SUBTASK 6.4 – IMPROVED CORROSION RESISTANCE OF ALUMINA REFRACTORIES

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SUBTASK 6.4 – IMPROVED CORROSION RESISTANCE OF ALUMINA REFRACTORIES

EXECUTIVE SUMMARY

Appropriate refractory selection is critical in optimizing productivity, energy efficiency, manufacturing, and labor costs in industries employing high process temperatures. Many factors need to be taken into account to select the optimum refractory. Some include material performance with respect to physical and chemical stability, installation issues, and the potential for contaminating the product pool (glass or steel). The greatest challenge is finding refractory that can withstand the harsh environments and yet be cost-effective since the cost for repairs between relines can be several million dollars. The final consideration for refractory selection is reuse and recycling of the used materials since environmental regulations are becoming more restrictive as to which materials can be landfilled.

The initial refractory work under the base cooperative agreement focused on the use of rare-earth oxide (REO) additives to castable alumina refractory to determine if the additives could increase the resistance of the material to slag corrosion in coal combustion systems. It was found that the REOs were not effective because they did not form continuous reaction products at the concentrations used, nor did they increase the sintered strength of the refractory. Therefore, in the spring of 1999, the focus of the project was changed to understanding refractory corrosion by flowing corrodents in other types of fossil-fueled thermal systems. A literature survey was performed to help define some of the major issues affecting refractories in thermal systems. The survey indicated that the single largest consumer of refractory materials is the steel industry, which typically purchases about 50% by weight of the refractories produced annually, with another 25% by ferrous and nonferrous foundries. Much of the remaining refractory materials are used by the glass industry. In addition, some of the most severe conditions for refractory corrosion in coal-fired power systems occur in gasification, not combustion systems. Therefore, it was decided to expand the capability of the EERC to perform flowing corrodent corrosion tests under diverse conditions by building a bench-scale furnace system to perform such tests in any atmosphere. This report summarizes the literature survey begun in the spring of 1999, as well as the initial construction of the bench-scale system up to the conclusion of Task 6.4 at the end of May 2001. The work is being continued under Task 6.6, Activity 2.

The initial objective of this project was to do a literature search to define the problems of refractory selection in the metals and glass industries. It was used to determine the areas in which the EERC can provide the most assistance through bench-scale and laboratory testing. The problems were found to fall into three categories: Economic – What do the major problems cost the industries financially? Operational – How do the major problems affect production efficiency and impact the environment? and Scientific – What are the chemical and physical mechanisms that cause the problems to occur? This report presents a summary of the results of the survey.

In the steelmaking industry, the operating conditions are particularly difficult: temperatures generally between 1500° and 1700°C; corrosion by molten metal, slag, iron oxide, dust, and gases;

thermal shock; and erosion. Refractory research in the steel industry should focus on applications "downstream" from the furnace. Much improvement has been made in the last decade in refractories and methods of repairing them. Therefore, the greatest gains still to be made can be achieved through research directed toward the ladle, tundish, and continuous casting refractories.

The operating conditions of the glass manufacturing industry are equally as difficult as the steel industry. Typical hot face refractory temperatures range from 1100° and 1700°C. The main refractory problems occur above the glass melt where temperatures are the hottest and products of combustion reside. The fastest growing technology in the glass industry in the past few years is the conversion from air–fuel combustion to oxy-fuel systems. The benefits include reduced NO_x and SO_x emissions and particulate carryover, as well as the improvement in glass quality and higher throughput. But the greatest disadvantage is the increased rate of corrosion to the crown and superstructure refractories in oxy-fuel furnaces because of the higher concentrations of water vapor and alkali in the gas caused by the absence of nitrogen which is a nonreactive dilutent. Hot-face corrosion and ratholing have proven to be very aggressive in oxy-fuel furnaces.

Once the problems were defined, the second goal of this project was begun: to design and build a bench-scale high-temperature controlled atmosphere dynamic corrosion application furnace (CADCAF). The furnace will be used to evaluate the corrosion resistance of refractories in the presence of flowing corrodents (slag, metal, glass) to temperatures of 1600°C under controlled atmospheres for extended periods of time. The conditions of the test will be chosen to simulate especially corrosive situations occurring in steel or glass-making operations or in coal gasification systems.

