

Refractories Applications *and News*



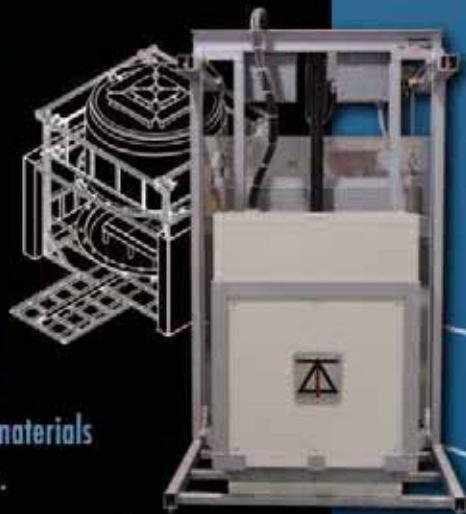
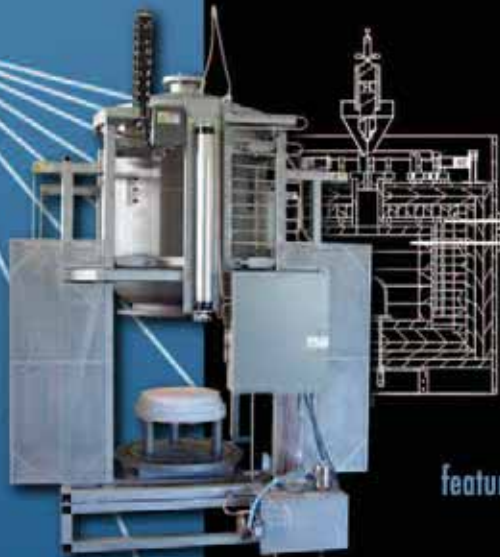
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is pleased to announce the availability of a new award-winning DVD entitled,

“Taming the Flame: The Story of Refractories”

Intended for a general audience, the DVD discusses the range of refractory products, how they are made, and the importance of refractories to modern manufacturing and society.

(8.5 minutes)



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A NATIONAL ASSOCIATION PROMOTING THE INTERESTS OF THE REFRACTORIES INDUSTRY

Jeffrey D. Smith, Editor, jsmith@mst.edu




Jeffrey D. Smith

Just a short note this issue as things are incredibly busy now that the holiday season is upon us. With all the craziness of trying to get our jobs done in the midst of parties, family reunions, vacation days, etc., the season is hectic for all.

It's also a common time to reflect upon all the good that we have in our lives, to look past the current economic difficulties and be thankful for all that we have. Health, family, friends, trusted coworkers and an industry that has provided us a degree of wealth and perhaps now importantly a sense of community that in my perspective is second to none.

Looking through this issue you will see mention of William Davis accepting a position at Alsey Refractories. This news was wonderful to me personally as Bill had worked with me for a number of years here at Missouri S&T. I wish him and his family the very best as they begin a new phase in their lives. I see also Charlie's reflections on 20 years of UNITECR and again it gives me great hope. I attended UNITECR 2009 and was changed by the experience. I am personally re-energized having renewed old friendships and having seen that, independent of the worldwide economic downturn, my colleagues continue to be creative and continue to be excited about engineering solutions to refractory related problems. Amidst these "worst times in history" we continue to excel as we always have. The two technical contributions in this issue are excellent examples of just the kind of efforts to which I refer.

So then are we to be pessimist and call these the worst of times or see the opportunities be creative and make these the best of times? I'll choose the latter if that's okay with you. 

If you would like to submit an article to be published in *Refractories Applications and News* or in *Transactions*, please contact Mary Lee at leemj@mst.edu.

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and News

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leemj@mst.edu
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Technology Bimonthly for the Global Refractories Industries

JOINTLY SPONSORED BY THE REFRACTORIES INSTITUTE AND REFRACTORY CERAMICS DIVISION OF THE AMERICAN CERAMIC SOCIETY

"Refractories Applications and News" founded by Robert E. Moore in 1996 at MS&T.

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: rbradt@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: jlmendozab@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.

Refractories Applications and News, the premier technology journal for the global refractories industries, covers the latest advances in raw materials, finished products, installation and research. *Refractories Applications and News* is published six times a year. Printed in the United States of America.

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Refractories Applications and News (ISSN 1537-6443) is a bimonthly non-profit publication provided free to U.S. subscribers.

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Refractories Applications and News is being indexed by Cambridge Scientific Abstracts in Ceramic Abstracts/World Ceramics Abstracts, and by Chemical Abstracts Service, CODEN RACECN.

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REFRACTORIES RELATED MEETINGS

2010

January 24-29, **34th International Conference and Exposition on Advanced Ceramics and Composites**, Hilton Daytona Beach Resort and Ocean Center, Daytona Beach, FL.

Feb. 21-24, **Materials Innovation in an Emerging Hydrogen Economy**, 2010 Hilton Cocoa Beach Oceanfront - Cocoa Beach, FL.

March 24-25, **St. Louis Section and the Refractory Ceramics Division 46th Annual Symposium**, St. Louis, MO.

May 3-6, **AISTech 2010 The Iron & Steel Technology Conference and Exposition**, David L Lawrence Convention Center, Pittsburgh, PA.

June 6-18, **12th International Ceramics Congress CIMTEC 2010**, Florence Italy, www.cimtec-congress.org/2010/.

September 6-10, **The 25th 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, www.impc210.org, PO Box 660, Carlton South, Victoria 3053, Australia.

October 3-6, **COM 2010-Conference of Metallurgists, 5th International Symposium on Advances in Refractories**, Vancouver, BC, Canada, George Oprea: oprea@interchange.ubc.ca, www.metsoc.org

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

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

**Send meeting announcements to Mary Lee at:
leemj@mst.edu**

**Announcements must be received a minimum of
four months prior to the meeting date.**



Rob Crolius

IN MEMORIAM: NICHOLAS C. MITCHELL, SR.

TRI members and the refractories community are mourning the loss on November 11, 2009, of Nicholas C. Mitchell, Sr., owner and CEO of Fibercon International, a TRI Associate member company that produces steel reinforcing fibers for refractories and concrete. An entrepreneur and respected businessman, Nick Mitchell, among many business endeavors, took

Fibercon from a plant that had been shut down for two years with no sales and no customers to the multinational company it is today, with operations on three continents and customers around the world. He will be remembered as a man who loved life, loved his family, and who also loved a good story. Our condolences go out to Nick Mitchell's family and the employees of Fibercon International.

TRI VIDEO "BEST IN SHOW"

The recently completed TRI video, "Taming the Flame: The Story of Refractories" has won a 2009 Best in Show award in the Accolade Video Competition. In recognizing the video, the competition said the video, "pays tribute to non-metallic materials that can withstand high-heats and which are used for the linings for furnaces, kilns, incinerators and reactors. This well-crafted and tightly edited film manages to make a topic which most people would think uninteresting both entertaining and educational."

Many thanks and kudos to TRI's production partner, Panta Rhei Media, and all the TRI members and allied groups who participated in, and contributed to, the project.

For more on the Accolade Awards, go to: www.accoladecompetition.org. To see the award and the TRI listing, you can click on videography on the right side and then Best in Show at the top left.

Copies of the 8.5 minute video in DVD format are available from TRI for \$20 for TRI members and \$30 for non-members. Call (412) 244-1880 for specifics.

TRI 2010 SCHOLARSHIP PROGRAM

The TRI Board of Directors has agreed to continue the Institute's scholarship program in 2010. Up to three \$5,000 scholarships for students in degree programs who have demonstrated through course work, research projects and/or summer jobs or co-op programs that they might be considering a career in the refractories industry. Applications are due to TRI by February 26, 2010, with scholarships to be awarded in June for the 2010-2011 academic year. For application requirements, call TRI at 412-244-1880.

2010 WILLIAM T. TREDENNICK AWARD

The TRI Board of Directors is now soliciting nominations of candidates for the William T. Tredennick Award. Named for long time TRI Board member Bill Tredennick, founder of Resco Products, the award recognizes an individual who has made a lasting and significant contribution to the refractories community. Nominations should include a one page letter describing the individual's contribution to the industry and any background materials you consider appropriate in justifying the nomination. You do not have to be a member of The Refractories Institute to submit a nomination. Nominations are due to TRI by February 19, 2010.

DAVIS JOINS ALSEY REFRACTORIES

William A. Davis has been named General Manager Quality Assurance, Mining and Compliance at the Alsey Refractories plant in Alsey, Illinois.

MANUFACTURERS GAIN EXPANDED NOL TAX RELIEF

President Obama has signed into law expanded net operating loss (NOL) tax relief which allows companies of all sizes to "carry back" current losses to offset taxes paid in profitable years. In turn, this will provide manufacturers needed cash to finance ongoing operations, retain jobs and in many cases, stay in business. It was included as part of an emergency unemployment benefits extension bill.

The expanded NOL relief allows manufacturers to "carry back" losses in 2008 or 2009 for a period of five years. Previously, manufacturers could only "carry back" losses for two years, which did not provide enough relief given the prolonged economic downturn.

GOVERNMENT WEBSITES ADDRESS H1N1 FLU

The federal government has provided resources to help manage the current pandemic and to control the further spread of the H1N1 outbreak. The Occupational Health and Safety Administration (OSHA) has recently developed a new website: <http://www.osha.gov/h1n1> that contains several fact sheets on how to reduce the risk of exposure to the 2009 H1N1 virus, including steps that manufacturers can take to prevent further spread of this virus. Additionally, <http://www.flu.gov/> from the Department of Health and Human Services provides extensive general recommendations to address the public health concerns posed by the H1N1 outbreak.

LEGISLATIVE - Estate Tax Reform Likely Kicked Down the Road Again

Reversing plans to have comprehensive reform of the estate tax in 2009, House Democrats are now looking at a one year extension again. The current estate tax rate is 45% on estates exceeding \$3.5 million. If Congress does nothing, the estate tax would disappear in 2010 but revert back to the pre-Bush Administration levels of 55% over \$1 million in 2011. By moving for a one year extension, Congress will throw the estate tax issue into the major tax initiative that has to be undertaken in 2010 when the Bush tax cuts are due to expire.

President Obama has supported efforts make the 2009 rate permanent. It is estimated that would cost the government \$256 billion over ten years, causing some in Congress to balk.

REGULATORY - OSHA Moving International Hazard Communication System

A proposed rule to align the Occupational Safety and Health Administration's Hazard Communication Standard (HCS) with provisions of the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS) was published in the September 30 Federal Register.

The current HCS requires chemical manufacturers and importers to evaluate the hazards of the chemicals they produce or import and provide information to subsequent users and requires all employers to have a hazard communication program for workers exposed to hazardous chemicals. In moving to align with GHS, OSHA will require employers to make a number of adjustments in their hazard communications programs to conform with the world-wide framework.

Continued on page 23

REFLECTIONS ON REFRACTORIES, 1989-2009

Charles E. Semler, Refractories Consultant, Semler Materials Services, Chandler, AZ, CESemler@aol.com



Charles E. Semler

BACKGROUND

Over the 20 years since 1989, when the first Unified International Technical Conference on Refractories (UNITECR) was held in the United States, the world's refractory users and producers, and their suppliers, as well as academics, consultants, and journalists, have convened every two years at various international locations (11 meetings to date), as shown below:

The 11 UNITECR meetings have provided a valuable forum for the international refractories community to share and discuss the latest practical and technical information, and to develop and promote business. UNITECR'09 in Brazil was a successful meeting, in spite of the global economic concerns during '08-'09. There were promising signs for the refractories industry, because by September '09, world steel production had progressively increased 28% from the lowest monthly production in February '09.

Each registrant at UNITECR meetings receives a Proceedings and/or disk, which contains all of the papers presented. The series of UNITECR Proceedings provides an excellent published record of the refractory activity and progress worldwide for the last 20 years, by which the state of the technology can be monitored and reviewed. It is now common for published refractories articles worldwide to include references to UNITECR articles.

REVIEW OF REFRACTORY TOPICS

A limited review of the program at three UNITECR meetings (#1, #6, and #11) is shown below to provide an indication of the relative interest in iron/steel and monolithic refractory papers, as well as selected other topics that were included on the programs:

These data indicate that there has been an increase in the number of sessions and papers on iron/steel topics over the years. Some of the iron/steel topics in 2009 were: carbon-containing refractories (MgO-C, Al₂O₃-SiC-C, castables, etc.), blast furnace applications, torpedo car applications, continuous casting refractories, ladle refractories, slide gates, submerged entry nozzles (SEN), etc. It should be noted that the activity/interest in monolithic refractories has also increased over the years, with a significant increase in papers at UNITECR'09, where there were more monolithics papers than iron/steel papers. The 2009 program also included an increased emphasis on high-tech topics (55 papers), i.e., basic science, advanced testing, nano-materials, and modeling/simulation.

STATUS OF THE STEEL INDUSTRY

Refractories are critical materials that enable the steel industry to make steel and operate profitably. Because the steel industry is the world's major consumer of refractories, at each UNITECR meeting, presentations on iron and steel applications are a main topic. As a very general indication of the business climate for the refractories industry, the production of steel since 1989, in China, United States, and the world, is shown in **Figure 1**.

Year	Location	Host Organization	Attendance	Papers
1989	Anaheim - USA Theme: Global Advances in Refractories	American Ceramic Society	900	160
1991	Aachen, Germany Theme: Global Advances in Refractories	German Refractories Assn.	970	115
1993	Sao Paulo, Brazil Theme: Refractories for the New World Economy	Latin American Refractory Makers Assn.	700	125
1995	Kyoto, Japan Theme: Global Development of Refractories	Technical Assn. of Refractories-Japan	900	186
1997	New Orleans - USA Theme: Refractories - A Worldwide Technology	American Ceramic Society	1200	200
1999	Berlin, Germany Theme: Refractories 2000	German Refractories Assn.	900	144
2001	Cancun, Mexico Theme: None	Latin American Refractory Makers Assn.	570	158
2003	Osaka, Japan Theme: ECO Refractory for the Earth	Technical Assn. of Refractories-Japan	700	181
2005	Orlando - USA Theme: Refractories - A Worldwide Community	American Ceramic Society	775	226
2007	Dresden, Germany Theme: United European Refractories Meet the World	German Refractories Assn.	875	138
2009	Salvador, Brazil Theme: Refractories in a Shifting Globalized World	Latin American Refractory Makers Assn.	630	203

	1989	1999	2009
Total Number of Sessions	18	27	28
Number of Papers	160	144	203
Number of Iron/Steel Sessions	7	9	11
Number of Iron/Steel Papers	44	45	60
Number of Monolithics Sessions	1	4	7
Number of Monolithics Papers	23	28	62
Selected Other Topics/Sessions	Glass	Glass	Glass
	Non-Ferrous	Non-Ferrous	Non-Ferrous
	Cement	Cement	Cement/Lime
	Petrochemical	Ceramics	Petrochemical
	Testing	Testing	Testing
	Raw Materials	Raw Materials	Raw Materials
	Basic Science	Production	Basic Science
	Production	Environment	Nano-materials

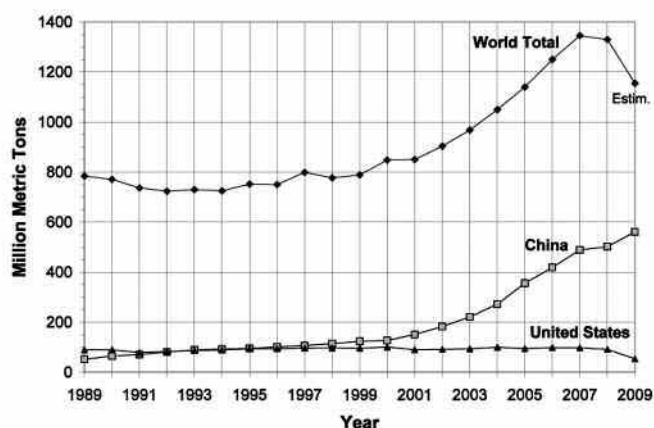


Figure 1. Annual steel production by the World, China, and United States for the two decades (1989-2009) of UNITECR meetings. The 2009 figures are estimated, based on the 9 month production results. Data from World Steel Assn.(www.worldsteel.org).

