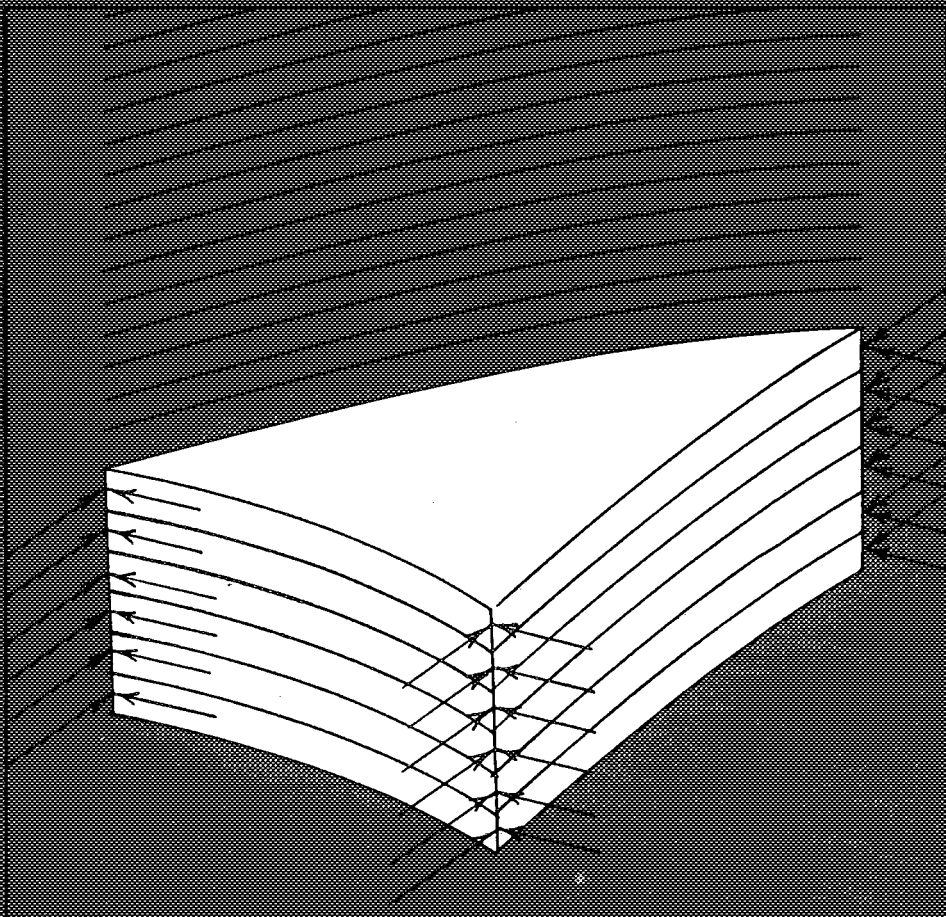


MONOLITHIC REFRACTORIES



Publication SP-74



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MONOLITHIC REFRACTORIES

David R. Lankard
Editor



Publication SP-74
American Concrete Institute
Detroit

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PREFACE

American Concrete Institute Committee 547, Refractory Concrete, was established in 1969 to provide a much-needed function of disseminating information on refractory concretes and related monolithic refractories to those involved in the production, installation, and use of this widely used class of refractory materials. Since its inception, the committee has conducted a number of seminars/workshops around the country; developed several state-of-the-art reports; and, in 1977 and 1980, organized symposia which were held in conjunction with ACI annual meetings.

The first symposium (San Diego, Calif., March 1977) had the theme "Refractory Concretes: Past, Present, and Future." The written proceedings (thirteen papers) were published as ACI Publication SP-57, 1978 (titled "Refractory Concrete"--pp. 1-307).

The present publication contains the written proceedings (ten papers, all invited) of the second symposium held in Las Vegas, Nev., March 1980 and structured on the theme "Premature Failure in Monolithic Refractory Constructions: Preventative and Remedial Treatment."

The symposium keynote address was given by Wate T. Bakker, who set the stage with his discussion of recent advances in refractory concrete technology that have led to improved performance in a variety of applications. Refractory problems (and solutions) unique to a number of these applications (coal gasification equipment, aluminum melting and holding operations, refining and petrochemical operations, and steel plant operations) were then considered in greater detail by subsequent speakers. Refractory producer and user viewpoints were both represented in these discussions.

Timely presentations were also made on the traditional and newly evolving procedures for designing monolithic refractory constructions and for nondestructively assessing the in-place quality and performance of these installations.

The information, insights, and recommendations presented at the 1980 symposium should be of great value to everyone concerned with the production, selection, installation, performance, and

maintenance of monolithic refractory constructions. Committee 547 is pleased that ACI has chosen to make them available through this publication.

David R. Lankard
Symposium Chairman
Chairman of ACI Committee 547
on Refractory Concrete

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SP 74-1**Recent Advances in Refractory Concrete Technology****By Wate T. Bakker**

Synopsis: Recent research on refractory concretes for use in energy conversion applications has provided data, useful in other areas. It is shown that refractory concretes, especially those containing a calcined fireclay aggregate, are very tolerant to environments, generally considered corrosive, such as gases containing CO, CO₂, H₂, H₂S and steam at high pressures. Even when the hydrated calcium aluminates are decomposed and some of the CaO is leached out, a refractory with acceptable physical properties remains. In many cases the strength of the material increases during service.

Improved design methods for refractory concrete were also developed. A computer program to calculate heat losses from refractory concrete lined pressure vessels was developed and experimentally verified. This model takes into account the effect of cracks, anchor spacing and different gases in the pores of the concrete. The thermo mechanical behavior of refractory concrete was studied experimentally and modelled by computer. Design and materials selection criteria were developed. To minimize cracking, shrinkage and creep of the concrete should be low, preferably less than 0.1%. Anchor spacing should be wide and the anchors coated with a compliant or combustible material to avoid stress concentrations. Bond barriers between the vessel shell and the refractory and between various refractory layers are also beneficial. Long holding periods during initial heat up of the lining were found superfluous.

Keywords: aluminum oxide; anchors (fasteners); bonding; calcium aluminates; clay minerals; coal gasification; compressive strength; computer programs; corrosion resistance; cracking (fracturing); creep properties; curing; dehydration; drying; feldspars; fire-clays; high-alumina cements; high temperature; linings; models; pressure; refractory concretes; research; shrinkage; silica; structural design; thermal expansion.

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Wate T. Bakker is presently Program Manager for Refractories and Ceramics at the Electric Power Research Institute. Previously he was Branch chief, materials in the Fossil Energy Directorate of DOE, where he managed a program on Refractory Concrete for Coal Gasifiers, and research associate in charge of High Alumina Refractories and Refractory Concrete at General Refractories Company

INTRODUCTION

U. S. Bureau of Mines Statistics presented in an earlier paper (1)* indicate that the production of refractory concrete is the fastest growing segment of the refractory industry. Although no recent statistics are available, there is little doubt that the rapid growth in refractory concrete production is still continuing. Several new developments, which were discussed at the 1977 ACI Symposium on Refractory Concrete have found considerable commercial acceptance. Examples are:

- Fiber reinforced Refractory Concrete
- High density, low cement refractory concrete
- Gun casting of refractory concrete

Research on refractory concrete has also increased considerably. Much of this increased activity is in the area of proprietary product development. Prospective applications of refractory concrete in emerging energy conversion processes, have spawned a sizable research effort in the public sector, sponsored mainly by DOE and, to a lesser extent, by EPRI. (2,3)

Standards development by ASTM has also been quite intense and has resulted in the introduction of four new recommended practices, covering the casting, gunning and firing of refractory concretes and the abolition of two obsolete standards. (4) Parallel activities are taking place overseas, especially in Europe, and have resulted in several new DIN standards.

It appears, therefore, that the stage is set for a continued rapid growth of refractory concrete usage in various areas such as emerging new energy technologies: coal gasification and liquefaction, fluidized bed combustion and combined cycle power plants. In this paper, we will discuss some of the pertinent results of recent research in refractory concrete technology of interest to the refractory community in general. Firstly, I will address interactions between refractory concrete and the service environment. Secondly, I will discuss the design of refractory concrete linings and their

*Superscripts indicate references pages

response to thermo-mechanical loads. Most of the work discussed here was carried out in various research institutes and universities. Summaries of these programs can be found in the proceedings of the fourth annual conference on materials for coal conversion and utilization.(3)

STABILITY OF REFRACTORY CONCRETE IN SERVICE

In air, the hydraulic phases in refractory concrete, CAH_{10}^* or C_3AH_6 are known to dehydrate at 200-350°C to CA or C_{12}A_7 . Other bonding phases such as AH, decompose to gamma alumina at the same temperature (Figure 1). (5) It is also well known that dehydration generally results in a drop in strength, (6) (Figure 2), although careful formulation of the concrete can minimize the strength loss. At higher temperatures, the calcium aluminates react with the aggregate to form CA_2 , CA_6 , or calcium aluminum silicates if silica is present.

For many applications, especially those at atmospheric pressure, this sequence of events is plausible and explains the behavior of refractory concrete in service adequately. However, since the matrix of most refractory concretes is extremely fine, it reacts quite readily with gases which may be present in the furnace such as CO , CO_2 and steam, especially at elevated pressures. This can lead to the formation of different compounds such as calcium carbonate or formate, Boehmite (AH), the high pressure hydrated calcium aluminate $\text{C}_4\text{A}_3\text{H}_3$ and Anorthite CAS_2 . The high pressure gas environment of dry ash gasifiers is a good example of such a reactive service environment and has been extensively studied in the last few years. (7, 8, 9) Although the service conditions in coal gasifiers are rather extreme, it is likely that similar reactions may occur in other service environments in the chemical and steel industries.

In a coal gasification atmosphere* at 500-1000 psi, Boehmite (AH), calcite and, less frequently, calcium formate are formed at temperatures below about 300°C. The formation of Boehmite markedly increases the strength of all concretes regardless of the aggregate used (Figure 3). The strength increase is related to the amount of Boehmite formed, which in its turn depends on the degree of steam saturation of the gas mixture. Calcium oxide has a tendency to leach out under these conditions especially when the CO content of the gas mixture is high (Figure 4). Fortunately, the strength of the concrete is not affected. This indicates that Boehmite is the most effective binder phase here.

*Concrete terminology C = CaO A = Al_2O_3 H = H_2O S = SiO_2 .

*Nominal 18% CO , 2% CO_2 , 5% CH_4 , 24% H_2 , 40% H_2O , 1% H_2S .

