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**Impact of Alternate Fuels on  
Refractories and Refractory Insulations**

**Proceedings of a Seminar, Washington, D.C.,  
September 21, 1976, Energy Research and  
Development Administration, Division of  
Industrial Energy Conservation**

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**OAK RIDGE NATIONAL LABORATORY**

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National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
Price: Printed Copy \$4.50; Microfiche \$3.00

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ORNL/TM-5895  
Addendum to  
ORNL/TM-5592

Contract No. W-7405-eng-26  
Metals and Ceramics Division

IMPACT OF ALTERNATE FUELS ON REFRACTORIES  
AND REFRACTORY INSULATIONS

PROCEEDINGS OF A SEMINAR, WASHINGTON, D.C., SEPTEMBER 21, 1976  
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION  
DIVISION OF INDUSTRIAL ENERGY CONSERVATION

prepared by  
Washington Scientific Marketing, Inc.  
Washington, D.C.

Date Published - May 1977

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Program Agenda

IMPACT OF ALTERNATE FUELS ON REFRACTORIES  
AND REFRACTORY INSULATIONS

September 21, 1976  
Washington, D.C.

Program Chairman's Welcome	R. W. Anderson, ERDA
ERDA Program Plan	M. Savitz, ERDA
Opening Remarks	R. G. Donnelly, ORNL Technical Chairman
Assessment of the Impact of Alternate Fuels on Refractory Insulations	V. J. Tennery, ORNL
Alternate Fuel Experience in Refractory Manufacturing	J. Bowman, Kaiser Refractories
Alternate Fuel Slagging in Refractories	T. C. McGee, Iowa State University
Substitution of Coal for Natural Gas in Face Brick Production	J. F. Edwards, General Shale Products Corp.
Alternate Energy Supplies	R. B. Rosenberg, Ins Institute of Gas Technology
Panel Discussion - Industrial Problems Associated with Use of Alternate Fuels	V. J. Tennery, ORNL Panel Moderator
Panel Members	
R. B. Rosenberg	IGT
J. Bonar	Carborundum Corp.
F. Schmidt	DuPont & Co.
C. T. Thompson	Bartlesville Energy Center
Summary and Closing Remarks	R. G. Donnelly, ORNL

PROCEEDINGS OF THE ERDA SEMINAR ON  
IMPACT OF ALTERNATE FUELS ON REFRACTORIES  
AND REFRACTORY INSULATIONS

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## INTRODUCTION

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## Introduction

Industrial users of natural gas have found that the present shortage and potential complete cutoff of this fuel to industrial consumers necessitates consideration of alternate fuels. In high temperature direct fired systems, the refractory and insulations used would be subjected to new and in some cases damaging combustion products. Thus conversion requires a careful match between the fuel and the refractory composition to minimize deterioration by combustion products. In assessing that match, all industrial concerns should address a set of questions pertaining to their fuel choice.

- 1) How will the fuel impurities affect refractory performance?
- 2) What effects will the match have on product quality?
- 3) What are the added capital costs of the match?
- 4) How will it affect the life cycle of the capital equipment?
- 5) How will it affect heat recovery systems?
- 6) How can increases in operating and maintenance costs be minimized?
- 7) What are the environmental effects of converting to the alternate fuel?

These are questions that companies cannot afford to ignore.

In this regard Oak Ridge National Laboratory (ORNL) conducted a survey which resulted in the document, Impact of Alternate Fuels on Refractories and Refractory Insulation Applications: An Assessment, authored by G. C. Wei and V. J. Tennery. Approximately 100 companies representing the most energy intensive industries were contacted during this survey. The findings of the authors were that, with the curtailment of natural gas as an industrial fuel:

- 1) Distillate oils such as No. 2 grade are favored in the immediate term because fuel delivery and combustion system requirements for these oils have the least incremental capital cost increase compared with natural gas; and the combustion characteristics are such that they can be used

directly in much equipment in place of natural gas. Impurities in No. 2 oil tend to be low compared to those in residual oil; thus No. 2 oil offers a lower risk of equipment deterioration through detrimental chemical reactions with fuel combustion products. (1)\*

- 2) Residual oils require a larger incremental capital cost relative to natural gas for their use than do distillate oils, and their impurity levels are usually significantly higher. The potential of residual oils to play a major role as an alternative fuel . . . is presently hampered by concerns about possible detrimental effects some of the combustion products of residual oils may have on high temperature industrial equipment . . . Relatively little specific technical information of industrial operating experience is available to aid designers in selecting refractory systems for use in conjunction with residual oil combustion. (2)
- 3) Many industrial firing processes that were developed for natural gas are not readily amenable to coal conversion. Most bituminous coal slags fuse or melt at temperatures slightly above 1204°C. (2200°F.); therefore, a simple combustion process using coal is essentially limited to this maximum temperature in order to permit use of relatively simple ash removal systems . . . The high retrofit cost for installing coal combustion equipment is a major negative factor in considering conversion from natural gas to coal. There is limited industrial process combustion experience with coal in the U.S. at this time compared to three decades ago. Many of the older processes operated at lower temperatures than those now used, so the experience of the past may not necessarily be directly transferable to modern process applications. (2)
- 4) Producer gas or low Btu gas is a potential alternate fuel for natural gas, and in fact,

\*Page numbers in the Assessment are referenced parenthetically

was used industrially before the wide use of natural gas. Extensive use of producer gas appears to be hampered by present lack of producer gas supplies and the reluctance of companies to provide their own producer gas plant because of cost. (3)

- 5) Electricity is now a serious contender as an alternate fuel or energy form for some applications. One major disadvantage is the relatively high cost of energy in this form; and secondly, much industrial heating process equipment will require major modifications in order to use electricity. (3)
- 6) Based on the assessment of industrial fuel conversion and the analysis of refractory deterioration due to interactions with combustion products, such as those containing vanadium, alkalis, and sulfur; future work is needed to better define phase relations and kinetic data for the fuel impurity and refractory material interactions. (10)

Using the Assessment as a baseline document in the Materials Optimization Subprogram, the Energy Research and Development Administration's Division of Industrial Energy Conservation has begun laboratory experiments on the effects of alternate fuels on refractories. These experiments are to begin in March 1977.

Before the experiments on alternate fuel effects on refractories were initiated, the Division of Industrial Energy Conservation held a seminar on the Impact of Alternate Fuels on Refractories and Refractory Insulations on September 21, 1976, in Washington, D.C. Approximately ninety persons -- representing users and manufacturers of refractories, and relevant government programs -- were in attendance. The purpose of this seminar was to inform industry of the survey results and to generate feedback from the industrial participants on the conclusions of the survey and the combustor experiments which were to commence a few months later. The material which follows in this report is the substance of the seminar.

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PRESENTATIONS



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Assessment of the Impact of Alternate Fuels on  
Refractories and Refractory Insulations\*

V. J. Tennery  
Oak Ridge National Laboratory

The U.S. industrial fuel supply situation, potential conversion from natural gas to alternate fuels, and the effect of alternate fuel combustion on industrial refractory furnace linings and refractory insulations was assessed from February through April 1976. Distillate and residual fuel oils were identified as the favored industrial alternate fuels in the near term. Relatively large capital investments, questionable supplies, and concern over emission standards and ash disposal currently make coal a less likely candidate for selection as an alternate fuel in the next five years.

Significant industrial conversion from natural gas to other fuels is underway and will become much more significant in the next three years. Energy intensive industries were assessed to identify refractory applications most likely to be impacted by fuel conversion.

The current state of information on refractory and insulation performance in conjunction with residual oil or coal combustion was assessed by means of personal contacts and a search of the literature. Major emphasis was placed on residual oil as it appears a most probable alternative to natural gas if satisfactory equipment performance can be assured. Critical impurities in residual oils are vanadium, alkalis, and sulfur. A lack of specific quantitative information on interactions of these impurities with various generic types of refractories under real combustor conditions was identified. Limited data on refractory performance under long term high temperature residual oil combustion was found. Typically, impurities result in fluxing, cracking, and spalling of refractories of various types.

\*See G.C. Wei and V.J. Tennery, Impact of Alternate Fuels on Industrial Refractories and Refractory Insulation Applications: An Assessment (ORNL/TM-5592)

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## Alternate Fuel Experience in Refractory Manufacturing

Jan Bowman  
Kaiser Refractories

The U.S. refractory industry produces both clay refractories and non-clay refractories. Annual shipments are over 7,000,000 tons of material with a value approaching \$900 million. The industry is vital to the economy, with over \$1,200 of GNP produced for each \$1 of refractory sales. Clay refractories include fire clay and alumina products containing natural clays and bauxitic materials. Non-clay refractories include a number of relatively small volume refractories such as fuse-cast products, crucibles, etc. However, approximately 70% of this category consists of products made from magnesia, dolomite and chrome ore.