Production was generally static from 1989 to 2000, and from 2000 to 2007 there was a significant increase. However, a decline in production began in 2008, with a drastic drop in 2009. But there are promising signs in 2009, as there has been a steady increase in steel production since the lowest monthly production in February 2009, with a 28% increase thereafter, through September 2009.

Another feature of **Figure 1** is the mega-increase in steel production by China, since 2000, which has had, and will continue to have a major impact on the global economy and steel market, especially because China has a large production overcapacity (240 million metric tons). There are directly related effects on refractories, raw materials, cargo rates/availability, etc. For the years 1989-2009 and 2000-2009, China's increase in steel production is 340% and 980%, respectively. Although the world's steel production will be significantly lower in 2009, China's production will be about 12% higher than 2008.

Figure 2 shows that refractory production in China also increased rapidly from 2000 to 2006 in parallel with the big increase in steel production. Whereas the steel production continued to increase in 2007 and 2008, the refractory production apparently decreased. This decrease could be the result of various factors in combination, such as:

- Ongoing improvement of refractories in China, resulting in more durable products.

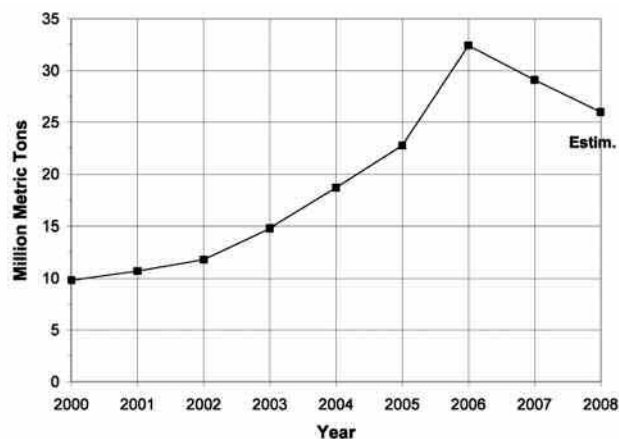


Figure 2. Annual refractory production in China during the years 2000 through 2008. Data from Editors of China's Refractories, Luoyang.

- Less use of lower grade, variable quality refractories from lower tier manufacturers who are being forced out of business.
- Government requirement that refractory production overcapacity be reduced.
- Elimination of smaller, less efficient steel plants with high refractory consumption.
- Improved operating conditions and control thereof, to further reduce the refractory consumption rate by the steel industry; e.g. the refractory consumption rate by the steel industry in China was estimated to be 30 kg/ton of steel in 2002, and 25 kg/ton of steel in 2005. However, the refractory consumption rates in China are still higher than Brazil, Germany, Japan, United States, etc.

With the ongoing improvement in refractories, installation methods, maintenance practices, and lining design, as well as improved steelmaking operations, there is a counter effect that contributes to a decline in the refractory consumption rate, and thus a decrease in refractory production, as has occurred in Japan, United States, and other countries. Japan has achieved a world class refractory consumption rate and it is continually decreasing, as shown below (Japan Refractories Assn.); related thereto, the annual refractory production in Japan has decreased 38% from 1989 to 2008.

Refractory Consumption Rate Steelmaking operation

Year	Consumption Rate (kg/ton of steel)
1989	12
1994	10.3
1999	9.5
2004	7.4
2009	???

TREND IN MONOLITHIC REFRACTORIES

Based on the many practical and technical developments since the 80's, the interest in, and usage of monolithic refractories (and pre-cast shapes) has greatly increased, and the trend is expected to continue. The UNITECR data above document the increased interest in monolithic refractories since 1989. **Figure 3** is included to show the production of monolithic refractories in Japan, United States, China, and India, from 2000 to 2008. It is seen that the monolithic production in Japan and United States is over 50% of the total refractory production each year (bricks/shapes + monolithics), and the production trend in China is increasing toward 50%, while India is lower (<20%), but also increasing, per the Indian Refractory Makers Assn. (IRMA), although current published figures were not found for China and India.

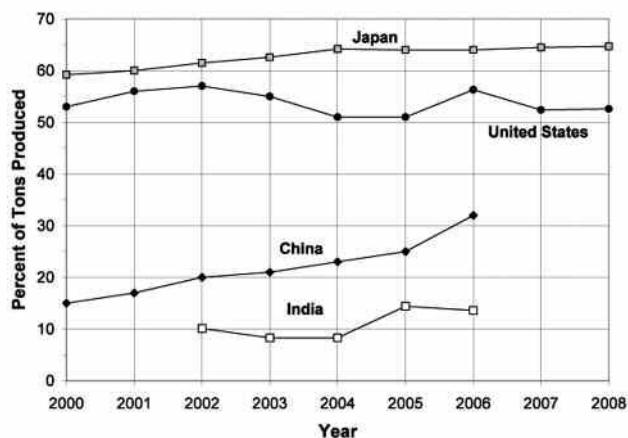


Figure 3. Graph showing the monolithic refractory production (percentage of total annual production) in Japan, United States, China, and India, since 2000.

INCREASED POPULARITY OF SPINEL

Over the last 20 years there has been a big increase in usage of spinel ($MgAl_2O_4$, $FeAl_2O_4$, etc.) in refractories, because of various benefits such as better refractoriness (vs. alumina), resistance to corrosion and slag/chemical penetration, expansion, in-situ phase development, the capability of replacing many Cr-containing refractories, and more. The increased popularity of spinel over the last 20 years can be inferred from the number of paper presented at UNITECR, with four papers in 1989 vs. 17 in 2009.

R&D in Japan, to replace their conventional steel ladle linings containing zircon contributed to the increased interest in and usage of spinel castables. For example, a Japanese paper at UNITECR'89 showed that an alumina-spinel castable had a wear rate of 1.2 mm/heat vs. 5 mm/heat for the traditional refractory (zircon-roseki), and this improved wear of the alumina-

spinel castable resulted in a big increase in lining life - 160 heats compared with 40 for the traditional refractory.

Several examples of "spinel" papers presented at UNITECR'99 (1-3) and UNITECR'09 (4-7) are shown below:

1. Experience with Alumina-MgO (Spinel-forming) Precast Shapes for Steel Applications
2. How to Formulate Spinel-forming Castables
3. MgO-Hercynite ($FeAl_2O_4$) – An Innovative Burned Basic Refractory (for cement kilns)
4. Nano-engineered Alumina-MgO Castables
5. Novel Spinel Family Refractories for High Temperature, High Alkaline Conditions
6. Improved Quality Spinel Brick for Rotary Cement Kilns
7. In-Situ Spinel-Bonded Basic Castables for Non-Ferrous Applications

RAW MATERIALS ISSUES

Concerning refractory raw materials in general, it should be noted that the unprecedented changes in China are being felt worldwide. It should not be surprising that China has been taking steps to insure that their steel production (integral with their economic growth) will continue, which must involve steps to (a) preserve and protect their refractory raw materials, and (b) continue to develop and manufacture higher grade, more durable refractories, of consistent quality. It is interesting to note several quotes of Prof. X.C. Zhong of Zhengzhou University about China's raw materials and refractory development, before (1, 2) and after (3) the huge increase in steel production:

1983 – "To meet the more stringent requirements of modern steelmaking, considerable R&D has been concentrated on high performance refractories of higher purity and better properties, with emphasis on natural raw materials (magnesite, dolomite, bauxite, etc.), which occur in abundance in China".

1985 – "Mother Nature has endowed China with many varieties of refractory raw materials, but we still have a long way to go to fully exploit and utilize this fortune".

2001 – "In the New Century, one of the main trends of technical development in China's refractories industry should be the development of a new generation of sophisticated synthetic refractory raw materials with Chinese characteristics, based on our rich resources of bauxite and magnesite".

The raw materials situation is very complex and has become a major concern for the refractories industry worldwide, because of the critical importance of raw materials for the ongoing, consistent production of high quality refractories, and for developing improved/new products. The refractories world was lured to Chinese raw materials in the 1980s, which resulted in major changes in the global production and supply of raw materials, and the market competition was greatly elevated. A dependence on Chinese raw materials developed, along with a sense of security. As a result, the recent big price increases, decreased/variable quality, and reduced availability of Chinese raw materials, which seemingly are related to China's huge increase in steel production and the associated increase in domestic refractory demand, to maintain their economic growth, have created big problems and withdrawal pains for the refractories world, whereby difficult choices and changes must be

made. Whereas the world refractory producers have benefited from Chinese raw materials for several decades, there is now a new reality, which requires action, and appropriate changes.


When thinking about the raw materials issues, it is important to remember that “raw materials are limited, but creativity is unlimited”. There are many options available today for developing alternatives that can help to minimize or eliminate the raw materials problems. Based on the increased emphasis on high-tech topics at UNITECR’09, it appears that the refractories industry has recognized the situation, and is proceeding with the R&D, strategic alliances, etc., to overcome the raw materials concerns that have arisen.

CONCLUDING COMMENTS

This paper presents a generalized overview of the 11 UNITECR meetings, and some refractories-related happenings, over the 20 year period from 1989 to 2009, including updated information on iron/steel production, trends in monolithic refractories, and raw materials issues. It can be concluded that the UNITECR concept of bringing the world refractory community together

every two years (uniting the refractories world), for discussion and sharing of technical information, and for promotion of business, has been very successful. Even with the severe global economic crisis of ’08-’09, UNITECR’09 (Brazil) still attracted good attendance. The next UNITECR meeting (#12) will be organized and hosted by the Technical Assn. of Refractories – Japan (TARJ), and will be held in Kyoto, Japan, Oct. 30 – Nov. 2, 2011.

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Industry News

CERAM PROVIDES GUIDELINES TO SUPPORT RISE IN USE OF COMPUTATIONAL MODELLING IN HIGH TEMPERATURE INDUSTRIES

The use of computational models to assess the feasibility and safety of industrial components is standard in manufacturing sectors such as the aerospace and automotive industries. However, the use of these computational techniques is a comparatively new idea for refractory and associated high temperature industries, and is often regarded with a certain amount of suspicion. CERAM, a global expert in materials testing, analysis and consultancy, has produced a set of guidelines for refractory manufacturers, lining designers, installers and users. Titled *Obtaining Valid Data for Computational Modelling of Refractory Structures* the free report provides guidance on the data required to produce meaningful computational models with which to assess the feasibility and safety of industrial vessels and components during operation at high temperatures.

Refractory linings are complex structures made of complex refractory materials. CERAM’s guidelines provide readers with an overview of the computational modelling process, which is based on the Finite Element Method, highlighting the essential data that must be obtained in order to create a useful and meaningful model. Effective computational modelling for refractories depends on the availability of data with which to produce both thermal and stress profiles, which play an important role in the design of refractory structures.

“Computer technology has developed and advanced almost unimaginably over the last two decades,” commented Sarah Baxendale, Refractories Consultant at CERAM, “and with it the scope for more sophisticated and accurate computational modelling.”

“Improvements in computer hardware and software have allowed the use of finite element modelling to cascade down to


desk top level within a wide range of industries, allowing us now to characterize in-service behavior of refractory linings and components with significant confidence – dependent, of course, on the accuracy of the data provided in the first place, which is where our guidelines can help.”

CERAM works with clients from a broad range of high temperature industries, including glass, cement, petrochemical, iron, steel, environment and energy, and offers computer modelling services for a variety of applications including the validation of refractory designs and the identification and solving of causes of failure. *Obtaining Valid Data for Computational Modelling of Refractory Structures* can be downloaded free of charge at www.ceram.com/refractories.

CANCARB’S THERMAX PRODUCTS REACH REGISTERED

“Cancarb Limited is pleased to announce the successful REACH registration of all of Cancarb’s Thermax™ and Carbocolor thermal carbon black products by our “Only Representative” Global Energy Investments S.a.r.L.

The successful registration was confirmed by the European Chemical Agency (ECHA) on November 13, 2009 and comes well before the deadline of November 30, 2010. This milestone, after more than two years of sustained work, relieves the Downstream Users of Thermax™ and Carbocolor thermal carbon black products of their REACH obligations. Further, it guarantees the uninterrupted supply of these products to the European Union.

Cancarb is the world leader in thermal carbon black production and continues its REACH activities as a member of the Carbon Black Consortium. For further details please visit www.cancarb.com or Tel: 403-527-1121. 

SLAG – PIG IRON INTERFACE IMPACT ON REFRACTORY WEAR INSIDE THE BLAST FURNACE HEARTH

A. D. Mariotti^{1,2}, E. Brandaleze^{2*}, G. Buscaglia³

¹Instituto Balseiro, San Carlos de Bariloche, 8400 Argentina

²Departamento de Metalurgia, Universidad Tecnológica Nacional, Facultad Regional San Nicolás, San Nicolás, 2900 Argentina.

³Instituto de Ciências Matemáticas e de Computação, Universidade de São Paulo, São Carlos, 13560-970 Brasil

*Corresponding author: ebrandaleze@frsn.utn.edu.ar

The pig iron-slag interface in the hearth has an important role in the hearth refractory wear. To predict the location of the slag layer (pig iron-slag interface profile) is relevant for the design of the refractory lining to avoid the local wear on the wall of the hearth (chemical attack). In addition, the interface tilt near the taphole has important influence on the hole diameter evolution during tapping. The characterization of this behavior, it is useful for taphole clay selection and improve the hearth operation. The physical modeling represents an important tool to study the pig iron-slag interface effect on the hearth refractory wear. In this paper, a physical model to analyze this fluid-dynamical problem was built. An extensive set of experiments investigating the relationships between the interface shape and the different variables of the fluid-dynamical problem were carried out. Results indicate that the interface tilt is in relation with the slag volume fraction during the outlet flow. Relevant theoretical considerations explaining the pig iron-slag interface behavior were obtained. By means of a digital camera, the evolution of the interface angle near the taphole zone was obtained. This result is in good agreement with the same angle, calculated by a mathematical expression using real measurements.

