

# Refractories Applications *and News*

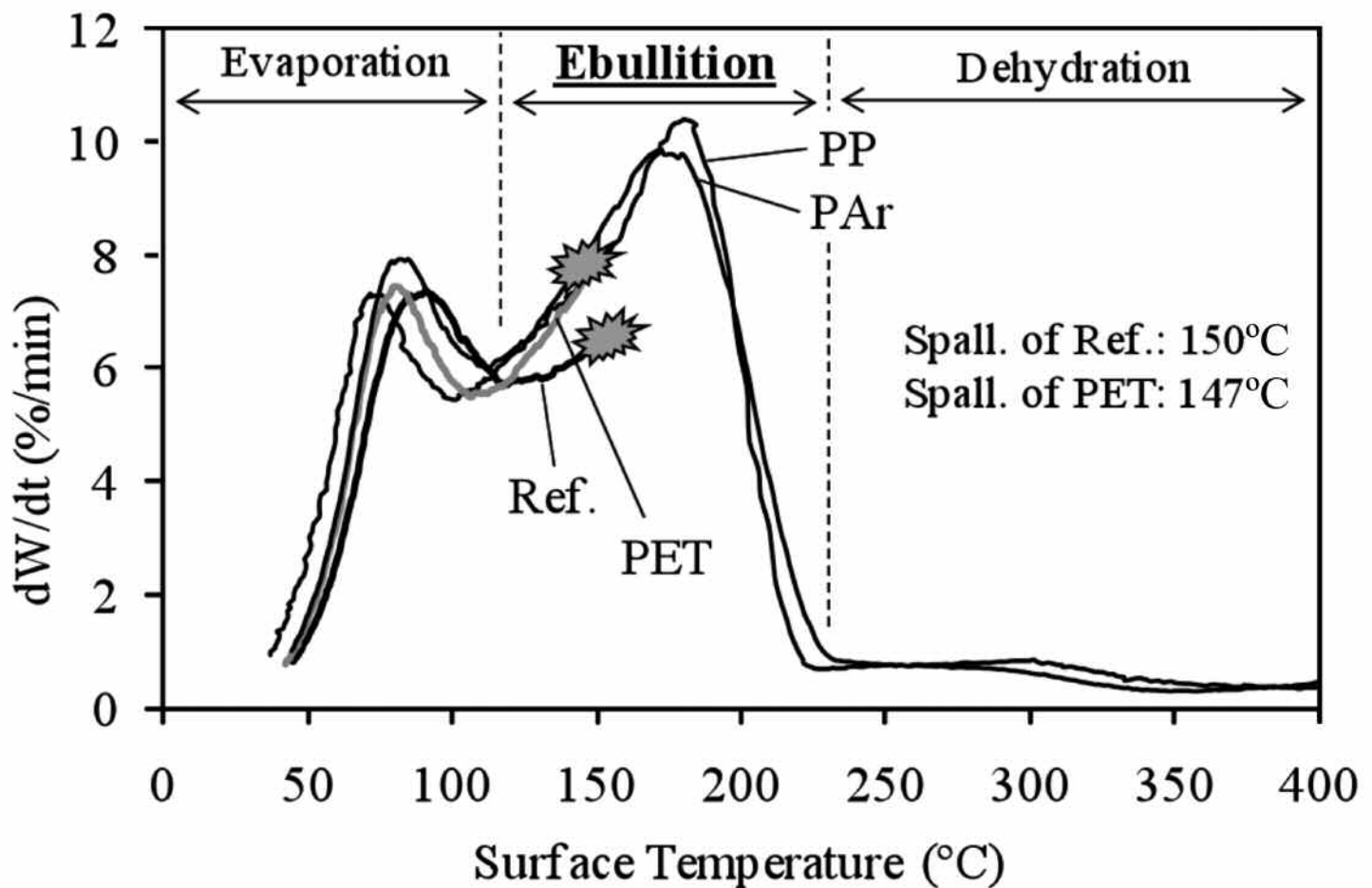


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Technology Bimonthly for the Global Refractories Industries

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## From the Editor . . .

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



Jeffrey D. Smith

Over the past few months, I have been approached several times by engineers and scientists in the refractories industry and have been asked about current graduate level research efforts in the United States. Each time the focus is somewhat different, likely related to the motivations behind the particular inquiry. Given the obvious interest, I felt compelled to discuss the topic in an upcoming editorial and since there is no time like the present . . .

The current economic environment has had a significant impact on industry funding of graduate level research in the US. This is especially true in the manufacturing sectors that were healing about the same time that the US and global economies began to decline. Many of these companies have done all they can to ensure retention of their own workforce. The concept of supporting graduate level education has not been a high priority. Although I have no doubt that many of these companies are well aware of the significance of such research efforts, the economic reality tends to define their immediate hierarchy of needs.

However, if we look back to “better” times and only consider the refractory and refractory related industries in the US, we have to go back a number of decades to find even modest levels of graduate level research support. Universities that elected to support the refractory community financed most of their graduate education and research with federal tax dollars and occasionally industry-supported efforts. As federal dollars became increasingly unavailable for refractory related efforts (Department of Energy funds were shifted to “green” programs and alternative energy initiatives) most universities headed for other areas.

Rolla has continued its involvement with the refractory industry, mainly through programs supported by end users and raw material suppliers. Most refractory manufacturer efforts were supplemented by significant DOE dollars. Such efforts continue today, albeit at considerably smaller levels. Graduate research and education costs continue to rise and industry and federal government dollars continue to fall. Consider the annual support required for a graduate student at MS&T today . . . \$24,000. Add to that number tuition (~\$6,000) and the university indirect charge; and a graduate student requires about \$45,000 each year, and that is without considering any dollars to support the equipment and testing associated with the effort.

These are the realities of the current situation in the US. The result is not terribly appealing. I currently have two graduate students in my group. The smallest number I have ever had and likely the smallest number working on refractories in many decades. As bleak as that may seem, it is considerably better than the situation at other US universities who, at least as far as I can determine, have no continuing refractory efforts. An occasional small project supported by a regional company, is likely although I don't see any associated presentations or publications related to such efforts.

So, what is the long-term impact? This is a question that will likely foster significant debate. I have strong opinions on the topic but will save most of those for another time. In closing, I will say that I know of no significant industries in the US that function without some type of graduate level training and research. RAM

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

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

## REFRACTORIES RELATED MEETINGS

### 2010

March 24-25, **St. Louis Section and the Refractory Ceramics Division 46<sup>th</sup> 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, **12<sup>th</sup> International Ceramics Congress CIMTEC 2010**, Florence Italy, [www.cimtec-congress.org/2010/](http://www.cimtec-congress.org/2010/).

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

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

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

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

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](mailto:leemj@mst.edu).

**Send meeting announcements to Mary Lee at:  
[leemj@mst.edu](mailto:leemj@mst.edu)  
Announcements must be received a minimum of  
four months prior to the meeting date.**



**Rob Crolius**

## LEGISLATION IN 2010

By the time this column is printed, the national debate on health care likely has come to some sort of end point, at least for now. Whether something good or bad was finally accomplished depends mostly on your point of view, and the final verdict on what President Obama and Congress ultimately got done or did not get done is probably years down the road. Regardless, what is certain is that

the Obama Administration and both parties in Congress are moving on to other important issues which will be pursued with much the same political infighting, rancor and grandstanding as we saw in the health care debate.

This column is devoted to what are expected to be the two giant legislative issues this year: (1) climate change and greenhouse gas emissions, and, (2) renewal and/or revision of a number of important provisions of the federal tax code.

Editor's Note: I applaud journalists who can provide factual, unbiased information. Unfortunately, I am not one of them. I find it impossible to discuss issues such as these without some editorial comment pro or con. Therefore, please let this document be only one of many you readers review as you work to inform yourselves on these matters. Like health care, these issues will affect each and every one of us directly—both professionally and personally—so it is past time to start paying attention.

## THE AMERICAN CLEAN ENERGY AND SECURITY ACT (H.R. 2454)

This is probably a good place to start on global climate change legislation because it actually has been passed by the House of Representatives. If enacted into law, this legislation will have major implications for both business and individuals, by imposing onerous costly new requirements on industry and increasing energy and consumer costs across the board.

H.R. 2454 has five key provisions:

- It requires utilities to meet 20% of their electricity demand through renewable energy sources and energy efficiency by 2020.
- It promotes investment in clean energy technologies and energy efficiency, carbon capture and sequestration, electric and other advanced technology vehicles, and basic science R&D.
- It establishes new energy-saving standards for buildings and appliances.
- It requires reduction of carbon emissions from 2005 levels from major U.S. sources of 17% by 2020 and 83% by 2050.
- While doing all the above, Congress intends to protect consumers from energy price increases at the same time!

The legislation as it currently stands will impact refractory producers in two major ways. First, the requirements imposed on electrical utilities and oil refiners will inevitably lead to higher utility rates. Congress allocates funds in the bill to offset increases, but realistically rates will be significantly higher. Opponents will argue that high-

er rates will impede U.S. competitiveness at a time U.S. industry is under the gun already. Proponents will argue that higher rates reflect the real energy and environmental costs to society and that the free, or at least cheap, ride must end. They will also assert that higher rates will encourage conservation. Hold on to your checkbooks.

The second and important issue for large refractory producers is the so-called "cap and trade" provisions for manufacturers emitting more than 25,000 tons annually of carbon dioxide or its equivalent. These large manufacturers are summarily lumped in with utilities and oil refiners and will be required to pay a fee per ton of emissions and to freeze or "cap" their emissions rates. The fee is currently projected to be in the range of \$13-17 per ton. Any increase in future emission allowances would require the purchase of additional carbon emission credits from sources that have accumulated excess credits through emission reductions in their own operations. The emission credits would essentially become a traded commodity. One can't help but see a comparison between the proposed energy credits and Chinese raw material export licenses, which started out at \$35 per ton and quickly soared to several hundred dollars per ton.

Congress allocates the income from this proposed program to fund a range of conservation and R&D programs and, believe it or not, to assist the very industries that are being regulated in the early years of the program. Why not just let them keep the money and invest it themselves in energy saving technologies? Also targeted for assistance under this program are industries being adversely affected by foreign competition. It would be nice if refractories could get in on some of that!

The legislation is now in the Senate. Despite all the sound and fury, it is unclear what, how much, and even if the legislation in its present form will get to President Obama for signature. It is unlikely that the Democrats can hold the coalition they put together for health care, and Americans, rightly or wrongly, are growing more wary of the climate debate, and a bunch of them will be voting in November. One thing is clear, however. Refractory manufacturers should be talking to their elected representatives in Washington right now. Information to have in hand for those discussions would be an estimate of company current emission levels and utility costs, what the company's current investment in, and cost of, government regulation and mandates already is, the number of employees and facilities in the representative's district (translates to payroll and potential voters), and, a list of the major issues the company is facing, from unfair foreign competition to tight credit to the need to attract trained employees to an industry which is absolutely critical to the economic success of the United States. One useful addition to the congressional dialogue might be a copy of the TRI DVD "Taming the Flame", which can help a senator or congressman understand just what refractories are and why they are important.

## RENEWAL AND REVISION OF EXPIRING TAX PROVISIONS

Note that we have not used the phrase "tax reform". Many will try to use it in the coming months, but any final tax legislation that is passed won't be real "reform". Actually, Congress technically does-

*Continued on Page 13*

# IT'S A REFRACTORY FAILURE...

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

Most people working in the refractory field are familiar with the statement “the refractories failed” or “it is a refractory problem”, although, upon investigation it can often be shown that the problem was not the result of a misapplied property intrinsic to the refractory. What these statements do point out is that the observed damage can easily be construed to be a refractory problem because they are the statement of the failure.

The saying also reflects an implicit expectation by the user of what the life of that component should have been and what needs to be modified to address the problem.

A true refractory failure consists of a refractory that does not support its own weight, its properties are not what they should have been, or it was manufactured with an incorrect chemistry. These problems do not occur very often and they can easily be determined through testing of the as-received product.

In this paper, I will review some of the items which are often categorized as a refractory failure but, may or may not actually be one.

**A wall/roof collapsed:** this certainly qualifies as a failure, but the statement does not tell you if indeed the culprit was a refractory property misapplication. The collapse of a wall or roof of a furnace is often the result of the anchoring system being compromised especially if it occurs early-on in a newly lined unit. Let us analyze this further. The anchors: metal clips, hex mesh, refractory brick, etc. have one role and that is to keep the wall or roof in close contact with the supporting shell. These anchoring systems can display several modes of failure all of which will lead to a shortened service life that generally can be traced back to improper design or installation problems. If no expansion joints were engineered into a lining, it may expand sufficiently to shear off the metal anchors and fall in. If using refractory anchors, the wall movement may have been so great as to have the anchor brick slip out of the ice tongs holding them in place. Installation problems can also lead to “refractory failures”. The welding of metal anchors or hexmesh to a shell has to be done correctly. This is a time consuming step which, if not carried out properly, will result in a failure that looks very similar to the previously stated case, i.e. the wall or roof is not supported and in the extreme collapses. Similarly, if there were not enough anchors installed, they were the wrong length, chemistry, etc. then they will not be able to support the refractory weight for the expected length of time and the wall or roof will fail.