I will discuss clay and basic refractory manufacturing operations with emphasis on high energy-consuming unit operations. Operating problems, capital and operating cost and environmental effects of alternate fuel use will be considered.

### Clay Refractories - Raw Material Processing

Clay refractories depend almost totally on naturally occurring minerals as their principle raw material. These materials are typically mined, sometimes beneficiated, sometimes dried in rotary driers and then crushed and sized for incorporation into refractory mixes. In addition, a substantial percentage of the minerals are calcined prior to the crushing step. Calcining is almost universally done in rotary kilns using between 3 and 8MM Btu/ton. Missouri flint clays, Alabama bauxites, some diaspores and so-called refractory bauxites are usually calcined before use in products. While natural gas has been the preferred fuel for "clay" calcination, light and heavy fuel oils are normally used in many places such as Guyana, where some 1,000,000 tons per year of refractory bauxite is calcined. No exceptional problems have been reported from these operations.

At Kaiser's Mexico, Missouri plant, two kilns calcine approximately 240,000 tons a year of clays. New air pollution regulations resulted in the installation in 1974 of wet scrubbers on kiln off-gases in place of cyclone collectors. The wet scrubbers do an excellent job of particulate control; however, the clays contain pyrite which evolves SO<sub>2</sub> on calcining, causing scrubber liquid to drop to a pH of around

4 when firing with natural gas. In other words, we solved the air pollution problem only to be faced with a water pollution problem! As you realize, EPA demands a water effluent pH limit of 6 to 9 for fluids entering a navigable stream. Since any water flow over 5 cubic feet/minute is considered a navigable stream, pH control of almost all effluents is mandatory and use of alternate fuels containing sulfur involves extra expense for soda ash to control pH. For this reason, we have limited liquid fuel use to 0.5% maximum sulfur #2 oil.

The use of coal as an alternate fuel was investigated and rejected on two counts: sulfur and ash content. The best available coals produce about 13,000 Btu/lb. with an ash content of 7-9%. Assuming 5MM Btu/ton heat input for calcination, we see a coal requirement of 384 lbs./ton of clay containing 30 lbs. of ash or equivalent to 1.5% of the clay. Laboratory tests indicate that this ash added to the clays would significantly lower the fusion point (refractoriness) of the material. I know of no successful use of coal for calcining high quality clays.

#### Ladle and Firebrick Production

Fireclay brick and ladle brick are formed from sized mixtures of various "clay" ingredients by one of three processes: dry press, stiff mud, or hand mould. The "shapes" are then dried in waste heat driers and fired in tunnel or periodic kilns. Firing temperatures vary from approximately 2000° to 2950°F., and alternate fuel use can depend on required firing temperatures. At temperatures up to 2300°, coal can be successfully used and is being used in ladle brick manufacture. At temperatures above 2300°, coal ash sticks to the product, causing fluxing and destruction of the ware and cannot be used.

Alternate liquid fuels are used for all firing temperatures with slight problems where good burner systems are installed. A recent refractories industry study indicated that only 10% of clay brick kilns had modern burner systems installed in 1972. Since then, perhaps 25% of the industry's kilns have been converted to modern high velocity dual fuel burner installations.

Kaiser's experience with old style liquid fuel burners was poor with uneven heat distribution in the kilns and too rapid heatup rates that resulted in excess breakage. Installation of high velocity dual fuel burners solved this problem, and the product quality has, if anything, improved over low-velocity gas firing. The capital cost of this conversion has been \$3-6 per annual ton and operation costs using oil have increased due to oil storage interest expense, higher maintenance expenses and the energy required for fuel atomization

and high velocity introduction into the kilns. Gas effluent problems from oil-fired tunnel kilns have been negligible at normal clay firing temperatures.

### Basic Refractories

Basic refractory products consist of brick or specialties composed of chrome ore, dolomite or magnesia either alone or as mixtures of magnesite and chrome. Chrome ore is purchased from South African, Philippine or Turkish sources and does not require high energy input to prepare it for the brick forming operation. Drying, crushing and sizing operations are straightforward and drier fuel sourcing is of small significance.

### Deadburned Dolomite

Dolomite for direct refractory use must be deadburned in rotary or shaft kilns. Deadburned dolomite kilns reach firing temperatures of 2900°F. and while normally gas-fired, have used coal, #2 or heavy oil sources for years.

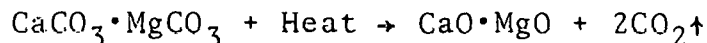
My company has used #6 oil standby fuel for deadburn dolomite firing in rotary kilns for 30 years with the usual boiler and handling problems associated with oil firing, but with no operating problems. Environmental problems similar to those discussed below under magnesite deadburning have been common.

### MgO Production

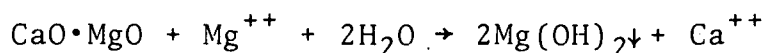
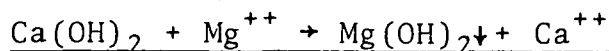
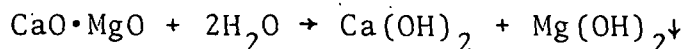
Magnesia, MgO, is normally produced in a two or three step process. The four unit operations involving high fuel use are:

- A. Dolomite calcination - rotary kilns
- B. MgO sintering - rotary kilns
- C. MgO calcining (lightburning) - multiple hearth furnaces
- D. MgO sintering - shaft kilns

Dolomite calcining kilns accomplish this reaction:



This reaction takes place at temperatures above approximately 1000°C. The resulting "dolime" is reacted with seawater or brine to precipitate  $\text{Mg}(\text{OH})_2$  by the following reactions:



The most harmful effect of liquid fuel alternatives to natural gas in dolomite calcining is the reaction of sulfur contained in the fuel with dolime.

Sulfur in the fuel oil that can be as much a 3.5% S by weight, is converted to SO<sub>2</sub> in the combustion zone of the kiln. Some of this SO<sub>2</sub> reacts with CaO and oxygen in the kiln to form CaSO<sub>4</sub>. This can contaminate the dolomite product. Calcium sulfate, particularly as reactive anhydrite, in the dolime can cause problems in the seawater precipitation process. This is apparently caused by precipitation of CaSO<sub>4</sub>·2H<sub>2</sub>O as selenite from metastable seawater with the active anhydrite serving as nuclei to initiate the sulfate precipitation. This is a serious problem as insoluble calcium salts markedly degrade the MgO product quality.

Tests at Kaiser's Natividad dolomite plant and Moss Landing, California Magnesia plant indicate the quality effects of the reaction are considerable and have limited the sulfur content of liquid fuels to 0.5% maximum.

In the single-burn MgO sintering process the sulfur content of the oil causes considerable operating problems in another area. This process is a classic example of solving one problem only to create a different and more severe one.

In the past years, most MgO sinter kilns collected dust, entrained in kiln exhaust gases, in cyclones and electrostatic precipitators with efficiencies up to 98%. The more stringent air quality laws passed in recent years required collection efficiencies exceeding 99.5%. In fact, in California, the efficiency must be at least 99.9%\* or an approximate maximum particulate emission of 25 lbs./hr. from a kiln using 31,000 lbs./hr. of feed.

Several methods of obtaining this efficiency were considered and rejected for various reasons, and wet scrubbers have been installed in most U.S. installations. High energy wet scrubbers do an excellent job of particulate capture and also, in the MgO process, do a super job of capturing SO<sub>2</sub> gas emissions from the kiln. Our stack data shows SO<sub>2</sub> content below 10 ppm. Unfortunately, the SO<sub>2</sub> cleaned from kiln gases ends up in the solid phase of the water effluent from the

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\*Efficiency actually depends on grain loading out of the back end of kiln. Assume 20 lbs./min. to scrubber. K-3 at 130 TPH product. Legal emission= $E=4.1P^{0.67}$  Here P=TPH Kiln Feed=130÷24x.35 P=15.5TPH : E=25.7 lbs./hr. Efficiency= $\frac{2000 P-25.7}{2000 P}=99.9\%$

Grain loading out of kiln  $\approx$  7.3 grains/SDCF.

scrubbers principally as  $\text{CaSO}_3$ . This material is about the most miserable cementitious agent a process plant could be cursed with. It sets up the dust as a cement in thickeners, blinds filters, and plugs the pipelines.

