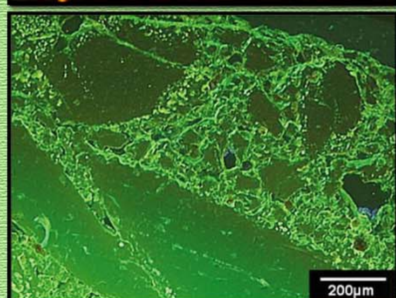
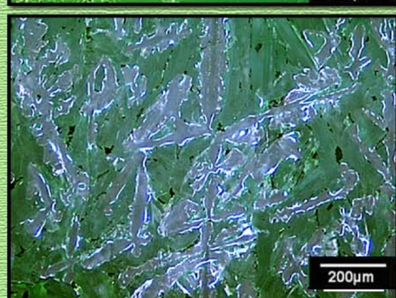
Refractories for Industrial Processing: Opportunities for Improved Energy Efficiency





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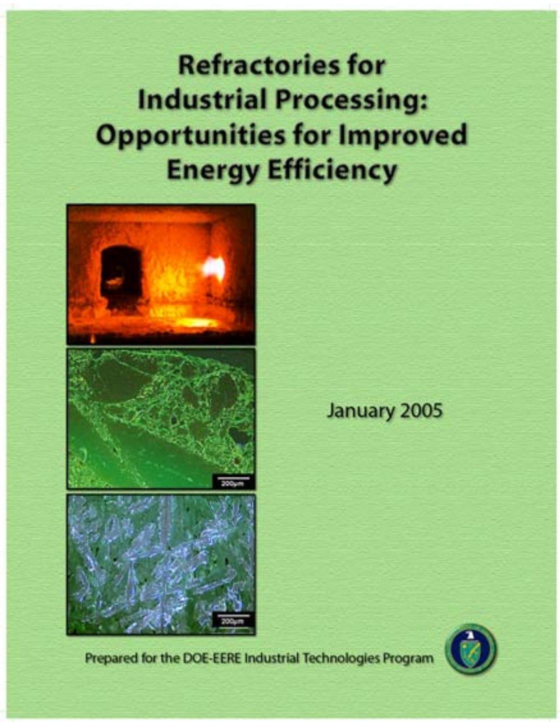
The photographs on the cover are an example of an aluminum furnace featured on the Harbison Walker web page (top), cathodoluminescence of a fusion-cast spinel refractory (center), and cathodoluminescence of a fusion-cast alumina refractory (bottom).



Refractories for Industrial Processing: Opportunities for Improved Energy Efficiency

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Executive Summary

Refractory materials with properties suitable for high-temperature applications are used throughout U.S. industry as insulation and/or containment vessel linings in high-temperature and corrosive environments. Indeed, it would be difficult to identify an industrial process that does not use refractory materials in one aspect or another. These materials must not only be capable of performing these tasks at elevated temperatures, but may also be called upon to bear mechanical loads and transfer heat. Refractories are characterized by two aspects that qualify them as strategic materials in support of American industry: (1) their ability to contain heat, chemicals, and melts; and (2) the crosscutting nature of their utility.

Figure ES.1 shows the ranges of usage temperatures for numerous industrial applications of refractories. This report and the attached appendices describe the current furnace technologies used by U.S. industries with specific highlighted analysis focused on four furnace types—kilns/calciners, reverberatory furnaces, boilers and reactor systems, and gasifiers—which are common to multiple industries and are representative of areas where significant energy improvement could be made through future refractory improvement. Analyses of these four types of furnaces alone suggest potential energy savings of over 400 trillion Btu/year. In addition to identifying areas of opportunity, this report describes possible crosscutting research and development (R&D) pathways for overcoming refractory-related performance barriers which could lead to improved energy efficiency through both the alteration of current materials and practices and the development of new materials, furnace designs, or redesigned processes of varying sizes.

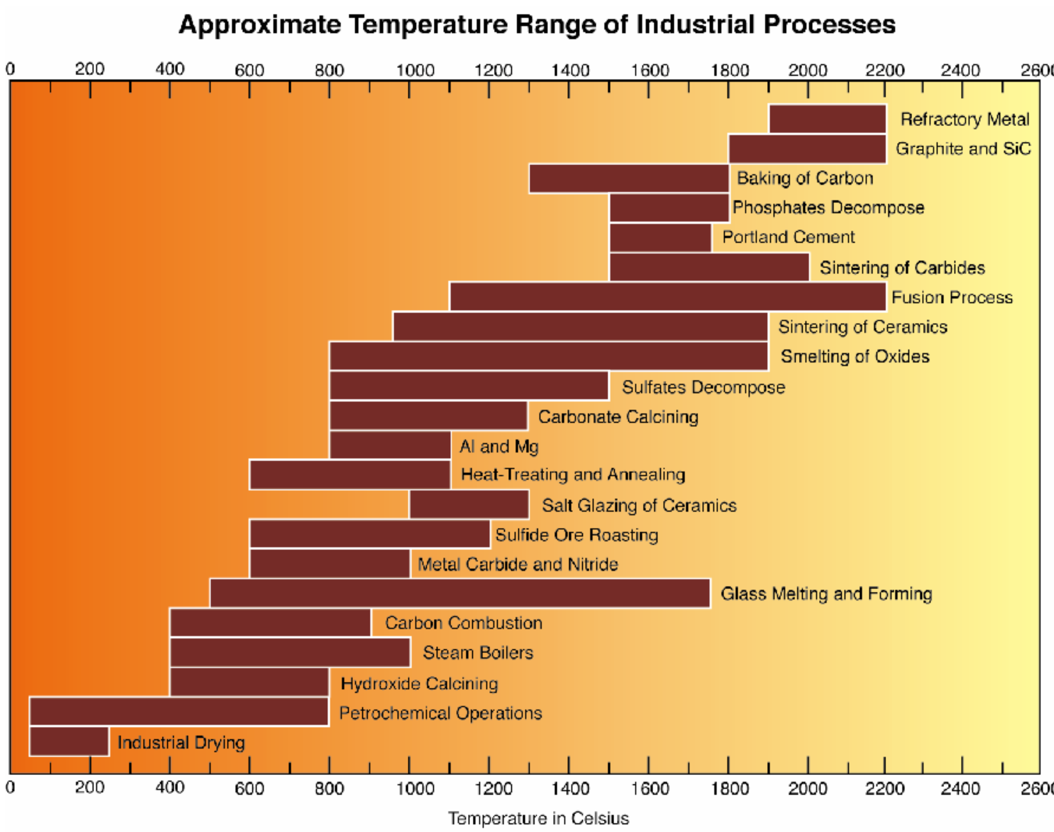

Fig. ES.1. Temperature regimes for industrial applications of refractories.

Abbreviations and Acronyms

BLS	black liquor solids
BOF	basic oxygen furnace
Btu	British thermal unit
DOE	U.S. Department of Energy
EAF	electric arc furnace
EERE	Energy Efficiency and Renewable Energy (DOE)
FCCU	fluidized catalyst cracking unit
ITP	Industrial Technologies Program (DOE)
MECS	Manufacturing Energy Consumption Survey
ORNL	Oak Ridge National Laboratory
R&D	research and development
TBtu	trillion Btu

1. Introduction

The Industrial Technologies Program (ITP), part of the Department of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE), seeks to improve the energy intensity of the U.S. industrial sector through a coordinated program of research and development (R&D), validation, and dissemination of energy efficiency technologies and operating practices. To achieve its mission, ITP partners with industry, equipment manufacturers, and other stakeholders to develop technologies that enable industry to use less energy per unit of output. Refractories are a class of materials of critical importance to manufacturing industries with high-temperature unit processes. This study describes industrial refractory applications and identifies refractory performance barriers to energy efficiency for processing. The report provides recommendations for R&D pathways leading to improved refractories for energy-efficient manufacturing and processing.

2. Current Refractory Status

There are many different types of furnaces used in industries in the United States, each with different refractory needs and challenges. A discussion of the refractory issues for several energy-intensive processing industries can be found in Appendix A. Fifteen classifications of furnaces with several common issues can be identified. Typical industrial applications of these fifteen furnace types are shown in Table 1. Refractory challenges and problems related to these furnace types, as reported by industry personnel and discussed in detail in Appendix A, are shown in Table 2.

Of these fifteen furnace types, four are highlighted in this document: kilns/calciners, reverberatory furnaces, boilers and reaction systems, and gasifiers. These were selected because they are common to multiple industries and representative of areas where significant energy savings [on the order of trillions of Btu (TBtu)/year] could be realized through future refractory improvement. Although emphasis was placed on blast furnaces, basic oxygen furnaces (BOFs), and other furnace types found in the steel industry, we have chosen not to focus on these furnaces because of their design practice of intentionally leaking energy so as to induce a steep thermal gradient through the lining. Additionally, BOF refractories are known to last thousands of heats, and little improvement is expected in improving refractories for these applications.

Analysis and discussion will address refractory improvements leading to higher energy efficiency and improved product yield for each of these four furnace types. Discussion will focus on the energy-intensive industries of the United States including aluminum, cement and lime, chemicals and petrochemicals, forest products, glass, heat treatment and annealing, iron and steel, and metal casting.

Table 1. Types of furnaces utilized in American industry

Furnace type	Industrial furnace applications								
	Aluminum	Cement & lime	Chemical/ petro-chemical	Forest products	Glass	Heat treat	Iron & steel	Metal casting	Other[a]
Blast furnace							X		1
Basic oxygen furnace							X		
Reverberatory furnace	X						X	X	2
Multiple hearth									2
Ladle/tundishe/trough	X						X	X	3
Electrolytic smelting	X								4
Kilns	X	X	X	X	X		X		5, 6
Electric arc furnace (EAF)				X			X		7
Cupola							X		
Heat treat	X			X	X	X	X	X	5,8
Still			X						9
Reactor/reformer			X						
Boiler	X	X	X	X		X			10
Gasifier			X	X					
Heat exchanger	X	X	X	X	X	X	X	X	

[a] Key to "Other":

1. Lead
2. Copper
3. Molten metal handling
4. Magnesium
5. Ceramics
6. Mining
7. Oxide melting
8. Various metal products
9. Organic and inorganic products
10. Virtually all industries

Table 2. Refractory barriers for furnaces utilized in American industry

Furnace type	Refractory challenges								
	Abrasion	**Caking/ agglom-eration**	**Contami-nation/ fouling**	**Corrosion/ wear**	**Erosion**	**Mechanical degradation**	**Thermal insulation**	**Thermo-mechanical degradation/ shock**	**Refractory life/ repairs**
Blast furnace	X				X	X		X	
Basic oxygen furnace			X	X	X	X	X	X	X
Reverberatory furnace			X	X	X		X	X	X
Multiple hearth	X						X		
Ladle/tundishe/trough			X	X	X	X	X	X	
Electrolytic smelting			XX	X		X	X		X
Kilns	X	X	X	X	X	X	X	X	X
Electric arc furnace (EAF)				X	X		X	X	
Cupola			X						
Heat treat									
Still	X						X	X	X
Reactor/reformer	X						X		
Boiler	X		X	X	X	X	X	X	X
Gasifier	X				X	X	X	X	X
Heat exchanger	X				X			X	

X
X

X
X

2.1 Usage in Industry

Although refractories are used in most, if not all, of U.S. industries, the iron and steel industry consumes 70% of the refractories produced globally, while the cement and lime industry consumes 7%, the ceramics industry 6%, the glass industry 3–4%, and the oil industry about 4%.[1] In 1998, a survey was conducted by the U.S. Advanced Ceramics Association and Oak Ridge National Laboratory (ORNL) to determine opportunities for advanced ceramics to meet the needs of manufacturing industries.[2] These industries included aluminum, chemicals and petrochemicals, forest products, glass, metals casting, and steel. Additionally, the supporting industry of heat treating and annealing was considered. From this survey, a number of critical areas were identified in each of these industries where improvements could lead to substantial economic and energy savings.

Additionally, the general practice of most industries is to choose fuel types and sources based primarily on cost and availability. This, in many cases, leads to variations in fuel quality and purity which will directly impact the performance of the refractory materials used in the respective furnaces. This must be considered when choosing furnace materials and when evaluating energy efficiency.

2.2 Current R&D Status

Substantial changes that have occurred in refractories technology over the past 25 years have resulted in crosscutting impacts on a number of manufacturing industries,[2] including the use of fibrous and high-strength porous insulation to reduce energy consumption in heat-treating furnaces. In the steel industry, the use of resin-bonded MgO-C-metal linings in basic oxygen furnaces significantly increases the number of heats between needed relinings, and SiC-based refractories have led to increased furnace life for steel blast furnaces. In the glass industry, the advent of oxy-fuel melting has led to renewed interest in alternative refractory materials that will allow for processing at higher temperatures and greater corrosion resistance to high alkali and water-rich environments. Additionally, many more recent ceramic compositions have received limited evaluation but have not reached maturity or production status. All of these events are representative of industrial process improvements that can be accomplished through advances in refractory materials, yet additional improvements could lead to even greater energy savings throughout the various industries.

The choice of refractory materials for a certain application is often dictated by the trade off between cost and performance. In the past economic considerations have led to the selection of lower cost/poorer performing refractories over higher performance/higher cost materials. Yet, with rising energy costs, environmental regulations, and economies of scale; higher priced premium refractory materials are receiving renewed interest and may prove cost effective in many applications for which they were previously deemed unsuitable.

3. Estimated Metrics for Overall Energy Savings Opportunities

Energy usage in several of the industries and estimates of potential energy savings through improvements in refractories are shown in Table 3. The values shown in this table are based primarily on DOE Manufacturing Energy Consumption Survey (MECS) data describing manufacturing energy consumption in the year 1998.[3] The estimates of energy usage affected by refractories are based on evaluation of industry roadmap documents and discussions with industry leaders. Energy savings goals are based on the needs of the industries and estimates for the four typical furnace types (Table 1) used throughout many of the industries, which are presented in detail in Appendices B, C, and D. These analyses are based on heat balance studies where the energy supplied to the system through combustion is equal to the sum of (1) latent heat in the furnace exhaust gases, (2) heat lost through the furnace walls and roofs, and (3) heat required for heating reactants to the process temperature and phase transformations at that temperature. The achievement of theoretical efficiency would require that items 2 and 3 be equal to zero. From a practical point of view, perfect efficiency is not probable, but improvements in furnace refractories could help facilitate improvements of furnace efficiency beyond the levels of present technology. The projected saving opportunities in the range of 166 TBtu/Yr to 830 TBtu/Yr are equivalent to the yearly residential electrical usage of New York state and the yearly residential air conditioning usage of the US, respectively.

Table 3. Energy analysis by industry with estimated short-term and long-term energy savings opportunities from improved refractories

Industry	NAICS codes	Total TBtu/year[a]	Usage affected by refractories		Energy savings goals for improved refractories (TBtu/Yr)	
			Percent	TBtu/Yr	Near-term 2%	Long-term 10%
Aluminum	3313XX1	441	90%	397	7.9	39.7
Chemical	325XXX	3,704	50%	1,852	37.0	185.2
Fabricated metals[b]	33281	445	90%	401	8.0	40.1
Forest products	321XXX, 322XXX	3,248	40%	1,299	26.0	129.9
Foundries	3315XX	233	90%	210	4.2	21.0
Glass	3272XX	203	70%	142	2.8	14.2
Iron & steel	33111	1,672	85%	1,421	28.4	142.1
Petroleum & coal products	324XXX	3,622	50%	1,811	36.2	181.1
Stone, clay products[c]	327XXX[d]	766	100%	766	15.3	76.6
All		**14,334**	**—**	**8,299**	**165.8**	**829.9**

[a] TBtu = trillion Btu/year. *Source:* U.S. Department of Energy, Energy Information Administration, *1998 MECS Consumption,* Table N3.2, Fuel Consumption, 1998.
[b] Includes heat treatment.
[c] Primarily cement and lime.
[d] Excludes category for glass, 3727XX.