**Excessive wear:** This can be seen in many areas, but often occurs when refractories are in an erosive or corrosive environment. Although it is possible that the refractories did not meet their expected physical properties, the problem is more often due to operational or installation factors. Higher operational temperatures than designed for, increased holding times, increased particulate loading, changes in particulate size, etc. by themselves all accelerate the refractory’s wear, but if two or more of these parameters are combined their effect can quickly become catastrophic.

Lack of chemical compatibility between the refractory and what they enclose can also manifest itself as excessive wear. Slags are a prime culprit of this phenomenon. If a slag’s composition is not carefully balanced so as to be in chemical equilibrium with the refractories it comes in contact with, it will attack the refractories and dissolve them. In addition, the rate of attack is greatly accelerated the higher the operating temperature. Long holding times exacerbate the problem. The extreme case is defined as a burn through or break out whereby all refractory is lost and there is a breach in the integrity of the holding container. In this case, the analysis or testing of the “used refractory” is not possible because the evidence was destroyed. The assumption that the material surrounding the hole is of the same chemistry and has the same properties as the failed one can be risky and should be pursued with care even though often there is no choice.

In all of these cases, there was a “refractory failure” as that was the manifestation of the problem. Nevertheless, its cause was not due to a true refractory problem, but a reflection of a poorly controlled operation, unknown operating parameters, or engineering design issues. The next section will discuss the effect of some true refractory issues.


**Installation factors:** years ago, when the use of brick was much more prevalent, installation issues were fewer as the refractory manufacturer was the one responsible of assuring the material met chemistry and had the expected physical properties. Today, the ubiquitous use of monolithics, leads to a sharing of responsibility: the manufacturer is responsible for providing a refractory material with the proper chemistry, grain sizing and that ultimately can achieve published physical properties; the installer has to mix and place it in such a way that its expected properties can be achieved in service; and the user has to bring the unit to service temperature in a manner that allows the refractory material to develop the specified properties. If any of these steps are not carried out properly then the refractory properties will be compromised and their life foreshortened.

**Selection concerns:** the proper selection of a refractory should be based on the chemistry, physical properties and form: brick, castable, plastic, etc. that are most compatible with the operating parameters. If only partial knowledge about the environment is

available then several iterations will be needed to determine the best lining concepts by basing each new refractory selection on improving upon the failures of the previous ones.

Worn refractories provide tangible evidence of the quality, design, installation and usage history of a unit. Their analysis should be one component of the unit's history undertaken to determine the reason for their unexpected short life. In some cases the problem will indeed be solely due to refractory issues

but often the answer is more complex and requires a careful analysis of the worn remains, unused refractories and operational parameters to develop a coherent scenario for the observed problem. In summary, the statement "it is a refractory problem" is often only partially true.

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

## Industry News

### GLOBAL DEMAND FOR KAOLIN TO REACH 24.8 MILLION METRIC TONS IN 2013

Global demand for kaolin is forecast to grow 1.7 percent per year to 24.8 million metric tons in 2013, exceeding the growth achieved between 2003 and 2008. Demand for kaolin in paper production is expected to improve, offsetting an expected slowdown in the ceramics market. In general, kaolin demand in advanced economies is projected to recover from the declines of the 2003-2008 period, while demand in the faster growing emerging markets will decelerate somewhat. These and other trends are presented in World Kaolin, a new study from The Freedonia Group, Inc., a Cleveland-based industry research firm.

Developing countries are becoming increasingly important to global kaolin demand. Strong demand gains in China and other developing countries in Asia are expected to account for the majority of global kaolin demand in 2013, with China alone accounting for over one-half of the global gain. China is forecast to surpass the US as the largest market for kaolin by 2013, as its kaolin consumption continues to grow faster than that of any other major national market. China's market for kaolin in paper is forecast to lead gains, driven by a rapidly expanding domestic paper industry. Imports into China are expected to grow especially fast, as the country's kaolin consumption outpaces production.

Demand for kaolin in paper -- the largest end use -- is forecast to rebound from its declines between 1998 and 2008. Over that period, kaolin suffered from competition with alternative materials (notably calcium carbonate), and that competition is expected to moderate in coming years. By 2008, much of the practical substitution of kaolin by calcium carbonate had already taken place. In addition, emerging markets such as China are expected to post strong gains as their paper industries expand.

International trade in kaolin is widespread, with approximately one-half of kaolin being consumed outside of its country of origin in 2008. This is in part due to the concentration of kaolin production in

the US and Brazil. By 2013, Brazil is expected to surpass the US as the world's leading exporter of kaolin, gaining market share in Western Europe and Asia at the expense of the United Kingdom and the US. Brazil boasts sizable deposits of high-quality kaolin, making it economical to produce kaolin there, despite the additional shipping costs.

World Kaolins (published 12/2009, 232 pages) is available for \$5,700 from The Freedonia Group, Inc., 767 Beta Drive, Cleveland, OH 44143-2326. For more information contact: Corinne Gangloff, Media Relations, Tel: +1 440-684-9600, Fax: +1 440-646-0484, [pr@freedoniagroup.com](mailto:pr@freedoniagroup.com). Information may also be obtained through [www.freedoniagroup.com](http://www.freedoniagroup.com).

### THERMAL ANALYSIS CAPABILITY

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For pricing and availability contact: Dr. Joseph Homeny, Tel: 614-818-1323, [homeny@ortonceramic.com](mailto:homeny@ortonceramic.com), Edward Orton Jr. Ceramic Foundation, P.O. Box 2760, Westerville, OH 43082

### REVITALIZED WEBSITE

Expert materials testing, analysis and consultancy firm CERAM has boosted its web offering to customers in the refractories and associated high-temperature industries with the launch of a revitalized website that provides expanded industry-specific services and a large resource of reports, white papers and guidance documents. The free downloads cover 'hot topics' across the breadth of CERAM's industry expertise, which for refractories include guidance on purchasing monolithic refractory materials and obtaining valid data for the computational modeling of refractory structures.

Customers visiting the new website will find it easy to navigate the full inventory of testing, analysis and consultancy services that CERAM offers, while the clear focusing of industry sections will enable visitors to quickly access a wealth of information specifically constructed to meet the needs of the refractories sector.

Chief Executive, Tony Kinsella, commented: "In response to the rapid growth of some of CERAM's business areas over the last 12 months, and the unrivaled industry breadth of our offering, we are

WORLD KAOLIN DEMAND (thousand metric tons)					
Item	2003	2008	2013	% Annual Growth	
				2003-2008	2008-2013
Kaolin Demand	21300	22850	24800	1.4	1.7
North America	5450	5040	4800	-1.6	-1.0
Western Europe	7080	6890	7040	-0.5	0.4
Asia/Pacific	5760	7190	8640	4.5	3.7
Other Regions	3010	3730	4320	4.4	3.0

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making sure that visitors to our website have a clear and easy way of accessing the information they need. We are proud of the expertise we have accumulated at CERAM and don't want to keep it to ourselves – we want to make sure that we provide as much information as we can in an easily accessible manner”.

Highlights of the new website include sign-up options for a range of industry-specific newsletters, an ‘Experts Biographies’ section where visitors can find out more about the leading materials experts in their sector, and an extensive collection of new downloads and case studies.

For further information please contact: Mandy Rymill, CERAM Marketing Communications Manager, Tel: +44 (0)1782 764 326, email: mandy.rymill@ceram.com, www.ceram.com.

## **MBO SEES IPS CERAMICS IN KILN FURNITURE**

IPS Ceramics Ltd is pleased to announce its Management Buyout (MBO) of the former Dyson Group business, Dyson Thermal Technologies Kiln Furniture. This MBO, concluded on December 23, 2009, includes the existing order book, manufacturing and intellectual properties associated with the Company's whole kiln furniture range (one of the largest in the world) and global agency agreements.

Existing customers are assured of a direct line of communication to the Senior Management Team and existing contacts in the commercial office to ensure continuity of supply, fulfillment of orders and access to the wide-ranging technical expertise that they have come to expect from this historic ceramic business.

The MBO Team behind IPS Ceramics comprises Managing Director Sukhjinder Singh (formerly MD Ceramics Division and Program Director, Dyson Group), Operations Director Ian Wright (formerly Senior Operations Manager, Dyson Thermal Technologies) and Sales Director Phil Green (formerly Commercial Business Manager, Dyson Thermal Technologies Kiln Furniture).

Sukhjinder Singh, a Dutch national, originally joined Dyson Group in April 2008 as its new Program Director, and subsequently also took on the role as Managing Director of the Ceramics Division. He holds an MSc in Business (specializing in Strategy, Finance and Marketing) and has a post-graduate Supply Chain qualification. He began his career in The Netherlands as a Management Consultant with KPMG, moving on to work for Shell and Univar, where he held Financial Controller, Strategy, Marketing and Project Leader roles.

Following the MBO, Mr. Singh said of the new venture: “One of the main drivers in my move to the UK was the strong entrepreneurial element to the job. I am delighted that this development and the creation of IPS Ceramics gives free rein to this aspect of my management role and promises to test all the strengths that brought me to the business in the first place”.

Mr. Singh's two fellow directors are experts in kiln furniture and are well known operationally and commercially all around the world. Between them they boast 70 years' experience in the Ceramic Industry.

Ian Wright joined Hewitt Refractories in 1977, adopting roles involving technical, laboratory back-up and quality control issues, and subsequently production management. When Hewitt Refractories became part of Dyson Group, Ian was appointed as Manufacturing Manager for what, at that time, was a business spread over three sites. Ever since the kiln furniture manufacturing was con-

solidated onto the one site in Stoke-on-Trent, Ian has been responsible for managing operations at senior level.

Phil Green gained his ceramic manufacturing and technical experience during 17 years with Wedgwood, after which he joined kiln furniture company Acme Marls in an export sales role (in 1989). Acme Marls was another business which became part of Dyson Group in 2000 and Phil progressed from export sales to his subsequent appointment as Commercial Business Manager of the new set-up. In addition to his broad technical knowledge of the product, Phil has travelled all over the world and has strong links with all the major international and UK ceramics manufacturers.

In addition to marketing products from the Hartshill factory, Dyson Thermal Technologies had formed a strong alliance with Asia's leading cordierite kiln furniture manufacturer, Beijing Trend Industrial Ceramics (Tongzhou, Beijing, China). The companies began working together in 2006 as partners to supply kiln furniture to the global market. By training personnel at Beijing Trend, sharing techniques and integrating quality standards, it quickly became possible for Beijing Trend to make its whole range according to Dyson's high quality process and specification. The IPS Ceramics Team has announced that this manufacturing and commercial cooperation will continue following the MBO.

Guo Haizhu, Managing Director of Beijing Trend, said: “IPS Ceramics will continue with what is already a long-term relationship with Beijing Trend. Trend and IPS will intensify this partnership in the future and capitalize on each other's respective strengths in order to offer our global customers quality products, the highest levels of service, quicker delivery and the most competitive prices. We are confident that IPS/Trend will be the leader of the global kiln furniture market”.

“In pursuit of this even closer relationship, I will initially be spending an increased amount of time at the Trend facility in China,” confirmed Ian Wright. “It is important at this stage for me to continue to assist the 320-strong team in Beijing with our ambitious program of technical enhancement and new product development. We have already discussed exciting prospects for our future cooperation and the MBO gives us full scope to exploit our excellent relationship with the Trend management”.

The establishment of IPS Ceramics means the continuation of a 150 year-old tradition in kiln furniture design and manufacture and, at the same time, a driving forward of the business by an experienced and dedicated team which is fully committed to maintaining all the close links it has with ceramic companies around the world.

“A carefully planned MBO was the only real option for the Kiln Furniture business and we are grateful to the Board of Dyson Group for having given us its support and encouragement,” said Phil Green. “We are recognized as a team that, above all, understands the complexities of all our customers' manufacturing operations and we will find a way to come up with the right products at the right price, delivered according to the required schedule.

“We have already begun visiting and calling customers to introduce IPS Ceramics, and our future actions will demonstrate that we aim to continue with product development, to enhance technical performance at every level, to always set quality values as a priority and to maximize the potential of all facets of the business – from human resources to manufacturing capabilities to leveraging our geographical advantage.”

IPS Ceramics has customers in major production sectors, such as tableware, sanitaryware, tiles, powder metallurgy, electroporcelains and special applications. These remain the focus for developing the business at this stage and, accordingly, one of the initial targets of the MBO Team has been to retain key skill sets in these areas. In a strongly competitive environment, price obviously remains an equally important consideration; therefore the agreement between IPS Ceramics and Beijing Trend is essential in enabling the Company to deliver exactly what its customers require.