In addition, high sulfur fuel forms a complex compound in the lower temperature zone of the rotary kiln that promotes ring formation in the kiln requiring shooting or even kiln shutdowns for scaling.

Frankly, I do not know what sulfur content can be tolerated in MgO rotary sinter kiln liquid fuel, but any level will significantly increase product cost because of these problems.

In the double-burn process, light oil (#2) burners are used in multiple hearth furnaces with some problems with sulfur pickup in the MgO product and subsequent problems in the sinter kiln. Again, the need to clean gaseous effluents results in the capture of  $\text{SO}_2$  and subsequent problems in removing it from the product. Btu input for these furnaces approaches 10MM per ton MgO.

Shaft kilns for briquette sintering depend on intimate mixtures of fuel with air in the kiln to provide efficient combustion. The kilns are very fuel efficient, using 3MM Btu/ton product compared to 12-18MM Btu/ton in single-burn process rotary kilns. The problem with liquid fuels, in addition to sulfur pickup in dusts, is proper fuel atomization. This can be accomplished by air or steam atomizing or by pre-gasification of the fuel prior to entering the kiln burners. Since shaft kiln temperatures exceed  $2100^\circ\text{C}$ ., one can visualize the problem with carbonizing liquid hydrocarbons that are not properly atomized or pre-gasified. Refractory lining problems with liquid fuels in these kilns are minimal when proper burner design and operation is used.

Coal firing is impractical for any of the above processes for two reasons: sulfur pickup and ash contamination of MgO would destroy product quality.

To summarize, use of liquid fuel in MgO production causes problems with:

- 1) Lime contamination from sulfur poisoning of dolime
- 2) Scrubber system problems in single-pass MgO sintering
- 3) Sulfur contamination of double-burn dusts
- 4) Oil atomization problems in shaft kilns



## Basic Brick Production

Finished basic refractories can be classified as specialties (mortars, dry mixes, plastics), chemically bonded brick, tarbond brick, regular burned and direct bonded brick. Of these specialties, chemically bonded and tarbonded brick have a minimal fuel requirement. Regular burned and direct bonded brick, however, must be fired in tunnel or periodic kilns to temperatures in the range of 2600°-3100°F. and 3150°-3400°F. respectively.

Kaiser fires basic brick at 6 worldwide locations using natural gas, LNG, #2 oil and #4 oil at various locations. In terms of product quality and normal operations, we see little difference due to fuel type. Btu input required appears to be fairly independent of fuel type. The problems we have experienced because of change to liquid fuel are in the economic and effluent areas. Conversion from gas to oil systems is an expensive process in terms of capital required and operating expenses. Kaiser's experience is that a direct bond (3000°F. firing temperature) tunnel kiln conversion from gas to oil costs between \$7 and \$10 per annual ton of production (1976 dollars).

In addition to conversion capital costs, operating costs with liquid fuels will be substantially higher than gas (assuming equal cost per MM Btu from fuel) for these reasons:

- 1) Interest cost of funds tied up in oil inventories
- 2) Maintenance costs of fuel storage, circulating systems, and burners
- 3) Cost of energy for fuel atomization and heating (in cold climates)

The tight federal and state EPA requirements on tunnel kiln emissions have most high-fire kilns on the ragged edge of compliance when firing with natural gas. It appears that some complex reaction products are formed when using liquid fuels that may cause kiln effluents to be out of compliance. If these problems cannot be solved by process changes, substantial capital outlays (on the order of \$500,000 per tunnel kiln) may be required to install scrubbers or baghouses to collect less than 10 lbs. per hour particulate effluents from a typical 20,000 TPY direct bond kiln.

## Summary

- 1) The refractory industry is converting from over 80% natural gas fuel sourcing to a high reliance on liquid fuels.
- 2) Some coal firing is done where process temperature does not exceed 2300°F.
- 3) Liquid fuels cause process problems in clay raw material calcining because of effluent controls and in the MgO manufacturing because of liquid fuel sulfur content.
- 4) Operating problems with liquid fuels versus gas are negligible if the inherent added expense (both capital and operating) of liquid systems is ignored.

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## Slagging of Refractories by Ash from Alternate Fuels

Thomas D. McGee  
Engineering Research Institute  
Iowa State University

This nation has an enormous variety of industrial furnace processes using natural gas or fuel oil. The depletion of natural gas will require conversion of many gas-fired furnaces to oil or coal in the very near future -- conversion from gas to oil has already begun. A few conversions to coal have also occurred. Conversion of most processes to coal will be very difficult and capital costs will be high. However, it is apparent that energy costs and petroleum depletion will force many processes to convert to coal in the next decade or two. Such conversions will introduce impurities from the oil or coal that will react with and corrode the refractory lining of the furnaces.

Slagging, or slag attack, can be defined as the alteration and corrosion of refractory furnace linings by liquid fluxes associated with the process. The impurities in oil or coal are added to those already existing in the process to cause corrosion or slagging of the refractories.

The refractories to which I refer are the furnace linings and components used to resist high temperatures, insulate, and contain the process material. They are made from a small number of relatively inexpensive compounds with high melting points, such as alumino-silicates, MgO, Al<sub>2</sub>O<sub>3</sub>, SiC, chromite, dolomite, silica, zircon, zirconia and graphite. Refractories are used in tonnage quantities and are made from incompletely refined natural materials. The trend for many years has been to increase purity, at a concomitant increase in cost, and thus obtain better service life.

Refractories are available in a wide variety of forms: huge fusion cast blocks, dense refractory brick, porous refractory insulating brick and fibrous blankets or board. Refractory concretes are refractory aggregates bonded together with hydraulic cements, usually pure or impure calcium aluminates. Refractory ramming mixes are refractory aggregates with a small amount of fine material to make them plastic. They frequently contain a source of acidic aluminum phosphate or sodium silicate as a bonding agent. Therefore, in general, each refractory product has a unique set of properties. When one discusses slagging of such a diverse collection of materials, he finds that each unique material may respond

differently. He may have to specify not only the general class of materials, but even a particular product from a particular manufacturer for a particular slagging problem.

Refractories are seldom completely dense. The open pores connected to the surface provide a pathway for slag absorption and increase the surface area in contact with the slag. Therefore, refractories should have high density for slag resistance. However, the most common method of improving the thermal insulating character of a refractory is to increase its porosity -- lessening slagging resistance. Existing furnace processes successfully utilizing insulating fibers, brick or castables may be seriously harmed by the conversion from gas to an alternate fuel.<sup>1</sup>

### The Alternate Fuels

#### Oil

Crude oil, depending upon its source<sup>2</sup>, may contain:

0 to 100 lbs. salt per 1000 barrels

1 to over 5% sulfur

0 to 1200 ppm. vanadium

0 to 150 ppm. nickel

Additional salt can be added by contact with seawater if it is shipped by tanker; the amount will vary from tanker to tanker.

The impurities are concentrated in the residual oils. The amount of ash depends upon the source of the crude oil blends, the grade of the oil, the blend of refinery products produced from the crude, and the impurity removal process employed by the refiner. Limits on the ash analysis and sulfur content should be specified when purchasing.

Conversion to fuel oil requires control of combustion to minimize hot spots and control the furnace atmosphere. A large number of industrial processes can be converted from natural gas to #2 fuel oil without difficulty, although sulfate emissions increase. Conversion to the heavy residual oils is more difficult.

The ash removed from fuel oil-fired boilers has  $V_2O_5$ ,  $Na_2O$ , and  $SO_3$  present in proportion to the sodium and vanadium

in the fuel. In other words, the amount of sulfur in the ash appears to be about the amount needed to react stoichiometrically with the sodium to make sodium sulfate.<sup>3</sup> Excess sulfur goes up the stack as  $\text{SO}_2$  or  $\text{SO}_3$ . Therefore, the salt content in the oil, not the sulfur content, is the key to sodium sulfate corrosion, although other basic cations in a process may also retain sulfur. Sodium sulfate is a fluid, water-like liquid which does not dissociate readily and contributes to slag attack. It can react with aluminum oxide, for example, to produce a sodium aluminate liquid, bubbling with released  $\text{SO}_3$  as the dissociation progresses.