INTRODUCTION

The refractory linings of the blast furnace hearth are subjected to chemical attacks and wear promoted by the extreme conditions inside the hearth. For this reason, it is necessary to design refractory bricks that have a high mechanical and chemical resistance. Current trends in blast furnace technology lead to larger more efficient production units and today a service live of 15 years is expected from a relined blast furnace [1]. The hearth is the most critical area of the furnace, so it is a normal practice to shut down the installation when repairing or reconstructing the refractory lining, causing huge economical losses. Therefore, iron and steel companies try to operate the blast furnace for as long as possible. Analyses of refractory materials as well as the study of the refrigeration systems play an important role. Recent developments of specialized hardware and software allow modeling different mechanisms that take place in the hearth in relation principally with temperature, providing refractory lining corrosion profiles [2].

In the **Figure 1**, a blast furnace hearth during tapping is sketched. Nevertheless, from a fluid-dynamical perspective, the system consists of three immiscible fluids flowing through the hearth porous medium. Two of them are liquid (pig iron and slag) and the other

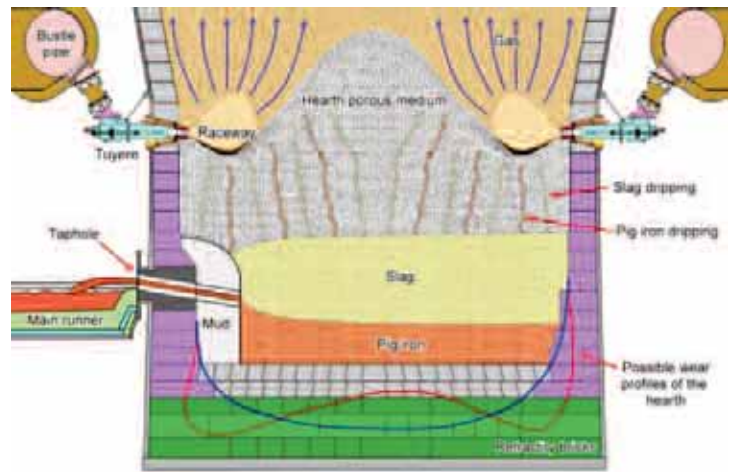


Figure 1. Sketch of the blast furnace hearth operation.

is a gaseous mixture that is at a pressure higher than the atmosphere. These fluids are immiscible and have different densities. For this reason three different layers are generated (from top to bottom: gas, slag and pig iron). Also, two interfaces between the fluid layers are present. When the hearth is drained through the taphole (drainage orifice in the side wall of the hearth), a complex flow takes place in which the interfaces move, tilt and bend. The understanding of this flow is crucial for the proper design and management of the blast furnace hearth. To predict the location of the slag layer (pig iron-slag interface profile) is important for the design of the hearth refractory lining to avoid the local wear on the wall of the hearth. In addition, the interface tilt near the taphole is relevant on the hole diameter evolution. During tapping, while the interface angle is decreased, the slag volume fraction in the outlet flow is increased and the taphole pressure drop grows.

This behavior provokes an enlargement of the shear stress on the hole wall and an increment in the hole wear. Thereby, this behavior is useful for clay selection to improve the hearth operation.

This drainage problem has been studied by several authors [3-11], both experimentally and numerically. Fukutake and Okave [3] simplified the problem assuming that the pig iron-slag interface remains horizontal during drainage and carried out experiments on a small three-dimensional physical model. They obtained a "flow out coefficient" which they related to the volume of slag retained inside the hearth.

In turn, Tanzil and co-workers [4] designed a two-dimensional physical model based on the Hele-Shaw viscous flow analogy, to avoid the complexity of measuring in a 3D porous medium. They used two immiscible fluids and showed that the pig iron-slag interface would be below the taphole level while the liquids are drained. They demonstrated how this affects the relation between the retained slag volume and the flow out coefficient. In addition, the paper presents pictures of the interface tilt and how this phenomenon is interpreted by them. Their simplified model was not able to represent the inertial effects at the taphole zone promoted by the high velocity near of it. The Hele-Shaw viscous flow analogy has been extensively used in the investigation of groundwater flows, in which velocities are much lower than in the taphole zone [12].

More recently, Nouchi and co-workers [7] built a small and geometrically complex 3D physical model. They used liquid paraffin and fluoride as fluids, which roughly match the non-dimensional parameter between model and prototype. Their experiments involved all the phenomena mentioned previously, and they analyzed the effects promoted by free coke zones. They measured the tap time, the maximum liquid level, the paraffin ratio and the drainage velocities of the fluids and concluded that the free space has a significant effect on the taphole conditions. However, they did not discuss the detailed behavior of the pig iron-slag and gas-slag interfaces.

Several studies about the drainage of the hearth are summarized by Zulli et al. [6]. They enhance the importance on the hearth drainage of the coke free spaces in the hearth and the taphole zone properties.

Nishioka and co-workers [5], on the other hand, compared a set of experiments (similar to those of Tanzil et al. [2]) to numerical simulations. Once their code had been validated by means of this comparison, they extended their numerical calculations from 2D to 3D and they carried out several parametric studies. They concluded that the coke size is very important in the residual volume of slag in the hearth and that the taphole conditions (geometry, flow regime, etc.) determine the total drainage rate. Keep in mind that the flow in the taphole, being a two-phase flow, strongly depends on the volume fraction of each fluid [13,14], which is unknown and varies with time. We refer the reader to Xu [15] for a review on recent research concerning oil-water flow in a pipe, the possible flow patterns, and some discussion about phase inversion phenomena and the calculation of pressure drop.

In this paper a physical model to analyze this fluid-dynamical problem was built. An extensive set of experiments investigating the relationships between the interface shape and the different variables of the fluid-dynamical problem were carried out and relevant theoretical considerations explaining the pig iron-slag interface behavior were obtained.

DIMENSIONAL ANALYSIS

The physical model we propose must be compared to the real furnace in terms of the non-dimensional parameters that govern the fluid-dynamical problem. **Figure 2** sketches the physical setup.

Assuming incompressibility of the fluids, mass conservation requires:

$$\text{div}(\vec{q}_1) = 0 \quad (1)$$

$$\text{div}(\vec{q}_2) = 0 \quad (2)$$

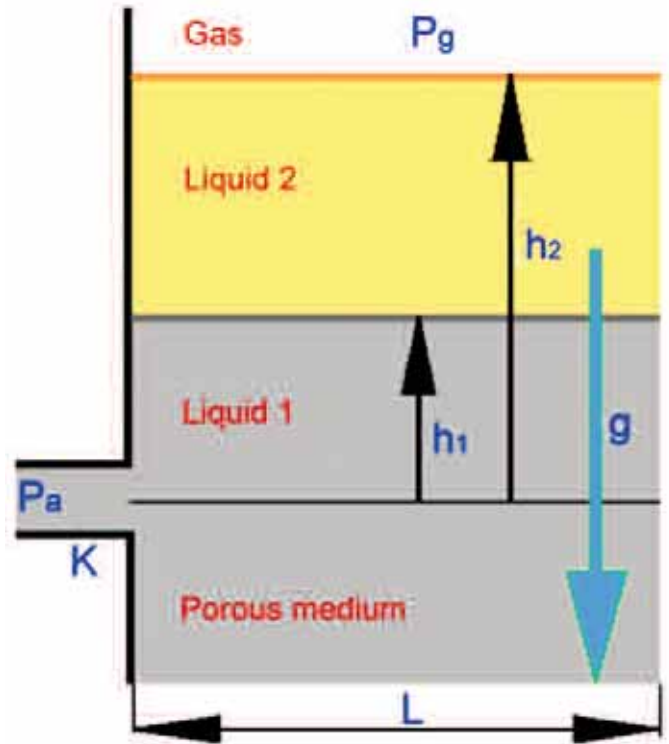


Figure 2. Sketch of the problem.

where q is the (porous-medium-averaged) velocity and the subscript differentiates the domains occupied by fluid 1 or 2. The equation relating the pressure gradient to the fluid velocity in a porous media was first suggested by Forchheimer (1901), but Ergun (1952) proposed some corrections at the equation constants [12].

$$\vec{\nabla}p - \rho_1 \vec{g} = -(A_1 + B_1 |\vec{q}_1|) \vec{q}_1 \quad (3)$$

$$\vec{\nabla}p - \rho_2 \vec{g} = -(A_2 + B_2 |\vec{q}_2|) \vec{q}_2 \quad (4)$$

where:

$$A = 150 \frac{(1 - \varepsilon)^2}{\varepsilon^3 d^2} \mu$$

$$B = 1.75 \frac{(1 - \varepsilon)}{\varepsilon^3 d} \rho$$

d : Particle equivalent diameter

μ : Dynamic viscosity

g : Gravity

ρ : Density

d_i : Particle irregular diameter

ϕ : Form factor or sphericity

p : Pressure

ε : Porosity

$$d = \phi d_i$$

The main data of the fluid-dynamical problem are h_1 , h_2 , ρ_1 , ρ_2 , A_1 , A_2 , B_1 , B_2 , ΔP , g , K , L where: h is the level of liquid over the

outlet pipe, $\Delta P = (P_g - P_a)$, P_g is the air internal pressure, P_a is the atmospheric pressure, K is the pressure drop constant and L is the hearth diameter.

From these $f = 12$ parameters with $r = 3$ primary dimensions (length, time and mass) we get the $n = f - r = 9$ non-dimensional parameters [16] shown in **Table 1**, in which the reference velocity u^* is defined by:

$$u^* = \sqrt{\frac{2[\Delta P + (\rho_1 g h_1 + \rho_2 g (h_2 - h_1))]}{\rho_1 K}} \quad (5)$$

Table 1. Non-dimensional parameters

$\Pi_1 = \frac{h_2}{h_1}$	$\Pi_2 = \frac{B_1}{B_2}$
$\Pi_3 = K$	$\Pi_4 = \frac{\rho_1}{\rho_2}$
$\Pi_5 = \frac{A_2}{A_1}$	$\Pi_6 = \frac{L}{h_1}$
$\Pi_7 = \frac{\Delta P}{\rho_1 g h_1 + \rho_2 g (h_2 - h_1)}$	
$\Pi_8 = \frac{B_1 u^*}{A_1}$	$\Pi_9 = \frac{B_2 u^*}{A_2}$

Table 2 shows the numerical values of some data both in the model and in the prototype (the blast furnace hearth). A value of 0.3 for packed bed porosity of the blast furnace hearth was considered [7], while 0.36 to 0.41 would correspond to the model, since it is a mono-size random packed bed [17]. The tabulated value of ϕ corresponds to a non-uniform coke particle [18]. The pig iron viscosity μ_1 corre-

Table 2. Parameters numerical values

	Prototype	Model
Π_1	1.65	1.65
Π_2	2.50	1.17
Π_3	22.45	22.9
Π_4	2.52	1.17
Π_5	80.0	35.0
Π_6	6.9	6.9
Π_7	2.3	2.3
Π_8	1911.0	164.5
Π_9	9.55	4.00

sponds to a 4% content of carbon [19]. The values of h_1 , h_2 , ρ_1 , ρ_2 , ΔP , L , u^* , μ_2 and d were obtained from the operation variables of a real plant. From these values, the K value for the prototype was obtained from **Equation 5**. The calculation of K in the model will be explained in the experimental results section.

Table 3 shows the non-dimensional parameters of both, prototype and model. The experimental model was designed so as to roughly

Table 3. Numerical values of the main variables

Data	Prototype	Model	Unit
ϵ	0.3	0.36	--
ΔP	300000.0	10160.0	Pa
L	10.4	2.0	m
h_1	1.5	0.29	m
h_2	2.5	0.48	m
ϕ	0.7	1.0	--
d_i	0.05	0.008	m
d	0.035	0.008	m
ρ_1	7000.0	998.0	Kg/m ³
ρ_2	2800.0	850.0	Kg/m ³
μ_1	0.005	0.001	Kg/ms
μ_2	0.4	0.035	Kg/ms
A_1	11111.0	20576.0	Kg/m ³ s
A_2	888888.0	720165.0	Kg/m ³ s
B_1	9074074.0	2994685.0	Kg/m ⁴
B_2	3629630.0	2550583.0	Kg/m ⁴
u^*	2.34	1.13	m/s
K	22.45	22.9	--

match the non-dimensional parameters of the prototype, aiming at qualitative agreement. We select water and oil to simulate de pig iron and the slag respectively, because an exact match would require uncommon, dangerous fluids. Other authors [4,7] present experiences using other kind of fluids like mercury and fluoride that turn into a complex proposal.

EXPERIMENTAL SET-UP

A schematic view of the experimental model is shown in **Figure 3**. The model size is significantly larger than others models presented in previous studies [3-5, 7], so as to keep inertial effects non-negligible. The vessel dimensions were 2 m in width, 1.2 m in height and 0.03 m in depth. Inside it, a rigid, homogeneous and isotropic porous media was arranged. This medium was conformed of acrylic plastic spheres of 8 mm in diameter.

Several quantities were measured in all the experiments: the total flow rate at the outlet, volume fraction of each liquid phase in the outlet flow, the static pressures at several positions and the evolutions of the interfaces for different conditions of pressure.

The instrumentation was as follows:

- A turbine flow meter was installed on the outlet pipe to measure the total flow rate.

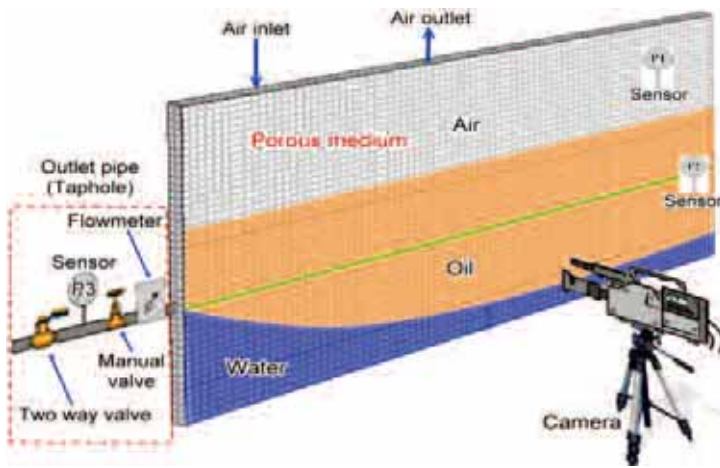


Figure 3. Schematic of the physical model and the experimental set up.

