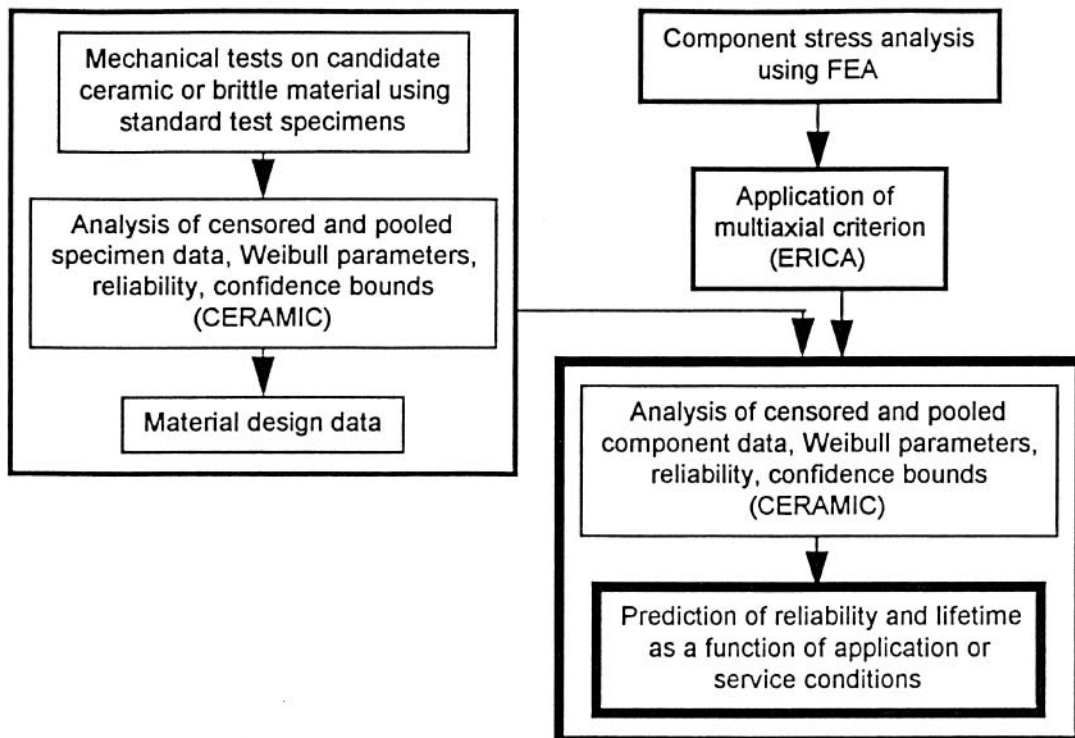
Where  $P_f$  is the cumulative probability of failure,  $K_v$  is a load factor ( $K_v = 1$  for uniaxial tension),  $V$  is the volume under uniform tension (the product  $K_v \cdot V$  is often referred to as the effective vol-

ume),  $V_0$  is unit volume,  $s$  is the magnitude of stress,  $m$  is the Weibull modulus and so is a normalizing parameter. The compression strength of ceramic and brittle materials tends to be at least an order of magnitude more than their tensile strength, so the more conservative tensile strength values are used for probabilistic life design or failure probability analysis. **Equation 1** portrays volume (or volume-type-flaws) as the strength – limiter, with higher strengths measured for smaller volumes. An analogous function may be used to relate failure probability to stress for surface flaws (e.g., strength of glass), but for the present analysis, a single volume flaw population was assumed to limit strength in the MgO-G refractory specimens, so **Equation 1** was used.

### II.B. Probabilistic Life Prediction Algorithm

Probabilistic life design of a brittle component combines three elements: material strength data represented in the form of **Equation 1**, finite element analysis of the component subjected to service conditions (or conditions of interest), and a multiaxial fracture criterion. A flowchart of the algorithm is shown in **Figure 1**.