In the meantime, the Company is dedicating itself to maintaining full customer service during this transitional period and the close liaison with all global clients is expected to result in a smooth takeover.

For more information contact: IPS Ceramics Ltd, Shelton New Rd., Hartshill, Stoke-on-Trent, Staffordshire, ST4 6EP, England, Tel: +44 (0)1782 711511, Fax: +44 (0)1782 717078, Commercial Office: [enq@ipsceramics.com](mailto:enq@ipsceramics.com), Website: [www.ipsceramics.com](http://www.ipsceramics.com).

#### **FIRST EVER CHINA REFRACTORY DIRECTORY 2009/10 JUST PUBLISHED**

An English-version CHINA REFRACTORY DIRECTORY 2009/10 has just been published and is now available to the business public.

New to market, CHINA REFRACTORY DIRECTORY 2009/10 is the only source of the English-language information available on refractory industry in China. It is the first of its kind and only comprehensive Chinese refractory directory that has ever been published. This powerful directory is your connection to the entire Chinese refractory industry sector.

The 339-page directory (ISBN: 978-0-9733166-3-6) provides a comprehensive listing of 2,184 refractory companies throughout China. The information given includes company name, names and titles of key persons, brief description, product lines, and contact details (address, telephone and fax numbers, e-mail addresses and websites).

Dr. James Han, president of Business Data International Inc., believes the directory fulfills a need for the delivery of quality data on the Chinese refractory industry.

"For marketers or researchers targeting China's markets, trying to find reliable, current data has always been a troublesome task, with very few information in English being available to them. What this directory aims to do is plug this gap, offering those looking for such information a real choice."

The directory is available for US \$199.95 from Business Data International Inc., [info@businessdataintl.com](mailto:info@businessdataintl.com) or Fax: +1 (450) 619-2532, [www.businessdataintl.com](http://www.businessdataintl.com).

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

Demonstrating a commitment to consistent delivery of quality products and services, Rath Incorporated has announced that it has achieved ISO 9001:2008 certification.

ISO 9000 is a series of five major standards for quality management and quality assurance established in 1987 by the International Organization of Standardization, representing a consensus on quality systems from more than 100 countries. ISO 9001 is considered the master model and the most rigorous certification to obtain, as it has more than twenty criteria to be met in areas such as management responsibility, contract review, process control, design, development, production, installation, service, and training.

At the heart of ISO 9001 is a close analysis of current documentation and quality systems. "In the industrial sector, documented processes that demonstrate continual improvement of business practices are critical to ensuring consistent delivery," said Frank Rowe, Technical Manager for Rath USA. "ISO certification is about commitment – to delivering the best, high-quality products and service to our customers. It means delivering what we say we deliver, and having the processes in place to prove it. The industry recognizes that commitment by making ISO certification an entrance requirement for doing business." Adds Vice-President Ralph Grizzel, "It is with great pride that we announce our successful achievement of ISO 9001:2008 certification. We truly hope that our commitment to quality is apparent in everything that we do."

While ISO 9000 standards are becoming necessary for conducting business internationally, only 12% of U.S. companies have completed the registration process, as reported in Quality Management Journal.

Rath Incorporated's successful achievement of ISO 9001:2008 registration now completes certification for Rath USA, which includes Rath Refractories in Milledgeville, Georgia. In addition to the Newark, Delaware and Milledgeville, Georgia plants in the U.S., Rath is ISO 9001 certified in Austria, Germany, and Hungary. Rath USA is the North American subsidiary of the Rath Group, a world leader in refractory materials and the practical application of ceramic fiber technology. More than 100 years ago in Vienna, Austria, Rath AG began as a manufacturer of specialty bricks for home heating systems. Since then, Rath has evolved into a leading provider of refractory solutions around the world.

For additional information, contact Tel: (302) 294 4446, Fax: (302) 294 4451, email [info@rath-usa.com](mailto:info@rath-usa.com), or visit <http://www.rath-usa.com>.



**Ads must be received by  
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# THE DRY OUT PROFILE OF STEEL MICRO-FIBER CONTAINING REFRACTORY CASTABLES

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Polymeric fibers have been shown to improve the dry out of castables by at least two different mechanisms: (i) permeability increase after fibers burn out and (ii) mechanical reinforcement. Polypropylene and polyaramid are examples of fibers which perform with these characteristics, respectively. This paper shows that steel fibers are also capable of improving the dry out of castables by reducing the risk of explosive spalling through mechanical reinforcement. To accomplish this, however, they need to be distributed as close as possible to each other in the matrix, which depends on their size and volume concentration in the refractory. Steel micro-fibers (20  $\mu\text{m}$  diameter) were effective in avoiding castable explosion (0.36 vol%), whereas regular fibers (450  $\mu\text{m}$  diameter) attained an outstanding performance when used in a much higher quantity (30 vol%).

## INTRODUCTION

Over the last decades, castable technology has evolved significantly, leading to denser and more resistant materials. Conversely, this advance has imposed more difficulty on the water withdrawal from inside the refractory bodies during heat up. To overcome this, a number of technologies have been developed, including the use of fibers.

**Figure 1** depicts the three different stages of water removal from castable specimens during dry out. Previous studies [1] have shown that, for low-cement high-alumina castables, the critical range is between 130 and 200°C, which is called the water ebullition stage.

Polymeric fibers are an efficient way of enhancing castable resistance to spalling upon drying, either by increasing their permeability or by mechanical reinforcement of their matrices.

Based on the polymeric fiber mechanisms pointed out, this paper presents the potential benefits for improving the castable dry out with regards to the heating rate, speed of water withdrawal and safety.

## EXPERIMENTAL PROCEDURE

The castables analyzed consisted of white fused alumina in the aggregate fraction and different types of reactive aluminas in the matrix. Calcium aluminate cement (2 wt%) was used as a binder. The formulations were based on Andreasen's packing model with  $q=0.24$  and particles ranging from 0.1 to 4750  $\mu\text{m}$ . Casting was performed using 4.2 wt% water and 0.05 wt% citric acid for dispersion.

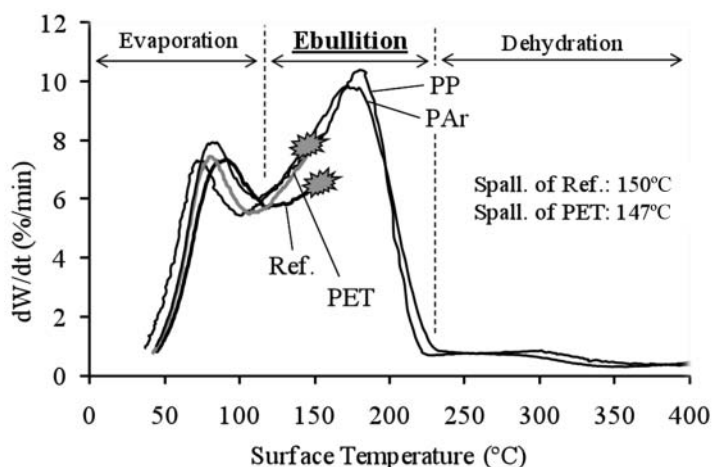


Figure 1. Thermogravimetric analysis of refractory castables containing polymeric fibers (heating rate: 20°C/min) [5].

An exception to the above formulations was the castable with 30 vol% steel fiber (**Table 1**), which requires a special particle size distribution and placing technique.

Five types of stainless steel fibers with varying shapes and sizes were used in the experiments. They are listed in **Table 1** according to their diameter, length and volume concentration in the castables. Their producers were Bekaert (B. S.), Gervois, Stax and Daoli. The polyaramid fibers (PAr) were provided by DuPont under the trade name of Nomex®.

The number of fibers per unit volume ( $N/V_C$ ) and the mean distance among them ( $S$ ) were evaluated according to **Equations 1** and **2**.

$$N/V_C = p/V_{\text{single fiber}} = 4p/\pi d^2 L \quad (1)$$

$$S = (V_C/N)^{1/3} = (\pi d^2 L/4p)^{1/3} \quad (2)$$

Where  $p$  is the volumetric fraction of fibers in the castable, and  $d$  and  $L$  are the fiber diameter and length, respectively.

The castables were cured at 8°C for 7 days in a moisturized environment in order to attain the formation of the  $\text{CAH}_{10}$  phase, which has a higher molar volume and leads to lower permeability, thereby providing the most critical condition for drying.

The work of fracture ( $\gamma_{\text{wof}}$ ) was the property selected to evaluate the mechanical performance. The detailed procedure for this test is described in reference [2].

**Table 1. Characteristics of the fibers and some of their features in the castables**

Fiber	Concentration (vol%)	Diameter ( $\mu\text{m}$ )	Length (mm)	N/VC ( $\text{cm}^{-3}$ )	S (mm)
PAr	0.36	20	6	1910	0.8
B.S.	0.36	20	6	1910	0.8
Gervois	0.36	70	2	468	1.3
Stax 130	0.36	130	4	68	2.5
Stax 225	0.36	180	6	24	3.5
Daoli	0.36	450	25	0.9	10.3
Daoli 2	30.0	450	25	75	2.4

The mass loss on drying (thermogravimetric analysis) was assessed using an apparatus developed by Innocentini et al. [3]. The derivative of the weight loss with the time ( $dW/dt$ ) was recorded as a function of the specimen surface temperature up to  $400^\circ\text{C}$  under a preset heating rate.

A “conventional” drying test [4] was also used to evaluate the castables with regular steel fibers (Daoli). It consisted of inserting the just cured specimens into a furnace previously heated at  $400^\circ\text{C}$  and monitoring the occurrence of explosion or physical damage within 20 minutes at this temperature. The fraction of surviving specimens (out of 4) was recorded.

## RESULTS AND DISCUSSION

### Polymeric Fibers

It has been demonstrated that by adding polymeric fibers to refractory castables can improve their resistance to explosive spalling during dry out. In addition, industrial practice has already consolidated this technology by using polypropylene (PP) or polyvinyl fibers in concentrations varying from 0.05 to 1 wt%, whenever faster drying schedules are required.

More recent research [2] has revealed that the fibers act using at least two different mechanisms:

1. Permeability increase;
2. Mechanical reinforcement.

**Figure 1** illustrates the drying profile of castables containing different types of fibers (0.36 vol%) [5]. It can be observed that those with additions of PP and polyaramid (PAr) were able to withstand the severe heating schedule imposed, whereas those with polyethylene terephthalate (PET) and with no fibers (ref.) did not survive the test.

PP starts to melt close to  $150^\circ\text{C}$ , thereby generating a porous structure in the refractory body, which increases its permeability. This mechanism takes place in the temperature interval where the pressure builds up due to the fact that ebullition of the free water in the castable is in the critical range ( $130$  to  $200^\circ\text{C}$ ). Therefore, the water vapor can be released through the porous channels generated by the fibers without causing damage to the refractory integrity.

Conversely, PAr does not undergo any significant physical change up to its degradation temperature, at approximately  $370^\circ\text{C}$ , where most of the water initially present in the castable has already been released [5]. In this case, the fibers provide mechanical reinforcement, giving rise to a toughening effect, which can be described as follows: during the ebullition period ( $110$  to  $250^\circ\text{C}$ ), if a high heating rate is applied, cracks will be generated and start growing. However, they will cross a large number of fibers in their way, which will dis-

sipate their energy and prevent them from growing beyond a critical size, ultimately reducing the risk of explosive spalling.

Nevertheless, for the latter mechanism to work properly, the fiber must possess good mechanical properties between  $110$  and  $250^\circ\text{C}$  [5]. This explains why PET was not as effective as PAr in the test shown in **Figure 1**. PET has a glass transition temperature of approximately  $70^\circ\text{C}$ , whereas its melting point is at around  $250^\circ\text{C}$ , meaning that in the critical temperature range it will be in a soft state, offering no mechanical benefit. Besides this, the fibers will still be there, not contributing to increase the permeability.

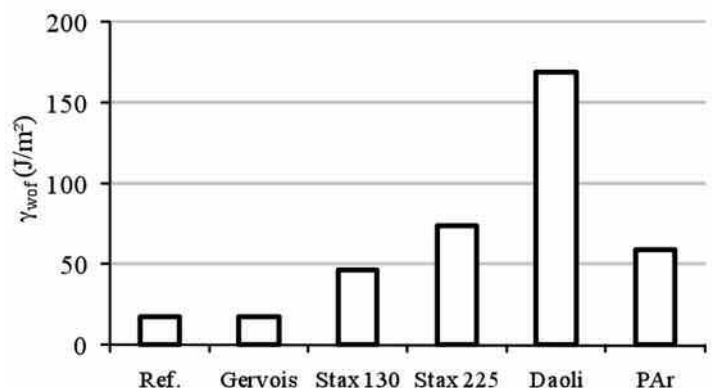
### STEEL FIBERS

Steel fibers are well known for their application as reinforcement of Portland and refractory castables. In the latter case, they have been shown to improve the resistance to thermal shock, to impact and to fatigue when used in quantities varying from 3 to 5 wt%. Additionally, Peret and Pandolfelli [6] have also investigated their potential regarding the optimization of castable drying schedules. Based on the results obtained for PAr fibers, the steel ones would be able to prevent explosive spalling by mechanical reinforcement.