- The oil volume fraction was measured using the two-way valve installed at the end of the outlet pipe. Every ten seconds, a three-second sample was diverted into a graded cylinder.
- Three pressure sensors measure the internal pressure (P1), the static pressure on the right extreme of the vessel (P2) and the outlet pipe static pressure (P3).
- An electrical valve installed at the air inlet allowed for controlling the internal pressure (P1).
- The density and viscosity of the oil were 850 Kg m^{-3} and $0.035 \text{ Kg m}^{-1} \text{ s}^{-1}$ respectively. Low-viscosity oils being transparent, an additive was used to make it visible under UV light inside a dark room.
- The interface was recorded on a digital camera. Post-processing of the images allowed for extraction of the interface location.

EXPERIMENTAL RESULTS

The study of the pig iron-slag interface applying a physical model, it allows to predict the behavior of the interface during the drainage. It is possible to determine that, during the drainage the interface is great part of the time below the taphole level. In this case, the refractory chemical attack by slag is promoted in this area and it could cause a hearth break out below the taphole level. For this reason it is pertinent to determine the angle of the pig iron-slag interface to predict refractory wear and operative problems.

In this article, we focus on the behavior of the liquid-liquid (water-oil) interface. For this reason, in the four experiments considered the oil-gas interface is as far from the water-oil one as possible. This condition is different to the actual hearth drainage (except when the slag layer is very large), with the goal of isolating the phenomena that take place at the liquid-liquid interface. The existence of a second interface (the gas-slag interface), the top dripping of slag and pig iron, the time dependent change of the taphole conditions (clay quality, diameter, length and roughness) during a tap or the porous medium conditions (permeability, free coke space, etc) are other additional factors that are left for future work.

The main ideas in the experimental design are:

- To control the experiment by means of only one main parameter: specifically, we choose the horizontal pressure difference (PD: P2-P3), since it is the main driving force for the flow. If the gas is not pressurized the height of liquid above the taphole would vary with time as fluid is drained. In turn, this would lead to a time-varying horizontal pressure differ-

ence (PD:P2-P3). Consequently, it was decided to pressurize the gas and control its pressure so as to keep PD constant during each experiment. Four constant values of PD were chosen: 8270 Pa, 9650 Pa, 11030 Pa and 12410 Pa.

- To keep the taphole conditions fixed: in the blast furnace the taphole conditions (diameter and length) change during the tap because of the wear produced by the flow of pig iron and slag. Each blast furnace has a behavior curve of the diameter growth that depends on the kind of taphole refractory clay, the operative procedure and a lot of other conditions. Each curve promotes a unique behavior of the interface for the same PD. Keeping the taphole conditions fixed we treat a non-specific, generic situation.

Taphole conditions

Figure 4, shows the time evolution of the total flow rate at the outlet pipe while Figure 5 shows the oil volume fraction (OVF) in the outlet flow for the four experiments. The time zero was defined when oil first reaches the taphole. Before that, during what will be denoted by the “single-phase regime”, the total flow rate (Figure 4) remains fairly constant, confirming that PD is in fact the main factor governing the flow.

When the oil reaches the outlet, a transition phenomenon that lasts for approximately one minute takes place in the four experiments.

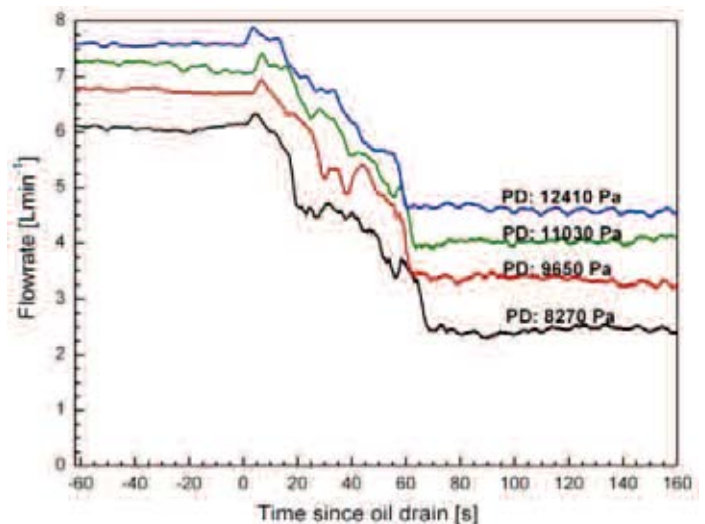


Figure 4. Total flow rate at the outlet pipe.

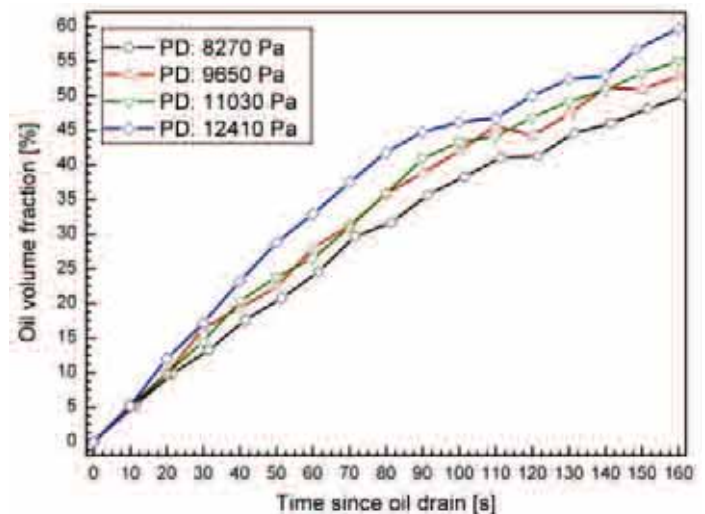


Figure 5. OVF evolution.

This transition leads to a new stable regime (“two-phase regime”) in which the total flow rate is significantly smaller than before. Notice that, when the oil start flowing through the outlet pipe, the flow rate presents a sudden, small increase, followed by a steady decrease and then a sudden decrease to a new, steady value. This behavior of the flow rate is not due to the applied pressure, since PD remains quite constant through the experiment (see **Figure 6**).

The transition is clearly due to the establishment, at the taphole mainly, of a two-phase condition, which significantly increases the flow resistance over the pure-water value. Though this, is obviously a consequence of the OVF. The end of the transition does not coincide with any noticeable change in the OVF curve, which keeps growing steadily throughout each experiment.

We use the results in (**Figures 4, 5 and 6**) to calculate the K coefficient:

$$K = \frac{P2}{\frac{1}{2} \rho(OVF) V^2} \quad (6)$$

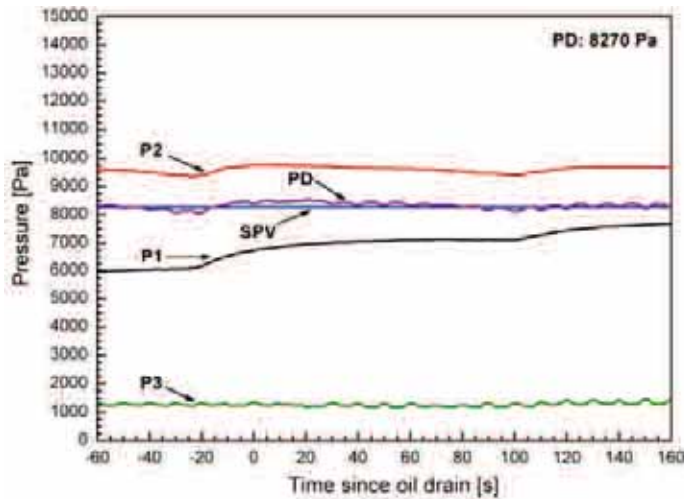
where $\rho(OVF)$ is the mixing density, $\rho(OVF) = \rho_{H_2O} (1-OVF) + \rho_{Oil} OVF$ and V is the flow velocity through the outlet pipe.

In **Table 4**, we report the temporal average of K and the total flow rate in the two stable regimes for the four experiments. The mean value of the time-averaged K in the single-phase regime is 22.9, confirming the similarity of prototype and model.

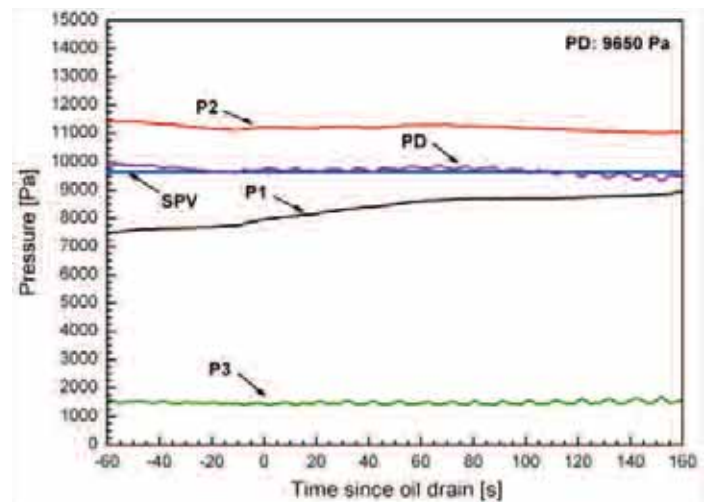
It is possible to see in **Figure 7**, the time evolution of K, where the fairly constant behavior before and after the transition can be confirmed. The oscillatory behavior after transition is a consequence of the velocity fluctuations shown in **Figure 4**. These fluctuations are larger in the two-phase regime because the flow rate is smaller (i.e., smaller denominator in (6)). For the same reason, the fluctuations are smaller in the experiments with larger PD.

Table 4. Temporal averages of K and total flow rate for the experiments before and after transition

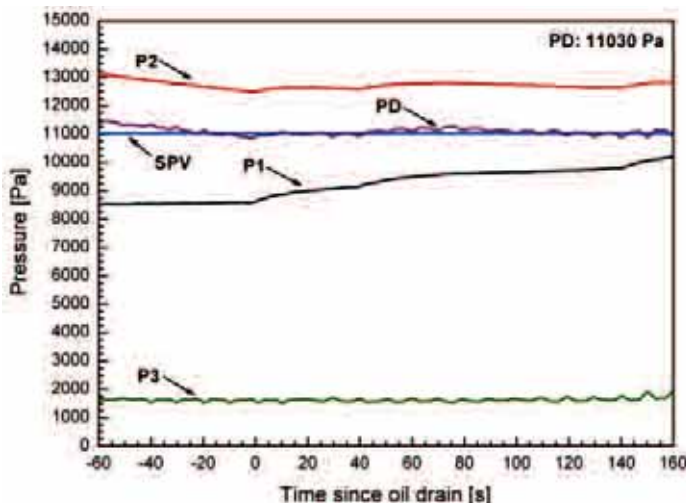
PD [Pa]	K (average)		Total Flow rate (average)	
	Before	After	Before	After
8270	23.7	156.9	6.1	2.45
9650	22.7	97.2	6.75	3.35
11030	22.7	77.2	7.2	4.05
12410	22.6	66.3	7.6	4.6



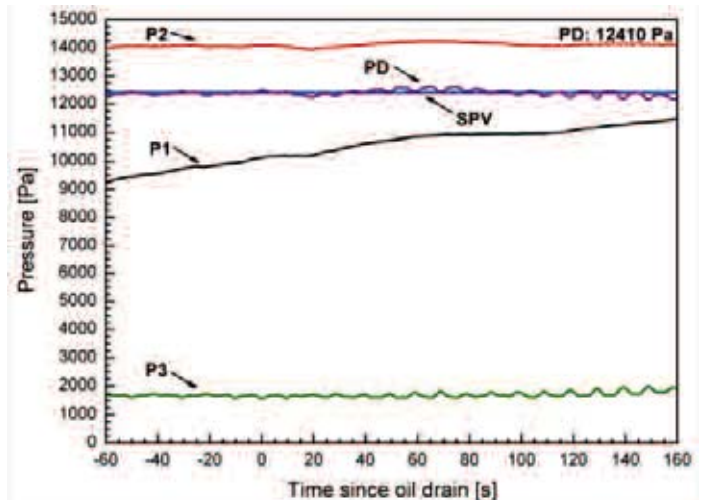
(a) Set point value (SPV) = 8270 Pa.



(b) Set point value (SPV) = 9650 Pa.



(c) Set point value (SPV) = 11030 Pa.



(d) Set point value (SPV) = 12410 Pa.

Figure 6. Pressure behavior for the four experiments.

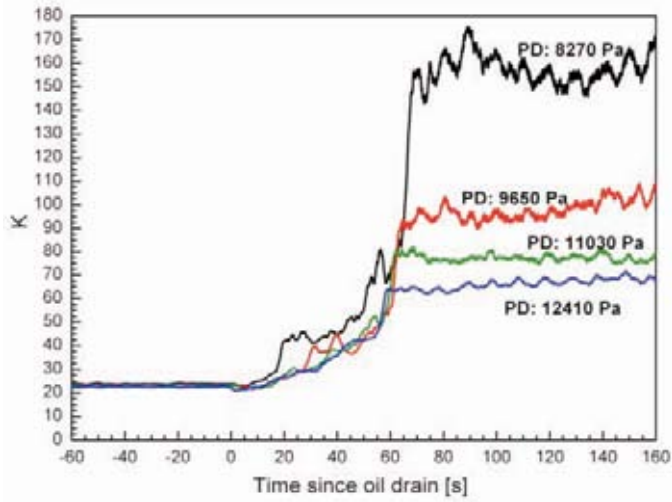


Figure 7. Evolution of K for the different PD.

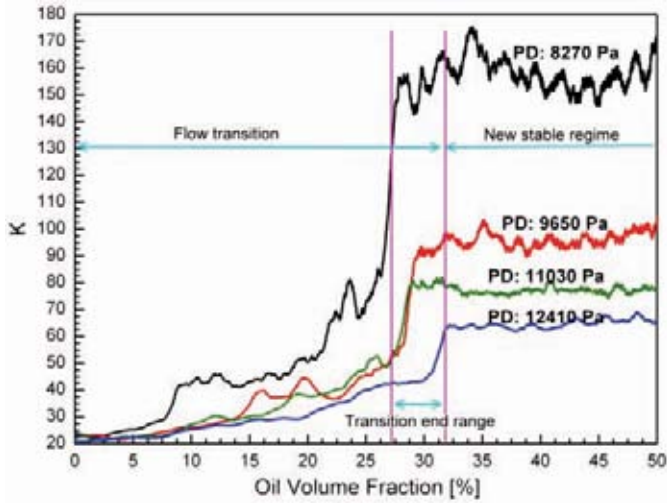


Figure 8. Transition and the new stable regime.

The end of the transition regime occurs in an OVF band that is between 27% and 33%, as it is shown in **Figure 8**. This suggests that the change in regime is linked to the OVF and the two-phase regime is stable when OVF in the main flow reaches 33%. It is quite clear from these data that the flow regime at the outlet, and in particular the OVF, is the most important factor determining the draining flow rate of the system.