Strength data are generated in the laboratory using a tensile specimen, flexure specimen, diametral compression specimen, etc. The strength data are ranked and applied to **Equation 1** with Maximum Likelihood statistics, and are scaled to a unit size ( $V_0$  in **Equation 1**) where the scaling parameter and Weibull modulus ( $s_0$  and  $m$  in **Equation 1**, respectively) are determined. The scaling parameter and Weibull modulus are then described as the material design data, because they are independent of specimen size and are material descriptors. The ceramic community often uses the characteristic strength ( $s_q$ ) in discussions. Although the characteristic strength is related to the scaling parameter, they are not the same entity. If one neglects the volume combination of test specimen size, loading configuration, and flaw type, the  $s_0$  term is replaced



**Figure 1.** Probabilistic life design algorithm (using AlliedSignal’s CERAMIC/ERICA computer programs) used to predict failure probability of a refractory component used in steel casting.

by  $s_q$  in that instance. The characteristic strength then effectively acts as a “scaling parameter” but its value is only valid for that particular specimen size so it is not strictly a material design parameter. The scaling parameter would be the same for different sized refractory flexure specimens; however, the characteristic strengths of the two-flexure specimen geometries would be different. The only time the scaling parameter of a material and the characteristic strength of a specimen made from that same material are equal is when the specimen coincidentally has unit size. For more thorough descriptions of this function, the reader is encouraged to review ASTM C1239 [8].

The second input needed to predict failure probability of a brittle component is a FEA model which takes into account the component’s service conditions (e.g., mechanical loads, constraints, temperature, and any time- and temperature-changes in strength) and geometry, and the material’s elastic properties.

The third and last required input to predict the failure probability is a multiaxial failure criterion. The results from the FEA model are used as input to determine a stress gradient factor as a function of Weibull modulus. Probabilistic life prediction computer programs (e.g., AlliedSignal’s CERAMIC/ERICA<sup>3</sup> and NASA’s CARES/LIFE<sup>4</sup>) were developed to specifically analyze this multiaxial criterion (and also a more detailed analysis of Equation 1 and its programs [9-10]). The use of the multiaxial fracture criterion effectively allows the material design data (which are usually generated with a uniaxial strength test) to be coupled to the multiaxial stress state, which is likely to exist in the component. This multiaxial failure criterion is very applicable for brittle load bearing materials which are designed for service stresses below which crack initiation will not occur, and which make it applicable for the conditions of thermal shock resistance in refractories which Phillips, et al., [1] proposes.

In the last step, all three inputs are combined (bottom-right box in Figure 1) to predict the failure probability of the component in question. Besides being used for the prediction of failure probability, this algorithm is also used for design because the component geometry may be iteratively changed in the FEA until its failure probability under service conditions is minimized.

### III. FAILURE PROBABILITY PERDITION OF MGO-G REFRACTORY COMPONENTS

Room temperature strength was measured for MgO-G refractory for three different exposure temperatures. The refractory composition consisted of 80.95 wt% MgO, 14.29 wt% graphite, and 4.76 wt% metal, with the later being a 50/50 blend of aluminum and silicon. A more detailed description of the material, specimen preparation, and strength testing is summarized in Reference [7]. For the present study, two components were modeled with FEA, one being a MgO-G prismatic bar and the other a MgO-G nozzle. The failure probability as a function of stress was then determined for both components and all three-exposure temperatures yielding six different failure probability prediction sets.

### III.A. MgO-G Strength Distributions

MgO-G disk-shaped specimens with a nominal diameter of 38.1 mm (1.5 in) and a 19.05 mm (0.75 in) thickness were core drilled parallel to the fabrication pressing direction. The specimens were then enveloped in graphite foil to reduce surface oxidation during exposure at 1000, 1300, or 1550°C (1800, 2370, and 2820°F) for 3 hours in flowing argon environment. A diametral strength (or Brazil) test at room temperature was performed (crosshead speed of 1.27 mm/min = 0.5 in/min) on the specimens in which an axially applied compressive load causes the specimen to fail from a consequential transverse tensile stress [11]. Graphite foil was employed as a padding material between the two specimen contact locations and the load train’s loading platens. The strengths were then determined using:

$$S_{DC} = (2P) / (\pi Dt) \quad [2]$$

Where  $S_{DC}$  is the diametral strength, P is the ultimate compressive force, D is the diameter, and t is thickness.