### Coal

Our coals are natural deposits which contain associated minerals such as pyrites or marcasite, clays such as kaolinites and illites, mica, sand and alkaline earth carbonates or silicates. These are not distributed uniformly through the bed, and when heated in burning coal are never at their equilibrium phase relationships for their average composition. There are many reports of coal ash composition, softening temperature and melting temperature.<sup>4</sup> When approaching these, one should be very cautious about accepting a representative ash composition at face value. Different coal basins do have different average ash analyses. But coal-fired furnaces are often fired just below the ash softening point. A fluidized bed is an example. In such situations it is not the average composition that causes disaster, but the most fusible composition. Therefore, beware of representative ash analysis. For some processes, acceptance sampling will be essential to successful utilization of coal.

### Mechanisms of Slag Attack

Slagging can be considered from two basic points of view:

- 1) thermodynamic equilibrium
- 2) heterogeneous chemical kinetics

### Thermodynamic Equilibrium Concepts

Many slag attack situations do not take place at chemical equilibrium even though they occur at very high temperatures. However, equilibria may be useful in predicting the direction a reaction will go. Where gaseous species are involved, equilibria is established more easily.

Slag reactions depend upon chemical equilibrium considerations. The free energies of the reactants and the products establish an equilibrium relationship that can be represented on an appropriate equilibrium phase diagram. Because of free energy changes, impurities usually increase the amount of liquid phase. This is the reason that refractories have become higher in purity in recent years, and that the impurities associated with alternate fuels will be harmful.

For example, the phase diagram for the reaction of  $V_2O_3$  with  $Al_2O_3$  shows that below the eutectic temperature of  $640^\circ$  rapid slag attack will not occur because the system will be completely solid. This is also true of  $MgO - V_2O_5$  where the eutectic temperature is only  $639^\circ$ . However, the refractoriness of vanadates is highly dependent on the external oxygen pressure. At lower oxygen pressures the  $MgO - V_2O_3$  system has an eutectic temperature of  $1830^\circ C$ . Therefore, small changes in oxygen partial pressure for a Venezuelan fuel oil containing vanadium might have a tremendous effect on the corrosion of magnesia refractories.

In most refractory installations there is a temperature gradient within the wall. Equilibrium considerations (and also kinetics) prevent reactions in the cold part of the wall. Attempts to conserve fuel by insulating a wall can lead to failure of the wall by raising its average temperature to a dangerous level.

The equilibrium diagram for sodium and aluminum sulfates also shows a low melting eutectic. But the aluminum sulfate portion of the diagram has not been determined because of the instability of aluminum sulfate. This reminds us that equilibrium considerations help us only if we consider the correct chemical reactions. If one of the important reactions is overlooked, attempts to predict equilibria from free energy calculations are certain to fail.

Equilibrium considerations are very important in choosing a refractory. For a given process environment the appropriate equilibrium diagrams will make it possible to predict the temperature at which slag attack will occur with a given refractory. Sometimes it is possible to saturate the slag by adding a chemical containing the refractory constituent, and thus prevent corrosion of the refractory. Addition of an organic magnesium compound to oils containing vanadium is an example.

## Heterogeneous Chemical Kinetics of Slag Reactions

Corrosion of refractories can be considered a case of heterogeneous chemical kinetics. The corrosion process is a chemical reaction. The shape of the slag-refractory interface adds geometric considerations. And it is necessary to transport material to and from the interface. Any of the three can dominate. Often a process change will affect the chemical reaction rate, the geometry, or the mass transport more than other factors and change the rate controlling mechanism. This is the reason two process or two furnaces, which appear to be identical, may perform very differently. In some slagging situations the corrosion will take place in a series of steps -- the slowest will be rate controlling. In other situations, parallel slagging processes take place. If one happens to be much faster than the others, it will be rate controlling. Often, parallel corrosion mechanisms do occur and often it is not possible to sort them all out.

### 1) Slagging Reactions

Slagging reactions take place at quite high temperatures where chemical reaction rates are very high. Most of these reactions are not controlled by the chemical reaction rates. However, if the slag attack is controlled by the rate of chemical reaction then changes in the mass transport, such as stirring, will have no effect.

### 2) Interface Geometry

The geometry of the interface is very important and this manifests itself in the effect of changes in structure and porosity. The simplest possible geometry is a pure nonporous refractory with a plane surface exposed to a liquid slag. For this condition, we can study the mass transport effects. There are three situations to consider: diffusion control, free convection, and forced convection.

## Transport

### 1) Diffusion Control of Mass Transport

If, for a pure refractory being dissolved in a viscous slag, the mass transport by diffusion of the refractory into the slag is rate controlling, then the corrosion rate will be parabolic in time. This is the situation when the corroding liquid has a small diffusion coefficient for the diffusion species -- often associated with viscous liquids at low temperatures. Under these conditions, the slagging rate is



given by

$$a = \frac{y}{2} / \sqrt{D^*t}$$

where  $y$  is the thickness corroded away,  $D^*$  is the effective molecular diffusion coefficient,  $t$  is time, and  $a$  is a constant whose value depends on

$$\pi^{1/2} e^{a^2} \operatorname{erfc} a = \frac{-\bar{V}_i (C_i - C_\infty)}{(1 - \bar{V}_i C_i)}$$

Here  $C_i$  is the concentration of the diffusing species at the interface,  $C_\infty$  is concentration in bulk, and  $\bar{V}_i$  is the partial-volume at the interface (the incremental change in the volume of the solution per incremental change in solute).

For sapphire dissolving in a  $\text{CaO} \cdot \text{SiO}_2$  slag

$$\bar{V} \approx \frac{\rho_o}{\rho} \approx \frac{\text{Solute density}}{\text{Liquid density}}$$

Then

$$\pi^{1/2} e^{a^2} \operatorname{erfc} a \approx - \frac{W_i - W_\infty}{1 - W_i}$$

where  $W_i$  is weight fraction at interface and  $W_\infty$  is weight fraction  $\text{Al}_2\text{O}_3$  in bulk.

Experimental measurements of the solution of  $\text{Al}_2\text{O}_3$  dissolving in  $\text{CaO} \cdot \text{SiO}_2$  slag were made using cylindrical sapphire rods, where the change in radius,  $\Delta R$ , was taken as a measure of  $Y$ . The time dependence was parabolic. Calculations for  $D^*$  made from the data gave reasonable values for slags with  $C_\infty = 0$  and 20%  $\text{Al}_2\text{O}_3$ . Thus, at low temperatures a solution of  $\text{Al}_2\text{O}_3$  in  $\text{CaO} \cdot \text{SiO}_2$  slags is parabolic in time and diffusion controlled.

## 2) Free Convection

If the viscosity is low and the partial volume effects are large then the kinetics may be governed by convection. Then the flow of slag will produce a stagnant boundary layer at the surface (Fig. 1).

The corrosion is controlled by

$$J = \text{flux} = \frac{dy}{dt} = \frac{D (C_i - C_\infty)}{\delta^* (1 - C_i \bar{V})}$$

where

$$\delta^* = \frac{(C_i - C_\infty)}{\left(\frac{dc}{dy}\right)_i}$$

and

$$\left(\frac{dc}{dy}\right)_i$$

is the concentration gradient at the interface.

The effective boundary layer,  $\delta^*$ , was calculated for cylindrical specimens by Elenbass as

$$\delta^* = 1.835 \left( \frac{Dv\rho_\infty}{gx^3 (\rho_i - \rho_\infty)} \right)^{1/4}$$

where  $g$  is gravity,  $x$  is distance along the length, and  $v$  is kinematic viscosity.

Substituting in the previous expression gives

$$J = 0.726D \left( \frac{g(\rho_i - \rho_\infty)}{Dv\rho_\infty} \right)^{1/4} (C_i - C_\infty)$$

Cooper and Kingery found their experimental results of  $\text{Al}_2\text{O}_3$  corroding in  $\text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot \text{SiO}_2$  slags at  $1500^\circ\text{C}$ . were linear, as predicted.

### 3) Forced Convection

When slag is forced to flow over the surface, the boundary layer becomes thinner. Theoretical calculations of the mass transport away from a rotating disk gives

$$\delta^* = 1.611 \left(\frac{D}{\nu}\right)^{1/3} \left(\frac{\nu}{\omega}\right)^{1/2}$$

where  $\omega$  = any velocity and  $\nu$  = kinematic velocity. Then the flux is

$$J = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \left( \frac{C_i - C_\infty}{1 - C_i \bar{V}_i} \right)$$

Again, Cooper and Kingery's experimental measurements confirmed the theoretical predictions.