Previous work on PP fibers [2] revealed that the influence of the fibers on the mechanical properties of the castables is much more evident in the work of fracture than in the tensile strength. Therefore, only the former one is considered here.

The first attempts were made by using long (25 mm) and short fibers (**Table 1**) with the same volumetric concentration used for the work on PAr (0.36%), as described in **Table 1**. **Figure 2** depicts the effect of the steel fibers in the work of fracture ( $\gamma_{wof}$ ) of the castables, highlighting how they can significantly improve their mechanical properties.

It can be observed that the longer the fiber is, the higher the  $\gamma_{wof}$  value (**Figure 2**), however, there seems to be a minimum length,



**Figure 2.** Work of fracture ( $\gamma_{wof}$ ) for castables with different types of fibers (0.36 vol%); “Ref”: no fiber [6].

around 4 mm (Stax 130), below which the so-called bridging phenomenon (fiber anchoring and pullout) is not activated in the castable matrix [7].

Despite the good mechanical properties, when tested for different drying rates, none of the steel fibers presented in **Figure 2** was able to prevent the castable specimens from experiencing explosive spalling under the most severe test conditions (20°C/min) [6]. That is, the metallic fibers were not as efficient as the PAr ones, although their effect on the mechanical reinforcement was considerably more significant.

Therefore, the work of fracture alone cannot fully explain why some fibers do improve the drying performance, whereas others do not. By analyzing **Table 1**, one can notice that the number of fibers per unit volume (N/VC) can vary dramatically for the same volume concentration (0.36 vol%), ranging from 0.9 to 1910 cm<sup>-3</sup>, depending on their length and diameter. Accordingly, the mean distance between two adjacent fibers (S) also decreases as N/VC increases (from 10.3 to 0.8 mm). According to Betterman [8], shorter distances reduce the size to which a crack can grow, thus protecting the refractory.

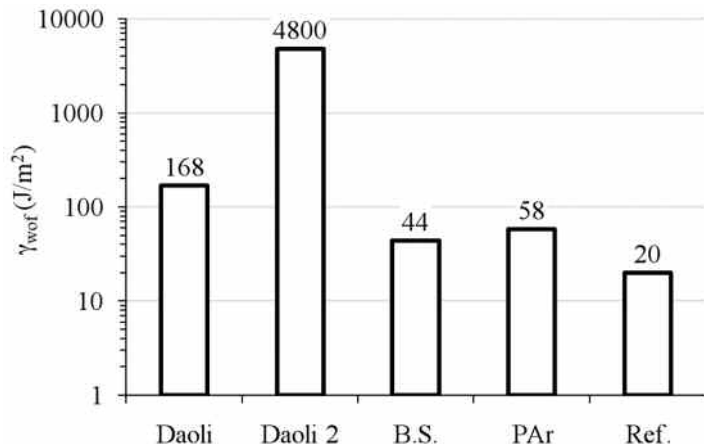
### STEEL FIBERS OPTIMIZATION

In order to increase the number of steel fibers per unit volume, two approaches were assessed. The first one consisted of using fibers with the same dimensions as those for PAr (B.S.), herein called steel micro-fibers, while the second one was to increase the concentration of regular steel fibers (25 mm length) up to 30 vol% (Daoli 2). In the latter case, a special installation method had to be employed to cast the specimens.

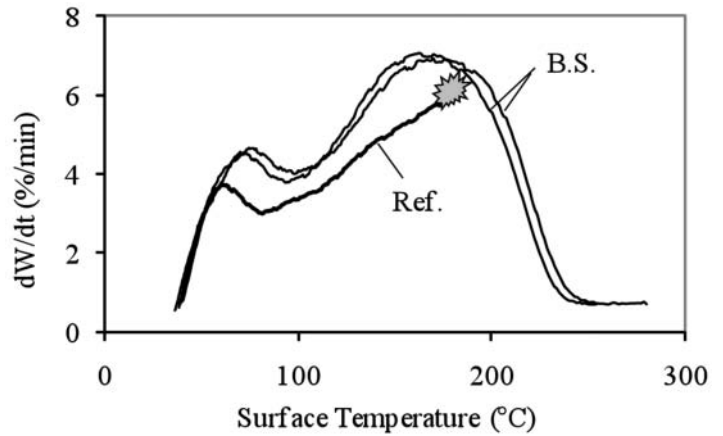
**Table 1** shows that in the case of B. S. both N/VC and S were the same as for PAr, whereas for Daoli 2 they were 75 cm<sup>-3</sup> and 2.4 mm, respectively. The effect of these new fiber additions on the work of fracture is presented in **Figure 3**.

It is worth noting that the  $\gamma_{wof}$  value for the castable with 30 vol% fibers (Daoli 2) was one order of magnitude higher than that with 0.36% (Daoli), and two orders greater than that with PAr. The steel micro-fibers (B. S.) attained a work of fracture similar to that of PAr, which was somewhat higher than the castable with no fibers (Ref.).

The drying behavior of the steel micro-fiber containing material was assessed by thermogravimetric tests (**Figure 4**). Conversely to the regular steel fibers, in this case the castable specimens survived the test. This result is compatible with the theory that for the same



**Figure 3.** Work of fracture for castables with new fiber formulations (Daoli 2 and B. S.).



**Figure 4.** Thermogravimetric analysis of refractory castables containing steel micro-fibers (heating rate: 15°C/min).

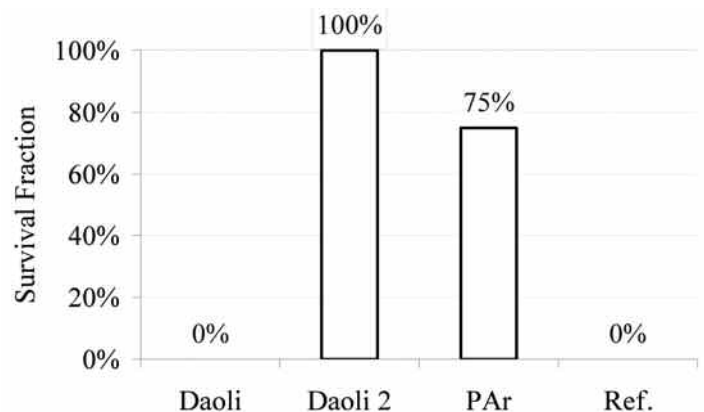
volumetric concentration of fibers, the higher the number of fibers per unit volume and the shorter the distance among them, the lower the risk of explosive spalling.

An additional feature provided by the steel micro-fibers in **Figure 4** is the faster drying rate (dW/dt) of the castable when compared to the reference one. As they are thoroughly and homogeneously distributed throughout the specimen volume, they have the capacity to increase its thermal conductivity, thereby speeding up the generation and the withdrawal of the water vapor.

A faster water release can be an advantage because it may shorten the time required for drying, but at the same time it might mean a higher risk of explosion, since the steam pressurization will be more intense. Therefore, the steel fibers used must be properly selected in order to optimize the drying rate and to avoid undesired side effects.

The castable with high fiber concentration (Daoli 2) was subject to a qualitative test in order to evaluate its tendency to explosive spalling during dry out (**Figure 5**). The results showed that its performance was even better than the castable with PAr, indicating that a very high work of fracture combined with a relatively short distance between fibers provide the optimum conditions for a safe and fast drying schedule.

It is also important to note that, unlike polymeric fibers, the steel ones remain in the castable up to temperatures around 1100°C depending on their oxidation resistance, thus contributing to the



**Figure 5.** Fraction of specimens surviving the qualitative drying test (room temperature to 400°C).

mechanical properties not only during the drying period but also throughout the castable operational life.

Nevertheless, they may require a different design of the refractory lining in order to compensate for the higher thermal conductivity, which increases the heat flow from the hot to the cold face.

## CONCLUDING REMARKS

It has been shown that steel fibers can be used not only to improve castable mechanical properties, but also to speed up their drying behavior. To accomplish this, a high volume concentration of fibers or the use of micro-fibers (20 µm diameter) is needed.

Besides avoiding the growth of micro-cracks in the castable matrix, the steel fibers also provide a faster drying rate due to their high thermal conductivity.


Therefore, as far as the design of high performance monoliths is concerned, it is recommended that the steel micro-fiber approach should be considered not only from the mechanical point of view, but also as an alternative to resume operation in a shorter time.

## ACKNOWLEDGEMENT

The authors are thankful to FAPESP and Magnesita S. A. The producers of the fibers are acknowledged for providing the samples used in this work.

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TRI News Continued from Page 4

n't have to address any tax provisions this year, but it is certain it will. No member of the House or Senate facing reelection in the fall can sit by and just let things be. Consider the following:

- The Bush individual and corporate tax cuts expire at the end of the year. Maximum individual rates will automatically revert to 39%.
- Provisions which decrease the "marriage penalty" expire this year.
- The Alternative Minimum Tax continues to impact significantly more Americans than Congress ever intended.
- The capital gains rate reverts to 20% at the end of the year. The president has said he wants that to happen.
- As of this writing, the federal estate tax, the infamous "death" tax, does not exist. It expired on December 31, 2009, as did the "stepped up" cost basis for capital gains and generation skipping provisions and Bush era changes to the gift tax limits.
- Currently, there is no corporate tax credit for R&D. It expired for the 14<sup>th</sup> time at year-end.

All the above-mentioned issues will be addressed in some manner, and whatever is enacted likely will be made retroactive to January 1, 2010. For example, the House of Representatives in December passed a one-year extension of the R&D tax credit, which would increase the alternative simplified research credit from 14% to 20%, but the Senate did not address it. That one, at least, is half way home at least for another year! Also, an agreement on a revision to/extension of the estate tax seems to be close which may set a 45% maximum tax on estates valued at over \$3.5 million.

Whatever happens, it is clear that the practice of putting piece-meal patches on the tax code as well as the tradition of kicking tough decisions down the road for immediate political expedience have all come home to roost. We now are faced with a perfect storm of financial woes where Congress has to work on the tax code at a time when the federal deficit has skyrocketed due to the economic crash and the resulting bailouts, increasing health care costs—both current and projected--the funding for the wars in Iraq and Afghanistan, and a 10% unemployment rate which results in significantly less tax income flowing to the U.S. treasury. Hold on to your check-books. 



# BASICS OF THE VERTICAL SECTION

Jeffrey D. Smith, Associate Professor, Department of Materials Science and Engineering, Missouri University of Science and Technology, [jsmith@mst.edu](mailto:jsmith@mst.edu)

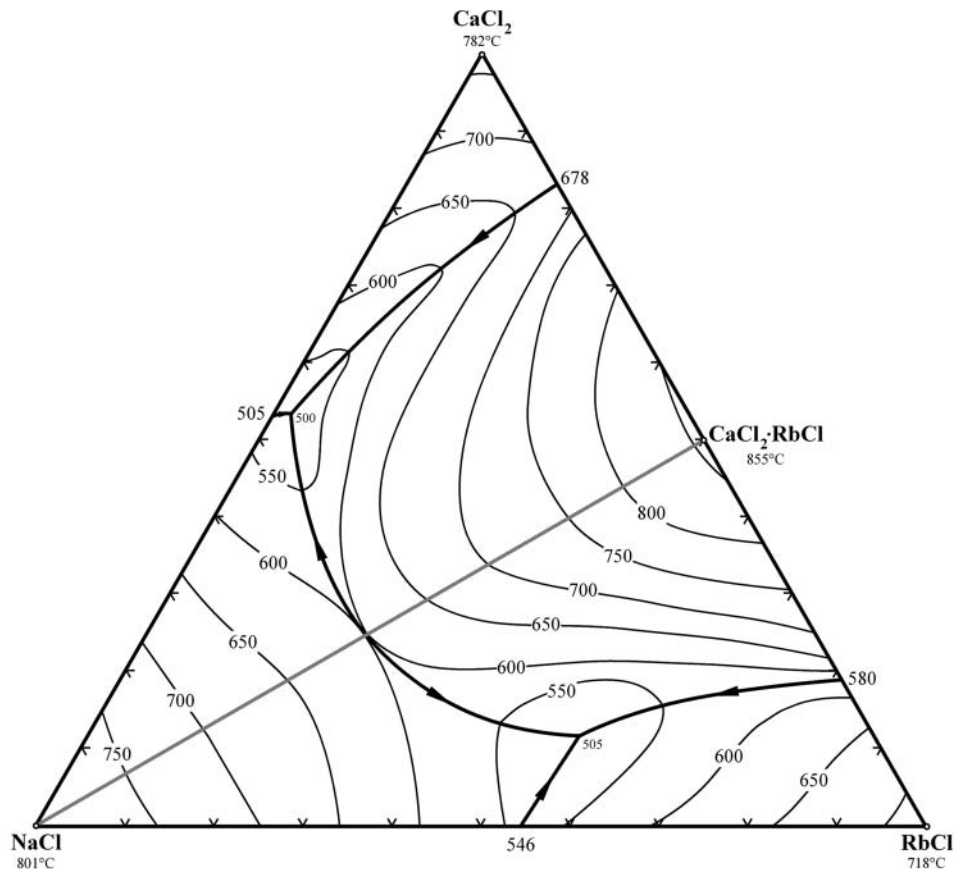
Phase equilibrium diagrams of three components are comprised of a wealth of information. Details of approaches to extract such data were provided in previous installments of *Phase Rules* [1-2]. Understanding and applying the previous tutorials doesn't necessarily provide the data in a form that is easily used to solve engineering problems. Given that most materials engineers and scientists have far more experience (and comfort) working with phase diagrams of two components, the goal then would be to present ternary equilibria data in a manner similar to that which they are already familiar. Vertical sections are just that, ternary phase diagrams projected into a binary phase diagram format.