The CADCAF is an electrically heated bench-scale box furnace with a removable top, made of stainless steel. The furnace has a sealed cylindrical inner chamber where the test samples are located. It has the capability of testing two refractory test samples simultaneously, up to a maximum of 1600°C. The gas mixture will be introduced through a gas inlet valve located on the side of the corrodent hopper. It will exit the system through a gas outlet vent located on one side of the catch pot and then exhaust through the fume hood.

As of the end of Task 6.4 at the end of May 2001, the furnace and corrodent feed systems had been purchased, and a stand to hold the furnace and the corrodent catch pot had been built. In addition, the inner containment vessel had been cast, but will not be fired until the furnace is fully operational. Operational status for the furnace has been delayed because several of the molybdenum disilicide heating elements were broken during shipping of the furnace system, and we are awaiting their replacement.

SUBTASK 6.4 – IMPROVED CORROSION RESISTANCE OF ALUMINA REFRACTORIES

INTRODUCTION

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Through the base cooperative agreement and other U.S. Department of Energy programs, the Energy & Environmental Research Center (EERC) has developed expertise and equipment to accurately simulate the conditions leading to high-temperature corrosion of refractories in coal-fired combustion systems. The initial refractory work under the base cooperative agreement focused on the use of rare-earth oxide (REO) additives to castable alumina refractory to determine if the additives could increase the resistance of the material to slag corrosion in coal combustion systems. It was found that the REOs were not effective because they did not form continuous reaction products at the concentrations used, nor did they increase the sintered strength of the refractory. Therefore, in the spring of 1999, the focus of the project was changed to understanding refractory corrosion by flowing corrodents in other types of fossil-fueled thermal systems. It was found through literature survey that the single largest consumer of refractory materials is the steel industry, which typically purchases about 50% by weight of the refractories produced annually, with another 25% by ferrous and nonferrous foundries. Much of the remaining refractory materials are used by the glass industry. In addition, some of the most severe conditions for refractory corrosion in coal-fired power systems occur in gasification, not combustion systems. Therefore, it was decided to expand the capability of the EERC to perform flowing corrodent corrosion tests under diverse conditions by building a bench-scale furnace system to perform such tests in any atmosphere. This report summarizes the literature survey begun in the spring of 1999, as well as the initial construction of the bench-scale system up to the conclusion of Task 6.4 at the end of May 2001. The work is being continued under Task 6.6, Activity 2.

OBJECTIVES

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summary of these problems. It was used to determine the areas in which the EERC can provide the most assistance through bench-scale and laboratory testing.

The final objective of this project was to design and build a bench-scale high-temperature controlled atmosphere dynamic corrosion application furnace (CADCAF). The furnace will be used to evaluate refractory test samples in the presence of flowing corrodents for extended periods, to temperatures of 1600°C under controlled atmospheres. Corrodents will include molten slag, steel, and glass. This test should prove useful for the glass and steel industries when faced with the decision of choosing the best refractory for flowing corrodent conditions.

ACCOMPLISHMENTS

Steel Industry Overview

In the United States, two methods are used to produce steel: the ore-based, or integrated process, and the scrap-based, or electric arc furnace (EAF) process. Two different approaches are used to prepare semifinished billet: the integrated process uses a blast furnace, while the scrap-based process is done in a minimill which uses an EAF. Once steel is in the semifinished state, further processing is required in both the integrated steelmaking process and the minimill.

The integrated process is "old line big steel," with facilities encompassing several thousand acres. The manufacturing process uses a complex series of capital-intensive units to produce high-quality steel. Annual production of an integrated steel mill is 3 to 5 million metric tons. The minimill is much more compact and can fit within an area as small as a city block. Annual production of a minimill is 0.5 to 2 million metric tons. The minimill initially focused on lowest-quality steel markets but has recently taken over the structural steel market and is competing effectively in hot-rolled products.

Refractories and ceramic coatings are currently being used throughout the processes, although advanced ceramics are emerging slowly because of their longer life but higher cost. Steelmaking refractory development is moving away from the standard "single component" refractory materials to multicomponent composite materials composed of high-purity oxides, carbon, and graphite. Magnesia–graphite refractories (with and without metallic additions) have been used successfully in steelmaking vessel barrels and slag lines. Castable refractories, including self-flow types, are increasingly used to line low-wear areas of steelmaking vessels, while dry vibratable magnesia-based tundish linings have emerged as an alternative to sprayed magnesia linings.

