

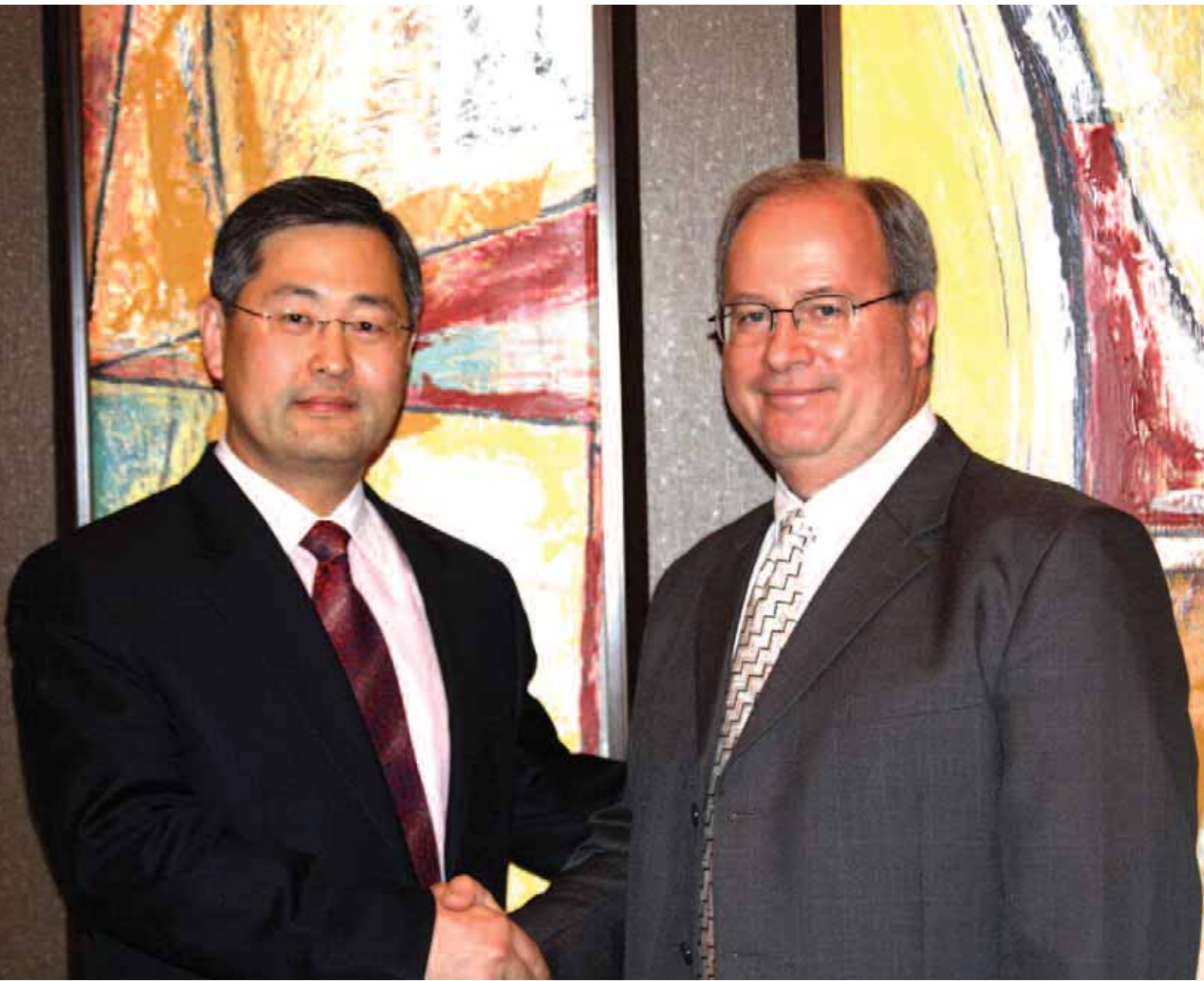
# Refractories Applications *and News*



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Technology Bimonthly for the Global Refractories Industries



**2008 Allen Award winner, Chang Min Chun, Exxon Mobil Research and Engineering (left). Presented by Mike Alexander, Chairman of the Refractory Ceramics Division (right).**



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Jeffrey D. Smith

My editorial that appeared in the last issue was written with the goal to illicit feedback related to the journal. I was pleasantly surprised as to the degree of such feedback and I had fully intended to comment on some of the responses that were received. In light of a recent issue, I have elected to delay that discussion until the next issue of RAN. Instead I want to discuss what turns out to be a related issue.

RAGBRAI is an annual seven-day bicycle ride across the state of Iowa. The ride averages about 500 miles traveling from the Missouri River on the western boarder of the state to the Mississippi River along the eastern boarder. The ride isn't a race but instead a nice week long enjoyable ride with friends, often hundreds participating. In my days as an undergraduate at Iowa State University I can recall my discussions of the ride and often seeing the riders as they made their way across the state.

I bring this up as at this year's event, tragedy struck. That tragedy being the death of a friend and colleague of mine at Missouri S&T, Don Myers, who was involved in what seemed to have been a very innocent looking crash from which he never regained consciousness.

Although most of you would have had not reason to meet Don, a professor in our engineering management department, I worked very closely with him over the past several years in the faculty governance of the university. Don was very committed to this university, devoting considerable time to what we refer to as university service. He was willing to get in and do the thankless work simply because it needed to be done.

So why am I discussing this in this forum? Two reasons. First, I wanted at least to a limited degree, to pay homage to one of my colleagues. Second, I wanted to call attention to the fact that at times the people we rely on, the ones we count on to do things, the ones we might well be taking for granted, may not be willing or able to continue in that role indefinitely.

Death, retirement, promotion, even simply becoming jaded or disinterested, are all reasons that we might lose the volunteers we rely upon. As an industry like ours becomes smaller and smaller in terms of people, we rely more and more heavily on fewer and fewer volunteers.

Who are these people in our industry? These refractory champions, these tireless volunteers. If I asked everyone in the industry to name them, I'm confident that eight or ten would end up on everyone's list.

Perhaps more importantly, how would we respond if they were no longer available to do the things that we have become perfectly happy to allow them to do? I suppose such questions are common in all groups, and I suppose we as with other groups would find people to pick up the slack. I would suggest, however, that we prepare for such inevitable events by encouraging more and more people to share the load so that the loss of any one would be more easily managed.



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## REFRACTORIES RELATED MEETINGS

### 2009

September 23-24, **52<sup>nd</sup> International Colloquium on Refractories 2009**, Aachen, Eurogress, Germany, Forschungsgemeinschaft Feuerfest e.V. – Feuerfest-Kolloquium – An der Elisabethkirche 27, 53113 Bonn, Germany, Tel:+49-(0)228-91508-45, Fax:+49-(0)228-91508-55, E-Mail: [info@feuerfest-kolloquium.de](mailto:info@feuerfest-kolloquium.de), [www.feuerfest-kolloquium.de](http://www.feuerfest-kolloquium.de).

October 13-15, **13<sup>th</sup> Annual Met Coke World Summit 2009**, Hilton Pittsburgh, PA, Tel: +1 207 781 9635 Fax: +1 207 781 2150 Contact: Brian Santos, [brian.santos@pira-international.com](mailto:brian.santos@pira-international.com), [www.metcokeworldsummit.com/](http://www.metcokeworldsummit.com/)

October 13-16, **UNITECR 2009 - 11<sup>th</sup> Biennial Worldwide Conference on Refractories**, Pestana Bahia Hotel, Salvador, Brazil, [www.unitecr2009.org/](http://www.unitecr2009.org/).

October 25-30, **Materials Science & Technology 2009 Conference and Exhibition - MS&T '09** combined with the **ACerS 111<sup>th</sup> Annual Meeting**, [www.matscitech.org/](http://www.matscitech.org/), David L. Lawrence Convention Center, Pittsburgh, PA.

### 2010

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

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

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

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 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.

**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 Crollius**

## **USTR ADDRESSES BAUXITE, SILICON CARBIDE, OTHER MINERAL EXPORTS FROM CHINA**

In June, U.S. Trade Representative Ron Kirk announced that the United States has requested World Trade Organization (WTO) dispute settlement consultations with the People's Republic of China regarding China's export restraints on numerous important

raw materials. China's measures which, according to Kirk, appear to be part of a troubling industrial policy aimed at providing substantial competitive advantages for the Chinese industries using these inputs. The materials at issue are: bauxite, coke, fluorspar, magnesium, manganese, silicon metal, silicon carbide, yellow phosphorus, and zinc. These are key inputs for numerous downstream products in the steel, aluminum, and chemical sectors across the globe. China ranks as a top global producer of these materials. The European Union also requested formal WTO consultations with China on the matter.

Ambassador Kirk said, "We are going to the WTO to enforce our rights, so we can provide American manufacturers with a fair competitive environment and put more American workers back on the job. China is a leading global producer and exporter of the raw materials in question, and access to these materials is critical for U.S. industrial manufacturers. The United States is very concerned that China appears to be restricting the exports of these materials for the benefit of their domestic industries; despite strong WTO rules designed to discipline export restraints.

"U.S. industries and workers can compete against anyone in the world if there is a level playing field, but China's policies on these raw materials appear to tilt that field in favor of Chinese producers," Kirk added. "We are deeply troubled at what appears to be a conscious policy to create unfair advantages for Chinese industries that use these raw materials. Now, more than ever, we must fight against this kind of domestic favoritism."

TRI has been working with USTR on the China trade issue for some time and recently suggested that magnesite be added to the list of subject exports.

The entire USTR news release may be found at [www.ustr.gov](http://www.ustr.gov).

## **ALLIED MINERAL PRODUCTS, INC. EXPANDS AMERICAN PRECAST REFRACTORIES FACILITY AND WAREHOUSE**

Allied Mineral Products, Inc. completed construction of a 92,000 square feet addition March 1 and began operating out of the new space April 1. This brings Allied's total production and warehouse area to just under 500,000 square feet at its Columbus headquarters. Allied's new, enlarged facility includes 50,000 square feet for its American Precast Refractories Division (APR). The remainder of the area will be used to store and warehouse materials for Allied's global operations.

The increased space will expand APR's precast refractory shape making capabilities with specialized and enhanced shapes. The larger APR area houses seven new furnaces which will improve flexibility in firing schedules. Another, new crane with a lift capacity of 20 ton also was installed bringing APR's crane lift capacity to 35 tons. The new APR space also includes a specialty shapes room for controlled castings and a material hot room to optimize material casting properties. There is an area to accommodate high volume production of small shapes and a grinding room to meet precise tolerances. A drive in dock door was added that can be served by the 20 ton crane to easily load and ship large shapes.

## **LEGISLATION**

### **House Health Care Bill Would Raise Taxes on Most Manufacturers**

Leaders in the House of Representatives in July unveiled a 1,018-page health care reform bill – H.R. 3200, the America's Affordable Health Choices Act. Expected to cost more than \$1 trillion over 10 years, the legislation would levy a new tax on those individuals and businesses that file at the individual rate and make more than \$350,000 a year (families/S-corps/partnerships, etc.). The National Association of Manufacturers estimates that the new tax would affect nearly 70 percent of all U.S. manufacturers. Concerns from many different groups about costs vs. benefits may slow the legislation which has been on a fast track up until now.

Of particular concern to some employers is that the House bill would significantly change requirements under the Employee Retirement Income Security Act (ERISA) which currently allows employers to provide standardized employee health insurance plans across state lines. This historically has been one part of our nation's healing care system which has worked pretty well.

### **Plant Closure Bills Introduced**

Legislation to expand the federal 1988 Worker Adjustment and Retraining Notification (WARN) Act was introduced in both houses of Congress at the end of June. Under the WARN Act, employers with more than 100 employees must provide a 60-day advance notification when layoffs of more than 50 workers are expected within a 30-day period. The new legislation (S. 1374/H.R. 3042), dubbed the Forewarn Act, would lower the threshold to companies with 75 or more workers, and to 25 or more layoffs, while expanding the notification time to 90 days. The legislation could be the subject of hearings later this year. Note that some states already have plant-closing regulations more strict than the current federal requirements.

### **Business Interests Call for NOL Relief**

Business interests in Washington are calling on policymakers to seriously consider prompt enactment of Net Operating Loss (NOL) relief legislation, as job losses continue to mount and access to credit markets continues to be tight. Enactment of temporary NOL relief legislation (S. 823/H.R. 2452) would extend the carry back period from two to five years for losses incurred in 2008 and 2009 for companies of all sizes and would help address both of these challenges.

*Continued on Page 18*

# FLUE WALL BRICK CORROSION MECHANISMS IN ANODE BAKING FURNACES

P. R. T. Tiba<sup>1</sup>, B.H. Teider<sup>2</sup>, J. B. Gallo<sup>2</sup>, V. C. Pandolfelli<sup>1</sup>, *tiba\_em03@yahoo.com.br* or *vicpando@power.ufscar.br*

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<sup>2</sup>Alcoa Alumínio S.A., Application, Development and Special Products Sales Area, Rod. Poços – Andradas, Km 10, Poços de Caldas, MG, Brazil

## ABSTRACT

The flue wall brick used in anode baking furnace plays an important role in the aluminum process as its selection and performance has a direct impact on both, furnace costs and the amount of metal produced. In this aspect, the search for optimized compositions which could increase the refractory's working life is always a target due to the close correlation between the brick performance and the furnace maintenance costs. Throughout the anode heat treatment process, some parameters can affect the flue wall brick's working life such as operational practices, baking conditions and the furnace environment. Nevertheless, in some plants, the chemical attack of the brick can be quoted as the main parameter used by the aluminum producer in order to evaluate its replacement. Therefore, the present work aims to present a review about the main mechanisms of corrosion observed on flue wall bricks and, then a case study of a high chemical attack which resulted in their replacement and a major increase of the anode furnace maintenance costs. The results show that the materials chemical attack increase was related to a change in the furnace process. Additionally, it is pointed out that the quality control of the green anode, of recovering coke and of refractory's compositions is essential, when a reduction in the brick corrosion is the aim.

## INTRODUCTION

The large numbers of aluminum producers and the current worldwide economic crisis have induced companies to adopt strategies of reducing energy consumption and metal production costs [1]. Considering the pre-baked technology plants, anode baking furnaces have become an important issue due to the high expenses on fuel, operational practices and refractory materials. Additionally, the baked anode quality also has a direct impact on the pot room performance and, consequently, on the amount of aluminum produced [2].

