**Impact of Alternate Fuels on
Industrial Refractories and Refractory
Insulation Applications**

An Assessment

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MASTER

OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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METALS AND CERAMICS DIVISION

IMPACT OF ALTERNATE FUELS ON INDUSTRIAL REFRACTORIES
AND REFRACTORY INSULATION APPLICATIONS
AN ASSESSMENT

G. C. Wei and V. J. Tennery

SEPTEMBER 1976

Prepared for

Division of Industrial Energy Conservation
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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SUMMARY

Current U.S. industrial planning for conversion to fuels other than natural gas was estimated from February through April 1976, by contacting more than 100 companies in a number of industries, including: chemical, petrochemical, steel, aluminum, copper, glass, cement, ceramics, and others. The potential effects of planned fuel conversions upon industrial refractory furnace linings and refractory insulations were also assessed by means of personal contacts and investigations of available literature.

The general opinion of those industrial energy users polled in this study was that the future industrial energy supply situation is confused at present, especially in possible areas of governmental control and regulation and that as a result, it is difficult to make any definite plans. Distillate and residual fuel oils were identified as the favored industrial alternate fuels in current plans. The 1975 and the projected 1979 fuel use by categories for eight energy intensive industries is presented in the following. Although these estimates are only approximate, they do indicate certain trends in each industry regarding fuel conversion. Distillate oils are easiest to use in place of natural gas for many industrial applications. The capital investment for converting from natural gas to distillate oil for most boiler and process heater applications is about twice the investment required to burn natural gas. Conversion to residual oil combustion systems requires an additional capital investment of about 20% compared to distillate oil systems. Conversion from natural gas to coal combustion costs about four times the capital investment required for natural gas systems. These ratios tend to become smaller as the size of the combustion unit is increased to very large size (e.g., >2 MW).

1975 and Projected 1979 Fuel and Energy Mix for Selected Industries

Industry	Fuel Type or Energy Source, %			
	Natural Gas	Fuel Oils	Coal	Electrical
Aluminum	37 (0) ^a	10 (39)	1 (1)	52 (60)
Cement	42 (0)	16 (5)	34 (85)	8 (10)
Ceramics	68 (5)	12 (73)	13 (15)	7 (7)
Copper	64 (5)	18 (75)	9 (10)	9 (10)
Glass	90 (0)	3 (90)	0 (0)	7 (10)
Iron and Steel	20 (5)	9 (22)	67 (68)	4 (5)
Petrochemical and Chemical	59 (5)	23 (57)	10 (30)	8 (8)
Petroleum Refining	33 (0)	64 (96)	0 (0)	3 (4)

^aThe number in the parentheses represent the projected values for 1979 and are estimates judged currently accurate to perhaps $\pm 15\%$.

The detrimental effects of the impurities in residual oils upon refractory linings in furnaces and process heaters is clearly inhibiting wider consideration of this fuel at the present time. Potential contamination of manufactured products by residual oils is also a restricting consideration of heavy oils. Impurities present in typical bituminous coals and problems associated with fusion of the ash at temperatures above about 1150°C (2102°F) were also cited as major concerns that are retarding wider consideration of this alternate fuel. Fusion of the coal ash and subsequent slag deposition and reactions including fluxing, slagging, and corrosion of refractories by this fused material with combustion chamber surfaces, furnace walls, and products being heat treated plus problems with air pollution regulations and ash disposal will all tend to inhibit direct substitution of coal for natural gas in a large number of industrial furnacing applications. This present assessment identified the following industrial heating applications that involve refractories and refractory insulations and are potential areas where refractory degradation could be a major problem caused by the conversion from natural gas to heavy oil and/or coal. The various refractory applications are listed by industry:

<u>Industry</u>	<u>Refractory Applications</u>
Aluminum	Reverberatory melting furnaces, anode bake ovens, holding furnaces
Cement	Kilns
Ceramics	Kilns
Chemical	Boilers, process heaters, reboilers
Copper	Reverberatory melting furnaces, converters
Glass	Glass melting furnace linings, combustion air preheating regenerators
Iron and Steel	Soaking pits, reheating furnaces, heat-treatment furnaces
Petroleum Refining	Catalytic reactors

There is currently limited experimental or industrial refractory operating experience with residual oils at combustion chamber surface temperatures above about 1100°C (2012°F). Most available literature data on residual oils and their combustion products clearly indicate that the alkali metals, principally sodium, plus vanadium and sulfur are the primary causes of observed detrimental reactions with commonly used bulk refractories. The situation with refractory fibrous insulations is less clear, since little information is in the literature. Most of

the available information on refractory-alternate fuel combustion product interactions has been obtained under experimental conditions that have been poor simulations of actual combustor environments and usually are more typical of classical phase equilibria work. Little quantitative information is known of the degradative reaction mechanisms, the reaction kinetics, or the dependence of either of these on temperature, combustion gas impurity composition, or oxygen potential for most of the generic classes of refractories currently used industrially. This situation is indicated for various kinds of refractories and insulations in the following table.

Current State of Information on Refractory Performance With Use of Residual Oils or Coal as Alternates to Natural Gas^a

	Generic Refractory Type	Pertinent Phase Diagrams Known ^b	Long-Term Industrial Distillate Oil Firing Experience Available ^b
1	Alumina	✓	✓
2	Alumina-phosphate bonded		✓
3	Aluminosilicate (Alumina-silica) (fireclays and insulation fire bricks)	✓	✓
4	Glass fiber insulation		
5	High-alumina monolithics		✓
6	Intermediate- alumina monolithics		✓
7	Magnesia	✓	✓
8	Magnesite-chrome	✓	✓
9	Magnesite-silica		✓
10	Oxide fiber insulations	✓	
11	Silica	✓	✓
12	Zircon		

^a Information lacking on corrosion and spalling mechanisms, degradation reactions and kinetics, long-term combustor tests, and long-term residual oil combustion tests.

^b ✓ = Extensive operating experience or technical data currently available.

It is apparent from this table that there is a scarcity of information of the type required for industrial operational and investment planning regarding selection of refractories for use with either residual oils or coals. There is probably sufficient industrial operating experience with distillate oil combustion effects on refractories to consider this oil to be a safe and reliable substitute for natural gas for the present.

1. INTRODUCTION

The use of natural gas in the United States and the rest of the world has been increasing about 8% yearly,¹ while U.S. production, declining in recent years, decreased by 5% in 1975. Natural gas presently supplies more than 18.5% of the world energy. The U.S. produces and consumes about 68% of the present world production; and since the early sixties, natural gas has been a primary energy source in this country. In 1970 about 35% of the U.S. energy requirements were satisfied by natural gas,² while 46% of industrial energy needs were provided by this fuel. The purity of natural gas combustion products has been a major consideration in the industrial choice of natural gas relevant to the present struggle against atmospheric pollution. The relatively low cost of this fuel, plus the ease in handling and combustion, have also provided a strong incentive for wide use of natural gas.

Recently in the U.S., the supply of natural gas available for industrial customers has been curtailed at various times in deference to residential customers. The number and length of these curtailments have been increasing rapidly.³

This situation has increasingly required the affected firms to provide an alternate fuel capability for their operations or to cease the operations. The alternate fuels available in the immediate term to most industrial customers are distillate oils, residual oils, coal, producer gas, and electricity. 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 it 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 the fuel combustion products. Distillate oils are more expensive than residual oils.

Residual oils require a larger incremental capital cost relative to natural gas for their use than do distillate oils; and the impurity levels are usually significantly higher in residuals. The potential of residual oils to play a major role as an alternate fuel at lower cost per unit of heat compared with distillate oils is presently hampered by concerns about possible detrimental effects some of the combustion products of residual oils may have on high-temperature industrial equipment. Much of the combustion experience in the U.S. with residual oil has been with steam boilers constructed primarily of water-cooled metal with the surface temperature limited to about 649°C (1200°F). At this temperature and below, corrosion rates of the boiler tubes are generally acceptable for the design life of the equipment under proper combustion conditions. For a great many industrial firing applications, temperatures well above 649°C (1200°F) are necessary; such operating temperatures require the use of ceramic refractories and/or refractory insulations in contact with the fuel combustion products. For these applications, relatively little specific technical information or industrial operating experience is available to aid designers in selecting refractory systems for use in conjunction with residual oil combustion. Few reports are available on the effects that residual oil combustion products have on refractory materials. Much more research needs to be done on this subject to provide information adequate for either equipment design or for industrial economic analyses.

Coal, propane, producer gas, and electricity are other candidate alternate fuels. 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. To use coal at higher temperatures, the reactions of coal slag with the product and with the internal parts of the firing equipment must be acceptable or controlled by means of equipment design. For many industrial firing processes this is not yet possible. The high retrofit cost for installing coal combustion

equipment is a major negative factor in considering conversion from natural gas to coal. There is a 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. There is also a lack of documentation in this area, which can be useful in planning industrial fuel conversion to coal. Combustion emissions from most bituminous coals are above those for an equivalent heating value from No. 2 or No. 6 oil. Therefore conversion to coal rather than oil creates a potential environmental problem unless pollution control equipment is also provided. The reactions between various refractory systems and coal slags are also of strong concern in ERDA's current programs in coal gasification, recuperators, and magnetohydrodynamics. Operating experiences from this work should provide information relevant to the use of coal as an alternate industrial fuel for high-temperature applications. However, it will be some years before this data base is established and available for use in materials selection and design.

Producer gas or low Btu gas is a potential alternate fuel for natural gas and, in fact, 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.

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.

The work described in this report was conducted over a period of three months (from February to April 1976). A selection of approximately 100 companies in energy intensive U.S. industries were contacted to determine their plans for converting to an alternate fuel, the anticipated time scale for these conversions, and their experiences with the effects that alternate fuels have on refractories and refractory

insulations. This assessment is the first task of a program whose objectives include:

1. determination of the physical and chemical properties of alternate fuels, their combustion technologies, and their cost and availability,
2. determination of the status of present U.S. industrial planning for conversion from natural gas to alternate fuels,
3. identification of industrial process systems that will most likely experience refractory deterioration with conversion to alternate fuels,
4. review of the present knowledge of alternate fuel combustion product-combustor material reactions, and
5. studies of the mechanism of the detrimental interactions.

The emphasis of this work is on the alternate fuel situation in the immediate term that extends from the present to 1980. Through selected refractory system-alternate fuel screening tests, this program will provide a data base for refractory material design and selection. The alternate fuels will include residual oils and coals of selected compositions. Refractory types to be tested in a controlled combustion environment will include: (1) dense refractory brick, including fireclay, alumina (fused and dry-pressed fabrication), phosphate-bonded alumina, magnesia, chrome-magnesite, and silica; (2) monolithic refractories, including plastic mixes (ramming and gunning compositions), and castables; (3) insulating refractory bricks of various maximum temperature ratings; (4) insulating refractory fiber materials including alumina-silica based fibers, all-alumina fibers, all zirconia fibers, and refractory fiber bat support structures, and (5) refractory mortars for dense refractory brick structures. After selected exposure times to alternate fuel combustion, the refractories or refractory insulations will be characterized in terms of changes in microstructure, phase content, chemical composition, and mechanical properties. The interpretation of the results from the screening tests will be based on the thermochemical and thermomechanical analyses described in this report along with the limited available industrial observations of these systems. The results of the screening tests will be used to provide parametric descriptions of the sensitivity

of various industrial refractories and refractory insulations to conversions to these alternate fuels.

Large-scale field tests that involve industrial furnacing operations using alternate fuels will possibly be conducted in cooperation with industrial firms and ERDA. Presumably, the results of these tests would provide confirmation of the results obtained in our smaller scale combustor evaluations and thereby accelerate industrial acceptance of the results.

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2. CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

This assessment indicates that, in the immediate term, there is a large amount of activity toward conversion away from natural gas in a variety of industries because of the scarcity of this fuel. Refractories and refractory insulations that are used in industrial furnace heating applications and that are likely to be affected in the near term by the impurities in the alternate fuels were identified. The interactions of the combustion ash, slag, and vapor with the refractory material that lead to refractory degradation were analyzed. Successful conversion to alternate fuels requires proper selection and design of the refractory systems. The conclusions are itemized as follows.

1. Due to the lifetime of combustion equipment and furnaces, the decisions on fuel conversion and refractory material selection made now will have an effect in the long term (1985-2000 period). This should be considered in any long-range planning. There is also a need for establishing a long time data base of alternate fuel combustion.

2. The alternate fuel for most industries in the immediate term is fuel oil, including both No. 2 and No. 6 grades.

3. The increase in the oil demand is expected to be matched by increased imports.

4. Coal combustion systems typically involve large capital investments relative to oil systems. Large industrial boilers (>25 MW) generally are planned initially for coal and can be converted to burn coal if they have been used for oil or gas. Medium and small boilers are more economically converted to residual or distillate oils. The cement industries and those parts of the ceramic industry using relatively low-temperature firing [$<1093^{\circ}\text{C}$ (2000°F)] are converting from natural gas to coal.

5. The vanadium, sodium, and sulfur that are the major impurities in both residual and distillate oils can cause fluxing, spalling, and cracking in aluminosilicate, magnesite-chrome, and zircon refractories used in brick and monolithic forms. These reactions are dependent upon

the combustion conditions. The impurity content in fuel oils varies widely, depending on the crude source, storage, and shipping conditions.

6. Refractory mortars usually contain a high percentage of calcium aluminate cement that is readily attacked by the vanadium and sodium in residual and distillate oils. Higher alumina, lower calcium oxide content, and higher density in mortars can give better resistance to fuel impurity attack.

7. Aluminosilicate refractories resist vanadium attack, but are readily corroded by sodium-containing solids, melts, and vapors at certain temperatures. The magnesite-chrome refractory system resists sodium attack, but is seriously fluxed by vanadium-containing solids, melts, and vapors. Therefore, in the presence of both vanadium and sodium, these two widely used industrial refractory systems will be degraded. Sulfur in heavy oils and coals generally attacks the refractory materials and tends to cause extensive deterioration in refractories and refractory insulations. Higher alumina or magnesia content, low alkali content, less glass phase, low calcium oxide content, and low porosity are essential factors for increased refractory resistance to attack by vanadium and sodium ash, slag, and vapor species.

8. Silicon carbide and Si_3N_4 reportedly resist fuel oil ash corrosion better than many other refractories. However, the high thermal conductivities of these materials requires increasing both the quality and the thickness of the backup insulation if these materials are used as the furnace hot face.

9. Some chemical and petrochemical companies are planning to make extensive conversions soon from natural gas in boilers and process heaters to No. 6 oil and No. 2 oil, respectively. Fireclay refractories, which are generally used in some of these boilers and particularly in process heaters, are subject to combustion ash corrosion at temperatures above about 800°C (1472°F).