In the steelmaking industry, the operating conditions are particularly difficult: temperatures generally between 1500° and 1700°C; corrosion by molten metal, slag, and iron oxide; thermal shock; and erosion (1). Refractory research in the steel industry should focus on applications "downstream" from the furnace. Much improvement has been made in the last decade in refractories, and methods of repairing them, used in the steelmaking furnaces. Therefore, the greatest gains still to be made can be achieved through research directed toward the ladle, tundish, and continuous casting refractories.

Integrated Steelmaking Process

An integrated steel mill starts with iron-bearing materials, principally iron oxides, which are reduced to molten iron in blast furnaces using coke as the reducing agent. Two primary processes are used to prepare the charge for the blast furnace: pelletizing and sintering. In pelletizing, unbaked balls are formed from iron ore combined with a binder. These balls are heat-treated in an oxidizing furnace at the mine and shipped to the mill where they are fed into the blast furnace along with coke, fluxes, and often sinter. In producing sinter, iron ore fines, coke fines, wastewater sludge, limestone, and air pollution control dust are agglomerated and heated. The heated mass is fused, cooled, and sized before being sent to the blast furnace.

Current applications of advanced ceramics in the integrated steelmaking process include wear surfaces on grinders, fans and crushers, coke rolls, refractory linings, and pollution control devices. New opportunities include single-piece fans, condensers, recuperators, and hot-gas filtration.

Blast Furnace Process

During the production of iron, ore, coke, limestone, and sinter are fed into the top of a blast furnace while heated air, sometimes augmented with fuel, is fed in through the bottom. As the charge descends through the furnace, carbon monoxide generated by the burning coke reduces the iron oxide in the ore to iron metal. The acid part of the ore reacts with the limestone to produce slag which contains unwanted impurities from the ore. The molten iron collects in the bottom of the refractory-lined furnace at a temperature of 1560°C. The slag is removed from the top of the molten iron and sold as a by-product. The molten iron is tapped from the bottom of the furnace and placed into refractory-lined cars for transfer to a desulfurization ladle.

Opportunities exist for improved refractories in the lower part of the blast furnace where coal is injected and in the desulfurization ladle. Opportunities also exist for the coal injection tubes themselves (tuyeres), which are short-lived because of wear. On average, 24 tuyeres are used for coal injection in a single furnace, each tuyere being 5–25 cm in diameter by 3 meters long.

Basic Oxygen Furnace Process

Basic oxygen furnace (BOF) steelmaking accounts for just under 60% of the liquid steel output in the United States and Canada (2). BOFs in operation today include conventional top-blown furnaces, bottom-blown furnaces, combinations of top- and bottom-blown furnaces, and inert gas-bottom stirring configurations. The predominant advantages of the BOF are very high production rates from few melting units and the tapping of low-residual-element (low-tramp element, low-nitrogen) liquid. The BOF is fed liquid pig iron, usually from blast furnaces, in amounts ranging from 65% to 90% of the total metallic charge; the balance is recycled scrap.

The top-blown BOF process generates heat by injecting high-purity oxygen into the molten iron from above. The oxygen reacts with the carbon and silicon to melt the scrap and remove impurities. No additional heat source is required. Various materials, including fluxing agents to produce metallurgical slags, are required for the refining process. Alloying materials, in the form of

alloyed scrap or ferroalloys, may be added singly or in combination to the molten steel during or after the carbon removal to produce steel.

According to Carniglia and Barna (3), the top-blowing process takes approximately 15 minutes, during which time the temperature of the charge rises, usually ending somewhat above 1700°C. The evolution of CO gas from within the charge churns it violently, intermixing the molten slag and metal, making voluminous froth and splashing it well up on the sidewalls of the "barrel." The atmosphere above the charge is principally a $CO–CO_2$ mixture, containing small amounts of SO_2 and other volatile oxides and much dust. It is exhausted through a movable hood and ducting. On completion of the "blow," the lance is withdrawn, and the vessel is tilted clockwise about 90°, so that the hot metal pours out the taphole while the cone restrains the overlying slag. Ordinarily, the vessel is then rocked back and forth to coat the upper walls with slag as much as possible; finally, it is turned all but upside-down to pour out the slag. If no lining repair or maintenance is needed, the BOF is ready for the next heat. The total elapsed time is about 30 minutes. Because of the advances in refractory materials and the benefits of slag splashing, BOF relines are down to once a year per furnace or less; lining life is in the 10,000 to 25,000 heat ranges (2).