Basically, anode baking furnaces consist of dense refractories, called flue wall brick and tie brick, and insulating refractories which are the thermal barriers that keep in the heat and save energy. Thus, refractory materials, mainly, flue wall brick, plays a primary role in the process as its selection and performance have a major impact on the furnace construction and the maintenance costs. Additionally, the demand for higher anode productivity using a shorter firing cycle also promotes the search for high quality materials [3-4].

Practical experiments confirm the importance of a suitable selection of these refractories due to the high costs of replacing refractories. However, as well as the quality of refractories, other parameters clearly affect the materials' working life during the anode heat treatment: operational practices, such as loading and unloading of the anodes, baking temperature range, furnace design and the chemical environment [5]. Among these factors, brick corrosion, which is primarily related to the furnace environment, can be quoted as the main variable used by aluminum producers to replace a used one [6].

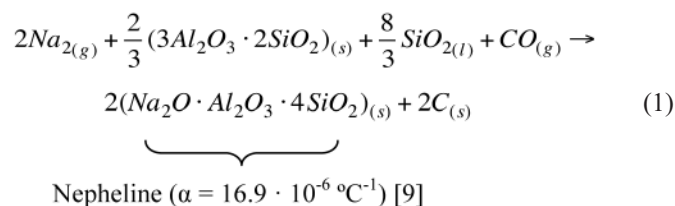
Some papers in the literature show that the brick corrosion mechanism is complex due to the various simultaneous reactions. Migration of CO<sub>(g)</sub> and CO<sub>2(g)</sub> into the brick pores, reduction of the oxide components on the anode side and recrystallization processes during cooling are some of these reactions [6-7]. Therefore, the refractory microstructure becomes a heterogeneous composite, which spoils a proper post mortem evaluation of the main chemical attack mechanism [8].

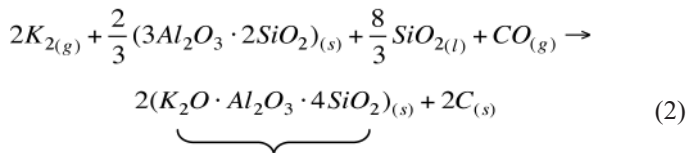
In order to better understand the corrosion mechanisms of refractories, a review highlighting the major compounds in the furnace environment and their reactions with the brick chemical phases is presented. In a further step, a case study of a post mortem chemical attack analyses in flue wall bricks for a specific anode furnace plant will also be presented.

According to the literature, five major elements present in the system can react with the refractories: alkalis, iron oxide, sulfur, fluorine and carbon monoxide [5].

## ALKALIS

Sodium oxide and potassium oxide sources are usually present in the process, including, refractory bricks, burned fuel, recovering coke and the recycled anode (butts) [5]. The main reactions among the alkalis and the refractory are shown below:





Kaliophilite ( $\alpha = 8.5\text{-}11.5 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ) [10]

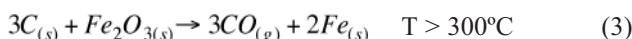
Several authors suggested that the alkali attack mechanism on silica-alumina refractories changes with the alumina content of the bricks [5, 11-13]. For an alumina level corresponding to a typical fireclay brick (around 50 wt% of alumina), the sodium gas reacts with the brick's microstructure, decomposing the mullite and generating nepheline and solid carbon (**Equation 1**), close to 1300°C (furnace operation temperature). This reaction is followed by a volumetric expansion of 10%, resulting in stress and, consequently, cracks in the bricks [12, 14]. Additionally, carbon deposition into the brick pores was detected, which induces mechanical stress in the material.

The reaction between potassium and silica-alumina brick is well known in the literature. The potassium vapor permeates the bricks and reacts preferentially with the matrix and the amorphous phase. Then, cracks are generated in the brick due to the formation of another expansive phase, kaliophilite, reducing the brick's working life [11-13, 15]. Additionally, a carbon deposition in the bricks pores is also detected, increasing the material damage (**Equation 2**).

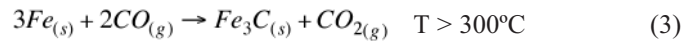
Therefore, one alternative to reduce the materials alkali attack can be the brick's mechanical strength increase in order to keep the brick's integrity throughout the furnace operation. Considering this, the stress generated by the reactions must be lower than the mechanical strength of the refractories. Another approach is to increase the alumina content in the brick's composition and, consequently, to reduce the free silica available for the reactions (**Equations 1 and 2**). However, the literature shows that the alkali's attack in high alumina refractory results in  $\beta$ -alumina, which is also an expansive phase (about 17% in volume). Previous studies confirm that high alumina refractories are susceptible to an alkali attack due to the high volumetric expansion associated to the  $\beta$ -alumina formation [12-13]. Nevertheless, some industrial experiments showed that these compositions present high chemical attack resistance, which is usually related to the lower reaction kinetic [16].

## IRON OXIDE

According to Ellingham's diagram [17], under certain partial pressure of  $O_{2(g)}$  and temperatures above 300°C, the presence of carbon and iron oxide induces the carbon monoxide formation due to the high affinity of the carbon with oxygen. Thus, the iron oxide is reduced, resulting in metallic iron and carbon monoxide, a common oxidation/reduction reaction (**Equation 3**).



In the range of 400°C and 800°C, this free metallic iron will react with CO gas from the environment, producing carbon dioxide and iron carbide which can be dissociated into solid carbon and metallic iron (**Equation 4**) [16, 18-19].



↓



Therefore, the presence of iron oxide also induces the solid carbon formation in the brick, leading to an earlier brick failure. Considering that the flue wall brick is mainly responsible for adding this harmful compound in the system, the aluminum producer must select the brick composition with a low iron oxide content.

## SULFUR

The brick's corrosion by  $SO_x$  follows a linear behavior (**Figure 1**) when the  $SO_{x(g)}$  concentration versus the "dew point" (temperature that the gas turns into a liquid) is plotted.

Firstly, the sulfur gas seeps into the bricks' pores and it is oxidized, resulting in  $SO_x$ . During the furnace operation, an increase in the  $SO_x$  concentration is observed in the brick, affecting the sulfur dew point temperature. For instance, at 1000°C, when the local sulfur content is higher than 650 ppm, the gas turns into a liquid, which fills in the voids of the bricks and reacts with the water vapor from the atmosphere. The combination of these elements and the high temperatures result in sulfuric acid which corrodes the materials' microstructure. Moreover, the simultaneous presence of  $Na_2O$  and  $SO_x$ , forms  $Na_2SO_4$  with, roughly, 10 molecules of combined water. In the heating and cooling cycles, over long periods, the water molecules are lost and recovered repeatedly, creating stresses and, consequently, cracks in the bricks [16].

Therefore, it is essential to reduce the sulfur content inside the furnace in order to avoid the sulfuric acid formation. Most likely, the fuel and the recovering coke are the main source of this compound in the system. However, further studies must be carried out in order to clearly understand its origin.

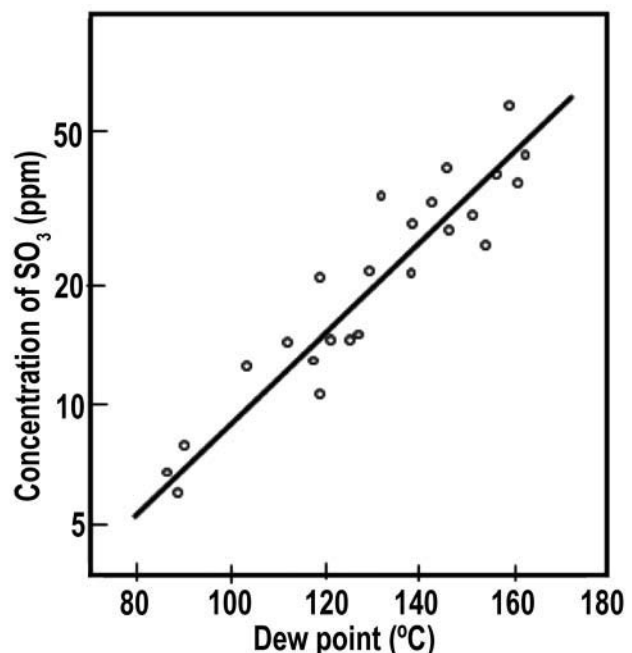
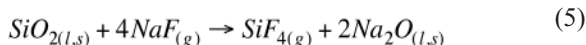


Figure 1. Concentration of sulfur (ppm) versus dew point ( $^\circ\text{C}$ ) [16].

## FLUORINE

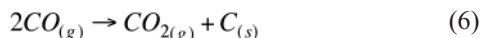
According to Carroll and Grobbelaar [5], the recycled anode used in the green anode composition is the main source of fluorine in the furnace. This element is vaporized at temperatures below 1260°C. Then, the fluorine gas reacts with the free silica of the refractories and generates  $\text{SiF}_{4(g)}$  (Equation 5). At high temperatures, this gas is released out of the brick, resulting in micro-cracks and voids [16]. Additionally, by the reaction below, it is possible to detect the sodium oxide formation, a harmful compound to the refractory, as previously presented.



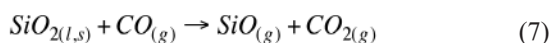
Therefore, the butts cleaning operation is fundamental for the fluorine content reduction and, consequently, to avoid the materials' micro-cracks due to  $\text{SiF}_4$  formation. On the other hand, the cost of this procedure must be taken into account in order to prevent an anode production increase.

## CARBON MONOXIDE

In a reducing atmosphere, as observed in anode baking furnaces, the carbon from the recovering coke and the green anodes react with the oxygen from the system, generating carbon monoxide. As previously quoted, cracks are generated in the bricks due to the mismatch of the thermal expansion coefficient among the phases generated in the microstructure (nepheline and kaliophilite) and the development of undesired products (sulfuric acid and  $\text{SiF}_4$ ). Thus, a higher surface area is available for the  $\text{CO}_{(g)}$  penetration into the bricks, inducing the carbon deposition (Figure 2). This reaction is known as "Boudouard Equation" (Equation 6).



Besides Equation 6, another one is observed at high temperatures. The free silica of the refractory reacts with carbon monoxide resulting in silicon monoxide and carbon dioxide (Equation 7). Hence, the free silica consumption modifies the original microstructure of the brick, spoiling the materials' hot properties.



Therefore, as mentioned previously, the brick's corrosion is not only carried out as described above, according to Pringent et al. [20], sodium oxide helps the formation of the liquid phase, decreasing its viscosity. Due to the capillary forces, this liquid permeates

the refractories, speeding up other chemical reactions such as, sulfur and fluorine attack, carbon deposition and  $\text{SiO}_2$  reduction on the anode side. Therefore, the search for optimized refractory compositions and a cleaner environment are essential when a reduction in furnace maintenance costs is the target.

Another objective of this paper is to apply this previous knowledge in a post mortem analysis as in a specific anode furnace plant; the flue wall bricks did not present the expected performance by the aluminum producer. The refractory's working life was reduced by half due to a high chemical attack and this increased the furnace maintenance cost. In order to understand the main reasons that can lead to an earlier replacement of the brick, a systemic analysis was carried out, based on the information of the previous review and considering the furnace operational practices. As a result, two hypotheses were formulated:

Hypothesis 1: Brick's physical properties – The aim of this approach is to verify whether changing the brick quality could have affected the materials' chemical attack resistance. This is an important feature because over time, for different batches of brick supply, a change in the flue wall brick chemical composition or in their firing conditions, could affect the phases present in the brick's microstructure, increasing the permeability and porosity of the materials and speeding up the bricks' corrosion.

Hypothesis 2: Anode furnace environment – The increase in the concentration of harmful elements present in the furnace can also speed up the corrosion reactions, even if the bricks present a high chemical attack resistance. Therefore, a post mortem analysis of the used bricks was carried out in order to evaluate the behavior of the brick's corrosion. Additionally, an evaluation considering the baking process, the green anode and the recovering coke compositions was carried out in order to investigate the impact of these raw materials on the intensity of the brick's corrosion.

## Methodology

### Hypothesis 1

In order to check if the as-received brick used in the anode furnace plant did not change its composition from batch to batch, some tests were carried out (Table 1) and the results were compared with the values obtained in the qualifying step [21]. It is important to highlight that the evaluated properties were performed with as-received bricks of different batches of the same supplier.

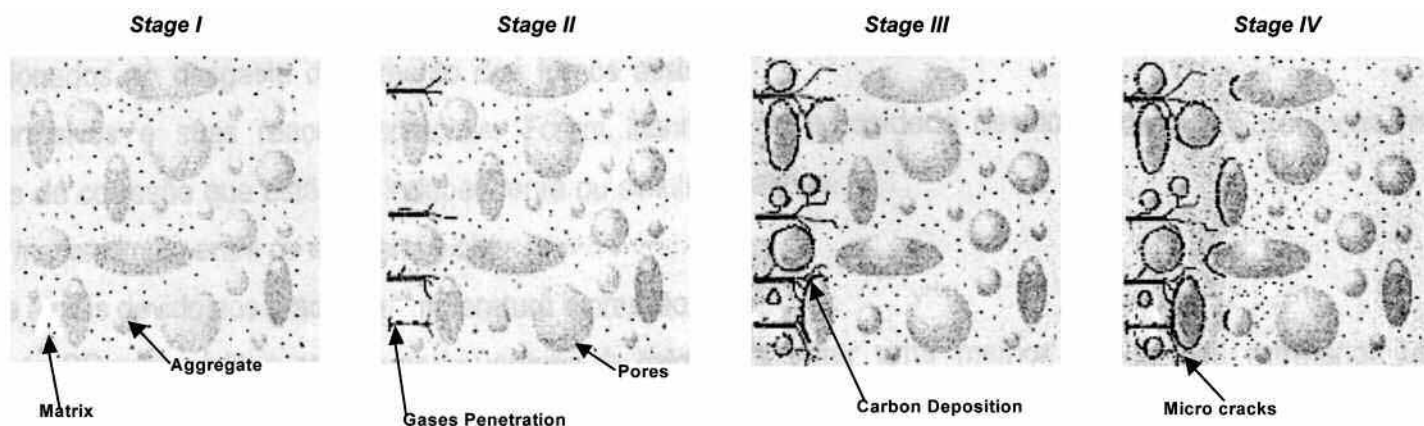


Figure 2. CO attack stages on the refractories [12].