10. The aluminum industry is converting to No. 2 and No. 6 oils in remelting and reheating furnaces that were built of high alumina ($>70\% \text{Al}_2\text{O}_3$) or phosphate bonded alumina refractories. The use of

No. 6 oil requires higher alumina content in the aluminosilicate refractory system. Anode bake ovens built of fireclay bricks probably will have to be upgraded to higher alumina content bricks before conversion to No. 6 oil.

11. Some steel companies are concerned about the contamination of their products by the impurities in the alternate fuels such as No. 6 oil or coal. In some plants, coke oven capacity is planned to be expanded for supplying coke oven gas to replace natural gas in soaking pits, heating and reheating furnaces. Nonintegrated companies that do not have coke ovens are converting to No. 6 and No. 2 oils. The refractories used in these furnaces cover a broad range of compositions and, in general, must be of high alumina or magnesia content, low porosity, and low alkali content for applications involving No. 6 oil.

12. Some of the glass companies are considering No. 2 oil for immediate-term conversion because of concern about detrimental reactions with No. 6 oil in their checkerwork brick in the furnace regenerators used to preheat the combustion air. Basic refractories that best resist the combustion ash attack are of high magnesium oxide content, direct bonded or forsterite bonded, low CaO/SiO_2 ratio, magnesite-chrome bricks. Some glass companies are seriously considering converting to electric melting.

13. The copper industry is converting to distillate and residual oils in their remelting furnaces and converters. Residual oil combustion requires the use of higher-purity materials in the basic refractories used for the side walls and the aluminosilicate refractories used in the roof.

14. Some refractory companies are converting to No. 2 oil because of concern about detrimental reactions that can occur in their kilns and products with the use of residual oils at the relatively high firing temperatures required.

15. Published information on alternate fuel combustion product (solid deposit, slag, liquid, and vapor) attack in refractory materials is sparse. There are few industrial observations from which detailed data could be extracted for this assessment. In some cases, the

information was regarded as proprietary. In most others, there was either no operational experience or the limited amount available was not amenable to interpretation. A systematic test program exposing generic types of refractory materials to alternate fuel combustion under controlled conditions of combustion time, mean temperature, temperature gradient, temperature cycling, and oxygen potential would provide guidelines to the sensitivity of various industrial refractory materials to alternate fuel combustion product attack. Large scale field test projects will help establish the magnitude of refractory deteriorations in various industrial furnacing applications under full-scale conditions.

16. The physical and chemical properties (e.g., density and standard free energy of formation) of certain phases (e.g., nepheline, β -alumina) resulting from combustion product attack of some refractories are still unknown and should be determined. Phase equilibrium and diffusion data in systems experiencing fuel ash attack (such as V_2O_5 - Na_2O - SO_3 - Al_2O_3 - SiO_2 , V_2O_5 - Na_2O - SO_3 - MgO - Cr_2O_3) are extremely limited and, in some cases, even contradictory. Additional experimental work is needed in determining these parameters as they are required in the thermochemical and thermomechanical prediction and analysis that are essential to understanding refractory degradation mechanisms. This type of information is essential to developing refractory materials that resist attack from the combustion products of alternate fuels.

2.2 RECOMMENDATIONS FOR SELECTION OF REFRACTORIES FOR USE WITH ALTERNATE FUELS

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, alkalies, and sulfur; future work is needed to better define phase relations and kinetic data for the fuel impurity and refractory material interactions. The thermochemical and thermomechanical parameters of the reaction products should also be determined. A laboratory test program and a field test program that covers a broad range of refractory and insulating materials

used in various combustion conditions for long times under high temperature test conditions are needed.

Six recommendations for selection of the presently available refractories for use with alternate fuels are:

1. Silica refractories should be replaced by other types of refractories that better resist combustion ash attack; since at temperatures above 1500°C (2732°F), silica bricks are seriously fluxed and cracked by sodium present in the combustion products of fuel oil.

2. The aluminosilicate materials in systems subject to the fuel conversion should be upgraded to higher alumina content, lower porosity, minimum glass phase, and low alkali content.

3. Phosphate-bonded alumina probably should not be used in alkali- and vanadium-rich environments characteristic of combustion of some residual oils.

4. Since plastic and castable refractories that contain calcium-oxide-based cements react with fuel oil ash, the use of these mixes should be carefully studied and attention directed to lowering the calcium-oxide content, lowering the glassy-phase content, and increasing the Al_2O_3 content.

5. The basic refractories, which are seriously fluxed by vanadium, should be upgraded by increasing the magnesium oxide content. Direct bonded, or forsterite bonded, low CaO/SiO_2 ratio, basic refractories are preferred.

6. The applications of zircon refractories probably should be limited to temperature lower than 1000°C (1832°F) at which decomposition will start in the presence of residual oil fuel ash components.

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3. ALTERNATE FUELS FOR THE IMMEDIATE TERM (1976-1980)

The total energy consumption in U.S. industries was about 29% of the total energy supply in the whole nation (73.1×10^{15} Btu) in 1974.¹ About 54% of the energy sources for industrial heating and power applications in 1971 (Table 3.1) was natural gas.² Industry's reliance on natural gas is evident. Natural gas is used to such an extensive degree that a wide variety of industries are dependent on it. For example, chemical and petrochemical, primary metal (steel and aluminum), copper, glass, cement, refractory, food, and paper industries have been using natural gas as a principal fuel to heat their furnaces, boilers, kilns, and reactors. Due to federal regulations, the price increase of natural gas in recent years (Fig. 3.1) is only moderate as compared to those of fuel oils and coal, even though the demand for natural gas from industry and residential customers has always been increasing.³ Clean, low priced, and relatively easy to handle, transport, and store, natural gas is far superior to other types of fuel.

Table 3.1. Distribution of Energy Sources in Industrial Heating and Power Applications in 1971

Fuel	%
Natural gas	53.9
Electricity	14.2
Fuel oil	12.1
Coal	13.0
Other	6.8

Source: 1972 Census of Manufacturers, p. 6-197, U.S. Census Bureau, Washington, D.C.

However, the production of natural gas, following an abrupt leveling off since 1970, experienced the first significant decline in 1974 despite the 7240 new producing wells completed in that year that represented the greatest number of new producing wells in the history of the natural gas

Fig. 3.1. Relative Increase of the Price Index for Fuels and Electricity (Price Index 1967 = 100). Reprinted with permission from G. C. Gambs, "The Case for Energy Management," in *The 1975 Energy Management Guidebook*, ed. by the editors of *Power Magazine*, McGraw-Hill, New York, 1975.

industry.⁴ The continuous shortage of natural gas (Table 3.2) will be as much as 12.2×10^{15} Btu by 1980 and has already resulted in serious curtailment to industrial users.⁵ In 1976 alone, the curtailment of natural gas in interstate pipelines may amount to nearly 2×10^{12} ft³.⁵ Such a shortage will have a serious and immediate impact on industries and electric power utilities. Industrial users get only short notice (one day to one month) that their gas supply is being reduced. Many industries facing the natural gas shortage, which is by no means short-term, are therefore converting their furnaces to other available fuels in order to keep their production constant. The principal reason for these conversions is not the cost of natural gas, but rather its shortage.

Alternate fuels such as distillate oils, residual oils, coal, and low-Btu gases, and other energy sources such as electricity, have been considered as replacements for natural gas. However, the use of these fuels requires an understanding of their physical and chemical characteristics as well as the installation of new fuel storage, piping, and combustion equipment that are usually capital intensive. The selection

Table 3.2. Comparison of Natural Gas Supply and Demand
(Btu $\times 10^{12}$)^a

	1975	1980	1985
Potential demand	30,268	34,700	40,119
Anticipated supply	22,420	22,480	22,180
Indicated shortfall	7,848	12,220	17,939

^aSource: *U.S. Energy Outlook - Gas Demand*, p. 4,
National Petroleum Council, Washington, D.C., 1973.

of the most suitable alternate fuel depends on its economics in terms of fuel cost, availability, and necessary capital investment, and the influence of fuel conversion on product quality and production rate. In addition, the direct impact of fuel conversion on the refractories and refractory insulation in furnaces has to be evaluated. An incorrect choice of the refractory materials can easily cost millions of dollars in repairs for a large installation, not including production losses because of downtime. The successful use of an alternate fuel thus hinges critically on the selection of a refractory based on an understanding of its interaction with the combustion products which, in turn, depends upon the physical and chemical properties and flame characteristics of the fuel to be used.

3.1 DISTILLATE OILS

Distillate oils have been used in many industrial heating installations and are considered one of the most ideal fuels to substitute for natural gas. There are two classes of distillates: namely, straight-run and cracked. Commercial distillate oils are usually mixtures of these two. A straight-run oil is distilled directly from crude oil while a cracked oil is produced from heavier fractions at high temperatures and pressures. The difference between these two types of oil is that cracked distillates contain a substantial amount of heavy hydrocarbons, which are more difficult to burn than the light hydrocarbons in the straight-run distillates. There are two commercial grades of distillate oils: namely, No. 1 and No. 2 (Table 3.3).

Table 3.3. Standards for Distillate and Residual Oils, D-396^a

Grade	Flash Point (°F)	Pour Point (°F)	Water and Sediment (vol %)	Maximum Ash (wt %)	Carbon Residue on 10% Bottoms (%)	Saybolt Viscosity (sec) ^b				Kinematic Viscosity (cSt) ^b				Minimum Gravity (deg API)	Sulfur (%)
						Universal at 100°F		Furol at 122°F		at 100°F		at 122°F			
						min	max	min	max	min	max	min	max		
1	100 ^c	0 ^d	Trace		0.15					1.4	2.2			35	0.5 ^c
2	100 ^c	20 ^d	0.05		0.35	(32.6)	(37.9)			2.0 ^d	3.6			30	0.5 ^{c,e}
4	130 ^c	20 ^d	0.5	0.1		45	125			(5.8)	(26.4) ^f				Legal
5 Light	130 ^c		1	0.1		150	300			(32)	(65) ^f				Legal
5 Heavy	130 ^c		1	0.1		350	750	(23)	(40)	(75)	(162) ^f	(42)	(81)		Legal
6	150	f	2 ^h			(900)	(9000)	45	300			(92)	(638) ^f		Legal

^aSource: "Petroleum Products and Lubricants," part 23, pp. 219-20, 1975 Annual Book of ASTM Standards, D56-D1660, American Society for Testing and Materials, Philadelphia.

^bViscosity values in parentheses are for information only and not necessarily limiting.

^cStatute value.

^dLower or higher pour points may be specified whenever required by conditions of storage or use. When pour point less than 0°F is specified, the minimum viscosity for Grade No. 2 shall be 1.8 cSt (32.0-S Saybolt Universal).

^eIn foreign countries, other sulfur limits may apply.

^fWhere low-sulfur fuel is required, fuel oil falling in the viscosity range of a lower-numbered grade down to and including No. 4 may be supplied by agreement between purchaser and supplier. The viscosity range of the initial shipment shall be identified, and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

^gWhere low-sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as low-pour (60°F max) or high-pour (no max). Low-pour fuel oil should be used unless all tanks and lines are heated.

^hThe amount of water by distillation plus the sediment by extraction shall not exceed 2%. The amount of sediment by extraction shall not exceed 0.5%. A deduction in quantity shall be made for all water and sediment in excess of 1%.

Number 1 oil is widely used for space heating. Number 2 oil is widely used in many industrial combustion installations such as melting furnaces, heat and reheating furnaces, kilns, glass tanks, packaged boilers, incinerators, and process heaters.

Distillate oils are relatively easy to handle, store, and burn as compared to residual oils and coal. They have good pumping properties and can be pressure atomized by air, steam, or ultrasonics. The maximum amount of sulfur is typically specified as 0.3 wt % for distillates.

The American Society for Testing and Materials has developed several standard test methods and procedures for determining the quality of fuel oils according to physical properties such as specific gravity, heating value, viscosity, water and sediment, and pour, flash, and fire points, all of which are important to handling and combustion. The heating value of No. 2 distillate oil varies with the gravity and the sulfur content, and is typically 142,000 Btu/gal. The gravity scale used in the petroleum industry is the American Petroleum Institute (API) scale and not the specific gravity of the oil. Number 1 oil has an API gravity range of 41 to 46 degrees; No. 2 oil, 30-39. Viscosity is an important factor in the design of the efficiency and sizing of pumps, pumping temperature, and pipeline sizing. Viscosity is the time in seconds that it takes 60 cm³ of oil to flow through a standard size orifice at standard temperature. The Saybolt Furol and Universal viscosimeters are generally used. The pour point of an oil is the lowest temperature at which it flows under standard conditions. Distillate oils usually pour freely above -12°C (10°F). Flash point is the temperature at which oil vapors flash when ignited and is a measure of the volatility of the oil. Distillate oils normally have flash points from 62 to 93°C (145 to 200°F). The total amount of water and sediment in distillate oils can be 0.2% of total volume. Water can lead to corrosion of storage tanks and piping and can cause inefficient combustion. Distillate oil generally contains impurities other than sulfur at levels <1 ppm. Depending on the crude source, handling, shipping, and storage conditions, impurities may include some sodium in the form of salt water and some lead from contamination by lead-bearing

gasoline. As many as 25 different metals can be found in distillate oils. Vanadium, sodium, iron, nickel, calcium, and aluminum are the most prevalent. A chemical analysis normally is not included in a distillate oil specification, except for the sulfur content. As a matter of fact, many oil companies are reluctant to release this kind of information. The metallic elements in oil are in the form of organometallic compounds that are extremely difficult to remove. Data from two oil companies (Table 3.4) indicate typical metallic impurity contents. Since low-level impurities in distillate oils are difficult to quantitatively determine, there is a continuing effort to develop more exact analytical methods.

The ash content of distillate oils is about $<0.1\%$. Although the percentage is low, a considerable amount of ash could accumulate during the life of the unit if the solids and some of the gaseous species react and remain in the combustion chamber. The fuel ash of distillate oils is composed of hydrocarbons, oxygen, nitrogen, sulfur, chlorine, and organometallic compounds. Beside reducing the heat transfer efficiency, ash deposits can also cause corrosion, cracking, spalling, and fluxing in the metals or ceramics in the combustion chamber. On the other hand, distillate oil combustion is similar to that of natural gas in flame length, flame geometry, and temperature range.