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At temperatures above 300°C Boehmite starts to decompose. Complete decomposition has occurred at 500°C. In low silica, high alumina concretes, this leaves $C_4A_3H_3$ and CA as the principal bonding phases and generally results in a decrease in strength. The actual strength loss depends on the heat up and cool down schedules used, but the room temperature bond strength after exposure to coal gas atmospheres at 500°C is generally about 25% less than the strength of similar samples fired in air. Thus, no catastrophic loss in strength occurs.

Refractory concretes containing silica or silicates, such as calcined clay base products, generally show a significant increase in strength after exposure to coal gas environments or high pressure steam at 500-1000°C, as compared to similar samples fired in air. Depending on the type of cement used, a strength increase of 100-200% may occur. Work at the NBS indicates that this strength increase persists at elevated temperatures up to at least 1200°C (Figure 5). This increase in strength is attributed to the hydrothermal formation of Anorthite by workers at the NBS. Formation of Anorthite is indeed common in samples exposed at 1000°C. However, specimens exposed at 500°C generally do not contain enough Anorthite to be detected by XRD, but do increase in strength. Workers at the Bureau of Mines attribute the increase in strength to the formation of an interlocking network of mullite crystals in the matrix as shown in Figure 6. As a further support for this hypothesis, they point out that calcined clay/fire clay brick also show a marked increase in strength when fired in high pressure steam instead of air (Table 1).

Since the strength of refractory concrete appears structure dependent, it may be possible to degrade the strength of concrete by repeated cycling across a phase boundary. At the University of Missouri at Rolla, (8) several concretes were, therefore, cycled across the Boehmite decomposition temperature. The modulus of rupture was measured after each cycle at room temperature. Results are given in Figure 7. It appears that the strength increase provided by the formation of Boehmite is retained even after several decomposition cycles in all concretes except the low silica concrete. XRD and TGA analysis indicate that not enough Boehmite formed in the latter to cause a strength increase. In previous tests strength increases similar to those of the other concretes were found. The other concretes, which all contain at least some silica, appear a little stronger than the same concretes, heated to 500°C or above and then exposed to the coal gas atmosphere. This indicates that a favorable bond phase, such as Boehmite, may transform to another mineral species such as Alumina, Anorthite, or Mullite, without losing the original microstructure which is responsible for the increase in strength. If this pseudomorphic transformation mechanism is true, there appears to be a fruitful area of further development here to optimize the microstructure of a refractory concrete at a low temperature in order to provide better properties at operating temperature.

In general, it can be concluded that refractory concretes, especially those containing some silica, are very tolerant to environments generally considered corrosive. Even when the

Calcium Aluminates are decomposed and most of the CaO is leached out, a refractory with acceptable physical properties remains. In many cases, the strength of the material even increases in service.

DESIGN OF REFRACTORY CONCRETE LININGS

Under ERDA/DOE sponsorship, a considerable effort was also made to better understand the behavior of refractory concrete during service in process vessels operating at high pressures and temperatures up to 1100°C. The two main issues addressed were:

1. Heat losses through refractory lined walls in service environments high in hydrogen, with partially cracked linings.
2. Thermo-mechanical stability of refractory concrete linings during heat up and cool down.

The program on thermal flux measurements carried out at the Battelle Columbus Laboratories has been completed and the resulting report (10) may be considered as a key reference for designers interested in heat losses from refractory concrete lined furnaces. A computer program to calculate heat losses for complex lining configurations has also been developed. The predictions of the computer program were experimentally confirmed using a highly instrumented 24 x 24" refractory concrete lining segment. Agreement was, in general, excellent.

The results of the Battelle study show that the traditional method of calculating heat losses through refractory brick linings is also an acceptable first approach for refractory concrete linings, provided that they are sound and the kiln atmosphere does not contain a high concentration of hydrogen.

The effect of anchors on the total heat loss was found to be surprisingly small (Figure 8). The effect of gas pressure was found to be negligible. Condensed water in the insulating concrete at the cold face has a more noticeable effect as shown in Figure 9.

Hydrogen in the kiln atmosphere and cracks parallel to the heat flow both give significant increases in heat loss. For the system studied at Battelle, which is fairly typical (Figure 10), a 30% increase in heat loss was found experimentally, when hydrogen is used instead of air. The computer program predicted a heat loss which was about 25% higher. It is speculated that some of the hydrogen in the pores may have oxidized. The effect of cracks on the heat flow was modelled and verified only for static conditions, without natural or forced convection through the cracks. Even without convection, 2 volume percent cracks extending parallel to the heat flow for 7-1/2" into the refractory lining will increase the heat loss by about 25% (Figure 12). This result agrees well with calculated heat losses which assumed heat loss by radiation along the crack. Table 2 shows

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some predictions for 12" cracks extending from the hot face to the cold face. Heat loss by radiation through open cracks becomes more pronounced as the temperature difference between hot and cold face increases.

The study of the thermo mechanical behavior of refractory concrete linings by Babcock & Wilcox Co. is still in progress. Modelling the thermo mechanical behavior of refractory concrete linings proved to be considerably more complex than modelling the heat flow. It is, therefore, not likely that a model for use as a design tool can be developed similar to that developed to calculate the heat losses. The main reason is that the stresses and strains generated in the concrete lining are very dependent on small changes in expansion, shrinkage and creep. These properties are very much dependent on the water/cement ratio and the dehydration schedule used and therefore cannot be determined or predicted with the required accuracy. Complex anchor/concrete interaction are also difficult to model. Thus, the design of refractory concrete linings will largely remain an experience based art for the near future. However, the very meticulous experiments carried out by Anderson and his coworkers have added greatly to our experience base. (11, 12) In a series of controlled heat up and cool down experiments on a 12" dual component refractory concrete lining a 5' diameter pressure vessel, the B&W team managed to reduce cracking of the hot face from very obvious 1/16 - 1/8" cracks to hairline cracks, which were only visible on very close inspection. This improvement is due to systematic changes in lining design and materials choice. Major contributing factors are listed below:

1. Material selection--Shrinkage and creep at all temperatures up to the operating temperature must be as small as possible. The linear shrinkage should preferably be less than 0.1%. Desired maximum creep rates are less well defined. Standard data using a 25 psi load are of little value, as stresses generated in a cylindrical pressure vessel during heat up and cool down can easily reach 1000 psi, before they are relieved through creep. The 50% Al_2O_3 low cement concrete, used by B&W in their most successful linings has about 1% deformation in a 10 hr creep test at 1100°C using a 1000 psi load. The thermal expansion should also be low, as most of the lining stress is generated by thermal expansion. Thus, if shrinkage and creep are equal, alumina-silica concretes crack less than tabular alumina base concretes. The newly developed relatively coarse grained low cement alumina-silica concretes have about the same shrinkage and creep of tabular alumina concretes at 1000°C and are, therefore, prime candidates for coal gasification vessel linings at temperatures below 1100°C.

Finally, the use of steel fibers appears to have a beneficial effect on crack propagation, probably because of their ability to distribute the thermal and mechanical loads more evenly.

2. Anchors and anchor spacing--Interaction between anchors and refractory concrete are a prime cause of cracking. Therefore, the widest possible anchor spacing should be used. At B&W a 36" anchor spacing definitely produced less cracking. Even wider spacings may be possible. Additional independent short anchors for the insulating layer resulted only in a more severely cracked insulator. A 100-250 mil coating on the anchors is needed to prevent anchor-refractory interactions and appears to reduce cracking. Without the coating, compressive stresses in the anchors exceed the yield strength of stainless steel (Figure 13).
3. Bond barriers--The use of bond barriers at the steel shell and the interface between the dense and the insulating layer is also beneficial. The barrier at the interface prevents cracks, initiated at the hot face, to propagate into the insulator and also allows the dense layer to expand and contract more freely, especially if coated anchors are used.
4. Heat up schedule--A slow steady heat up rate of 50-100 F/hr without holds for dry out and dehydration gave less cracking than more conventional heat up schedules. Explosive spalling did not occur and only modest steam pressures were generated inside the lining.

All the above improvements were obtained while using very well controlled casting and installation procedures, using always the lowest water content needed to vibrate the material in place.

Another interesting result of the B&W study is the interaction between the lining and the shell. Stiff linings without coated anchors and bond barriers using a 95% Al_2O_3 concrete with a relatively high thermal expansion can induce hoop stresses up to 11000 psi in the pressure vessel shell (Figure 14) at 1200°F. The use of bond barriers, coated anchors and a 50% Al_2O_3 concrete at the hot face reduced the hoop stresses to 4000 psi at 1700°F and about 7000 psi at 1850°F (Figure 14). Thus shell stresses are reduced considerably.

In general, it can be concluded that it will probably not be possible to design and install refractory concrete linings which will not crack during service. However, it is possible to reduce cracking to the point that is safe to assume that all cracks will be closed tight at operating temperature. The key materials properties to achieve this are shrinkage, creep and thermal expansion. All should be as low as possible. Of all presently available products, high density 50% Al_2O_3 concretes with a low cement content appear to come closest to meeting these requirements. It is reassuring that the raw materials for these products are available domestically and in great abundance.

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Table 1. Effect of high pressure steam on strength and mineral composition of refractories.

	Cold Crushing Strength (psi)		Mineralogy (X.R.D.)		CaO (percent)
	Air ⁽¹⁾	Steam ⁽²⁾	Air ⁽¹⁾	Steam ⁽²⁾	
Calcined clay plus raw kaolin	1,930	7,720	Mullite, Cristobalite, Rutile	Mullite, Cristobalite, Tridymite, Rutile	0.1
50% Al ₂ O ₃ concrete	3,310	11,180	Mullite, Cristobalite, C ₂ AS, CA, CA ₂	Mullite, Anorthite, Cristobalite, α Al ₂ O ₃	7.7

(1) 980°C, 250 hr, 1 atm

(2) 980°C, 1,000 psi, 250 hr

Table 2. Effect of through-cracks on heat flow-air and hydrogen comparison.