**Table 1. Properties evaluated for the flue wall bricks.**

Property	Unit	Standard
Apparent Porosity	%	ASTM C-830
Apparent Density	g/cm <sup>3</sup>	ASTM C-830
Permeability	k <sub>1</sub> (m <sup>2</sup> ) k <sub>2</sub> (m)	Internal Standard
Chemical Analysis	wt%	ASTM C-573
X-ray Diffraction	-	Internal Standard

The evaluation of the apparent porosity and bulk density was based on ASTM C830.

The air permeability at room temperature was evaluated using an internal standard procedure based on ASTM C577, with 70 mm diameter x 25 mm thick cylindrical samples. The pressure drop and the air velocity were measured and the permeability constants were based on the Forchheimer Equation (8) [22].

$$\frac{P_i^2 - P_o^2}{2 \cdot P \cdot L} = \frac{\mu}{k_1} \cdot v_s + \frac{\rho}{k_2} \cdot v_s^2 \quad (8)$$

where, P<sub>i</sub> and P<sub>o</sub> (atm) are the absolute pressure at the entrance and exit of the sample, respectively; P (atm) is the pressure at the moment that the flow rate is measured; L (m) is the sample thickness; μ (Pa·s) is the fluid viscosity; ρ (kg/m<sup>3</sup>) is the fluid density; v<sub>s</sub> (m/s) is the superficial fluid velocity; k<sub>1</sub> (m<sup>2</sup>) and k<sub>2</sub> (m) are the Darcian (viscous) and Non-Darcian (inertial) permeability constants, respectively.

The chemical analysis was performed according to NBR 3198. For each composition, 200 grams of powder were prepared by milling the brick in a tungsten carbide shatter box and the analyses were performed in fluorescence x-ray equipment (PW 1440 model from Phillips).

The x-ray diffraction analyses were performed in order to identify the mineralogical phases present in the materials using the Rigaku Rotaflex equipment, RU-200B model, with a copper tube and nickel filter. A comparison was made with the JCPDS data files, using Bruker Difrac Plus ® software.

### Hypothesis 2

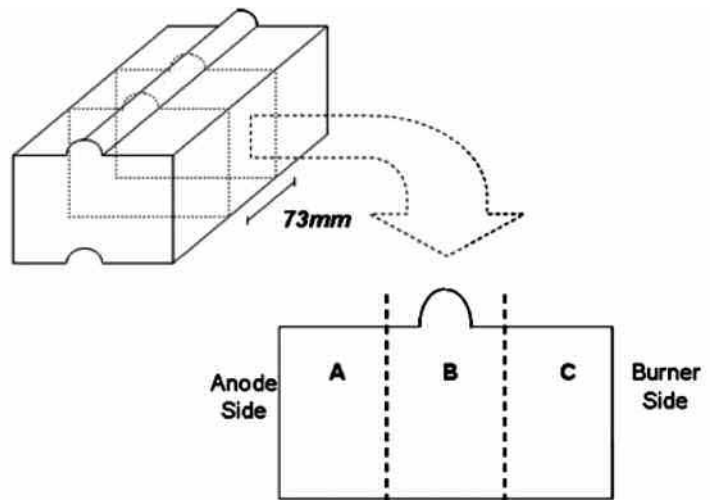
In order to check the interaction among the elements present in the furnace environment and the refractory microstructure, visual inspection and post mortem analysis were carried out.

### Visual Inspection

The first step to analyze the used bricks was the visual inspection. Features such as, brick color, volume change and carbon impregnation at the anode side were analyzed. Additionally, photographs were taken in order to record the refractory's physical changes.

### Post-Mortem Analysis

The second step to verify the degree of brick corrosion was the post-mortem analysis. From the same furnace, three used bricks from distinct regions and all submitted to 83 working life cycles were analyzed. From each used brick, three samples were withdrawn, using Clipper cut-off equipment. It is important to highlight that the letter "A" is related to the anode side of the brick, "B" stands for the middle area and "C" for the burner side (**Figure 3**). The chemical analysis and the x-ray diffraction were also used to analyze the brick's corrosion.



**Figure 3.** Sample regions from the flue wall brick for the post mortem analysis.

## RESULTS AND DISCUSSIONS

### The Brick's Physical Properties

Comparing the physical property results of the present brick and those obtained in the qualifying step, it can be observed that the refractory supplier did not change the quality of the brick. This can be confirmed by the porosity, density and permeability which, practically, maintained close values to the original ones (**Table 2**). Additionally, **Table 3** gives a strong indication that the flue wall brick holds the same chemical composition for different batches. The alumina and silica content remained constant, about 50% in weight and low content of alkalis, sulfur, iron oxides and fluorine were observed for both data. Moreover, the absence of carbon and sulfur in the as-received brick composition and their presence in the post mortem analysis is a clear

**Table 2. Flue wall bricks' physical properties for the qualifying test and the present one.**

	Qualifying	Present
Porosity (%)	14.00 ± 0.60	12.17 ± 0.32
Density (g/cm <sup>3</sup> )	2.41 ± 0.01	2.46 ± 0.01
k <sub>1</sub> (m <sup>2</sup> )	2.43 E-13	7.13 E-13
k <sub>2</sub> (m)	1.87 E-08	3.87 E-08

**Table 3. As-received flue wall bricks' chemical composition.**

(%)	Qualifying	Present
Loss on Ignition	0.09	0.08
SiO <sub>2</sub>	46.73	46.67
Al <sub>2</sub> O <sub>3</sub>	48.85	49.11
Fe <sub>2</sub> O <sub>3</sub>	1.39	1.28
TiO <sub>2</sub>	2.32	2.23
CaO	0.11	0.10
MgO	0.07	0.05
K <sub>2</sub> O	0.15	0.13
Na <sub>2</sub> O	0.02	0.03
ZrO <sub>2</sub>	0.06	0.06
P <sub>2</sub> O <sub>5</sub>	0.06	0.05
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.03
SO <sub>3</sub>	-	0.01

indicator that the source of each element inside the furnace must be investigated.

In order to ensure the materials performance during application and to check the brick heat treatment conditions, such as firing temperature and time, the crystallographic phases present in the bricks were analyzed. **Figure 4** shows the x-ray profile indicating the presence of mullite, cristobalite, rutile, quartz and corundum. A comparative analysis shows a very close profile for the brick compositions from different batches.

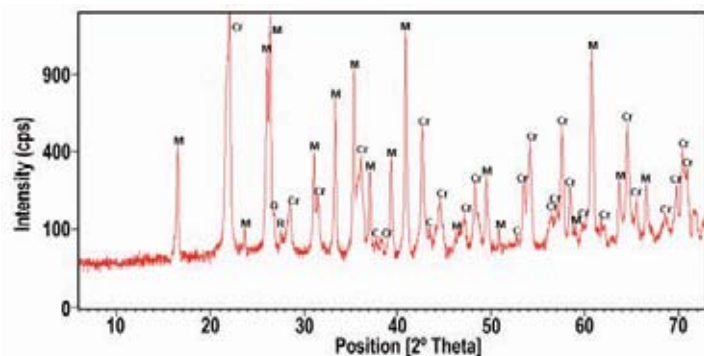
Therefore, if, throughout time, an increase in the chemical attack of the bricks was detected by the aluminum producer, most likely this could not be related, in this case, to the flue wall brick's properties and, hence, the second hypothesis must be checked.

## POST MORTEM ANALYSIS OF THE USED BRICKS

### Visual Inspection

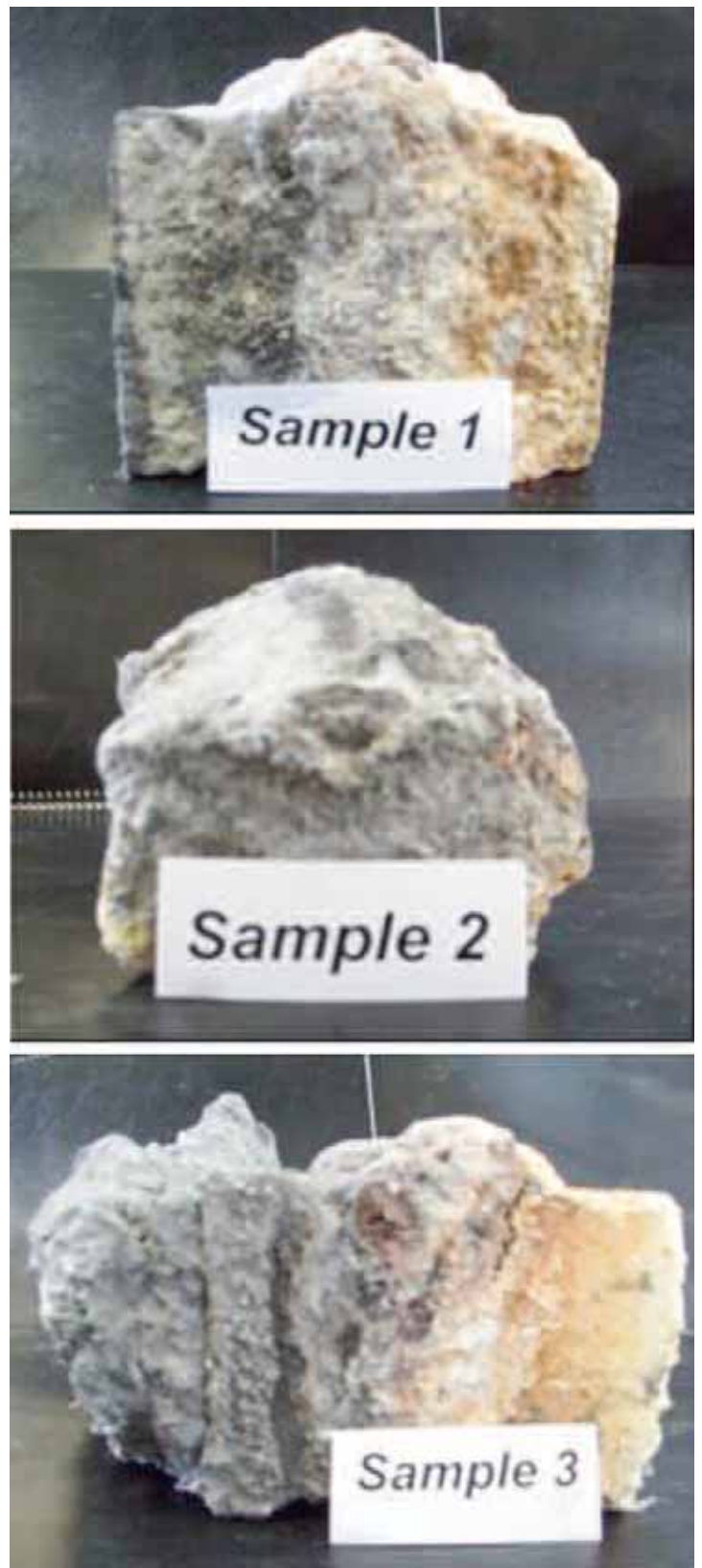
Three flue wall bricks from different regions of the furnace but with the same 83 working life cycles and the same composition were analyzed (**Figure 5**). The first important aspect is that all samples presented a color change along their cross section (from the anode to the burner side). This behavior is related to the carbon deposition on the anode side of the bricks.

Additionally, it is important to highlight the different behaviors observed for each used brick: sample 1 presented the highest dimensional stability as shown in **Figure 5** and a color change along the brick cross section; sample 2 presented high shrinkage, very likely, due to a severe chemical attack during its working life and the last sample presented a layer of coke impregnated on the anode side of the brick, which can increase the furnace maintenance cost due to the cleaning operation of the bricks. Therefore, these 3 individual behaviors can provide a strong indicative that the bricks' position inside the furnace walls can affect the corrosion level of each refractory. Most likely, the temperature gradient and the different thermo-mechanical conditions inside the furnace affected the refractories corrosion behavior.



M	-	$Al_6Si_2O_{13}$	-	Mullite
Cr	-	$SiO_2$	-	Cristobalite
R	-	$TiO_2$	-	Rutile
Q	-	$SiO_2$	-	Quartz
C	-	$Al_2O_3$	-	Corundum

**Figure 4.** Representative x-ray diffraction for the qualifying brick and the present one.



**Figure 5.** Cross sections of used samples 1, 2 and 3 after 83 working cycles.

### Chemical Analysis

In order to analyze the bricks' corrosion level, a chemical analysis was performed. The literature shows that five main elements react with the refractories microstructure, reducing the material's

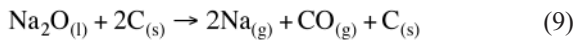
working life: alkalis, iron oxide, sulfur, fluorine and carbon monoxide.

## Alkalis

**Figure 6** shows the profiles of the alkali (sodium and potassium oxides) content for the used samples and for the as-received one. Thus, four distinct behaviors were observed: the as-received brick presented the lowest and constant values of alkalis in its cross section; sample 1 presented a high concentration of alkalis on the anode side and in the middle of the brick, with lower values at the burner side. Very likely, the alkali gases permeated the pores of the bricks and reacted with the microstructure, resulting in new phases such as kaliophilite and nepheline. After the attack, the alkalis filled in the brick pores and acted as a barrier to the gas penetration, reducing the alkali content on the burner side. It is important to highlight that this is just a hypothesis.

Sample 2 presented a distinct behavior when compared to the other used bricks: a high concentration of alkalis all through the brick. Most likely, this occurred due to the high chemical attack at high temperatures, inducing its shrinkage as observed in **Figure 5**. Hence, both the alkali content and the depth penetration along the brick cross section were high.