The availability of distillate oils is related to the crude oil supply and the demand for higher grade petroleum products such as gasoline and diesel fuel. The statistics of the American Petroleum Institute show that in 1974 about 10% of distillate fuel oil was apparently imported.⁶ If the imported crude oil that was later refined into distillates were included, the total import accounted for about 40% of the total supply of distillate oils (2,951,000 barrels per day). As industrial needs increase, the supply of distillate oil will rely heavily on imports in the immediate term. The average price of No. 2 oil in 1974 was \$2.59 per million Btu, or equivalently, \$10.50 per barrel.⁴ The price increase was nearly 70% in one year alone. It is expected that by 1980 industry will pay \$25 per barrel for fuel oils.³

Table 3.4. Typical Metallic Impurities and Sulfur Content (ppm)^a in Distillate and Residual Oils from Two Oil Companies

Impurity	From Company A		From Company B
	No. 1 Oil	No. 2 Oil	No. 2 Oil
Sulfur	350-1,500	1,200-2,500	0.3 wt %
Sodium	0.01-0.1	0.02-0.2	0.05-0.13
Lead	0.01-1.0	0.01-1.0	<0.10
Vanadium	0.01-0.5	0.01-0.5	<0.05
Copper	0.005-0.05	0.005-0.05	
Calcium	0.01-0.1	0.01-0.15	<0.002
Potassium	0.01-0.06	0.01-0.10	
	<u>No. 4 Oil (Low Sulfur)</u>	<u>No. 6 Oil (Low Sulfur)</u>	<u>No. 6 Oil (Domestic)</u>
Sulfur	5,000-10,000	5,000-10,000	2.9 wt %
Vanadium	1-65	12-100	50
Nickel	1-65	15-100	15
Iron	1-20	20-40	10
Sodium	1-25	25-50	4
Calcium	1-20	10-50	2
	<u>No. 4 Oil (High Sulfur)</u>	<u>No. 6 Oil (High Sulfur)</u>	<u>No. 6 Oil^b</u>
Sulfur	15,000-30,000	15,000-30,000	2.9 wt %
Vanadium	30-100	30-200	350
Nickel	15-100	15-100	25
Iron	5-50	5-50	115
Sodium	5-50	15-75	5
Calcium	5-50	15-75	5

^aUnit of impurity content is ppm unless noted.

^bFrom Caribbean crude containing vanadium below 500 ppm. Vanadium content of one Venezuelan crude can be as high as 1200 ppm.

The supply of distillate oils depends on international markets and a stable supply in the future is very questionable. In addition, No. 2 oil is expensive (about \$2.59 per million Btu vs \$0.68 per million Btu for natural gas),⁴ and sizable capital investments are necessary for combustion, storage, and piping equipment. Nevertheless, industrial users facing the severe curtailment of natural gas still consider distillate oils, especially No. 2, an ideal alternate fuel provided the refractory materials in furnaces and combustion chambers are selected properly.

3.2 RESIDUAL OILS

Residual oils are also promising alternate fuels. There are three grades of residual oils: Numbers 4, 5, and 6. Of these three, No. 6 or Bunker C is most widely used by industry. Basically, No. 6 oil is the residue left after most of the light volatile products have been distilled from the crude oil. Today's residual oils are usually blends of distillates and heavy residuals. The production of No. 6 oil historically has not been determined by its demand, but rather the demand for gasoline and distillates. However, the high market price of residual oils has encouraged some refiners to increase the production of residual at the expense of light distillates. The price index for residual oil doubled from 1970 to 1973.³ Coal prices also increased significantly. In comparison, natural gas and industrial electricity only showed modest price increases. In 1974, the price of residual oil was \$2.05 per million Btu, or equivalently, \$13.09 per barrel. Most recently, No. 6 oil prices have been increased to nearly equal that of No. 2 oil. Numbers 4 and 5 oil can be produced by blending from 20 to 85% of No. 2 oil with No. 6 oil to meet ASTM specifications, or it can be a straight-run product. Number 5 oil comes in two classes. Light No. 5 oil can be atomized while heavy No. 5 oil needs preheating. Separation of two components in the storage tank can cause blended residual oil to become an unstable fuel. If the storage tank system is properly designed so that the oil is conditioned by heating, agitation, and thermal insulation, the blended fuel oil should not separate.

In 1974 the total U.S. residual oil demand was 2,655,000 barrels per day, of which 73% was imported. The availability of residual oils is thus more dependent on foreign sources than light distillates. While it could be a good alternate fuel in the immediate term, its long-term supply could easily be interrupted by international market turmoil or instability.

The heating value of residual oil is typically 152,000 Btu/gal. The range of viscosities for residual oil is quite broad (Table 3.3). Its pour point usually ranges from -4 to 18°C (25 to 65°F). Normal heating of storage tanks, pipelines, and pumping equipment keeps the oil well above this range of temperatures. The flash point of heavy oil can be as high as 121°C (250°F). The amount of water and sediment in residual oil is from 0.1 to 2%. Sulfur content is generally at the level of 3 wt %, but the limit specified for a given application is that which is dictated by the local environmental regulations. The ash content in residual oil ranges from 0.2 to 1.5%. Vanadium, sodium, iron, nickel, lead, calcium, and aluminum are generally present at levels higher than a few ppm in most residual oils. Vanadium is present in small amounts in most U.S. domestic crudes, but may appear in substantial quantities in Venezuelan or Arabian crudes (Table 3.4) and, in some cases, can be as high as 2000 ppm (0.2%).

The difference in the impurity level among these oils can be an order of magnitude or more. For this assessment, oil companies were reluctant to release impurity specifications for their No. 6 oils. The general opinion expressed by oil chemists during this assessment is that the range of the properties of residual oil such as impurity content and viscosity will continue to be broad in the immediate future. It is generally agreed that no specification can presently be written such that the burning qualities of fuel oil are reproducible. Engineers therefore must consider accommodations for a wide range of properties in designing combustion, pumping, piping, and storage systems.

Experiences of combustion equipment builders indicate that, in general, the larger the size of the heavy oil burner, the better it works above a level of about 1.5 million Btu/hr. Efficient high velocity

light oil burners have been commercially available for some time. However, development of a high velocity heavy oil burner capable of low excess air firing without formation of carbon deposits in the burner tile is still unsuccessful.⁷

One of the inevitable results of the high metallic impurity content in residual oil is the deterioration in refractory materials in the combustion space. In addition to the sizable increased amount of maintenance work, the problems associated with conversion to residual oil firing are: (1) the flame temperature usually is higher than that of natural gas, (2) the flame length is longer than in the case of natural gas and is likely to impinge on the products and furnace walls, which were formerly at a distance from the flame, (3) the high level of contaminants in combustion products and in the exhaust gas often causes air pollution violations, and (4) the combustion products corrode, flux, and crack the refractory materials in the furnace and generate thick deposits in the cooler places in the furnace. These installations also require more capital investment than those using distillate oils. Despite these potential disadvantages, industrial heating apparatus in which very high temperatures [$>1482^{\circ}\text{C}$ (2700°F)] will not be used is being converted to heavy oils because the product contamination can be tolerated. Since residual oils are expected to be more readily available to industrial customers than distillate oil in the immediate term (1976-1980), respondents indicated that residual oil is expected to be a principal alternate fuel in the next five to ten years.

3.3 COAL

Coal is the most economical source of energy for many industrial heating applications. Identified and projected reserves of coal in the U.S. amount to 3224 billion tons, which is more than half of the world total reserves.⁸ About 5% of the total U.S. reserves are economically recoverable at this time. In 1970 the total U.S. coal demand was about 613 million tons. About 50% of this amount was used for electrical power generation and 34% was used in industrial heating and coking. The average price of coal in 1974 was \$18 per ton or

equivalently \$0.89 per million Btu.³ By 1980 it is predicted that coal prices will be close to \$50 per ton.³

The properties of coal vary greatly among different sources. For example, high sulfur Eastern bituminous and low sulfur Western subbituminous and lignite are very different in moisture content, ash content, ash-fusion temperature, sulfur content, alkali content, etc. The successful use of coal as an alternate fuel therefore depends on the careful evaluation of the performance of a particular type of coal in a particular furnace. Bituminous coal contains 1 to 5% moisture, whereas some Western lignites contain up to 45% moisture. Coal ash composition also varies widely. For example, Eastern coal ash has a greater percentage of ferric oxide than calcium oxide and magnesium oxide, while for Western coals the reverse is true. Ash contents of coals can vary from 3 to 30% (Table 3.5). Sulfur in coal is in the form of pyrite, marcasite, calcium sulfate, or organic sulfur, and ranges from trace quantities to almost 8%. The heating value of bituminous coal varies with those physical and chemical properties and is generally about 24,000,000 to 28,000,000 Btu/ton. Lignites have heating rates of 6,000,000 to 10,000,000 Btu/ton.

Pulverized coal, which is ground from the raw coal, is often used in industrial heating and steam generation. But the high capital cost of the necessary installations such as combustion equipment, storage, grinding, moisture treatment, flue gas cleaning, and transportation generally amounts to about triple the cost of an equivalent distillate fuel oil firing unit. This is a big obstacle to the wide use of coal as an alternate fuel. The high percentage of noncombustible materials in coal will lead to ash deposits in the furnace with the consequence of reduction in furnace efficiency and possible violations of local environmental regulations. Problems such as clinkering, corrosion, and slagging in a coal-fired furnace dictate that the temperature should be kept below approximately 1093°C (2000°F). In some cases, the refractory material in the combustion chamber or burner must be upgraded via compositional changes to be suitable for a specific type of coal. Despite these limitations and the high capital investment,

Table 3.5. Examples of Ash Composition in a Typical West Virginia Coal and a Montana Coal

Oxide	Average wt %	Oxide	Average wt %	Oxide	Average wt %
<u>West Virginia Bituminous Coal Ash^a</u>					
Li ₂ O	0.075	Ag ₂ O	0.0010	La ₂ O ₃	0.030
Na ₂ O	1.78	As ₂ O ₃	<0.07	MnO	0.046
K ₂ O	1.60	B ₂ O ₃	0.12	MoO ₃	0.016
Rb ₂ O	0.030	BeO	0.008	NiO	0.047
CaO	2.76	Bi ₂ O ₃	<0.004	P ₂ O ₅	0.35
SrO	0.38	Cb ₂ O ₅	0.010	PbO	0.048
BaO	0.22	CoO	0.010	Sb ₂ O ₃	<0.005
MgO	0.98	Cr ₂ O ₃	0.023	SnO ₂	0.020
Al ₂ O ₃	29.9	CuO	0.061	V ₂ O ₅	0.050
SiO ₂	43.9	GaO	0.022	WO ₃	<0.01
Fe ₂ O ₃	15.9	GeO ₂	0.011	ZnO	0.053
TiO ₂	1.52	HgO	0.011	ZrO ₂	0.029
<u>Station B Montana Subbituminous Coal Ash^b</u>					
SiO ₂	34.2	Fe ₂ O ₃	12	Na ₂ O	0.3
Al ₂ O ₃	15	CaO	18	K ₂ O	0.3
TiO ₂	0.8	MgO	4.5	SO ₃	17

^aH. F. Yancey and M. R. Geer, *Coal Preparation*, pp. 1-38, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, 1968.

^bW. R. Buckley et al., *Power Magazine*, p. 20 (July 1974).

coal as an alternate fuel is expected to play a major role in industrial fuel planning in the long run but only a limited one in the immediate future.

3.4 ELECTRICITY

Electricity is obviously a clean form of energy. The direct use of electricity in industrial processing and heating has several advantages over direct fuel use: (1) higher efficiency of heat utilization, (2) environmentally clean, and (3) less cost in capital investments such as storage, transportation, piping, pumping, and combustion systems. In terms of energy, the cost of electricity is presently much higher than fuel oil, coal, or natural gas simply because electricity is generated from these fuels at a typical conversion efficiency of about 35%. In 1974, the average price of electricity for industry was \$6 per million Btu.³ Despite its high price, electricity still is a nearly ideal substitute for natural gas in some processing furnace applications. In fact, several respondents indicated that the manufacturing industry is in general already converting to electric power where practical. For example, three years ago, one major furnace company manufactured only natural gas furnaces, but now 40% of this company's production is electric furnaces. As this was a general trend identified in this assessment, the question is raised regarding the electric power generation capacity to meet the needs resulting from this conversion. In view of the rapidly rising cost of electric energy and a potential shortage of investment capital for expansion of utility services, conversion from natural gas to electricity is not a generally desirable alternative at this time. The use of electricity to make up the shortage of natural gas appears to be relatively limited in the foreseeable future.

3.5 LOW BTU GASES

Low Btu gases that are produced from the gasification of coal or oil or reclaimed from steelmaking processes are also considered as alternate fuels in this assessment. The gas composition depends on its production process (Table 3.6). Since there is a significant amount

Table 3.6. Typical Compositions of Low Btu Gases and Natural Gas^a

Parameter	Natural Gas	Lurgi	Fluidized-Bed Coal Gas	BOM 7644	Winkler-1	Winkler-2	Producer Gas (from coal)	Blast Furnace Gas	Blue Water Gas	Coal Gas
O ₂										0.4
N ₂	0.5	30.2	50.4	54.7	55.3	1	52.4	60	4.5	6.2
CO ₂	1.8	10.7	0.5	7.2	10	19	4	11	4.7	4
CO		10.7	31.8	2.0	22	38	29	27	41	18
H ₂		15.7	15.6	15.5	12	40	12	2	49	49.4
CH ₄	93.3	4.4	0.5	2.8	0.7	2	2.6		0.8	20
C ₂ H ₆	3.49									2
C ₃ H ₈	0.68									
C ₄ H ₁₀	0.18									
C ₅ H ₁₂	0.04									
H ₂ O		27.8	0.5							
H ₂ S		0.5	0.7							
Stoichiometric fuel/air:										
Ratio (By vol)	0.103	0.923	0.815	0.899	1.141	0.488	0.817	1.448	0.450	0.252
LHV, Btu/scf	930	121	154	132	110	250	150	92.3	274	422
HHV, Btu, scf	1030	150	163	143	117	272	158	93.3	299	471
Stoichiometric temperature:										
Rise, °F	3495	2312	3007	2638	2438	3501	2871	2205	3769	3601
H ₂ /CO (by vol)		1.467	0.491	7.75	0.545	1.053	0.414	0.074	1.195	2.744

^aSource: Used with permission from *Power Magazine*, p. 62 (June 1974).

of CO and N₂ in these low Btu gases, the stoichiometric fuel/air ratios for low Btu gases are higher than for natural gas. The heating values of these low Btu gases are around 300 Btu/ft³. The technology of coal gasification to produce low Btu gases is such that this fuel is not economically feasible at present and may not be for ten years or more. However, in the iron and steel industries, both the coke oven gas and the blast furnace gas, which have traditionally been used as fuels, can replace natural gas to a great extent. For the immediate term, the use of low Btu gases as an alternate fuel is only applicable where their production occurs as a part of some other primary process.