Additionally, one must consider that declines in certain properties may have a direct influence on other related properties. This is evident for example in a furnace wall where lack of corrosion resistance may result in a reduction in thermal efficiency as decreases in wall thickness due to corrosion will lead to decreased insulating ability of the furnace wall. The furnace efficiency will now not only be impacted, but thinning of the refractory wall may also lead to shut-down of the furnace for maintenance causing loss of production and the need for additional energy to reheat the furnace. Energy considerations from all these areas are considered in Table 3.

Figure 1 shows the potential energy benefit opportunities represented by the four furnace types analyzed.

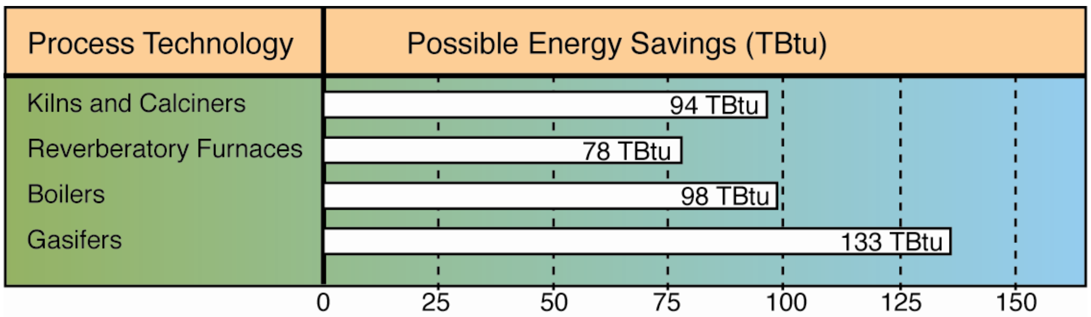

Fig. 1. Long-term energy benefit opportunities estimated for the four analyzed furnace types.

4. Process Technology and Performance Barriers

4.1 Kilns and Calciners

Kilns and calciners, or the products produced by them, are used in many industries (aluminum, cement, chemical, forest products, glass, iron and steel, and mining) and therefore have crosscutting interests. Analyses were performed to evaluate cases for both alumina and lime calcinations, based on use of rotary-type kilns for various flame temperatures, exhaust temperatures, and wall/roof losses (Appendix B). For all the heat supplied by combustion, the gross available heat is calculated from the heat content of the flame less the heat content of the exhaust gases, and a part of the heat supports wall loses while the remainder is available for the work of the kiln/calcinations of feed to product.

4.1.1 Industrial Applications of Process Technology

Aluminum — alumina, carbon, lime
Cement and lime — lime, cement
Chemical and petrochemical — lime
Forest products — lime
Glass - lime
Iron and steel - lime
Mining — raw materials

4.1.2 Current Technology

Two types of kilns typically found in the industries listed were selected for review. In the case of alumina calcination, we considered a kiln measuring 3.5 m in diameter by 80 m long with an output of approximately 250,000 tons/year; for lime calcinations, we chose a kiln measuring 5 m in diameter by 50 m long with an output of approximately 365,000 tons/year. In the lime calcination process, product is often lost through dust loss as loose powder is blown out of the kiln along with the exhaust gases. Therefore, in the lime analysis, both the case of no dust and the more realistic condition of up to 20% of the calcined product being lost as dust were considered. Calculated heat of reactions (at 77°F) of 634 Btu/lb and 1364 Btu/lb were used for the alumina and lime calcination processes, respectively, leading to a calculated total heat requirement of 1728 Btu/lb for the alumina calcination process and 2196 Btu/lb for the lime calcination process.

4.1.3 Energy Impact

Energy benefits resulting from refractories in kilns are related to the following operational improvements:

1. An increase in the adiabatic flame temperature of 200°F (as with modified oxy-fuel firing at about 20% enrichment) can lead to substantial fuel savings due to thermal efficiency.
2. A decrease in the exhaust temperature of 200°F (resulting in greater heat retained for the actual process) also leads to a substantial fuel savings.
3. A decrease in wall/roof losses of 200,000 Btu/ton of product can result in substantial energy savings (considering half the supplied energy goes up the stack, with the remainder available to support work and wall losses).
4. Process yield improvements will result in substantial energy benefits.

For the energy analyses, it was assumed that a little over half of the total calcined alumina produced in the United States (4.4 million metric tons in 2001) was produced using a rotary kiln. Similarly, it was assumed that of the 20 million short tons of lime produced in the United States in 2002, about 80% of the production was performed using rotary kiln calciners. It was also assumed that 80% of the 103 million metric tons of cement produced in the United States in 2002 was produced using rotary kilns operating in the temperature range of 2600 to 3000°F. Results of the analysis are shown in Table 4.

Table 4. Total effect of improved refractories on rotary kilns

Energy-intensive process industries	Product	Fuel decrease (Btu/ton)	Wall loss decrease (Btu/ton)	Tons affected per year	Energy benefits per year (TBtu)
Aluminum	Al_2O_3	413,000	200,000	2,500,000	1.5
Cement and lime	Cement	800,000	200,000	82,400,000	82.4
Cement and lime, chemical and petrochemical, forest products, glass, iron and steel	Lime:				
	No dust	413,000	200,000	16,000,000	9.8
	20% dust	885,000	250,000	16,000,000	18.3
All					**112**[a]

[a] Without carbon and sulfur contributions.
Source: Portland Cement Association, *Economic Industry Overview,* 2003.

4.1.4 Barriers Related to Refractory Materials for Kilns and Calciners

The central conclusion from the analyses for concerning kilns and calciners is that as flame temperatures increase and exhaust temperatures approach process temperatures, greater thermal efficiency is realized. Hence, improvements in reducing the thermal conductivity of the refractories, and improving the chemical and mechanical properties of the refractories, will have a significant payoff in overall fuel consumption. Addressing the following barriers associated with the performance of refractory materials used in kilns and calciners would improve energy efficiencies.

1. Unavailability of refractories with sufficient high-temperature strength, erosion/corrosion resistance, creep resistance, resistance to large temperature gradients, and stability at higher temperatures for use with elevated furnace flame temperatures.
2. Lack of sufficient high-temperature durability and corrosion/erosion resistance in current refractories for improved heat transfer through increased levels of stirring and agitation of the material being processed.
3. Unavailability of refractories with lower thermal conductivity and greater high-temperature stability needed to achieve substantial reductions in wall and roof heat losses.
4. Lack of knowledge concerning operations needed to increase refractory life, reduce product sticking, and increase levels of product recovery for the reduction of unscheduled outages, improvement of product yield, and the increase of furnace campaign lives.

4.2 Reverberatory Furnaces

Analyses of reverberatory furnaces were performed to evaluate cases of aluminum, copper, and glass-melting furnaces for various assumed values of flame temperatures, exhaust temperatures, and wall/roof losses. For all the heat supplied by combustion, the gross available heat is the heat content of the flame less the heat content of the exhaust gases. Additionally, part of the gross available heat supports wall losses and the remainder supports melting, the real job of the furnace. Reverberatory furnace schematics are provided in Appendix C.

4.2.1 Industrial Applications of Process Technology

Aluminum — metal melting	Metal casting — metal melting
Glass — glass melting	Copper — metal melting
Iron and steel — metal melting	

4.2.2 Current Technology

Analyses of reverberatory furnaces were based on a nominal furnace having a capacity for melting 20,000 lb of material per hour. This is a typical size used in the aluminum industry and is used for the other industrial analyses for comparison purposes. For the fixed melting capacity of 20,000 lb/h, the energy needed for melting is the same in all aluminum melting cases, 504 Btu/lb. In the analysis, wall and roof losses from 0 (really impossible) to 10 million Btu/h, or 0 to 500 Btu/lb of material, have been assumed. This range is expected to span the full spectrum of industrial practice. The gross available heat to do these jobs is the difference in flame and exhaust heat contents. It has been assumed that natural gas fuel with an adiabatic flame temperature of ~3600°F has been used as a base, with increasing flame temperatures that may be achieved through regenerators/recuperators or oxygen enrichment.

Exhaust temperatures ranging from 1400 to 2000°F have been assumed. Increasing exhaust temperatures at fixed flame temperatures results in total heat consumptions ranging from 777 Btu/lb (61% thermal efficiency) to 2261 Btu/lb (22.3% thermal efficiency). Furnaces in the aluminum industry generally fall in this range, as summarized below:

Furnace type	*Thermal efficiency*
Normal furnace (poor to good practices)	2500–1350 Btu/lb
State-of-the-art new furnace	1350–1200 Btu/lb
Furnace builders' lower limit for reverb.	1200–1000 Btu/lb
New/radical technology	1000–504 Btu/lb

Similar efficiencies are expected in the other two industries studied.

4.2.3 Energy Impact

Energy benefits that could result from improved refractories in reverberatory furnaces are related to the following operational improvements:

1. An increase in the adiabatic flame temperature of 200°F (e.g., oxy-fuel firing with 20% oxygen) leads to substantial fuel savings due to thermal efficiency.
2. A decrease in the exhaust temperature of 200°F (resulting in greater heat retained for the actual process) also leads to a substantial fuel savings.
3. A decrease in the wall/roof losses of 2.5 million Btu/h also results in substantial energy savings (considering half the supplied energy goes up the stack, with the remainder available to support melting and wall losses).

For the calculations, it was assumed that annually in the United States, 9.3 billion lb of aluminum (half of all the ingot and mill products in the aluminum industry in 1998) are melted in reverberatory furnaces, 0.36 billion lb of refined copper from scrap is processed in reverberatory furnaces, and an average of the 40 billion lb of glass is produced using reverberatory furnaces (based on 1999 numbers). In addition, 20% oxygen enrichment was assumed for the metal melting cases, while 100% oxygen enrichment was assumed for the glass melting case. The details of the calculations are presented in Appendix D. Results of the analysis are shown in Table 5.

Table 5. Total effect of improved refractories on reverberatory furnaces

Energy-intensive process industries	Product	Fuel decrease (Btu/lb)	Wall loss decrease (Btu/lb)	Pounds affected per year ($\times 10^9$)	Energy benefits per year (TBtu)
Aluminum, copper[a]	Metal melting	452	200	10	2 (20% enrichment)
Glass	Glass melting	476	100	40	76 (100% enrichment)
All					**78**

[a] Without iron and steel and metal casting contributions
Sources: American Metal Market, *Metal Statistics 1998,* 90th ed., 1998; DOE Office of Industrial Technologies, *Energy and Environmental Profile of the U.S. Glass Industry,* 2002.

4.2.4 Barriers Related to Refractory Materials for Reverberatory Furnaces

The central conclusion from these analyses is that as flame temperatures increase and exhaust temperatures approach process temperatures, greater thermal efficiency is realized. As shown in Appendices B, D, and E, the impact of reducing wall losses by 2.5 million Btu/h leads to corresponding savings of 4.5 million Btu/h for aluminum (232 Btu/lb), 7.5 million Btu/h for copper (333 Btu/lb), and 11.9 Btu/h for glass (595 Btu/lb). Hence, improvements in reducing the thermal conductivity of the refractories, and improving the chemical and mechanical properties of the refractories, will have a significant payoff in overall fuel consumption. Addressing the following barriers associated with the performance of refractory materials used in reverberatory furnaces would improve energy efficiencies.

1. Unavailability of refractories with sufficient high-temperature strength, erosion/corrosion resistance, creep resistance, resistance to large temperature gradients, and stability at higher temperatures for use with elevated furnace flame temperatures.
2. Lack of sufficient high-temperature durability and corrosion/erosion resistance in current refractories and materials for improved heat transfer through increased levels of stirring and agitation of the material being processed.
3. Unavailability of refractories with lower thermal conductivity and greater high-temperature stability.
4. Lack of knowledge concerning the interactions between refractories and process environment/operations which leads to reduced refractory life, product sticking unscheduled outages, low product yield, and limited furnace campaign lives.

4.3 Boilers and Reactor Systems

Boilers and reactor systems are found in most industrial settings and therefore are of key interest as a crosscutting unit process. For the following analysis, boilers for the production of steam are considered for the aluminum, cement and lime, chemical and petrochemical, forest products, and heat treatment industries. (See Appendix E for a schematic illustration of boiler furnace sections.) Additional areas for energy efficiency improvements also exist in chemical reactors utilizing catalysts and other reactions.

4.3.1 Industrial Applications of Process Technology

Aluminum — steam production
Cement and lime — steam production
Chemical and petrochemical — steam production
Forest products — steam production
Heat treatment — steam production

4.3.2 Current Technology

For the purpose of the performance analyses of boilers, a standard unit using a single header boiler system has been assumed.

4.3.3 Energy Impact

Improved refractory practice in boilers will result in energy benefits either from improving the boiler efficiency through improved vessel insulation and/or by reduced heat losses during steam transfer through improved transfer pipework insulation.

The DOE Best Practices Steam System Assessment Tool was used to analyze the effects of improving boiler efficiency from 85 to 87% through use of the following:

- Improved insulation for improved boiler efficiency
- Improved pipework insulation for improved steam transfer systems

The effects of increasing boiler efficiency by 2% and reducing heat losses during steam transfer by 10% are shown in Tables 6 and 7.

Table 6. Steam system assessment tool single header analysis results for improved insulation for improved boiler efficiency

Variable	85% efficient boiler case	87% efficient boiler case	Improvement	
Fuel cost, \$1000/year	4,000	3,908	92	(2.30%)
Fuel consumption, std ft^3/h	71,421	69,799	1,622	(2.27%)
CO_2 emissions, 1000 lb/year	66,403	64,876	1,527	(2.30%)
NO_x emissions, 1000 lb/year	131	128	3	(2.29%)

Table 7. Steam system assessment tool single header analysis results for improved pipework insulation for improved steam transfer systems

Variable	Current operation	10% improvement	Improvement	
Fuel cost, \$1000/year	4,000	3,924	76	(1.90%)
Fuel consumption, std ft^3/h	71,421	70,065	1,356	(1.90%)
CO_2 emissions, 1000 lb/year	66,403	65,142	1,261	(1.90%)
NO_x emissions, 1000 lb/year	131	129	2	(1.53%)

As shown in Table 6, a 2% improvement in boiler efficiency leads to a 2.3% improvement in fuel cost and consumption, while the 10% improvement in the efficiency of the transfer pipework insulation leads to a 1.9% improvement in fuel cost and consumption. As shown in the tables, there are also decreases in emissions associated with improvements in boiler efficiency and pipework insulation. If these fuel savings are then applied to the chemical, petroleum refining, and pulp and paper industries, estimates can be made concerning the possible energy savings resulting from implementation of these improvements in each industry. Table 8 shows the results of such an analysis.

Table 8. Potential energy savings from improved boiler efficiency due to improved refractories and improved transfer pipe-work insulation

IOF industry segment	TBtu	%	Capture basis (%)	Projected fuel savings (TBtu)
Chemical industry steam opportunities				
Present usage of fuel for generating steam	1,540			
Opportunity for improving boiler efficiency from 85 to 87%		2.3		
Fuel saved	35			
Opportunity for reduced line heat losses by 10%		1.9		
Fuel saved	30			
Chemical industry fuel reduction	*65*		*40*	*26*
Pulp and paper steam opportunities				
Present usage of fuel for generating steam	2,596			
Opportunity for improving boiler efficiency from 85 to 87%		2.3		
Fuel saved	60			
Opportunity for reduced line heat losses by 10%		1.9		
Fuel saved	49			
Pulp and paper industry fuel reduction	*109*		*40*	*44*
Petrochemical steam opportunities				
Present usage of fuel for generating steam	1,675			
Opportunity for improving boiler efficiency from 85 to 87%		2.3		
Fuel saved	39			
Opportunity for reduced line heat losses by 10%		1.9		
Fuel saved	31			
Petrochemical industry fuel reduction	*70*		*40*	*28*
Total steam opportunity	**244**		**40**	**98**

According to the DOE-EERE Best Practices report concerning steam usage in the chemical manufacturing, pulp and paper, and petroleum industries,[4] 1540, 2596, and 1675 TBtu of fuel, respectively, is used to generate steam per year by each industry (see Table 8). As can be seen, on a 40% capture basis (i.e., 40% of the existing plants will use the improved refractory and insulation systems), the levels of projected fuel savings are 26, 44, and 28 TBtu, respectively, for the chemical, pulp and paper, and petroleum refining industries. This results in a total projected fuel savings of 98 TBtu across the three industries.