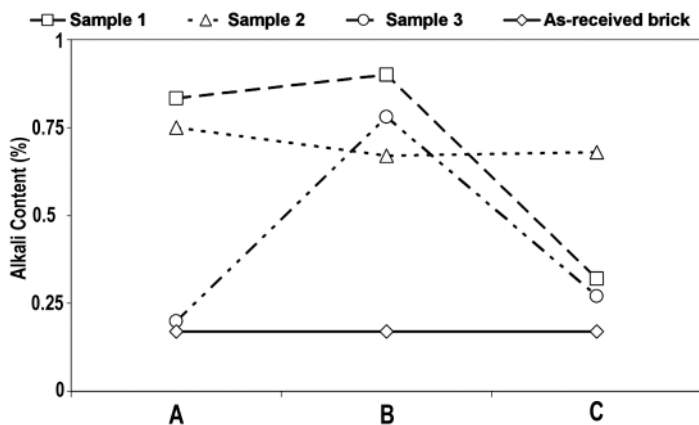
Sample 3 presented a similar behavior to sample 1 with high alkali content in the middle and on the burner side of the brick. However, on the anode side, the alkali content was close to the as-received brick. According to thermodynamic simulation (in equilibrium conditions), the reaction stated in **Equation 9** can occur at high temperatures (1250°C) and low oxygen partial pressure (in the range between  $1.52 \cdot 10^{-18}$  atm and  $3.70 \cdot 10^{-10}$  atm) [23]:



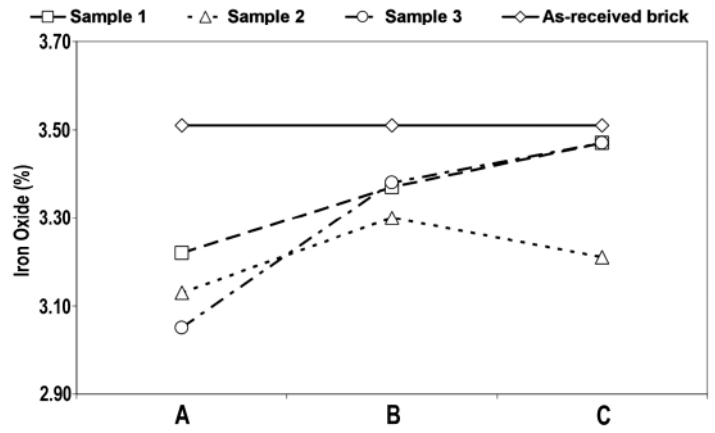
Therefore, the presence of solid carbon and sodium oxide can generate carbon solid and gases, such as sodium and carbon monoxide and this can be confirmed by the low values of alkalis (**Figure 6**) and high carbon content on the anode side of this brick (**Figure 10**). This reaction can also be carried out at low oxygen partial pressure.

## Iron Oxide

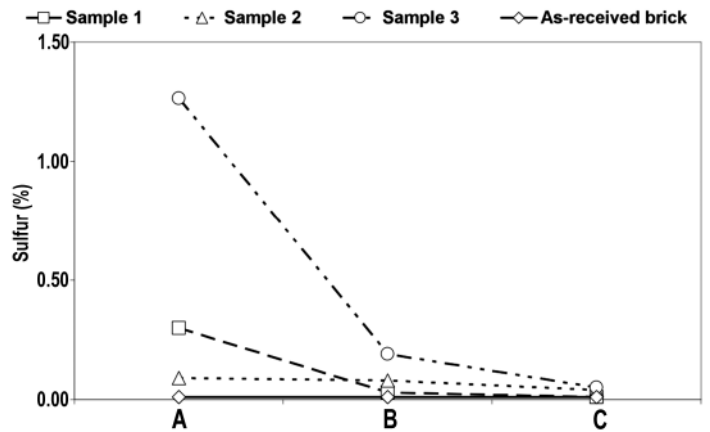
According to **Figure 7**, all used bricks presented a similar behavior: the iron oxide content was reduced from the burner side to the anode one. As previously shown, the iron oxide must have been reduced, generating metallic iron that could react with



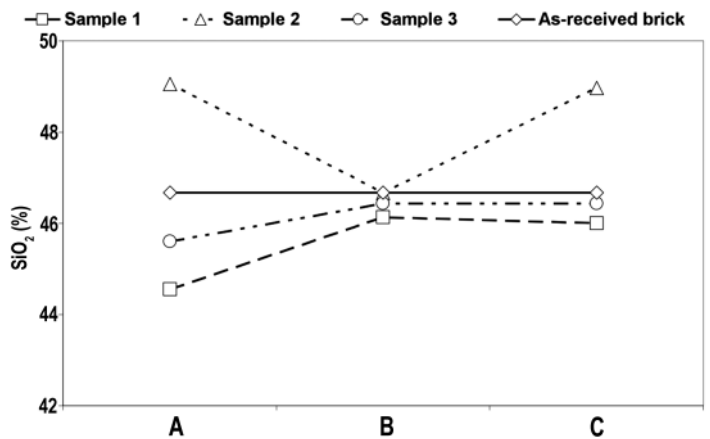
**Figure 6.** Alkali content in the flue wall bricks (the lines are just to guide the eyes).



**Figure 7.** Iron oxide content in the flue wall bricks (the lines are just to guide the eyes).



**Figure 8.** Sulfur content in the flue wall bricks (the lines are just to guide the eyes).

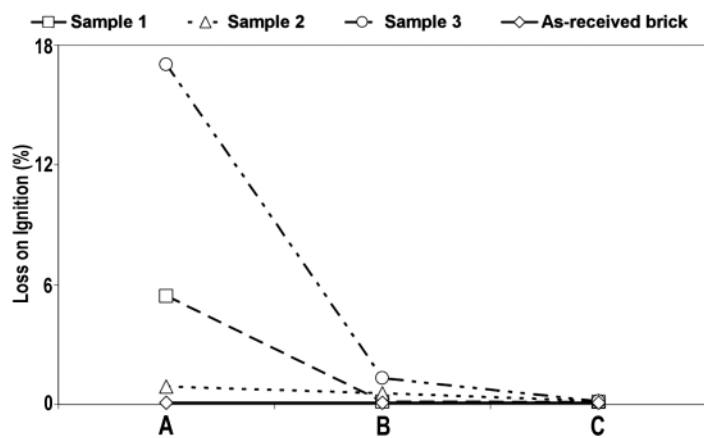


**Figure 9.** Silica content in the flue wall bricks (the lines are just to guide the eyes).

the carbon monoxide present in the system. As a final product of this reaction, the carbon is deposited into the pores of the bricks. Therefore, the search for flue wall brick compositions with lower iron oxide content is usually required in order to avoid mechanical stress due to carbon deposition.

## Sulfur

All used samples presented an increase in the sulfur content, mainly, on the anode side (**Figure 8**). Comparing these results with



**Figure 10.** Carbon content in the flue wall bricks (the lines are just to guide the eyes).

those observed in **Table 3**, it could be observed that the sulfur origin cannot be related to the brick's composition. Hence, the source of this element inside the furnace must be investigated. Additionally, this available sulfur present in the material can combine with the water vapor from the atmosphere, resulting in sulfuric acid which can spoil the materials' properties in the working conditions.

### Fluorines

**Figure 9** shows interesting behavior as the silica content of two used samples was reduced just on the anode side of the bricks. Most likely, a reaction between fluorine and silica occurred, generating  $\text{SiF}_4(\text{g})$  and damage to the refractories. However, the silica content of sample 2 presented an increase in the anode side. As previously presented, the chemical attack of this brick was intense along the furnace operation, leading to a non-expected behavior. Most likely, the brick's position inside the furnace affects the corrosion degree. Nevertheless, further studies must be carried out in order to clarify this aspect.

### Carbon Monoxide

By analyzing the samples and the obtained results of the chemical analysis, a correlation between the carbon content and the visual inspection of the bricks was attained. Sample 3, primarily, presented a thick layer of coke impregnated on the anode side and the highest value of carbon content. It is important to highlight that this behavior is not desired because it reduces the pit size and increases the furnace operational costs due to the cleaning process of the materials or their replacements.

Therefore, the chemical analysis of the bricks is a good indication of the materials' corrosion degree. In some cases, a correlation between the visual inspection and the chemical analysis was observed and, according to the obtained results, the bricks' position inside the furnace can influence the materials' corrosion level. However, the chemical analysis is not enough to guarantee all of these reactions were carried out. The x-ray diffraction was also performed and the results are shown in the next section.

### X-ray Diffraction

According to the chemical analysis of the samples before and after using, it seems that the bricks underwent a high chemical attack throughout their working life. However, the x-ray diffraction presented a similar phase distribution for all used samples, where,

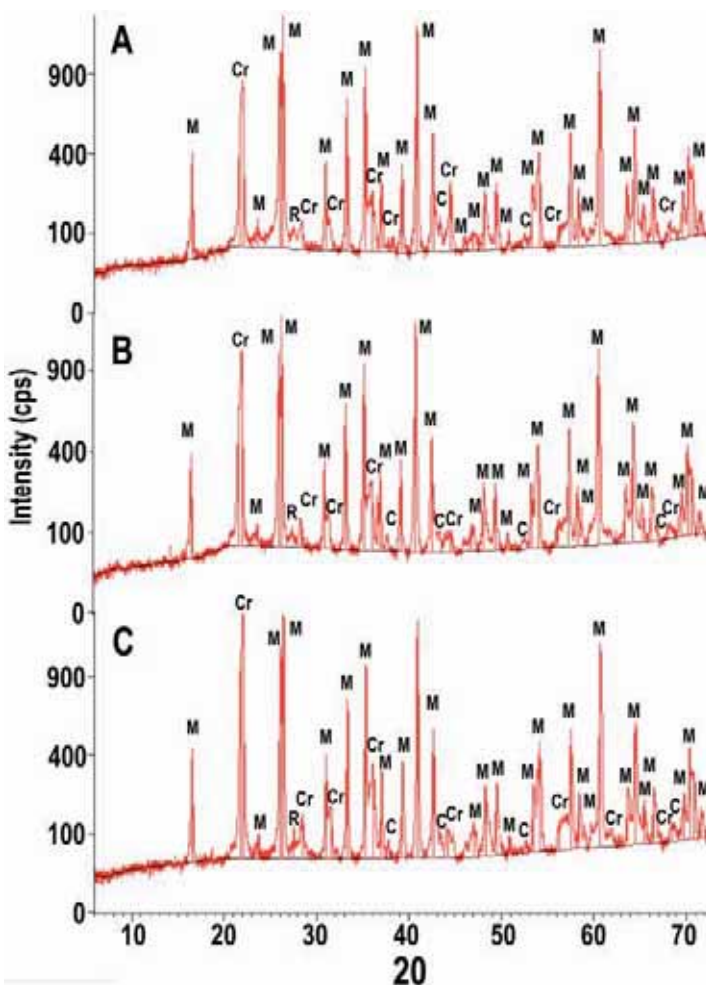
mullite, cristobalite, rutile, quartz and corundum were the main phases in the microstructure (**Figure 11**). Analyzing the cristobalite peak intensity, the behavior of the three used samples was similar, increasing from the anode side to the burner one. Very likely, this is associated to the silica reaction with alkalis and fluorine, which can generate phases such as kaliophilite and nepheline. These phases were not detected by the XRD, most likely due to their low content (< 5 wt% in the sample).

The post mortem analysis confirmed that the brick's failure was primarily related to the presence of some harmful elements that resulted in an intense chemical attack. Thus, the next step of this study was to identify the origin of each harmful component inside the furnace in order to reduce their contents and, consequently, decrease the materials' corrosion.

During the anode baking, another two components present in the furnace can be responsible for supplying the harmful components to the bricks: the green anode and the recovering coke. Hence, an investigation into their compositions over time was performed in order to verify the interaction between the brick's corrosion intensity and the chemical composition of these raw materials.

### GREEN ANODE

**Figure 12** shows two different situations occurring simultaneously in the furnace:



**Figure 11.** Representative x-ray diffraction of the used samples 1, 2 and 3.

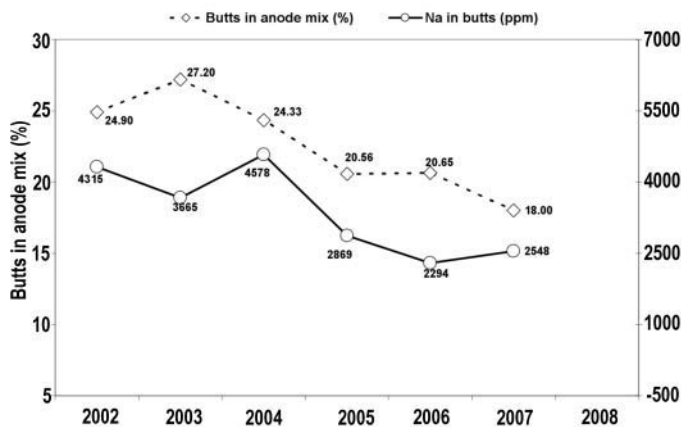


Figure 12. Butts and Na content in the green anode.

- Since 2003, the green anode, which is comprised of pitch, green coke and recycled anode (butts), has reduced its butt content (dotted line). As the recycled anode is the main source of sodium and potassium oxides, it seems that the furnace environment was less harmful, positively affecting the bricks' performance.
- The sodium content in the butts was also reduced over time (solid line). Hence, there was an improvement in the recycled anode cleaning operation, which reduced the sodium content in the furnace environment.

Nevertheless, according to **Figure 13**, the difference between the sodium content in the green anode and the baked one, increased in 2003 (dotted line). Therefore, the alkali content available inside the system to react with the brick increased significantly, resulting in a high chemical attack and, consequently, a reduction in the materials' working life.

To confirm the hypothesis that something special occurred in 2003, causing an increase in the harmful elements, sulfur and iron content present in the green anode composition were plotted. Thus, according to **Table 4**, the amount of both elements increased in 2003 and it must be considered that the green anode can also provide iron and sulfur to the system. Therefore, a time-to-time chemical control of the green anode is essential to follow the brick's performance.

## RECOVERING COKE

The recovering coke also has an important influence in the materials' performance. According to **Table 5**, the sulfur present

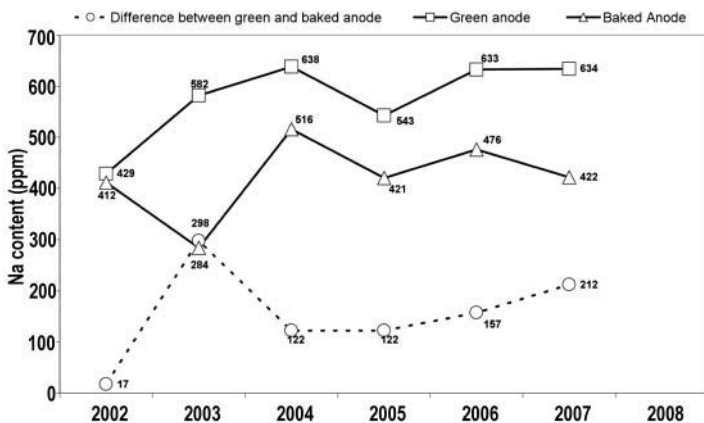


Figure 13. Sodium content in the green and baked anode.

Table 4. Sulfur and Iron present on the green anode composition since 2002.