#### Slagging by Coal Slags

The chemical analysis of coals varies widely. A range of analysis has been given as:

SiO <sub>2</sub>	20 - 60%
Al <sub>2</sub> O <sub>3</sub>	10 - 35%
Fe <sub>2</sub> O <sub>3</sub>	5 - 35%
CaO	1 - 20%
MgO	0.3 - 4%
TiO <sub>2</sub>	0.5 - 2.5%
Na <sub>2</sub> O + K <sub>2</sub> O	1 - 4%
SO <sub>3</sub>	1 - 12% (after oxidation) <sup>4</sup>

The above analyses are given on an oxide equivalent basis and the bulk of the composition is in the first four oxides. Under reducing conditions, the Fe<sup>+3</sup> would become metallic iron and not participate in the corrosion process. The CaO·SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub> corrosion of Al<sub>2</sub>O<sub>3</sub> is not a bad model system for comparison with coal slags, especially for the western coals; and the analysis of Cooper and Kingery reported above should be a reasonable model for a dense Al<sub>2</sub>O<sub>3</sub> refractory.

## Corrosion by Fuel Oil Slags

For fuel oil slags containing  $V_2O_5$  the corrosion of  $Al_2O_3$  single crystals by  $V_2O_5$  was also found to be parabolic at low temperatures, below  $850^\circ C.$ , and linear at high temperatures<sup>6</sup> (Fig. 2).

Polycrystalline  $Al_2O_3$  was similar, but the highest purity, B, corroded less (Fig. 3). (The slowing down at long times was due to the increased concentration of  $Al_2O_3$  in the slag.)

When corroded for longer time periods the polycrystalline specimen disintegrated at the corners due to grain boundary solution and the rate turns up despite the increased concentration  $C_\infty$  in the bulk (Fig. 4).

Beer and Richarz studied the corrosion of higher porosity alumina by  $V_2O_5$  and  $Na_2O - V_2O_5$  liquids.<sup>7</sup> They found the rate of capillary penetration was decreased slightly by the alkali addition; this they attributed to a viscosity increase.

Analysis by electron microprobe revealed the corrosion took place at the grain boundaries and attacked  $\beta$   $Al_2O_3$  and  $MgAl_2O_4$  spinel more rapidly than  $V_2O_5$  attacked  $\alpha$   $Al_2O_3$ . They found activation energies of 40.9 and 18.6 kcal/mole compared to Frischat's 27 kcal/mole. They ascribed these to chemical reaction control at low temperatures and capillary diffusion at high temperatures. This points out the difficulties encountered in assigning mechanisms based upon Arrhenius activation energies.

## Conclusion

The simplified model systems cited above confirm the theoretical considerations involved in slag attack. Even simple systems are difficult to analyze and experimental data is, in general, lacking. Real refractories are not pure systems and are not completely dense. The theoretical considerations provide a sound scientific basis for analysis -- but much more research is needed.

Every slag system is unique. The complexity of the various processes makes it necessary to rely on experimental data to determine how to control slagging in a particular situation. However, research to improve the purity of refractories and to reduce porosity will certainly be helpful.

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- <sup>2</sup>See "Guide to World Crude Oil Export Stream," Oil Gas J., March 29, 1976. See also F.F. and E.M. Shelton, "Heating Oils," BERC/PPA - 7614, N.T.I.S., 1976.
- <sup>3</sup>Yoshimi Ishihari, "High Temperature Corrosion of Stainless Steel by Fuel Oil Ash," Bull. Jpn. Pet. Inst. 10, 28-33, 1968.
- <sup>4</sup>For example, see W.A. Selvig and F.H. Gibson, "Analysis of Ash from United States Coals," U.S. Bur. Mines, Vol. 567, 1956.
- <sup>5</sup>The section on mass transport is based upon A.R. Cooper and W.D. Kingery, "Dissolution in Ceramic Systems: I Molecular Diffusion, Natural Convection and Forced Convection Studies of Sapphire Dissolution in Calcium Alumina Silicate," J. Am. Ceram. Soc. 47, 37-43, 1964.
- <sup>6</sup>M. Safdar, G.H. Frischat, and H.W. Hennicke, "Corrosion of Aluminum Oxide by Vanadium Oxide Melts," Ber. Dt. Keram. Ges. 54, 291-4, 1974.
- <sup>7</sup>H. Beer and W. Richarz, "Investigations on the Attack of Melts Containing Vanadium on Polycrystalline Alumina," Ber. Dt. Keram. Ges. 51, 201-5, 1974.

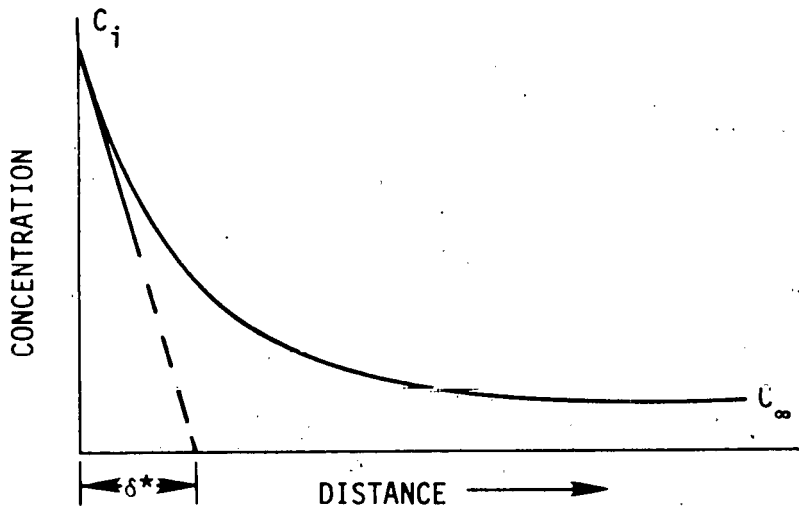


Fig. 1. Concentration gradient and effective boundary layer thickness,  $\delta^*$

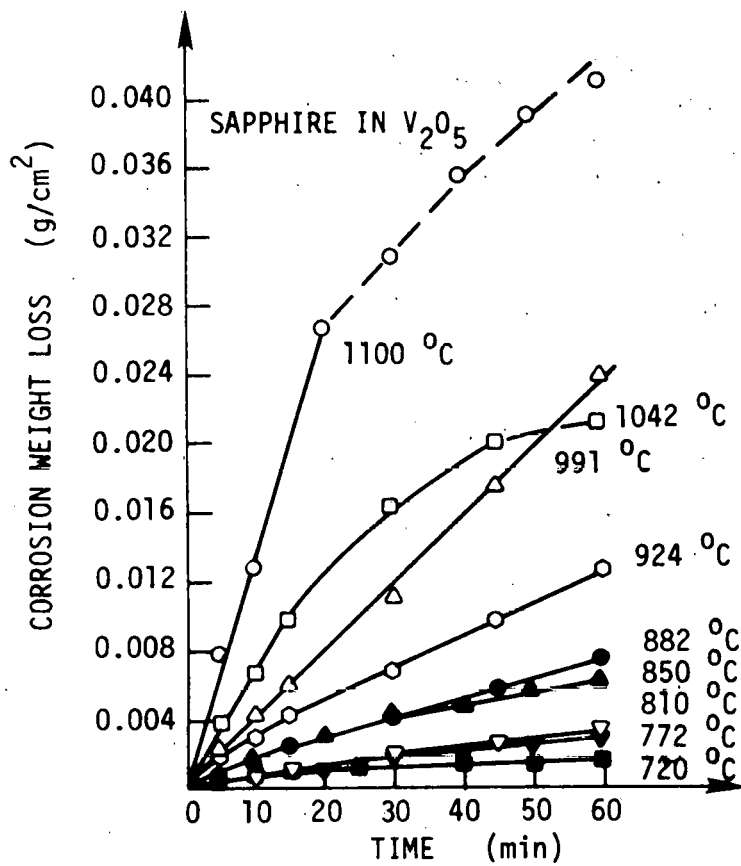


Fig. 2. Corrosion of single crystal sapphire by liquid  $V_2O_5$

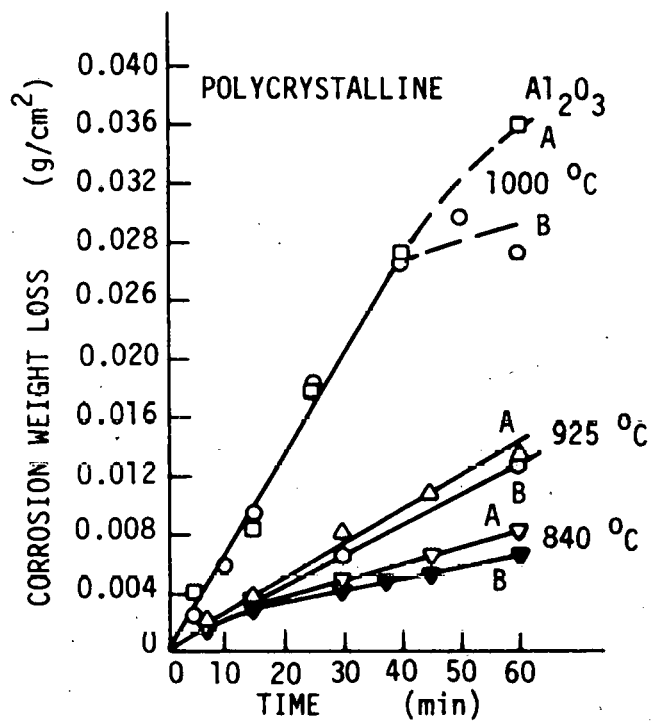


Fig. 3. Corrosion of polycrystalline Al<sub>2</sub>O<sub>3</sub> by liquid V<sub>2</sub>O<sub>5</sub>