4.3.4 Barriers Related to Refractory and Insulating Materials for Boilers and Reactors

The central conclusion from these analyses is that decreased fuel consumption resulting from improved boiler efficiency can be achieved through better insulation practices. As shown, the impact of increasing boiler efficiency by 2% and reducing heat losses during steam transfer by 10% will result in a total fuel savings of 98 TBtu for the industries studied. Addressing the following barriers associated with the performance of refractory and insulating materials used in boilers and reactors would reduce energy requirements:

1. Unavailability of insulating refractories with sufficiently low thermal conductivities to lead to increases in energy efficiency levels for boiler operations.
2. Unavailability of improved insulating materials for transfer pipework that could help reduce heat losses during steam transfer operations.

4.4 Gasifiers

Gasifiers are currently being used in the chemical and petrochemical industry for coal and biomass gasification and in the forest products industry specifically for black liquor gasification. This technology has the potential for biomass solid fuels to be converted into fuel gas “syngas” consisting largely of hydrogen (H_2) and carbon monoxide (CO). This gas can then be burned cleanly and efficiently in a gas turbine to generate electricity and/or used to synthesize clean transportation fuels or chemicals.

Gasification is currently used in the chemical industry as a means to produce clean energy, high-value energy products, and various petrochemicals from coal (including the possibility of producing hydrogen fuel, high-grade transportation fuels, and industrial-grade methanol). Experimental gasifiers are being applied in a few chemical and pulp and paper plants for coal or black liquor conversion, while gasification is also being used as a means of using biomass as an energy source rather than a waste product. In the future, the forest products industry may use gasification to replace Tomlinson boilers.

A limitation on the use of these experimental gasifiers is the lack of reliable refractories for containment. If the refractory requirement could be met, coal, black liquor, and biomass gasification could lead to greater reductions in purchased energy and even change these industries from net energy importers to net energy exporters.[5] Gasification holds the promise of generating 175% more electrical power than do current technologies, but the gasification technology currently in use requires frequent refractory relines of the vessels, hence reducing the economic and energy benefits.[5] Additionally, although chemical or pulp and paper manufacturing facilities are not currently used to produce transportation fuels from biomass, they may become a valuable asset for establishing an infrastructure for such technology. Future gasification-based “biorefineries” might produce a variety of renewable fuels, electricity, and chemicals in conjunction with pulp and paper products.

4.4.1 Industrial Applications of Process Technology

Chemical and petrochemical — coal and biomass gasification
Forest products — black liquor gasification

4.4.2 Current Technology

A coal gasifier generally consists of a metallic shell protected by a lining made up of two to six concentric layers of refractory protecting the interior of the vessel. Coal gasifers are expected to operate at high temperatures and moderate pressures, and with gas and particle flows containing H_2, CO, H_2O, C, H_2S, HCl, hydrocarbons, metallic impurities, and salts. These linings have average lifetimes on the order of 7000 run hours and generally fail because of excessive mechanical wear (erosion), chemical penetration of slag into the structure of the innermost brick (corrosion), or some combination of these two mechanisms. Erosive wear occurs as the feedstock itself causes physical decay of refractory hot-face surfaces when injected at high velocities. Corrosive attack occurs when the coal slag residues penetrate the refractory hot face surface, thus weakening the refractory by forming solid-solution phases.

The nominal scale of an average pulp and paper mill is 6 million lb/d of black liquor solids (BLS)—the equivalent of 1.5 million Btu/h or 438 MW fuel—corresponding to 1900 machine dry short tons per day of paper production (1725 metric tons).[5] Pulp mills processing more than 6 million lb/day BLS account for about one-third of all U.S. capacity today, and this fraction will grow over time as mill consolidations continue. A standard sized gasifier for this size mill is considered. This unit was assumed to have a BLS concentration of 80% and a steam pressure of 1870 psia.

4.4.3 Energy Impact

For the following analysis, we considered a combined-cycle gasifier typical of those used for coal or black liquor gasification with the requirements above. Combined-cycle black liquor gasification has the potential of producing more than twice the current output of electricity per ton.[5] In many cases, power in excess of a chemical or pulp mill's needs could be produced and exported. Further, if gasified coal or black liquor were converted to a high-quality synthetic gas similar to syngas produced from fossil residual oil, the energy and economic benefits would be even greater. Conventional processes could then be used to convert the gas to liquid fuels or hydrogen.

According to the economic and energy analysis performed by Larson et al.,[5] full implementation of the black liquor gasification initiative could achieve the following energy benefits by 2020:

1. Production of up to 8 GW of electricity from sustainable, renewable raw materials by 2020 through black liquor gasification alone.
2. Production of 16 GW or more of electric power for the application of black liquor gasification in conjunction with wood residual gasification by 2020.
3. Alternatively, displacement of more than 282 million barrels of oil per year if these technologies were applied to syngas production to be used for liquid fuels.

The total of these biomass energy sources consumed at pulp mills in 2002 was estimated at 1.6 quads (one quad is 10^{15} Btu).[6] The potential renewable energy generation potential from black liquor in the pulp and paper industry in the southeastern United States is shown in Table 9.

Refractories and insulation materials play key roles in many of the unit operations involved in both of these industries. It is estimated that processes affected by refractories account for about 40% of the industries' direct energy consumption. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for these two industries could lead to energy savings opportunities up to 129 TBtu/year.

Table 9. Renewable energy generation potential (billion kWh/year) from black liquor in the pulp and paper industry in the southeastern United States

Technology	Potential by 2020 (billion kWh/year)	Equivalent energy (TBtu/year)
Chemical		**440**
Conventional coal combustion (33–35% efficient)		726 (energy needed)
Combined cycle gasification (45–50% efficient)		660 (energy needed)
Total improvement		*66*
Forest products		
Tomlinson recovery boiler	4.4	15
High-efficiency Tomlinson recovery boiler	16.7	57
Combined cycle gasification	36.2	124
Total improvement		*67*

4.4.4 Barriers Related to Refractory Materials for Gasifiers

Addressing the following barriers associated with the performance of refractory materials used in gasifiers would reduce energy requirements:

1. Unavailability of advanced refractory materials with improved corrosion/erosion resistance, improved reliability, and reduced maintenance costs.
2. Lack of refractories with resistance to high alkali atmospheres and high levels of stress, which lead to gasifier containment issues.
3. Lack of alternate refractory designs which would provide refractory surfaces (using coatings, chemical alteration of refractory surfaces, physical alteration of refractory surfaces, etc.) that are more impervious to wear and corrosive attack.
4. Unavailability of refractory materials with greater thermal compatibility with metallic materials used in gasifiers.

5. Overall R&D Barriers and Pathways for Refractories

Evaluation of refractory usage, barriers, and needs of these several energy-intensive process industries shows that several common themes arise in the pursuit of improving refractory materials for greater energy efficiency. These themes relate to improving energy efficiency by reducing energy loss and increasing productivity through the development of higher-strength refractories capable of operating at higher temperatures, the development of refractories with lower thermal conductivity to reduce wall losses at higher service temperatures, the tailoring of thermal expansion capabilities of current refractories, and the development of refractories with greater resistance to chemical and mechanical wear (corrosion, erosion, abrasion, etc.). This concept is shown in Fig. 2.

Fig. 2. Improving refractory materials for improved energy efficiency.

Through analysis of current refractory use, current barriers, possible improvements in process energy efficiency, and R&D refractory needs for several process industries, many issues common to multiple industries become apparent. The research focus areas and technical R&D topics below have been identified as issues common to many applications of refractories.

1. *Understand the degradation mechanisms of refractories in different environments*
   Determine the mechanisms responsible for the chemical and mechanical degradation of refractories in the various environments in which they operate.

2. *Achieve improvements in thermal control*
   Determine the thermomechanical properties of refractory materials and develop materials that will allow furnaces to operate with longer campaigns and with higher levels of insulation to reduce heat losses. This may also involve the implementation of new furnace designs, the formulation of newly redesigned processes, or the re-engineering of existing industrial practices.

3. *Evaluate thermomechanical properties at elevated temperature*
   Determine the key properties of refractories at elevated temperatures, including hot modulus of rupture, hot crushing strength, creep behavior, refractoriness under load, physical and thermal spall resistance, dimensional changes (elastic modulus, thermal expansion, and growth from chemical alteration), and thermal conductivity.

4. *Form an expert advisory committee*
   Assemble a committee composed of current and retired industry experts to serve in an advisory role for industry-focused refractory R&D projects. Additionally, inventory and preserve existing industrial equipment and facility resources through systematic surveys of refractory experts (especially retirees) so that industrial furnaces and existing laboratories can be utilized, when possible, to augment new experimental system requirements.

6. Specific R&D Areas with Barriers and Pathways

The following text summarizes pathways for overcoming barriers for the six specific R&D areas that can yield the greatest returns in refractories.

6.1 Improved Castable and Monolithic Refractory

Barrier

Inadequate resistance to corrosive and mechanical wear, which limits the use of castable and monolithic refractories.

Pathways

- Fabricate fusion-cast refractories (such as alumina zirconia refractories) that do not include silica or other glass formers. These refractories should possess greater corrosion resistance and thermoelastic properties. The refractories would be of use to industries such as glass, pulp and paper, and many others.
- Fabricate components for continuous measurement of parameters such as temperature, bath chemistry, etc., that will have long-term stability in high-temperature industrial solvents, such as cryolite for the electrolytic production of aluminum. Candidate materials such as HfB_2, HfC, ZrB_2, ZrC, and TaC should be considered.
- Develop oxide/nitride grain boundary additives leading to closure of open porosity in silica, mullite, and magnesium aluminates as used by the glass and other industries.

6.2 Modified Fiber Materials

Barrier

Lack of fiber insulation materials with lower thermal conductivity, greater chemical resistance, and higher temperature stability limits.

Pathways

- Produce frothed latex/fiber mixes for gunning to reduce airborne fibers during installation. Enhance adhesion of materials to steel and other metals for application in heat treatment furnaces. Develop new inorganic binder systems.
- Fabricate fibrous materials with greater strength and lower friability for use in heat treatment and chemical and petrochemical industries.

6.3 Surface Modification (Coatings, Physical or Thermal Alteration)

Barrier

Lack of techniques and materials for applying surface coatings or inducing physical alteration of refractory surfaces through either mechanical or thermal means.

Pathways

- Modify surfaces or near-surfaces of sintered alumina and mullite refractories by applying corrosion/erosion-resistant coatings such as spinel phases (or additional corrosion-resistant materials) for use by industries such as glass, pulp, and paper.
- Determine the effects of "preexisting" refractory heating conditions that, when applied concurrently with high-intensity infrared heating, modifies the surface of bonded refractories and results in the residual compression of a modified surface at service temperatures. One advantage of this could be an increase in the "strain-free" temperature of refractories used in process industries.
- Determine the applicability of radiation-heating attenuation/mitigation, and if applicable, simulate refractory structures that would maximize its effect to optimize radiant heat transfer (e.g., improve oxy-fuel fired systems for the aluminum, glass, metal casting, and iron and steel industries).
- Investigate the effects of radiative heating and transmittance in refractories on thermal conduction for minimizing thermal losses from various types of furnaces used throughout the selected industrial areas.

6.4 Synthetic Aggregates and Powders

Barrier

Lack of higher-performance aggregates that would increase the life and durability of refractory products used across the various industries and lack of higher-quality matrix materials that would increase the durability of refractories.

Pathways

- Measure and model strength as a function of aggregate size distribution. Tailor microstructure so that flexure and compression strengths are increased.
- Explore candidate aggregate coatings as "additives" that control or binder grain boundary effects (e.g., diffusion, heat transfer, corrosion-resistance, etc.) for improved refractory processing.

6.5 High-Temperature Properties of Refractories

Barrier

Lack of information on the high-temperature thermomechanical and corrosion properties of current and newly developed refractory materials.

Pathways

- Develop realistic test methods and environmental tests systems in order to evaluate elevated temperature properties. Evaluate corrosion behavior of refractories for various effects of water/CO/CO_2/alkali content on the corrosion and phase stability of refractories used in gasifiers and in the glass, aluminum, steel, and metal casting industries. Develop lab-scale systems to evaluate the degradation of refractories up to 2000°C.
- Systematically characterize and model reheat-generated permanent expansion effects in fusion-cast and bonded refractories, a phenomenon known to occur in many refractory systems used throughout the various process industries, but not currently understood.

- Perform postmortem analysis on failed refractory components from several industries and identify service-limiting flaw types. Use component samples for measurement of strength distribution and compare to strength distribution of virgin materials. Perform probabilistic strength-size-scaling analysis using both distributions as input and predict failure time of components.
- Measure the corrosion resistance of bonded refractories as a function of refractory sintering temperature and interpret the performance in reference to service temperature.
- Investigate the effect of specimen size in refractories by measuring strength (modulus of rupture) as a function of specimen size in bonded or fusion-cast refractories. Determine if variations in strength can be represented by a Weibull distribution and if strength is size-scaled.

6.6 In Situ and Graded Refractories

In situ refractories are defined as brick or unshaped products that react internally or with furnace atmospheres and/or slag components to enhance their performance. Natural in situ formation of Fe-Mg-O spinels in steel-making furnaces permits improved life and durability of these furnaces.

Barrier

Lack of R&D to improve existing in situ refractory systems and for development of new in situ systems for additional industrial applications

Pathways

- Model crack initiation and growth as a function of material, depth, and service properties using microstructure-based finite element analysis (e.g., μ-FEA, OOF). Simulate and optimize hypothetical microstructures that hinder crack growth.
- Develop high-intensity infrared heating techniques to fabricate optimized graded refractory structures, and measure thermomechanical stability and corrosion resistance.
- Model, simulate, and design refractory microstructures that promote maximum creep and erosion resistances.
- Determine the effect of crystallography of base and in situ phases on the development of thermal stresses and the stability of in situ layers.
- Determine and optimize “substrate” surface geometries (e.g., dimples, corrugated, saw-tooth) that will minimize shear stresses in thermo-environmental barrier refractory coatings that are subjected to a thermal gradient.

6.7 Sensors for Materials Performance

Barrier

Lack of sensors to monitor refractory-related issues including wall thickness regression, gas phases, and other environmental conditions.

Pathways

- Develop sensors and methods for the measurement of spectral emissivity for application in glass tanks and metal melting furnaces.
- Develop sensors and methods for the monitoring of wall regression due to corrosion, erosion, and wear in glass tanks and metal melting furnaces.

- Develop continuous real-time measurement techniques for parameters such as temperature, pressure, melt analysis, flue gas analysis, and environmental gas phases.

The tasks and the industries which will benefit from the projects described above are shown in Table 10. As is evident from the table, these suggested R&D pathways are crosscutting. Although there is a current trend for many of these industries moving overseas, it is believed that the R&D pathways proposed will directly benefit U.S. industry. Even as processes such as aluminum smelting and glass production move off shore, there will still be a need for remelting and other production domestically.