Crack Configuration	Hot Face Temperature (°F)	Gas	Total Heat Flux (Btu/hr ft ²)	Increase in Heat Flux Relative to Standard Case (Btu/hr ft ²)	Increase in Heat Flux Relative to Standard Case (percent)
No cracks	1500	Air	468	0	0
No cracks	2000	Air	621	0	0
No cracks	1500	H ₂	795	0	0
No cracks	2000	H ₂	1044	0	0
12 in. through-crack	1500	Air	791	323	69
12 in. through-crack	2000	Air	1248	621	101
12 in. through-crack	1500	H ₂	998	203	26
12 in. through-crack	2000	H ₂	1502	458	44

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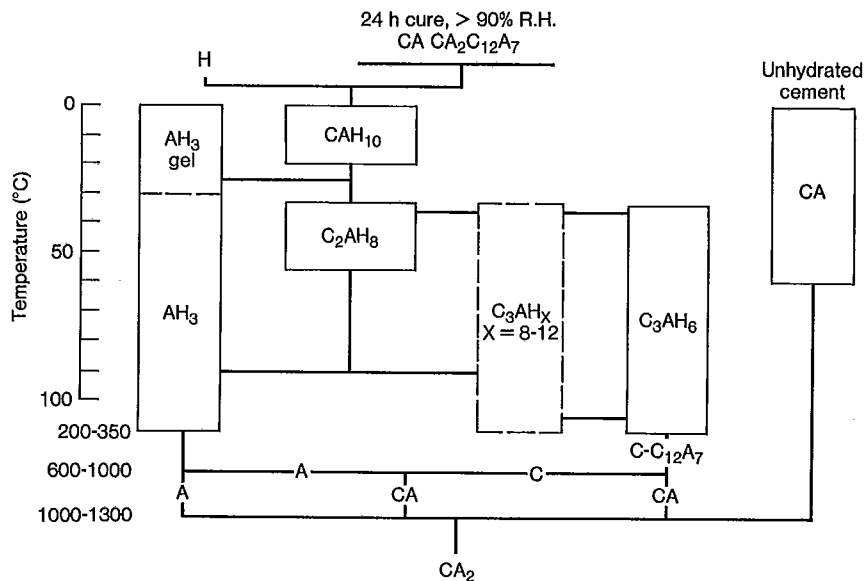


Fig. 1--Hydration and dehydration of calcium aluminate cement

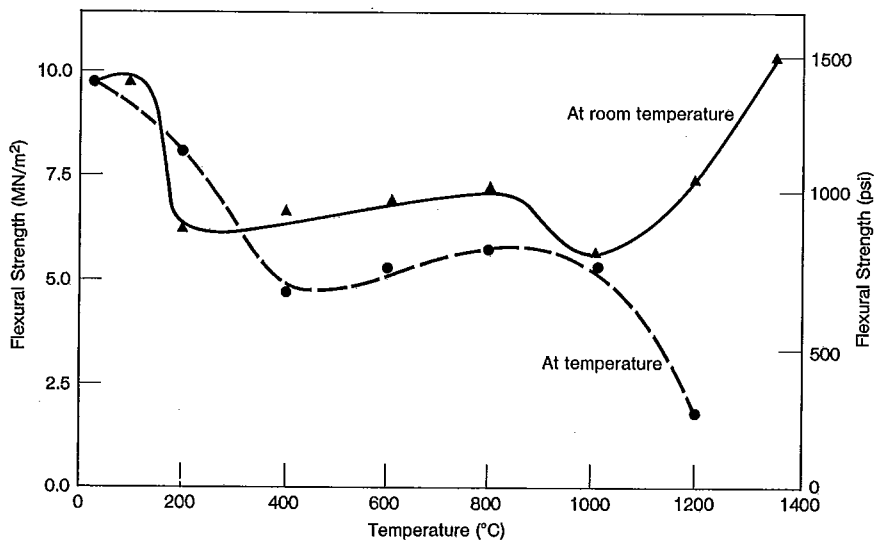


Fig. 2--Strength of 50 percent Al_2O_3 concrete as a function of temperature

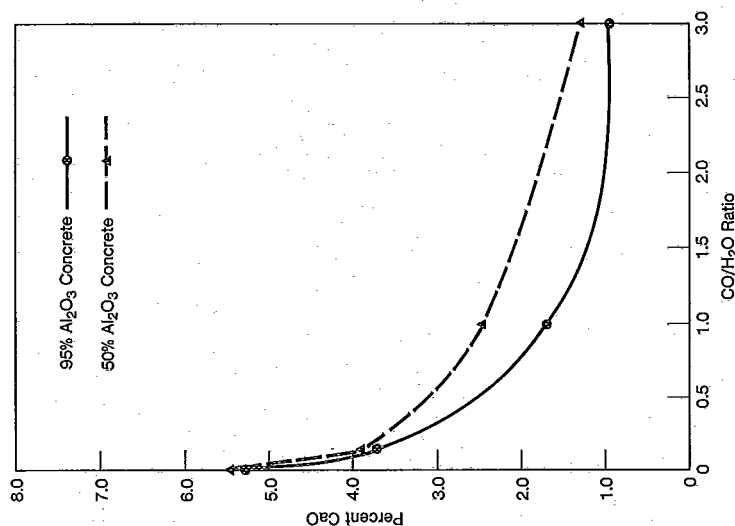
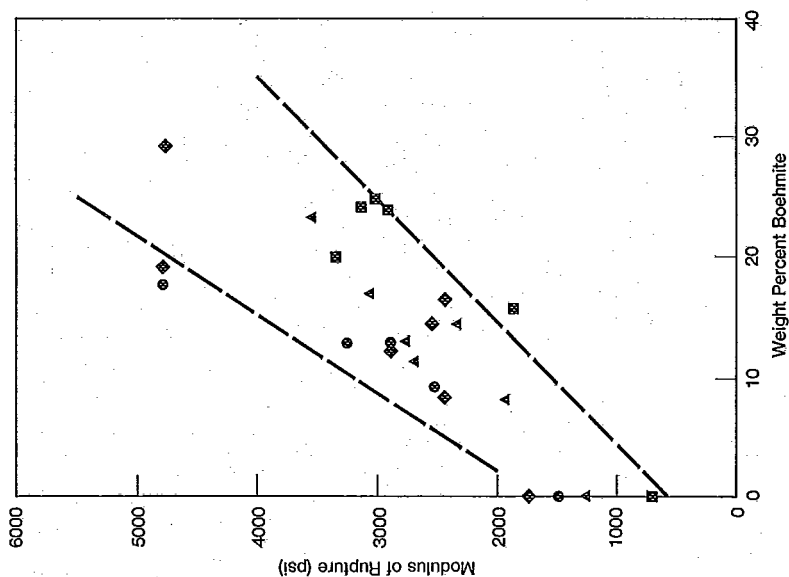


Fig. 4--Decrease of CaO content of high and intermediate alumina concretes after 20 days' exposure in various coal gas mixtures



3--MOR of 95 percent Al₂O₃ concretes after exposure to coal gas atmospheres--Effect of boehmite content

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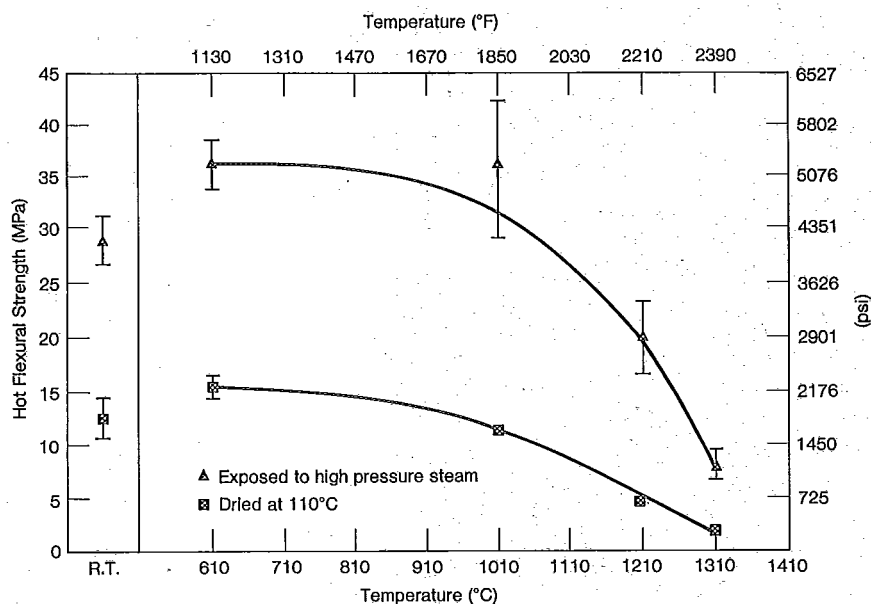


Fig. 5--Hot modulus of rupture of a 56 percent Al_2O_3 refractory concrete before and after exposure to high pressure steam

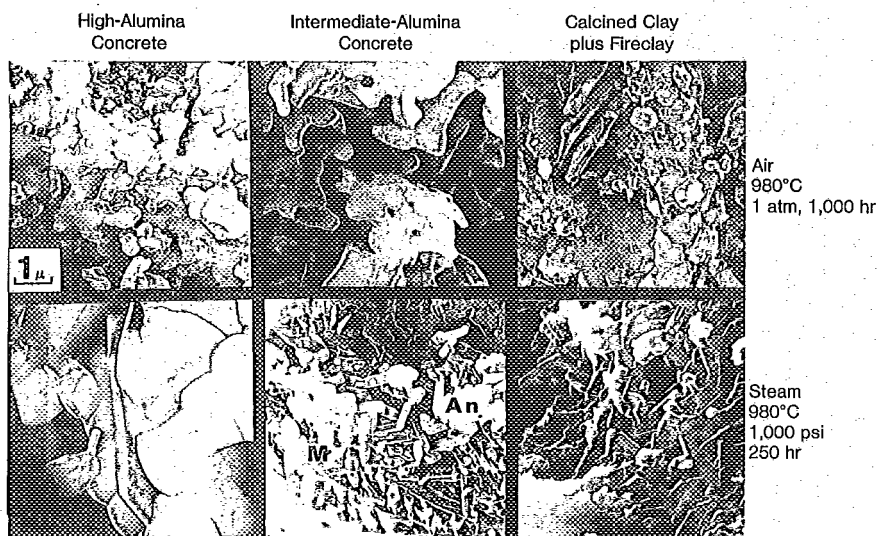


Fig. 6--Mullite formation during exposure to high pressure steam

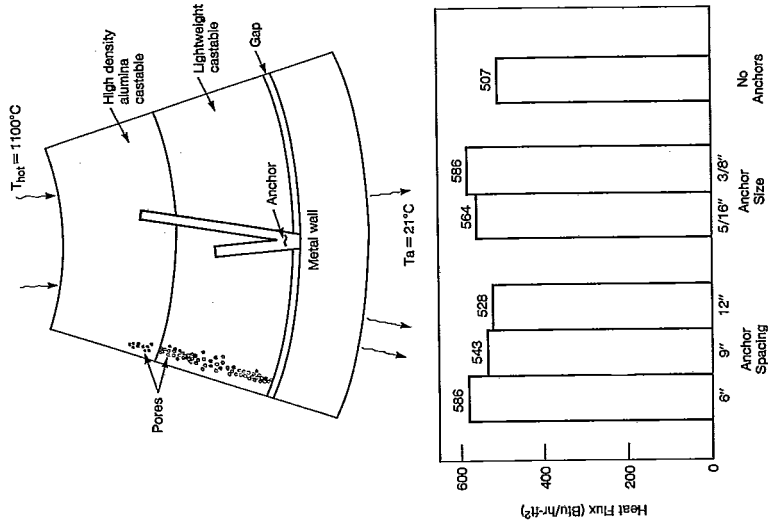


Fig. 8--Effect of anchor size and spacing on heat flux through refractory concrete lining