	Sulfur (wt%)	Iron (ppm)
2002	1.48	961
2003	1.50	1483
2004	1.60	1125
2005	1.59	1217
2006	1.57	1364
2007	1.63	1150

Table 5. Recovering coke composition.

(wt%)	Iron	Vanadium	Sulfur	Silicon	Ash
Recovering Coke	0.0022	0.135	5.1	0.0018	0.5

inside the furnace environment is mainly related to the recovering coke. Additionally, a new element was detected: vanadium. The alkalis combined with vanadium results in low melting phases, reducing the brick's refractoriness [11]. Hence, the recovering coke must also be chemically controlled in order to decrease the brick's damage.

## CONCLUSIONS

Comparing the data obtained for the material supplied in qualifying test and the present one, no change in the brick's composition was observed. Therefore, the shorter brick's working life was not related to the flue wall brick's quality. Considering this, a suggestion for the aluminum plants is to perform periodical quality control tests for as-received brick to ensure that they do not change from batch to batch. Usually, data-sheets last much longer without changes than the actual compositions.

The post mortem analysis confirmed severe corrosion in the bricks. Hence, in order to increase the flue wall brick's working life, the aluminum producer must also reduce the concentration of the harmful elements inside the furnace environment using a time-to-time chemical quality control of the green anode raw materials and the recovering coke. Additionally, the search for bricks with low alkali, free silica and high alumina should always be kept in mind.


The analyses pointed out that something occurred in the furnace in 2003 that could have sped up the flue wall bricks corrosion. This hypothesis was confirmed by the aluminum company, as in that year, a high amount of green anodes were bought from another anode paste plant, which enhanced the concentration of the harmful compounds in the furnace and, consequently, the anode furnace maintenance costs increased due to the flue wall brick's working life reduction.

## ACKNOWLEDGMENTS

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next issue.**

# BEHAVIOUR OF ANDALUSITE AND MULLITIZED ANDALUSITE CRYSTALS UNDER THERMAL SHOCK

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## ABSTRACT

The thermal shock resistance of raw or mullitized single crystals has been studied between 1200°C and room temperature. Damaging of andalusite crystals occurs mainly during the first thermal shock with a move of the cleavages and a generation of cracks. The composite microstructure of mullitized andalusite crystals seems to be a strong advantage in order to increase thermal shock resistance. It can explain the good behaviour of fired andalusite bricks regarding thermal cycling.

## INTRODUCTION

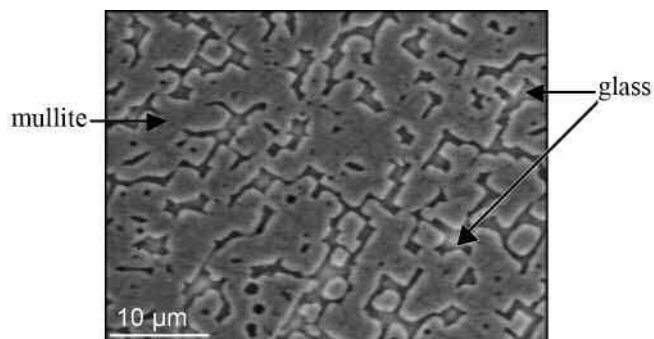
Andalusite based refractory products are used satisfactorily in applications where thermal shock resistance is required [1, 2].

By heating, andalusite ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) is converted into mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and silica rich glass [3, 4]. Mullitization of andalusite single crystal leads to a composite: about 83% of this composite is mullite and the other 17% is silica rich glass [5, 6] which becomes a glassy phase by cooling (**Figure 1**). The composition of the mullite is close to 72% of  $\text{Al}_2\text{O}_3$  and 28% of  $\text{SiO}_2$ ; it corresponds to a 3:2 mullite.

The purpose of this paper is to understand how the mullitization process affects thermal shock resistance of andalusite and mullitized andalusite raw materials.

## STUDY OF THERMAL SHOCK: ULTRASONIC TECHNIQUE AND EXPERIMENTAL PROCEDURE

With an ultrasonic method, it is possible to determine Young's modulus which is an adequate characteristic to study the thermal shock of andalusite and mullitized andalusite raw materials [7, 8].



**Figure 1.** Polished section of an andalusite grain transformed into a mullite-glass composite by heating to 1700°C (backscattered electrons SEM micrograph).

The velocity of the propagation of the ultrasonic waves depends on several parameters: mineralogical phases, porosity, cracks network, and chemical composition.

In the “long bar mode”, the velocity of the longitudinal waves is:

$$V_{L_{BL}} = \sqrt{\frac{E}{\rho}}$$

where E is the modulus of elasticity and  $\rho$  is the bulk density.

There is a direct relation between E, V and  $\rho$  [9]. Therefore, in this paper, the elastic characteristics of refractories will be presented in terms of ultrasonic velocity, which is the measured parameter, in order to calculate the modulus of elasticity. The ultrasonic system is a SOFRANEL EPOCH equipment using two kinds of sensors: M106 (2 MHz) or X1020 (100 MHz). The choice of the frequency of the sensors depends on the material. The method of measurement is the transmission mode method. The time between two successive echoes corresponds to the time required for the ultrasonic wave to go through the sample.

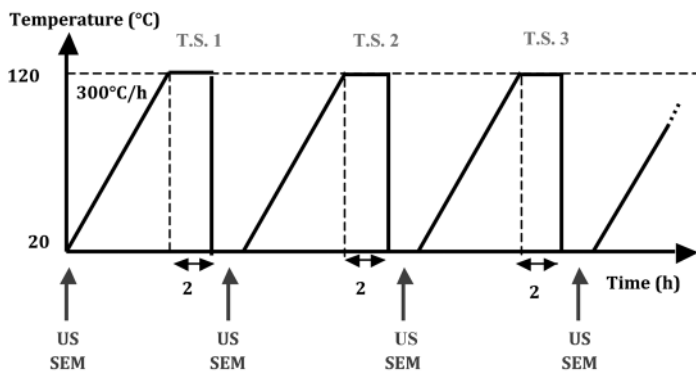
As thickness L of the sample is known, time t is measured, ultrasonic velocity V is calculated:

$$V = \frac{L}{t}$$

Large well-formed crystals of andalusite (5.8 mm diameter) were carefully selected. Mullitized andalusite crystals were prepared by firing andalusite crystals up to 1500°C with a 900°C/h slope and a six-hours dwell time at maximum temperature. The crystals were cut perpendicularly to their c-axis and one face (001) was polished.

The thermal shock resistance of andalusite or mullitized andalusite single crystals has been studied between 1200°C and room temperature. 1200°C has been chosen because at this temperature, the associated minerals melt providing a liquid phase and mullitization is beginning.

The polished grains are put into an electric furnace and heated at 1200°C (at a heating rate of 300°C/h). After two hours heating to homogenise temperature in the crystal, the samples are submitted to thermal shocks in the air. Quenching time from 1200 to 20°C was less than five seconds. Prior to testing and after each quench, the velocity of propagation of ultrasonic waves, perpendicular to the c axis was measured with Sofranel EPOCH equipment and the polished face was examined by scanning electronic microscope (SEM) using secondary or backscattered electron imaging. The **Figure 2** shows the experimental procedure of the successive thermal shocks.



**Figure 2.** Experimental procedure applied for thermal shock study on andalusite and mullitized andalusite crystals.

## RESULTS AND DISCUSSION

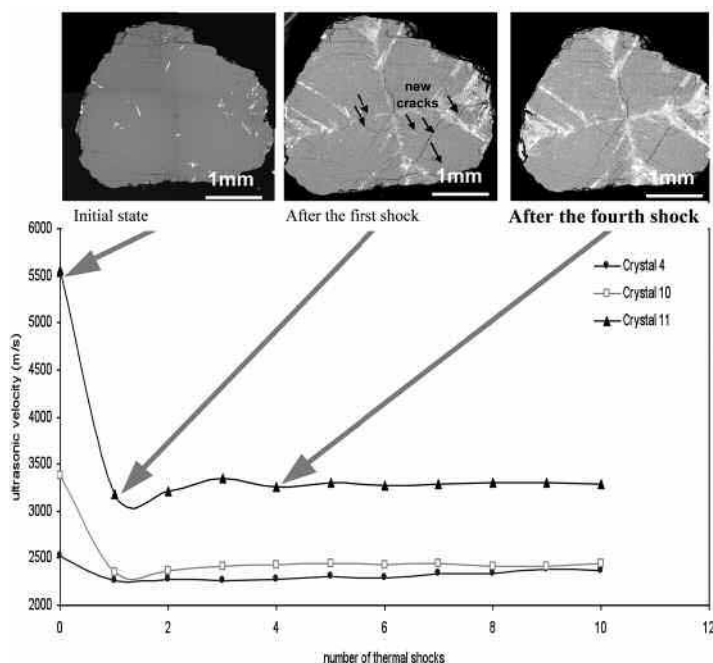
### Evaluation of the thermal shock performance of andalusite crystals

**Figure 3** shows the evolution of the velocity of ultrasonic waves for three representative crystals of andalusite after ten successive thermal shocks. The first thermal shock is the most damageable. After the other thermal shocks, ultrasonic velocity and the modulus of elasticity are then found to be stable.

The initial andalusite contains some inclusions and exhibits an initial network of cracks, even before the first thermal shock. The initial cracks result from opening of the (110) cleavage planes. After the first thermal shock (one cycle), the surface has already changed considerably:

- The amount of cracks has increased and large cracks appear.
- A white new phase appears, located in geometrical figures.

This is the reason why ultrasonic velocity decreases. There is no micro-structural relation between the initial cracks (before the first thermal shock) and the cracks created by thermal shocks. The new



**Figure 3.** Evolution of the velocity of ultrasonic waves for three representative crystals of andalusite after 10 successive thermal shocks.

cracks are generated by the successive thermal shocks which contribute to the advanced thermal shock performance.

They may develop:

- With the same orientation. The orthogonal cracks are in fact the traces of andalusite cleavages;
- Or without any relation to the cracks created during the previous thermal shock.

After 4 cycles, the pattern observed after 1 cycle remains. We only see an increase in the surface of the white phase which is a glass resulting from the melting of associated minerals. The associated mineral inclusions are located in a particular area of the crystal called chistolite. The chistolite is revealed by the melting of these inclusions.

After each thermal cycle, interesting changes are observed (**Figure 4**).

- The initial cracks of the crystals are partly sealed by a glass as soon as the first cycle has been completed.
- In the same time, new cracks appear elsewhere.
- Cracking and sealing can occur during each cycle. Coalescence of droplets at the surface reveals that more glass is expelled cycle after cycle.

SEM micrographs reveal that during two hours heating at 1200°C before each thermal shock, a silica-rich vitreous phase appears which may fill, by capillarity, the network of cracks created by the thermal shocks. This melting phase, due to alkalis and iron oxides contained in minor mineral inclusions (quartz, phyllosilicates, ilmenite) of andalusite grains cures the existing cracks and stops the new cracks which are generated by the next thermal shock.

Simultaneously, the mullitization of andalusite begins at 1200°C, through a dissolution precipitation mechanism [10, 11]. Mullite develops in andalusite from defect-rich zones and participates in the cure of the network of cracks (**Figure 5**). Two “antagonistic” phenomena occur simultaneously: the heating allows the formation of a liquid phase, which cures some micro cracks and may increase Young’s modulus. But the thermal shocks generate small cracks, which may decrease Young’s modulus. The result is a stable Young’s modulus. Consequently, andalusite provides excellent thermal shock resistance. There is a relation between ultrasonic elasticity properties and the evolution of microstructures: cracks are deflected or healed by glass-mullite zones.

Evaluation of the thermal shock performances of mullitized andalusite crystals, comparison of the ultrasonic velocity of andalusite and mullitized andalusite is included below.

**Figure 6** shows the evolution of the velocity of ultrasonic waves for three representative crystals of mullitized andalusite after four successive thermal shocks.

A sealing of the initial cracks after one cycle occurred (**Figure 7**). The silica glass is expelled from the crystal and precipitation of iron oxides occurs in the glass.

The evolution of the ultrasonic velocity as a function of the thermal shock cycles shows a strong difference between andalusite and mullitized andalusite (**Figure 8**).

- For andalusite, the decrease in the velocity occurs from the first cycle and is stable afterwards. This decrease

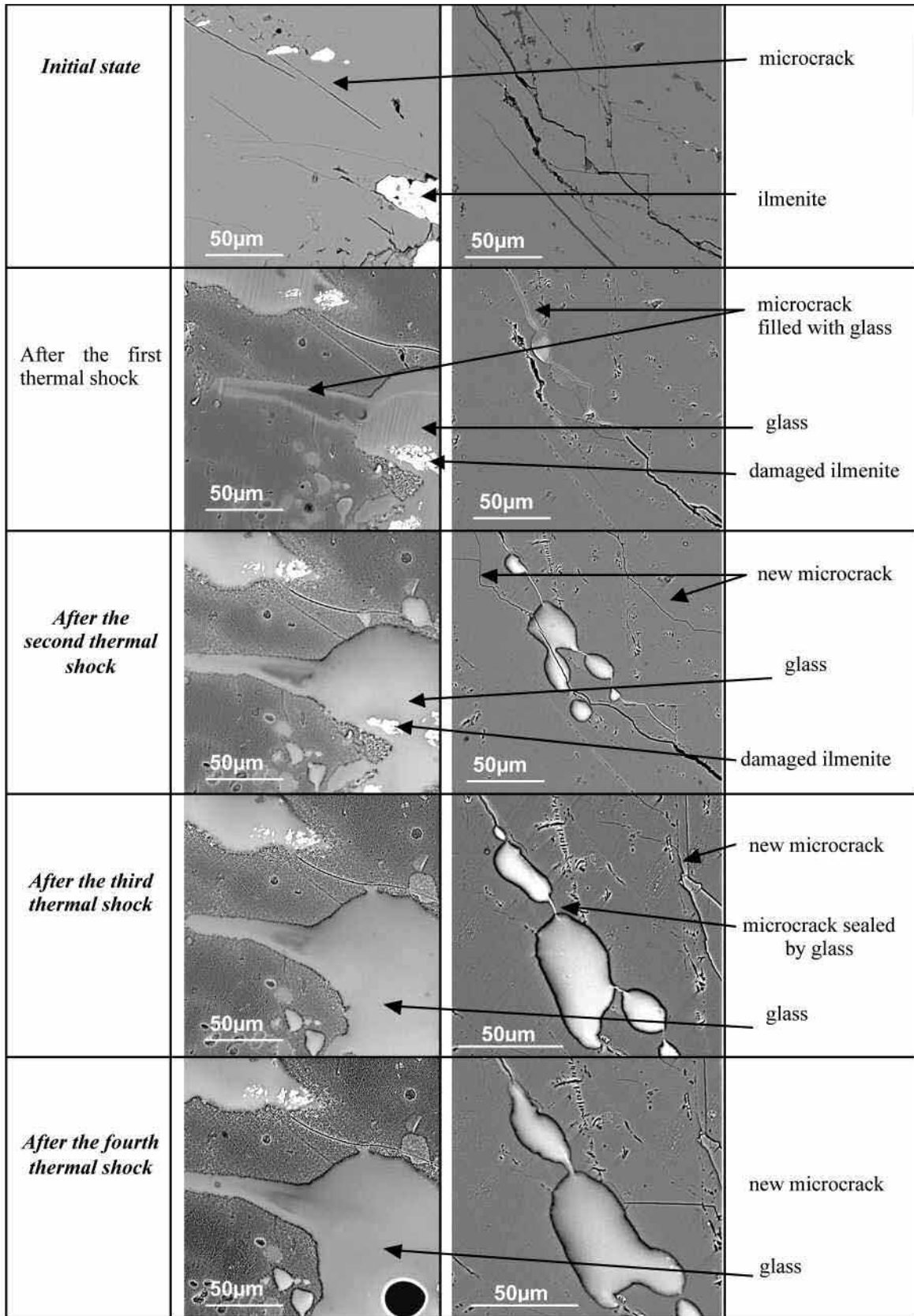


Figure 4. Backscattered electron image of the initial aspect of andalusite crystal and the aspect of the crystal after thermal shocks.