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4. ASSESSMENT BY INDUSTRY OF FUEL CONVERSION IMPACT ON INDUSTRIAL REFRACTORIES AND REFRACTORY INSULATIONS IN THE IMMEDIATE TERM

As discussed previously, natural gas has become a primary fuel for most industries in the U.S. during the past two decades. As this fuel became more available following World War II, industrial and residential users converted from other fuels, primarily coal, to natural gas because of:

1. its relatively low cost per Btu,
2. the desirable flame properties peculiar to natural gas,
3. the relatively clean combustion products from natural gas compared to coal, and
4. the relatively low capital investment required for conversion to use of natural gas.

Within the past five years or so, the demand for natural gas has exceeded the supply in various regions of the U.S. and the suppliers have begun to limit the gas available to industrial users during periods of high demand in order to ensure gas availability to residential and commercial customers.

The interruptable nature of most of the industrial contracts now available for natural gas has caused some companies to install alternate fuel supply systems that could be used during the period when the natural gas supply is interrupted by the supplier. The availability of natural gas for industrial use has been decreasing in many areas; therefore, some industrial firms are planning to make relatively permanent conversion to an alternate fuel where possible. The relatively low cost of natural gas compared to any other fuel, on a heat equivalent basis, still provides a strong incentive for industry to use it wherever and whenever possible. To determine the present status of industrial planning for conversion from natural gas to alternate fuels, an assessment was conducted during February, March, and April 1976. About 100 selected companies were contacted by phone to determine their present plans, and several were subsequently visited in order to obtain more detailed information or to see specific equipment operated with an

alternate fuel. Certain companies within the more energy-intensive industries were identified and contacted to determine:

1. the present mix of fuels that provide the firm's energy needs,
2. future plans for conversion from natural gas to alternate fuels, and
3. direct company experience with alternate fuels and the effect of these fuels upon refractories in combustion equipment.

Most firms cooperated with this assessment, although some were openly negative. In general, industrial interest in alternate fuels was quite high with most interest in oil. Many firms are confronted almost daily with interruptible natural gas supplies and have by necessity installed alternate fuel systems.

4.1 THE CHEMICAL AND PETROCHEMICAL INDUSTRIES

Some chemical and petrochemical companies plan to convert boilers and process heaters from natural gas to alternate fuels in the near future. One large chemical and petrochemical company indicated that in 1976 its energy use according to fuel type is expected to be 40% natural gas, 30% fuel oil, and 30% coal; they plan to decrease the use of natural gas to only 10% in 1979. For 1974, another company had used 67% natural gas, 15% fuel oil, and 18% coal. In this case, they plan to reach the goal of 29% natural gas, 52% fuel oil, and 21% coal in 1980. One large company experienced a natural gas shortage in 1975 alone of one trillion cubic feet or about 5% of the total they needed. While exploring the possibility of opening their own natural gas wells, this company plans to convert to fuel oil and coal as soon as practical. While initiating such large scale fuel conversion activities, many companies indicated they have assumed an available supply of alternate fuels such as No. 6 and No. 2 oils and coal in both the immediate and in the long term. One major petrochemical manufacturer admitted that the long-range planning on energy resources and fuel use was risky because of their assumptions on the availability of alternate fuels. Their policy was to change natural gas burners to dual fuel burners completely by 1978 and only to invest in new coal-fired

steam boilers in the future, assuming environmental regulations could be met while burning coal.

A comparison of costs shows that boiler and process heaters converted to No. 6 oil are typically 20% more expensive than those operating with No. 2 oil, and coal firing unit costs are about triple that of No. 6 oil firing units. The present and future transportation costs for coal are a major concern of many companies contacted. One source indicated that, in one particular case, the conversion cost for coal-fired boilers is more than the original cost of the steam plant that is being converted. Small industrial boilers are less adaptable to fuel changes than larger boilers. These small units become uneconomical with the high cost of control, fuel storage, and piping equipment required. Since fuel costs are a more protracted expenditure, the company can often better afford higher priced natural gas and fuel oils than the expensive sulfur removal devices and the fuel handling equipment required to burn coal. Therefore, the small and medium size industrial boilers will probably continue to use natural gas and distillate or residual fuel oils.

Present plans in some of the chemical and petrochemical industries are to use No. 6 oil in cold-wall boilers because of the belief that this will be relatively safe as far as boiler life and integrity is concerned. This safety is assumed because the firebox of cold-wall boilers contains a minimum of ceramic refractories or insulations in contact with the flame and combustion products. In some cases, a double-mode firing with coal and heavy oil in boilers helps to reduce fuel oil costs and to meet local emission standards.

One company mentioned their experience with No. 6 oil-fired boilers in the late 1960s. The No. 6 oil used was from Venezuelan crude oil, which contains relatively high sulfur and vanadium contents. Problems such as tube clogging and reduction in heat transfer characteristics due to the huge amount of solid deposits in the combustion chamber soon developed and led to shutdown and costly cleaning. Because of this incident, this company later imposed a tight control over the sodium and vanadium contents in the No. 6 oil they purchased; i.e., sodium less than 50 ppm and vanadium less than 150 ppm.

McMullen,¹ Walls and Proctor² and Palfreyman³ also reported marine and stationary boiler problems associated with the use of Bunker C oil, which is essentially equivalent to the No. 6 grade. Fireclay bricks and castables are usually used in these boilers. These fireclay refractories are typically classified as low-duty, medium-duty, high-duty, or super-duty in the order of increasing service performance at high temperature. More than 20 years ago, Jones and Hardy⁴ pointed out that heavy oils containing vanadium are highly destructive to fireclay brick in boilers. The other impurities such as alkali and alkaline earths are less detrimental as compared to vanadium. These experimental observations were based on results of a slagging test. Unfortunately, the seriously detrimental effect of heavy oil ash on fireclay refractories in boilers and process heaters has apparently been known by relatively few people, and was unknown to many technical personnel in the chemical and petrochemical industries. The improper choice of refractory for use with residual oils has cost the chemical and petrochemical industries many millions of dollars in maintenance costs and repairs.⁵

Due to present concerns about potential detrimental effects of impurities in No. 6 oil, present industrial plans are generally to use No. 2 oil in process heaters since these units contain a significant amount of refractories. The chamber wall temperature in this application is relatively high, about 982–1093°C (1800–2000°F) as compared to 593°C (1100°F) for boilers. Some respondents commented that sulfuric acid as a combustion product penetrated through fiber refractory insulations in their equipment and corroded the metal lining in their reactors and process heaters. Because of the high permeability of sulfur oxides through such insulations as fiber blankets, a protective coating on the inner surface of metal liners is required if high sulfur oil is to be used.

There are some heating processes that require either a high degree of cleanliness or precision control of temperatures. These requirements cannot readily be met if alternate fuels are used. An example of this was a food-related product cited by one company in the manufacturing of a particular phosphate compound.

The need for precise control of temperature to prevent hazardous explosions in the ammonia reformer in the fertilizer industry dictates that natural gas be used. Other than specialized requirements such as these, the conversion to distillate and heavy oils in the chemical and petrochemical industries can be extensive.

4.2 THE IRON AND STEEL INDUSTRY

According to the American Iron and Steel Institute,⁶ natural gas accounted for 17% of the total amount of energy consumed in the iron and steel industries in 1974 and this amounted to 7% of the industrial natural gas demand in the whole country. There are three principal methods of steel melting: open hearth, basic oxygen, and the electric arc. Open-hearth furnaces, because of their relatively low productivity and high capital investment, are gradually being phased out and replaced by basic oxygen and electric furnaces. Open-hearth furnaces consume much more natural gas than the other two types of furnaces. Because of this trend away from open-hearth furnaces, the need for natural gas for steel melting will steadily decline. The most energy-intensive process in the steel industry is the operation of blast furnaces. This process consumes about 18 million Btu of energy per ton of iron, of which 0.5 million Btu typically comes from natural gas, which has been used as a supplemental fuel in the blast furnace to reduce the quantity of coke required and to increase the production rate.⁷ In this application, fuel oil probably will replace natural gas. The blast furnace usually is lined with super-duty or high-duty fireclay refractories, which could be subjected to attack by fuel oil ash following such a fuel conversion.

Certain steel companies have indicated that they are planning to expand coke oven capacity where applicable and thus provide sufficient coke oven gas to make up for a lack of natural gas. Those companies that do not have coke ovens are facing a necessity for fuel conversion.

In converting to alternate fuels, steel companies are concerned about possible contamination of their products by trace elements in the fuel. For those heat-treatment furnaces where a clean annealing

environment and high degree of uniformity in temperature are required, natural gas was mentioned as the only suitable fuel at present. Soaking pits, heating, and reheating furnaces for metal rolling and forming, which in the past used a high percentage of natural gas and blast furnace gas, are being scheduled for conversion to No. 2 and No. 6 oils. The types of refractory used in these applications cover a broad range; fireclay (26-45% Al_2O_3), sillimanite (45-65% Al_2O_3), mullite (65-75% Al_2O_3), bauxite based (75-90% Al_2O_3), chrome-magnesite, chrome, and magnesite in brick form or monolithic form have all been used. All these refractories are subjected more or less to attack by vanadium and sodium in fuel oils at temperatures ranging from 1149 to 1427°C (2100 to 2600°F), which is the typical temperature in the walls of the soaking pits and reheating furnaces. In general, higher Al_2O_3 or MgO content together with low impurities (such as calcium, boron, and alkalies) tend to increase the corrosion resistance of a refractory. One company reported that in their soaking pits, which were fired by No. 6 oil, the wall opposite the burner and the roof were essentially washed out or fluxed away due to the interactions between the refractory material and the combustion products in the fuel oil. Another company commented that in their experience the refractories used in steel soaking pits and reheating furnaces must be upgraded by increasing the Al_2O_3 or MgO content prior to conversion to No. 6 oil.

At present, some steel companies feel that investments in waste heat recovery systems are good investments. However, conversion to a fuel such as No. 6 oil will result in a large quantity of combustion ash deposit in recuperators or waste heat boilers associated with soaking pits, heating or reheating furnaces, and cupolas. This indeed was recently discovered by one steel company. The reduced heat recovery efficiency and the increased maintenance labor were unanticipated costs.

As the steel continuous-casting process (in which soaking pits and reheating furnaces could be eliminated) becomes more popular in steel-making, the total fuel consumption per ton of steel may be reduced by about 8% and such furnace problems would be reduced accordingly.⁸ It was estimated by one contact that by 1985 about 50% of the total U.S. steel production will come from the continuous-casting process.⁸

In the forging and fabrication part of the steel industry, the shortage of natural gas has been severe. One major steel forging company experienced nearly 50% curtailment of its natural gas requirement over the previous year. While considering drilling natural gas wells for their own use, these companies rebuilt furnaces and converted to dual burners to use No. 2 oil as standby. The furnace walls, which were formerly ceramic bricks as thick as 18 in., were rebuilt to consist of 2 in. of fiber refractory materials backed up by 4 in. of mineral wool insulation. The temperature in the refractory in this application is about 871°C (1600°F). As a result of these modifications in their forging furnaces, the warm-up time was reduced significantly and the total savings in fuel was almost 75%. Long-term operational performance of this furnace design has not been determined to date. In the forging and fabrication part of the steel industry, No. 2 oil is widely adopted because its use will be more compatible with the refractories used.

4.3 THE ALUMINUM INDUSTRY

Aluminum companies are interested in conversion from natural gas in the melting and remelting furnaces, as well as in the heating and reheating furnaces. One major aluminum company estimated that its use of natural gas will be negligible by 1979 compared with today's use, which represents more than 60% of the total energy spent on furnace heating and melting applications. Natural gas is widely used in all steps of aluminum production, including bauxite drying, alumina separation and calcination, melting, anode electrode manufacturing, rolling, extrusion, milling, and fabrication.

The general trend in the aluminum industry is to convert the reverberatory melting and remelting furnaces, heating and heat-treating furnaces, and anode bake ovens to No. 2 oil because of the curtailment of natural gas supplies. Propane currently is used by some of these companies as a standby fuel. One company contact expressed concern over the detrimental effect of combustion products of residual oils on the fireclay refractories used in anode bake ovens in which the temperature ranges from 1038 to 1316°C (1900 to 2400°F). The main potential

problem in these applications is refractory deterioration due to fuel ash attack. In an aluminum reverberatory furnace, the molten aluminum temperature is about 704°C (1300°F), but the temperature in the refractory above the metal line is usually 1093 to 1316°C (2000 to 2400°F). The furnace below the metal line is typically lined with 75–90% Al₂O₃ brick or 85% Al₂O₃ phosphate-bonded brick. Above the metal line, super-duty fireclay, plastic or castable refractory is typically used. The flue is lined with high-duty firebrick and the charging door is filled with super-duty castables. Silicon carbide brick bonded with silicon dioxide or silicon nitride and zircon brick are also used in the melting furnace. One company found that the roof and the wall above the metal line in the aluminum reverberatory melting furnace were seriously fluxed by the combustion products of No. 6 oil. Refractory linings had to be replaced by a higher Al₂O₃ content type of refractory. Although formerly not feasible, it now becomes economically attractive to invest in recuperators to preheat the combustion air. The main problem related to alternate fuel conversion is the recuperator material corrosion by the combustion products and traces of halide contained in the flue gas.⁹

Coal firing in aluminum reverberatory furnaces is being actively explored by one company we contacted. However, the test results are considered proprietary and were not available for this assessment. It is expected that the main difficulties with coal use will be coal ash slagging and corrosion in refractories, ash removal, and contamination in the aluminum melts.

4.4 THE COPPER INDUSTRY

Some copper companies using a significant quantity of natural gas in their smelting and melting furnaces and converters are actively converting to alternate fuels. Currently, some copper companies have distillate oil on standby to supplement natural gas used in converters and reverberatory melting furnaces. One contact indicated that the energy sources for current production of each ton of copper (which requires about 100 million Btu) is: electricity, 54%; natural gas, 27%; fuel oil, 14%; and coal, 5%. More than 50% of the total energy consumed

in the smelting and melting processes, which use about 48% of the total production energy, comes from natural gas. The curtailment of natural gas forced the copper companies to convert mainly to fuel oils (distillate and residual). One company pointed out that their reverberatory melting furnaces that were converted to No. 6 oil were later changed to No. 2 oil because of observed deterioration in furnace refractories. Another company said that the high cost of using residual oil and the similarity of costs of residual and distillate oil made residual oil uneconomical.

The side walls of the copper reverberatory furnace usually are lined with chrome-magnesite or magnesite chrome, burned or chemically bonded brick, depending on the copper ore and melt. The roof is usually silica refractory, and basic bricks or high Al_2O_3 bricks are also used. The temperature on the inner furnace wall is about 1649°C (3000°F). Oxygen enrichment of the combustion air was considered by many of these companies.¹⁰ Such enrichment will increase the flame temperature as well as the melt temperature and will require linings of higher purity magnesia compositions. Coal firing in the copper reverberatory furnaces is in the exploratory stage. In addition to the inherent refractory degradation associated with coal firing, a main concern is the capital cost of converting to coal. Thus, in the near term, distillate and residual oils will continue to be the main alternate fuels in the copper industry.