Once completed, the sections can be used to conduct qualitative isoplethal analyses to determine primary and secondary crystals, and crystallization temperatures, resorption, reaction sequences, solidus temperatures and polymorphic transformations, among others. Obtaining quantitative data from vertical sections is slightly more complicated but the lever rule still holds. The difficulty arises in determining the conjugate phase(s) at the ends of the tie line. Unlike the special case of true binary systems, most vertical

sections are pseudo-binary and the conjugate phases are actually mixtures of two phases. This complication will be addressed in a subsequent issue of *Phase Rules*. The current installment concentrates on explaining the procedure for constructing a vertical section using a fairly simple system.

The NaCl-RbCl-CaCl<sub>2</sub> system was selected for detailing the approach for constructing vertical sections. Although this could not be considered a refractory system, it is relatively simple, containing only one binary compound (CaCl<sub>2</sub>•RbCl) and no ternary compounds. The system contains only congruent compounds further simplifying the procedure. More complex diagrams follow the same set of steps that are described in this manuscript, but add a number of iterations that make the process more tedious. The next installment of *Phase Rules* will address the considerable more complex situation using the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> diagram that has been used previously.

The NaCl-RbCl-CaCl<sub>2</sub> ternary phase diagram is included as **Figure 1**. This diagram was constructed from data published previously in the *Phase Diagrams for Ceramists* compilations [3]. A



**Figure 1.** Ternary phase diagram of the NaCl-RbCl-CaCl<sub>2</sub> system. This fairly simple diagram contains only one binary compound, only two ternary eutectics, and no ternary compounds.

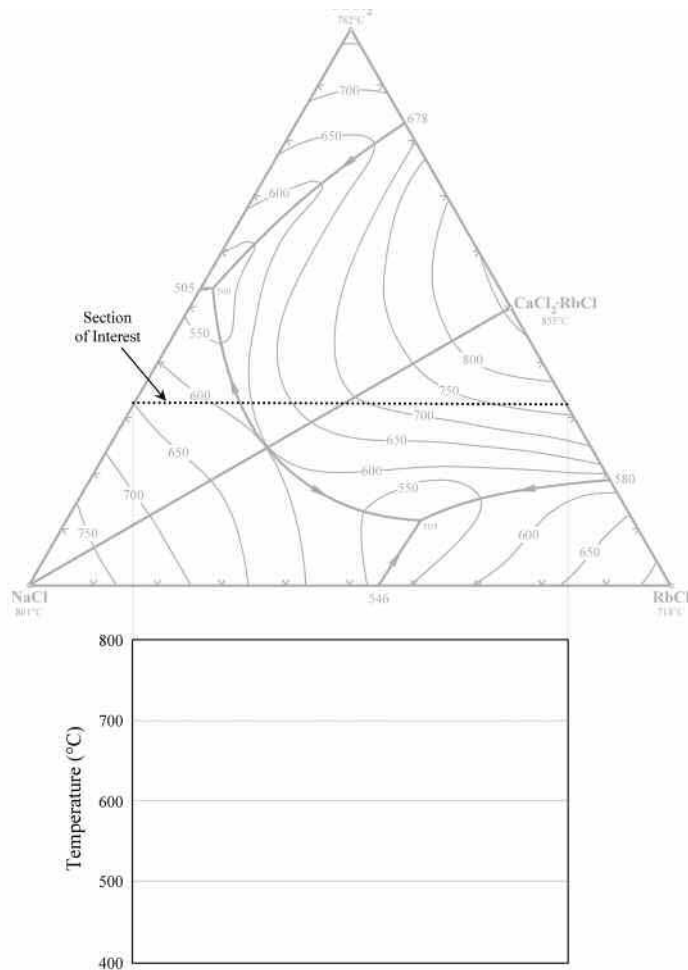
number of small errors (whether of omission or commission) were corrected, including a mislabeled ternary eutectic temperature and a labeling of the binary compound. All other data remain as originally published.

## METHODOLOGY

Vertical sections can be constructed along any line within a ternary phase diagram. The procedure for constructing these sections is straightforward, although at times quite tedious.

The easiest way to construct the vertical section is to select a section line of interest and then rotate the diagram until the section line is horizontal on the page. A box can then be constructed by dropping vertical lines from both ends of the section and then adding a top and a bottom to complete the box. A temperature scale can then be established although it is often difficult to predict an appropriate scale until more information is known.

In the case of the NaCl-RbCl-CaCl<sub>2</sub> system, a composition of roughly 33 mol% CaCl<sub>2</sub> was chosen with the molar ratio of NaCl and RbCl allowed to vary from 0-1 as shown in **Figure 2**. This particular section was selected more for the ease with which the principles could be explained and graphed than anything else. This section is not any more or any less complicated than others that might have been selected.



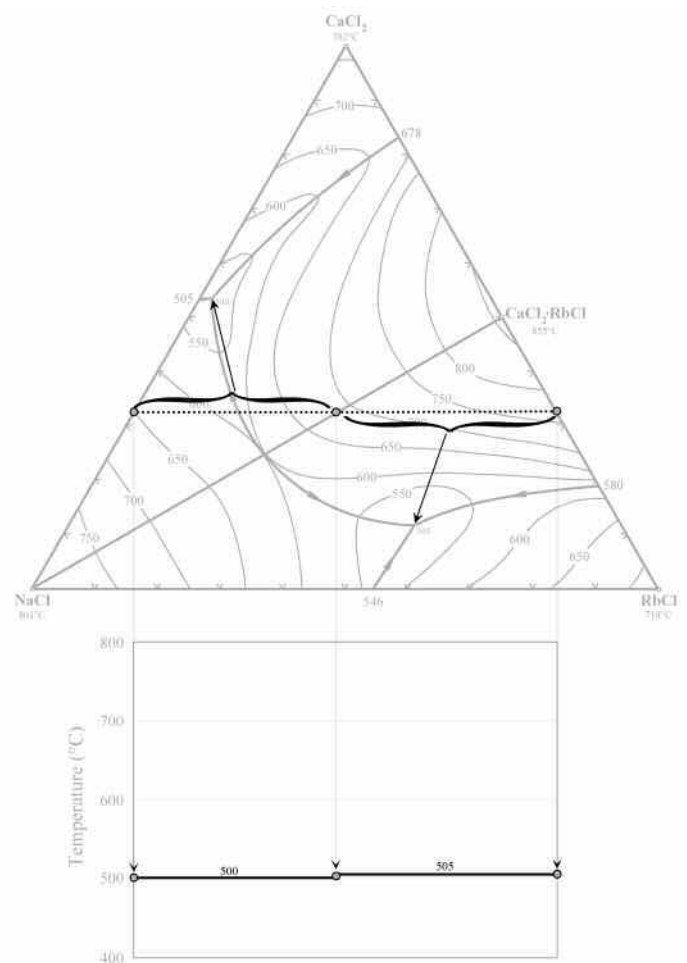
**Figure 2.** A selected section of interest and initial preparations for constructing the associated vertical section.

Once the section of interest is established, the vertical section can be constructed as described in the following sections. The goal of this procedure is to divide the diagram into chemistry ranges that follow the same reaction sequence.

## Solidus Line(s)

The first step in constructing a vertical section is to determine the solidus temperature for each Alkemade triangle that the section line crosses. Recall that for every composition within an Alkemade triangle, the final liquid solidifies at exactly the same point (same temperature and composition). As such all compositions along the section line that lie within a given Alkemade triangle have the same final crystallization temperature. This set of points will appear as a horizontal line similar to the solidus line in a typical binary phase diagram.

**Solidus Lines in the NaCl-RbCl-CaCl<sub>2</sub> System** - The section line, detailed in **Figure 3**, crosses two Alkemade triangles. The first is the NaCl/CaCl<sub>2</sub>/CaCl<sub>2</sub>•RbCl triangle. All compositions within that Alkemade triangle solidify at the temperature specified by the point where the NaCl, CaCl<sub>2</sub>, and CaCl<sub>2</sub>•RbCl phase fields touch (500°C). Vertical construction lines can be extended from the two points where the section line intersects the Alkemade triangle to define the range and then the solidification temperature can be indicated on the vertical section diagram. This results in a



**Figure 3.** The vertical section resides in two Alkemade triangles. The eutectics associated with compositions along the section are identified in the ternary, allowing the solidus lines associated with the eutectic reactions to be constructed in the vertical section.

horizontal solidus line. Repeat the procedure for the other Alkemade triangle, NaCl/RbCl/CaCl<sub>2</sub>•RbCl. For this Alkemade triangle, the corresponding invariant is 505°C.

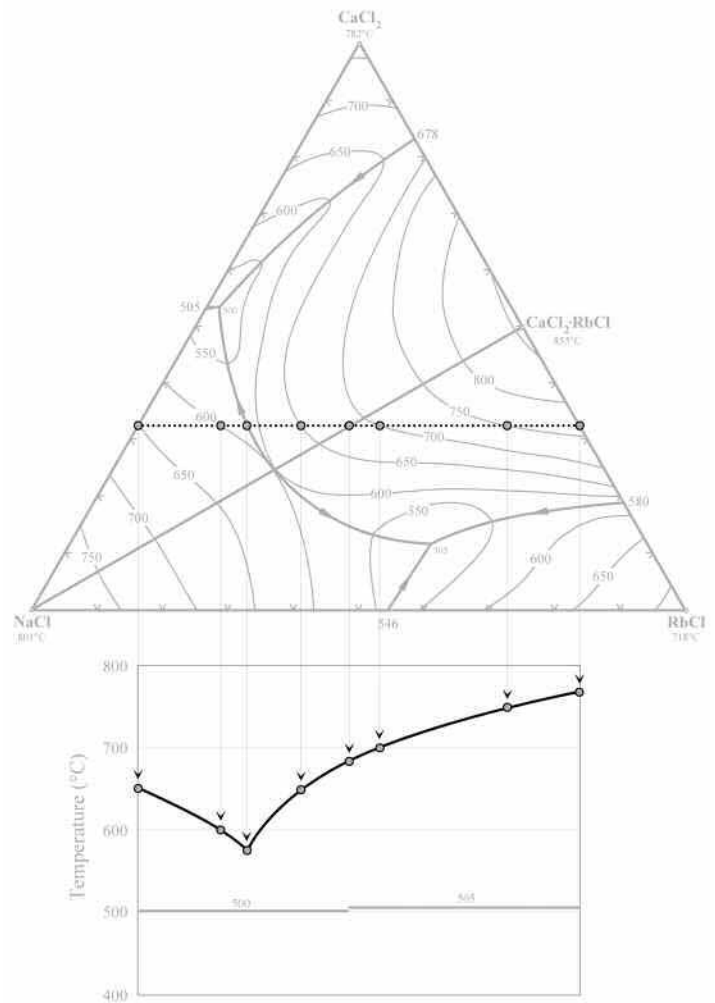
## Liquidus Curves

The second step is arguably the simplest as it only involves plotting the liquidus temperatures along the section line. This requires nothing more than plotting the points where isotherms cross the section line. In true binaries the liquidus curve will contact the solidus line(s). In most vertical sections, however, the liquidus curves and solidus lines will not intersect.

**Liquidus Curves in the NaCl-RbCl-CaCl<sub>2</sub> System** - The procedure for establishing the liquidus curves is presented graphically in **Figure 4**. The process begins by selecting appropriate points along the section line and plotting the corresponding temperature on the vertical section diagram. Many points can be chosen, but it is normally only necessary to plot a few points to get the curvature close. Recall that the temperature change will be smooth within phase fields and that change will occur at phase boundaries and possibly at Alkemade intersections.

Each time the section line crosses an isotherm, that temperature is plotted on the vertical section. Additionally, the ends of the section line and the point where the section line and the NaCl-CaCl<sub>2</sub>•RbCl Alkemade cross should also be included. In these cases, the temperature must be estimated or extrapolated, as specific temperatures are seldom included on the ternary phase diagrams.