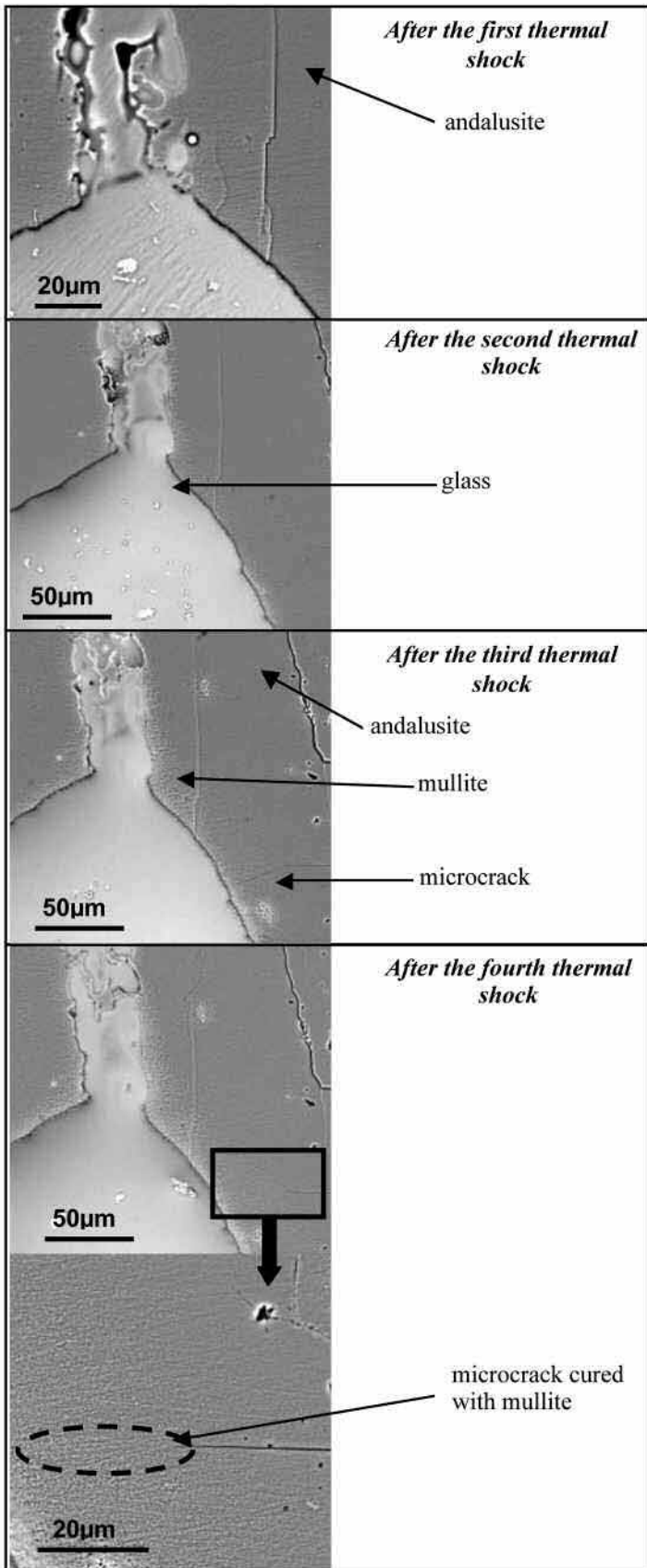


Figure 5. Backscattered electron image of the andalusite crystal after thermal shocks (curing of a crack with mullite).

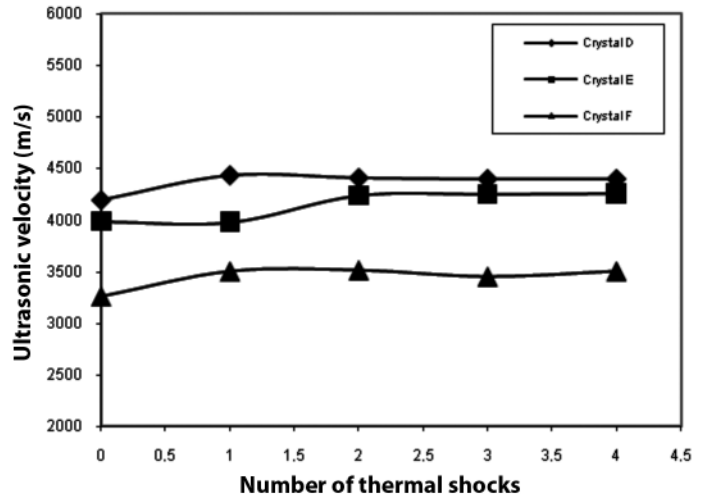


Figure 6. Evolution of ultrasonic velocity mullitized andalusite crystals.

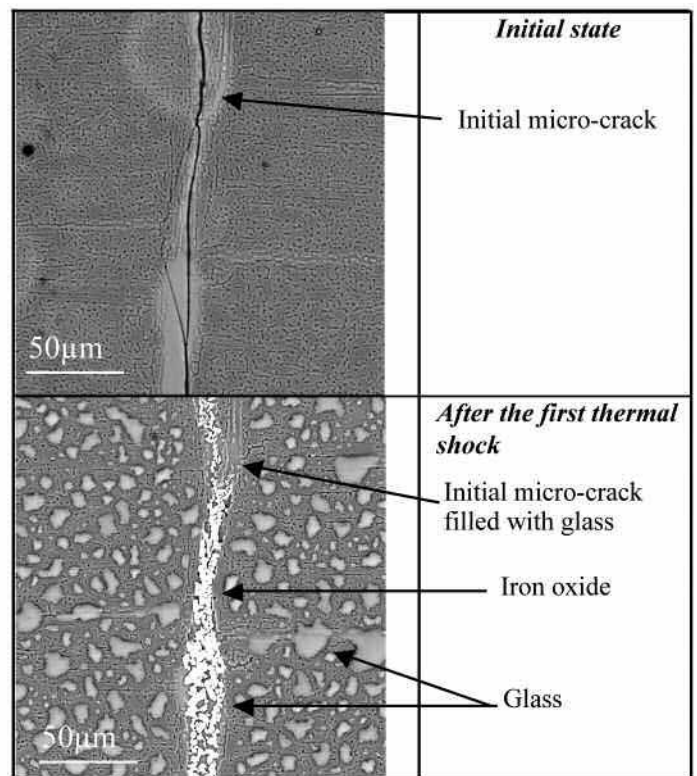


Figure 7. Backscattered electrons image of a mullitized andalusite crystal.

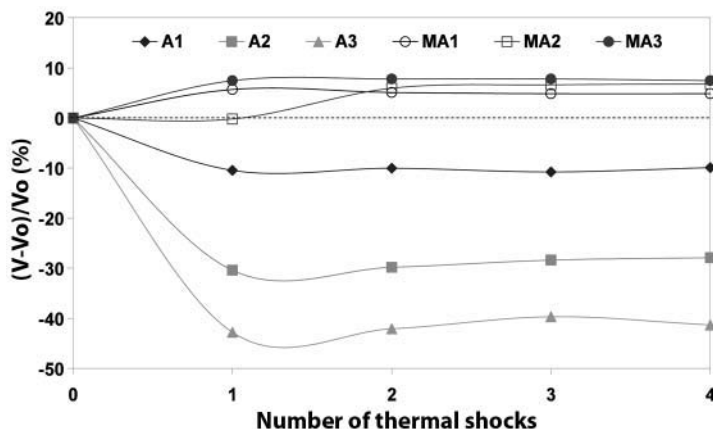
depends on the initial state of the crystal. The crystal that shows the highest initial velocity shows also the sharpest drop;

- For mullitized andalusite, ultrasonic velocity does not decrease but increases slightly. The behaviour is also stable for the next cycles. Homogeneity of the behaviour of mullitized andalusite is confirmed.

## CONCLUSION

Ultrasonic velocity measurements and microstructure study lead to several conclusions:

- The behaviour of andalusite crystals under thermal shocks depends on the initial state of the crystal (amount of associated mineral and amount of cracks);




**Figure 8.** Evolution of ultrasonic velocity of andalusite (A1, A2, A3) and mullitized andalusite crystals (MA1, MA2, MA3) – Vo initial velocity.

- Cleavages of andalusite seem to move during thermal shocks and could contribute to decreasing fracture energy;
- If the firing temperature is high enough, the melting of associated minerals provides a recovery of the cracks initiated by the first thermal shock and consequently decreases the damage;
- Cycle after cycle, the mullitization of andalusite occurs even at 1200°C and is concentrated in the stressed areas;
- Transformation into mullite of andalusite crystals during firing improves their behaviour under thermal shock because it homogenizes the microstructure of the initial crystal (building up of a unique mullite-silica glass network, sealing of cracks, and melting of associated minerals).

Damaging of andalusite crystals occurs mainly during the first thermal shock with a move of the cleavages and generation of cracks. During the short dwell time at 1200°C between each thermal shock, the melting of associated mineral and mullitization occurs. The liquid phase limits the effect of the thermal shock because it enables crack recovery. The crack healing process seems to occur as early as the first thermal shock for mullitized andalusite crystals. The composite microstructure of mullitized andalusite crystals seems to improve thermal shock resistance. It can explain the good behaviour of fired andalusite bricks regarding thermal cycling.

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### TRI News Continued From Page 4

Similar NOL relief legislation was previously passed by the House and Senate early in 2009, but was significantly pared back as part of the final stimulus law.

## REGULATORY


### OSHA Moves on Crystalline Silica

The Occupational Safety and Health Administration announced that it plans to complete its peer review of the Health Effects Analysis and Quantitative Risk Assessment for Crystalline Silica by September. By setting this early milestone, OSHA is signaling that work on its long-awaited comprehensive health regulation to address occupational exposures to crystalline silica will now begin to move forward in

earnest. The peer review had been stalled under the Bush Administration. The agency could publish a proposed rule in early 2010.

## CONFERENCES AND SEMINARS

### TRI Fall, Spring Membership Meetings

Planning is underway for the TRI Fall Membership Meeting to be held at the Embassy Suites Hotel near the Pittsburgh Airport, September 30-October 1, 2009. Mark your calendars now. While you have them out, make a note to be in Napa Valley in California June 2-4, 2010 for the TRI Spring Membership Meeting. 

# THERMAL STRESS DYNAMICS

Alfred W. Allen, Professor, Ceramic and Nuclear Engineering, University of Illinois, Urbana, Illinois

Presented at the Refractories Symposium, The St. Louis Section of the American Ceramic Society, April 6, 1973 Engineers Club of St. Louis

Applying the term “dynamics” to thermal stress implies a force and its relation to the motion and equilibrium of a body of matter. Thermal stress is indeed a dynamic phenomenon referring to stress gradients induced by differential thermal strain under a temperature gradient in a refractory. The driving force for the temperature gradient is the heat flux to the refractory combined with the resulting heat transfer response in the refractory. In classical interpretations reference is made to Biot’s modulus,  $\beta$ , which is the ratio:

$$\beta = \frac{r_m h}{K}$$

where  $h$  is the coefficient of heat transfer from the surrounding to the body,  $K$  is the thermal conductivity of the refractory and  $r_m$  is the factor related to heat transfer path length.  $r_m$  is the normal distance from a center, an axis, or a midplane to the heated surface depending on the shape under consideration. The coefficient,  $h$ , may be altered considerably by the nature of the boundary layer at the heated surface.

Editor’s Note - A number of years ago I poured through all of the past St. Louis Symposium proceedings looking for particularly good and still relevant manuscripts. I am confident, although saddened, that we have likely the only complete set in existence. It is that realization that prompted me to begin these historical reprints in *RAN*. Although we are nearing the end of my original list, I have expanded my search to include other, obscure or largely unavailable, sources for reprint consideration. The current two manuscripts are from Al Allen. Along with two associated inserts that I thought would be appropriate as well as the front cover of Chang Min Chun receiving the most recent Al Allen Award. I decided to include them both as a mini-tribute to Professor Allen.

If  $\beta$  is increased this means that the rate of ambient heat energy transfer to the refractory has increased relative to the energy transfer within the refractory. An impact analogy is useful here in that the  $\beta$  increases the phenomenon becomes similar to a sharp impact loading. The effect of the boundary layer could be to “soften the blow”.

Quantitatively, for larger values of  $\beta$ :

1. The magnitude of the stress at the heated surface increases;
2. The time interval to achieve maximum surface stress is shortened;
3. The time duration of maximum surface stress is shortened.

The thermal stress wave has therefore started at the heated surface and is propagated to cooler regions with the transfer of heat. The thermal stress generates a strain depending on the elastic response of the material. Note here that a simplifying assumption is complete elasticity.