4.5 THE GLASS INDUSTRY

The glass industry is gas-intensive. From batch handling and melting to forming and postforming, natural gas is extensively used. One major glass manufacturer reported that their energy use data in recent years clearly indicates a trend in the reduction of natural gas use, which has been largely compensated for by the increased use of fuel oil and electricity. In fact, some glass company representatives spoke of entering into an "electricity age."¹¹ The mixing of fossil fuel and electric power has been a common practice in glass pots and tanks in the past. The electric boosters using molybdenum electrodes to generate strong convection currents in the molten glass can increase the melting efficiency from 10 to 40%. This higher efficiency offsets the high

electric rates (\$6/million Btu) relative to natural gas and fuel oils. However, the refractory life of an electric melter is only about half the life of an equivalent conventional glass tank. A technical breakthrough in the near future regarding refractory technology and materials is required to make the electric melter more attractive to glass manufacturers. The glass industry, facing the severe curtailment of natural gas, is intensely interested in better refractory use and combustion control for gas or oil fired tank or pot furnaces.

Glass melting furnaces are operated at high temperatures ranging from 1538 to 1649°C (2800 to 3000°F). The batch normally consists of silica and glass-forming components such as lime, soda, and borates. Most of the glass furnaces are equipped with regenerators in which the checkerwork bricks are first heated by the furnace exhaust gas. Large valves then redirect the gas flow, and combustion air is then passed through the checkerwork to be preheated. While one set of regenerators is supplying preheated air, the other set is being heated by the furnace exhaust gas. The crown of a glass tank furnace is built of silica brick covered on the cold side with refractory insulation. The bottoms are built of insulating firebricks covered by layers of high-duty firebricks on which high Al_2O_3 brick will form the support for the fused-cast Al_2O_3 or sintered zircon blocks that are supporting the melt. Side-walls are usually made of high Al_2O_3 (higher than 45%) or fused cast alumina refractories. The crown and upper sidewalls of the regenerator usually are built of basic or mullite refractory, while the lower sidewalls are super-duty firebricks. The upper checkerwork is usually basic bricks while the lower checkerwork is either basic or super-duty fireclay, depending on the service condition.

One company indicated that they were allotted only 85% of the natural gas they used in 1975, so they had to change to No. 6 oil. In this case, refractories were selected with greatest caution to ensure proper corrosion resistance. So far, little operational experience has been obtained from this particular facility. Because of refractory degradation, one company had to shut down their glass tanks, which were fired with high vanadium No. 6 oil.

In addition to fuel oil, producer gas is also an alternate fuel. One respondent indicated that producer gas combustion needed preheating as well as combustion air preheating, and this required better design and selection of the checkerwork bricks in the regenerator.

Contacts in the glass industry generally indicate strong interest in alternate fuels and especially No. 2 oil for immediate term conversion due to their concern about potential detrimental reactions with No. 6 oil in their regenerators. The cost of constructing residual oil combustion systems has also been cited as a barrier to the wider use of No. 6 oil. Where the color requirement of the product glass is unaffected by the contaminants from coal ash, powdered coal has been experimentally used in a 100 ton/day glass tank for container manufacturing.¹² But experience with the combustion of powdered coal in the glass industry is still very limited. It appears that coal burning in glass tanks is primarily of long-term interest. Number 6 oil and coal mixture slurry combustion is presently being actively investigated by a joint effort-involving more than 20 companies from several sectors of industry. The main technical problems are the prevention of separation of coal particles and oil, which leads to incomplete combustion and the refractory degradation by the combustion products. This type of alternate fuel seems unlikely to become practical for glass manufacture in the immediate future. In general, distillate oil and residual oils are considered by the glass industry as near-term alternate fuels.

4.6 THE CERAMICS INDUSTRY

The ceramics industry as a natural gas-intensive industry has been actively converting to alternate fuels due to recent severe gas curtailments. One major refractory producer plans to install dual burners to reduce within four years their consumption of natural gas from a present 60% of their total heating energy supply to less than 40%. Due to the relatively high firing temperatures required for their products, refractory companies are concerned about potential detrimental reactions that can occur with use of residual oils. The ceramics industry is thus changing their kilns to dual burners with No. 2 oil as standby. Tunnel

kilns are the primary method for firing all types of refractories. The temperature in the hot zone or burning zone of a tunnel kiln ranges from 1093 to 1760°C (2000 to 3200°F). The hot zone is usually built of super-duty, high-alumina firebricks or basic bricks. Medium-duty firebricks are used in the heating and cooling zones and air-lock zones. The arched roof in this region is usually silica brick or may be a basic brick in high-temperature kilns.

One structural clay product company successfully converted to powdered coal a large tunnel kiln firing face brick. The kiln has been operated with this fuel for two years. The temperature in the hot zone is kept at temperatures below 1093°C (2000°F), since the ash of the particular coal used fuses at temperatures of 1149 to 1260°C (2100 to 2300°F) and will corrode the refractories at these high temperatures.

Coal combustion is only applicable where the contamination from coal ash on the fired products can be tolerated. Coal-firing kilns currently cost about three times their oil system equivalents. Despite the high cost of the capital investment, the moderate price and abundant supply of suitable coal as compared to high-priced oil and scarce natural gas has been a strong incentive for the ceramics industry to begin to convert to coal for application temperatures lower than 1093°C (2000°F). One ladle brick company stated that they planned to convert to coal from today's zero percent to 35% of the total combustion units by 1979.

In the area of No. 6 oil burning, two companies pointed out that they burned No. 6 oil in their calcining kilns many years ago, but problems of refractory interactions with fuel ash ruled out the continuing use of this type of fuel. Today the calcining kilns generally are fired with No. 2 oil or natural gas. In the immediate term, respondents indicated that distillate oil is the main alternate fuel to replace natural gas. The effects of No. 6 oil conversion on refractories in high-temperature ceramic kilns could obviously be serious, and is a major concern in this industry.

4.7 THE CEMENT INDUSTRY

The cement industry is steadily converting to coal. Six years ago, about 99% of all cement kilns in this country were fired with natural gas. At present, only slightly over 50% of the cement kilns are fired by natural gas. Pulverized coal combustion is apparently satisfactory for this application. One company contact predicted that by the end of 1979 essentially all their cement kilns will be coal fired.

There are two types of kilns for cement production, the vertical-shaft kiln and the rotary kiln. For lime kilns, the operation temperature in a vertical-shaft kiln is at least 1093°C (2000°F), while it is 1427°C (2600°F) in a rotary kiln. The burning zone is built of super-duty, basic, or high-alumina dense bricks. Medium-duty fireclay bricks or castables are used in the colder portions of the kiln. The highest temperature in the hottest zone of a cement kiln is about 1649°C (3000°F). The main function of the hot zone lining is to support a coating on the refractory 2 or 3 in. thick, which is constantly renewed during cement production. The composition of the coatings is similar to that of the clinker and serves as a protection for the refractories.

At present, the supply of coal is adequate and coal combustion is suitable for this industry. The high price of fuel oils relative to coal makes fuel oils less favored. The cement industry's primary fuel will continue to be coal.

4.8 OTHER INDUSTRIES

In addition to the above major industries, other industries also face problems in converting to alternate fuels. This section outlines fuel conversion prospects and their effects on refractories in other industries and in electric power utilities. Petroleum refining companies burn natural gas and oil in their boilers and process reactors. One company indicated that the distribution by fuel types in 1975 was 90% oil and 10% natural gas. During that year, this company's conversion to fuel oil cut by half their consumption of natural gas to an overall total of only 5%. The major increase in the use of residual oil was with boilers in which the small amount of refractory lining and the

relatively low operation temperature [593°C (1100°F)] would cause only an ash problem with minimal metal corrosion. On the other hand, the linings of reactors such as those used for the hydrodesulfurization reactions, which are normally operated at elevated temperatures and under high pressures, would be subject to attack by the fuel ash of residual oils. These reactors were thus converted to distillate oils. The refractory linings in chemical reactor vessels are usually super-duty fireclay, insulating castable, or gunning mixes in monolithic forms. Although producer gas is also an alternate fuel, the general trend in the petroleum refining industry is to use residual and distillate oils.

In the food industry and paper industry, boilers to generate steam and other miscellaneous relatively low-temperature furnaces are the major heating applications. Companies within these industries facing natural gas curtailment are converting their boilers to fuel oil and coal. One paper company burned waste wood in their boilers to make up the shortage of natural gas. The food industry must use natural gas in some of their heaters and driers due to the stringent cleanliness and quality requirements for their products.

In 1973, electric power utilities accounted for more than 50% of the national total demand for residual oils and for about 7% of the total amount of distillate oils in the U.S.¹³ These energy needs were almost equal to the total national industrial demand for both residual and distillate oils. The fuel conversion plans of electric power utilities will therefore greatly influence the availability of different types of fuels to industrial users. The federal government is requiring certain electric power plants to convert to coal from oil.¹⁴ A total of 155 boilers at 79 power stations that were originally designed for coal combustion have capacities larger than 25 MW. These boilers were later converted to fuel oil or gas. Their conversion back to coal now would reduce domestic fuel oil demand by 0.5 million bbl/day, and natural gas by about 550 million ft³/day. Correspondingly, the coal demand would increase by 48 million tons/year.

Despite the high investment cost, some industrial steam plants will be converted to coal. In smaller units, electrode boilers are becoming widely used. Because of the very different combustion properties of coals from different sources, consideration must be given to the fuel/air ratio, heat transfer characteristics, and flame geometry suitable for the particular type of coal burned. A respondent indicated that, in one case, improper burner adjustment resulted in severe damage to the burner tile that was built of 99% fused cast alumina. The combustion of coal containing 25% ash reduced the service life of this dense refractory from six years to only six weeks because of severe erosion and slagging. The effects on the furnace refractories of conversion to coal by steam generation plants will require better control of the combustion and better selection of refractories.

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5. INTERACTIONS OF ALTERNATE FUEL COMBUSTION PRODUCTS WITH REFRACTORIES AND REFRACTORY INSULATIONS

5.1 COMBUSTION PRODUCTS FORMATION

Since fuel oil was identified previously as the alternate fuel for most industries in the immediate term, the impact of industrial fuel conversion will thus be assessed primarily from the analysis of the interactions between the fuel oil combustion products and the refractory materials in the furnace.

The most abundant impurities in fuel oils and particularly residuals, are usually vanadium, sodium, and sulfur. At combustion temperatures, these elements form oxides such as V_2O_5 , Na_2O , and SO_3 . Under appropriate atmospheric conditions, other vanadium oxides could be formed as well. Notably, the refractory oxides V_2O_3 and V_2O_4 , which have melting points of $1970^\circ C$ ($3578^\circ F$) and $1637^\circ C$ ($2979^\circ F$) can be produced at sufficiently low oxygen potentials. When compared with V_2O_5 , which melts at $690^\circ C$ ($1274^\circ F$), V_2O_3 and V_2O_4 are in fact quite refractory. As a result, it has been suggested that the atmosphere in a combustion chamber containing vanadium should be kept at reducing conditions by using a minimum amount of excess air to suppress the formation of V_2O_5 , but favoring production of V_2O_3 and V_2O_4 .¹ It is generally believed that this condition will reduce the extent of vanadium oxide corrosion in refractories. Systematic operational verification of this hypothesis is very scarce.

The system $Na_2O-V_2O_5$ has been the subject of many investigations, but results are inconsistent and sometimes contradictory. Wilson² recently reinvestigated the system $V_2O_5-Na_2O$ (Fig. 5.1). An important feature of this system is that the liquidus temperature and the melting points of sodium vanadate compounds depended on the oxygen partial pressure. The melting points of $Na_2O \cdot 3V_2O_5$ and $Na_2O \cdot 6V_2O_5$ decrease with increasing oxygen partial pressure. The melting point could be suppressed as much as $100^\circ C$ ($180^\circ F$) if the oxygen partial pressure is increased from 0.2 atmosphere to 1 atmosphere. Thus the corrosion in pressurized conditions such as gas turbines and petrochemical reactors

Fig. 5.1. The Binary V_2O_5 - Na_2O Phase Diagram at Two Oxygen Partial Pressures. Reprinted with permission from R. C. Kerby and J. R. Wilson, *Can. J. Chem.* 51: 1033 (1973).

will be significantly higher from ambient atmosphere applications. This phenomenon also explains the scatter in the melting points and liquidus temperatures in earlier investigations in which the oxygen activity was not controlled. There are three eutectics, one peritectic, and five compounds identified (Table 5.1). The lowest eutectic temperature is 525°C (977°F).

Sulfur trioxide and dioxide formed by combustion of sulfur bearing fuel oil will be at equilibrium and their chemical potentials will be determined by the oxygen partial pressure associated with the reaction:

Table 5.1 Invariant Points in the V_2O_5 - Na_2O Binary System

Composition (mole %)		Temperature (°C)	Type of Invariant	Equilibrium Solid Phases
V_2O_5	Na_2O			
69	31	575	Peritectic	$Na_2O \cdot xV_2O_4 \cdot (6 - x)V_2O_5 + 5Na_2O \cdot xV_2O_4 (12 - x)V_2O_5$
54	36	525	Eutectic	$5Na_2O \cdot xV_2O_4 \cdot (12 - x)V_2O_5 + NaVO_3$
37	63	562	Eutectic	$NaVO_3 + Na_4V_2O_7$
32	68	645	Eutectic	$Na_4V_2O_7 + Na_3VO_4$

The production of SO_3 from fuels has been related to the amount of excess air used in the burner. Reid³ found that the formation of SO_3 can be prevented by burning residual oil with a minimum amount of excess air, preferably with less than 0.5% of oxygen remaining in the flue gas. At temperatures higher than 1200°C (2192°F), most sulfates decompose and sulfur is thus present only as SO_3 or SO_2 . At lower temperatures, sulfates will be formed. Foster⁴ et al., examined the system Na_2SO_4 - V_2O_5 . They found that $NaVO_3$, $Na_2O \cdot 3V_2O_5$, $Na_2O \cdot 6V_2O_5$ are the only compounds formed with the evolution of SO_3 at temperatures above 871°C (1600°F). Baldwin⁵ et al., reported similar compounds with the exception of $Na_2O \cdot 3V_2O_5$. Instead, they observed formation of $5Na_2O \cdot 12V_2O_5$. Niles⁶ later confirmed that only three sodium vanadates can exist. Depending on the Na/V ratio, the following reactions occur:

At temperatures lower than 1093°C (2000°F), SO₃ may lead to the formation of sulfates. The stability of the condensed sulfate phase is determined by the temperature and the equilibrium SO₃ pressure on the deposit. Other metallic contaminants in fuels such as potassium, iron, calcium, aluminum, lead, and silicon will also form oxides at combustion temperatures. These oxides will react then with vanadium pentoxide, make less of it available for reaction with sodium, and thus result in a higher effective Na/V ratio. This will produce sodium vanadates of higher Na/V ratios.