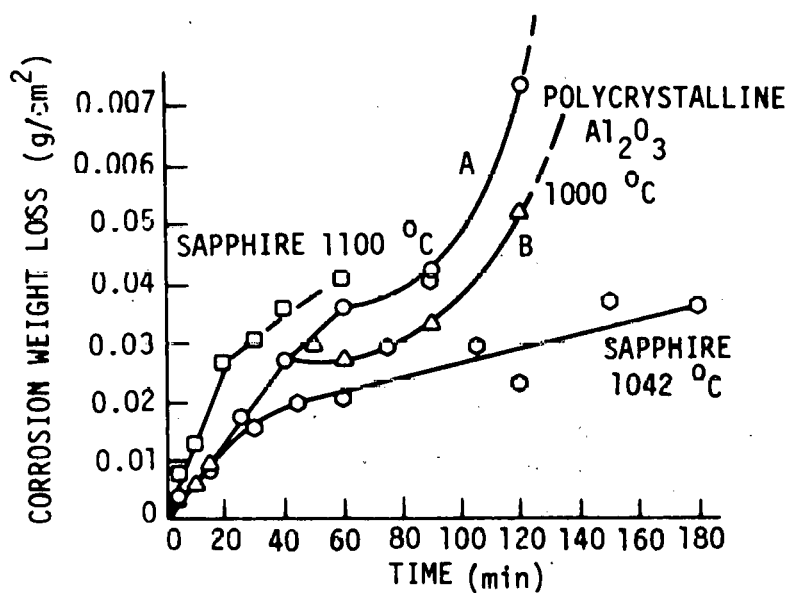


Fig. 4. Corrosion of single and polycrystalline Al<sub>2</sub>O<sub>3</sub> for longer times

Substitution of Coal for Natural Gas  
in Face Brick Production

Joseph F. Edwards  
General Shale Products Corp.

The United States brick industry produces about 8 billion brick per year using mostly natural gas or petroleum-based fuels. The future outlook, both regarding availability and price of these fuels, suggests that the development of coal-firing capability is critical to the long term survival of the industry. Such a capability would conserve about 320,000,000 gallons of oil annually from the brick industry alone, which is only a small part of the total ceramic industry.

General Shale Products Corporation produces approximately 600 million brick per year or roughly seven and one half percent of the U.S. brick output. It became apparent to us in the early 1970's that future supplies of cheap natural gas were in jeopardy and there were warning signs of a worldwide shortage of all petroleum products with the implied threat of sharply rising prices. By contrast, coal reserves were extensive and our plants were located near the heart of the eastern coal producing region. We were convinced that coal would eventually become the only economical fuel available to the brick producer.

Beginning in 1972, four teams of management personnel visited England and Germany to look at coal-fired tunnel kiln plants. A limited number of coal-fired tunnel kiln plants were found and even these were not completely suited to our purposes, but we gained enough information to confidently pursue a research program of our own to attempt to fire our modern side-fired tunnel kilns directly with coal. The direct-fired method was chosen over the coal gasifier approach because of economics and the then nonexistent efficient coal gas producer which could use bituminous coal.

In early 1973, we committed one producing tunnel kiln (30 million brick per year production) to research on coal-firing. The basic theme that has persisted throughout the whole project is the introduction of finely ground coal directly into the tunnel onto and into the ware.

Many innovations in coal preparation, coal handling, coal delivery, safety, cleanliness and pollution control were a necessity. The major innovation has been a metering and feeder system for the controlled injection of small quantities of coal in the magnitude of 5 to 60 lbs. per hour at multiple feed



points. This invention, called the "solid fuel metering and delivery system," made it possible to introduce finely ground coal at rates comparable to the fuel input of existing gas or oil burners.

The original research kiln is now on 100% coal with no reduction in production capacity. A second kiln at the same location is being converted to coal-firing. A third at a different site is now on 80% coal and two more kilns are in the process of being converted. Fuel costs at these plants have been cut in half in comparison to the oil-firing costs. Costs with oil were running in the neighborhood of \$10 per thousand brick, and it now costs approximately \$5 per thousand to utilize coal.

As of July 1976, General Shale has spent nearly two million dollars on coal-firing research and coal conversion projects. Payback if all kilns in the company are converted to coal would be approximately three million dollars annually in fuel savings. But most importantly, we are not at the mercy of foreign oil embargoes.

PANEL DISCUSSION

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## Impurity Problems with Alternate Fuels

One issue in the forefront early in the discussions was the impurity levels of some alternate fuels. These impurities come from a number of sources, including refining processes, transportation and storage procedures, as well as initial impurities. One panel member offered some information relating to impurities added during the refining process:

Some heavy metals are added as a product of corrosion. A substantial amount of iron in residual oil is corrosion product as well as lesser amounts of nickel and chromium. Salt is also a frequently found impurity. Some refiners neutralize the distillation columns with sodium hydroxide to prevent hydrolysis of magnesium chloride. This causes corrosion in the upper part of the distillation towers and adds more sodium to the residual oil.

Although there are no hard data at hand regarding the amount of impurity contributed by transportation and storage, there were some serious concerns over it. Several participants had found in their experiences that transportation and storage of fuel oils was casually handled and few safeguards had been instituted to ensure the fuels' purity:

The fuel oil customer does not know how his supplier is handling the oil. The supplier could have a number of different grade oils at the bottom of his tanks which can get into your shipment.

Along this line another participant stated:

If your company is receiving a No.2 distillate from a supplier and the last delivery with his truck was a No.6 oil, then you can expect to have your shipment contaminated with sulfur.

One solution which was offered is to follow TVA's procedure in fuel oil purchases. When ordering fuel oil, TVA writes up specifications for the oil it needs, and then buys only that which matches the specifications. Companies that do not have the facilities or the market power to write specifications can turn to the Bartlesville Energy Research Center's published survey report, Heating Oils for 1976, for guidelines.

This report covers data on a total of 297 samples of heating oils. The fuels were manufactured by 30 petroleum refining companies . . . average, minimum and maximum results were published from the analysis of these samples. The range of samples includes grades 1, 2, 4, 5 light, 5 heavy, and number 6 oils from five different regions of the U.S. The type of properties included in the report are: gravity, flash point, viscosity, cloud point, pour point, sulfur content, carbon residue, water, sediment, and distillation temperatures.

Attempts to solve the impurity problem of fuels can produce unanticipated problems. This point was brought forth in relation to the supplementing of fuels with additives:

Additives can be used as a means to control fuel ash corrosion. The electric utility industry has used additives to retard alloy corrosion in boilers. You will find that on systems with regenerators, such as glass tanks, there are major fouling problems, as the refining people have found. Fouling will cause high pressure drops which will force you to shut your equipment down.

It is important to also note that although additives have been utilized to retard alloy corrosion in boilers, much less is known about their use with refractories.

Initial impurities are the primary problem in fuel oils. This is especially true with regard to residual oils. With this problem in mind, a caution in the use of residual oils as a refractory fuel was contributed by a representative of ERDA:

Every crude oil is different. Most refineries are different in that they are geared to the particular crude they are working with. The whole process of refining is to take the good products out to get higher quality products, such as gasoline. This works down the line to distillates and so on. After the refining process is finished, what is left is the residual oil. Thus, anything you had in the crude to begin with is concentrated back to the residual oil. Your approach to choosing a residual oil, then, should be carefully thought out.