Table 10. Recommended R&D pathways for advanced refractories

Technical R&D potential pathways	Industry segment							
	Alumi-num	Cement & lime	Chem. / petro-chemical	Forest products	Glass	Heat treatment	Iron & steel	Metal casting
Improved castable and monolithic refractories	X	X	X	X	X	X	X	X
Modified fiber materials			X			X		X
Surface modifications (coatings, alterations)	X	X	X	X	X		X	
Synthetic aggregates and powders	X	X	X		X	X	X	X
Elevated temperature refractory properties	X	X		X	X	X	X	X
In situ and gradient refractories	X	X	X	X	X		X	X
Sensors for materials performance	X	X	X	X	X	X	X	X

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APPENDICES

Appendix A: Discussion of Refractory Usage by Process Industries

A.1 Aluminum

Current Industry Operations and Refractory Use

Aluminum production is energy-intensive, consuming about 0.4 quads of electrical energy per year in the United States.[1] Additionally, the industry faces many of the same competitive pressures as the steel industry, including global competition, energy consumption issues, and pollution abatement. Therefore, a technology road map has been created to address these issues by targeting areas such as energy consumption, productivity, emissions, recycling, quality, alternate technologies, and by-products.[2]

Many systems are used in the production of aluminum and its alloys, all of which depend on the proper selection and management to ensure the cost effectiveness of the metallurgical and refractory practices. These systems include steam boilers for Bayer plants, calciners, and carbon baking furnaces used for the production of the anodes which are consumed in the Hall-Heroult reduction process. In Hall-Heroult electrolytic reduction cells, the key refractories are those used to support the cathode hearth and to minimize the penetration of bath constituents into the carbon cathode and underlying refractories. Melting furnaces for alloy production by the primary and secondary producers include large fossil-fuel-fired reverberatory furnaces as well as a variety of induction furnace designs dominated by the coreless and the channel induction types. Temperatures and corrodant chemistries, as well as furnace atmospheres, determine the lining used for each of these processes. The refractories used for each will be briefly reviewed.

Primary Aluminum Production

The production of primary aluminum metal is based on three major steps. The first involves the *mining of bauxite ore.* There are no high-grade deposits in the United States; therefore, refractories play little role in this process.

The second process involves the *conversion of bauxite to metallurgical grade alumina*. The Bayer process is based on digestion of bauxite in caustic solution heated with superheated steam to form sodium aluminate. Impurities are removed from the pregnant caustic by chemical reactions with dissolved species (primarily SiO_2) and filtration of insoluble impurities (primarily iron oxide). The saturated solution is then cooled in precipitator tanks in which aluminum trihydrate is precipitated and then recovered by filtration. The aluminum trihydrate is converted to alumina by calcination. Two methods of calcination are employed in the industry: use of fluid bed calciners and use of rotary kilns.

The third process involves conversion of alumina to aluminum by *electrolytic reduction* using the Hall-Heroult process. In the reduction process alumina is dissolved in a molten bath (cryolite, Na_3AlF_6, with additions of AlF_3, CaF_2, and sometimes LiF and MgF_2). The cell for this process utilizes a containment system consisting of a steel shell lined with a castable refractory, a porous insulating refractory, a less porous semi-insulating refractory, and finally firebrick. A carbon cathode acts as the bottom of the cell for molten aluminum containment. The side-wall refractories are generally phosphate-bonded alumina brick or alumina castable materials. Because the sides of cell have less insulation, more heat is lost through the walls than the floor. The lower wall temperature is actually beneficial, causing electrolytes in contact with the wall to solidify and form a "frozen ledge" which protects the walls of the cell from penetration by molten cryolite. This practice is successful, but involves a trade-off between energy efficiency and electrolytic cell stability and lifetimes in terms of energy consumption.

Reduction cells currently employ various refractories just below the carbon cathode which during service degrade in various ways, permitting bath constituents to move into the cathode carbon and refractories. The systems in place today include fireclay bricks, castable refractories, semi-insulating refractories, and insulating bricks. Systems for primary aluminum production involve several different designs depending on the level of amperage and the numbers and array of anode blocks. The current intensity for operating reduction cells throughout the world ranges from 60,000 to 500,000 A. Yet, they all still involve a carbon cathode hearth and consumed carbon anodes in which the bauxite ore charge and the systems of alkali fluoride fluxes are placed and held while the reduction process is carried out continuously. Typically the reduction process is carried out at a temperature in the range of 960 to 970°C. The refractories are key components in reduction cells. The atmosphere inside the cavity of a reduction cell is very reactive, containing a mixture of CO_2, CO, HF, SO_2, and particulate fluoride salts.

In all cases it seems that the formation of a feldspathic composition at the interface between the cathode and the barrier is highly desirable but that other bath species can still penetrate the barrier and lead to highly shortened cell life. Further, downward movement of alkalis and bath constituents through the hearth toward the subhearth insulation eventually results in the failure of the furnace, an event which is still quite unpredictable. Because of this, furnace lives vary from hundreds to thousands of days.

Taberaux[3] has reviewed the failure mechanisms of aluminum reduction cell systems. Fireclay brick in one reported case lasted over 3000 days, showing that the material itself can meet the challenge, all other factors being optimal in their selection and control. Castables have disadvantages in cast-in-place systems, and currently the preference is for precast monolithic systems, which have had good success. Two types of dry barrier refractories are currently being used. Their advantages rest on ease and rapidity of installation and lack of joints. They include aluminosilicates on the one hand and anorthite feldspar on other, chosen because it undergoes beneficial in situ reactions and is, in fact, patented.

Carbon anode baking furnaces have historically been constructed of aluminosilicate bricks. These bricks have sufficient refractoriness that efforts to replace them with alumina-reinforced versions have not been cost-effective. The challenge to the brick comes from its coking and from the alkalis present in the electrode feedstock. Most recently, fireclays with very low alkali content have been used for the production of bricks increasingly designed with surface locking systems that reduce the bowing of walls, which is the principal reason for the replacement of the refractories. Because such large numbers of bricks are used in carbon baking furnaces, attempts have been made to recycle them, but past efforts have not resulted in the formulation of a cost-effective protocol.

Schubert[4] recently addressed the basic issues of movement of the flue walls, and points to the findings in postmortems that the insulation may be inadequate for the support role that it plays. The many challenges to the flue walls include (1) alkali infiltration and attack from bath carryover, via recycled anode butts in the recipe; (2) fluoride salt attack from bath carryover, via recycled anode butts in the recipe; (3) minor "squatting" from elevated temperatures and load; (4) mechanical damage from impact of the anode and/or the crane during loading and unloading; (5) thermal shock, especially during the cooling cycle; (6) construction details that aggravate normal wear and tear; (7) various problems due to improper expansion allowances; and (8) coke sticking to refractory, aggravated by alkali content.

Semifabricated and Secondary Aluminum Production

Secondary aluminum production involves *recycling of aluminum metal scrap*. This is carried out in a variety of furnace designs. When large volumes of alloy are required, reverberatory furnaces are traditionally used. These furnaces have seen a constantly evolving refractory practice. Monolithics replaced bricks in the distant past, and currently monolithics in the form of precast "big blocks" are receiving renewed interest. A recent paper by Canon[5] reports that the real advantage of precast furnace components rests in the time savings rather than in the extension of service life.

As in the case of the subhearth refractories used in pot furnaces, it is essential to develop a freeze zone in the walls of all the furnaces. This is done by selection of refractories and appropriate thicknesses. It is also essential to restrict the penetration of the aluminum alloy into the refractory, which is achieved by incorporation of additives, some of which are proprietary. As it is impossible to keep oxygen from reacting with the aluminum metal, a so-called bellyband develops in all types of melters. Because of the fluctuating level of the metal in some furnaces, the bellyband can be quite wide and eventually extend into the furnace to such an extent that it must be removed. In the case of the largest reverberatory types of furnaces the removal is sometimes carried out using large robotic devices. In many instances the furnace has to be shut down to effect adequate removal. In the hearth region of the melter, linings of silicon nitride–bonded silicon carbide are used for molten aluminum contact areas.

After melting, the molten aluminum flows through refractory-lined troughs between the various process steps. These troughs are typically lined with oxide ceramics such as fused silica or mullite with 10–15% porosity and special additives to resist wetting. These materials are installed in board or castable form and are used due to their low thermal expansion and good thermal shock resistance. Still, erosion and abrasion issues are of concern. SiC-based materials have been considered for this application but are more expensive than oxide refractories.

Bellyband buildup is the overriding issue in melting furnaces. Quesnel et al.[6] have reviewed the problem for aluminum holding furnaces and melters. There is a lack of understanding concerning the mechanisms of bellyband formation. The two types of tests typically used in the study of candidate refractories are a bellyband corrosion test (which is a simple cup test) and an immersion test (which really looks at the penetrability of the refractory by the metal). Long use of these tests has produced inconclusive answers about the mechanism of attachment, and it is apparent that new approaches are needed.

Barriers

Refractories play key roles in most of the unit operations involved in the production of primary and secondary aluminum. It is estimated that about 90% of the direct energy use by the industry is in processes affected by refractories. Recommended improvements for refractories include applications for refining, reduction, carbon anode baking, and melting operations. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for the aluminum industry could lead to energy savings opportunities up to 29.2 TBtu/year. The specific barriers are as follows:

- *Aluminum Refining*

  Unavailability of improved refractories for superheated steam generation, as well as improved refractories for calcining operations, particularly rotary kilns for alumina and lime, which could lead to improved energy efficiency for refining operations.

- *Aluminum Reduction*

  Lack of understanding concerning the mechanisms and degradation scenarios leading to the failure of reduction cell refractories and, ultimately, the reduction cell. Further, there is a lack of improved linings and refractories with improved resistance to bath penetration that would permit extended lives for reduction cells.

- *Carbon Anode Baking Furnaces*

  Unavailability of stronger insulating shapes for components of carbon baking furnaces.

- *Aluminum Melting Furnaces*

  Lack of understanding regarding the mechanisms of bellyband buildup formation. This is complicated by the inability of current tests to provide conclusive answers regarding the mechanism of attachment and to provide sufficient performance projections.

R&D Pathways

- *Refining*
  - Develop improved refractory and insulation systems for high-temperature steam generation.
  - Improve refractory materials for calcining operations, particularly for rotary kilns.
- *Reduction*
  - Develop a fuller understanding of cell refractory failure through chemical and physical modeling of the reactions and transport mechanisms. Develop knowledge and control of all aspects of the chemical and physical properties of the refractories, and optimized refractory design approaches for reduction cells carrying increasing current intensities.
  - Develop a sidewall refractory design that would allow direct contact with the molten cryolite bath, permitting elimination of the “frozen ledge.”
  - Develop refractories with improved toughness, impact resistance, and abrasion resistance for the hearth region of reduction cells.
- *Carbon Baking*
  - Develop understanding of the manner in which insulation components are being affected chemically and mechanically by the loads from the overlying charge and wall refractories. Perform studies of the mechanical properties of such used refractories to provide answers to these and related questions tied to assuring thermomechanical stability.
  - Develop improved refractories and furnace designs for reducing energy consumption in carbon melting furnaces though modeling of design, process control, quality control, and selection of hot-face refractories, not only in the flue walls but in other components of the furnaces.

- *Melting Furnaces*
    - Develop more accurate simulations of the melting process.
    - Develop a materials approach that involves the development of graded monolithic linings, cast in place or precast, which have much denser surface regions and might also contain additives to dissuade penetrants. Determine the key factors which affect penetration and attachment such as the permeability of the surface region to the metal or altered metal.
    - Develop improved refractories for aluminum melting and casting operations, including advanced refractories for reverberatory melting furnaces and prefired refractory riser tubes for low-pressure aluminum die casting applications that are economical, strong, thermal-shock-resistant, and nonwetting to molten aluminum, and that have low gas permeability.
    - Develop efficient, long-life degassing components for aluminum alloy production.

A.2 Cement and Lime

Current Industry Operations and Refractory Use

The United States is the third largest cement-producing country in the world (after China and India). The production of cement and its intermediate product, cement clinker, has risen steadily over the last decade, with consumption increasing 40% while production has only increased 27%. This has led to increased imports in the short term, mainly from Canada and Mexico, but could lead to further expansion of the domestic industry in the long term. Currently, there are 115 cement manufacturing plants in the United States, with about 75% of the total plants owned by only 10 large companies: Lafarge North America, Inc.; Holcim (US), Inc.; CEMEX, SA de CV; Lehigh Cement Company; Ash Grove Cement Company; Essroc Cement Corporation; Lone Star Industries, Inc.; RC Cement Company; Texas Industries, Inc. (TXI); and California Portland Cement Company.

The 1997 Economic Census report (sampling 279 establishments) shows that refractories (clay or non-clay) account for 2.5% of the total cost for the cement industry, or approximately \$61.5 million of the total \$2.5 billion spent.

A typical modern cement plant may include the following refractory lined units: (1) a preheater equipped with several cyclones as a heat exchanger, (2) a precalciner with a burner for the decarbonization process, (3) a kiln, and (4) a kiln cooler. The preheater, cyclones, and heat exchangers heat the cement raw meal or slurry before it is passed to the rotary kiln. This aids fuel economy by decreasing the amount of heat that the kiln must supply. The precalciner uses preheated combustion air from the clinker cooler and/or kiln exit gases with separate burners to calcinate up to 95% of the raw material. A precalciner kiln system consisting of a rotary kiln with an external furnace may also be used for heating cement raw meal to calcination temperatures. This system also often has a multistage cyclonic preheater attached to it for further heating efficiency.

The kiln is where cement raw mix is dried, calcined, and burned into clinker at temperatures of 2600–3000°F. Kilns can be rotary (rotating at one to three revolutions per minute) or shaft type and use coal, oil, gas, or other fuel for heating. A rotary kiln will generally be divided into zones for drying, preheating, calcining, burning, and cooling. Kilns having a preheater and/or precalciner do not usually contain the first three zones. The molten batch emerges from the lower end of the kiln in the form of very hot, marble-sized chunks known as “clinker.” Once out of the kiln, the clinker goes through a cooling process in the kiln cooler. When cool, the clinker is ready to pass through a series of grinding and milling processes that result in the gray powder we know as cement.

The kiln is the heart of the plant and is generally lined with fired bricks. Monolithic refractories are used only in tapered parts of the inlet chamber, the manhole of the calciner, and the charging inlet of the kiln. These monolithics are required to posses high resistance to reaction with cement raw materials, high resistance to penetration/infiltration of alkalis, as well as high resistance to mechanical stress. Generally, dense low-cement, high alumina castable with service temperatures of 1700–1800°C (3092–3272°F) is used here.

A typical long kiln will include a drying zone, a preheating zone, a calcining zone, a burning zone, a transition zone, and a cooling zone to create a temperature profile in the kiln. Generally, fireclay bricks or high-alumina bricks are used in the drying and calcining zones. Lightweight insulating bricks are used to reduce the heat loss from the kiln. In these zones, refractories are subjected to abrasion and structural spalling caused by reactions with alkali from the cement raw materials. The temperature is relatively low in these zones, but because of the use of various wastes as fuel and constant temperature fluctuations, the refractory wear can become severe. Fuel types vary among petroleum coke, tires, solid wastes, etc., resulting in increased concentrations of alkalis (Na, K), sulfur (S), and chlorine (Cl) as well as other environmentally detrimental metals (Pb, Zn). As a results, the refractories are subjected to harsher alkaline sulfate [$(K_3Na(SO_4)_2$, K_2SO_4] and alkaline chloride (KCl, NaCl) condensation at cooler zones. Sulfur additionally combines with the cement component (CaO) to form $CaSO_4$ cotectic liquid. These liquid and vapor phases infiltrate into bricks, resulting in refractory densification, increased thermal conductivity, and thermal expansion which ultimately reduces the structural flexibility of kiln linings. Additionally, the increase in thermal conductivity often damages the steel shell.

Monolithic refractories are also used in sections of cement kilns, typically at the outlet where wear rates are very high. At these zones, dense silicon carbide–based castables are often used. The cyclones in the preheater section of cement plants are also lined with dense castables, due to the complexity of their shapes and the wear resistance required. The shell of the exhaust gas duct is made from both dense and insulating castable material. In the cooler section of the plant, monolithic refractories are used to line the ceiling. The upper and middle cyclones of the calciner are generally lined with fireclay castable or equivalent gunning materials possessing a service temperature of 1400–1500°C (2552–2732°F). One common problem with this arrangement arises when cement raw materials reach the inlet chamber and riser because they adhere (stick) to the refractory lining and thus cause clogging. This clog is either mechanically removed or removed with high-pressure water.