The vapor pressure of V₂O₅ has been measured and is expressed by⁷

$$\log P \text{ (mm Hg)} = -\frac{7100}{T(\text{K})} + 5.05 \quad (5.7)$$

At 1500°C (2732°F) the vapor pressure of V₂O₅ is thus 1.46×10^{-2} atmosphere (11.1 torr). In a high temperature environment such as the glass tank and glass tank regenerator, vanadium pentoxide is thought to be present only as vapor. V₂O₅ can also cause color changes in both glasses and refractories. Small amounts of V₂O₅ such as 0.1 wt % will produce a distinct gray-green in refractories;⁸ this sometimes causes concern among furnace operators.

The combustion products as presented above will react with refractories and refractory insulations. The interactions of these combustion products and the refractory materials will be analyzed according to the composition system of the refractory material.

Fibrous refractory insulations including alumino-silicates, and alumina and zirconia as well as insulating fire brick will probably be much more susceptible to reaction and attack by alternate fuel combustion products than the equivalent compositions in the form of a dense refractory. The much larger available surface area per unit mass in these insulations compared with dense refractory brick or a monolithic form

would provide ready access for gaseous species to react with the refractory fibers or pore walls of the insulating brick. There is apparently no available experimental information regarding the structural stability of these thermal insulations in high-temperature atmospheres containing gaseous species of sodium, vanadium, and sulfur or of the effects of these interactions on the thermal transport properties of the thermal insulation materials.

5.2 ALUMINOSILICATE SYSTEM

The aluminosilicate family includes fireclay, high alumina, mullite, and corundum refractories. These are basically composed of alumina, silica, mullite, sillimanite, and silicate glass. The end members of the aluminosilicate series are silica and alumina. There are few industries operating processes above a few hundred degrees centigrade that do not make use of refractories of this family. As outlined by Chester,⁹ the application range of the aluminosilicate system in various fields is broad.

Vanadium pentoxide forms a low temperature eutectic 650°C (1202°F) with Al_2O_3 . The phase diagram of the V_2O_5 - Al_2O_3 system is presented in Figure 5.2. The intermediate compound is $\text{Al}(\text{VO}_4)$ which melts at 695°C (1283°F). Therefore, if kinetics permit, V_2O_5 is a good flux for Al_2O_3 . In comparison, the eutectic temperature of V_2O_5 and silica is 649°C (1200°F) with no intermediate compound formation (Fig. 5.3). Vanadium pentoxide increases the crystallization, but not the nucleation rate of glass, and acts as a mineralizer enhancing the phase transformation of silica glass and quartz to cristobalite.¹⁰ If the work on the ternary system V_2O_5 - Al_2O_3 - SiO_2 by Shimotakahara¹¹ is reliable, a ternary compound ($\text{V}_2\text{O}_5 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), two ternary eutectics [mullite-ternary compound- V_2O_5 , 657°C (1215°F), and silica-ternary compound- V_2O_5 , 656°C (1213°F)] and one peritectic [Al_2O_3 -mullite- V_2O_5 , 657°C (1215°F)] are present.

The kinetics data for the interaction of V_2O_5 with Al_2O_3 or SiO_2 are lacking and are even contradictory. Beer and Richarz¹² examined the rate of V_2O_5 and NaVO_3 attack in Al_2O_3 . They concluded that at temperatures from 725°C (1337°F) to 870°C (1598°F), the rate of reaction is

Fig. 5.2. Proposed Phase Diagram of the V₂O₅-Al₂O₃ System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., p. 124, American Ceramic Society, 1969.

Fig. 5.3. Phase Diagram of the V₂O₅-SiO₂ System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., 1969 Supplement, p. 110, American Ceramic Society, 1969.

controlled by a chemical reaction with an activation energy of 40.9 kcal/mole. From 870°C (1598°F) to 1300°C (2372°F), these authors report the reaction is diffusion controlled. For corrosion by NaVO_3 , the process is controlled by a chemical reaction with an activation energy of 45.5 kcal/mole at temperatures from 1000°C (1832°F) to 1275°C (2327°F). On the other hand, Frischat et al.,¹³ investigated the dissolution of Al_2O_3 in V_2O_5 melts and observed a diffusion-controlled process below 850°C (1562°F).

The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system has been extensively examined. The ternary phase diagram gives the sodium silicates: $2\text{Na}_2\text{O}\cdot\text{SiO}_2$, $\text{Na}_2\text{O}\cdot\text{SiO}_2$, and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$; two sodium aluminates: $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ and β -alumina $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$; three ternary compounds: albite ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$), nepheline and its high temperature polymorph carnegieite ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$); two aluminum silicates: sillimanite ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) (Fig. 5.4). Na_2O is a good glass network modifier and readily forms glasses with Al_2O_3 and SiO_2 . Upon exposure to Na_2O , the crystalline phases such as mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), sillimanite ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), and corundum, which are usually present in $\text{Al}_2\text{O}_3-\text{SiO}_2$ refractories will form sodium aluminum silicates. The corrosion of mullite by Na_2CO_3 vapor was studied by Okawara and Yamaguchi.¹⁴ They report that mullite first decomposes into carnegieite and corundum. Corundum then gradually reacts to form sodium silicate and nepheline. Similarly, mullite exposed to sodium vanadate may decompose according to the following reactions:

Unfortunately, the standard free energies of formation for albite, nepheline, and β -alumina are presently unknown. It is thus uncertain that the above reactions are thermodynamically favorable. Since NaVO_3 melts at temperatures lower than either V_2O_5 or Na_2O , mullite is expected

$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

Fig. 5.4. Phase Diagram of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., p. 181, American Ceramic Society, 1969.

to decompose upon NaVO_3 exposure at lower temperatures than in the case of V_2O_5 or Na_2O exposure alone. In fact, the above reactions have been confirmed by experiments at temperatures higher than 900°C (1652°F).¹⁵ Similarly, sillimanite and corundum may react with the combustion product NaVO_3 as follows:

Rigby and Hutton¹⁵ found that, in the aluminosilicate refractory system, Na_2O first reacts with Al_2O_3 and SiO_2 to form sodium aluminate and sodium silicate. Mullite also starts to decompose and to form nepheline, sodium aluminate, and β -alumina. The final phase relations at equilibrium are calculated using the Na_2O content, and the Na_2O - Al_2O_3 - SiO_2 phase diagram (Fig. 5.4). Generally speaking, the fluxing effect of Na_2O can be summarized (Table 5.2).

Vanadium pentoxide in the combustion ash will reduce the amount of free Na_2O available to react directly with the refractory because the V_2O_5 reacts with Na_2O to form sodium vanadate. However, sodium vanadate acting both as a flux and a mineralizer may react with the Al_2O_3 - SiO_2 compositions at much lower temperatures and generate more liquid phase than would either Na_2O or V_2O_5 alone. Indeed, in the presence of both Na_2O and V_2O_5 , nepheline is formed at 800°C (1472°F), whereas it is not formed even at 900°C (1652°F) when Na_2O alone is present. Albite, which also is not formed in the presence of Na_2O alone, is formed if NaVO_3 is present with Na_2O because of the powerful mineralizer action of NaVO_3 . That the sodium vanadates are strong fluxing agents in the Al_2O_3 - SiO_2 system was observed by Rigby and Hutton,¹⁵ MacLaren and Richardson,¹⁶ and Jones and Hardy.¹⁷ However, the total amount of Na_2O and V_2O_5 used in these investigations all exceeded 10 wt %, and were high compared to levels more typical of combustor concentrations. Busby¹⁸ conducted an experiment using samples containing lower concentrations of V_2O_5 and Na_2O (less than 5%). He concluded that the 2% of Na_2O can cause a lowering of about 20°C (36°F) in the refractoriness (indicated qualitatively by the amount of liquid phase present) of silica and 43%- Al_2O_3 bricks, but 2% of V_2O_5 probably only causes a reduction of a few degrees

Table 5.2. Temperatures at Which Aluminosilicate Refractories are Fluxed by Na_2O , and $\text{Na}_2\text{O} + \text{V}_2\text{O}_5$

Composition, wt %		Fluxing Temperature, ^a °C	
Silica	Alumina	Na_2O Alone ^b	$\text{Na}_2\text{O} + \text{V}_2\text{O}_5$ ^b
100	0	800	900
80	20	800	900
60	40	1000	900
40	60	1400	1200
20	80	1500	1300
0	100	1600	1500

^aThe fluxing temperature means the temperature at which significant amounts of liquid phase are formed. To ensure no liquid formation, the refractory should be used at temperatures 100°C below the fluxing temperature.

^bThe amounts of Na_2O and V_2O_5 exceed 10 wt %.

centigrade. If the total amount of V_2O_5 is less than 0.5 wt %, the lowering in the refractoriness of the Al_2O_3 - SiO_2 system is negligible.¹⁹

When silica refractories are subjected to fluxing by Na_2O , a glassy or amorphous phase will be formed in the composition range of Na_2O less than 34 wt %. Morsanyi²⁰ found that vanadium pentoxide alone can cause the transformation of quartz to cristobalite. There was no apparent reaction between V_2O_5 and SiO_2 , under the conditions of these experiments. In contrast, NaVO_3 fluxes SiO_2 and produces a brownish-glass phase which contains about 2–5 wt % V_2O_5 . In addition to cristobalite, tridymite is also formed, with the formation of tridymite attributed to the presence of Na_2O . While NaVO_3 reacts with high silica refractories, the result and products are essentially similar to those formed from silica by reaction with Na_2O . It thus seems from these investigations that V_2O_5 does not have a pronounced detrimental effect on silica refractories. Furthermore, V_2O_5 tends to increase the viscosity of the liquid phase formed by reaction at high temperatures of Na_2O and silica. The increased viscosity will retard transport of sodium or vanadium

species through this liquid phase and will make reaction of silica more difficult than with only Na_2O and silica. This phenomenon also explains the very similar fluxing temperatures in 20% alumina refractories under attack by $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$ and Na_2O (Table 5.2).

Plastic and castable refractories, which are widely used in monolithic forms generally contain bonding phases usually consisting of calcium aluminate cements such as $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$. The binary system $\text{CaO}-\text{V}_2\text{O}_5$ has a series of eutectics and intermediate compounds (Fig. 5.5). The bonding phases in the

Fig. 5.5. Phase Diagram of the V_2O_5 - CaO System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., p. 109, American Ceramic Society, 1964.

monolithic refractories may react with the combustion product sodium vanadates as follows:

Since no gas phase is involved and the total number of moles of the reactants are approximately equal to the total number of moles of the products in these reactions, the standard enthalpy of reaction at 298 K (ΔH_{298}°) can be used as a reasonable indicator to determine if the reaction is thermodynamically favorable. The calculation of the standard enthalpy of reaction is based on the thermochemical data from various sources (Table 5.3). The negative values of these reactions indicate that they are thermodynamically favorable. Therefore, sodium vanadates will be expected to flux and react with calcium aluminates. The attack by sodium vanadate is expected to be more serious than for Na_2O or V_2O_5 alone. Calcium oxide is known for resisting reaction and attack by Na_2O .⁹ Vanadium pentoxide will flux calcium aluminate and Na_2O can reduce the viscosity of the liquid phase formed; both actions will facilitate the further transport of vanadium through the liquid phase to the calcium aluminate interface and thereby favor more corrosion.

Phosphate bonded alumina refractories, which have a high strength at high temperatures and are widely used in many severe applications, probably will react more readily with the combustion product sodium vanadate than the corresponding alumina refractories. Phosphorous pentoxide forms low temperature eutectics and an intermediate compound

Table 5.3. Selected Thermochemical Data for Some Refractory Materials

Material	ΔH_{298}°	ΔS_{298}°	Reference
V ₂ O ₅	-370.65	-0.105	a
NaVO ₃	-273.75	-0.0638	a
Al ₂ O ₃ (α)	-400.4	-0.0749	b
SiO ₂ (quartz)	-217.2	-0.436	b
3Al ₂ O ₃ •2SiO ₂	-1629.83	-0.303	b
Al ₂ O ₃ •SiO ₂	-618.81	-0.118	b
Na ₂ O•Al ₂ O ₃ •2SiO ₂			
Na ₂ O•Al ₂ O ₃ •6SiO ₂			
Na ₂ O•11Al ₂ O ₃			
Na ₂ O•SiO ₂	-373.19	-0.0754	b
CaO•Al ₂ O ₃	-555.2	+0.0273	c
CaO•2Al ₂ O ₃	-954.6	+0.0425	c
2CaO•Al ₂ O ₃ •SiO ₂	-933.2	+0.0430	c
2CaO•V ₂ O ₅ (C ₂ V)	-736.95	-0.152	a
3CaO•V ₂ O ₅ (C ₃ V)	-902.95	-0.174	a
Na ₂ O•Al ₂ O ₃	-541.7	-0.0513	b
Na ₂ O•Al ₂ O ₃ •4SiO	-1393.3		d
2CaO•SiO ₂ (C ₂ S)	-539	+0.0288	d
3CaO•MgO•2SiO ₂ (C ₃ MS ₂)			
CaO•MgO•SiO ₂ (CMS)	-539.9	+0.0270	d
2MgO•SiO ₂ (M ₂ S)	-520.30	-0.0954	b
2MgO•V ₂ O ₅	-677.75	-0.153	a
ZrSiO ₄	-483.736	-0.0918	b
Na ₂ ZrSiO ₅			
ZrV ₂ O ₇			

^aA. D. Mah, *Thermodynamic Properties of Vanadium and Its Compounds*, RI-6727, Bureau of Mines, Washington, D. C. 1966.

^bJANAF *Thermochemical Tables*, 2nd ed., NBS-37, National Bureau of Standards, Washington, D. C., 1971.

^cBarin and Knacke, *Thermochemical Properties of Inorganic Substances*, Springer, New York, 1973.

^d*Selected Values of Chemical Thermodynamic Properties*, NBS Cir. 500, National Bureau of Standards, Washington, D. C., 1959.

$P_2O_5 \cdot V_2O_5$ with vanadium pentoxide. The bonding phase, aluminum phosphate, which has an excellent hot strength is therefore subject to potential degradation by vanadium compounds. Unfortunately, published data on phosphate bonded alumina refractories relevant to sodium and vanadium attack, such as phase diagrams and kinetics data, are lacking.