It should be noted that any time the section line crosses a boundary curve there will be a change in the curvature of the liquidus. In this case, the point represents a minima. This crossing of the section line and a boundary curve also impacts the pseudo-liquidus curves that will be described in the next section.



**Figure 4.** Liquidus temperatures along the section in the ternary diagram are identified and transferred to the vertical section to define the liquidus line.

## GLOSSARY OF TERMS

*(refer to the previous installment [1, 2, 4, 5, 6, 7] for additional terms of interest)*

**Pseudo-binary** – Any line drawn on a ternary diagram between two compounds where the equilibria is of three components, instead of two.

**Pseudo-liquidus** – A term used to describe lines separating a phase field consisting of two solids and liquid from another phase field also consisting of two solids and liquid, although one of the solids is different.

**True Binary** – A line drawn between compounds on a ternary diagram where the equilibria is of two components. True binaries are characterized by the end members melting congruently and the Alkemade between the components only extending through the phase fields of the two components being considered.

**Vertical Section** – A projection technique where three phase equilibrium is presented in a format loosely consistent with binary phase diagrams.

## Pseudo-liquidus Curves

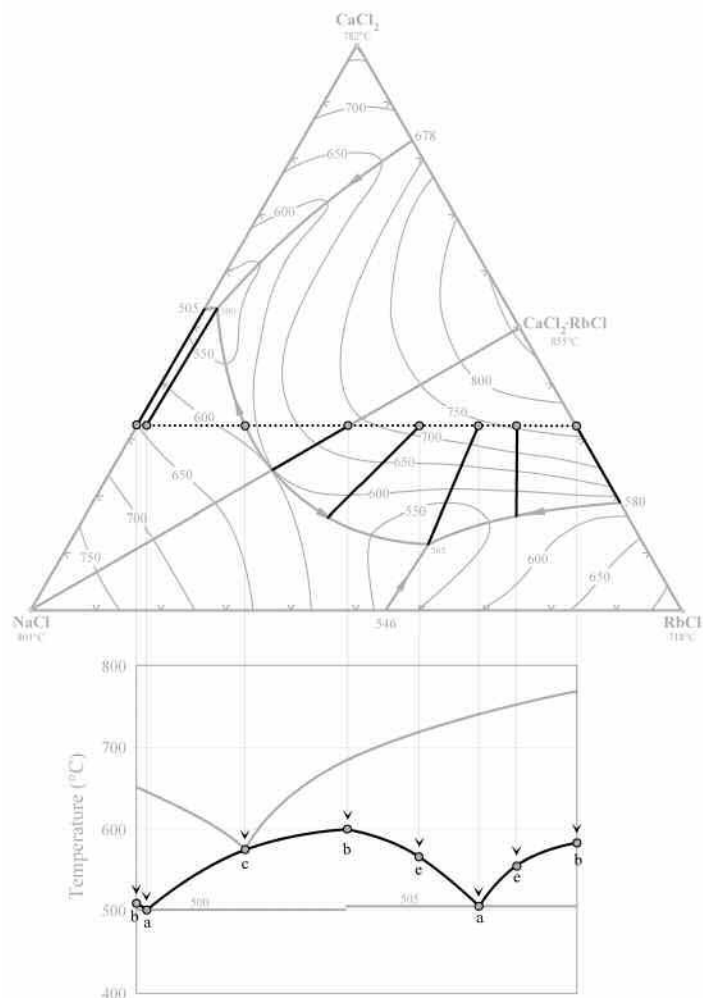
The third step for constructing a vertical section involves adding the pseudo-liquidus curves or lines. This is the first appearance of the term pseudo-liquidus in the literature. In the past, most references to these curves/lines have used the term sub-solidus. Extensive review of the origins of the sub-solidus term have not provided a compelling rationale for the name and, given that the definition of solidus is the minimum temperature at which a liquid can exist, using the term sub-solidus is at best, confusing. As such the term pseudo-liquidus is proposed. The liquidus curves separate the liquid phase field from the phase fields containing liquid and one other solid. The pseudo-liquidus curves/lines separate phase field containing liquid and one solid from fields containing liquid and two solids.

Pseudo-liquidus construction involves considering multiple compositions within each Alkemade triangle. In cases where the section line crosses more than one primary phase field within an Alkemade triangle, compositions within each phase field will be required.

- (a) Identify compositions that will not result in crystallization of two solid phases prior to solidification. Within each phase field, this composition is determined by drawing a line between the component for the phase field in question and the invariant point for the associated Alkemade triangle. The intersection of

this line and the section line defines the composition where the pseudo-liquidus will contact the solidus.

- (b) Identify compositions where the section line and Alkemade lines intersect. These points represent the compositions that will have the highest degree of two-phase crystallization (crystallization progresses along the full length of the two-phase boundary). Note that the compositions considered should be slightly off the Alkemade lines but so close that the temperatures are effectively the same. Solidification of the composition directly on Alkemade lines are somewhat different and are addressed later in this manuscript.
- (c) Identify compositions where the section lines intersects a boundary curve. Such compositions will not result in crystallization of a single solid, but instead two solids will crystallize from the liquid compositions where the section line and a boundary curve intersect are, therefore, points where the liquidus curve and the pseudo-liquidus curve intersect.
- (d) Identify compositions that intersect lines drawn from the component composition for the phase field, through the section line and on to any additional invariant that touches the phase field. In systems where there is only one invariant associated with each phase field, no such additional compositions exist. In more complex systems, as will be described in the next installment of *Phase Rules*, compositions of this type will be quite frequent.
- (e) Identify other compositions to help establish the curvature of the pseudo-liquidus curves. Normally only one or two compositions are necessary to provide reasonable precision.



**Figure 5.** Important compositions along the section in the ternary diagram are identified along with their partial crystallization paths (shown in heavy line). The paths in the ternary are used to identify the temperature at which each composition begins to crystallize more than one solid phase. These temperatures are transferred to the vertical section in order to define the pseudo-liquidus. The designations (a, b, c, e) are detailed in *Pseudo-liquidus Curves* in the text.

### *Pseudo-liquidus Curves in the NaCl-RbCl-CaCl<sub>2</sub> System -*

Consider the compositions at the edges of the phase boundaries. Determine the temperature at which the composition transitions from one solid phase plus liquid to two solid phases plus liquid. Include these temperatures on the diagram for those compositions, as shown in the diagram included as **Figure 5**. These points relate to the (a) compositions described in the previous section. For NaCl, the composition furthest to the left on the section line begins to crystallize two-phases (NaCl and CaCl<sub>2</sub>) at 505°C. For the same phase field the composition furthest to the right begins to crystallize two-phases (NaCl and CaCl<sub>2</sub>•RbCl) immediately upon cooling so no crystallization of a single-phase from the liquid occurs, meaning the pseudo-liquidus must contact the liquidus at that composition. This point relates to the (c) composition described in the previous section.

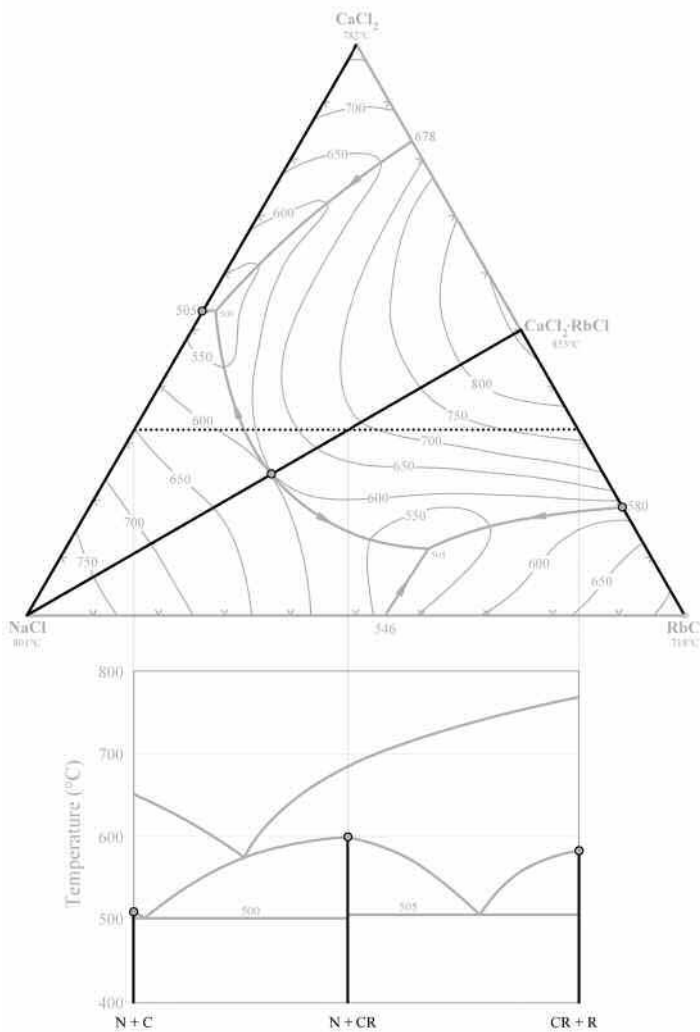
Repeat the procedure for the other phase field and plot all the temperatures on the diagram and connect the lines. Finally consider the composition that falls along the NaCl/CaCl<sub>2</sub>•RbCl Alkemade line within the CaCl<sub>2</sub>•RbCl phase field. Because the composition falls along a true binary, it will solidify at 600°C, the binary eutectic temperature for the NaCl-CaCl<sub>2</sub>•RbCl system. These points relate to the (b) compositions described in the previous section.

Finally select additional points for pseudo-liquidus curvature, detailed as (e) compositions in the previous section. In this case, two such compositions were selected within NaCl/CaCl<sub>2</sub>•RbCl/RbCl Alkemade triangle. Although no additional compositions were chosen within the NaCl/CaCl<sub>2</sub>/CaCl<sub>2</sub>•RbCl Alkemade triangle, two (one on either side of the composition where the section line and boundary curve intersect) could have been to improve the precision of that curve as well.

### **Component Lines**

In two component phase equilibria, component lines indicate how a single-phase compound behaves upon heating. As indicated previously [5] these vertical lines are actually one-component systems within the binary system. If congruent, these compounds will melt into a liquid of the same chemistry. If incongruent, the compounds would decompose into a solid and a liquid, each having a different chemistry than the compound itself.

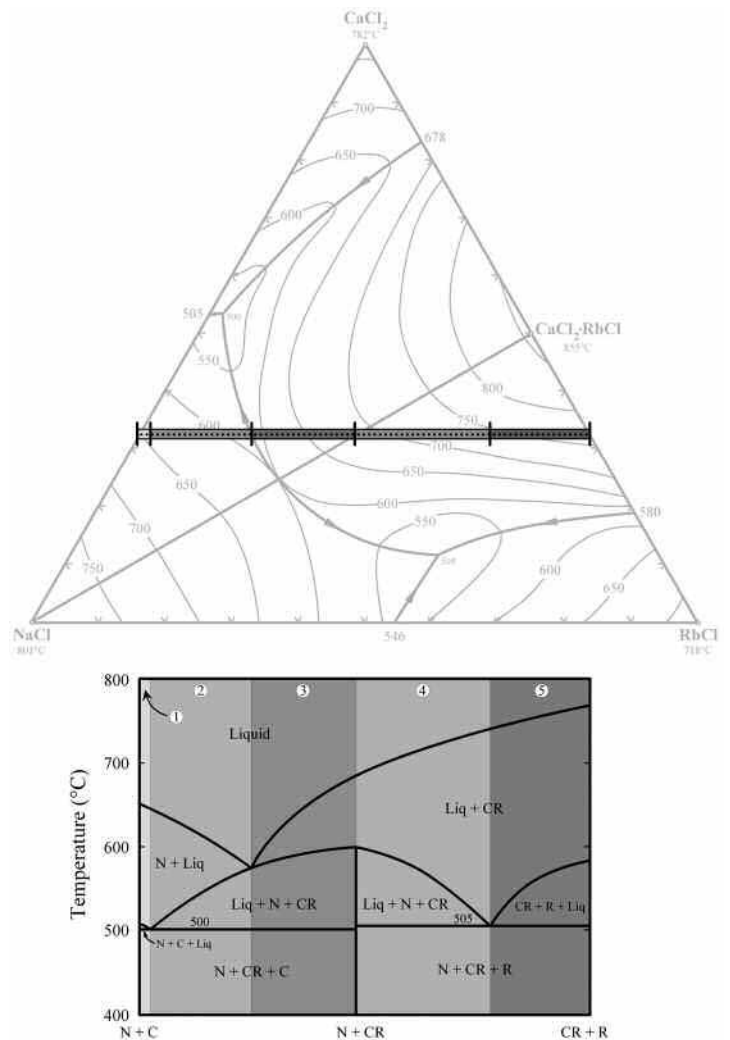
The same logic applies to vertical sections. In this case two different situations can exist. The first is the same as described previously, a single-phase compound that may be either congruent or



**Figure 6.** The compound lines are identified and added to the vertical section. The extreme ends of the section on the ternary intersect the parent binaries and therefore will have binary phase stability upon crystallizing these compositions to temperatures below the binary eutectic temperatures. The section line in the ternary also crosses the NaCl-CaCl<sub>2</sub>-RbCl Alkemade and will have binary phase stability upon cooling below 600°C. Note that N=NaCl, C=CaCl<sub>2</sub>, CR=CaCl<sub>2</sub>•RbCl, and R=RbCl.

incongruent. For such a vertical line to exist in a vertical section, the section of interest would have to be drawn directly through a compound, whether it is a unary, binary or ternary compound. The second situation occurs when the section line crosses an Alkemade line. In this instance the component is actually a mixture of two compounds, each defined by the ends of the Alkemade line in question. These are two-component systems within the ternary system. These vertical lines will always appear as incongruent, dissociating into a solid and liquid or in special cases, two solids and liquid. The latter case will be addressed in a future installment of *Phase Rules*.