The diametral strength distributions for the three exposure temperatures were determined using AlliedSignal’s CERAMIC/ERICA computer programs<sup>5</sup>. The computer program uses maximum likelihood estimation to determine the distributions. The results from this are illustrated in Figures 2-4 for the three exposure temperatures. Within 95% confidence, the strength data fit quite well to a Weibull distribution for all three-exposure temperatures. The Weibull moduli were 8.3, 5.8, and 9.4 and the characteristic strengths for this specimen geometry were 3.17, 2.29, and 2.16 MPa (460, 332, and 313 psi). Also, within 95% confidence (upper and lower estimates in parenthesis in Figures 2-4), the Weibull moduli for the 1000 and 1550°C exposed specimens were equivalent and the Weibull modulus for the 1300°C exposed specimens was lower valued. The characteristic strength for the 1000°C exposed specimens was higher-valued than those for the 1300 and 1550°C exposed specimens. The strength distributions for the three sets of data were then scaled to unit size using

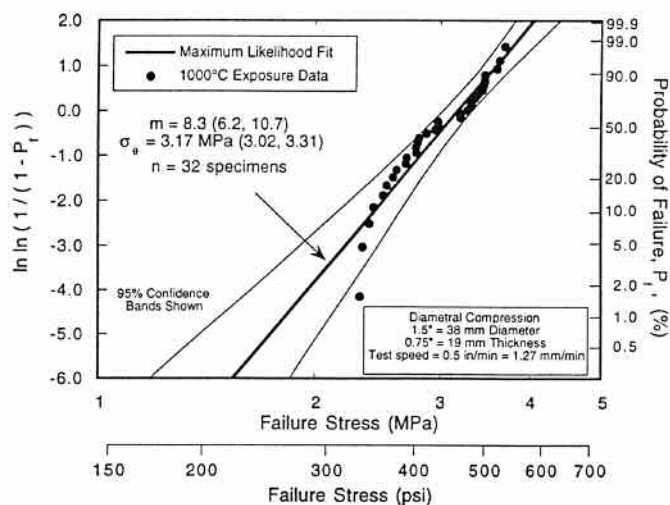


Figure 2. Room temperature strength distribution for MgO-G diametral compression specimens pre-exposed to 1000°C.

3. AlliedSignal Inc., Phoenix, AZ.

4. NASA Lewis Research Center, Cleveland, OH.

5. The use of the AlliedSignal CERAMIC/ERICA computer programs does not indicate that its use is preferred over the NASA’s CARES/LIFE program could have been in the present study as well.

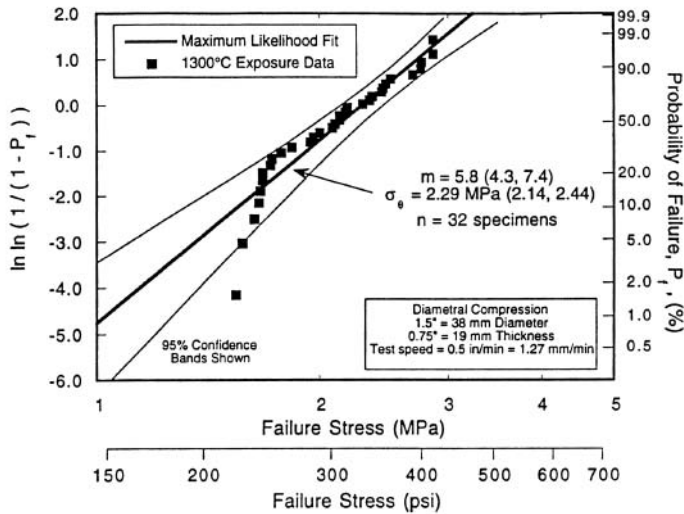


Figure 3. Room temperature strength distribution for diametral compression specimens pre-exposed to 1300°C.