Herein arises the concept of thermal shock. Thermal shock refers to the damage to the refractory produced by the propagation of the stress (strain) wave. Many test methods specify the evaluation of the degree of mechanical deterioration by determining elastic or strength moduli before and after repeated heating and cooling cycles. Thus it may be expected that the refractory could “absorb” thermal strain damage without sufficient deterioration to completely lose structural integrity. In “absorbing” the energy of thermal shock it may undergo permanent changes in micro or macro structure, which lead to physical property changes but not to complete mechanical failure. These concepts indicate that effects due to thermal shock are not unlike those related to impact or fatigue.

If the propagation of thermal shock damage is sufficient to cause loss of structural integrity or actual loss of material from the structure then the dynamic process has proceeded to thermal spalling. The standard ASTM test for spalling is based on a weight loss determination of a panel subjected to a series of heating and cooling cycles sufficiently exaggerated to take the process of thermal shock to thermal spalling. The condition of heat transfer in the original test was designed to simulate boiler service. When results from this test are difficult to correlate from one laboratory to another, it may well be that heat transfer conditions are not duplicated. Only a temperature is specified in the operation of the test.

Some degree of restraint, anisotropy, or inhomogeneity always exists in a refractory material under conditions of dynamic heating. Even in equilibrium heating the inertial resistance to thermal strain offers enough restraint to make normal thermal expansion a stress producing property. If elasticity is assumed then:

$$\frac{\text{Expansion stress, } \sigma}{\text{Expansion strain, } \epsilon} = \text{Elastic Modulus}$$

Also

$$\epsilon = \alpha \Delta T$$

where  $\alpha$  is the linear coefficient of thermal expansion and  $\Delta T$  the temperature change. If this expansion is modeled as a heated bar restrained longitudinally, the elasticity involves shear, tension and compression and

$$\sigma = \frac{E \alpha \Delta T}{1 - \mu}$$

where  $E$  is flexural modulus and  $\mu$  is Poisson’s ratio. Because

$$\sigma = \frac{E}{2G} - 1$$

this expression for the thermal stress then also considers shear by the incorporation of the shear modulus,  $G$ .

The temperature gradient  $\Delta T$ , therefore produces the stress gradient. Steady state heat transfer within the body generally leads to a uniform temperature gradient and hence a uniform stress gradient. Unsteady state heat transfer is the condition in

many refractory structures where heating and cooling cycles are rapid. This leads to nonuniform and changing temperature gradients, hence, the thermal stress distribution is quite complex.

If the stress is considered to be an incremental stress at a point in the refractory, the maximum allowable stress would be a strength parameter,  $S$  or

$$\sigma_{\max} = S$$

$\Delta T$  at this point then would be the temperature gradient to initiate failure at the point,  $\Delta T_f$ . Or as the stress analyst would say: “to nucleate cracks”. Therefore

$$\Delta T_f = \frac{S(1-\mu)}{E\alpha}$$

When the actual geometry of the refractory shape is considered the temperature gradient is also a result of the heat transfer properties and shape. It can be shown that

$$\Delta T_f = \left[ \begin{matrix} \text{mechanical} \\ \text{property} \\ \text{factor} \end{matrix} \right] \times \left[ \begin{matrix} \text{thermal} \\ \text{property} \\ \text{factor} \end{matrix} \right] \times \left[ \begin{matrix} \text{shape} \\ \text{factor} \end{matrix} \right]$$

This relationship becomes the basis for thermal shock criteria or for the nucleation of thermal stress cracking.

Each application for the refractory must be assessed to determine which of these factors is controlling. Most often the shape is dictated by other considerations and cannot be modified to improve thermal shock. It is interesting that criteria of good aerodynamic design lead to optimized geometry insofar as thermal shock is concerned. If the heat transfer coefficient is so large as to be essentially infinite, then the mechanical factor alone is controlling. If the thermal conductivity is very high in relation to the heat flux input (low  $h$ ), then the mechanical property factor may be of little importance at least in dictating resistance to thermal stress.

If the thermal expansion coefficient approaches zero then  $\Delta T_f$  would approach infinity. A silica refractory approaches this behavior above 800°F. But between room temperature and 800°F, the silica refractory has a very large expansion coefficient. The problem then relates to operation in getting and keeping the silica refractory above 800°F. Fused silica glass has a very low expansion curve from room temperature up, but it will devitrify to cristobalite. Cristobalite has an essentially infinite expansion coefficient in the range of room temperature to 500°F.

All of the above considerations have been related to the criteria for nucleating cracks by thermal stress. When all of the requirements for a refractory material are considered related to such considerations as slag resistance, cost, thermal cycling and ease of installation, it seems improbable that a material would ever perform its function completely free of thermal crack patterns. In the design of the refractory structure it is feasible, however, to assume that thermal crack propagation could be limited. This propagation requires that the strain energy released during cracking be greater than or equal to the energy dissipating mechanisms available. The limitation of thermal crack propagation and resulting improved thermal spalling resistance then requires a microstructure that would interrupt the scatter strain energy. Studies have shown this mechanism to be related primarily to types of surface energy:

1. Thermodynamic surface free energy;
2. Anelastic deformation at crack tip surfaces;

*The following biographical data is reprinted from The St. Louis Section of the Eighth Annual Symposium on Refractories (Theme: Mass Transportation in Refractories) sponsored by The American Ceramic Society at the Engineer's Club, St. Louis, MO on April 21, 1972*

**Alfred W. Allen - University of Illinois**

Professor Allen received his Bachelor of Science Degree in Ceramic Engineering at the University of Missouri at Rolla in 1941 and a Master of Science Degree in Ceramic Engineering at Virginia Polytechnic Institute in 1942. He was a research engineer with Harbison-Walker Refractories Co. from 1942 to 1943. After a tour of duty in the Army Air Force as a navigation and meteorology instructor (1<sup>st</sup> Lieutenant) he came to the University of Illinois in 1945. He started as special research associate and is now Professor of Ceramic and Nuclear Engineering. Since coming to Illinois he has also held positions with Bendix Aviation Corporation, U.S. Steel, and the University of California. He is a member of Tau Beta Pi, Keramos and Alpha Chi Sigma honorary societies. His technical society memberships include AIME, American Society for Engineering Education, American Ceramic Society, British Ceramic Society and the American Powder Metallurgy Institute. He is Past President of the Ceramic Educational Council, Past Chairman of the Materials Division of ASEE and Past Chairman of Nomenclature of ASTM Committee C-8 on Refractories. He is the author of numerous papers.

3. Plastic or viscous deformation on new surface formed by crack nuclei;
4. Charge on fresh surfaces.

In polyphase, heterogeneous refractory microstructures the strain energy introduced in the material may be less than the surface energy at grain and pore boundaries. This heterogeneity may actually promote essential absorption of strain energy released in localized thermal shock and slow down crack propagation. Boundaries between brittle and plastic (or viscoelastic) phases provide regions for strain energy dissipation by inelastic deformation. The plastic or viscous layer of heated material may act as a kind of boundary layer in which relaxation of the stress gradient occurs. This “pyroplastic” condition may sustain large magnitudes of load-induced stress and be markedly resistant to thermal stress propagation. This is often exhibited by silica rich refractories, which maintain structural stability by virtue of the high viscosity of the liquid. This is not generally true of basic refractories, which have low viscosity liquids. Composite microstructures of phases having widely different elastic moduli also exhibit a type of boundary strain dissipation.

Hasselmann has shown, in fact, that thermal stress crack nuclei may present a kind of self-limitation to crack propagation. He shows that the stored energy is the sum of the elastic energy plus the energy stored in crack nuclei. This crack system can be quite stable and not promote propagation if the temperature gradient is below a critical value. The critical gradient is dependent on elastic properties, number of cracks and crack length. It is possible then to have a heterogeneous refractory microstructure containing crack nuclei all of which interrupt thermal stress propagation.

The stored elastic energy is:

$$W = \frac{S^2(1-\mu)}{E\alpha}$$

If this is compared to the previous equation for,  $\Delta T_f$ , the temperature gradient to nucleate cracks, it can be seen that both of these indicate that a high strength to flexural elastic modulus ratio is desired. If the limit of Poisson's ratio is zero, then the shear modulus should be half of the flexural modulus. Mechanically this is a material of high resiliency. Thus a material of high strength and high modulus would be inferior to a material of moderate strength and low modulus. Required is a high extensibility, a large area under the stress strain curve, and a high strain to fracture, regardless of the strength.

The importance of grain size distribution and heterogeneity had been shown to be important in the days of development of open-hearth silica brick. A grain size distribution with coarse quartzite with added iron oxide proved to have a safe heating rate twice that of conventional silica refractory.

A somewhat different aspect of the thermal spalling problem is illustrated by refractories that have been subjected to long-term service so that zones have developed due to the temperature gradient and conditions of slag attack. This has been referred to as "metasomatism" in previous symposia. Illustrated is a silica brick from extended use in the crown of a glass tank. (EDITOR'S NOTE: Figure not included with original manuscript printed.) The zoning shown is the result of the changing equilibrium polymorphic content of the silica as well as the penetration of alkali into the hot face. The hot face in this case is primarily tridymite. Behind the hot face is a zone having primarily cristobalite and tridymite, while still a third zone exists that has the polymorphic content of the original refractory. Because silica transformation temperatures occur in definite ranges, distinct discontinuities in both reversible thermal expansion and in permanent volume change occur at these zone junctions. The crown becomes more sensitive to thermal cycling. It also may be unstable at the elevated temperature of the crown because of the permanent volume change mismatch. The elastic modulus discontinuity in these zones is also noted.

Rigby showed recently the possibility of elastic modulus discontinuities in magnesite-chrome brick as being contributory to the shelling or peeling of basic refractory walls. In a single phase material the elastic modulus would be expected to decrease with temperature. But in a magnesite-chrome refractory the sharp composition gradient at the magnesia-chrome interface produces a spinel reaction layer by diffusion. (This was discussed in some detail at the 1972 symposium). There is a thermal expansion mismatch between the spinel and magnesia grains generating a thermal stress at these micrograin boundaries. This prestressed condition in the microstructure causes a stiffening effect in the refractory seen as a measured increase in elastic modulus. Combined with slag penetration this physical property discontinuity can produce an unstable refractory structure even though the temperature in the furnace is not cycling.


These effects could be considered to be a kind of stress-corrosion condition peculiar to the process and the particular furnace operation. A detailed understanding of the use of the refractory in a materials system that makes the total structure less dependent on the thermal shock behavior of the refractory is the only answer here. The evolution of the internally plated brick with hold-up, hold-down

suspension in the basic open-hearth roof is an example of a highly developed system of this type.

## SUMMARY

1. The proper condition of heat transfer must be analyzed to assess the probable role of such parameters as Biot's modulus, thermal conductivity, and thermal diffusivity in relation to thermal stress dynamics.
2. Resistance to thermal stress nucleation and thermal shock propagation is favored by a material having a high extensibility or thermal resiliency.
3. The grain boundary condition and grain size distribution of a refractory can limit the propagation of thermal shock.
4. Designs which offer thermal stress relief by mechanical prestressing are often feasible in making the structure stable in a thermal stress environment.
5. Altering the boundary layer of a material to influence Biot's modulus and hence affect the magnitude and build of surface thermal stress is possible.
6. Low thermal expansion coefficient favors low thermal stress but the expansion coefficient may not always remain constant with changing conditions of service.

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# ELASTICITY AND ANELASTICITY IN REFRACTORIES

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The pivotal role of microstructure in the progress of characterization of a refractory has been discussed in previous lectures at this symposium. It has also been pointed out that the chemical characterization of refractories has been optimized to a degree compatible with their economics of production. Product development in refractories is emerging to an era where more sophisticated mechanical characterization is becoming a requirement. This dictates a need to understand the role that phase placement (microstructure) and its relation to mechanical behavior plays in the total characterization of the refractory.

Correlation between the microstructure of refractory oxides and mechanical properties at room and elevated temperatures is being improved by interpreting the stress-strain response as a model anelastic phenomenon. Not only do such studies help in the understanding of mechanical behavior at the continuum level, but they also help define the mechanism of deformation at the microstructural and atomistic levels providing information on structure not discernable by other means.

The definition of anelasticity has its origins in an examination of the strain response of a material to a simple square wave stress program. In perfect elastic response the strain follows the stress with no time lag, responding instantaneously so that a mirror image square sine wave results. In anelastic response a portion of the strain response is always time dependent so there is a stress level at which the strain begins to lag the stress. This response has a mechanical analog as shown where the portion of the response which is elastic is shown as two springs in parallel and the time dependent portion is shown as a dashpot in series parallel with the springs. Upon application of the stress the springs extend until they are strained to the level  $\epsilon_u$  during which time the dashpot was in an unrelaxed position. At the strain level  $\epsilon_u$  the dashpot begins to move (or relax). This is the level at which the time-dependent movement of the dashpot governs the strain response. As the stress is released the elastic deformation  $\epsilon_u$  of the springs is immediately recovered followed by a relaxation in the dashpot again until the time dependent  $\epsilon_R$  is recovered.

This gives rise to two definitions of elastic moduli, the unrelaxed modulus,  $E_u$  and the relaxed modulus,  $E_R$ . The latter modulus must consider the strain and stress rates ( $\dot{\sigma}$  and  $\dot{\epsilon}$ ) and the relaxation times at constant stress ( $t_\sigma$ ) and constant strain ( $t_\epsilon$ ) as indicated.

$$E_u = \frac{\sigma_o}{\epsilon_o}$$

$$E_R = \frac{\sigma_o + \dot{\sigma} t_\epsilon}{\epsilon_o + \dot{\epsilon} t_\sigma}$$

For the simple square wave stress assumed the strain at any time,  $\epsilon_o$ , is a function of the instantaneous stress,  $\sigma_o$ , the instantaneous

strain,  $\epsilon_o$ , the relaxation time at constant stress,  $t_\sigma$ , and the relaxed modulus,  $E_R$ , as indicated. Note that since the stress rate is zero essentially the entire time,  $E_R$  is only a function of instantaneous stress and strain, strain rate and relaxation time at constant stress.

$$\epsilon_t = \frac{\sigma_o}{E_R} + \left( \epsilon_o - \frac{\sigma_o}{E_R} \right) e^{-\frac{t}{t_\sigma}}$$

Also when  $\dot{\sigma} = 0$ ,

$$E_R = \frac{\sigma_o}{\epsilon_o + \dot{\epsilon} t_\sigma}$$

Erroneously the relaxation is often considered to be instantaneous with the stress, which is a way of saying that  $t_\sigma$ , also equals zero and then the relaxed and unrelaxed moduli must be equal. This simplifying assumption is certainly not true particularly at elevated temperatures.