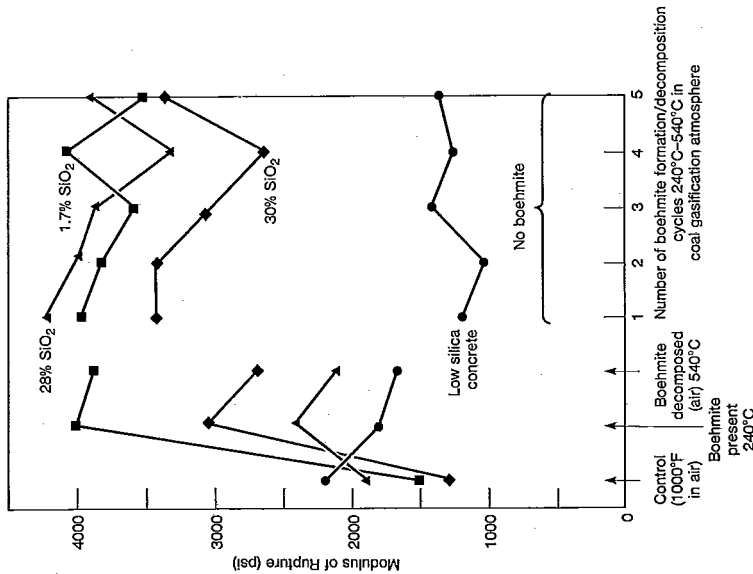


Fig. 7--Room temperature modulus of rupture of refractory concretes before and after repeated boehmite formation/decomposition cycles

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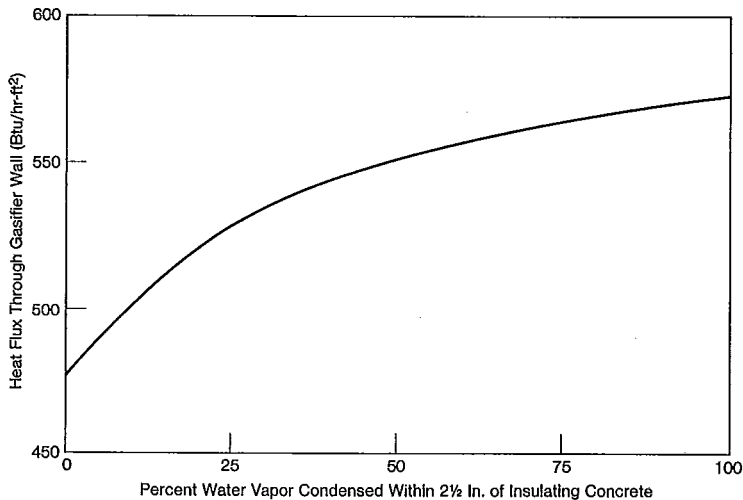


Fig. 9--Increase in heat flux through a refractory lining caused by condensed water at the cold face (hot face temperature 815 C)

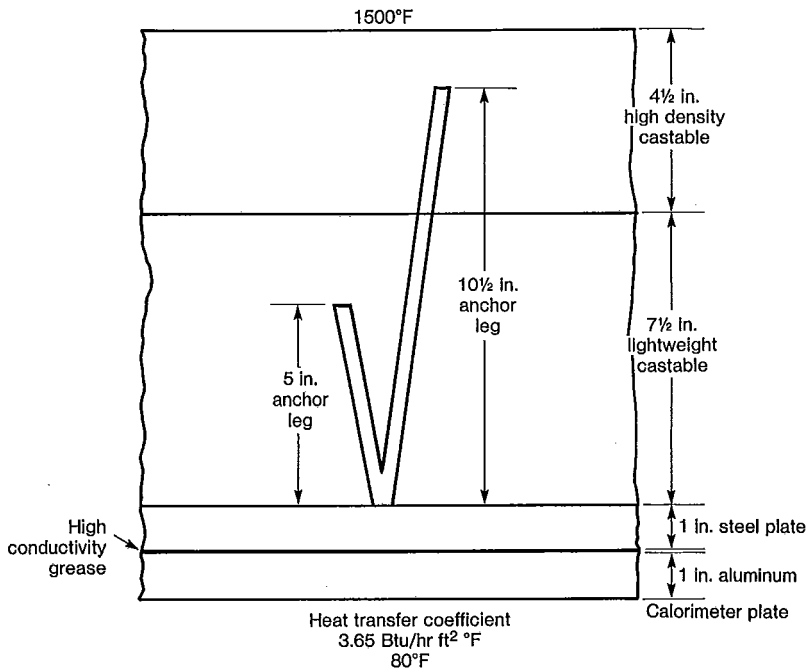


Fig. 10--Experimental material system A

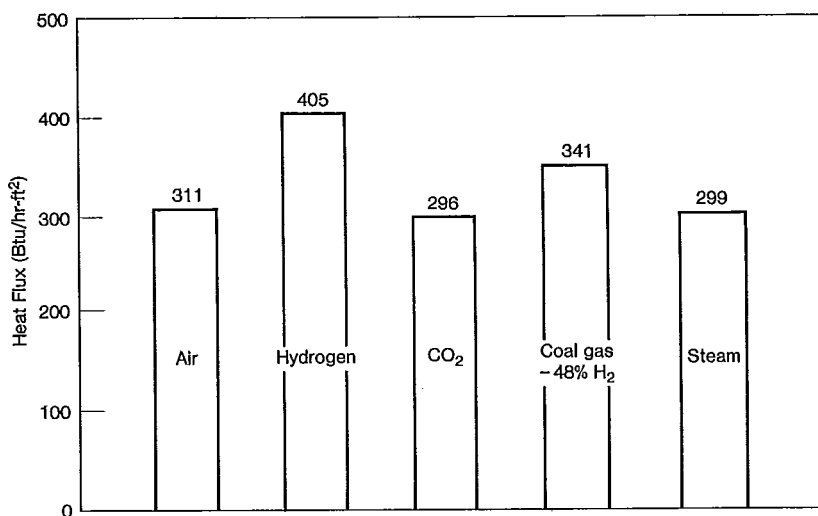


Fig. 11-- Effect of gas composition on heat flux through composite, 12" refractory lined wall

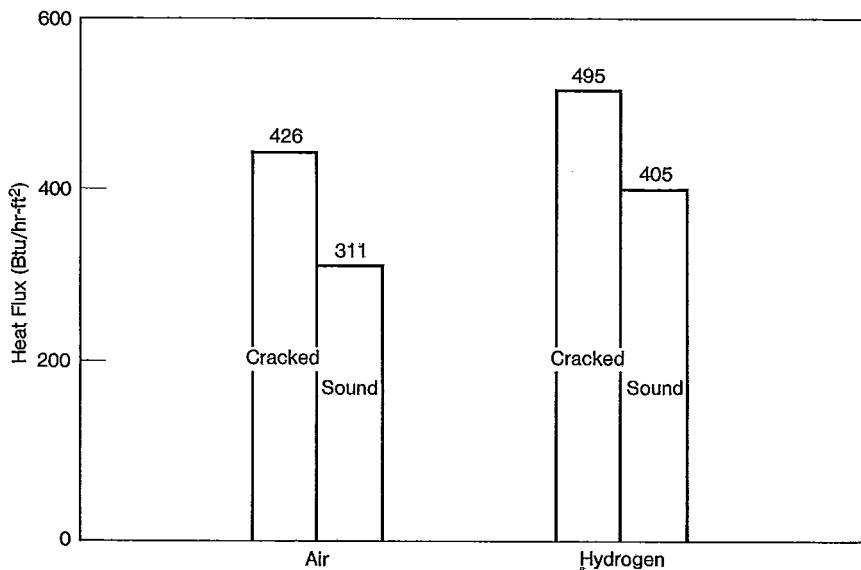


Fig. 12--Effect of 7 in. deep cracks on heat flux in air and hydrogen

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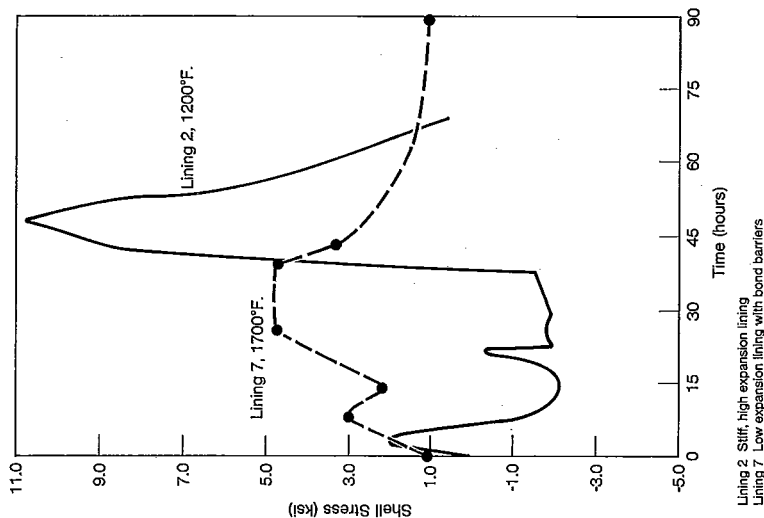


Fig. 14--Stresses induced in pressure vessel shell by refractory lining during heat up and cool down

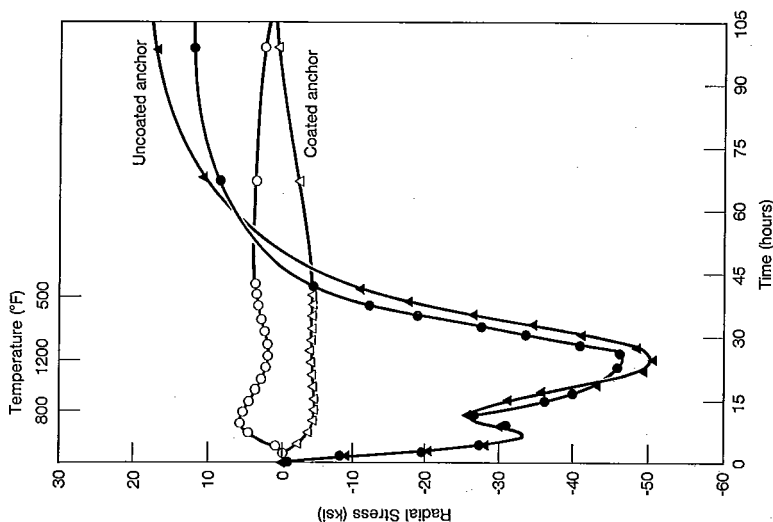


Fig. 13--Effect of coating on anchor stresses during thermal cycling

Castable Refractory Design Requirements

By S.A. Bortz, R.F. Firestone, and M.J. Greaves

Synopsis: Refractory is a construction material which is used in hot, hostile environments where plain concrete fails. Although concrete practice can be used as a guide, there are many special factors which must be taken into account to develop an optimum design. A thorough understanding of these factors is essential for successful refractory castable application.