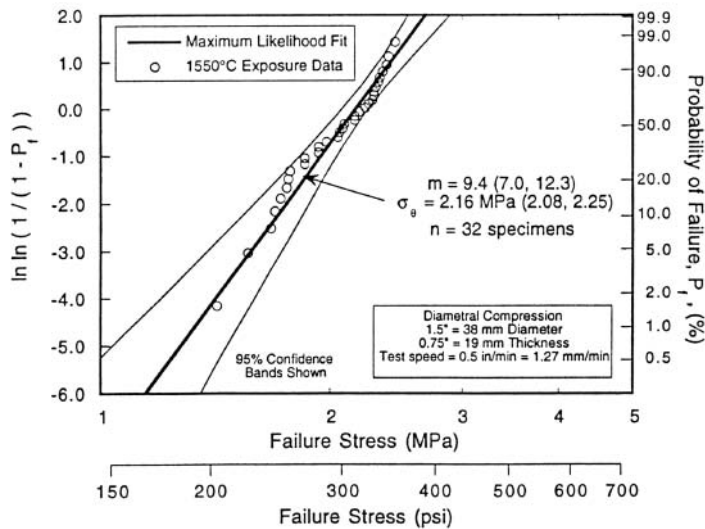


Figure 4. Room temperature strength distribution for diametral compression specimens pre-exposed to 1550°C.

AlliedSignal's CERAMIC/ERICA computer program to determine the material design data.

The changes in characteristic strengths and Weibull moduli for the three exposure temperatures were believed to be a consequence of the specific phases formed in the refractory. Specimens exposed to 1000°C had the largest characteristic strength and this was attributed to the presence of the mechanically strong  $Al_4C_3$  phase. However, unlike the forsterite, and remnant  $Al_4C_3$ , which resulted from mutual reactions of the  $Al_4C_3$ , Si, and the MgO. The relatively low Weibull modulus for 1300°C exposed specimens represents a relatively wide scatter in measured strengths. If each of these phases could concurrently act to limit strength in this refractory material, then greater scatter in strength would be anticipated. Only spinel and forsterite remained in the specimens exposed to 1550°C. The characteristic strength of these 1550°C

exposed specimens was also relatively low, but the Weibull modulus was higher than that of the 1300°C exposed specimens. The low strength is consistent with the absence of  $Al_4C_3$  and the relatively high Weibull modulus is consistent with the absence of the other phases, which were present in the 1300°C exposed specimens.

## IV. FEA MODELING OF THE MGO-G COMPONENTS

### III.B. 1. MgO-G Three-Point Bend Bar

A MgO-G prismatic bend bar with dimensions of 25.4 x 25.4 x 152.4 mm (1 x 1 x 6 in) in three-point flexure (101.6 mm or 4 in span) was modeled using commercial finite element analysis software<sup>6</sup>. This geometry is a commonly employed strength test specimen for refractories [12]. A Young's modulus of 200 GPa (29 Msi) and Poisson's ratio of 0.25 were used. An arbitrarily chosen load of 1000N (224 lbs) was applied<sup>7</sup>. The results from this FEA model were put into AlliedSignal's CERAMIC/ERICA computer program with the material design data for each of the three temperatures.

The predicted strength distributions for MgO-G three-point-bend specimens exposed to 1000, 1300, and 1550°C are shown in Figure 5. For any stress, the failure probability of the 1000°C exposed specimens was the lowest, with the 1550 and 1300°C exposed specimens in turn having higher failure probabilities. The ranges of predicted stresses for this three-point-bend specimen are larger than that for diametral compression because its effective volume (the term  $K_v \cdot V$  in Equation 1) is smaller than that for the diametral compression specimen. The intent of this Section III. B. 1. Exercise was to illustrate the strength-dependence on size for two commonly employed refractory test specimen geometries.