Once established the component lines separate the horizontal solidus lines in the vertical section. Normally these lines will extend until they contact the pseudo-liquidus curves, although not always. To be certain, consider crystallization from that composition on the section line, but take care as these compositions will often fall on a true binary join so final solidification occurs at the binary invariant point as opposed to the ternary invariant point.



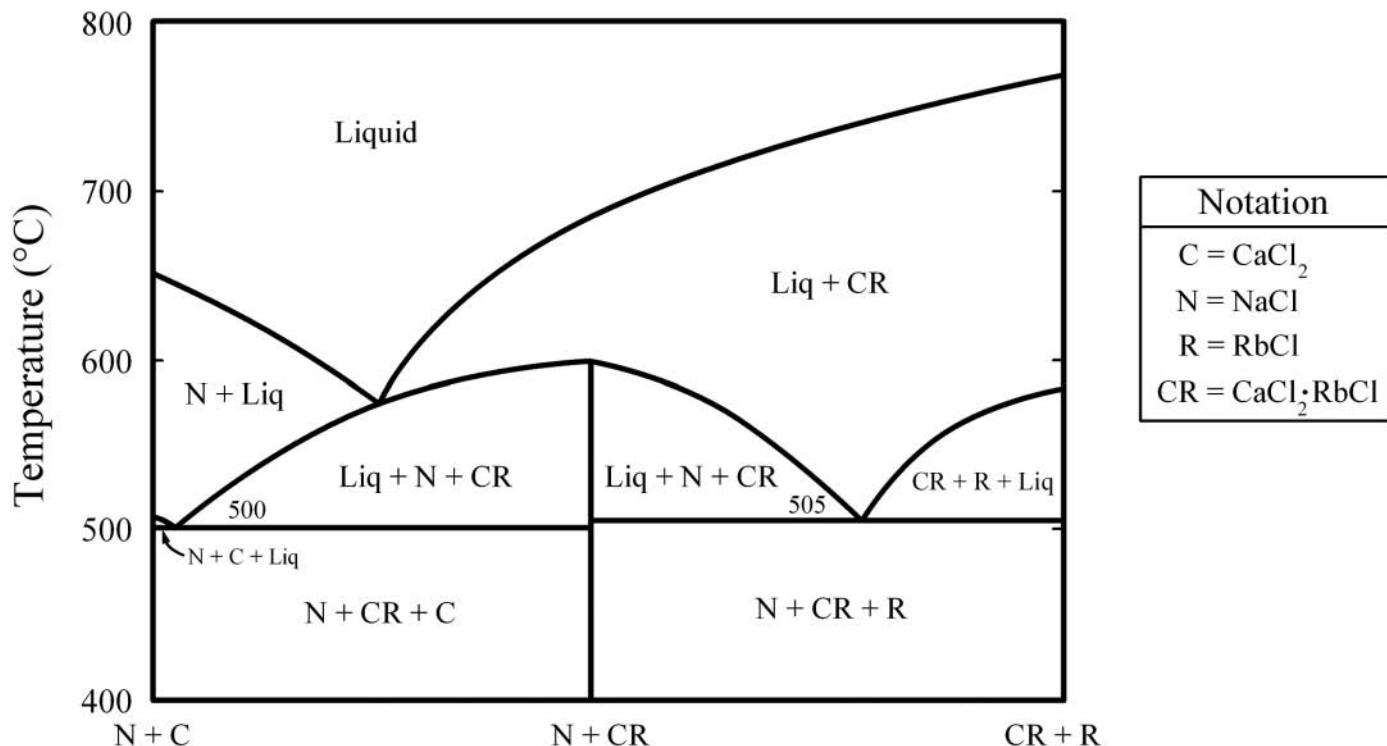
**Figure 7.** The section line in the ternary diagram is divided into five regions of identical crystallization/reaction sequences. All compositions within each region on the ternary section line will undergo the same reactions (although at different temperatures), this can be used as a qualitative check of the vertical section.

### Component Lines in the NaCl-RbCl-CaCl<sub>2</sub> System -

Include a component line on the diagram for each Alkemade line that the section intersects. In this example the section intersects the NaCl/CaCl<sub>2</sub>, the NaCl/CaCl<sub>2</sub>•RbCl, and the CaCl<sub>2</sub>•RbCl/RbCl Alkemade lines. Extend the line up to the temperature at which liquid begins to form (binary eutectic temperatures). For NaCl/CaCl<sub>2</sub> the temperature is 505°C, for NaCl/CaCl<sub>2</sub>•RbCl the temperature is 600°C, for CaCl<sub>2</sub>•RbCl/RbCl the temperature is 580°C. All of these are indicated on the diagram included in **Figure 6**.

### Labeling the Vertical Section

Labeling regions is a fairly simple matter of indicating the conjugate phases for a particular region. Keep in mind that regions above the liquidus can be either one or two liquids. Regions below the liquidus but above the pseudo-liquidus must be two-phases (liquid and one solid) and regions below the pseudo-liquidus must be three phases (liquid and two solids above the solidus line; three solids below the solidus line).



**Figure 8.** The completed vertical section from the NaCl-RbCl-CaCl<sub>2</sub> system with the liquidus, pseudo-liquidus, solidus, and compound lines defined. In addition, all the phase fields have been labeled.

### Labeling the Vertical Section in the NaCl-RbCl-CaCl<sub>2</sub> System

The labeled vertical section is included as **Figure 7**. The labels are obtained by considering crystallization for a number of chemistries. For this vertical section five different regions have a unique reaction sequence. The regions are shaded to different degrees to help highlight the transitions. For example, upon cooling from liquid all compositions within the middle region of the vertical section (indicated as 3) crystallize CaCl<sub>2</sub>·RbCl from the melt, then crystallize NaCl simultaneously with the CaCl<sub>2</sub>·RbCl, and finally CaCl<sub>2</sub> crystallizes with the other two at the solidus temperature.

**Figure 8** is the completed vertical section for the compositions selected. The diagram looks somewhat like a standard binary phase diagram, except for the inclusion of the pseudo-liquidus curves. One must be careful in using the diagram, as the compositions indicated along the ordinate are not as straightforward as in the typical binary diagrams. In this case the far left of the diagram is a combination of NaCl and CaCl<sub>2</sub> while the far right is a combination of CaCl<sub>2</sub>·RbCl and RbCl. Knowing the amounts of each that are present allows determination of the location of a particular chemistry along the diagram.

Determining the concentration of each phase in a component mixture is accomplished using the binary lever rule at the intersection of the section line and each Alkemade line. The conjugate phases for that composition are the phase at each end of the particular Alkemade. In this example the NaCl plus CaCl<sub>2</sub> component line is 67 mol% NaCl and 33 mol% CaCl<sub>2</sub>, the NaCl plus CaCl<sub>2</sub>·RbCl component line is 35 mol% NaCl and 65 mol%

CaCl<sub>2</sub>·RbCl and the CaCl<sub>2</sub>·RbCl plus RbCl component line is 65 mol% CaCl<sub>2</sub>·RbCl and 35 mol% RbCl.

The methodology for constructing a fairly simple vertical section is detailed in this manuscript. Very few ternary diagrams useful to refractory engineers and scientists are so straightforward. The next installment of *Phase Rules* will address a much more complex system. The vertical sections in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system will be used to provide one of the most complicated vertical sections that might be encountered. Extending the basic methodology described in this manuscript will result in constructing a number of vertical sections pertinent to high temperature materials research development and engineering.

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# POLLUTION REDUCTION AS A REFRACTORY SELECTION AND PROCESS IMPROVEMENT METHODOLOGY

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## AUTHOR'S NOTE 2010

This article was written in 1997 and is as true today as it was then in relationship to waste management, however, it is even more important today to expand the survey and team efforts to include not only waste reduction but energy reduction. The refractories using industries are by nature also the energy using industries. Improvement team efforts today must also include energy reduction as a goal. Technology changes abound, for burner control, reduced heat transfer materials, emissivity modification coatings, and lining designs that enable "go cold" practices.

It is as true today as in 1997, the only way to improve is to empower your teams to make change, the manufactures that will win in this century are those that will manage their process the most effectively, working on waste and energy reduction is one way to improve your chances for survival.

Since the creation of the EPA, the focus of industry and regulators has been to control pollution. Millions of dollars have been spent in the process of collecting our emissions and then disposing of them. This process has given us better air quality, better water quality and more controlled land disposal methods; but has done little to reduce the pollution generated by industry. Recently there has been a wind of change blowing through industry and government. This change can be best expressed as the movement from control towards prevention of pollution.

We all are aware of horror stories about adding control technology to process to stop one problem only to create another even larger problem. During the 70's, industry added dust collectors and scrubbers to their processes. This new technology effectively reduced the air emissions but often created new solid or liquid waste problems. The focus had been how do we control our emissions not how do we reduce them.

Because of these past problems, the concepts of Multi-Media Pollution Prevention have begun to take hold in industry and government. Multi-media Pollution Prevention means we must look at all sources of pollution when we make a change, even if the change is to control an emission.

The key concepts of pollution prevention are simple:

- Make as little pollution (waste) as possible.
- If you make pollution, make it as low in toxicity as possible.
- If you make waste, recycle it in the process that generated it.
- If you can't recycle, reuse it in another industrial process.

- If you can't reuse it, reclaim a portion of the waste.
- If you can't reclaim the waste, treat it to reduce the toxicity and dispose of it in the safest manner possible.

The interesting thing about the above concepts is that they not only lead to reduced pollution but also often lead to cost reductions. In today's environment of pollution control, the idea that environmental improvements can be cost reductions may seem a paradox. However, if you look at the dramatic changes that have taken place in our basic industries in the past two decades it becomes clear that pollution reduction and cost reduction have often come together.

We will explore some examples of pollution reduction that have occurred in the refractories-using industries over the past decades. In doing so we will try to develop a methodology that exploits the effort to reduce pollution to yield an added benefit of cost reduction.

## MAKE LESS OF IT

One classic example is the increase in production of steel by the mini-mill. The mini-mill is a classic example of a reuser; scrap steel from many sources is converted to new usable steel. In the process, less energy (re: pollution source) is used and a one-time waste becomes a raw material.

The refractories-using industries all have examples of changes in refractories selection and in their processes that have greatly reduced pollution and cost. The driving force to these changes has been cost reduction, however, pollution reduction often occurs simultaneously.

The Basic Oxygen Furnace (BOF) is a great example of changes to reduce costs having resulted in reduced pollution. In the early 80's, the average BOF would need a reline in less than 1000 heats of steel. The refractories at that time were pitch-impregnated or pitch-bonded magnesia. In most cases, one or two high wear areas would cause the vessel to need a full reline. This meant that in some areas of the vessel most of the refractory was still intact. The interest of the BOF managers to reduce the cost associated with rebuilding and downtime caused the refractories industry to introduce new products (zoning). This enabled the BOF to last on average 4,000 heats. Further improvements in refractories and process changes such as slag splashing and improved gunning repairs have take BOF life over the 10,000 heat life in the last few years.

The BOF process now has a lower refractory cost per heat – while realizing the great reduction in the amount of solid waste generated. Each BOF that lasts 10,000 heats produces less than 1/10 of the solid waste that it did in the 80's. Improved refractories and changes in our processes have led to reductions in pollution in all refractory using industries, but few rival the BOF.

## **MAKE LOWER TOXICITY WASTE**

The cement industry had relied on low cost mag-chrome refractories since the 60's. As our understanding of the hazards of some chrome compounds increased, it became clear that mag-chrome refractories used in the highly alkaline environment of the cement kiln presented an environmental hazard after service.

Due to the penetration of fluxes in and coatings on the refractories used in the cement kiln, reuse was not possible. Some cement manufacturers tried recycling their linings back into their kilns. However, this potentially caused an increase in chromate level of the cement produced.

In the 80's most major refractories companies began to develop new chrome-free products for cement kilns. Many of these new products failed to provide the service life that mag-chrome products had given. However, after more than a decade of improvements and process changes the cement industry has non-chrome products that perform as well as the traditional mag-chrome.