Keywords: aluminate cements and concretes; chemical attack; coal gasification; compressive strength; corrosion; corrosion resistance; creep properties; density (mass/volume); erosion; failure mechanisms; high temperature; linings; modulus of elasticity; refractory concretes; spalling; stresses; structural design; thermal conductivity.

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INTRODUCTION

Design Consideration as Applied to a Coal Gasifier

For the purpose of this paper, the design process for a slagging gasifier lining will be used as an example. The consideration presented are similar for refractory linings for other processes as well.

The first consideration in designing a refractory lining is to find a material that will withstand the expected temperature in an atmosphere which can include hydrogen, steam, carbon monoxide, hydrogen sulfide, and/or sulfur dioxide. In addition to withstanding the high temperature process atmospheric condition, a lining must also withstand the fluxing action of either acidic or basic slag. A third consideration is to find a material that can withstand the erosion to which it will be subjected under operating conditions.

Reducing gases, primarily H_2 or CO , will attack silica-containing refractories at low pressures and high temperatures, whereas steam and CO_2 are aggressive at high pressures and high temperatures. In a reducing atmosphere ash, which contains iron, is more corrosive to alumina-silica refractories than it is in an oxidizing atmosphere of the same temperature. Magnesia, on the other hand, may dissolve relatively large amounts of ferrous oxide in a reducing atmosphere without apparent damage. High pressure (1000 psig) steam-rich atmospheres tend to accelerate refractory deterioration. Lower pressures (0-100 psig) favor attack by hydrogen-rich atmospheres.

There is probably no one material which will meet all these requirements. High-alumina refractories, which are inherently abrasion resistant and are inert to an acid slag, can usually contain coal gasification atmospheres and will effectively resist attack by steam, the most aggressive agent at high pressures. Under some conditions, it is necessary or desirable to include chromic oxide in the formulation of high-alumina refractories manufactured for coal gasification service. One purpose of the chromic oxide is to react favorably with ferrous oxide in preference to alumina.

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Another reason is to take advantage of the very high melting point of chromic oxide (over 4100°F) which is about 400°F higher than the melting point of pure alumina. Fortunately, there are no low-temperature eutectics in the alumina-chromic oxide system.

Corrosion of refractories by steam involves extraction of soluble oxides or hydroxides and formation of silicic acids from aluminosilicates. Since most pre-fired alumina refractories develop their strength and coherence through siliceous bonds, steam at elevated temperatures and pressures can readily cause softening and deterioration. High-alumina castables, in which calcium aluminates bind the alumina or aluminosilicate aggregates, do not exhibit such surface deterioration and are a better choice for lining some vessels than pre-fired materials of the same alumina content.

High-alumina materials which are phosphate bonded may also be preferred for some applications. The extraction of phosphorus pentoxide present as AlPO_4 ($\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 = 2 \text{AlPO}_4$) in hydrogen-rich atmospheres has not proved as damaging as previously predicted. This lack of reaction between phosphorus and hydrogen may indicate that atmospheres with a high partial pressure of steam are oxidizing with respect to phosphorus bonds and not reducing even though there is an apparent excess of hydrogen and carbon monoxide. Phosphate bonded materials need to be used with caution for service under highly reducing conditions with very low partial pressures of steam.

The temperature and the oxidizing or reducing characteristics of the process gases as simultaneously expressed in terms of the ratios $\text{H}_2/\text{H}_2\text{O}$ and CO/CO_2 need to be established before the lining of a unit can proceed. The partial pressure of steam in the gas must also be considered independently of the foregoing ratios. In order to classify an atmosphere where the foregoing ratios are not known, it has been found useful to calculate the atom fractions of oxygen, hydrogen, and carbon and plot them on a normalized ternary system diagram (1).

For this calculation, oxygen includes all atoms of oxygen in combustion air, steam, and fuel except those bound in minerals forming the ash. Hydrogen includes all atoms of hydrogen in fuel and steam. Carbon includes carbon atoms in gaseous species plus solids and liquids, if any.

For purposes of this discussion, it is convenient to classify atmospheres as oxidizing or reducing in terms of stoichiometric combustion ratios (FSA)* or pure hydrocarbons as follows:

FSA	Atmosphere
0-0.25	Reducing
0.25-0.50	Reducing/transition
0.50-1.00	Oxidizing/transition
over 1.00	Oxidizing

*FSA = Fraction of stoichiometric air.

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If the composition of the products of partial oxidation in a coal gasifier falls in the oxidizing/transition or the reducing/transition range of FSA values, the atmosphere may be either oxidizing or reducing depending on the temperature, pressure, minor constituents, relative reaction rates, etc. These conditions are shown graphically on the ternary system diagram of Fig. 1. Lines representing $FSA = 1.0$, $FSA = 0.5$ and $FSA = 0.25$ for any hydrocarbon, CH_n , containing no oxygen, can be found on lines drawn through a common point on an extension of the carbon-hydrogen axis with virtual coordinates (1.33H-0.33C.)

The line connecting H_2O and CO_2 represents complete (stoichiometric) combustion of CH_n . The point found at the intersection of this line and the line through CH_n and O_2 define the atom fractions of oxygen, hydrogen, and carbon for $FSA = 1.0$.

The line connecting $H_2O_{1/2}$ (.033 O, 0.67 C) represents combustion of CH_n with 25 percent theoretical oxygen. The point found at the intersection of this line and line through CH_n and O_2 defines the atom fractions of oxygen, hydrogen, and carbon for $FSA = 0.25$.

The atmosphere is reducing in processes represented by atom fractions in the zone, $C-CO_{1/2}-H_2O_{1/4}-H_2$.

In the reducing/transition zone, $CO_{1/2}-CO-H_2O_{1/2}-H_2O_{1/4}$, other factors such as temperature, pressure, and presence of sulfur and catalysts determine whether the atmosphere is oxidizing, neutral, or reducing with respect to any particular refractory. The products or combustion under boiler, where less than stoichiometric air is used to suppress nitrogen fixation, fall in the oxidizing/transition zone.

The atom fractions can be calculated from the quantities and ultimate analysis of the materials going into a process or from the volumetric analysis of the gas coming out (2).

Refractory Failure Mechanisms

Material exposed in gasifiers and similar environments are known to fail by gaseous corrosion, slag corrosion, erosion, and spalling.

- Gaseous corrosion of high-temperature refractory materials can occur at temperatures as low as 1350°F. Silicon carbide is subject to deterioration in oxidizing atmospheres at this temperature. The corrosive components of coal gasifier atmospheres include hydrogen, steam, carbon monoxide, hydrogen sulfide, sulfur dioxide, carbon dioxide, alkali vapors, and aerosols.

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- Molten slag attacks all refractories presently used in slagging coal gasifiers unless they are water-cooled to form a protective layer of frozen slag on the surface.
- Erosion and abrasion by particulate matter is normally not a major problem in slagging gasifiers since most refractories are inherently abrasion resistant and the velocities in gasifiers are normally low except possibly at localized areas. Graphite refractories are soft and may need special protection.
- Spalling and mechanical failure is difficult to characterize because it is usually not a factor, but when it is, the results can be catastrophic.

Thermal stresses in the lining are one cause of spalling. These stresses are particularly important at low temperatures during heat-up when the refractories are relatively brittle and when the maximum thermal gradients occur. Thermal stresses that can lead to low-temperature spalling failures can be caused by three distinctly different loading conditions:

- a. Heating and cooling without external restraints
- b. Heating and cooling with external dimensional restraint
- c. Heating and cooling with external load restraint.

Of these, the second causes the highest thermal stresses while the third can cause progressive failure as the load is transferred from one part of the lining to another.

The effect of thermal stresses and the avoidance of premature failure due to spalling can be minimized by slow heating and cooling, properly providing for thermal expansion, and distributing the loads on the refractory. The organization responsible for the start-up and operation of the plant should maintain control over the rate of heating and cooling during start-up and shutdown. It is possible to incorporate a sacrificial inner lining to protect the permanent lining during initial heat-up and operation.

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Design Parameters

Service conditions for representative processes have been investigated. These conditions have been characterized in such a way that an appropriate lining can be specified and designed. The most important factors to be considered in the selection of refractories process environments over 2300°F are thermal cycling, process atmospheric corrosion, and for some processes, corrosion by ash slags. Erosion is a function of operating conditions and must be considered but generally does not govern a design. Spalling is not normally a function of normal operation conditions but is of concern to designers, refractory manufacturers and operators. All refractories suitable for use in high temperature processes have a limitation on how fast they can be brought to operating temperature. Blast furnace start-ups are planned to limit temperature rise of refractories to 150°F per hour.

The presence of hydrogen must be taken into account because of its high conductivity and its effect on the conductivity of porous refractory materials.

Many processes are highly endothermic, and part of the difference among processes depends on how energy is supplied to and removed from the reactor unit and how the temperature is controlled.

Attention must also be given to the following details, particularly as they affect the refractory lining.

- Heat losses through the walls
- Expected refractory life
- Stress and strain in lining due to heat-up, cooldown and thermal cycling
- Design and construction of internal supports and access through the lining
- Reliability of cooling systems
- Usage of rejected heat, if any
- Effect of operating pressure on lining design.

Each process has its own set of operating conditions and constraints. A design based on a complete evaluation of all refractory requirements for all processes is beyond the scope of this paper. An examination of some of the common refractory lining problems encountered illustrate the range of possibilities and include most of the problems expected to be found in the design of a lining.