Anelastic stress-strain response in tension may also be considered as a cyclic thermodynamic phenomenon wherein work is done during the stress increase portions of the cycle and recovered when the stress is released. The difference in these two work functions is reflected in the mechanical hysteresis and represents energy dissipated during the process of deformation. If this cycle is at an extremely rapid stress rate, the energy (heat) dissipated is not transferred from the material and its internal energy change is isentropic (constant entropy). Its temperature will fall with tensile strain at constant entropy according to:

$$\left[ \frac{\partial T}{\partial \epsilon} \right]_s = - \frac{V \alpha E T}{C_V}$$

where  $V$  is the molecular volume,  $\alpha$  the coefficient of thermal expansion,  $E$  is Young's Modulus, and  $C_V$  the specific heat at constant volume. For most oxides  $\alpha$  is positive and the isentropic assumption may be valid. For compression the algebraic sign of this function is +.

When the stress cycle occurs as very low stress rates the energy dissipated is easily transferred, the deformation is isothermal and the entropy is probably not constant.

Anelastic response to cyclic stress is usually between these thermodynamic limits, the energy loss per cycle being dependent on the frequency of stress cycling. The ability to produce this energy loss in the acoustical spectrum is termed damping capacity. It is often determined on a vibrating specimen whose geometry is such that the frequency is in the audible range and occurs at very low stress levels. The dynamic elastic moduli are thus determined near the origin of the stress-strain curve. A characteristic stress frequency,  $F_o$ , is found at which the damping capacity is a maximum.

The period of this vibration, i.e. the reciprocal of the characteristic stress frequency, should be the relaxation time of the process producing the energy loss.

Rather than conduct the extensive experiments necessary to establish the characteristic stress frequency it is expedient with ceramic materials to analyze the vibration of one of the fundamental modes of vibration in a prismatic specimen or a long rod. The two fundamental modes of vibration which are relatively easy to excite are the first mode of flexural vibration and the first mode of torsional vibration. From the resonant frequency,  $F_R$ , of the first mode of vibration, Young's modulus of elasticity,  $E$ , may be determined by

$$E = C_1 W F_R^2$$

where  $W$  is the weight of the specimen. Note that with a prismatic section vibration in this flexural mode requires that the inertia of the vibrating nodal section be overcome. The constant  $C$  is therefore involved in this inertial correction being dependent on the moment of inertia of the nodal section and the ratio of its radius of gyration to the length of the prism. From the frequency of the first mode of torsional vibration the modulus of rigidity may be calculated in a somewhat similar manner. Since the frequencies of these transverse modes of vibration are often in the audible range, the technique is referred to as "sonic testing".

If the specimen is forced to vibrate in a fundamental mode like the first mode of flexure, a record of the frequency-amplitude response near the characteristic resonant frequency,  $F_R$ , for that mode can be analyzed to yield a value for damping capacity. This damping is the energy dissipation discussed before. Since it presumably arises from time-dependent movement of structural elements within the material, it is termed internal friction. By analogy to electrical circuits the reciprocal of the capacitance,  $Q^{-1}$ , is actually the tangent of the phase angle between the stress wave and the strain wave, the stress leading the strain.

The internal friction may also be determined from decay of free vibration at the resonant frequency for a fundamental mode. These methods supplement one another. When the internal friction is low, the half width,  $\Delta F$ , of the amplitude-frequency plot becomes small and difficult to determine. When the damping is large the attenuation of the free vibration is very rapid, making the time interval for the amplitude decrement,  $\Delta t$ , difficult to determine.

Instrumentation as shown will allow determination of the resonant frequency for a specimen suspended for flexural vibration. When the oscillator is turned off the trigger sweep actuates the storage oscilloscope and a record of the attenuation of the vibration is made. By motorizing the oscillator sweep and providing it with an energized rotary potentiometer, the frequency may be plotted against the output of the amplitude-sensing pickup using a flat bed function plotter. Either of these may be analyzed to produce the damping capacity. Appropriate corrections, however, must be made for the suspension system. The unrelaxed Young's modulus is determined from the resonant frequency  $F_R$ .

If the measuring system can be established to provide information on a specimen at elevated temperature it can lead to much information relative to the deformation mechanism. It must be considered, however, that the complexity of the microstructure of an oxide may complicate the interpretations somewhat. Ceramic

materials might be thought of as being in a structural series with the single crystal as one end member and a complex, polyphase, polycrystalline material with its assemblage of defects, pores, and impurity phases as the other end member. Proceeding from the single crystal the first degree of complexity is introduced by the presence of grain boundaries. These boundaries are, of course, regions of change in entropy and represent defective regions in themselves. Herein reside two sources of anelastic response.

When solute atoms are present within the structure of the oxide they occupy selected sites which can only be accommodated in a relatively strain-free state. Under stress the unit cell will elongate parallel to the direction of stress. Poisson contraction in directions normal to the stress may force solute atoms to diffuse or "jump" into a position between atoms in line with the direction of applied stress. The energy loss accompanying this process will usually be detected if the internal friction is determined as a function of temperature. The diffusion of  $Cr^{+3}$  in alumina and the movement of  $Na^{+1}$  in glass have been detected by this method.

Grain boundary relaxation is a primary source of internal friction often occurring at a characteristic temperature. The classical interpretation shows a discontinuity in the decrease in elastic modulus at the grain boundary relaxation temperature. But this is not always true in a polycrystalline complex having highly anisotropic expansion characteristics. In the case of a silica refractory an initial expected drop in elastic modulus is followed by a sharp increase. This seems to imply that the anisotropic expansion combined with displacive polymorphic changes in the quartz, tridymite, and cristobalite present produce internal grain boundary stress which compensates for the relaxation expected. Again in the case of polycrystalline nickel oxide internal anisotropy generates a stress compensation in the region of the ferromagnetic transformation temperature. An antiferromagnetic to paramagnetic change near 300°C is shown. An internal strain component is generated which is additive with the usual strain component causing  $E$  to increase until at the transformation temperature, the strain is released and normal relaxation begins.

The structure of  $UO_2$  is somewhat typical of so-called pure oxides and represents this degree of microstructure complexity. The internal friction at room temperature is strongly dependent on the grain size or grain surface contact indicating the overriding influence of grain boundaries on anelastic energy loss. The other prominent feature of the microstructure is the grain boundary porosity. The strong dependence of elastic modulus is well known for oxides. The next degree of complexity of microstructure is quite characteristic of oxide systems. The exsolution of a second phase is the consequence of the cosolubility at elevated temperatures with a rapidly decreasing solubility as the temperature is lowered. When the oxygen to uranium ratio is increased (to  $UO_{2.071}$ ) and the material is quenched through a solubility boundary this degree of complexity is illustrated.  $U_4O_{9-Y}$  is precipitated within the boundaries of the primary  $UO_{2+X}$  to produce a Widmanstatten-type structure. The three phase assemblage: pores, primary  $UO_{2+X}$ , and the exsolved  $U_4O_{9-Y}$  is well developed. If the grain size is kept constant and porosity normalized, the internal friction and elastic modulus are strongly dependent on this second phase.

In other approaches to the study of stoichiometry and boundary effects in urania the boundary region has been treated as a highly

## Refractory Ceramics Division Alfred W. Allen Award

This biennial award was established to honor Alfred W. Allen's legacy as an educator, technical contributor and supporter of the Refractory Ceramics Division. The award committee selects as the biennial award recipient, from the technical literature of the last two years, the author(s) of the technical paper on refractory ceramics which reflects the highest level of technical quality.

Year	Author(s)	Paper
2008	Chang Min Chun, Narasimha-Rao V. Bangaru, Neeraj Thirumalai, John R. Peterson, Christopher J. Fowler and Robert L. Antram	"Erosion-Corrosion-Resistant Titanium Diboride Cermets for High-Temperature Process Applications," International Journal of Applied Ceramic Technology, Volume 5, Issue 6, pp. 597-609, November 2008
2006	Y.A. Marques, R.G. Pileggi, F.A.O. Valenzuela, M.A.L. Braulio and V.C. Pandolfelli	"Setting Additives Influence on the Thermomechanical Properties of Wet Shotcrete Refractory Castable Matrices," Ceramic Bulletin, pp. 9201-9206, 2005
2004	S. Ramachandran, K.D. Peaslee, and J.D. Smith	"Thermochemistry of Steel-Refractory Interactions in Continuous Casting Nozzles," Iron and Steelmaker, 11 (2003) pp.55-63
2002	Michel Rigaud, Stefan Palco, and Ningsheng Zhou	"Alumina and Magnesia-Based Castables Containing Graphite: Comparison"
2000	A.A. Weresczak, T.P. Kirkland, and W.F. Curtis	"Creep of CaO/SiO <sub>2</sub> -containing MgO Refractories," J. Mater. Sci., 34 (1999) pp. 215-227
1998	Gord Cuthbert, Reg White, Brian Martin, Chris Doyle, Juan Hrepic and Carlos Diaz	"The Effect of Slag Composition Control on the Performance of Magnesite-Chrome Refractory Linings in Top Blown Rotary Converters," pp.381-392, Advances in Refractories for the Metallurgical Industries II, Canadian Institute Mining, Metals, Petr., 8/96 Montreal.
1996	K.N. Singh, C.R. Beechan, T.J. Russo, W.S. Howanski and B. Brezny	"Reducing Thermally Induced Stresses in BOF Linings," pp. 491-498, 1995 Steelmaking Conference P di Proceedings
1994	J. Tu, R.B. Fortuna, and S.C. Su	"Microstructure, Phase Composition and Properties of an Olivine Based Castable," pp. 506-516, UNITECR '93
1992	Claude Allaire, Michel Rigaud, and Serge Dallaire	"Basic Phosphate-Bonded Castables from Dolomitic-Magnesite Clinkers," Journal of the American Ceramic Society, 72 (9) 1698-1703 (1989)
1988	Phil L. Smith, James E. White, and Philip G. Whiteley	"Ultra High Alumina or Silicon Carbide Refractories for Critical Areas in Blast Furnace Linings," The Technical Association of Refractories, Japan, pp. 101-117
1987	Gary D. Morrow and Robert O. Russell	"Thermal Modeling in Melt Shop Applications, Theory and Practice," American Ceramic Society Bulletin, 64 (7) 1008-12, (1985)
1986	Brian Rand and O. Serdar Ozgen	"Kinetics of Oxidation of the Graphite Phase in Alumina/Graphite Materials," Brit Ceram Trans J, Vol. 84, No. 2, pp. 70-76, 1985.
1985	Wate T. Bakker, Ulrich Gerhardus, Sherman Greenberg and Meinhold Trondt	"Refractory Practice in Slagging Gasifiers," Ceram. Bull., pp. 870-6, July 1984.
1984	Robert O. Russell and Gary D. Morrow	"Characteristics of Refractories Used in Teeming Ladles," Iron & Steelmaker, July 1983.
1983	John Sweeney and Mark Cross	"Analyzing the Stress Response of Commercial Refractory Structures in Service at High Temperature: A Simple Model of Viscoelastic Stress Response" and "II. A Thermal Stress Model for Refractory Structures," Trans. J. Brit. Ceram. Soc., Vol. 81, No. 1, pp. 25-28 and No. 2, pp. 47-52, 1982.
1982	Ranjit K. Ghose and James E. White	"Constitutional Factors Affecting the Relationship Between CaO/SiO <sub>2</sub> Ratio and Hot Strength in Magnesia-Based Refractories," Trans. J. Brit Ceram. Soc., Vol. 79, pp. 146-53, 1980.
1981	Robert H. Herron and Kenneth A. Baab	"Silicon Carbide Brick for Blast Furnaces," Iron and Steelmaker, 7 (4) 39-44, (1980)
1980	John H. Ainsworth and John A. Kaniuk	"Creep of Refractories in High Temperature Blast Furnace Stoves," Ceramic Bulletin, July 1978

disordered phase so that the grain boundary viscosity is determined. Generally this "viscosity" is simply the stress divided by the strain rate in a creep experiment. This type of experiment may be difficult to reconcile with the internal friction studies because the long heat treatment necessary to obtain the creep data produces mass transport which changes the microstructure.

In the classical internal friction experiment, activation energies can be calculated if the determination can be made at at least two frequencies. This can be done by changing the geometry of the specimen while keeping all microstructural factors constant.

It is axiomatic that raw materials for refractory oxides can be beneficiated only to a degree compatible with the economics of production and utilization of the final product. Therefore, the need for considering the most complex end member of the microstructural series is evident. Impurity phases may be present simply because they come with the major desirable phase and were not economically feasible to remove. Such phases often exist at the boundaries as shown in the model and are considered to be a viscous liquid at elevated temperatures which is retained as a supercooled or glass phase a room temperature. This phase may thus control the internal friction in a manner which produces a high background level in anelastic response. Superimposed on this background would be the internal friction peaks accompanying the various processes of deformation.

In modern basic refractories the liquid phase has been carefully controlled so that it is isolated by the direct-bonded solid phase. The diffusion interface formed during use of the refractory thus becomes an important feature of the microstructure. As the periclase regions and the high chrome regions undergo codiffusion a secondary spinel interface is formed. Mechanical behavior as evidenced by grain boundary anelasticity and the elastic modulus-temperature function will depend on maintenance of the integrity of this interface.


If the change in the elastic modulus of a chemically bonded refractory is followed as the temperature rises, the relaxation accompanying the degradation of the chemical bond is readily observed. As the ceramic bond begins to develop, the elastic modulus begins to increase again as the modified structure begins to develop.

In summary, internal friction studies along with dynamic modulus-temperature functions combined with microstructure characterization should further define origins of deformation in refractory oxides. Understanding of mechanical behavior should be the net result.

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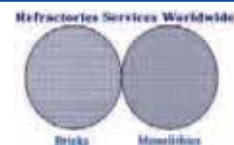
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Tel: (708) 344-7600, Fax: (708) 344-7636  
dthurman@sunrockceramics.com  
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ifbinc@aol.com  
www.insulatingfirebrick.com

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www.appliedceramics.com

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### NABALTEC AG

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### Minelco Inc.

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minelco.inc@minelco.com www.minelco.com

### Unimin Corporation

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metalcaster@unimin.com www.metalcaster.com

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