INTERFACE BEHAVIOR

Let us now turn to the shape and motion of the interface within the porous medium. In **Figure 9**, it is possible to visualize the evolution of the oil-water interface for the different values of PD. The interface bends towards the taphole until it reaches the outlet. Once the oil has reached the outlet ($t = 0$), the interface remains attached to it, even though by the end of the experiments the mean water level is significantly below the taphole. The interface angle at the taphole thus starts by being positive and decreases with time, taking negative values about 20-30 seconds after $t = 0$ (depending on the applied PD).

To characterize this behavior, the interface angle in the immediate vicinity of the outlet pipe (θ_0) was measured. **Figure 10**, shows the evolution of this angle for the different values of PD as a function of time. It is observed that increasing the applied PD leads to a more rapid evolution of the interface angle.

In **Figure 11**, the interface angle at the taphole is plotted as a function of OVF for the four experiments. The angle strongly correlates to the OVF, implying that the interface tilt at the outlet pipe can be thought as mainly determined by the OVF in the outlet flow

Fitting the experimental points obtained in all the experiments, a relationship between the water-oil interface angle and the OVF in the outlet flow for the flow rates managed in these experiments can be obtained:

$$\theta_0 = -54.3 + 98.8e^{\left(\frac{OVF}{17.1}\right)} \quad (7)$$

THEORETICAL DISCUSSION

The results obtained by the hearth physical model increase the knowledge on the interface behavior and permits to predict the impact on the hearth refractory wear.

The interface between two immiscible liquids flowing in a porous medium is narrow compared to the dimensions of the domain occupied by each liquid alone. Hence, one may assume a well-defined interface separating the domains of the two fluids [12].

Neglecting capillary pressure at the interface, the continuity of the pressure requires that the pressure be the same when a point on the interface is approached from either side. Hence, the component of the pressure gradient tangential to the interface must also be the same on both sides of the interface [12].

The flow in the direction s in both domains (see **Figure 12**) is thus ruled by:

$$-\left(\frac{1}{\gamma_1} \frac{\partial p}{\partial s} + \frac{\partial z}{\partial s}\right) = \frac{\mu_1}{k\gamma_1} q_{1s} + \frac{C}{g} q_{1s}^2 \quad (8)$$

$$-\left(\frac{1}{\gamma_2} \frac{\partial p}{\partial s} + \frac{\partial z}{\partial s}\right) = \frac{\mu_2}{k\gamma_2} q_{2s} + \frac{C}{g} q_{2s}^2 \quad (9)$$

where:

$$k = \frac{\varepsilon^3 d^2}{150(1-\varepsilon)^2}$$

$$C = 1.75 \frac{(1-\varepsilon)}{\varepsilon^3 d}$$

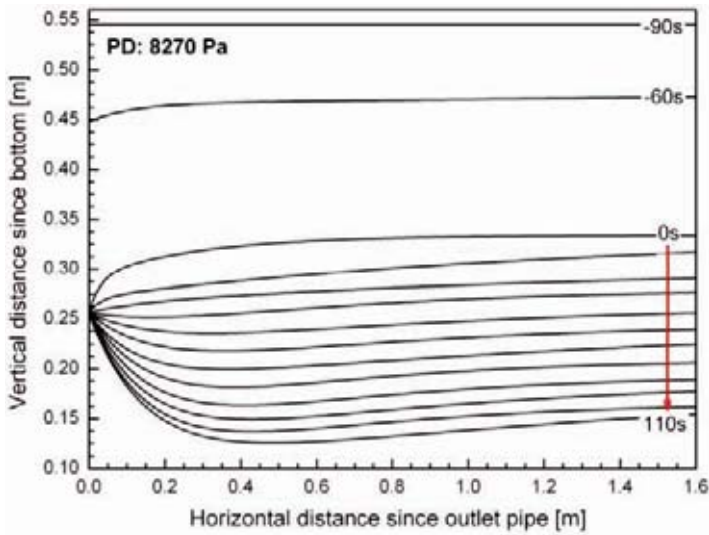
$$\gamma_1 = \rho_1 g$$

$$\gamma_2 = \rho_2 g$$

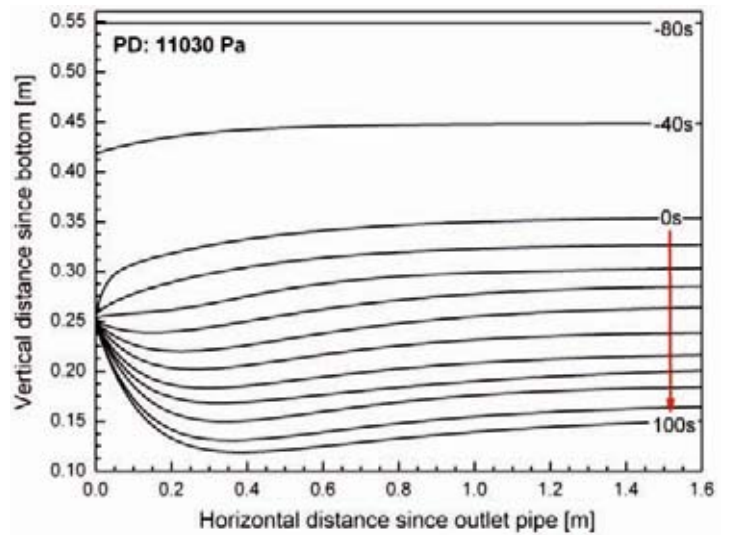
s : Tangential direction at interface

By eliminating $\frac{\partial p}{\partial s}$ from **Equation 8** and **9**, we obtain a relation between the interface tilt (θ) and the porous medium velocities:

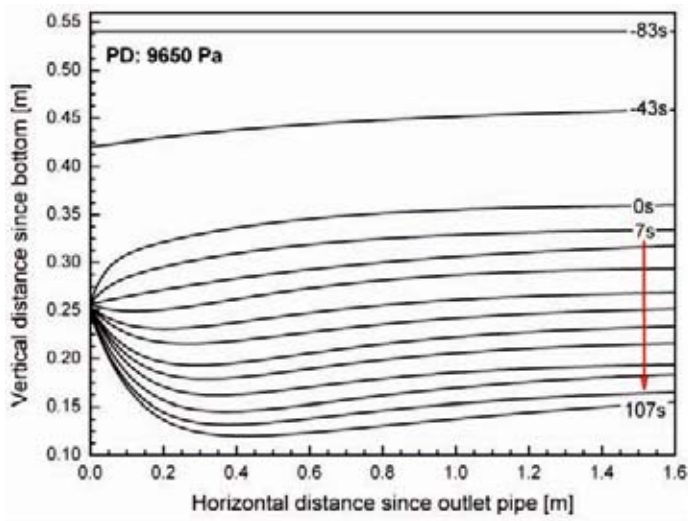
$$\frac{\partial z}{\partial s} = \text{sen}\theta = \frac{1}{k(\gamma_1 - \gamma_2)} [\mu_2 q_{2s} - \mu_1 q_{1s}] + \frac{C}{g(\gamma_1 - \gamma_2)} [\gamma_2 q_{2s}^2 - \gamma_1 q_{1s}^2] \quad (10)$$



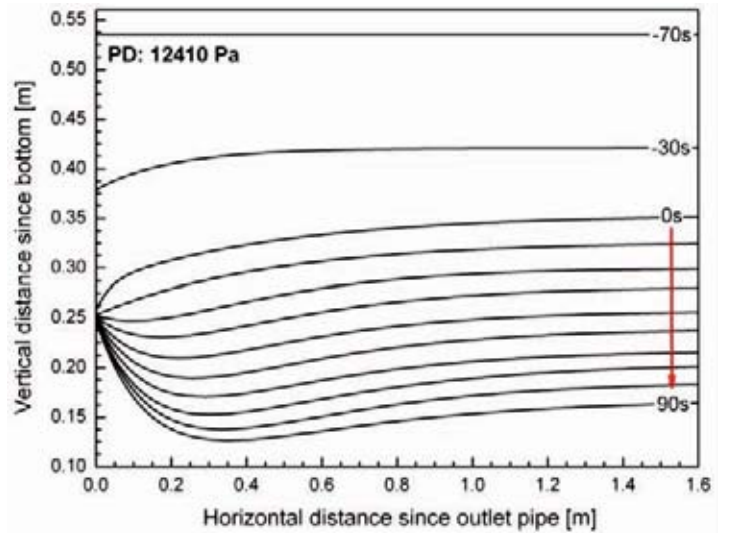
(a) PD=8270Pa



(c) PD=11030 Pa



(b) PD=9650 Pa



(d) PD=12410 Pa

Figure 9. Evolution of the water-oil interface profile for the four experiments.

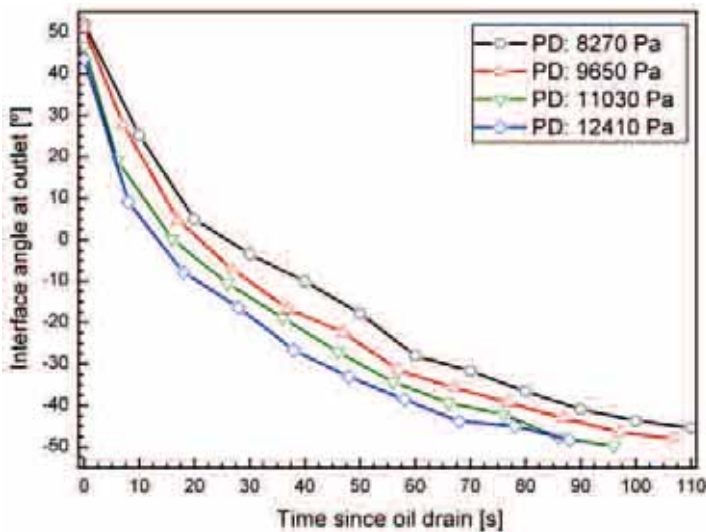


Figure 10. Evolution of the water-oil interface angle at outlet for different PD.

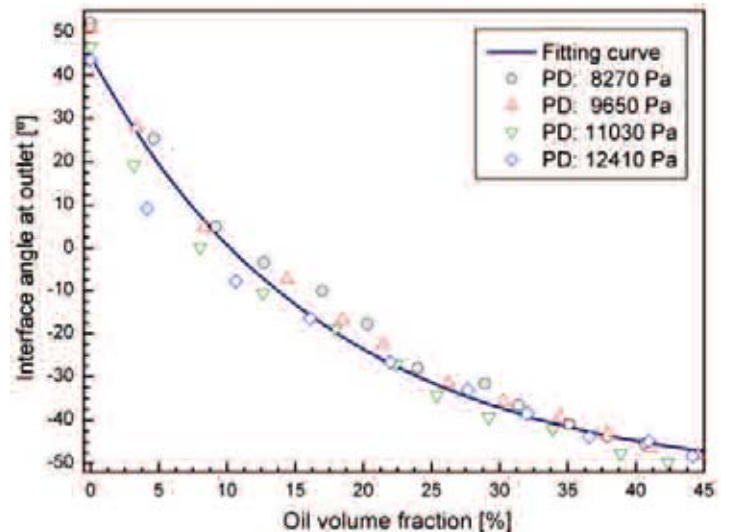


Figure 11. Interface angle behavior vs OVF and fitting curve from the points.

To simplify the analysis, let us drop the quadratic terms, so that Equation 10 becomes:

$$\frac{\partial z}{\partial s} = \tan\theta = \frac{(q_{2s}\mu_2 - q_{1s}\mu_1)}{k(\gamma_1 - \gamma_2)} \quad (11)$$

Analyzing Equation 11, θ depends on the flow tangential velocities at the interface. This behavior is sketched in Figure 13. Some interesting consequences of this equation are:

- If the liquid 1 is stagnant, $q_{1s} = 0$, the interface has a positive slope if the flow of the liquid 2 is in the +x direction.
- If the liquid 2 is stagnant, $q_{2s} = 0$, the interface has a negative slope if the flow of the liquid 2 is in the +x direction.
- If $q_{2s}\mu_2 - q_{1s}\mu_1 = 0$, the interface is horizontal.

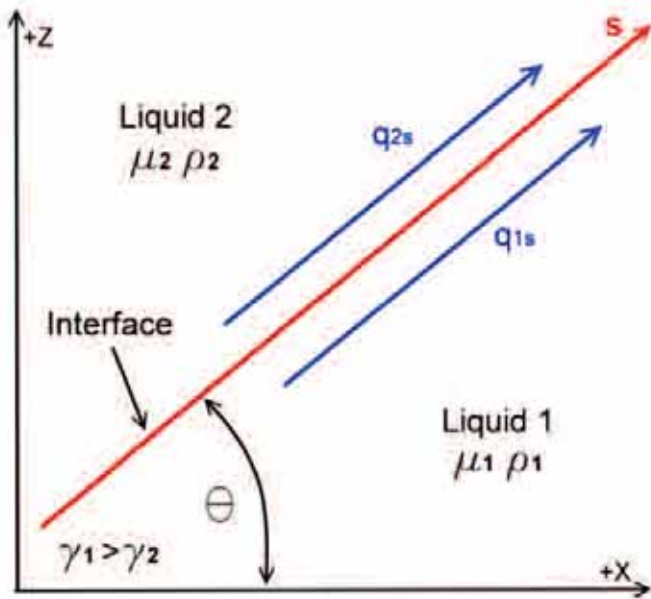


Figure 12. Sketch of the flow near to an interface.

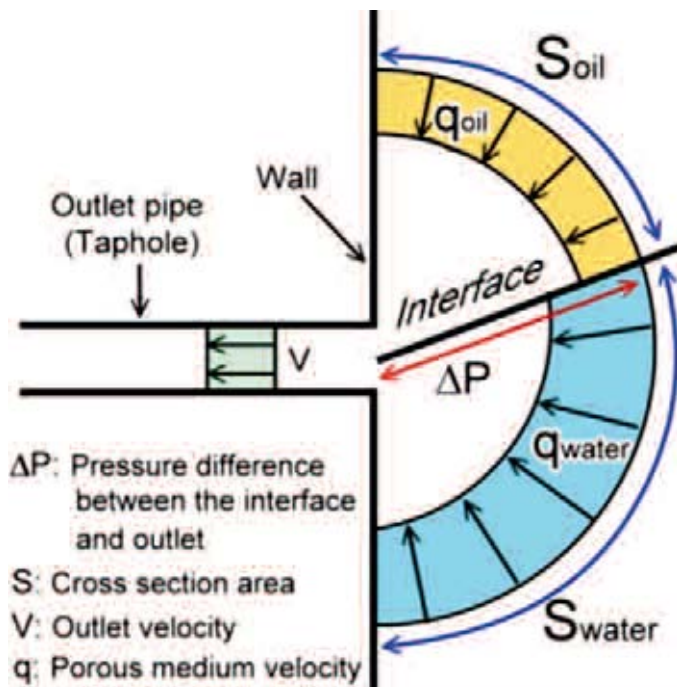


Figure 13. Interface tilt affected by tangential flow velocities at the interface.