- a) Process atmospheric corrosion (oxidation or reduction).

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- b) All forms of corrosion depend on the operating temperature level. High temperatures are generally, but not always, more damaging than moderate temperature (fluxing).
- c) Erosion is related to corrosion and abrasion.
- d) A fourth consideration, spalling, depends on the thermal expansion and other physical properties of the refractory details of the design and installation of the refractories and temperature changes during start-up, during normal operations and during shutdown. Frequently, damage is cumulative, limiting the life expectancy of a lining to the number of such cycles.

Each of the above problems is treated in relation to the other because of the interaction that is always present.

However, in general, the design parameters used by engineers for refractory liners have been simplified as indicated in the following paragraphs, and as indicated in the above discussion, these are inadequate for good refractory design.

When designing a castable refractory lining, the following six important assumptions are generally made by design engineers:

- (1) steady-state thermal conditions exists, and transient heating and cooling can be neglected;
- (2) thermal conductivity is uniform throughout the lining, and thermal gradient therefore is linear;
- (3) shrinkage varies linearly with temperature, and the shrinkage gradient therefore is linear;
- (4) the reversible thermal expansion coefficient is constant over the temperature range considered;
- (5) the elastic modulus is uniform throughout the lining;
- (6) stress-strain relationships are purely elastic.

The first assumption relates to operating conditions. All of the others relate to properties and behavior of the refractory which are usually obtained under steady-state uniform temperature conditions. In reality, departures occur from all of these assumptions.

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Refractory Castable Properties

There have been numerous published studies of alumina or aluminosilicate refractory castables; some of the more recent ones are listed in the References. Studies have been made of the composition, cement/aggregate ratio, and mineralogy of green and fired castables (2-6). Mixing and curing conditions have been shown to influence strongly the properties of castables (2,3, 6-8). However, data on mechanical properties of castables at high temperatures are quite limited. This may be due to the complex nature of refractory castables compared with refractory bricks. In use, the castable is cured and then fired from one side only so that a temperature gradient exists through the material. Thus, if the temperature is high enough, the hot face will have a ceramic bond; the cold face will retain the original hydraulic bond; and the interior will have a mixture of both bond types. The variation in bonding causes a variation in thermal conductivity, elastic modulus, strength, density, and other properties. In contrast, a refractory brick is already fired so that a uniform ceramic bond exists throughout the material.

Most studies of the mechanical properties of refractory castables consist of measurement of room temperature strength and modulus before and after firing at various temperatures. These studies (2-4, 6,7, 9-12) have led to an idealized curve (6) for the variation of strength versus distance and temperature for a castable furnace wall (see Fig. 2). According to these studies, the cold face has the highest strength, the hot face has the lowest, and the interior of the wall shows large variations in strength with distance and temperature. The minimum at 1500°F (or 5 inches from the cold face) in Fig. 2 is due to the destruction of the original cement bond at a temperature which is too low for formation of a strong ceramic bond. The maximum at 2000°F (or 9 inches) is due to the formation of a strong ceramic bond whose strength then decreases as the temperature increases.

However, the few studies of hot strength (8, 13-16) show that this idealized curve is in error and that the variation of strength with temperature is actually much less. This is not surprising since many refractory castables have good spalling resistance, which is unlikely if there were a marked variation in strength. A typical curve from an early study on hot strength (13) is shown in Fig. 3. The lower curve shows the strength at temperature while the upper curve shows the room-temperature strength after heating to various temperatures. The actual variation in hot strength is much less than the idealized curve of Fig. 2, although there is still a decrease with increasing temperature and the hot strength is always less than the room-temperature strength.

Recently, castable refractories have been developed which have much higher hot strengths than room-temperature strengths. Figure 4 compares the hot strength of an early refractory (Castable K), such as shown in Fig. 3, with that of an improved refractory (Castable H-30). For the latter refractory, the hot strength at 1000°C

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is more than twice the room temperature strength although there is still a drop in strength at 300-400°C due to dehydration of two major hydrates in the cement, AH_3 and C_3AH_6 (16).

However, even these hot strength studies probably do not accurately reflect the variation in strength with temperature of a castable in actual furnace walls, because the specimens were heated and measured under constant temperature conditions. In use, the refractory castable is fired from one side only--that is, in a temperature gradient. Thermal conductivity is of necessity measured in a temperature gradient, and studies of this property (17-19) have shown that there is a significant difference between thermal conductivities of castables fired at constant temperature and fired in a temperature gradient. This difference reflects a difference in the degree of bonding which should cause similar differences in mechanical properties. The one study of the mechanical properties of castables fired under both condition (20) showed that the variation of density and room-temperature strength through the thickness of the castable was much less for temperature gradient firing than for constant temperature firing. This was ascribed to migration of fluxes from the hot face to the cold face making the hot face more refractory and the interior more strongly bonded. Thus, the change in strength of refractory castables with temperature may be even less than shown in the curves of Figs. 3 and 4.

Thermal Conditions and Gradients

Thermal conductivity in refractory castables is a function of both temperature and bonding condition (which itself is a function of temperature). As previously discussed, the thermal conductivity varies significantly for castables fired at a uniform temperature or fired in a temperature gradient. The differences are due to varying degrees of cement and ceramic bonding. Three behavior zones are observed corresponding to temperature levels consistent with: (1) maintenance of hydrate material; (2) loss of chemically combined water; and (3) development of a ceramic bond. Furthermore, the existence of these regions is time-dependent since dehydration and ceramic bond formation are time-temperature dependent.

Nonlinear Thermal Expansion

The physical changes in the refractory discussed in the previous sections also produces a nonlinear thermal expansion through the thickness of the refractory as well as that due to changes in temperature. In the latter case expansion increases slightly with rising temperature. Thus, there is not only a difference in expansion due to the temperature gradient through the refractory but also due to the fact that the bonding mechanism is different, i.e., cement, transition, and ceramic.

Effect on internal stresses tends to be the same for nonlinear thermal conductivity and nonlinear thermal expansion. Both will increase the hot-face compressive stresses when compared to linear gradients of these properties.



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Nonlinear Strength

Strength of the castable refractory will also be nonlinear through the wall, depending on the temperature gradient and final hot and cold side temperature. The effect of this strength variation could have drastic effects on the ability of the refractory to withstand its own dead load and its ability to resist the thermal loads to the differential thermal expansion and shrinkage during initial firing.

Nonuniform Elastic Moduli

The determination of elastic moduli of monolithic refractories is complicated by the fact they do not follow Hooke's law at elevated temperatures under realistic rates of loading. Elastic moduli diminish sharply and permanently when refractory concretes are heated. The situation is further complicated by the nonuniform temperature gradient through the wall. This condition will cause the neutral axis of the refractory wall to be located off-center, nearer to the cold face than to the hot face. The result is the cold face will carry higher stresses due to dead load compression than the hot face. In addition, the biaxial stressed due to expansion will be very complex because the differential strength and coefficient of expansion through the wall. Properties of the refractories through the wall must be obtained if the true states of stress are to be determined and a cost-effective refractory lining designed.

Creep and Stress Relaxation

There have been no systematic studies of the creep of refractory castables; the high-temperature studies discussed previously have measured either modulus of rupture or compressive strength. There are some data given in the manufacturers' literature which indicate that properly cured castables are as resistant to creep as refractory bricks. We have observed that at low loads, high alumina castables at temperature up to 3200°F have approximately the same deformation rate as comparable refractory bricks, but that at high loads the deformation rate of a castable is much greater than a brick.

Castable refractories will creep, and there will be stress relaxation under compressive and tensile stresses. At stresses below failure strength, the creep will diminish with time and approach zero. Work has been done (21) which indicates that total creep deformation does not vary much with either load or temperature, although early creep rates and elastic deformation do. This is not the normal expected behavior.

Creep occurs under normally constant stresses. When strain instead of stress is constant, the stress relaxes by the same mechanisms that causes creep, but rate behavior is different because the driving force (stress) is constantly diminishing.

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Castable refractories usually contain highly elastic refractory aggregates. Under load, both creep and stress relaxation probably occur chiefly by yielding or flow of interparticulate cement films, and stop when enough aggregate grains are in direct contact to bear load. A similar effect is noted in polycrystalline bodies containing viscous grain boundaries (22). This may explain the indifference of creep deformation to temperature and load mentioned above.

Castable refractories containing weaker aggregates or more cements or having large pore volumes show high creep rates and larger total creep deformations. They may be expected to show greater stress relaxation also.

Conclusion

A castable refractory must be an engineering material of construction which maintains a degree of chemical and physical identity in an environment characteristic of a particular process, high temperature being a major condition of such an environment. In addition to temperature, the environment must be further defined by conditions of erosion, corrosion, thermal cycling, and mechanical stress as imposed by the expected configuration of the refractory structure and its heat distribution. Once this information is well understood, rational design of castable refractory linings can be undertaken.

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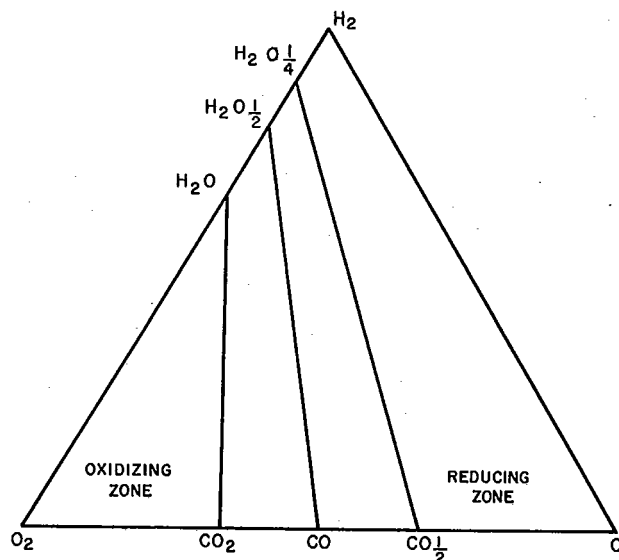


Fig. 1--Oxidizing, reducing, and transition zone for coal gasification processes (Reference 1)