Opportunities for advanced refractories or ceramics in the BOF process include the taphole gun nozzle, taphole sleeve, sensor shields, refractories in runners used to flow the molten steel from the furnace to refining ladles, and bottom-stirring elements. There is also a need for either metallized or refractory coatings for lower hoods to help furnace availability by extending hood life to that of the refractory lining (2).

The main differences between the top-blown furnace and the bottom-blown furnace are that the gas is injected from the bottom and the steel is removed through a hole drilled (tapped) through the refractory liner. A taphole gun is used to plug the hole with a refractory clay mix. The nozzle of the taphole gun must have high-thermal-shock resistance, high-temperature capability, and high-impact resistance. Monolithic ceramics of silicon carbide and mullite have been evaluated, but success with these ceramics has been limited because of their unpredictable, brittle behavior. Tapholes also see high-velocity metal and slag; the main concern there is maintenance of a constant diameter (3).

Shields are sought for sensors that can monitor melt temperature, uniformity of the melt, and offgas composition. Although lightly loaded, these sensor shields must operate at temperatures in excess of 1650°C while exposed to highly oxidative and corrosive gases (4). Runners for transferring the molten steel from the BOF to the refining ladle are often fireclay brick maintained with plastic and ramming mixes. Because of their high maintenance cost, castable refractories high in aluminum oxide and chromium oxide are being used, although operating life is still limited to 1 to 2 weeks. Further environmentally acceptable improvements in the lifetime of the runner refractories are sought. The main type of attack in the runners is from erosion by the molten flowing steel.

Bottom stirring based on gas injection is used in the BOF to reduce slag buildup and improve temperature and metal uniformity. Bottom-stirring elements include water-cooled metal pipes enclosed in refractory (tuyeres) and porous plugs. Problems with tuyeres include burning back the metal pipe with a loss of flow control, plugging by molten metal flow into the tuyere, cupping of the

tuyere end, and loss of furnace energy efficiency when water-cooled. The problem with porous plugs is low gas flow and low abrasion resistance. Improved temperature capability is also sought for porous plug materials.

Electric Arc Furnace Steelmaking Process

The EAF is the second highest producer of steel in the United States (3). The conventional top-charged EAF process now accounts for 40% of the U.S. raw steel production (2). It is versatile as to size and as to feed, receiving scrap and blast furnace hot metal or the output of an oxygen furnace. It may be fed some coke, and either acid or basic slagging may be used. In the United States, the latter predominates.

Freitag and Richerson (4) describe the EAF process. Unlike the integrated steel process, electric arc steelmaking furnaces use scrap metal as the charge that is melted and refined using primarily electricity. Cylindrical, refractory-lined arc furnaces are equipped with carbon electrodes that are lowered through the furnace roof. During charging, the furnace roof is removed, and scrap metal is placed into the furnace. Alloying agents and fluxes are added through doors on the side of the furnace. The electrodes are lowered to within 1 inch of the metal surface, and current is applied to generate heat above the metal. Oxygen is injected through a consumable lance to decarburize the steel and to supplement thermal energy. During melting, oxidation of impurities occurs and forms a slag on the molten metal surface. Similarly, as in the integrated process, unwanted materials are removed and alloying agents added. The final product is removed from a taphole on the side of the furnace.

EAFs have the highest refractory wear of steel production furnaces. Refractory consumption averages 2 pounds/ton of steel for brick and 9 pounds/ton for gunned repair materials (5). The slag line is a high-wear area because of the turbulence created by the metal–slag mixing. Below the slag line, the refractory is exposed primarily to metal and slag; above it, to splash, CO–CO_2, and dust and direct radiation from the arcs. Hot spots occur in sidewalls where this radiation is most intense. Except for these areas, the sidewalls and bottom see common maximum steelmaking temperatures of about 1700°C with basic slagging and about 1600°C with acid slagging (3). Opportunities exist for advanced ceramics in EAFs in longer life electrodes, oxygen injection lances, oxy-fuel burner nozzles, recuperators, runners for transferring the hot metal to the refining ladle, and as a replacement for high-maintenance refractories applied to the water-cooled panels of the sidewalls and top of the EAF. Current refractories are repaired on a weekly basis.