Figure 14, sketches the interface behavior at the outlet pipe where the cross-sectional area of each phase changes until the velocity in each phase satisfies both the mass continuity and pressure field conditions imposed by the outlet pipe. In a porous medium viscous coupling is negligible, making it reasonable to locally approximate the radial velocity field in each liquid by constant on each circular region. The outlet pipe rules the flow rate of each phase in relation to the flow regime through it. The interface tilt at the outlet pipe thus results from a compromise between the pressure field and the mass continuity in the vicinity of the outlet.

To examine this concept, the experiment with PD:9650 Pa was further studied.

Figure 15 shows, a zoom of Figure 9 (b), where the values of the interface tilt was obtained. The grey straight segments show the interface tangent at 0.1 m radius (R) from the outlet pipe. The angle formed between the interface tangents with the horizontal (θ) was measured to compute the approximate cross-sectional areas of water and oil along the interface evolution. The simplified equations for the cross-sectional areas for the two fluids are:

$$S_{oil} = \left(\frac{\pi}{2} - \theta\right)eR \quad (12)$$

$$S_{water} = \left(\frac{\pi}{2} + \theta\right)eR \quad (13)$$

where are the cross section areas at the liquids, e is the vessel depth (0.03 m) and R is the radius (0.1 m) showed in Figure 15.

Figure 16, shows the evolution of the cross section areas for the oil and the water. The tangential velocities at the interface can be obtained using the cross-sectional areas and the flow rate of each phase. The resulting velocities for the experiment can be seen in Figure 17.

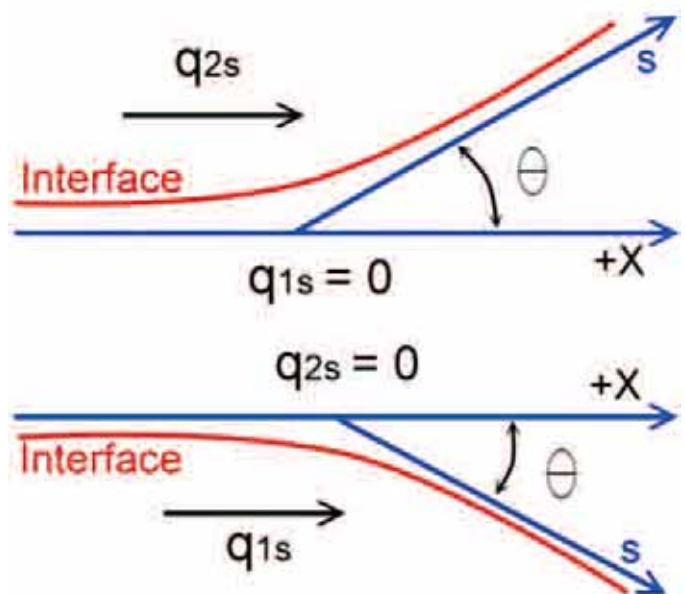


Figure 14. Sketch of the compromise between the pressure field and the mass continuity.

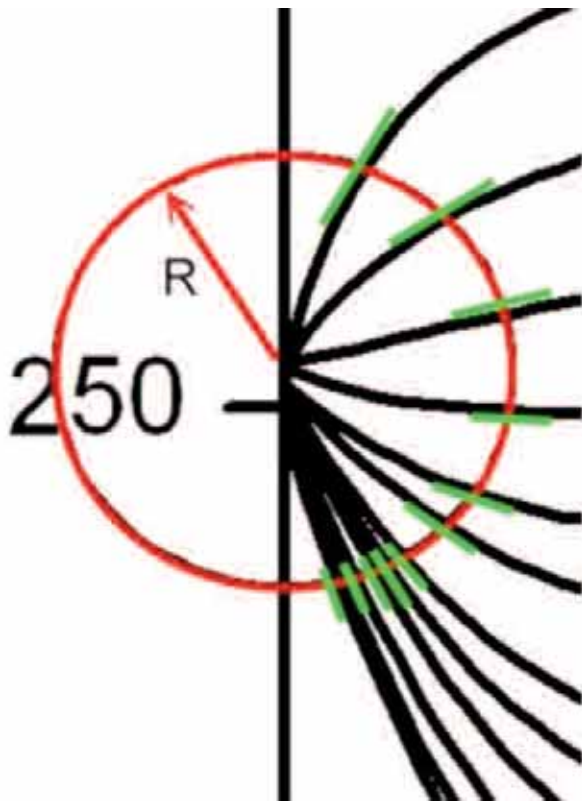


Figure 15. θ angle values on the 0.1 m radius form the outlet pipe.

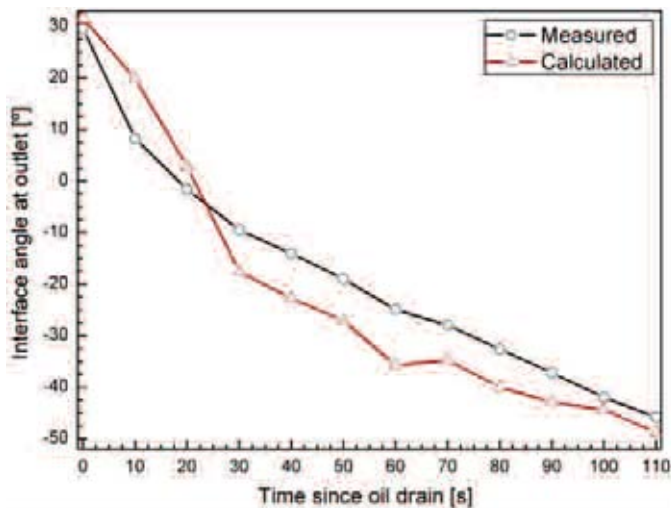


Figure 16. Cross section area evolution for the oil and water.

Figure 18, shows the comparison between the measured and calculated (by means of Equation 10 and Figure 17) θ values. The good agreement proves that the previous analysis is consistent with the physics of the problem.

CONCLUSIONS

By means of a 2D physical model we studied the behavior of the pig iron-slag interface in the drainage process in detail. The understanding of this flow is crucial for the proper design and management of the blast furnace hearth. To predict the location of the slag layer (pig iron-slag interface profile) is important for the design of the hearth refractory lining to avoid the local wear on the wall of the

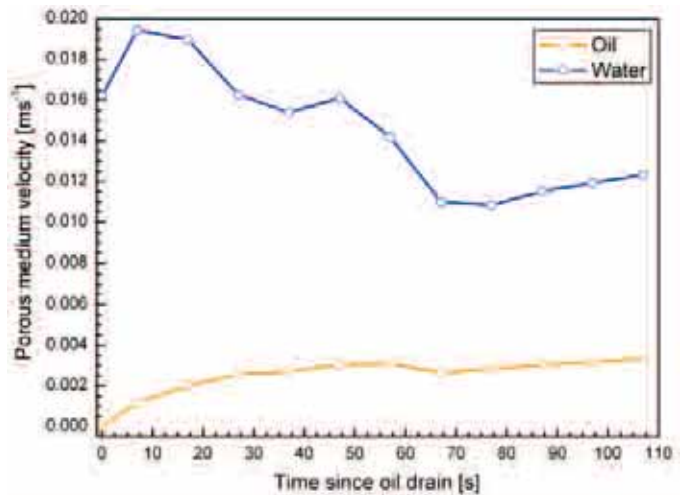


Figure 17. Porous medium velocities for oil and water at R.

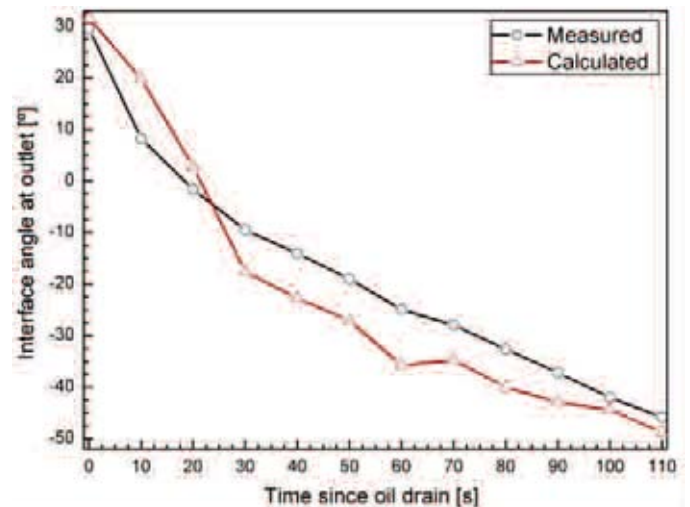


Figure 18. Comparison between the measured and calculated θ values.

hearth. In addition, the interface tilt near the taphole is relevant on the hole diameter evolution. During tapping, while the interface angle is decreased, the slag volume fraction in the outlet flow is increased and the taphole pressure drop grows. This phenomenon provokes an enlargement of the shear stress on the hole wall and an increment on the hole wear. Thereby, this behavior is useful for taphole clay selection to improve the operation.


Dimensional analysis was carried out and it suggests that the main physical phenomena in the model should be well represented by the prototype. The drainage was controlled by keeping constant the horizontal pressure difference (PD) as the main parameter that rules the phenomenon. Maintaining PD constant we avoid the hydrostatic effect of the liquid over the taphole level and attain that the gas-liquid interface does not have effect on the liquid-liquid interface. Four constant values of PD were chosen and for each of them one experiment was carried out. Several quantities were measured in all the experiments: the total flow rate at the outlet, volume fraction of each liquid phase at the outlet, the static pressures in different points and the interface evolution for the experiments. From the interface evolution, the water-oil interface angle was determined to characterize the interface behavior.

From the measurements, some conclusions were obtained:

- A transition phenomenon takes place when the oil-water interface reaches the taphole. A new regime (two-phase regime) is established, in which the flow rate is significantly lower than in the previous, single-phase regime. The decrease in flow rate is most probably a direct consequence of the dispersion of oil drops in the water. For this reason, the taphole pressure drop grows and the shear stress on the hole wall is increased. This provokes an increment on the hole diameter by the abrasion of the two-phase flow. By other hand, the flow rate in the stable two-phase regime is fairly independent of the OVF, which increases monotonically as the fluids are drained.
- The interface angle in the immediate vicinity of the outlet shows an exponential dependence with time, tending to a final angle that is quite similar in all the experiments. During the evolution, the interface tilt at the outlet strongly correlates to the OVF. It is possible to observe that, during the drainage the interface is great part of the time below the taphole level. In this case, the refractory chemical attack by slag is promoted in this area and it could cause a hearth break out below the taphole level. By means of numerical studies, the influence of the other parameters on the **Equation 7** is being studied and will be reported in a future work.
- The value of the interface tilt is in good agreement with a simplified analysis that considers pressure continuity and mass conservation equations, neglecting viscous terms, wall effects, etc.

In the blast furnace hearth, there are different variables that have effect in the drainage of the pig iron and the slag: the internal pressure, the liquid height above the taphole, the fluid-dynamical properties of the pig iron and the slag, the permeability of the coke packed bed and the physical properties of the taphole (clay quality, diameter, length and roughness). When the quality of the coke is good, the liquid level in the hearth is correct, the internal pressure is stable and the viscosity of the slag is good, the taphole operation determines the flow regime through the taphole and rules the drainage of the liquids. With a specific taphole conditions, despite that the pig iron-slag interface cannot be observed, the interface tilt is related to the slag volume fraction in the outlet flow. Therefore, to know that the phenomenon of increment in the taphole diameter during tapping is caused mainly by the abrasive mechanical process of the two phase flow, it contributes to the design of taphole clays that they can achieve the hearth behavior looked for according to the wanted blast furnace production.

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Ads must be received by
Jan 21st for publication in the
Mar/Apr 2010 issue.

Ads received after the 21st will be placed in the next issue.

THERMO-MECHANICAL PROPERTIES OF COLLOIDAL SILICA CONTAINING CASTABLES

Marina R. Ismael¹, Paschoal Bonadia², Victor C. Pandolfelli¹, vicpando@power.ufscar.br

¹Federal University of São Carlos - Materials Engineering Department Rod. Washington Luis, Km 235, 13565-905, São Carlos – SP, Brasil

²Magnesita Refratários S/A – Research and Development Center, Cardeal Eugenio Pacelli Av., 815, 32210-902, Contagem – MG, Brasil

Calcium aluminate cements (CAC) are the most used hydraulic binders for refractory castables. However, when added to Al_2O_3 - SiO_2 and Al_2O_3 -MgO castables, the CaO from the cement can negatively affect the refractoriness of these systems. For this reason, colloidal silica has been pointed out as an important alternative for the traditional CAC binders, since it has the potential to speed up drying, reducing the amount of liquid phase at high temperatures and inducing mullite formation. Additionally, previous work indicated that the combination of colloidal silica with microsilica or hydratable alumina can lead to improved compositions. Nevertheless, investigations on the properties of these enhanced systems after firing and at high temperatures are scarce in the literature. Therefore, in order to fill this gap, this work presents the characterization of optimized colloidal silica formulations based on permanent linear change (PLC), apparent porosity (AP) and cold (MOR) and hot (HMOR) modulus of rupture. The results are compared with those of a CAC reference castable. It was shown that the alternative binder systems are superior in terms of MOR (250-1500°C) and HMOR (1150-1450°C) due to their lower porosity and higher amount of mullite in the matrix.

INTRODUCTION

Calcium aluminate cements (CAC) with chemical compositions varying from 50 to 80% Al_2O_3 are the most used hydraulic binders for low temperature strength in refractory castables. The reasonable cost/benefit ratio of these binders has strongly consolidated their use throughout the last decades. Among the properties that the CACs impart to castables, the most relevant ones are the high mechanical strengths attained after curing and drying and the good resistance to corrosion agents [1-3].

The main drawback of CAC binders is that they add calcium oxide (CaO) to refractory systems. When the CaO is present in typical castable formulations, which commonly comprise Al_2O_3 - SiO_2 or Al_2O_3 -MgO raw materials, components of low liquidus temperature may form. Thus, the high temperature properties of the refractories are negatively affected.

Additionally, the calcium aluminate cements lose most of their strength in the 300 to 900°C temperature range due to the decomposition of the hydrated phases. Accordingly, the dehydration process is also followed by steam release, which increases porosity. This feature forces the refractory engineer to use a number of additives and other technologies in order to avoid damage to the castable integrity at these intermediate temperatures. Above 900°C,

ceramic bonding starts to take place and the cement supplies CaO and Al_2O_3 to the system [1-5].

In order to overcome these problems, colloidal silica has been pointed out as an alternative for the calcium aluminate cements [6-12]. The use of SiO_2 -sol, which is the colloidal form of silica, as a binder for refractory castables, has brought about the most significant advances in these systems since its first commercial application in the 1980s [2]. The principle is based on a sol-gel bonding system, where colloidal silica particles gel around the refractory particles of the castable, providing mechanical strength to the structure [9, 13].