In the United States, as in most industrialized countries, two types of manufacturing processes have become prevalent in the cement industry; these are known as the “wet process” and the “dry process.” Although in many respects these processes are the same, or very similar, in the older wet process, ground raw materials are mixed with water to form a thick liquid slurry, while in the dry process crushed limestone is used and raw materials are mixed together without the addition of water, leading to higher energy efficiency, since drying is not needed. Currently there is a general trend in the United States to convert wet kiln technology to dry kiln technology; as a result, in 2000 there were 32 wet and 77 dry kilns.

The major fuels used in U.S. cement plants are coal and coke, or coal and petroleum, and are used for the clinkering process. After 1980, however, other fuels—including tires, solid and liquid hazardous wastes, and nonhazardous wastes such as oils and solvents—began to be gradually used. The use of these alternative fuel types has significantly increased in recent years, as shown in Table A.1. Overall, this suggests that there have been no major changes in energy-efficient fuel use in cement kilns since 1990, although more modern plants have been built. The survey, by the Portland Cement Association (PCA), suggests slightly lower average energy uses of 4.73 GJ per million metric ton of clinker and 4.91 GJ per million metric ton of Portland cement for 2000. Further, the 1997 Economic Census report (sampling 279 establishments) showed that energy costs (fuel costs and purchased electricity costs) account for 40% of the total cost for the cement industry, with approximately $485 million spent on fuel and a similar amount spent on electricity.[7]

Table A.1. Feedstock for energy use in the cement industry, 1993-2001 (thousand metric tons)

	1993	1994	1995	1996	1997	1998	1999	2000	2001	% change
Coal	10,034	10,484	8,241	8,764	9.035	9,066	9,206	10,095	10,240	2.05
Coke from coal	NA	NA	455	458	351	432	343	442	420	–7.69
Petroleum coke	NA	NA	1,475	1,295	1,288	1,197	1,622	1,351	1,370	–7.11
Fuel oils[a]	46	49	42	64	86	73	82	124	93	102.2
Natural gas[b]	668	650	1,069	710	672	720	653	338	397	–40.5
Tires	70	120	158	191	277	269	685	374	300	328.6
Solid wastes	90	74	68	72	68	74	816	1,016	320	255.6
Liquid wastes[a]	744	600	885	910	835	1,268	906	929	829	11.4

[a] Millions of liters.
[b] Millions of cubic liters.

Barriers

Refractories play key roles in calcining operations, the core production method for the cement and lime industries. It is estimated that almost all of the energy consumption is affected by refractories. Recommended improvements for refractories include applications for all of the thermal zones of typical rotary calciners. Based on subsequent analyses of typical furnaces and unit processes, improvements to refractory systems for the cement and lime industries could lead to opportunities for energy savings of up to 42.3 TBtu/year. The specific barriers are shown below.

- Unavailability of chrome-free refractories for use in the transition zones of lime kilns, where refractories are subjected to large temperature fluctuations by the repeated detachment and adhesion of the cement coating.
- Unavailability of refractories with adequate corrosion resistance and adhesion (coating) ability for use in the burning zone of lime kilns, where temperatures reach to above 1450°C (2642°F).

- Unavailability of refractory monolithics with high abrasion resistance as well as high resistance to mechanical and thermal spalling for the inlet chamber and riser of kilns to replace less adherent silicon carbide castables and precast shapes.
- Unavailability of monolithic refractory materials with resistance to alkali reaction for use as clinkers in the cooling zone of the kiln to replace low-cement, high-alumina castables used in the area.

R&D Pathways

- Develop monolithics with better abrasion resistance and low or no adherence properties.
- Develop methods to modify the surfaces of clinker zone brick, so as to encourage the formation of protective coatings by physically altering the refractory surface or through chemical alteration of the surface. Develop and improve magnesia-spinel brick and demonstrate the effect of zirconia additions.
- Identify non-chrome-containing refractories which possess increased corrosion resistance to the environment present in cement manufacturing.
- Develop nondestructive techniques for monitoring wear of refractories.
- Develop and improve silicon carbide castables to produce products with improved thermal properties and even less adherence to cement raw materials.

A.3 Chemical and Petrochemical

Current Industry Operations and Refractory Use

The chemical industries have processing equipment that spans a broad range of types, with associated processing temperatures ranging from as low as 370–425°C (700–800°F) to as high as 1870°C (3400°F). The refractory-lined units in a typical full-spectrum refinery can include fluidized catalyst cracking units (FCCUs), catalytic reformers, fired heaters, boilers, hydrogen reformers, ethylene furnaces, incinerators, and carbon furnaces. Some of these units are designed to have substantial insulating capability in their linings, while others are low-temperature-process units, like FCCUs that contain only a single layer of refractory designed to withstand the extremely severe abrasion caused by the catalyst.

The estimated cost of refractory lining installation and maintenance work for the chemical and petroleum industries is relatively low (as low as 1% of the total operating cost) compared to other equipment construction and maintenance costs; yet, refractory lining degradation and failure are leading factors for frequency and duration of shutdowns. Due to lower operating temperature, as compared to other industries, refractory is not normally affected by high temperatures, yet refractory degradation may be caused by erosion, corrosion, and mechanical stresses caused by thermal cycling, depending on location of the refractory within the unit. Another problem that can affect refractory reliability is the manner in which the refractory is installed (i.e., pneumatically gunned, shotcreted, vibration cast, pump cast, and/or hand packed). Additionally, with operating time, minor imperfections can become locations of exacerbated lining degradation. Lining design (i.e., anchoring, lining thicknesses, and design of construction/expansion joints) can also add to lining degradation.

Also, the total tonnage of refractories in an average-sized full-spectrum refinery can be as high as 1000 tons of refractory for a single lining that is intended to last for at least a decade: a typical refinery requires approximately 2500 tons of refractory. Some of the more critical units are put on maintenance, with annual turnaround, and the replacement and repair of refractories for a single unit can amount to 250 tons, or a fourth of the lining.

Virtually all of the refractories used by chemical plants are monolithics. These include castables, cast vibration mixes, gunning mixes, low- and no-cement castables, plastics, and a variety of insulating refractories. Because many of the temperatures of refinery processes are too low to promote a ceramic bond to replace the hydraulic bond of calcium aluminate–bonded castables, the refractory practice has been based largely on phosphate-bonded plastics, which develop the needed properties at or below the process temperatures. Refractory practice varies widely from one company to another. Some companies have incorporated castables, especially vibratables, into their practice, and today companies are evaluating shotcretable refractories in locations where a ceramic bond can be developed at the process temperature.

However, the place where advances in refractories may have the greatest impact on efficiency in the chemical industry is in the boilers used to produce steam for power generation. Improvements in the thermal efficiency of boilers themselves, through improved insulation, and in the insulation used on transfer pipework could lead to reduction in heat loss and lower fuel consumption.

In the petrochemical and synthesized gas industries in particular, new designs in the catalyst support media and the installation of refractory insulation have increased operation life and efficiencies of reactors of various types. New refractory designs for support media have allowed increased flow rate and longer productive life for expensive catalyst materials. More attention being paid to the use of sprayable refractory ceramic fiber lining materials as well as new microporous silica backup materials. More attention is also being paid to the use of precast parts for component of the various unit processes, and wider use of precast technology is anticipated. Because it is so important to maintain shell temperatures of vessels and reactors above a threshold temperature to avoid condensation onto the shell, designers are trying to refine the models for predicting temperature gradients and cold face temperatures. Lack of data on the thermal conductivity of many commercial monolithic refractories is holding back progress in this area.

Barriers

Refractories and insulation materials play key roles in most of the varied unit operations involved in the production of chemical and petrochemical products; it is estimated that about 50% of the industries' direct energy consumption is in processes affected by refractories. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for the chemical and petrochemical industries could lead to energy savings opportunities of up to 266.4 TBtu/year. The specific barriers are shown below.

- Lack of understanding of high-temperature properties such as creep rupture, short-time strength, thermal conductivity, thermal expansion, ductility, and stability for the monolithic refractories used in this industry.
- Lack of understanding of the corrosion properties of refractories used in the chemical and petrochemical industries, which subject materials to conditions ranging from hot-oxidizing environments to environments that contain hot halogen gases or gases with entrained particles.

- Lack of understanding regarding turnaround times and maintenance costs, which have become increasingly more important cost elements. Lack of understanding regarding the reduction of energy consumption and air pollution.
- Lack of understanding regarding high-temperature and corrosive environments which limit refractory life and increase maintenance costs in numerous chemical and petrochemical reactors.

R&D Pathways

- Develop improved refractories for minimizing mechanical damage to refractory-lined refining vessels through reduction of the amount of mechanical stresses on the lining.
- Perform work to optimize the physical properties of refractories (i.e., thermal insulation, erosion resistance, corrosion resistance, thermal shock resistance, strength, porosity, and permeability) under known required operating conditions for specific unit types. Develop realistic and reproducible product development and quality control testing that can be used to relate step improvements in needed physical properties of the current refractory lining materials in service.
- Develop improved methods of analysis for high-temperature equipment through techniques for online refractory inspection.
- Develop longer-life refractories that are field-repairable, less brittle, and more shock-resistant.
- Acquire thermophysical, kinetic and mechanical data on refractories.
- Develop ceramic-metal-matrix composites with improved stability and explore surface modification and/or coatings for use in corrosive environments.
- Develop materials to withstand high temperatures (1000–3000°F) while retaining superior strength, ductility, corrosion and wear resistance to resist damage due to corrosion and high temperatures present in the chemical process industry.
- Develop materials with enhanced resistance to organic acid environments and improved materials for chlorine-based processes, to improve plant operations and maintenance requirements and reduce costs.
- Develop refractories and refractory coatings for high-temperature furnaces to reduce energy and maintenance costs. Develop high-temperature nonstick surfaces that do not degrade or become volatile at high temperatures to help reduce needed maintenance of chemical process equipment.

A.4 Forest Products

Current Industry Operations and Refractory Use

Although the pulp and paper industry is not a substantial user of refractories, the forest products industry is the third largest consumer of energy in the United States, at approximately 3.3 quads per year.[8] To its credit, the industry generates 63% of its own energy using recycled woody waste products and other renewable sources for fuel (bark, wood, and pulping liquor). Since 1972, the industry has reduced its use of fossil fuels and purchased energy by about 2% while increasing total production by nearly 64%. In the future, black liquor and biomass gasification will lead to greater reductions in purchased energy and could even change the pulp and paper industry from a net energy importer to a net energy exporter. Gasification holds the promise of generating 175% more power than do current Tomlinson furnaces, but the gasification technology currently in place requires yearly refractory relines of the vessels.[9]

Lime recovery kilns are used in most forest products industries as an integral component of the Kraft pulping process, with lime recovery kilns operating at a level of 7 million Btu/ton of lime recovered. Yet, these kilns have the disadvantages of cyclic production rates, poor product quality, dust cycles, rings, material buildups, and blockages. Most of these deficiencies can be related to premature brickwork failure and buildups, with loss in production of up to 35 days per year being attributed to ringing.

Barriers

It is estimated that about 40% of direct energy consumption by the forest products industry is in processes affected by refractories. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems could lead to energy savings opportunities of up to 129 TBtu/year. Specific barriers are shown below.

- Lack of understanding regarding problems associated with sticking of reactants and products to the refractory linings of lime kilns, limiting their operating lives.
- Unavailability of materials with corrosion resistance to the harsh, high-alkali black smelt environment (consisting of steam, sulfur, hydrogen, and CO) and abrasion/erosion resistance, spall resistance, and thermal compatibility with metallic materials used in the gasifiers.
- Unavailability of improved materials for containment which do not react with the high-alkali atmosphere present in the gasifier. Such reactions result in slabbing, which limits the lining life.
- Lack of a database on the properties of the castable materials used in this industry, information which is not provided by the refractory producers.
- Unavailability of improved refractories for Tomlinson recovery boilers to replace fireclay, alumina brick, or similar monolithic compositions used in the floor. Improved refractories could decrease the amount of furnace downtime needed for repairs and would decrease energy usage due to shutdown and restart cycles.
- Lack of refractory systems with sufficient alkali corrosion resistance for storage container linings used for hot pulping chemicals.

R&D Pathways

- Develop improved refractories for lime kilns to reduce downtime due to ringing and buildups, thus leading to increases in energy efficiency due to better thermal management and increases in lime kiln lining lifetimes.
- Develop advanced refractories to provide suitable materials for use in black liquor and biomass gasifiers. Advanced refractories could lead to substantial improvements in energy efficiency for the forest products industry, which currently requires yearly refractory relines of the vessels.
- Develop materials with greater resistance to the corrosion in molten salt environments, greater abrasion/erosion resistance, and greater spall resistance. In addition, develop alternate refractory schemes to provide refractory surfaces which are more impervious to wear and

corrosive attack through coatings, chemical alteration of refractory surfaces, physical alteration of refractory surfaces, etc.

- Develop refractory materials which are more thermally compatible with metallic materials used in gasifiers.

A.5 Glass

Current Industry Operations and Refractory Use

The glass industry produces a wide variety of products using different process technologies. Perceived differences across the segments of the glass industry remain a barrier to broad-based industry collaboration. These differences have led individual segments to select different melting technologies, prefer different refractories, and operate furnaces that differ in size and scale. Capital and operating costs for the individual segments reflect these product and process differences. Further, differences in glass types and industry segments and the needs of large versus small furnaces limit the ability to define common interests. There are also concerns with project definition and management for cooperative efforts: costs, timing, and sharing of technical and financial risks and the intellectual property generated.

Melting of the batch is accomplished using different types and sizes of furnaces, with refining occurring in the melting chamber. Furnaces may be discontinuous (<5 ton/day) or continuous (large operations, estimated to last up to 10–12 years today). Continuous furnaces may be direct-fired (units fired with natural gas and producing 20–150 ton/day), recuperative furnaces (direct-fired furnaces fitted with recuperators to recover heat from exhaust gases), regenerative furnaces [the most commonly used furnaces, with capacities of 100–1000 ton/day, and with the furnace heat collected in a regenerator that is used to preheat combustion air as high as 1260°C (2300°F) and achieve higher energy efficiency] or all-electric melters.

Commonly, alumina-zirconia-silica refractories are used as sidewalls, with zirconia content ranging from 33 to 41%. Chrome-containing refractories are also used in the fiberglass industry because of their additional corrosion and erosion resistance, but their use is decreasing because of environmental concerns about chrome. Refractories containing chrome are not used in the flat, container, or pressed/blown glass industries because chrome impurities can discolor the glass. Silica is commonly used for the crown of the furnace, or sometimes mullite if oxy-fuel firing is employed. Due to chemical incompatibilities, a layer of alumina-zirconia-silica is often used as a buffer between the crown and sidewall.[1]

Significant progress has been made in reducing energy intensity in areas of the glass industry over the last ten years. This increase in efficiency has been accomplished mostly through improved process control systems, the development and use of advanced refractory materials, and technologies such as oxy-fuel firing and electric boost, which increase production capacity. Advanced technology has reduced the fuel consumed per ton of glass melted by 25% since the early 1980s, and energy use has declined in the fiberglass sector by 30% since 1978.[10]

Still, energy efficiency depends on the size of the operation and the production rate. For example, a large (120 ton/day) all-electric furnace uses electricity at 66% overall efficiency, while a small all-electric furnace (4 ton/day) has about 34% overall efficiency.[11] Electric glass-melting furnaces are more thermally efficient than oxy-fuel because there is less mass (melt basin only) and less surface area for heat losses. Average oxy-fuel melters consume 3–5 MMBtu from fossil fuel per ton of glass melted. This is in comparison with the average electric consumption of all-electric direct resistance glass melters of about 2.7 MMBtu/ton.