### III.B.2. MgO-G NOZZLE

A MgO-G nozzle having dimensions of 203 O.D. x 101.6 I.D. x 1524 mm length (8 O.D. x 4 I.D. x 60 in length) was modeled using FEA. The nozzle was vertically suspended from one end, so the

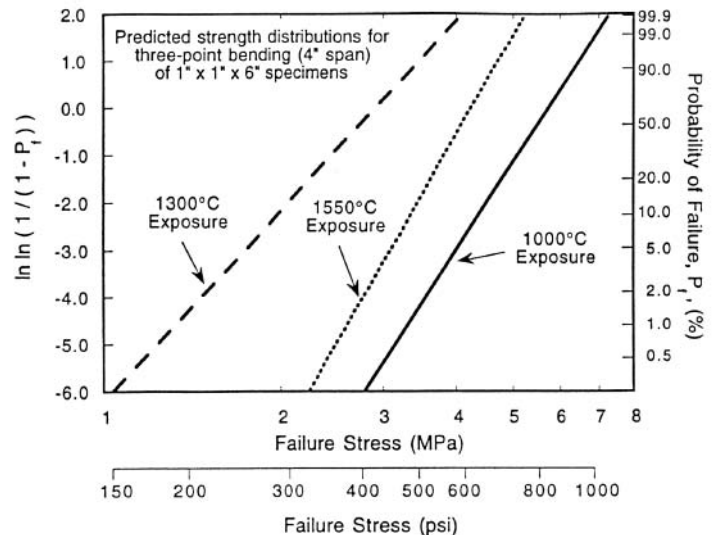


Figure 5. Predicted room temperature flexure strength distributions for the MgO-G refractory exposed to 1000, 1300, and 1550°C.

6. ANSYS, Inc. Canonsburg, PA.

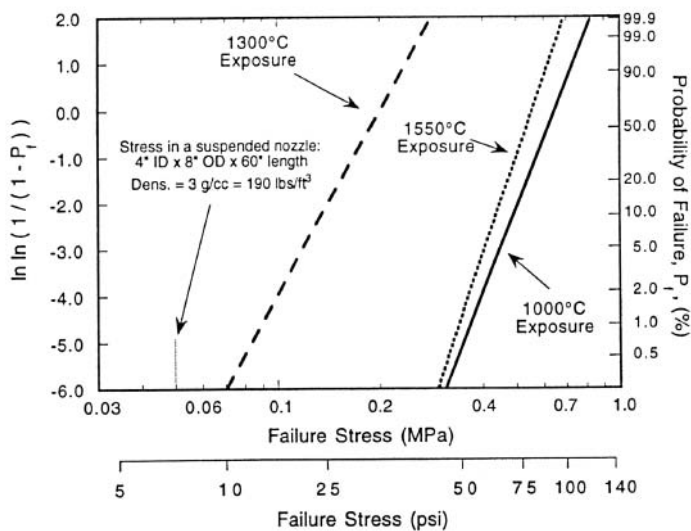
7. The multiaxial fracture criterion uses the stress gradient as input. This gradient is independent of stress because the material is linear elastic. Consequently, any load may be applied as long as linear elasticity exists.

stress state within it was due entirely to gravity acting on its mass. A Young's modulus of 200 GPa, a Poisson's ratio of 0.25, and a density of  $3 \text{ g}\cdot\text{cm}^{-3}$  ( $\approx 190 \text{ lbs}\cdot\text{ft}^{-3}$ ) were used. The results from this FEA model were input into AlliedSignal's CERAMIC/ERICA computer program with the material design data from the three exposure temperatures.