This problem was echoed in a panelist's comments early in the proceedings:

U.S. residual oil does not have the impurity content that oil out of Venezuela can have. Venezuelan residual oil can have from 500 to 3,000 ppm of vanadium just as it comes off the bottom of the still.

Although ERDA perceives that there will be a conversion by industries to No.2 and No.6 oils from natural gas, ERDA representatives urged industry not to view petroleum as a long range alternative to natural gas. It was felt that petroleum should remain only an immediate or mid-term alternative until suitable substitutes can be found.

The conversion process to alternate fuels has been perceived as a major problem by refractory manufacturers and users because of the increased impurities in these fuels. However, a representative of a primary metals company stated that the changeover would not place any undue strains on the primary metals industry since the industry has had past experience with coal and oil as primary fuels:

There is little interest in our industry regarding alternate fuel usage. As you probably know, we used coal as a fuel about 30 or 40 years ago. Thus, converting back to coal creates no problems for us, with the exception of questions of heat control, which are being resolved.

One attendee saw the conversion process as analogous to changing slagging practices. The conversion to alternate fuels would present some problems, but none that are impossible to solve.

Refractory manufacturers have spent much time and money performing tests similar to Oak Ridge National Lab's combustor tests, but they have performed them with different slagging practices, not with different fuels.

What you are really talking about is a change in slagging practices. You are converting from a nice clean fuel to one that is dirty. At very high temperatures, there might be some unusual effects. But in a severe environment you are still limited in the directions you can go by your refractory materials.

The same polarity in viewpoints was found by the authors of the Assessment during their field survey:

The refractories manufacturers that we spoke with during this exercise are reflective of the attitudes that all is well in hand. They felt that there was very little to be concerned about if these fuel choices work in the near term. It was only a matter of changing refractory compositions or something of that nature. . . Other refractory manufacturers we spoke with had quite a different point of view. They took the position that there was a considerable lack of coherence and understanding.

Although some attendees believed that industrial firms could cope with the problems of converting to alternate fuels, the majority of the participants welcomed the development of any information which would ease their transition problems.

## The Data Base on Refractory Parameters

One topic which engaged the attention of the attendees was whether the data base on refractory parameters and the knowledge of deleterious reactions of the refractory wall with combustion products is sufficient to meet the problems of converting to alternate fuels. This question was manifested in several ways: Is the present data base accurate? Do coupon tests contribute to a valid data base? Do ASTM tests provide reliable indicators of product performance? Is there a need for fuller evaluation of the data as it is presently accumulated?

The basic problem concerning the knowledge of refractory parameters and attack mechanisms is whether the present data base is accurate by contemporary standards. It was initially pointed out by several participants that the data base is sizeable, and is aimed towards those problems that have constantly plagued refractories.

We had trouble with sulfur and vanadium twenty years ago. I think there is quite a bit of information on the metal alloys in the literature regarding the effects of corrosion.

Another participant indicated that he felt the data base provides an accurate lead for the company that has a problem with refractory attacks:

If you cannot predict which direction to go to overcome reaction problems in order to maximize refractory lifetime, then you are in trouble. The answer, of course, might be just to use more expensive brick, and that is what your tests will probably lead you to conclude. But when you get in the phase relationships, if you cannot tell which way to go to reduce the attacks of refractory linings, then you are missing much of what is in the literature . . . You should know what materials to use to minimize the effects of refractory attacks, even in the high temperature region, just based on past experience. This is not a new science. It is a very old science. The amount of literature on the reaction range and the phase diagrams is huge.



It was also emphasized that if the data base were sufficient, the technical expertise of the companies to assimilate and interpret the information is another major factor.

You have a situation where people have been called upon to match refractory compatibility to slags for a long time. Now you are talking about one more slag; it may be highly corrosive, but it is just one more slag. You should be able to handle that with your normal developmental procedures.

Much of the opinion which followed accepted the initial premise that there is a large amount of information, but that this information is either too limited or it does not account for variables relevant to modern firing conditions. One participant stated, "Just the turbulence that might exist in equipment is a very important factor to consider." Another attendee found that the basic information is available, but that it is not amenable to long range planning:

The refractory manufacturer, in general, can tell you which direction to go to get better service, and so forth. But the user is interested in how long that refractory material will last if he installs it. That is what the manufacturer cannot tell him. We can tell him what direction to go, but we cannot say, "If you do this, your refractory life is going to double." We just do not know without simulative tests.

Another aspect of the data base problem and its quality was brought up during this discussion. This concerned the validity of the test base upon which the data on refractory materials has been generated. Essentially this issue revolved around whether information formulated from coupon type tests was of sufficient quality for industrial use. There was nearly uniform agreement that information generated by these tests is of limited applicability.

I would like to hazard a couple of generalizations. One is that extrapolation of coupon type test data to real life equipment is dangerous. Secondly, if you try to double sulfur content and triple vanadium content, and then try to extrapolate the results, you would be better off if you saved your time, money, and effort.

It was also stated that:

You will need in-service testing to get information necessary for predicting refractory performance or at least for choosing refractories for further, on-going tests.

There were a few additional comments which did not dispute these points, but rather focused on the fact that coupon tests are much less expensive than combustor tests and simulation testing. The participants also spoke of industry's need for immediate results. The conclusion, though, of one participant was:

There is nothing wrong with these tests. But the results which you get from them are that refractory materials either are or are not worth full-scale testing.

There followed a delineation of what types of coupon tests provide the most valid results:

I think there are two kinds of coupon tests. First, you have a sample that is just immersed like a cup or a pencil test. The whole pencil is at the high temperature of the device you are heating it in and it is being attacked on all sides. The second type of coupon test is where you have a reactor or a piece of equipment that is already operative and you place a piece of refractory in the wall. I think the data from that type of test is quite valuable. The difference between this test and the pencil test is that the brick in the refractory wall will experience the same thermal gradients that the equipment experiences, whereas a stick of refractory in a cup will not. The rates of corrosion of these two coupon tests are vastly different.

The conclusions offered by the attendees pointed to simulative testing as a means by which a data base of higher quality could be formulated. Both combustor tests and modeling methods were advocated as the means of creating that high quality data base.

It has been said a number of times, and I cannot agree with it more, that simulating the process and really running it with combustors and refractories is vital.

I think with all the tests and basic research, many researchers are learning of the great potential of simulative testing. You have to get very close to modeling whatever it is that you are concerned about. Just the turbulence that might exist in the equipment is very important. I would advocate simulative testing. This means we would have to get into testing to a greater extent than we are right now.

I think mechanism modeling is very useful. You have to understand the slag attack to really understand the mechanism. This understanding you get from modeling will then translate to the direction you will pursue to control furnace slag attacks. People can also apply mathematical modeling of furnace processes and other kinds of modeling. These methods can be very good low cost representations for a processor.

In conclusion, one of the panelists urged that we follow the path which the Europeans have established in simulative testing:

The Europeans have recognized the importance of simulative testing before we have. They have a range of units located at universities and institutes, which have very extensive test firing capabilities. There is almost no equivalent in the U.S. We do not have any industry-wide or academically-available test furnaces where a reasonable simulation test can be run.

The next subject brought out during the panel discussion was whether ASTM tests constitute accurate measures of performance for refractory materials. Several comments from the audience and the panel highlighted the fact that the variability of some refractory compositions make it very difficult to rely totally on the ASTM tests.

My question centers around the accuracy and precision, specifically accuracy, with which the thermo-physical properties of a refractory wall can be determined. My experience is that many of the monolithic refractory compositions change continuously as the raw materials supply market situation changes. The material which you buy this year will not be the same as it is next year. The property variations in each year's batch will make for unknown variations in your production lots.

This problem of variability of the composition led one industry representative to conclude:

The most unscientific, inexact process is the making of castable refractory products. This whole process is dependent on the type of water and the type of mixture being used. Maybe it is an art!

Another cause of variability in refractory properties is related to the exposure of the furnace environment.

The properties of castable rammed cements change drastically with time in the furnace. If you are melting metal in a rammed refractory, metal will permeate it.

Thus, calculations based on the ASTM tests may not be in line with the actual properties of refractory products a company puts out.

When you assume in a calculation of thermal-conductivity through a component wall a uniform thermal-conductivity based on a value from the previous batch, you are being naive! All you are giving the customer is a ballpark figure.

But even though there are questions about applicability and accuracy, the ASTM tests are still considered the best basis for property determination of refractory materials.