The main advantages of colloidal silica based castables are: (i) their lower energy mixing requirements; (ii) high permeability structure, which enables the composition to be easily dried, reducing cracks and explosive spalling; and (iii) low temperature sintering characteristics [9-11]. Moreover, no CaO is added to the system.

Previous work of the authors indicated that microsilica and hydratable alumina addition to colloidal silica containing castables could further optimize these systems [10, 11]. The presence of microsilica in colloidal silica bonded castables enhances the mechanical strength attained by the SiO_2 -sol gelling mechanism. Moreover, this superfine addition can increase sinterability and mullite formation, most likely leading to lower creep deformation [10].

The combination of colloidal silica and hydratable alumina can result in important advantages to the processing and properties of castables, such as porosity reduction and increase of mechanical strength at temperatures below 350°C [11]. Nevertheless, very few results have been reported on cold (after firing >350°C) and high temperature properties of these castables [14].

In this paper, colloidal silica containing castables, in combination or not with microsilica and hydratable alumina, are assessed regarding permanent linear change, apparent porosity and cold and hot modulus of ruptures. All the results are compared with those of a CAC reference castable.

MATERIALS AND TECHNIQUES

The castable particle-size distribution (PSD) was adjusted to a theoretically self-flow continuous curve (Andreasen $q=0.21$ and $D_{\max}=4.750 \mu\text{m}$) [15]. Brown fused alumina was used as an aggregate, whereas fine calcined alumina comprised the matrix (**Table 1**) [10].

Table 1. Castable formulations and raw materials

Raw-Materials (Specification - Supplier)	Compositions			
	CS	MS	ABS	CAC
Calcined Alumina (wt %) (E-SY PUMP 1000 – Almatris U.S.)	34.0	31.0	30.0	33.0
Microsilica (wt %) (971-D – Elkem Norway)	-	3.0	-	-
Brown Fused Alumina (wt %) (Elfusa - Brazil)	66.0	66.0	70.0	67.0
Binder (wt %) CAC (CA-14M – Almatris U.S.), CS (Colloidal Silica - Nalco), AB (Alphabond 300 – Almatris U.S.)	7.5 CS	7.5 CS	5.0 CS and 3.0 AB	3.0 CAC
Total Water Content (wt %)	4.5	4.5	4.5	4.5
Dispersant (mg/m³) [PEG* or Citric Acid (CA)]	0.36 CA	0.78 PEG	0.36 CA	0.36 CA
Gelling Agent (wt %)** (MgO Sinter)	0.6	0.6	0.6	-

* PEG: polyethyleneglycol.

**wt % relative to the colloidal silica amount.

The mixing of the compositions was carried out in a rheometer at a constant speed of 44 rpm [16], after which they were cast into 150x25x25 mm shapes. Curing was performed in an acclimatized chamber (Vötsch 2020) at 50°C for 24 hours. The colloidal silica containing compositions (CS, MS and ABS) were kept at a ventilated atmosphere whereas the CAC based castable was cured in a closed saturated environment (sealed plastic bags) [9-11]. After demolding, the samples were dried at 110°C for 24 hours and then heat treated (at a 3°C/min heating rate), for 12 hours, at 110°C, 250°C, 500°C, 750°C, 1000°C, 1250°C and 1500°C. The cooling rate applied was 10°C/min.

The permanent linear change was measured according to **Equation 1**. The initial (L_0 , before firing) and final (L_f , after firing) lengths were measured at three different regions in the specimens, so as to obtain an average value. For each composition, a total of five specimens were assessed.

$$\text{Permanent Linear Change (\%)} = \left(\frac{L_f - L_0}{L_0} \right) \cdot 100 \quad (1)$$

Apparent porosity was determined according to the ASTM C 20-87 standard (immersion test), using kerosene as the immersion liquid. The modulus of rupture (MOR) was measured in MTS equipment (model 810) in the three point mode (ASTM C133-97), taking the average value of five specimens. Each specimen was machined (with water as a coolant agent) to attain smooth surfaces and dried (110°C/24h) before being tested. The MOR was calculated according to **Equation 2**.

$$MOR = \frac{3}{2} \cdot \frac{P_{max} \cdot L}{b \cdot d^2} \quad (2)$$

where P_{max} is the maximum load, L is the span between the rods (125 mm) and b and d, are the width and the depth of specimen, respectively.

The hot modulus of rupture (HMOR) was measured according to ASTM C 583-80 (Standard Test Method for Modulus of Rupture of Refractory Materials at Elevated Temperatures), using three-point loading (High Bending Strength Tester, 422, Netzsch), for 5

samples of each castable composition. The load was applied at a rate of 12.5 N/s and the HMOR value was obtained from **Equation 2**. The specimens were sintered for 12 hours at the same temperature they were to be tested (1150, 1300 and 1450°C – heating rate = 3°C/min). All the specimens were machined and dried (110°C/24h) after the heat treatment (and before the test).

RESULTS AND DISCUSSION

The permanent linear change (PLC) of the castables up to 1500°C is shown in **Figure 1**. The change in the specimen dimensions as a function of the temperature is controlled by the loss of free and chemical water (from 110 to 500°C), sintering (above 1000°C) and the formation of new phases (above 1000°C). Generally, water withdrawal and sintering are related to shrinkage, whereas new phases may be accompanied by either expansion or shrinkage. Therefore, the net result of the PLC is a balance among the simultaneous operation of these mechanisms.

From **Figure 1**, it can be observed that the CS castable is the only one that shows virtually no linear change at 250°C. This feature may be related to the consolidation mechanism of the colloidal silica, whereby a permeable structure is attained upon curing, which allows the withdrawal of almost all the water in the castable already at 110°C. Therefore, no significant shrinkage is observed

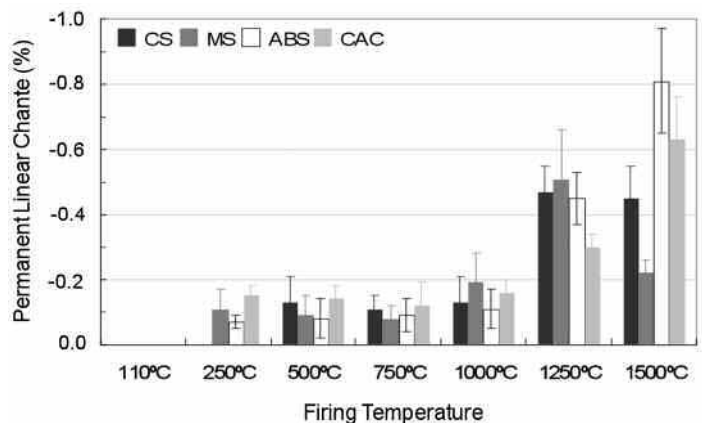


Figure 1. Permanent linear change as a function of firing temperature for CS, MS, ABS and CAC.

at 250°C. From 500 up to 1000°C, no relevant differences are seen among the different compositions.

At 1250°C, the CAC castable presents the lowest shrinkage (lowest PLC). This composition contains CaO from the calcium aluminate cement, which may react with the alumina from the castable matrix and form the CA_6 ($CaO \cdot 6Al_2O_3$) phase. The formation of CA_6 is known to be an expansive reaction and may partially compensate for the specimen sintering, thus leading to a lower net shrinkage value (Figure 1).

The MS castable contains two sources of SiO_2 (Table 1), namely the colloidal silica and the microsilica. Therefore, its composition is richer in silica than the other ones, which means that a higher amount of mullite ($3Al_2O_3 \cdot 2SiO_2$) may form when firing. Similarly to the CA_6 , mullite formation is an expansive reaction, which can partly offset the shrinkage effect resulted by the sintering of the system. Most likely this is the reason why MS displays the lowest PLC at 1500°C. Conversely, composition ABS contains the lowest amount of SiO_2 , which is consistent with its high shrinkage measured at that temperature (Figure 1).

Figure 2 depicts the behavior of the castables apparent porosity (AP) as a function of the temperature. It is interesting to note that the compositions with a higher colloidal silica content (CS and MS) start with a relatively high AP, but then at 1250 and 1500°C this porosity tends to decrease. The opposite trend, however, is observed for ABS and, more significantly, for CAC. These latter compositions have an initial low AP, but as the firing temperature is raised up to 1250°C their porosity increases accordingly. At 1500°C, this trend seems to invert and the porosity decreases.

The low AP of compositions CS, MS and even ABS at 1500°C might be associated to a more significant liquid phase sintering [17]. The phase diagram presented by Risbud and Pask [18] (Figure 3) shows a metastable liquid formation at temperatures as low as 1260°C on the silica rich side of the system. Therefore, if a local higher silica concentration is found out in the castable matrix, this liquid may enhance densification and promote pore reduction.

The increase in porosity for the compositions with the hydratable binders (ABS and CAC) from 250 to 1250°C may be explained by the decomposition of the hydrated phases. Within this temperature range, the chemically bonded water is withdrawn from the castable, thereby leaving voids in its structure. These voids, or pores, remain in the specimen up to the sintering temperature

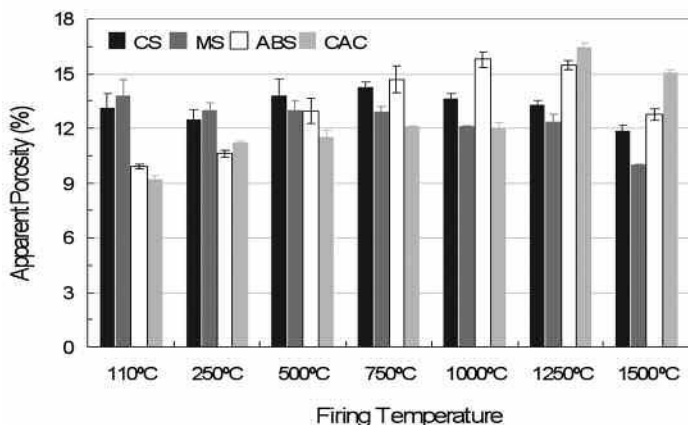


Figure 2. Apparent porosity as a function of firing temperature for CS, MS, ABS and CAC.

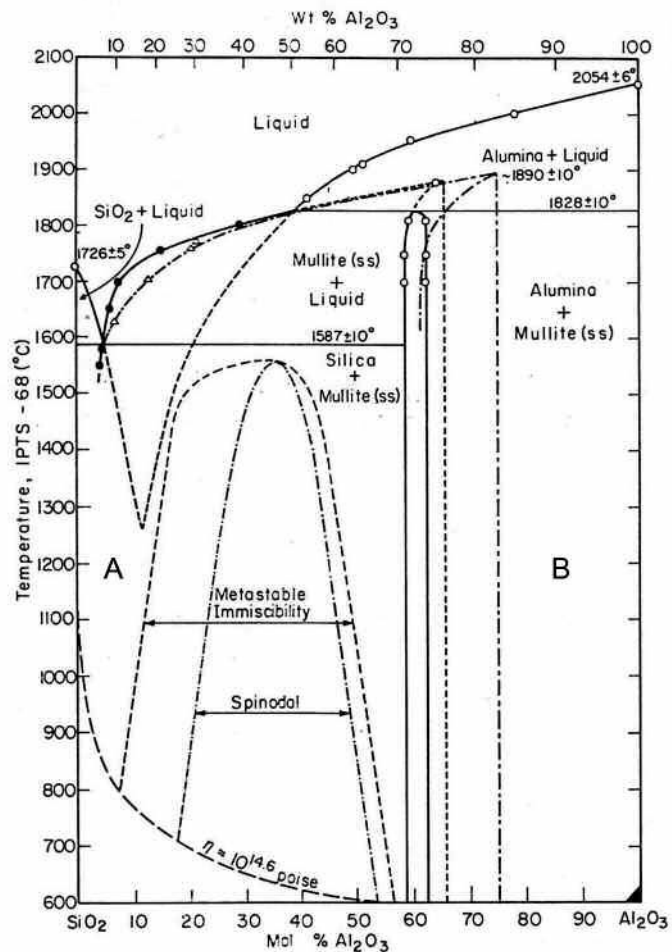


Figure 3. Al_2O_3 - SiO_2 binary system by Risbud and Pask [18].

(1250 to 1500°C), where the ceramic bonding starts and densification takes place.

The negative effect of hydrates decomposition in castables CAC and ABS can also be assessed from the modulus of rupture (MOR) results (Figure 4). It is clear that they lose more strength between 110 and 750°C, when compared to CS and MS. This temperature range is critical for hydratable binders, because their tridimensional network of hydrated phases is gradually decomposed, thus losing their ability to hold the castable particles together. In the range of 1000 to 1250°C, sintering begins and the mechanical strength increases again.

For the castables containing colloidal silica (CS, MS and ABS), the development of the MOR displays a different behavior (Figure 4). As this binder promotes no hydrate formation, but a silane (Si-O-Si) network, no loss on mechanical strength is observed from 110 up to 750°C. In fact, the modulus of rupture tends to slightly increase within this range.

Therefore, although CAC has a higher initial strength (at 110°C), CS, MS and ABS attain much better properties as the temperature rises, especially above 750°C (Figure 4). This fact may be associated with the high colloidal silica reactivity and to the formation of mullite.

According to Figure 4, it seems that colloidal silica anticipates sintering, leading to high mechanical strengths already at 1000°C. Additionally, the formation of mullite, with its needlelike

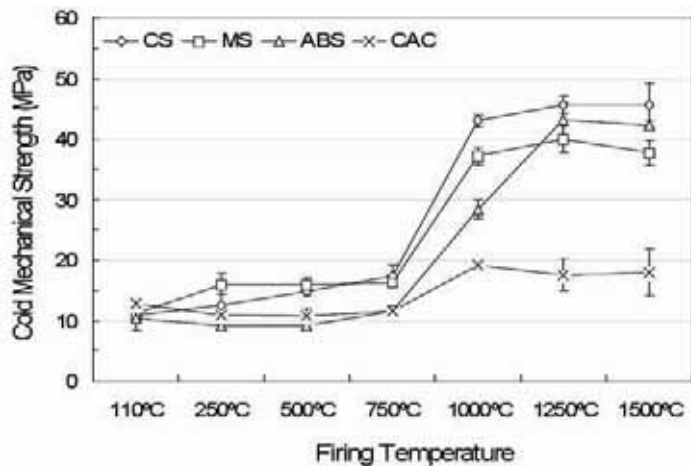


Figure 4. Modulus of rupture as function of firing temperature for CS, MS, ABS and CAC.

microstructure, improves the MOR. This feature is highlighted by the poor properties of CAC at 1000-1500°C, which contains no silica, and hence no mullite, in its composition.