At lower temperatures [$1150^\circ C$ ($2102^\circ F$)] sulfidation can produce stable sulfates such as Na_2SO_4 and $MgSO_4$. Their presence decreases the amount of free Na_2O and sodium vanadate available for reactions in the Al_2O_3 - SiO_2 system. But, the sulfate may react directly with refractories with the evolution of SO_3 . The degradation in refractories due to the detrimental interaction between refractory oxides and sulfur combustion products is generally more serious than the case of sulfur-free combustion conditions. Formation of sulfates can cause a volume change and thus generate cracks in the refractory. These will lead to more surface area in the refractory to be exposed to the reacting species and also offer faster transport paths for them into the refractory. Therefore, the net result of sulfate formation is probably enhanced refractory degradation.

5.3. THE MAGNESIA-CHROME SYSTEM

The basic refractory family including magnesite, magnesite-chrome, chrome-magnesite, and chrome has increased in its importance in recent years. The application is not only in the iron and steel industry, which requires the magnesite-chrome family in BOF and arc furnaces, but also from nonferrous metals, cement, and glass producers. The main advantage of this system is its excellent resistance to attack by iron oxide, alkali, and lime fluxes. But it is also well known for its poor thermal shock resistance. To a degree similar to the Al_2O_3 - SiO_2 system, the magnesite-chrome system has been investigated in its interactions with typical fuel combustion products.

Kerby and Wilson² examined the systems Na_2O - V_2O_5 - Cr_2O_3 and Na_2O - V_2O_5 - MgO (Fig. 5.6 and 5.7). Dependence of phase equilibria on the oxygen partial pressure was not observed in the binary systems Cr_2O_3 - V_2O_5 , Fe_2O_3 - V_2O_5 , or MgO - V_2O_5 . Addition of Na_2O results in a region of the liquidus temperatures, which is dependent upon the oxygen

Fig. 5.6. Phase Diagram of the V_2O_5 - Na_2O - Cr_2O_3 System. Binary phase compositions: I = $Na_2O \cdot 6V_2O_5$, II = $5Na_2O \cdot 12V_2O_5$, III = $NaVO_3$, IV = $Na_4V_2O_7$, V = Na_3VO_4 , VI = $CrVO_4$. Reprinted with permission from R. C. Kerby and J. R. Wilson, *Can. J. Chem.* 51: 1037 (1973).

Fig. 5.7. Phase Diagram of the V_2O_5 - Na_2O - MgO System. Binary phase compositions: I = $Na_2O \cdot 6V_2O_5$, II = $5Na_2O \cdot 12V_2O_5$, III = $NaVO_3$, IV = $Na_4V_2O_7$, V = Na_3VO_4 , VI = $Mg_2V_6O_{17}$, VII = MgV_2O_6 , VIII = $Mg_2V_2O_7$, IX = $Mg_3(VO_4)_2$. Reprinted with permission from R. C. Kerby and J. R. Wilson, *Can. J. Chem.* 51: 1039 (1973).

partial pressure. The phase diagrams for V_2O_5 - Cr_2O_3 and V_2O_5 - MgO are shown in Figs. 5.8 and 5.9. The compound $CrVO_4$ is formed; the eutectic temperature is $655^\circ C$ ($1211^\circ F$). Interactions with Na_2O will produce several compounds and eutectics with the lowest eutectic temperature being $505^\circ C$ ($941^\circ F$) (Table 5.4). The system MgO - V_2O_5 has four compounds and several peritectics and one eutectic with a temperature of $604^\circ C$ ($1119^\circ F$). The inclusion of Na_2O results in several compounds, one eutectic, and four peritectics with the lowest one at $470^\circ C$ ($878^\circ F$). These phase diagrams show that sodium vanadate is a strong flux for the magnesia-chrome system. Basic refractories in general are resistant to reaction with alkalis. Chromia will react and form alkali chromates, but most often it is the bonding phase that is degraded in these refractories. Vanadium pentoxide will flux the magnesia-chrome system. The presence of Na_2O will increase the fluidity of the liquid phase generated by vanadium pentoxide. This will enhance the solubility of the refractory in the slag and the transport rate of vanadium through the melt as well. Therefore, the corrosion from a mixture of Na_2O and V_2O_5 in this refractory system is far more serious than from either V_2O_5 or Na_2O alone.

Since CaO is usually present in the bonding phase in the magnesia-chrome refractory, attention should also be paid to the CaO - V_2O_5 and related systems. The phase diagram of the system CaO - V_2O_5 (Fig. 5.5) indicates the formation of three intermediate compounds, CaO - V_2O_5 , $2CaO \cdot V_2O_5$, and $3CaO \cdot V_2O_5$ with an eutectic point at $618^\circ C$ ($1144^\circ F$). The ternary system CaO - MgO - SiO_2 has been investigated extensively (Fig. 5.10). For V_2O_5 exposure, the following reactions have been considered. The symbols used in these equations are indicated in Table 5.3.

Fig. 5.8. Phase Diagram of the V_2O_5 - Cr_2O_3 System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., p. 130, American Ceramic Society, 1964.

Fig. 5.9. Phase Diagram of the V_2O_5 - MgO System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., 1969 Supplement, p. 89, American Ceramic Society, 1969.

Table 5.4. Invariant Points in the Systems V_2O_5 - Cr_2O_3 , V_2O_5 - Na_2O - Cr_2O_3 , V_2O_5 - MgO , V_2O_5 - Na_2O - MgO , V_2O_5 - CaO , V_2O_5 - SiO_2 , V_2O_5 - Al_2O_3 , V_2O_5 - ZrO_2

Composition (mole %)			Temperature (°C)	Type of Invariant	Equilibrium Solid Phases
V_2O_5	Cr_2O_3				
76	24		655	Eutectic	$V_2O_5 + CrVO_4$
52	48		902	Peritectic	$CrVO_4 + Cr_2O_3$
V_2O_5	Na_2O	Cr_2O_3			
76	3	21	630	Eutectic	$V_2O_5 + Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5 + CrVO_4$
56	26	18	545	Peritectic	$Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5 + CrVO_4 + 5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5$
52	28	20	505	Eutectic	$5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5 + NaVO_3 + CrVO_4$
43	17	40	555	Eutectic	$CrVO_4 + NaVO_3 + Cr_2O_3$
35	39	26	520	Eutectic	$NaVO_3 + Na_4V_2O_7 + Cr_2O_3$
V_2O_5	MgO				
77	23		604	Eutectic	$V_2O_5 + Mg_2V_6O_{17}$
72	28		640	Peritectic	$Mg_2V_6O_{17} + MgV_2O_6$
56	44		742	Peritectic	$MgV_2O_6 + Mg_2V_2O_7$
37	63		980	Peritectic	$Mg_2V_2O_7 + Mg_3(VO_4)_2$
V_2O_5	Na_2O	MgO			
77	1	22	602	Eutectic	$V_2O_5 + Mg_2V_6O_{17} + Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5$
61	23	16	535	Peritectic	$Na_2O \cdot xV_2O_4 \cdot (6-x)V_2O_5 + 5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5 + Mg_2V_6O_{17}$
49	30	21	510	Peritectic	$Mg_2V_6O_{17} + NaVO_3 + 5Na_2O \cdot xV_2O_4 \cdot (12-x)V_2O_5$
46	21	33	540	Peritectic	$Mg_2V_6O_{17} + Mg_2V_2O_7 + MgV_2O_6$
47	26	27	505	Eutectic	$NaVO_3 + Mg_2V_6O_{17} + Mg_2V_2O_7$
24	37	39	495	Peritectic	$NaVO_3 + Mg_3(VO_4)_2 + Mg_2V_2O_7$
15	44	41	470	Peritectic	$Mg_3(VO_4)_2 + Na_4V_2O_7$
22	48	30	480	Peritectic	$Mg_3(VO_4)_2 + Na_4V_2O_7 + NaVO_3$
V_2O_5	CaO				
78	22		618	Eutectic	$CaO \cdot V_2O_5$
58	42		778	Peritectic	$2CaO \cdot V_2O_5$
36	64		1015	Peritectic	$3CaO \cdot V_2O_5$
V_2O_5	SiO_2				
96.7	3.3		661	Eutectic	none
V_2O_5	Al_2O_3				
98.4	1.6		640	Eutectic	$AlVO_4$
V_2O_5	ZrO_2				
80	20		650	Eutectic	ZrV_2O_7

CaO-MgO-SiO₂

Fig. 5.10. Phase Diagram of the CaO-MgO-SiO₂ System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., p. 210, American Ceramic Society, 1964.

Therefore, the existence of forsterite M_2S was predicted and indeed was confirmed at 1450°C (2642°F) by Eke and Brett.²¹ They also discovered a solid solution phase of C_2S and C_3V , $(CaO)_{2.5} SiO_2 (V_2O_5)_{0.2}$ and a phase field of MgO , M_2S , and liquid at 1500°C (2732°F) and 1450°C (2642°F).²² The presence of forsterite in high lime compositions indicate stability of forsterite relative to C_2S upon V_2O_5 exposure.

The presence of V_2O_5 will increase the amount of the liquid phase in the psuedo-ternary system CaO-MgO-SiO₂, which becomes glass upon quenching. Dicalcium silicate and C_3MS_2 will be converted by V_2O_5 to liquids at 1450°C (2642°F). The liquid phase between grains will lead to grain growth, reduction in hot strength, and consequent failure of the refractory. For magnesite bricks containing forsterite with low lime content, the forsterite will act as a stable second phase that will limit the

liquid penetration and the grain growth, and will promote bonding of the grains.

The corrosion resulting from both V_2O_5 and Na_2O together in the basic refractory will be more serious than for V_2O_5 alone. The sodium oxide may attack the bonding phase to form glassy phases since the V_2O_5 - CaO - SiO_2 system has large compositional ranges in which glasses are formed. The presence of V_2O_5 somehow reduces this tendency, perhaps by the increased viscosity in the liquid phase.²⁰ Sodium vanadate may react with $2CaO \cdot SiO_2$, $CaO \cdot MgO \cdot SiO_2$, and $2CaO \cdot Al_2O_3 \cdot SiO_2$ according to the reactions as follows:

The calculation of the standard enthalpy of formation indicates that $2CaO \cdot SiO_2$ and $2CaO \cdot Al_2O_3 \cdot SiO_2$ will be decomposed by sodium vanadates. In comparison, if only V_2O_5 is present, the following reactions may be considered:

$$\Delta H_{298}^\circ = -38.5 \text{ kcal/mole} . \quad (5.25)$$

The negative values of the standard enthalpy of reaction indicate that all these reactions are thermodynamically favorable. Again, as described before, the presence of Na_2O will render the liquid phase less viscous and increase the solubility of the bonding phases in the liquid phase which will lead to more extensive fluxing and penetration.

Evans and Cholerton²³ conducted an experiment involving V_2O_5 vapor attack in basic refractories. They observed that dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$) and monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$), which are initially present in the bonding phase or are produced as a result of batch carryover of silica and CaO , are readily fluxed by V_2O_5 to form a low surface tension liquid, which will completely surround and wet the periclase grains and result in significant grain growth. Under a thermal gradient, because of the tendency of the liquid to decrease its free energy upon cooling, such liquid will migrate toward the relatively cooler central region of the brick and could leave outer zones of the bricks devoid of bonding silicates. The problem with forsterite bonded basic bricks is that the batch carryover can radically change the original CaO/SiO_2 ratio from 0.5/1 to about 4/1 which leads to mechanical disintegration. In applications involving no thermal cycling, chrome-magnesites and magnesite-chrome refractories in which a second solid phase exists, can resist the V_2O_5 attack better than the magnesite bricks. Evans and Cholerton²³ finally suggested that magnesite bricks should not be used above 1450°C (2642°F) in the presence of vanadium and not above 1500°C (2732°F) in vanadium free atmospheres. Their observations were in general agreement with earlier works by Pressley,¹⁹ Robijn and Dekeyser,²⁴ and Lehman et al.²⁵

At lower temperatures, sulfates [Na_2SO_4 , MgSO_4 , CaSO_4 , $\text{Cr}_2(\text{SO}_4)_3$] could contribute to the disintegration in the basic bricks due to their accompanying volume expansions. Mörtl and Zednicek²⁶ found that in the range $600\text{--}900^\circ\text{C}$ ($1112\text{--}1652^\circ\text{F}$), the basic bricks are often completely spalled in the surface region according to the reaction:

Glazer and Boggum²⁷ reported that if present, arsenic compounds will catalyze the formation of SO_3 and thus increase the formation of MgSO_4 . The dissociation temperatures of MgSO_4 and CaSO_4 are 1124°C (2055°F) and 1350°C (2462°F) respectively. Busby and Carter²⁸ reported that the rate of formation of MgSO_4 is accelerated by the presence of Na_2SO_4 . Both V_2O_5 and As_2O_3 increase the formation rate of MgSO_4 and reduce its dissociation temperature. In general, sulfate is more detrimental to the basic system than to the aluminosilicate system, mainly because of the reactions of MgO and SO_3 .

5.4. OTHER REFRACTORY SYSTEMS

Zircon refractories are used mostly in the glass industry. They consist of a zircon phase (ZrSiO_4) which will decompose into ZrO_2 and SiO_2 at a temperature of 1200°C (2192°F) in the presence of alkali vapor according to the following reaction:²⁹

The ZrO_2 - V_2O_5 system has been reported (Fig. 5.11). A low temperature eutectic: 650°C (1202°F) is also present in this system. With sodium vanadate exposure, the following reactions may occur.

Unfortunately, the standard free energies of formation for $\text{Na}_2\text{ZrSiO}_5$ and ZrV_2O_7 are not available and thus it is uncertain that the above reactions will occur, or at which temperatures they will occur.

Dolomite refractories, which consist of CaO and MgO will be seriously attacked by the combustion product sodium vanadate. Of all

Fig. 5.11. Phase Diagram of the V_2O_5 - ZrO_2 System. Reprinted with permission from *Phase Diagrams for Ceramists*, E. M. Levin, C. R. Robbins, and H. F. McMurdie, eds., 1969 Supplement, p. 112, American Ceramic Society, 1969.

refractory types, dolomite refractories are the most susceptible to reaction with V_2O_5 .

Bratton et al.,³⁰ have investigated the corrosion rate of V_2O_5 and/or Na_2O in SiC , Si_3N_4 , and silicon-aluminum-oxygen-nitride systems proposed for use in gas turbines. At temperatures as high as 1371°C (2500°F), there is essentially no corrosion, but rather erosion due to the high speed liquid particles of V_2O_5 and Na_2O in the pressurized condition in a gas turbine.