Yet, modern glass melting still requires a high-temperature device that consumes a significant quantity of energy, with melting energy representing about 15% of the manufacturing costs. Although there are some proven energy-reduction technologies for melting that are not currently being implemented and some concepts which have been identified to further reduce energy consumption (improvements in corrosion-resistant refractories, insulation, combustion, process control), the economic incentive for adopting these proven technologies and developing these new concepts may not currently be sufficient to justify the cost and the effort. This may be because the industry views minimizing the energy cost per ton of glass produced as more important than reducing the energy content as measured in thermal units and because the *value* of the energy saved at the current cost of energy, with an assumed low rate of cost escalation, is not sufficient to justify many energy-saving technologies. In particular, technologies that require any significant capital investment are usually discarded by the glass industry or looked upon unfavorably, with many glass manufacturers expecting a one- to two-year payback for capital investments.[12] Specific energy usage by sector is shown in Table A.2.

Table A.2. Estimated energy use in melting and refining

Glass sector	Av. specific energy use (10^6 Btu/ton)	Annual energy use (10 TBtu)
Flat	8.6	42.9
Container	5.5	53.1
Pressed/blown	7.3	18.1
Fiber	8.4	25.6

Source: DOE, *Energy and Environmental Profile of the US Glass Industry,* DOE/GO -102002-1590, Office of Industrial Technologies, April 2002.

Oxy-fuel firing is also still a viable technology and could improve efficiency in the glass industry. The trend towards using oxy-fuel firing is steadily increasing because an oxy-fuel furnace can produce the same amount of glass as with gas and/or air, but at a lower fuel input.[13] Additionally, when regenerative furnaces are converted to oxy-fuel firing, the regenerator refractory structure is not needed, eliminating the exhaust volume by as much as 75%.[14] As of 1998, only 20% of the glass furnaces in the United States had been converted from air-fuel to oxy-fuel technology, with the greatest conversion rate found in the fibers sector.[15] To date, it is estimated that the number of conversions has increased only to around 25% of the total industry.[15] A breakdown of the number of conversions to oxy-fuel technology completed by 1998 in each sector of the glass industry is shown in Table A.3, along with estimates of the number of conversions made to date. Therefore, there is still a great opportunity for further improvements in the energy efficiency of the glass industry through further utilization of oxy-fuel fired furnaces. Further improvements in refractory technology are needed to fully utilize the benefits of oxy-fuel technology.

Boosting with oxygen firing will result in increased production but will also increase the melting cost per ton of glass. This trade-off is accepted by the industry because the additional capacity gained is at a much lower capital cost than that associated with building new furnaces. Sampling of the industry indicates that to date, 125–150 of 500–550 total glass furnaces have been

Table A.3. Conversion of North American glass melters to oxy-fuel firing as of 1998 and as of 2004

Glass sector	No. of oxy-fuel conversions	Total no. of glass tanks	% converted
As of 1998			
Containers	23	210	10
Fibers	41	110	37
Textiles	(30)	(70)	(42)
Insulation	(11)	(40)	(27)
Flat	2	45	5
Specialty	54	235	23
All sectors	**120**	**600**	**20**
As of 2004 (estimated)			
Containers	27	180	15
Fibers	46	100	46
Textiles	(35)	(62)	(56)
Insulation	(11)	(38)	(29)
Flat	3	45	7
Specialty	60	225	27
All sectors	**136**	**550**	**25**

converted to oxy-fuel firing. This is only 25% of all the furnaces in the industry, leaving a large number of furnaces that could be converted to the more efficient technology, leading to pollution abatement and higher energy efficiency, if improved alternate refractories with sufficient corrosion resistance and thermal efficiency could be found. Of the various segments making up the glass industry, the fiber area has made the most use of oxy-fuel firing, with nearly 50% of these furnaces having been converted; in second place is the specialty area, with over 25% of the furnaces converted. Great opportunities exist in the flat and container glass segments, which have conversion rates on the order of 5 to 15%.

Barriers

Refractories and insulation materials play key roles in many of the unit operations involved in the glass production; it is estimated that about 70% of the direct energy consumption is in processes affected by refractories. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for the glass industry could lead to energy savings opportunities of up to 13.9 TBtu/year. Specific barriers are shown below.

- Unavailability of durable and inexpensive materials for use for refractories in constant contact with molten glass, combustion gases, and hot glass products in glass furnaces which operate continuously at temperatures exceeding 1400°C in the molten bath and 1600°C in the combustion atmosphere for operating lives of 8–10 years.
- Unavailability of parts and installation equipment to replace parts and materials that fail during production campaigns, without major furnace shut-downs and loss production.
- Limitations on energy efficiency and degrading glass quality, particularly in oxy-fuel environments, due to limitations of refractory performance.
- Lack of knowledge that would improve the performance and quality of existing refractories and lead to increased production life and lower installation costs.

- Lack of modeling of corrosion mechanisms that would help determine solutions for reducing corrosion in refractories and for providing adequate on-line sensors that would optimize operation control, leading to longer-life, corrosion-resistant refractories, thereby reducing capital costs for glass melting and forming applications.
- Lack of knowledge in the form of a materials property database, identification of new melting techniques and their associated refractories, and better methods for the evaluation and repair of refractories in service.

R&D Pathways

- Develop integrated furnace models for the prediction of methods for improving thermal efficiency, for developing new glassmaking technologies, and for projecting performance of alternate refractory materials.
- Develop refractories (particularly for furnace crowns) having sufficient strength and corrosion resistance at higher operating temperatures when using oxygen enrichment.
- Develop monolithic and/or coated refractories that will be more resistant to penetration of corrosive liquid and gaseous species.

A.6 Heat-Treating and Annealing

Current Industry Operations and Refractory Use

Heat-treating is a $20 billion industry in the United States and represents $75 billion or more in value-added manufacturing globally.[16] It is also crosscutting, enabling technology that affects most of the industries found in the United States, including aluminum, glass, iron and steel, and metal casting. The goal of the Heat Treating Industry Vision 2020 is to reduce energy usage in the heat-treating industry by 80%. To achieve this goal, cooperation is needed between all the related industrial groups, including the heat treating community, metal producers, foundry and forging groups, fabricators, government, and academia.

One of the most important research needs for this industry is the development of integrated process models. Heat treating today is viewed as an experience-based art. However, in the future it must function in a scientific, predictive environment, where processes are truly understood and capable of being simulated. For example, it has been demonstrated that the solutionizing time for a cast aluminum alloy could be reduced from 12 to 2 h with no loss of quality or properties. This magnitude of heat treatment cycle time reduction could result in increased productivity and/or reduced energy consumption of greater than 50%. Validated databases for multicomponent alloys and predictive models will enable comparable results to be achieved for a wide range of alloys and applications.[17]

Barriers

Refractories and insulation materials play key roles in various furnace systems used in the heat-treating and annealing industries; approximately 90% of direct energy consumption is in processes affected by refractories. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for the heat treatment and annealing industries could lead to energy savings opportunities up to 45 TBtu/year. Specific barriers are shown below.

- Unavailability of high-performance refractories for the improvement of thermal efficiency in furnace systems that would lead to reduced cycle times, lower required energy input, and lower processing costs.
- Unavailability of gradient refractory systems with lower thermal conductivity and high-temperature strength and corrosion/erosion resistance for reducing heat losses and improving chemical compatibility.
- Unavailability of refractory materials with longer lifetimes due to improved corrosion resistance, extended temperature resistance, and mechanical thermal stability, while also possessing reduced costs.

R&D Pathways

- Develop improved insulation materials to achieve higher operating temperatures, reduce heat losses, and eliminate reheating while also reducing process time and production costs.
- Develop higher-efficiency insulation materials to increase the thermal efficiency of current processes and simultaneously lower heat-treatment times, leading to significant reduction of energy consumption levels. This could then lead to the development and application of accelerated heating technologies, which will require alternative insulation materials with greater thermal shock resistance and high-temperature stability.

A.7 Iron and Steel

Current Industry Operations and Refractory Use

In the steel industry, competitive pressures such as worldwide overcapacity, the high cost of energy, environmental and safety regulations, competing materials, customer demand for high quality, and the high cost of capital have led to a need for sweeping changes across the industry. Therefore, four critical areas for improvement or targets of opportunity were identified: (1) process efficiency through improved throughput, quality, and energy efficiency, (2) increased recycling, (3) new processes to avoid or reduce air and water pollution, and (4) product development.[18]

As part of the approach to address these areas, refractories currently used throughout the steel making process were analyzed. Oxide-based ceramics of aluminum, calcium, zirconium, chromium, magnesium, and carbon are primarily used in steel contact in an effort to reduce contamination and interaction with the highly alkaline slags. Nonoxide ceramics consisting of combinations of silicon, titanium, tungsten, and aluminum are used for hot handling applications where thermal shock resistance, creep resistance, wear resistance, and resistance to acidic species is desired. These materials may be in the brick or castable form. In many areas of steel furnaces refractory life is extended by splashing slag against the refractory walls. This slag solidifies on the wall, forming a protective layer. This process, though highly successful, is very inefficient thermally.

Today, steelmaking from pig iron commences in the transfer ladle ahead of the basic oxygen furnace (BOF) and continues after the BOF to the ladle stations and on to the tundish, which distributes the steel into the continuous casting or stationary molds. Refractories for all these unit processes are selected on the basis of their longevity and the cleanliness of the steel that passes through them. The cost per pound of refractories for all the various components, with few exceptions, has increased markedly with the awareness that advanced refractories can meet the goals of greatly extended service and contribute to the quality of the steels.

In steel ladles, maintenance costs are high and heat efficiency is poor. Currently, high-alumina and magnesia-based castable refractories are preferred for ladle linings at and below the slag line due to the high process temperatures, erosion from the stirred bath, and the high corrosiveness of the slag. Life is short for these refractories; they typically last for only 30 to 50 heats. Higher-temperature-capable oxide/carbon mixtures have been evaluated for use to provide a balance between purity, thermal shock resistance, and erosion resistance, along with other alternative refractories with longer life, lower cost, and safer disposal. Yet, no material of choice has been identified.

Monolithics (refractory concretes and gunning mixes) comprise at least 60% of all refractories used in iron and steelmaking in the United States today (over 70% in Japan), and there is a strong trend to increased use of precast versions of monolithics. Installation practice has undergone some major advances which translate to much more rapid original construction, replacement of working linings, and repair. The adaptation of shotcreteing methods from construction concrete technology has resulted in significant reductions in downtime and in some cases longer service life as well. In the ladle lining practice, it has been possible to successively repair the original lining such that complete relining is no longer necessary.

Improved materials for runners (used to flow the molten steel from a BOF or an electric arc furnace to the refining ladles) are needed. These components are generally constructed from fireclay brick, alumina castable, or chromia castable. They experience corrosion, wear, and thermal stresses that limit their lives to one to two weeks. Similar improvements are needed for water-cooled pipes and stirrers enclosed in refractory. They also experience corrosion, wear, and thermal stresses that limit their life and require weekly repair.

Energy consumption in the various unit processes found in the iron and steel industry has changed substantially due to advances in refractory practice, but it is difficult to identify the role of refractories in energy savings because many changes are being made in designs and combustion practices as well as in metallurgical and slag practices. Some unit processes like blast furnaces and BOF melters are designed to leak energy to induce a steep thermal gradient through the lining. In an extreme example of this process design concept, the walls and roofs of electric arc furnaces are water-cooled to cause the steepest possible thermal gradient. Consequently, it is in the other unit processes where refractory practice contributes to energy savings in several ways (e.g., more efficient insulation, extension of the time between maintenance shutdowns, reduction in the amount of refractory scrap and reduction in metal scrap through improved cleanliness of the final steel products).

As mentioned, blast furnaces and BOF melters are designed to leak energy, and even in the case of most ladles, insulation is minimized in the walls and bottoms in an effort to induce a thermal gradient in the interest of reducing the refractory wear. Ladle covers, on the other hand, are absolutely necessary to conserve the temperature of the contained metals and are made from increasingly advanced materials. There are many opportunities for direct energy savings in all of the unit processes and components in iron and steel plants that are not designed to incorporate steep thermal gradients. There are also opportunities to extend refractory life through the use of lining thickness monitors and other sensors and instruments which improve the combustion efficiency and reduce stack losses as well as release of undesirable products of the processing of the iron and steel.

Significant improvements are needed for meeting operating challenges for monolithic refractories. Monolithic linings possess many inherent problems. Ideally, steelmakers would like to have monolithic linings for all of the ladles and even for the basic oxygen furnace. The so-called basic lining has received considerable research attention, but no reports of success in a BOF have been reported to date. Problems exist with the hydratability of the basic components of the products, which are based on MgO, magnesite, doloma (calcined dolomite, $CaCO_3{\cdot}MgCO_3$), and spinel. Further, monolithics for BOF linings need to incorporate substantial amounts of carbon in the form of graphite, and research is ongoing to resolve the problem that derives from the interference of the high volumes of graphite with the binder systems of the monolithics.

Barriers

Refractories and insulation materials play key roles in the smelting, refining, and melting operations used in the iron and steel industries; it is estimated that 85% of the industries' direct energy consumption is in processes affected by refractories. Based on subsequent analyses of typical furnaces and unit processes, improvement of refractory systems for the iron and steel industries could lead to energy savings opportunities up to 148.5 TBtu/year. Specific barriers are shown below.

- Lack of adequate corrosion resistance for refractories in contact with molten metal, which leads to undesirable equipment lifetimes. This is especially important for refractories used in parts of furnaces, ladles, and tundishes.
- Unavailability of improved materials for runners (used to flow the molten steel from a BOF or an electric arc furnace to the refining ladles), water-cooled pipes, and stirrers enclosed in refractory.
- Lack of utilization of advanced monolithics in ladles due to problems with their explosive tendencies and lack of data on some of the key input properties and parameters for most of the monolithic products that meet the requirement for steel ladle practice.
- Unavailability of improved impact pads at the bottom of ladles, which experience high wear, thermal shock, and abrasion.
- Unavailability of thin-walled alumina refractory ladle shrouds that are used to reduce oxygen pick-up during pouring with lifetimes of greater than ten heats in the extreme conditions of this application.

R&D Pathways

- Develop methods for suppressing the hydration of magnesites.
- Develop refractory linings with improved life and reduced maintenance requirements, to reduce the yearly or even monthly maintenance shutdowns generally necessary to repair refractory problems. Reducing the frequency of or eliminating these shutdowns would provide significant cost reduction, not to mention associated energy savings.
- Develop advanced materials (such as refractories with in situ coatings or externally applied coatings) for resisting corrosion/erosion damage.
- Develop new materials along with improved materials databases for members of the industry to adapt to new materials in their operations.
- Develop improved refractories for use in various parts of furnaces, heat processing equipment, ladles, and tundishes.

- o Develop improvements in runners, water-cooled pipes and stirrers, which all experience corrosion, wear, and thermal issues that can limit their life and require weekly repair.
- o Develop improvements in materials and installation methods for ladle bottoms and impact pads by using ceramic coatings or alternate localized materials.
- o Develop long-lived, economically feasible, prefired refractory crucible linings for induction melting of stainless steel in air-melt operations.
- o Develop improved ceramic/refractory materials for net shape steel casting, eliminating rolling mill operations.

A.8 Metal Casting

Current Industry Operations and Refractory Use

Energy consumption for the metals casting industry is on the order of 0.2 quads per year.[20] This resulted in an estimated energy cost for the foundries industry in the United States of $1.2 billion in 1997[7] and $1.5 billion in 1998,[20] or about 10% of the total material cost put into production and 4–5% of the value of total shipment.[21] Therefore, the industry wishes to optimize melting, holding, and heat-treating furnaces to conserve energy (i.e., to reduce energy usage by 20%) and minimize pollutant emissions. Further, the industry wishes to increase the life of refractories and other ceramic components that are exposed to molten metals and/or furnace environments and develop in-line sensors that are stable in the molten metal environment.[10]

The unit processes utilized in the metal casting industry are lined with a wide range of refractory compositions (including silica, alumino-silicate, high alumina, zircon, magnesia, spinel, chrome, and magnesia-carbon) and forms (monolithics, precast shapes, and bricks). Most metals casting industry melting and holding furnaces are lined with ceramic refractories which are selected to minimize reaction with the specific metal being processed. Major refractory lined units include reverberatory furnaces, crucible (pot) furnaces, channel induction furnaces, coreless induction furnaces, electric arc furnaces, and pouring ladles. These furnaces are lined with wide ranges of refractory compositions, including silica, alumino-silicate, high alumina, zircon, magnesia, spinel, chrome, and magnesia-carbon.