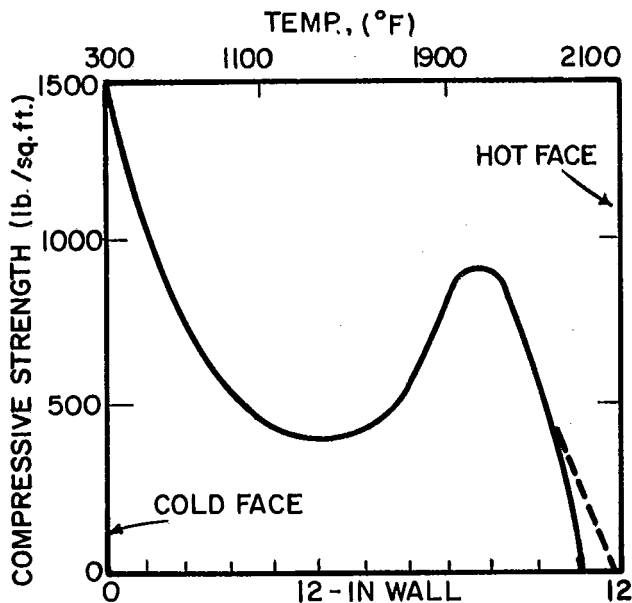


Fig. 2--Strength versus distance and temperature in a 12-in. refractory castable wall (Reference 5)

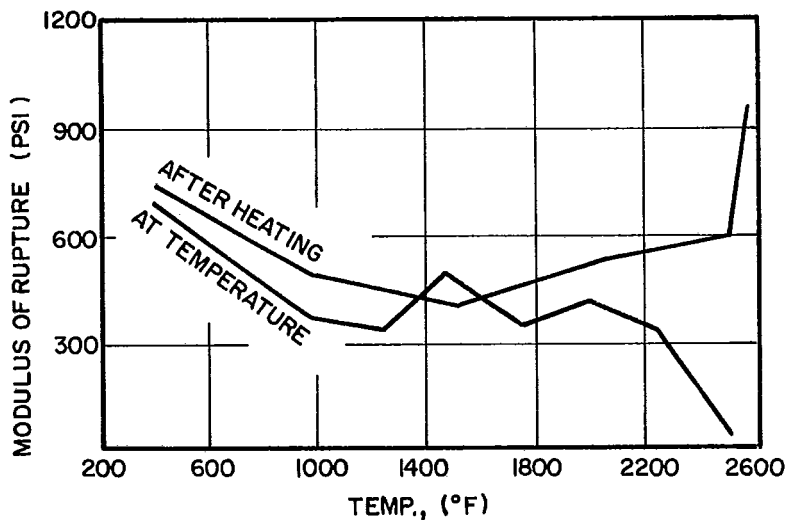


Fig. 3--Strength versus temperature for high alumina refractory castable after heating and at temperature (Reference 12)

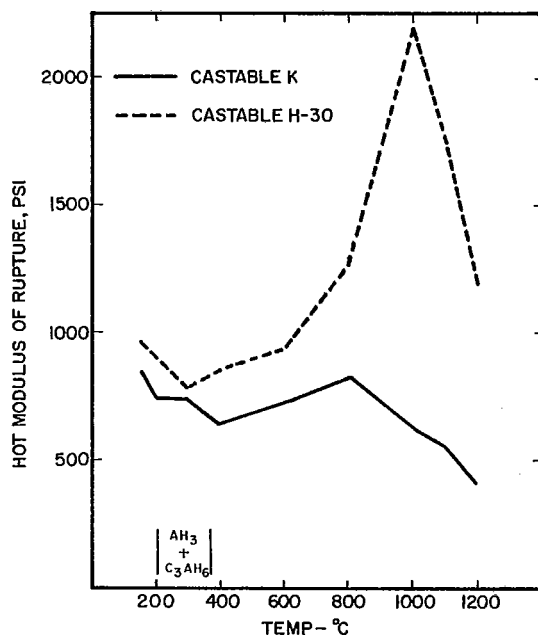


Fig. 4--Strength at temperature for two high alumina castable refractories (Reference 16)

SP 74-3

Advances in Nondestructive Evaluation Methods for Inspection of Refractory Concretes

By William A. Ellingson

Synopsis: Refractory concrete linings are essential to protect steel pressure boundaries from high-temperature aggressive erosive/corrosive environments in many energy-intensive commercial processes such as blast furnaces and petrochemical plants, and in new industries such as synthetic fuel production. Advanced nondestructive evaluation methods are being developed for assessing the integrity of refractory linings. Radiographic techniques, thermography, acoustic-emission detection, and optical laser interferometry have been shown to yield information on the structural status of refractory concrete. Methods using ^{60}Co radiation sources can yield measurements of refractory wear rate and images of cracks and/or voids in pre- and post-fired refractory linings up to 60 cm thick. Thermographic (infrared) images serve as a qualitative indicator of refractory spalling, although quantitative measurements are difficult to obtain from surface-temperature mapping. Acoustic emission has been shown to be a qualitative indicator of thermomechanical degradation of thick refractory panels during initial heating and cooling. Laser interferometry methods have been shown to be capable of completely mapping refractory lining thicknesses. This paper presents recent results obtained from laboratory and field applications of these nondestructive evaluation methods in petrochemical, steel, and coal-conversion plants.

Keywords: acoustic measurement; blast furnaces; coal gasification; corrosion; cracking (fracturing); erosion; gamma rays; high temperature; inspection; interferometers; lasers; linings; nondestructive tests; penetrameters (radiation); radiography; refractory concretes; thermography; ultrasonic tests; wear.

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INTRODUCTION

Refractory concrete linings are essential to protect steel pressure boundaries from aggressive high-temperature erosive/corrosive environments which exist in coal-conversion (1,2), petrochemical (3), and steel-production (4,5) processes. In any industry utilizing refractory linings, accurate information is needed (preferably during operation) on the status of the structural integrity of the lining: e.g., how much has it worn? Where has it worn? Are cracks developing? This information allows rational decisions to be made on process conditions as well as on the relative safety of nearby operations personnel. However, it is usually impossible to obtain this information directly because the refractory is inaccessible during operation. Advanced non-destructive evaluation methods such as acoustic-emission measurement, infrared imaging, and various techniques employing gamma radiation sources and optical laser systems are currently being developed to provide information about in-place castable refractory concrete used to line vessels and components. The purpose of this paper is to summarize recent progress in the development of non-destructive inspection methods for establishing the status of these critical refractory linings.

PENETRATING RADIATION

The two most commonly used nondestructive testing (NDT) methods are radiography and ultrasonics. These two techniques are applicable to any structural engineering material, including refractories. In general, however, ultrasonics do not yield high resolution in terms of crack detection or thickness measurements in porous media like refractory concretes because such media tend to be highly attenuating to ultrasonic waves. This is primarily because of scattering at the interfaces between aggregate and binder material as well as between the concrete and internal voids. Penetrating radiation, on the other hand, is not subject to severe scattering in these materials and has been found to be highly useful. Several examples will be presented; all use gamma radiation from ^{60}Co .

In conventional industrial radiography, as in medical radiography, sensitive film is used to detect the radiation. Although conventional radiography has long been a standard industrial

method for inspecting metals, little information has been available in the open literature on the application of this technique to refractory linings. Argonne National Laboratory (ANL), as part of a program to develop nondestructive evaluation methods for coal-conversion systems, has conducted several laboratory and field tests in which conventional radiography was used to examine coal-gasification plant main-process vessels and components with a wide variety of design cross sections employing refractory linings.(6) The first two applications discussed below utilized panoramic radiography, in which a ^{60}Co source is placed inside the component of interest and film is exposed at successive circumferential positions around the outside.

In coal-gasification plants, because of the highly aggressive environments (corrosive/erosive gases containing ash and char), carbon steel vapor barriers are usually welded to the outer shell at various elevations throughout the height of reactor vessels (see Fig. 1a). These vapor barriers are potential sites for air entrapment. The metal hangers (usually stainless steel) that are used in installing castable refractory linings also represent potential trouble spots, since the position and orientation of these hangers have been shown (7) to be critically related to crack location and initiation. Castable refractories require vibration during casting to settle properly; this vibration can change the orientation of certain hangers, bringing adjacent ones into close proximity. Knowledge of hanger position and orientation prior to process start-up could allow potential trouble spots to receive closer inspection. The panoramic radiographic image shown in Fig. 1b illustrates the capability of this technique to detect air voids and reveal hanger orientation.

More complex vessel-wall designs, which employ water-cooling tubes, have also been examined. Figure 2a shows a schematic wall section from the upper stage of the Bi-Gas coal-gasification pilot plant. Again, using panoramic radiographic techniques, reasonably high-quality images have been obtained; in the example shown in Fig. 2b, the horizontal cooling-pipe walls can be readily seen. Although the exact pipe-wall thickness cannot be determined from such a radiograph, severe wall-thickness reduction due to corrosion could easily be detected.

The small white ring seen near the center of Fig. 2b is an image-quality indicator (penetrameter)* that was developed at ANL to establish spatial resolution for refractory-layered structures. Experience suggests that for best results, penetrameters should be fabricated from the same material as the refractory to be radiographed, or of a refractory as close as possible in density to the one undergoing inspection. The penetrameters found to be most useful have been designed with a thickness equal to 2% of the total

*Penetrameters have been used in conventional metals radiography for many years, usually in the form of a metal bar with drilled holes of known diameter.

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(refractory + steel) wall thickness, and an inside hole diameter equal to the penetrometer thickness. Under these conditions, the processed film will indicate a contrast sensitivity of 2%.

A potential problem in the radiographic inspection of thick linings is the effect of refractory moisture content on the exposure time and general image quality. In experimental studies at ANL, water had little effect on image quality, but it decreased the film densities by up to 0.4 from the desired densities of 1.5-2.5. This simply meant that required exposure times for moist refractories were much longer.

The condition of refractory-lined ducts is also critical for continuous process operation. In piping carrying erosive media, critical erosion regions generally occur wherever the flow direction changes. An example is shown in Fig. 3: Ash and char flowing through a downcomer must change direction 140° and rise in a vertical riser, as shown schematically in Fig. 3a. It has been possible to inspect such linings periodically by means of double-wall ^{60}Co radiography (4), and measure the erosive wear (see Fig. 3b,c). In addition to assisting in evaluation of material performance, these results have led to improved lining design in the lift-line sections of coal-gasification plants.

Although additional studies are necessary to allow better image quantification, these results suggest that radiography can provide important input to refractory-lining designs. Results to date indicate that radiography with a 100-Ci ^{60}Co source can provide information on refractory linings up to 60 cm thick.