I think you have to accept the fact that the ASTM tests are not completely accurate, but at least you can extrapolate from them. If you do not start with the results of those tests, you really do not have anyplace

to start other than assuming you have designed a balanced test on your own. If I am doing something that will be used by several companies, I prefer to use the ASTM tests and extrapolate from the values.

Finally, it was pointed out that refractory materials can approach the qualities of engineering materials, but the costs get into the area of diminishing returns in quality based on the price increment. An attendee remarked that one cannot expect refractory materials to perform like engineering materials, such as steel, because the processes of manufacture are incomparable.

With all the previous factors in mind concerning the data base problems, the belief was expressed that evaluations must be made of the specific problems the refractory manufacturer or user has to face in converting to alternate fuels.

First, in the area of equipment, I see that there are two types of interest. In existing equipment, where we have already committed ourselves to specific designs and capital investment, we have to consider the dollar incentives for conversion to alternate fuels. Secondly, we have to know the technical feasibility of conversion. As I view it, there are some things that we do not know right now without changing the materials of construction, pertaining both to refractories and metals systems. . . So with an eye to building and construction of future plants and facilities, we would like to make these evaluations on a firm footing. The test work that would be done by industry and ERDA is important.

In response the panel chairman, Vic Tennery, suggested that a committee of refractory manufacturers and users be established to monitor and disseminate information on new developments and data:

The purpose is to try to stay current on the subject areas of alternate fuels and the potential impact of these fuels on ceramic refractories and insulations. This committee would communicate or help to communicate the information to industry

and users . . . The present situation with alternate fuels is that a multitude of programs are underway, and people are experiencing difficulty keeping track of them. A committee could monitor the on-going efforts and transfer the needed information to refractories manufacturers and users.

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## ERDA-ORNL Combustor Tests

During V. J. Tennery's presentation on the Assessment, he outlined the format of the upcoming combustor tests which Oak Ridge National Laboratory will be conducting on refractory materials. Below is an excerpt of his remarks about the program.

The present plan is to run the tests for approximately 1,000 hours each. It is an arbitrary figure. The tests will run at 2600°-2700°F. We tentatively plan to do four panel tests in the combustor simultaneously during each test. To some people, the soundness of this logic is not apparent, because of the potential synergistic effects between the various materials in the combustor. But we are going to try four panel tests in an effort to complete as many tests as possible in a reasonable time period. If we do single panel tests it would take too long to develop sufficient information which could be widely utilized. Initially, we will look at two compositions of alumina silicate refractory brick; one 50% alumina and the other one 90% alumina. Along with these refractory bricks we will examine two generic fibrous insulations. We intend to fabricate relatively small panels using recommendations made by the manufacturer of the refractory to simulate a wall.

The discussions relative to this test plan did not dwell on the information to be derived, but rather focused on the issue of whether the testing program should be limited to the 2600°-2700°F. range, or should be expanded to include other temperature ranges. The basic division was between the ceramics industry representatives, who felt that lower temperature testing should also be a part of the program, and several other attendees who believed that high temperature testing would generate the most valuable information.

The ceramics industry representatives emphasized two points: 1) extrapolation of high temperature tests downward for the low temperature refractory users would not be valid, and 2) the undercapitalization of their industry makes it difficult to conduct their own simulative testing program.



The first point was made when an advocate of high temperature tests stated:

It would probably not be as fruitful to try to simulate a 2000°F. test as it would be to simulate a 2500°F. test. You can extrapolate back from 2500°F. to get the kind of performance data you want at 2000°F. That, of course, would not be an optimization.

Another attendee responded with the contrary viewpoint:

Regarding the problem of trying to extrapolate down to lower temperatures, silicon carbide brick is a good example. Silicon carbide will stand up very well in oxidation resistance at 1570°C. With essentially the same gas atmosphere, you may have bad problems at 1100° or 1150°C. because the mechanism of oxidation of the surface and the protective layer of silica forms on silicon carbide as a much less dense layer of silica. Therefore, you have got a completely different oxidation mechanism. Thus, to extrapolate rates of oxidation from 1570°C. down to 1100°C. would constitute a dreadful mistake.

Regarding the second problem, one ceramics industry representative noted that the undercapitalization of his industry made a testing program at lower temperatures more desirable and valuable.

The ceramics industry, up until quite recently, has been characterized as small, family-owned companies which are undercapitalized. They do not have R&D money. The steel companies, on the other hand, have rather sizeable laboratories. You will not find this in the ceramics industry. Thus, it may be quite important to solve the steel industry's reaction problem, but there is still this \$9 billion industry that needs even more help in solving its reaction problem than the steel industry does.

The advocates of high temperature tests stated that a testing program at high temperatures would have greater relevance for refractory users since the high temperature range involves complex factors which are difficult to predict.

When you are talking about high temperature processes, you are talking about processes where a refractory is crucial. It appears that the 1800°-2000°F. range can be tooled up with slightly inferior refractories, with perhaps some minor deterioration problems as a result. I am suggesting that possibly the reason why ERDA has preferred to look at high temperature refractory problems is simply because the economic impact is potentially greater.

The observation was added that refractories are utilized for high temperature applications in the majority of cases.

I think we tend to forget where refractories are used. The steel industry uses better than 70% of them. Thus, when you are talking about establishing a testing program, you should be thinking in terms of 2500°F. or above.

The final, and most important, point made in this discussion was that the knowledge of high temperature refractories needs to be supplemented.

If you need a testing program at all, you need it in the high temperature range because the reactions are much more complicated. There, you have a limited ability to predict phase reactions. Phase diagrams going with four to six compounds present real difficulties.

There was also some interest expressed in testing the effects of design and installation of refractories. But these factors would not be specifically addressed in the testing program under discussion at this seminar.

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SUMMARY AND CLOSING REMARKS

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## Summary and Closing Remarks

R. G. Donnelly, ORNL

In this morning's session we learned that there will be a large shortfall in the natural gas supply for a number of reasons in a very short period of time. We learned also that the industry is preparing a massive shift from natural gas to oil, but surprisingly, not much to coal in the near future.

On the negative side, there are problems which are due to the impurities in the oil and coal, the major ones being sodium, vanadium, and sulfur. These impurities cause problems with ceramic linings and there are many potential mechanisms for deleterious interaction. Thus, experimental data appears to be necessary, especially at the higher temperatures, and these experiments should be conducted under very realistic conditions. These impurities cause problems with the products that are being produced. Switching to oil or coal also gives greater environmental problems to overcome and larger capital outlays are required for both the additional equipment necessary to burn these alternate fuels as well as for the additional equipment necessary to overcome the environmental problems.

There were a number of conflicts in the development of ceramics which were brought out. These complications include the fact that a more porous ceramic for a better insulative ability is needed. More dense ceramics are also required to minimize penetration by the alternate fuel impurities. Another conflict is that if furnaces are better insulated and the hot wall temperature is raised, then the slagging attack of the ceramics is increased.

On the positive side, we learned of some successes in conversion to alternate fuels. There have been some reduced fuel costs and some cases of improved product quality and production rate, and improved heat transfer, so the picture is not totally negative.

In the afternoon session panel discussion, the major point of discussion had to do with testing the effects of the alternate fuels on refractories and refractory insulations. There was not uniform agreement on the need for testing or the conditions of testing if done. Some refractories manufacturers suggested that no further testing is needed. However, the majority opinion appeared to be that additional testing is required, and that this testing should closely simulate the actual usage conditions. Combustion testing is of this nature, and it was generally

recommended. Also, there are many conditions of the testing which must be controlled. These include oxygen partial pressure, temperature, geometry, composition, etc. Thermal gradients are important as well as turbulence. A significant point discussed was the interpretation of the results. In order to be able to extrapolate the test results either to higher or lower temperatures, an understanding of the mechanisms of interaction is required so that valid analytical models can be constructed. Sampling of the industrial specimens appears to be favored by many, and the need for standard refractory materials and test methods was also identified.

In closing, I want to thank our speakers and the panel members for their fine contributions to this conference. I particularly want to thank Dr. George Wei and Vic Tennery of Oak Ridge who put a lot of effort into preparing the program and lining up the speakers.

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- 367. J. F. Wosinski, Corning Glass Works, Box 432, Corning, NY 14830
- 368. Albert Yee, Dolomite Brick Corp., 232 E. Market St., York, PA  
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- 369. J. S. Young, Babcock & Wilcox Refractories, Old Savannah Rd.,  
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- 370. Neil Young, International Paper Co., 220 East 42nd St., New York, NY  
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