Substantial problems do still exist with molten material containment and handling. For example, cupola linings for ferrous alloy melting usually require weekly repairs because of corrosion and mechanical damage. An alternative to refractory linings is “skull melting” (in titanium melting, for example) where in a mechanism similar to the slag splashing in the steel industry or the formation of a “frozen ledge” in the aluminum industry, a protective layer of metal is solidified on the containment vessel surface, creating a corrosion-resistant layer but lowering the thermal efficiency of the system.

Iron foundries are the major energy consumer for this sector, representing about 12% of the industry, followed by steel foundries at about 10%. Within each process, approximately 55% of the total energy cost is used for the melting of the metal, with other processes (core making, mold making, heat treatment, and post-casting processes) accounting for the other 45%. Although the total energy cost (fuel + electricity) accounts for only about 10% of the total material cost, it can be as high as 20% or more for many foundries depending on efficiency and the materials processed. Specific energy usage by the metals casting industry is given in Table A.4.

Table A.4. Process and energy data for U.S. metals casting industry

Process	Energy consumption
Core making and mold making	7–20% energy, 1–3 × 10^6 Btu/ton
Cupola melting	Total: 8.6 × 10^6 Btu/ton Coke: 5.8 × 10^6 Electricity: 1.1 × 10^6 Natural Gas: 1.6 × 10^6 Oxygen: 0.1 × 10^6
Electric melting	Induction furnace: 4.3–7.6 × 10^6 Btu/ton Electric arc furnace: 4.3–5.2 × 10^6 Btu/ton Electric-resistance heated reverberatory furnace: 5.2–7.9 × 10^6 Btu/ton
Gas-fired melting furnace	Crucible: 1.8-6.8 × 10^6 Btu/ton Reverb.: 2.5-5.0 × 10^6 Btu/ton
Refining and pouring processes	Electricity: 0.4 × 10^6 Btu/ton Natural gas: 0.2 × 10^6 Btu/ton
Cleaning and finishing processes	1.0 × 10^6 Btu/ton
Investment casting	Electricity: 3.0 × 10^6 Btu/ton Natural gas: 4.0 × 10^6 Btu/ton
Lost foam casting	2.5 × 10^6 Btu/ton
Die casting	Electricity: 4.0 × 10^6 Btu/ton Natural gas: 5.0 × 10^6 Btu/ton
Other casting processes	Permanent: 2.5 × 10^6 Btu/ton Shell mold: 2.5 × 10^6 Btu/ton Plaster mold: 3.0 × 10^6 Btu/ton

Source: Energy and Environmental Profile of the U.S. Metal Casting Industry.

Although the service life of refractory linings for all foundry practices has been extended greatly in the last decade, many of the problems identified above still persist. For example, most channel and coreless induction furnaces in iron and steel foundries use spinel-forming dry-vibratable castable, a shift from the wet ramming practiced in the past. This extended the service campaign of the foundries, but metal penetration and chemical corrosion by slag still persists. Also, there are few case studies that show good refractory maintenance management, new refractory development, or proper selection methods resulting in great energy savings and reduced melting cost. With the ever-increasing demand for quality cast metal, alloy composition, and innovative melting technologies, refractories sections have been pushed to more challenging positions. Research programs in refractories science and technology in the United States have never been as large and as comprehensive as R&D programs for other industry and technology sectors. Nonetheless, the metal casting industry is still one of the largest industry sectors in the United States, and the refractories industry is essential to it.

For steel casting, wear of refractories and reaction of the refractories with highly basic (calcia-containing) slag can generate defect-forming inclusions. High-alumina refractories are generally used throughout this area of the process, with application of zirconia-based materials in areas of high wear and thermal shock and magnesia-based materials in areas of high slag corrosion.

Carbon materials cannot be used for this application, as they react with oxide-based refractories to form CO and with aluminum in steel to form alumina. Similarly, silica-based refractories cannot be used because of contamination issues.

There is a serious lack of data on the mechanical, thermal, and chemical properties of monolithic refractories; and much of the data that exists is lacking in detail or is obsolete. There is only one reference source for such key data as strength, modulus of elasticity, thermal conductivity, heat content, permeability, thermal shock and creep behavior; and this source was first available 15 years ago. Hundreds of new and updated versions of monolithics are on the market today, but there is very little design and other technical data available aside from the product data sheets, which do not list much beyond bulk properties and some typical values (not to be used in design but only as guide for selection).

Barriers

Refractories are used throughout the various unit processes found in the metal casting industry; approximately 90% of the direct energy consumption is in processes affected by refractories. Based on subsequent analysis of typical furnaces and unit processes, improvement of refractory systems for the metal casting industry could lead to energy savings opportunities up to 8.5 TBtu/year. Specific barriers are shown below.

- Lack of methods and materials to reduce or eliminate refractory failure due to physical erosion and chemical corrosion by molten metal and slags in nearly all stages of metal melting, refining, and pouring processes where refractories make contact with molten metal.
- Lack of methods and materials to reduce or eliminate refractory failure related to fusion of refractories and chemical corrosion by MnO and FeO in steel foundries where the molten steel is generally tapped at high temperatures [up to 2150°C (3900°F)], and the common practice is to use low-cost silica, zircon, or alumino-silicate ramming mixes and plastics, especially in those foundries that apply acid melting practices in smaller furnaces.
- Lack of methods and materials to reduce or eliminate clogging or build-up formation in channels and throats is problematic for most metal casting operations.
- Lack of methods and materials to reduce or eliminate refractory wear in electric arc furnaces for the melting of steel, where reduced refractory wear and energy savings would be especially beneficial.
- Lack of methods and materials to reduce or eliminate wear and reaction of refractories with highly basic (calcia-containing) slags for steel casting.
- Lack of data on the mechanical, thermal, and chemical properties of monolithic refractories, with much of the data that exists lacking in detail or being obsolete.

R&D Pathways

- Develop improved refractories that will resist physical erosion and chemical corrosion by molten metal and slags. Specifically, develop material systems for steel containment that are chemically stable with the molten metal and that provide mechanical integrity against wear and abrasion.
- Develop improved refractories which are resistant to corrosion by MnO and FeO to prevent fusion of refractories in steel casting.

- Develop refractories which will resist the adhesion of molten metal that results in clogging or build-up formation in channels and throats.
- Develop improved refractories for use in electric arc furnaces for the melting of steel that will resist wear and provide energy savings though improved insulation.
- Determine the mechanical, thermal, and chemical properties of monolithic refractories used in the metal casting industry.
- Develop novel low-cost and high-performance monolithics (in particular for iron, steel, and aluminum foundries), basic gunning mixes, and MgO-graphite castable for rapid repair of electric arc furnaces.
- Develop and model slag chemistry compatible with refractory linings and maximize the slag foaming properties, along with efforts to reduce or eliminate repair and patching of electric arc furnaces due to refractory wear.

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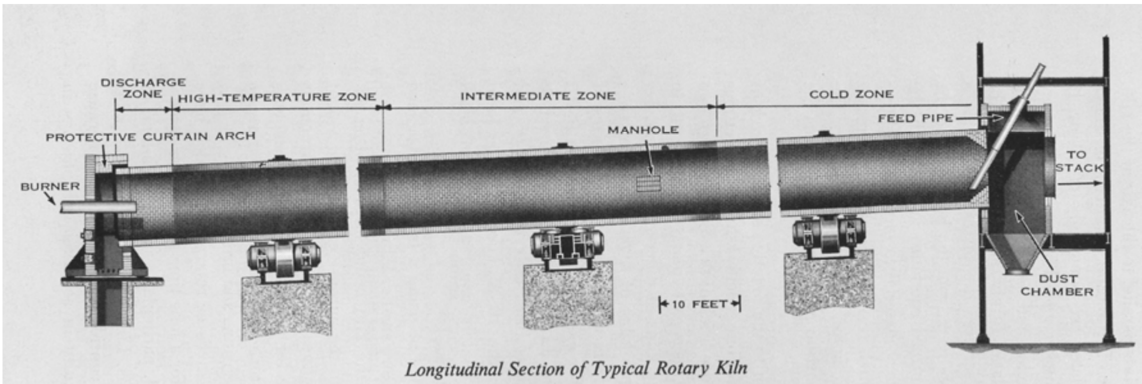
Appendix B: Rotary Kiln Analysis Schematic, Conditions, and Results



Longitudinal Section of Typical Rotary Kiln

Fig. B.1. Longitudinal section of a typical rotary kiln. Reprinted from *Modern Refractory Practice,* 3rd ed., Harbison Walker Refractories, Pittsburgh, 1950.

Assumptions for alumina calcination, rotary kiln

Plant production	500,000 tons Al_2O_3/year	
Assume two kilns		
Output per kiln, no downtime	277,778 tons Al_2O_3/year	
With 90% uptime	250,000 tons Al_2O_3/year	
Output per day	685 tons Al_2O_3/d	
Output per hour	29 tons Al_2O_3/h	
Kiln diameter	3.5 m (11 ft)	
Kiln length	80 m (262 ft)	
Kiln exterior surface	880 m^2 (9468 ft^2)	
Reaction	2 $Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$	
Heat of reaction at 77°F	634 Btu/lb Al_2O_3	
Assume reaction temperature of	1100°C	
	2012°F	
say	2000°F	
Heating products to 2000°F		
Al_2O_3	562 Btu/lb Al_2O_3	
3 H_2O	532 Btu/lb Al_2O_3	
Total heat requirement	1728 Btu/lb Al_2O_3	
	3,456,824 Btu/ton Al_2O_3	
Heat of reaction		
35.91 cal/mol	Reaction	634
64,638 Btu/#mol	Heating	562 Al_2O_3
634 Btu/lb	Heating	532 H_2O
	Total	1,728 Btu/lb Al_2O_3

Results of alumina rotary kiln analysis
(Temperatures in °F)

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	3,456,824	39.84%
Wall Loss Energy	400,000	4.61%
Exhaust Energy	4,821,030	55.56%
Total Energy	8,677,853	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	3,456,824	42.46%
Wall Loss Energy	400,000	4.91%
Exhaust Energy	4,285,360	52.63%
Total Energy	8,142,183	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	3,456,824	37.87%
Wall Loss Energy	600,000	6.57%
Exhaust Energy	5,071,030	55.56%
Total Energy	9,127,853	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	3,456,824	40.36%
Wall Loss Energy	600,000	7.01%
Exhaust Energy	4,507,582	52.63%
Total Energy	8,564,406	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	3,456,824	44.81%
Wall Loss Energy	400,000	5.19%
Exhaust Energy	3,856,824	50.00%
Total Energy	7,713,647	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	3,456,824	47.17%
Wall Loss Energy	400,000	5.46%
Exhaust Energy	3,471,141	47.37%
Total Energy	7,327,965	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	3,456,824	42.61%
Wall Loss Energy	600,000	7.39%
Exhaust Energy	4,056,824	50.00%
Total Energy	8,113,647	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	3,456,824	44.85%
Wall Loss Energy	600,000	7.78%
Exhaust Energy	3,651,141	47.37%
Total Energy	7,707,965	100.00%

Savings for alumina

Nature of saving	Btu/ton saved
Effect of 200°F increase in flame temperature	472,621
Effect of 200°F decrease in exhaust temperature	912,268
Effect of reducing wall loss energy from 600,000 to 400,000 Btu/ton	413,056

Assumptions for lime calcination, rotary kiln

Plant production	730,000 tons CaO/year	
Assume two kilns		
Output per kiln, no downtime	405,556 tons CaO /year	
With 90% uptime	365,000 tons CaO /year	
Output per day	1,000 tons CaO /d	
Output per hour	42 tons CaO /h	
Kiln diameter	5 m (16 ft)	
Kiln length	50 m (164 ft)	
Kiln exterior surface	785 m^2 (8,454 ft^2)	
Reaction	$CaCO_3 \rightarrow CaO + CO_2$	
Heat of reaction at 77°F	1364 Btu/lb CaO	
Assume reaction temperature of	1000°C	
	1832°F	
say	1800°F	
Heating products to 1800°F		
CaO	371 Btu/lb CaO	
CO_2	391	
Total heat requirement	2126 Btu/lb CaO	
	4,252,259 Btu/ton CaO	
Heat of reaction		
57.29 cal/mol	Reaction	1364
103,122 Btu/#mol	Heating	417 CaO
1,839 Btu/lb	Heating	415 CO_2
	Total	2,196 Btu/lb CaO

Results of lime rotary kiln analysis (neglecting dust loss)
(Temperatures in °F)

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	4,252,259	40.62%
Wall Loss Energy	400,000	3.82%
Exhaust Energy	5,815,323	55.56%
Total Energy	10,467,582	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	4,252,259	43.30%
Wall Loss Energy	400,000	4.07%
Exhaust Energy	5,169,176	52.63%
Total Energy	9,821,435	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	4,252,259	38.95%
Wall Loss Energy	600,000	5.50%
Exhaust Energy	6,065,323	55.56%
Total Energy	10,917,582	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	4,252,259	41.51%
Wall Loss Energy	600,000	5.86%
Exhaust Energy	5,391,399	52.63%
Total Energy	10,243,657	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	4,252,259	45.70%
Wall Loss Energy	400,000	4.30%
Exhaust Energy	4,652,259	50.00%
Total Energy	9,304,517	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	4,252,259	48.11%
Wall Loss Energy	400,000	4.53%
Exhaust Energy	4,187,033	47.37%
Total Energy	8,839,291	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	4,252,259	43.82%
Wall Loss Energy	600,000	6.18%
Exhaust Energy	4,852,259	50.00%
Total Energy	9,704,517	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	4,252,259	46.12%
Wall Loss Energy	600,000	6.51%
Exhaust Energy	4,367,033	47.37%
Total Energy	9,219,291	100.00%

Savings for lime, neglecting dust loss

Nature of saving	Btu/ton saved
Effect of 200°F increase in flame temperature	567,631
Effect of 200°F decrease in exhaust temperature	1,095,660
Effect of reducing wall loss energy from 600,000 to 400,000 Btu/ton	413,056

Results of lime rotary kiln analysis (assuming 20% dust loss)
(Temperatures in °F)

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	5,102,710	39.00%
Wall Loss Energy	400,000	3.06%
Exhaust Energy	7,581,767	57.94%
Total Energy	13,084,478	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	5,102,710	43.30%
Wall Loss Energy	400,000	3.39%
Exhaust Energy	6,283,012	53.31%
Total Energy	11,785,722	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	2000	
Reaction Energy	5,102,710	37.39%
Wall Loss Energy	600,000	4.40%
Exhaust Energy	7,944,267	58.21%
Total Energy	13,646,978	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	2000	
Reaction Energy	5,102,710	41.51%
Wall Loss Energy	600,000	4.88%
Exhaust Energy	6,589,678	53.61%
Total Energy	12,292,389	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	5,102,710	43.87%
Wall Loss Energy	400,000	3.44%
Exhaust Energy	6,127,936	52.69%
Total Energy	11,630,647	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	5,102,710	48.11%
Wall Loss Energy	400,000	3.77%
Exhaust Energy	5,104,439	48.12%
Total Energy	10,607,150	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3600	
Exhaust Temperature	1800	
Reaction Energy	5,102,710	37.39%
Wall Loss Energy	600,000	4.40%
Exhaust Energy	7,944,267	58.21%
Total Energy	13,646,978	100.00%

Parameter	Btu/ton	% Usage
Flame Temperature	3800	
Exhaust Temperature	1800	
Reaction Energy	5,102,710	46.12%
Wall Loss Energy	600,000	5.42%
Exhaust Energy	5,360,439	48.45%
Total Energy	11,063,150	100.00%