Ladle Refining Process

Ladle refining refers to the metallurgical processes done in the ladle (2). According to Freitag and Richerson (4), the cost of refining and casting steel accounts for 95% of the total cost of the finished product. Thus the use of new materials in these operations could potentially add high value by significantly lowering overall cost. A number of processes are often used to refine the molten steel in a ladle after it leaves the BOF or EAF prior to casting. Ladle refining processes include argon oxygen degassing, ladle metallurgy, vacuum arc remelting, and vacuum degassing. Processes selected are based on the desired metallurgy and purity.

Refining is performed in separate ladles to prolong the life of the furnaces. Ladle refining vessels range in sophistication from in-house designs built with plant equipment to engineered, multifunction stations (2). The refractory lining in a ladle arc furnace is exposed to severe service conditions (6). These conditions include high temperatures, corrosive slags, long holding times, and violent bath agitation. The steel ladle refractories must withstand corrosive attack at up to 1700°C.

Freitag and Richerson (4) explain the ladle refining process. It is generally performed by electric arc reheating. The molten metal bath is stirred throughout the process to provide for thermal and chemical homogenization and to accelerate metallurgical reactions. Stirring is provided by inert gas introduced near the bottom of the ladle using porous plugs, tuyeres, or lances. Gas injected from above using water-cooled, refractory-coated metal lances is considered safer than porous plugs or tuyeres, but maintenance is high, and heat efficiency is reduced. Porous plugs, which are the most commonly used during refining, last only 30 heats because of erosion by the flowing metal. Because of their many disadvantages, replacement of lances is a several million dollar a year business.

Although tap temperatures from the BOF and EAF typically are lower, temperatures at ladle slag lines are higher because of the submerged arc reheating. Slag temperatures have been measured in excess of 200°C higher than the temperature of the steel bath. The upper slag line (filled level) and lower slag line (discharged level) are foci of corrosive wear. The slag corrosion of refractories is directly proportional to slag fluidity and temperature (1). The possibility of "hot spots" in the ladle lining because of arc flare also exists.

Improving slag resistance, especially penetration resistance, of castables for making ladle linings has become the focus of research and development work in monolithic refractories. Structural spalling caused by slag intrusion is, in most cases, the main wear mechanism (7). Other requirements for the refractory used in ladles is that the refractory must not shrink from the shell over some 10 to 100 temperature cycles, nor crack under the thermal shock of being filled, and it must endure much mechanical abuse (3).

Because of the high temperatures, erosion from the stirred bath, and high corrosiveness of the metallurgical slag, high-alumina and magnesia-based (slag line) castable refractories are preferred for ladle linings. Still, life remains short (30–50 heats). In some instances, higher-temperature-capable oxide–carbon mixtures are being used to provide a balance of reasonable purity, high thermal shock resistance, and low erosion. Alternative refractories having longer life, lower cost, and safer disposal are sought.

In addition to use with porous plugs, tuyeres, lances, and refractories, opportunities exist for advanced ceramics in ladle recuperators and impact pads. Recuperators are exposed to corrosive gases, and impact pads are located at the bottom of the ladle and, ultimately, determine the life of the ladle. Materials with higher-strength capability at temperature, improved abrasion resistance, and high-thermal shock resistance are desired.

Steel Casting

After the steel has been refined, it is ready to be cast into ingots or continuous strips. Ninety-seven percent of all steel produced in 1995 was continuously cast, while the remaining 3% was ingot cast (4). Carniglia and Barna (3) describe continuous casting. In this process, a transfer ladle is placed at the top. A "ladle shroud" (vertical refractory tube) is affixed under its slide gate valve, by means of which molten steel is delivered intermittently to the tundish immediately below. This procedure keeps the tundish, a much smaller surge reservoir, always nearly full. Below the tundish is the "tundish shroud," another tube whose lower extremity is submerged in the steel, which it delivers by gravity feed down into a water-cooled copper mold. The casting machine can have either one (single strand) or multiple molds (multistrand caster) (4). The steel cools as it passes through the mold and forms a solid shell or "skin." As the steel proceeds onto the runout table with a series of hot-handling rollers, the center of the steel solidifies, yielding a semifinished shape at a specified width and thickness. A cutting torch is used at the end of the roll line to cut the steel to the desired length. Because of the harsh operating conditions, the life of many of the components of the caster pouring system is less than one heat.