The predicted failure probabilities for MgO-G nozzles exposed to 1000, 1300, and 1550°C are shown in **Figure 6**<sup>8</sup>. Shown in the lower left in **Figure 6** is the maximum tensile stress (0.05 MPa or  $\approx 7 \text{ psi}$ ) in the nozzle. The failure probability of the vertically suspended MgO-G nozzles exposed to 1000 and 1550°C is very low, while the failure probability of a nozzle exposed to 1300°C will indeed intersect the maximum tensile stress in the nozzle at some finite value. The shown stress range of failure is shifted to lower stresses than for the diametral compression or three-point flexure specimens because the volume of the nozzle is so much larger. The intent of this Section III.B.2. exercise was to illustrate how strength data generated on a standard test specimen made from a refractory can be used to predict the failure probability of realistic steel casting refractory component.

The MgO-G nozzle FEA model may be modified to be more representative of actual service. For instance, temperature profile boundary conditions could be applied to both the internal and external surfaces of the nozzle, and thermal conductivity and heat capacity properties could be accounted for to predict the transient and steady-state stress in the nozzle. If probabilistic strength data as a function of temperature were available, then the failure probability of the nozzle under realistic service conditions could be determined. For example:

- If this new service stress were too high, then one could revisit the nozzle FEA model to modify the geometry with the intent of lowering service stress. This process could be iteratively performed until an optimum nozzle design (i.e., a minimum or acceptable failure probability) and acceptable service stress state were determined.



**Figure 6.** Predicted room temperature failure probability for MgO-G nozzles exposed to 1000, 1300, or 1550°C. Gravity acting on the mass of the nozzle accounts for the stress state within it.

8. If MgO-G strength data were generated using different specimen geometries (e.g., a diametral compression specimen and a flexure specimen), then the data from both could be combined or pooled to increase the numbers of total MgO-G strength data points whose net effect would be more confidence in the failure probability prediction of the nozzle component.

- If this new service stress were relatively low, and a less conservative design would be more cost-effective, then this FEA model also could be iteratively modified until an optimum nozzle design and acceptable service stress state were found.

## V. Closing Remarks

The results and discussion from the present study suggest that probabilistic life design is applicable for use with refractory components used in steel casting. Firstly, the strength distributions for a MgO-G refractory were well-represented by a two parameter Weibull distribution. Secondly, if thermal shock resistance is dictated by avoiding the onset of crack initiation, then the described probabilistic life prediction algorithm should also be applicable. Thirdly, the analysis outputs a failure probability for a specific service stress, which is more realistic design criterion for ceramic and brittle material component design than a deterministic approach. Lastly, if data were available which describe the strength distribution of a refractory at service conditions, and the service conditions were known so a representative FEA model could be created, then probabilistic life design could be used for optimizing the refractory component's design and to promote longer and more predictable service lifetimes.

## SUMMARY


The failure probability of magnesia-graphite components was predicted using a probabilistic life design approach. The room temperature strengths of a magnesia-graphite refractory pre-exposed to 1000, 1300, and 1550°C were fitted to a two-parameter Weibull distribution. The strength data distributions were then combined with finite element analysis of two components and an appropriate multiaxial ceramic failure criterion to predict the failure probabilities of each. The two components were [i] at  $25.4 \times 25.4 \times 152 \text{ mm}$  ( $1 \times 1 \times 6 \text{ in}$ ) magnesia-graphite prismatic bar subjected to three-point flexure using a 101.6 mm (4 in) span, and [ii] a vertically suspended magnesia-graphite nozzle component 203 O.D.  $\times$  101.6 I.D.  $\times$  1524 mm length (8 O.D.  $\times$  4 I.D.  $\times$  60 in length). The latter exercise illustrated how laboratory-generated strength distributions may be used to predict the failure probability of an actual refractory component used in steel casting, while the former exercise provided useful information in regards to the strength-dependence on size between two common specimen geometries used for refractory strength tests. The results indicate an approach of probabilistic life design is applicable to refractory component design for the steel casting industry.