The hot modulus of rupture (HMOR), which enables the assessment of the materials mechanical strength at high temperatures, is shown in Figure 5. At 1150°C the colloidal silica compositions attain the highest HMOR values, especially the MS one. It is likely that the microsilica contained in this latter castable provides bet-

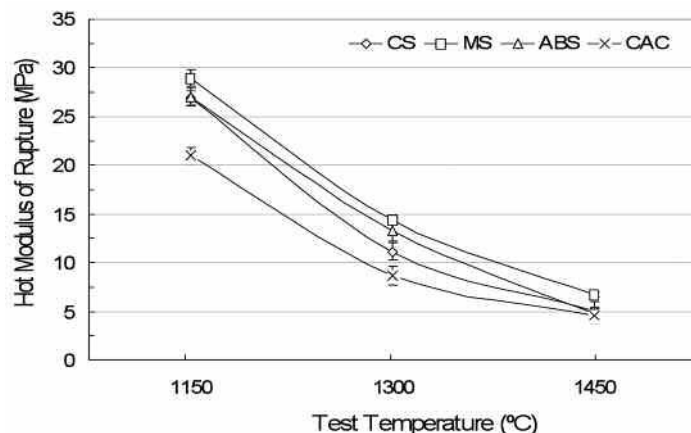


Figure 5. Hot modulus of rupture as a function of the temperature for CS, MS, ABS and CAC.

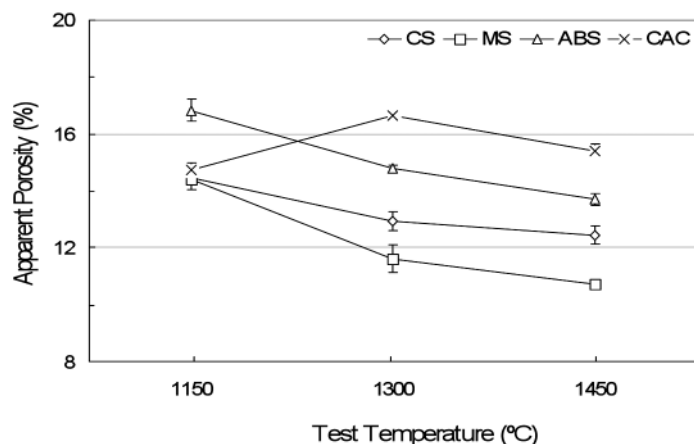


Figure 6. Apparent porosity as a function of testing temperature for CS, MS, ABS and CAC.

ter placing properties and denser particle packing [10], thus leading to an optimized microstructure and higher strength. This theory is supported by the lower porosity of this composition (Figure 6).

At 1300°C, a considerable drop in the HMOR value is observed for the silica rich compositions (Figure 5). This phenomenon has already been reported in the literature for silica containing castables [17], and is associated with the metastable liquid formation at approximately 1260°C (Figure 3).

Nevertheless, the diagram in Figure 3 shows that for the metastable liquid to be present, the reactive part of the castable (its matrix) should have an $Al_2O_3:SiO_2$ ratio close to region "A", which is not the case here. The compositions studied in this work are closer to region "B", as listed in Table 2, where there are no eutectic points.

A possible explanation for the low temperature liquid formation is that although colloidal silica particles are nanometric, they could form agglomerates during gelling. The stoichiometry around these agglomerates would be richer in silica, thereby shifting the local chemical composition towards the "A" region of the diagram (Figure 3).

Interestingly, the HMOR at 1450°C continued to drop compared to 1300°C, even though it was expected that at this temperature the presence of mullite would increase the system's hot strength. Possibly, the metastable liquid formed at around 1260°C consumed some of the silica present in the system, thereby preventing a more expressive mullite formation.

The CAC castable showed the same HMOR trend as that for the colloidal silica ones. Even with no silica in its composition, which could otherwise form the deleterious $Al_2O_3-CaO-SiO_2$ phases, the CAC composition attained a relatively low hot strength at 1450°C (nearly 5 MPa).

It is important to notice, however, that commercial castable compositions, which combine a number of different raw materials, may attain much lower HMOR values at 1450°C than those presented here. Therefore, further work should be carried out in order to compare the hot properties of the colloidal silica castables with those of more traditional ones.

The porosity values measured for the specimens, which were tested for HMOR are presented in Figure 6. The compositions with the silica binder (CS, MS and ABS) led to lower porosities, mainly above 1300°C. These results are consistent with those shown in Figure 2, where the higher sinterability of the colloidal silica promotes a significant pore reduction after the thermal treatment above 1000°C.

CONCLUDING REMARKS

When compared to the traditional calcium aluminate cements, colloidal silica attains better mechanical strengths at intermediate to low temperatures. As the silica binder develops no hydrated phases, its strength is not affected from 250 to 750°C. Additionally, its high reactivity favors sintering and mullite formation in the castable matrix, leading to a remarkable MOR evolution from 750 to 1500°C.

Table 2. $Al_2O_3:SiO_2$ ratio in the matrix of colloidal silica containing castables

Compositions	CS	MS	ABS
$Al_2O_3 : SiO_2$	92.0 : 8.0	84.0 : 16.0	94.0 : 6.0


The HMOR tests revealed that the colloidal silica containing castables outperform the cement bonded ones, especially for the composition with microsilica at 1150°C. At 1300 and 1450°C, a possible metastable liquid formation in the Al₂O₃-SiO₂ system causes a decrease in the high temperature strength.

Finally, besides the known faster drying schedules provided by colloidal silica bonded monoliths, this paper has shown that the thermo-mechanical properties of these refractories tend to be superior as well. However, further work still has to be done, investigating, for instance, the effect of different types of colloidal silica and their concentration in the high temperature properties of the castables. A companion paper dealing with these aspects has already been submitted to RAN.

ACKNOWLEDGMENTS

The authors are thankful to the Brazilian Research Funding CAPES and FAPESP for supporting this work and Almatiss (U.S.), Magnesita Refratários (Brazil), Forza (Brazil) and Elfusa (Brazil) for the raw materials supplied and to F. Valenzuela for helping in the processing and measuring steps.

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Changes will be mandated in a number of areas, including container labels, safety data sheets, and employee training.

A number of countries, including the United States, international organizations and stakeholders participated in developing the GHS to address inconsistencies in hazard classification and communications. The GHS was developed to provide a single, harmonized system to classify chemicals, labels and safety data sheets with the primary benefit of increasing the quality and consistency of information provided to workers, employers and chemical users. Under the GHS, labels would include signal words, pictograms, and hazard and precautionary statements. Additionally, information on safety data sheets would be presented in a designated order.

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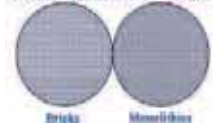
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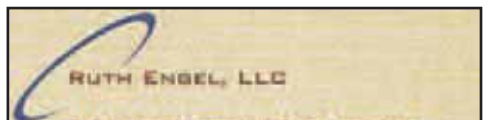
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Tel: 604-859-5288 or 604-851-4556
rdlane@clayburngroup.com

IFB, Inc.

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

Saint-Gobain Ceramics

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Worcester, MA 01615-0136
Tel: (508) 795-2963 Fax: (508) 795-5011
patrick.m.stephan@saint-gobain.com
www.refractories.saint-gobain.com

KILN/FURNACE FURNITURE

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5555 Pleasantdale Rd., Atlanta, GA 30340
Tel: (678) 735-4925 Fax: (770) 368-8261
Sean.McDevitt@AppliedCeramics.com
www.appliedceramics.com

Nth Degree Products

404 Laurel Ridge Rd., Hainesport, NJ 08036
Tel: (609) 518-9447 Fax: (609) 518-9445
nthdegreeproducts@Yahoo.com

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1 New Bond St., MS 301-432
Worcester, MA 01615-0136
Tel: (508) 795-2963 Fax: (508) 795-5011
patrick.m.stephan@saint-gobain.com
www.refractories.saint-gobain.com

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dthurman@sunrockceramics.com
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Kyanite Mining Corporation

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14025 N. Rivergate Blvd., Portland, OR 97203
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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

Saint-Gobain Ceramics

1 New Bond St., MS 301-432
Worcester, MA 01615-0136
Tel: (508) 795-2963 Fax: (508) 795-5011
patrick.m.stephan@saint-gobain.com
www.refractories.saint-gobain.com

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33765 Pine St., Abbotsford, BC, CA V2S 5C1
Tel: 604-859-5288 or 604-851-4556
rdlane@clayburngroup.com

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Penn Center West, Bldg. 2, Ste. 430
Pittsburgh, PA 15276
Tel: (412) 494-4491 or (800) 354-1211
Fax: (412) 494-4571
sales@rescoproducts.com www.rescoproducts.com

Saint-Gobain Ceramics

1 New Bond St., MS 301-432
Worcester, MA 01615-0136
Tel: (508) 795-2963 Fax: (508) 795-5011
patrick.m.stephan@saint-gobain.com
www.refractories.saint-gobain.com

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Penn Center West, Bldg. 2, Ste. 430
Pittsburgh, PA 15276
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sales@rescoproducts.com www.rescoproducts.com

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Kyanite Mining Corporation

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info@kyanite.com www.Kyanite.com

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

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Cincinnati, OH 45202
minelco.inc@minelco.com www.minelco.com

Unimin Corporation

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Tel: 281-590-8500 or 800-828-5002
Fax: 281-590-5342
tfl@tflhouston.com www.TFLHouston.com

ZIRCAR Ceramics, Inc.

100 North Main St., P.O. Box 519
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dph@zircarceramics.com www.zircarceramics.com

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1 New Bond St., MS 301-432
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inquiry@johnsonmachineco.com
www.johnsonmachineco.com

Alcon Tool Company

587 Baird St., Akron, OH 44311
Tel: 330-773-9171 Fax 330-773-8042
www.alcontool.com rd@alcontool.com

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VanceCeramics101, Inc.

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C-E Minerals

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Tel: 800-243-9004 Fax: 800-243-9005
metalcaster@unimin.com www.metalcaster.com

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info@unifrax.com www.unifrax.com

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rdlane@clayburngroup.com

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rdlane@clayburngroup.com

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www.rficonstructionproducts.com/

Lancaster Products,

Div. of Kercher Industries, Inc.
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rdlane@clayburngroup.com

SILICA BRICK

Utah Refractories Corp.

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Tel: (412) 851-2430 Fax: (412) 851-2425
tlmpgh@aol.com

SILICA MATERIALS

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104 Murphys Crossing Dr., Powell, OH 43065
Tel: (614) 284-9699 Fax: (614) 761-7722
vrestivo@hotmail.com www.sachtleben.com

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pormond@aluchem.com

Christy Minerals

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Tel: (636) 585-2214 Fax: (636) 585-2220
info@christyco.com www.christyco.com

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pormond@aluchem.com

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Refractory Specialties, Inc.

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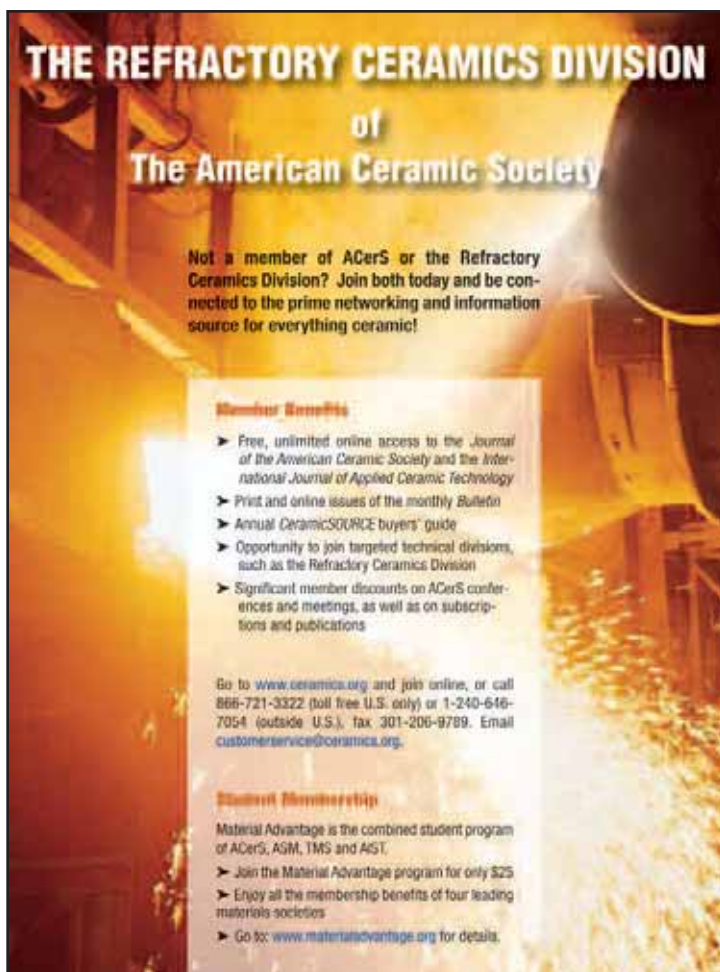
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One Landy Lane, Cincinnati, OH 45215
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ST. LOUIS SECTION AND THE REFRACTORY CERAMICS DIVISION 46th ANNUAL SYMPOSIUM

The St. Louis Section and the Refractory Ceramics Division of the American Ceramic Society will sponsor the 46th annual symposium on the theme "Innovative Materials for Energy Efficiency" on March 24-25, 2010, held in St. Louis, Missouri at the Hilton St. Louis Airport Hotel. Co-program chairs are Bill Headrick of Missouri Refractories and James Bennett of Albany Research Center.

Partial listing of papers to be presented:

“CDS on Drying”, A. Hall – CDS, Inc.

“Dry-Out Index”, J. Peterson – ExxonMobil

“Development of Materials (Proppants) for Oil and Gas Recovery (Invited Paper)”, J. Hellman – Penn State

“DOE Industrial Technology Program – R&D Projects Selection Process and Energy Efficiency Assistance Activities”, M. Jha – US Department of Energy, Golden Field Office

“Current Legislative and Regulatory Issues Potentially Impacting Refractories”, R. Crolius – The Refractories Institute

“Advantages of Dense Calcium Hexaluminate Aggregate for Back Lining in Steel Ladles”, D. Zacherl – Almatris

“New Gunning Technology for Rapid Refractory Turnaround”, S. Libby or J. Stendera – Vesuvius

“FIRE”, M. Rigaud - FIRE

“Ceramic Filters”, R. Olson – Selee Corporation

“Carbon Fiber”, J. Lebant – SGL Group / The Carbon Company.

If you are interested in participating in the Tabletop Expo, contact Mary Reidmeyer at (573) 341-7519, maryrr@mst.edu or Patty Smith at (573) 341-6265. psmith@mst.edu.

A block of rooms have been set aside for the evenings of March 22-26, 2010 at the Hilton (314) 426-5500. The rate is \$99.00 for a single or double. To receive the \$99 rate, please refer to the St. Louis Section of the American Ceramic Society when making your reservation. All reservations must be received on or before February 24, 2010

For further information please contact Patty Smith at Tel: (573) 341-6265, Fax: (573) 341-6151 or email: psmith@mst.edu.