According to the *Steel Industry Technology Roadmap* (2), submerged entry nozzles (SENs) are often the limiting material in refractories used for molten steel control. SENs are used in steelmaking to prevent reoxidation of molten steel directly from stream contact with the surrounding environment and from air entrapment and splashing when the molten stream strikes the liquid surface in the mold. Accretion formation and the associated clogging of tundish flow control systems are major problems that lead to decreased strand speed, premature changing of SENs, or strand termination and associated reductions in productivity, consistency, and steel quality.

SENs are replaced as often as once every 2 to 4 heats as compared to BOF linings that last more than 10,000 heats. Assuming a cost of $500 per SEN, a company would spend in excess of $2 million on SENs between furnace relines. This figure is even greater when other factors are considered, such as the cost of physically replacing the SENs and the cost associated with decreased productivity as nozzle accretion occurs. Similar cases could be made for ladle slag lines, tundish linings, and slide gates and shrouds.

Sliding glass plates are used for controlling the steel flow during the casting of steel. A typical material used for this application is pitch-impregnated corundum–mullite, zirconia, or SiAlON. The plates are subjected to two main types of attack: corrosion by steel, slag, and iron oxide and erosion by the steel flow. They also have to preserve the steel quality by minimizing inclusions (1).

Bitouzet and others (1) state that one of the most important problems for steelmakers is corrosion by the low levels of calcium present in steel. In the case of a corundum–mullite sliding plate, the mechanism of corrosion is the formation of CaO by reaction of the calcium with the refractory, followed by the formation of a low melting point liquid phase as the CaO penetrates into the refractory. The liquid phase is then washed away by the steel. The average service life is less than two heats. SiAlON is the preferred material because it is a reduced material, and the porometry is very fine which allows very little penetration of steel containing CaO. Therefore, the corrosion is much slower.

Refractory wear and reaction with the highly corrosive slag can generate defect-forming inclusions in the steel. Inclusions are formed from refractories contained in the ladles, tundish, and molds. Material systems used to contain the steel must be stable and not add to the inclusion count. High alumina refractories are commonly used throughout the process with application of zirconia-based (areas of high wear or thermal shock) and magnesia-based (areas of high slag corrosion) materials as required. Carbon-containing refractories have been considered throughout the pouring system, but they react with oxide-based refractories to form carbon monoxide. Aluminum contained in the steel also reacts with the refractory to form alumina. Silica-based refractories are not used because of the potential for steel contamination.

According to Freitag and Richerson (4), clogging of the caster pouring system is the single largest operational problem resulting in reduced quality and production delays. One source of clogging is from the interaction of the molten steel or slag with the refractory. Remedies to clogging include alternate refractory materials, application of glazes to the refractory, and reduction of residual porosity in the refractory. Currently available remedies do not completely eliminate clogging; therefore, alternate materials are being sought.

To limit oxygen pickup during pouring from the ladle, a thin-wall ladle shroud is attached to the bottom of the ladle. The shroud extends into the molten metal contained in the tundish. Common causes of ladle shroud failure include plugging, throat cracking, erosion in the throat, bottom slag line erosion, or bottom vertical cracking. A similar shroud is used to protect the molten metal stream as it leaves the tundish when not protected by the nozzle itself. The high-alumina refractories commonly used for the shrouds have a life expectancy of 1–10 heats before they need to be replaced.

Forming and Finishing

After casting, the slab, billets, and blooms are further processed to produce strip, sheet, plate, bar, rod, and other structural shapes through various hot-forming operations that can then be followed by cold-forming operations, depending on application (4). Finishing operations are often product-specific heat treatments (such as spheroidizing, normalizing, or annealing) or surface treatment operations (such as galvanizing, electroplating, carburizing, machining, or surface induction treating) (2).

The most common hot-forming process is hot rolling, which uses a series of water-cooled rolls to reduce the thickness of a heated steel slab. Surface scale is removed from the heated slab by a scale breaker and water sprays prior to entering the roughing stands containing the sets of rolls. At the end of the roughing section, the steel enters the finishing stands for final reduction, then it is cooled and coiled.