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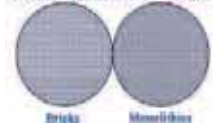
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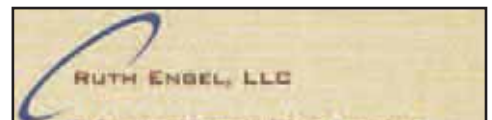
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2625 S. 21st Ave., Broadview, IL 60155  
Tel: (708) 344-7600, Fax: (708) 344-7636  
dthurman@sunrockceramics.com  
www.sunrockceramics.com

## HIGH PURITY MAGNESITE

### AluChem, Inc.

One Landy Lane, Cincinnati, OH 45215  
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aluchem@aluchem.com

## INSULATING BRICKS

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rdlane@clayburngroup.com

### IFB, Inc.

610 East Butler Rd., Butler, PA 16002  
Tel: (724) 282-1012 Fax: (724) 285-7673  
ifbinc@aol.com  
www.insulatingfirebrick.com

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patrick.m.stephan@saint-gobain.com  
www.refractories.saint-gobain.com

## KILN/FURNACE FURNITURE

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nthdegreeproducts@Yahoo.com

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patrick.m.stephan@saint-gobain.com  
www.refractories.saint-gobain.com

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2625 S. 21st Ave., Broadview, IL 60155  
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dthurman@sunrockceramics.com  
www.sunrockceramics.com

## KYANITE

### Kyanite Mining Corporation

Dillwyn VA 23936  
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info@kyanite.com www.Kyanite.com

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lesg@hightempinc.net www.hightempinc.net

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Penn Center West, Bldg. 2, Ste. 430  
Pittsburgh, PA 15276  
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Fax: (412) 494-4571  
sales@rescoproducts.com www.rescoproducts.com

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Worcester, MA 01615-0136  
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www.refractories.saint-gobain.com

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Fax: (412) 494-4571  
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www.refractories.saint-gobain.com

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Dillwyn VA 23936  
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### NABALTEC AG

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Tel: +49 9431 53-457 Fax: +49 9431 61557  
ceramics@nabaltec.de www.nabaltec.de

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### Minelco Inc.

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Cincinnati, OH 45202  
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### Unimin Corporation

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metalcaster@unimin.com www.metalcaster.com

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### TFL, Incorporated

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Fax: 281-590-5342  
tfl@tflhouston.com www.TFLHouston.com

### ZIRCAR Ceramics, Inc.

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www.johnsonmachineco.com

### Alcon Tool Company

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www.alcontool.com rd@alcontool.com

## PRODUCT ENGINEERING/QA SERVICES

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bvance23@comcast.net

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inquire@ceminerals.com www.ceminerals.com

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sales@rescoproducts.com www.rescoproducts.com

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cangrosales@ix.netcom.com  
www.rficonstructionproducts.com/

### Lancaster Products,

Div. of Kercher Industries, Inc.  
920 Mechanic St., Lebanon, PA 17046  
Tel: (717) 273-2111, (800) 447-7351  
info@lancasterprd.com www.lancasterprd.com

## REFRACTORY RECYCLING

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P.O. Box 58184, Pittsburgh, PA 15209  
Tel: (412) 821-5566 Fax: (412) 821-5577  
atencinci@verizon.net www.ceramicrecycling.com

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## REFRACTORY SHOTCRETE INSTALLATIONS

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rdlane@clayburngroup.com

## SILICA BRICK

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## SILICA FUME

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## SILICA MATERIALS

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### International Minerals, Inc.

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jk@imi-minerals.com www.imi-minerals.com

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## SILICON METAL POWDER

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info@basstechintl.com www.basstechintl.com

## SODIUM SILICATE POWDERS

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www.almatis.com

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info@fiberconfiber.com www.fiberconfiber.com

## TITANIA

### Sachtleben Chemical Company

104 Murphys Crossing Dr., Powell, OH 43065  
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## TOLL CRUSHING & GRINDING

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