Savings for lime, assuming dust loss

Nature of saving	Btu/ton saved
Effect of 200°F increase in flame temperature	1,565,167
Effect of 200°F decrease in exhaust temperature	965,410
Effect of reducing wall loss energy from 600,000 to 400,000 Btu/ton	885,374

Appendix C:
Reverberatory Furnace Schematics

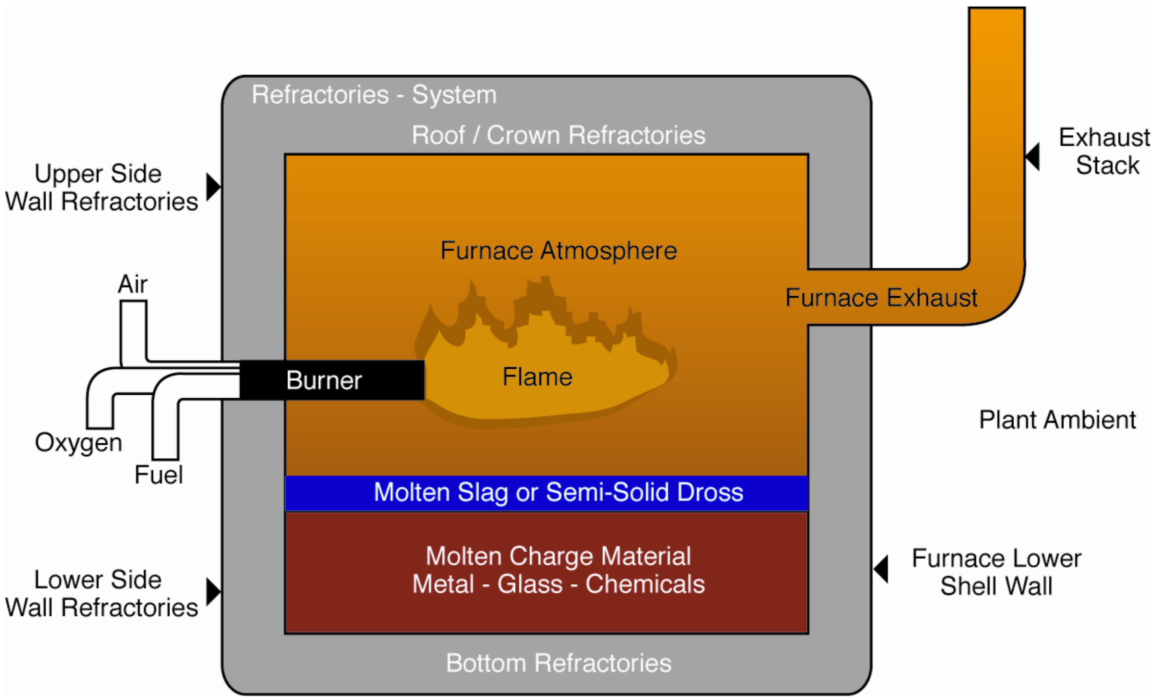


Fig. C.1. Reverberatory furnace schematic.

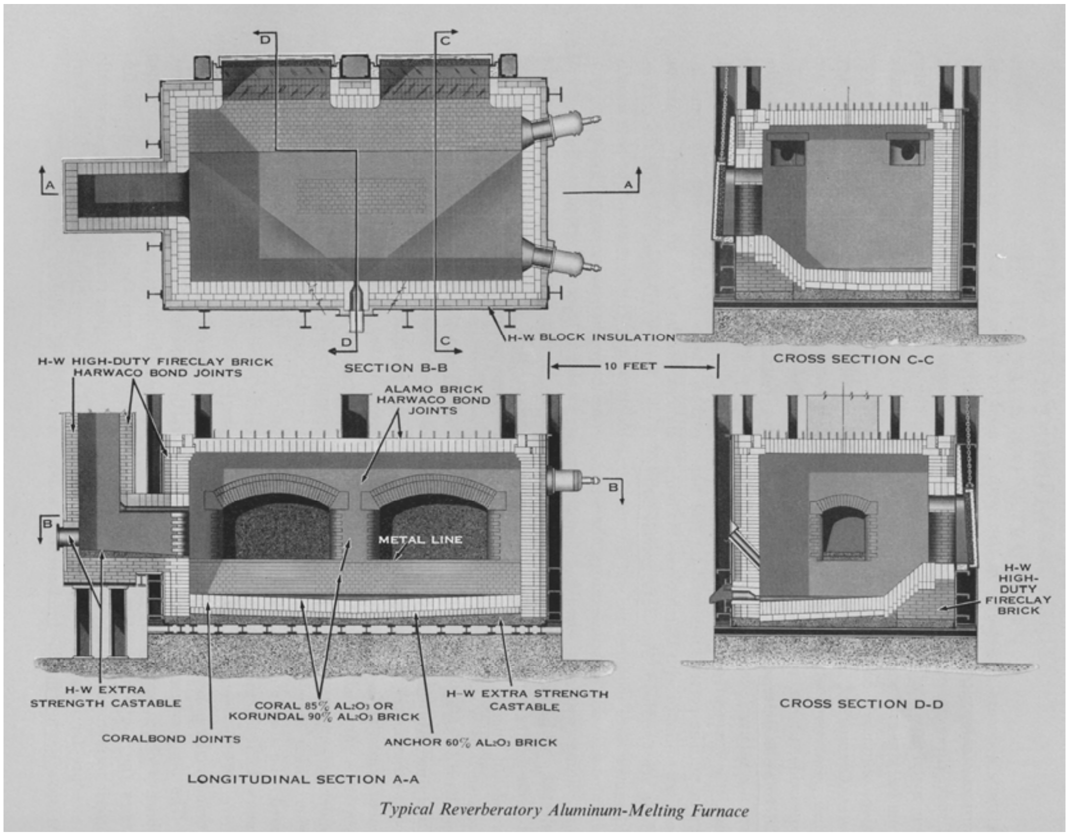


Fig. C.2. Typical reverberatory aluminum-melting furnace. Reprinted from *Modern Refractory Practice,* 3rd ed., Harbison Walker Refractories, Pittsburgh, 1950.

Appendix D: Reverberatory Furnace Analysis Conditions and Results

Results of aluminum reverberatory furnace analysis

	Temperature (ºF)		
Case	**Flame**	**Exhaust**	**Wall/roof Loss (Btu/h)**
Case 1	3600	1600	5,000,000
Case 2	3800	1600	5,000,000
Case 3	3600	1600	7,500,000
Case 4	3800	1600	7,500,000
Case 5	3600	1800	5,000,000
Case 6	3800	1800	5,000,000
Case 7	3800	1600	7,500,000
Case 8	3800	1800	7,500,000

Results of aluminum reverberatory furnace analysis
(Temperatures in °F)

Case 1		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	1600	
Melting Energy	10,095,271	37.2%
Wall Loss Energy	5,000,000	18.4%
Exhaust Energy	12,076,217	44.4%
Total Energy	27,171,489	100.0%
Case 3		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	1600	
Melting Energy	10,095,271	31.9%
Wall Loss Energy	7,500,000	23.7%
Exhaust Energy	14,076,217	44.4%
Total Energy	31,671,489	100.0%
Case 5		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	1800	
Melting Energy	10,095,271	33.4%
Wall Loss Energy	5,000,000	16.6%
Exhaust Energy	15,095,271	50.0%
Total Energy	30,190,543	100.0%
Case 7		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	1800	
Melting Energy	10,095,271	28.7%
Wall Loss Energy	7,500,000	21.3%
Exhaust Energy	17,595,271	50.0%
Total Energy	35,190,543	100.0%

Case 2		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	1600	
Melting Energy	10,095,271	38.7%
Wall Loss Energy	5,000,000	19.2%
Exhaust Energy	10,978,379	42.1%
Total Energy	26,073,651	100.0%
Case 4		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	1600	
Melting Energy	10,095,271	33.2%
Wall Loss Energy	7,500,000	24.7%
Exhaust Energy	12,796,561	42.1%
Total Energy	30,391,833	100.0%
Case 6		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	1800	
Melting Energy	10,095,271	35.2%
Wall Loss Energy	5,000,000	17.4%
Exhaust Energy	13,585,744	47.4%
Total Energy	28,681,016	100.0%
Case 8		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	1800	
Melting Energy	10,095,271	30.2%
Wall Loss Energy	7,500,000	22.4%
Exhaust Energy	15,835,744	47.4%
Total Energy	33,431,016	100.0%

Savings for aluminum reverberatory furnaces

Furnace change	Btu/h saved	Btu/lb Al saved
Effect of 200°F increase in flame temperature	1,411,637	70.58
Effect of 200°F decrease in exhaust temperature	3,486,046	174.30
Effect of reducing wall loss energy from 7.5 to 5 million	4,642,045	232.10

Results of copper reverberatory furnace analysis

(Temperatures in °F)

Case 1		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2200	
Melting Energy	6,272,301	21.6%
Wall Loss Energy	5,000,000	17.2%
Exhaust Energy	17,713,616	61.1%
Total Energy	28,985,917	100.0%
Case 3		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2200	
Melting Energy	6,272,301	17.7%
Wall Loss Energy	7,500,000	21.2%
Exhaust Energy	21,642,188	61.1%
Total Energy	35,414,489	100.0%
Case 5		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2400	
Melting Energy	6,272,301	18.5%
Wall Loss Energy	5,000,000	14.8%
Exhaust Energy	22,544,602	66.7%
Total Energy	33,816,904	100.0%
Case 7		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2400	
Melting Energy	10,095,271	24.4%
Wall Loss Energy	7,500,000	18.2%
Exhaust Energy	23,721,632	57.4%
Total Energy	41,316,904	100.0%

Case 2		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2200	
Melting Energy	6,272,301	23.4%
Wall Loss Energy	5,000,000	18.7%
Exhaust Energy	15,499,414	57.9%
Total Energy	26,771,715	100.0%
Case 4		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2200	
Melting Energy	6,272,301	19.2%
Wall Loss Energy	7,500,000	22.9%
Exhaust Energy	18,936,914	57.9%
Total Energy	32,709,215	100.0%
Case 6		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2400	
Melting Energy	6,272,301	20.5%
Wall Loss Energy	5,000,000	16.3%
Exhaust Energy	19,323,945	63.2%
Total Energy	30,596,246	100.0%
Case 8		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2400	
Melting Energy	6,272,301	16.8%
Wall Loss Energy	7,500,000	20.1%
Exhaust Energy	23,609,659	63.2%
Total Energy	37,381,960	100.0%

Savings for copper reverberatory furnaces

Furnace change	Btu/h saved	Btu/lb Al saved
Effect of 200°F increase in flame temperature	3,018,769	150.94
Effect of 200°F decrease in exhaust temperature	5,791,405	289.57
Effect of reducing wall loss energy from 7.5 to 5 million	6,662,946	333.15

Results of glass reverberatory furnace analysis
(Temperatures in °F)

Case 1		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2800	
Melting Energy	13,771,643	16.3%
Wall Loss Energy	5,000,000	5.9%
Exhaust Energy	65,700,751	77.8%
Total Energy	84,472,394	100.0%
Case 3		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	2800	
Melting Energy	13,771,643	14.4%
Wall Loss Energy	7,500,000	7.8%
Exhaust Energy	74,450,751	77.8%
Total Energy	95,722,394	100.0%
Case 5		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	3000	
Melting Energy	13,771,643	12.2%
Wall Loss Energy	5,000,000	4.4%
Exhaust Energy	93,858,216	83.3%
Total Energy	112,629,859	100.0%
Case 7		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3600	
Exhaust Temperature	3000	
Melting Energy	13,771,643	10.8%
Wall Loss Energy	7,500,000	5.9%
Exhaust Energy	106,358,216	83.3%
Total Energy	127,629,859	100.0%

Case 2		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2800	
Melting Energy	13,771,643	19.3%
Wall Loss Energy	5,000,000	7.0%
Exhaust Energy	52,560,601	73.7%
Total Energy	71,332,244	100.0%
Case 4		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	2800	
Melting Energy	13,771,643	17.0%
Wall Loss Energy	7,500,000	9.3%
Exhaust Energy	59,560,601	73.7%
Total Energy	80,832,244	100.0%
Case 6		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	3000	
Melting Energy	13,771,643	15.4%
Wall Loss Energy	5,000,000	5.6%
Exhaust Energy	70,393,662	78.9%
Total Energy	89,165,305	100.0%
Case 8		
Parameter	**Btu/h**	**% Usage**
Flame Temperature	3800	
Exhaust Temperature	3000	
Melting Energy	13,771,643	13.6%
Wall Loss Energy	7,500,000	7.4%
Exhaust Energy	79,768,662	78.9%
Total Energy	101,040,305	100.0%

Savings for glass reverberatory furnaces

Furnace change	Btu/h saved	Btu/lb glass saved
Effect of 200°F increase in flame temperature	19,521,102	976.06
Effect of 200°F decrease in exhaust temperature	31,173,901	1,558.70
Effect of reducing wall loss energy from 7.5 to 5 million	11,906,250	595.31

Appendix E: Boiler Schematic

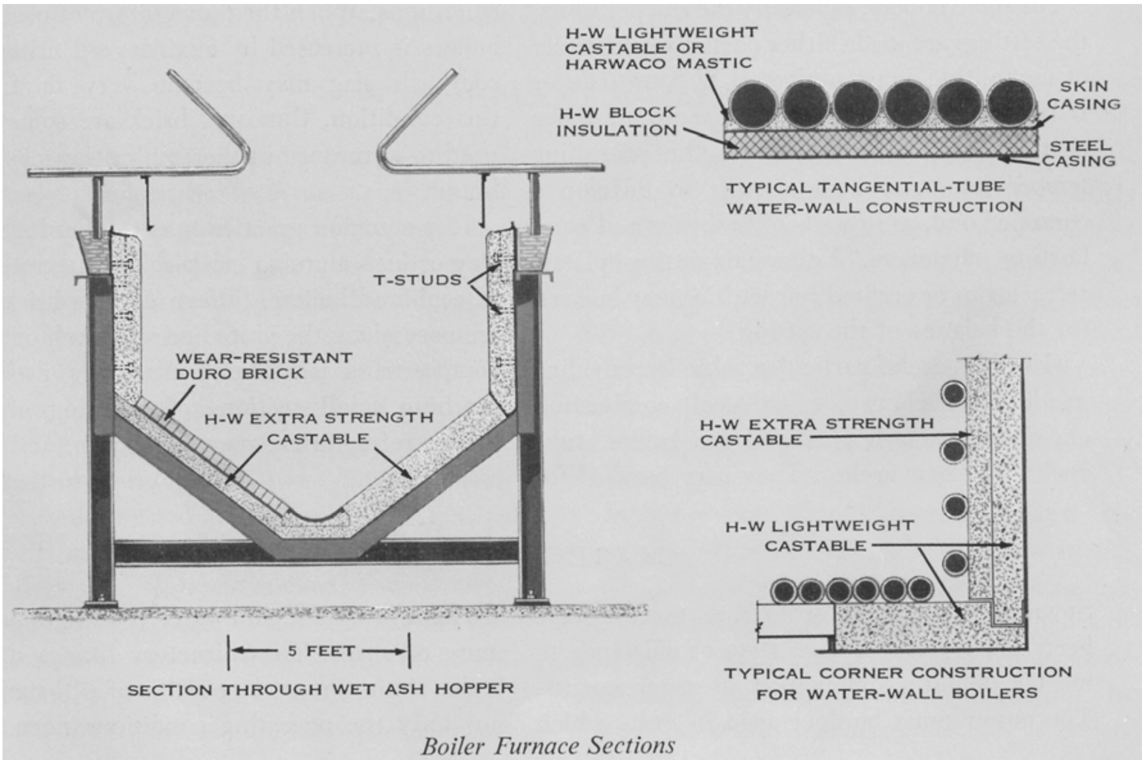


Fig. E.1. Boiler furnace sections. Reprinted from *Modern Refractory Practice,* 3rd ed., Harbison Walker Refractories, Pittsburgh, 1950.