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6. ANALYSIS OF DEGRADATION MECHANISMS IN REFRACTORIES AND REFRACTORY INSULATIONS

6.1 RESULTS

Many experiments reported in the literature on combustion ash corrosion of refractories used solid-solid or solid-liquid reactions. Normally, such experiments involved mixing the characteristic combustion product compounds such as Na_2SO_4 and V_2O_5 with the phases of the refractory system of interest such as Al_2O_3 and SiO_2 , or MgO and Cr_2O_3 . The samples were usually heated to high temperatures, then quenched and examined to determine the new phase compositions. Alternately, these experiments involve contacting solid-combustion product phases with a piece of test refractory at various temperatures and times. The reaction products formed and strength degradation are later determined. Vapor phase tests reacting Na_2O or V_2O_5 vapor with the refractory more closely simulate actual combustion situations, but these tests have only been done in a few limited cases.

Table 6.1 lists the methods for testing V_2O_5 - Na_2O - SO_3 corrosion in the refractories as reported in the literature. The test result normally has direct application only to a limited temperature range and fuel ash composition range. Two degradation modes that have been identified are fluxing, and cracking of the refractory. Actually these two types of deterioration are related. In fluxing, a liquid phase is generated from the low-temperature eutectics existing between the combustion products and refractory oxides. The liquid phase will penetrate the pores in the refractory and later cause spalling and cracking due to thermal stresses generated upon thermal cycling. The cracks thus generated will produce new surfaces to be further attacked by the liquid phase generated by fluxing and thus cause more extensive cracking and spalling. The cracking and spalling result from the formation of new solid phases such as nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$), forsterite ($2\text{MgO} \cdot \text{SiO}_2$), MgSO_4 , and so forth, which have different specific or molar volumes than the host refractory

Table 6.1. Tests of V_2O_5 - Na_2O - SO_3 Corrosion in Refractories

Author and Year	Method	Corrosive Species	Refractories	Reference Number
Rigby and Hutton (1962)	Mixing refractory and corrosive powder and firing	Na_2CO_3 and V_2O_5	Al_2O_3 - SiO_2 system	15 (Chapter 5)
MacLaren and Richardson (1959)	Cone deformation	Na_2O , CaO , and V_2O_5	Al_2O_3 - SiO_2 system	16 (Chapter 5)
Jones and Hardy (1952)	Slag fusion and chemical reactivity	Petroleum ash	Fireclay refractories	17 (Chapter 5)
Pressley (1970)	Thermal cycling in the presence of SO_2 , Na_2SO_4 , and $NaVO_3$	SO_3 and Na_2SO_4	Al_2O_3 - SiO_2 system and basic system	19 (Chapter 5)
Busby (1963)	Mixing refractory and corrosive powders and firing	Na_2O and V_2O_5	Al_2O_3 - SiO_2 system	18 (Chapter 5)
Okawara and Yamaguchi (1969)	Vapor phase attack	Na_2CO_3	Mullite refractory	14 (Chapter 5)
Frischat and Hennicke (1974)	Dissolution	V_2O_5 melt	Polycrystalline alumina and sapphire	13 (Chapter 5)
Bonar (1976)	Slag corrosion	Na_2O and V_2O_5	Al_2O_3 - SiO_2 system and SiC	4 (Chapter 6)
Morsanyi (1963)	Slag corrosion	Na_2O and V_2O_5	Silica refractories	20 (Chapter 5)
Crouch et al. (1970)	Oil combustion	Oil ash	High alumina and magnesite refractories	1 (Chapter 6)
Morsanyi (1966)	Vapor phase attack	Na_2SO_4 , Na_2CO_3 , $NaVO_3$, and $NaCl$	Silica refractories	2,3 (Chapter 6)
Robijn and de Keyser (1970)	Field test, checkers of glass tank	V, Ni, and As	Basic bricks	24 (Chapter 5)
Evans and Cholerton (1972)	Vapor phase attack	CaO and V_2O_5	Basic bricks	23 (Chapter 5)
Busby and Carter (1971)	Mixing refractory and V_2O_5 , Na_2SO_4 , As_2O_3 powders, SO_3 vapor attack	SO_3 , V_2O_5 , Na_2SO_4 , As_2O_3	Magnesite bricks	28 (Chapter 5)

system. The expansion or shrinkage of these new phases relative to the original reactants will generate internal stresses that can cause cracking.

As a first-order approximation, the internal stress generated can be calculated by:⁵

$$\sigma = \frac{2E}{3(1 + \nu)} \cdot \frac{\Delta v}{v}, \quad (6.1)$$

where E is the elastic modulus, ν is Poisson's ratio, and $\Delta v/v$ is the volume fraction expansion or contraction due to the appearance of new phases. Considering thermal cycling, the liquid phase or the new reaction product, which has a different thermal expansion coefficient, will produce a mean linear thermal expansion coefficient for the system, α_m :⁶

$$\alpha_m = \frac{\alpha_1 f_1 E_1 / (1 - \nu_1) + \alpha_2 f_2 E_2 / (1 - \nu_2)}{f_1 E_1 / (1 - \nu_1) + f_2 E_2 / (1 - \nu_2)}, \quad (6.2)$$

where index 1 and 2 refer to the original phase and the new liquid or solid phase, respectively, α is the thermal expansion coefficient, ν is Poisson's ratio, f is the volume fraction, and E is the elastic modulus. If the temperature is changed by ΔT , the stress acting on the host phase (σ_1) and the new phase (σ_2) will be:⁶

$$\sigma_1 = \frac{\alpha_m - \alpha_1}{1 - \nu_1} E_1 \Delta T, \quad (6.3)$$

$$\sigma_2 = \frac{\alpha_m - \alpha_2}{1 - \nu_2} E_2 \Delta T. \quad (6.4)$$

In the case of aluminosilicate refractories, according to the molecular volumes, the formation of nepheline and alumina by the decomposition of mullite will show a volume contraction of 4.9% (Table 6.2). The formation of β -alumina will be accompanied by a volume expansion of 20%. When Na_2O reacts with mullite or alumina to form $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, the volume expansion is 14%. With an assumed elastic modulus of 10×10^6 psi (6.89×10^9 Pa) and a Poisson's ratio of 0.3 (Eq. 6.1), a compressive stress greater than 700,000 psi (4.82×10^9 Pa) can be expected when the reaction products mentioned above are formed. Since this is well

Table 6.2. Selected Thermophysical Properties of Some Refractory Materials

	Density ^a (g/cm ³)	Mean Linear Thermal Expansion Coefficient ^b (°C ⁻¹ × 10 ⁶)	Elastic Modulus ^a (psi × 10 ⁻⁶)	Poisson's Ratio ^a
Al ₂ O ₃	3.97 ^c	8.8 (0-1000) ^f	55 ^f	0.31 ^e
SiO ₂ (Cristobalite)	2.32 ^c	1.5 (25-1000) ^f		
SiO ₂ (Tridymite)	2.26 ^c			
SiO ₂ (Quartz)	2.64-2.66 ^c	1.0 $\perp$ and $\parallel$ C axis (25-1000) ^f	10.5 ^f	0.185 ^e
Na ₂ O·11Al ₂ O ₃	2.619 ^c			
Na ₂ O·Al ₂ O ₃ ·4SiO ₂	3.3 ^c			
Na ₂ O·Al ₂ O ₃	2.71 ^d			
Na ₂ O·SiO ₂				
2CaO·V ₂ O ₅				
3CaO·V ₂ O ₅				
3CaO·MgO·2SiO ₂				
CaO·MgO·SiO ₂				
2MgO·V ₂ O ₅				
3MgO·V ₂ O ₅				
2MgO·SiO ₂	3.21 ^c	11.0 (0-1425) ^e		
MgSO ₄	2.66 ^c			
Al ₂ O ₃ ·SiO ₂	3.247 ^c	6.58 (20) ^e		
Na ₂ O	2.27 ^c			
V ₂ O ₅	3.357 ^c			
2CaO·SiO ₂	3.28 ^e	14.36 (25-1000) ^e		
ZrSiO ₄	4.6 ^e	5.63 (25-1500) ^e	24 ^e	
MgO	3.60 ^e	15.11 (25-1500) ^e	30 ^e	0.163 ^e
NaVO ₃				
3Al ₂ O ₃ ·2SiO ₂	3.156 ^c	5.62 (25-1500) ^e	20.75 ^e	0.238 ^e

^aRoom-temperature values.^bApplicable temperature or range in °C in parentheses.^c*Handbook of Chemistry and Physics*, Chemical Rubber Company, Cleveland, Ohio, 1975.^dRigby and Hutton, *J. Am. Ceram. Soc.* 45(2): 68 (1962).^eP.T.B. Shaffer, *Handbook of High-Temperature Materials*, Plenum Press, New York, 1964.^fW. D. Kingery, *Introduction to Ceramics*, Wiley, New York, 1959.

above the fracture strength of most aluminosilicate refractories,⁷ microcracks will probably be generated. In the case of basic refractories, the formation of MgSO_4 will cause a volume expansion of 35%. Creation of forsterite ($2\text{MgO} \cdot \text{SiO}_2$) from periclase will cause a volume expansion of 12%. A stress on the order of 10^6 psi (6.89×10^9 Pa) can also be generated in magnesia-chrome refractories by these volume differences. Consequently, spalling throughout the refractory is expected from the formation of these phases.

The porosity of the refractories plays an important role in the degradation due to fluxing and cracking. Since the pores can generally be regarded as a trapping center for the microcracks generated by these stresses, the presence of pores would help to depress the further growth and extensions of the cracks, but would also result in lower initial strengths for the refractory. In fact, pores can stop crack growth to a great extent under certain conditions. On the other hand, the existence of both open and closed pores represents a rapid transport path for the combustion product reactants such as Na_2O or V_2O_5 . The corrosive species in vapor or liquid form can penetrate the pore, attack fresh internal surface in the refractory interior, and therefore cause extensive degradation. In addition, the presence of liquid phase among grains may enhance grain growth, lower the creep strength, and weaken the refractory at high temperatures. Microstructural changes are further complicated since liquid phase will migrate from the hot surface to a relatively cooler region in a refractory material with a thermal gradient. This migration then depletes the bonding phase in the region close to the hot surface, with a reduction in the hot strength and an increase in the creep rate of the refractory material. The quantitative aspects of these effects are largely unknown in most of the refractory systems currently used industrially. In view of these effects, dense refractories with small amounts of porosity are superior to more porous ones. In designing a refractory system resistant to fuel ash attack, the use of dense refractories that are relatively inert to the corrosion of the combustion products usually conflicts with considerations of cost and thermal insulation properties, which are typically a direct function of the amount of porosity.

The formation of liquid phase on the surface of the refractory may act as a barrier to the reaction with the combustion products if the viscosity is high enough. Fluxing and reaction rates depend on four factors: (1) the vapor-solid-liquid reaction at the interface, (2) the transport of the combustion product ions in the melt, (3) the amount of the refractory dissolved in the liquid, and (4) the transport of corrosive ions through the solid phase in the refractories. Each of these four steps could be the rate-determining step in the reaction of the combustion products with the refractory material. Little quantitative data of this type are available for most refractories at present. The most powerful corrosion characteristics of a mixture of Na_2O and V_2O_5 in the alumina-silica system are that both Na_2O and V_2O_5 act as a flux and a mineralizer with the former playing the major role. In the basic refractory system using MgO , V_2O_5 readily fluxes the refractory oxides and Na_2O tends to make the slag or melt less viscous, and this enhances the corrosion rates. The basic refractory is appropriate to use in an alkali-rich environment and the aluminosilicate refractory is appropriate for a V_2O_5 environment, but the combination of Na_2O and V_2O_5 renders either type of refractory prone to serious degradation. Magnesia- (ref. 8), dolomite- (ref. 8), SiC - (ref. 9), and Al_2O_3 -based (ref. 10) additives in fuel oil reduce vanadium corrosion in metal systems. The MgO reacts with V_2O_5 to form $3\text{MgO} \cdot \text{V}_2\text{O}_5$, which does not readily react with metallic materials in boilers. This appears to be a potential way to inhibit the corrosion in refractories. Much more research is required to examine the use of additives to prevent corrosion in refractories and refractory insulations.

Another point with regard to the fuel ash corrosion is that the phase diagram data, which represents equilibrium behavior, should be applied with great care to real combustion situations because the fuel ash corrosion reactions in refractories may never reach equilibrium.

6.2 INTERPRETATION OF FIELD TEST RESULTS

The field test results of oil ash corrosion in refractories were interpreted on the basis of the mineralogical and chemical examinations

of the refractories used. However, the results are not always reliable for several reasons: First, the amount of vanadium compounds formed in the bricks is usually small and irregularly distributed. (X-ray diffraction techniques often are not able to detect the expected phases.) Secondly, the compositions of many vanadates are still uncertain and their stoichiometry ranges under the conditions of interest are unknown. (Some vanadates, such as sodium vanadate, desorb oxygen upon cooling and thus change composition.¹¹) Thirdly, the optical properties of many vanadates are not sufficiently known to permit unequivocal petrographic analysis. (With electron probe microanalysis and other new techniques, it may be possible to identify the elements and their distributions in this type of material.)

With one exception, all the experiments identified in our literature review used solid-solid or solid-liquid reactions. Examinations of refractory field test samples in many of the reported cases often failed to consider that V_2O_5 and its compounds, which can form with the common oxides present in the generic types of refractories, have relatively high vapor pressures at the test temperatures. The absence of significant amounts of V_2O_5 in the exposed refractories often leads to the possibly false conclusion that V_2O_5 does not contribute to refractory deterioration. The V_2O_5 may not precipitate in significant amounts at temperatures higher than 1400°C (2552°F). However, the detrimental effect of V_2O_5 vapor can be even more serious than the slag containing V_2O_5 because the corrosive vapor can permeate through the pores and thereby attack both external and internal surfaces in the refractories.

In the reported interpretations of refractory field test samples, distinctions should also be made between pressurized and nonpressurized environments. Since the liquidus temperatures and the melting points of intermediate compounds in many ternary and quaternary systems involving Na_2O and V_2O_5 strongly depend on the oxygen partial pressure,¹² degradation in refractories due to Na_2O and V_2O_5 attack will be more serious in those applications involving pressurized oxygen-rich atmospheres.

When compared with isothermal situations, thermal cycling in applications such as the checkerwork in the regenerator of glass tanks

increases fluxing, spalling, and cracking. Any thermal gradient in the refractory that increases the microstructural changes involved in the refractory deterioration should also be included in the characterization of the field test samples, and these data have often been lacking from published reports.

In view of the very limited documentations on alternate fuel refractory interactions, an extensive laboratory screening test and a long-term field test are urgently needed. The data base generated will help industries to form a sound alternate-fuel refractory strategy as the conversion from natural gas to fuel oils and/or coal becomes a major problem of the immediate future.

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