These actions have clearly been driven by the concept to make waste less toxic. Cost savings from the change to non-chrome refractories may not seem to be possible, until you compare the cost of treatment and disposal compared to the cost of using a non-chrome refractory. With chrome refractories, treatment and disposal can be over \$300 per ton. Non-chrome refractories can be disposed of or recycled at a fraction of this cost.

## **RECYCLE IT**

In recent years, a number of steel manufactures have begun to reexamine that which once was considered waste and they have started using this material in their processes. The best example is the use of alumina-rich refractory rubble as bauxite replacement in the blast furnace. This process not only means that the steel maker has less bauxite to buy but also the disposal cost of the refractory has been eliminated. These two cost savings more than offset the added cost of separation and crushing. Similar success can be found in the use of magnesia refractory rubble as a raw material in slag conditioner.

The primary-copper industry has found the percentage of copper is greater in used mag-chrome refractories from their converter than in the ore that they mine! Today many primary-copper smelters process their spent linings in the same way they process their ore. This has meant more copper return and has reduced both the quantity and potential toxicity of their waste.

## **REUSE IT**

A great example of pollution reduction and reuse is the small electric furnaces used to make fiberglass. This industry had relied on alumina-zirconia-silica (AZS) refractories to line these high output furnaces. Typically, the furnace life was measured in days. There was a general understanding that chrome-alumina refractories could be better, but they cost much more than AZS and the problems with the disposal of chrome made this industry reluctant to change. Despite these problems, as the need for more furnace life increased, trials of chrome-alumina were made. With a 10% chrome product, the life increased markedly.

This led to more trials at higher concentrations of chrome. Today most of this industry is using a zoning concept with all chrome-alumina refractories ranging from 10% - 80% chrome. Furnace life is

no longer measured in days, but in months. Typical furnace life is 3 - 6 months.

Despite this increased life, the environmental problems associated with chrome remained an issue. Working with the fiberglass industry some refractories manufactures developed technology to permit the reuse of this material in the manufacture of new chrome-alumina refractories. This new technology has grown and improved to the point that today most of the chrome-alumina used in the fiberglass industry is returned to the manufactures for reuse. Less waste has been made and what is generated is reused and is no longer pollution!

Another example of reuse is the AOD and RH Degasser; both rely on mag-chrome refractories to give the best life. Since the early 90's many customers have been concerned with the future liability associated with the disposal of mag-chrome; to date no chrome free product has been able to match the life of mag-chrome refractories. Because of this concern some refractories producers have begun to take back the used mag-chrome refractories. With proper demolition methods, very little process contamination is in the used refractories. The used refractories are reused as raw material for the manufacture of new mag-chrome brick and monolithics. This process has removed the concern of disposal of mag-chrome products and permitted the AOD and Degasser to continue to use the type of refractories that give the longest lives (making less pollution).

In a similar example, the float-glass industry has relied on mag-chrome for some areas in their process, most notably the checker stack. Unlike the steel industry, the refractory from this application contains a high amount of process contamination including alkaline compounds and glass. Companies like Universal Materials and North American Refractories have worked with the float-glass industry to develop methods to permit the reuse of this material. This again has enabled the glass industry to choose chrome refractories when they are the best choice to extend lives. Longer life means less pollution and lower cost.

## **RECLAIM IT**

Some mag-chrome and chrome-alumina refractories contain too much process contamination to be considered for reuse. With the EPA Landban on chrome waste higher than the RCRA standards it became much more costly to dispose of this type of waste. Inmetco started a process in Ellwood City, PA, which not only dealt with this type of material in an environmentally safe manner but also reclaimed the chrome as metal for use in the stainless steel industry. Today much of the refractories of this type are processed by Inmetco as well as other chrome waste. Their process not only reduces pollution but also returns an important metal to the market.

Cost savings? Yes, this process can cost less than treatment and disposal, but the real savings are in the lowered liability of reclaiming over disposal. One thing that has become very clear to industry in the last decade is the total cost of waste is not just the present cost but future cost. If a company is involved one super fund, clean up, much greater cost is added to the bottom line than the cost of the refractory that was used.

## **TREATMENT AND SAFEST DISPOSAL POSSIBLE**

Of all the concepts of pollution reduction, this is the least cost effective. It is the last resort that we should use. Even this is a cost savings over the old "toss and keep going" attitude of the past.

How can this be? The answer is again liability. The cost of superfund cleanups and the lengthy and costly process of proving that you did not destroy the environment can destroy a bottom line. Though treatment and disposal is costly, it is the most cost effective method when all else fails. Sadly, it is often the most used method.

Why is this the case? It is simple, we do not account for our cost in a manner that weights the cost of disposal and refractory life. We let things like the cost of a refractory mean what we paid for the product, not what will this product cost from the time I buy it until I need to replace it. Refractory cost based on "cost/ton of product made" is a better method, but even this often fails to look at the full life cycle of the product. Only when all of these issues are taken into consideration can true cost savings and pollution reduction take place.

The above is not only true for the selection of refractories but for all of the materials we buy and use. How can a company develop systems that measure these costs and find the savings that are waiting in pollution reduction?

### THE TEAM EFFORT


First, it must be a team effort. No one department can make this type of project work. All aspects of your business must be

involved. Manufacturing, purchasing, environmental, safety, technical, accounting and legal all understand the cost of a process as it applies to them. Only this team can look at a process, material or combination and give the true cost.

One you have assembled this team where do you start? Start with what can be measured – waste. Look everywhere – air, water and solid waste. Be sure to include waste that is recycled, reused and reclaimed as well as controlled waste. Catalog the amounts, determine the hazards, and determine the cost!

List your waste by quantity (most to least), by toxicity (highest to lowest) and cost. Once you have this list set the team loose to find ways to reduce the top three from each class. Include your suppliers, your trade organizations and even your regulators.

Do not let the process be driven down by "that will never work" attitudes; each team member brings an understanding that only they have. This process is truly a case where the sum is greater than the total of the parts. In 1970, no one would have believed that BOF lives could be 10,000+ heats or that fiberglass electric melters could last six months.

Your list is your greatest source of pollution reduction and cost savings. Your team is the most important process change you can make. Don't wait for regulators to push new controls on your processes – get the savings today by reducing pollution. 

## ST. LOUIS SECTION AND THE REFRACTORY CERAMICS DIVISION 46<sup>th</sup> ANNUAL SYMPOSIUM

The St. Louis Section and the Refractory Ceramics Division of the American Ceramic Society will sponsor the 46<sup>th</sup> 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 – Almatix

"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.

# The Section Needs Your Help . . .

## Date and Subject of Annual St. Louis Section Symposia

Annual	Date	Topic
Forty-sixth	March 24, 2010	Innovative Materials for Energy Efficiency
Forty-fifth	March 25, 2009	Raw Materials
Forty-fourth	March 26, 2008	CSI Refractories
Forty-third	March 28, 2007	Thermal Management
Forty-second	March 29, 2006	Advances in Raw Materials
Forty-first	March 30, 2005	Monolithic Refractories
Fortieth	March 31, 2004	Refractories for Foundries
Thirty-ninth	April 9, 2003	Raw Materials and Monolithics
Thirty-eighth	March 21, 2002	Refractories for Continuous Casting of Steel
Thirty-seventh	March 23, 2001	Refractories for Aluminum
Thirty-sixth	March 26, 2000	Insulating Refractories: Their Production, Testing and Characterization
Thirty-fifth	March 26, 1999	Starting Materials for Refractory Monolithics
Thirty-fourth	March 19, 1998	Refractories for Casting Steel
Thirty-third	March 21, 1997	Refractories for Foundries
Thirty-second	March 22, 1996	New Material System and Placement Techniques for Refractory Monolithics
Thirty-first	March 16, 1995	TQM Models and Their Impact on Improving Refractory Processes
Thirtieth	March 25, 1994	Fundamentals of Refractory Castables
Twenty-ninth	March 26, 1993	Advances in Raw Materials and Binders for Refractories
Twenty-eighth	March 27, 1992	Standardization and Development of Testing of Steelplant Refractories
Twenty-seventh	March 23, 1991	Advances in Refractories for Incinerators, Waste Disposal and Petrochemical Applications
Twenty-sixth	March 30, 1990	Refractories for Worldwide Blast Furnace Melting Practice
Twenty-fifth	March 17, 1989	Refractory Applications in Glass Manufacture and Processing
Twenty-fourth	March 19, 1988	Refractories for Metals Handling
Twenty-third	April 10, 1987	Refractories for Ladle Metallurgy
Twenty-second	March 21, 1986	The Application of Test Data in Refractory Design
Twenty-first	April 12, 1985	Quality Management and Statistical Process Control
Twentieth	March 29, 1984	Changes in Refractory Technology - Applications of Micro Processor Control to Refractory Technology
Nineteenth	April 15, 1983	Changes in Refractory Technology-Characterization of Refractories
Eighteenth	March 12, 1982	Changes in Refractory Technology in Place Forming
Seventeenth	April 10, 1981	Changes in Refractory Technology Forming
Sixteenth	March 28, 1980	Changes in Refractory Technology - Raw Materials
Fifteenth	April 6, 1979	Refractories for Conservation
Fourteenth	April 7, 1978	Changes in Refractory Technology - Testing
Thirteenth	April 1, 1977	Changes in Refractory Technology - Specialties
Twelfth	March 26, 1976	Refractories in the Supply and Use of Energy
Eleventh	April 25, 1975	Material and Processes: Selection and Control
Tenth	April 5, 1974	The Bond in Refractories
Ninth	April 6, 1973	Thermal Failure
Eighth	April 21, 1972	Mass Transport in Refractories
Seventh	April 2, 1971	
Sixth	April 17, 1970	Hot Strength
Fifth	April 11, 1969	Corrosion of Refractories
Fourth	1968	
Third	April 14, 1967	General Refractories Theme (Frist proceedings)
Second	1966	General Refractories Theme (No proceedings)
First	April 1, 1965	General Refractories Theme (No proceedings)

The St. Louis Section of the American Ceramic Society is trying to collect and maintain a list of all past St. Louis Symposia. Any information regarding the symposia in 1965, 1966, 1967, 1968 and 1971 would be greatly appreciated. Information can be sent to Missouri Refractories, morco@refractories.net or (636) 479-7770.

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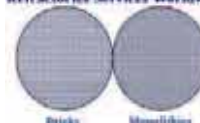
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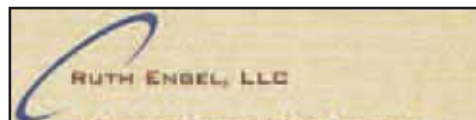
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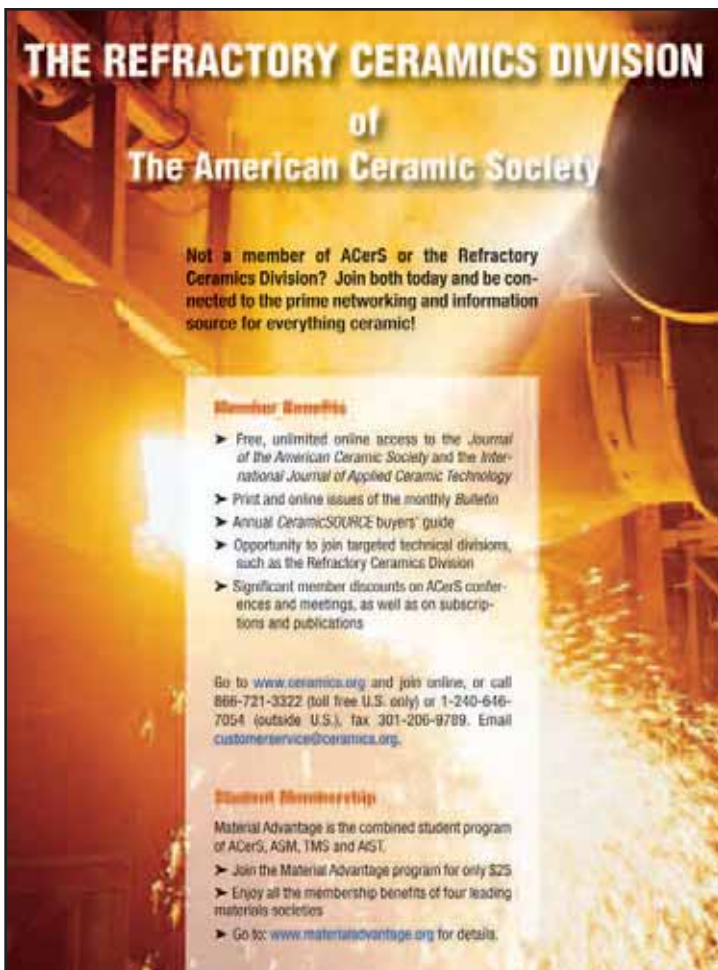
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