An unconventional method based on detection of gamma radiation from ^{60}Co has been used by Republic Steel (4) for nondestructively determining the wear status of refractory linings in blast furnaces. Blast furnaces are very large vessels up to 12.2 m (40 ft) in diameter, capable of producing in excess of 4.5×10^6 kg (5000 tons) of iron per day. During the long campaigns expected of blast furnaces, interim data (i.e., between lining installation and campaign completion) on refractory wear are essentially unavailable, and information on the performance of sophisticated and expensive refractory linings must be based on intermittent spot-checks. Republic has developed a method of embedding ^{60}Co capsules in refractory linings at known depths and detecting the emitted gamma radiation (which penetrates both the lining and the steel) from outside the vessel walls. Since some of the capsules are lost as the lining wears away, the rate of lining wear can be determined. A 1.5- to 5.0-mCi source was determined (4) to be strong enough for use in refractory linings up to 80 cm (31.5 in.) thick, as found in bosh sections of blast furnaces. This method has been used in castable as well as molded refractories. The ^{60}Co isotope was chosen because it has a high melting temperature (1273°C; 2323°F) (4) and a half-life of 5.3 years. Present federal radiation limits allow 5×10^{-4} μCi per ton of steel (4) or 454 μCi per ton of iron. Studies at Republic Steel have shown that the radioactivity of iron produced under these conditions is less than

10% of this limit.

Figure 4 is a schematic diagram of an axial section of a blast furnace, showing typical locations of ^{60}Co capsules as employed in tests at Republic. Table I presents wear-rate data for the Youngstown No. 1 furnace, obtained from incremental measurements. Similar studies have shown that wear rates are drastically different in different furnaces, as well as in various sections of the same furnace; in one furnace, a test showed all refractory to be completely worn away at one location in a matter of days, while in other sections the refractory lining lasted through the entire campaign.

In applications where this method can be used, it seems to have considerable potential for establishing wear patterns and allowing rational design modifications as well as material performance evaluations.

THERMOGRAPHY

Although refractory conditions can be directly measured by radiographic imaging methods, the high radiation source strength ($\sim 100\text{ Ci}$) necessitates evacuation of personnel from test areas. Also, the handling of ^{60}Co requires licensed specialists. This means that routine inspections must be well planned. Thermography (infrared photography), on the other hand, is a remote sensing method which requires neither special handling licenses nor the removal of personnel from the test area. Like most optical devices, thermography systems provide full-field views as opposed to point-by-point measurements. However, infrared images do not provide direct quantitative information about refractory status. Refractories are most often used as a lining; this leads to several problems when one attempts to make quantitative evaluations of material performance from thermal images which are only surface-temperature mappings. Quantitative infrared imaging involves analytical heat-transfer models that take into account such factors as surface emissivity, thermal conductivity, and thermal contact resistance at interfaces, which are difficult to determine in field applications.

An effort has recently been made (7) to establish the maximum wall thickness for which infrared imaging can be used to quantitatively determine wall-cavity configurations in refractory-lined ducts. Figure 5 shows the model used for study. One problem in such systems is the directional variation of the surface emissivity factor, which can lead to erroneous interpretation of full-field images. Figure 6 shows the theoretically predicted directional emissivity effect for a metal surface. Recent experimental studies at ANL on small-diameter ceramic tubes (8) have vividly demonstrated this effect (see Fig. 6). However, if thermal contact resistance is known or can be well estimated in a test, infrared images can perhaps be used to make quantitative predictions of internal refractory configuration. Figure 8 shows examples of

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synthesized temperature distributions for three different values of thermal contact resistance, and the cavity configurations predicted from these distributions. Recent studies (10) have suggested that for refractory-lined ducts, 20-cm-thick refractory linings on 1.2-cm-thick pipe walls can be examined quantitatively. Thicker steel boundaries tend to conduct heat so rapidly that up to 50% of the refractory thickness must be lost before satisfactory temperature gradients can be sensed on the test surface and used quantitatively in equations to predict cavity shape.

Infrared scans are routinely performed at several petrochemical installations. Hill and Bevers (10) have recently reported on the use of infrared scanning at the AMOCO Oil Co., including a discussion of the economic advantages. Figure 9 shows examples of field infrared scans of internally refractory-lined vessels at AMOCO's Texas City (TX) gasoline refinery.(10) Clearly, full-field infrared scans are qualitatively useful in the detection of locally high temperatures.

ACOUSTIC-EMISSION DETECTION

Acoustic-emission detection is a less well developed but rapidly advancing NDT technique. Acoustic emissions are generally defined as elastic waves generated by the release of energy stored internally in a structure. In refractories, such energy can be released as a result of crack formation or extension, friction mechanisms, or phase transformations. Refractory concrete materials are extremely heterogeneous structures and, as such, are prolific acoustic emitters when under stress. Unfortunately, this complex structure also makes detailed analysis very difficult, since it gives rise to considerable acoustic reflection and scattering. For these reasons, only comparative, qualitative tests have been conducted to date. However, acoustic emission tests on similar refractories, performed at different laboratories, show similar results.(11,12)

Advances in electronic instrumentation over the past decade have accelerated acoustic-emission signature analysis and have made it a potential tool for estimating the quality of installed concretes in order to prevent premature failures caused by inadequate installation methods or procedures. Failures of castable refractories generally occur during initial firing or during plant start-up or shutdown. During the past five years, the U. S. Department of Energy has funded studies (11,12) to characterize acoustic emissions from thick refractory-concrete linings during initial firing. These studies have been directed towards developing on-line surveillance methods to characterize the quality of thick lining installations. Tests have been conducted on 95% and 50% Al_2O_3 , as well as dual-layer refractory samples. Work at ANL and Babcock and Wilcox in the last two years has focused on tests of large panels heated under prototype conditions, i.e., with a thermal gradient through the sample. For the detection of acoustic emissions during initial firing, acoustic transducers must be not only acoustically coupled to the refractory concrete, but a

same time thermally decoupled from it, since acoustic sensing elements cannot be used reliably for extended time periods at temperatures above 300°C. Figure 10 schematically shows a typical test setup and instrumentation. The Babcock and Wilcox tests have shown that carbon steel rods welded to the outer wall can also be used as waveguides, although this usually exposes the transducer to a higher temperature.

Recent results obtained from tests on 22.9-cm (9-in.)-thick panels suggest that damage occurs during the heat-up part of the schedule for rapidly heated specimens, but during the cool-down period for slowly heated specimens. Figure 11 shows results obtained at ANL from tests on two identically cast panels. Panel A was subjected to a fast heating schedule followed by a fast cooling schedule; Panel B was subjected to a slow heating schedule followed by a fast cooling schedule similar to that used for Panel A. The total acoustic ringdown counts from a 175-kHz transducer and a broadband (125 kHz-2MHz) transducer are shown. For Panel A, significant acoustic activity is detected during heat-up, but when cool-down begins, little additional activity is noted. For Panel B, as soon as cool-down begins, a significant increase in acoustic activity is noted. Figure 12 shows the results of Farris' 1978 study (13) on emissions from a 900-kg (2000-lb), 76-cm-high x 76-cm-diameter cylinder made of 94% Al_2O_3 castable concrete (tabular alumina aggregate). As in the case of Panel B above, the heating rate was extremely slow; again, a significant increase in acoustic activity was detected as soon as cooling began. These two independent studies show remarkably similar results.

Studies using small (2.5 x 2.5 x 2.5-cm), uniformly heated samples of 50 and 95% Al_2O_3 castable refractory (as opposed to thermal gradient tests) were also performed at ANL; the samples were fired to 1000°C and cooled at various rates and then ruptured in four-point modulus of rupture (MOR) tests at room temperature. The results, shown in Table II, suggest that a higher acoustic ringdown count for a given refractory is correlated with a lower MOR. This implies that the higher acoustic activity detected during initial firing of refractory concretes is correlated with the occurrence of thermomechanical degradation. In an experiment at Babcock and Wilcox (11), a thick refractory panel, instrumented with acoustic-emission sensors, was rapidly heated with consequent explosive spalling. Figure 13 shows that prior to the spalling, acoustic activity increased significantly; this increase can perhaps be considered a precursor to the failure. Such information, if quantifiable relative to refractory mechanical properties, should allow on-line surveillance of refractory status during initial firing and plant start-up and shutdown periods.

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INTERFEROMETRY

A laser interferometry system for measuring wear of refractory linings has been developed jointly by AGA Corporation and Stora Kopparberg, Domnarvret of Sweden. (14,15) In this system, interferometric techniques are used to measure the time required for a beam of coherent light (generated in this case by a laser) to travel from the source to point(s) of interest on a lining and return. A helium-neon laser ($\lambda = 632.9$ nm), modulated at two frequencies (299.970 kHz and 29.970 MHz), is used to measure phase changes. Low-frequency modulation is employed first, yielding a coarse measurement (± 0.5 m) of object distance. This is followed by high-frequency modulation, which allows the previous measurement to be refined to ± 5 mm. Angular movement of the laser head allows a wide coverage which is restricted only by the size of the vessel opening.

Such a system appears to work well for applications where the light beam can be accurately directed into a vessel. Figure 14 schematically shows how the externally positioned laser head can be located relative to the vessel lining. Van Konijnenburg (15) reports that each distance measurement takes 3-10 s and that an entire vessel lining can be scanned in $\frac{1}{2}$ h of real time. Nagai et al. (16) of Kawasaki Steel Corporation have reported measurements inside converters used in steelmaking where temperatures reached 900-1200°C. Ståhl has reported the use of the laser interferometer in converters, yielding quantitative measurements of the effect of periodic gunning as various heats are produced during a given campaign (see Fig. 15).

CONCLUSIONS

Higher costs for both replacement materials and operation require that energy-intensive industries obtain longer service life from materials of construction. Prevention of premature failure and quantitative knowledge of the performance of critical refractory linings seem to be attainable through the employment of cost-effective NDT techniques. The recent progress discussed in this paper is indicative of the considerable efforts now being made to apply advanced NDE technology to refractory materials. One can only assume that as higher performance is expected of materials, the cost-benefit ratio associated with advanced NDE methods will become more acceptable.

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Table I. Wear-Rate Data^a for Castable Refractory Lining of Youngstown No. 1 Blast Furnace

Level	Location	Depth of Sources, ^b (Measured from Hot Face)	Time to Remove, weeks	Average Wear Rate of Refractory, cm/week
1	1.52 m above tuyere centerline	10 15-22	2.5 20.8	4.0 0.9
2	2.4 m above top of mantle line	12.7 25-38	10.8 59 ^c	1.2 0.5
3	4.9 m above top of mantle line	12.7	16.8	0.8
4	6.7 m above top of mantle line	12.7 17.8-51	59 ^c 59 ^d	0.2 -

^aData from Ref. 4.^bFour sources at each depth.^cThree of four sources removed.^dOne of four sources removed.