Cold rolling is used to reduce the steel to final dimensions and surface finish or to form pipes and tubes. Cold rolling is similar to hot rolling except the metal is not heated. During cold rolling, the steel is hardened and must be heated in an annealing furnace (800°–1200°C) before use to make it more formable. After the steel is softened in the annealing process, it is typically run through a temper mill to produce the desired flatness, metallurgical properties, and surface finish.

Finishing processes such as pickling and oiling are used to clean the surface of the semifinished, hot-rolled steel prior to cold rolling, forming, or coating operations. Mill scale, rust, oxides, oil, grease, and soil are chemically removed by a variety of chemical and physical processes. Acid pickling processes which use hydrochloric, nitric, sulfuric, and other combinations of acids are used to remove oxide scales. After pickling, alkaline cleaners may be used before cold rolling. Corrosion-resistant steels, ceramic-coated steels, graphite, engineered polymers, glass and, in some cases, advanced ceramics (primarily nonoxides) are used throughout these processes. Opportunities for use of advanced ceramics include condensers, exhaust fans, pumps, spray nozzles, and processing tanks.

Glass Industry Overview

Glass manufacturing encompasses numerous chemical formulations, melted at various temperatures and in several kinds of equipment (3). The glass industry consists of four major segments: container glass, flat glass, fiberglass, and specialty glass. While the container, fiber, and flat glass industries focus on producing soda-lime glass for large broad-based markets, the specialty glass industry focuses on higher-temperature glasses. Key drivers for investment in the glass industry include cost, quality, and increased productivity.

Ceramic-based materials commonly used in glass-processing equipment include fused silica, alumina, and alumina–zirconia–silica (AZS); graphite; precious metals; and water-cooled ferrous alloys. Ceramics are primarily used as refractories, with ceramic coatings increasingly being used for wear resistance. Glass contact refractories must be of oxide composition. Carbons, carbides, and even chrome-containing oxide formulations would release dark-colored particles into the melt by corrosion or otherwise, and glass products in general can tolerate neither color nor the presence of undissolved particles (stones) (3). Advanced ceramics are rarely used because of their high cost. Owing to the lack of suitable higher-temperature-capable materials, fluxes are commonly used to reduce glass-processing temperatures and permit the use of conventional materials.

There are four primary operations for glass manufacturing: batching, melting, refining, and forming. Batching, melting, and refining operations are common to all glass-manufacturing processes with some variation in furnace type. Various postprocesses are used, depending on the end product. Glass-melting furnaces can be divided into those heated electrically and those heated primarily by combustion. Starting with specialty glass compositions and then expanding to more common glass such as soda lime, oxy-fuel firing has been, over the past few years, the fastest growing technology in the glass industry.

The benefits of conversion from an air–fuel combustion system to an oxy-fuel system have been well documented in numerous articles. Depending on the driving force for conversion, these benefits include reduced NO_x and SO_x emissions and particulate carryover, as well as an improvement in glass quality and higher throughput (8). Oxy-fuel conversion can reduce NO_x emissions from a typical float glass plant from over 320 kg/hr to approximately 40 kg/hr (9), the greatest disadvantage being the increased rate of corrosion to the crown and superstructure refractories in oxy-fuel furnaces because of the higher concentrations of water vapor and alkali in the gas caused by the absence of nitrogen which is a nonreactive dilutent. For example, a typical flue

gas composition for an oxy-fuel soda-lime furnace would be 13% N_2, 52%–56% H_2O, 2%–4% O_2, 31% CO_2, and 200–220 ppm NaOH. A typical flue gas composition for an air-fueled soda-lime furnace is 68% N_2, 18% H_2O, 2% O_2, 12% CO_2, and 60 ppm NaOH (10, 11). Typical hot-face refractory temperatures in a glass furnace range from 1100° to 1700°C.

Batching

Raw material selection is based on chemistry, purity, uniformity, and particle size. Additional organic, metallic, and ceramic contaminants may be introduced throughout the delivery, storage, mixing, and sizing processes, as well as through the use of cullet (recycled glass). Because of the effects of contamination, the use of cullet varies within the industry according to the desired end product. Delivery, mixing, and sizing processes are highly abrasive, and equipment used commonly contains ceramic-coated wear surfaces or ceramic liners manufactured from alumina, silicon carbide, or tungsten carbide. While generally cost-effective and with adequate performance, lower-cost solutions offering lower risk of contamination are sought.

Melting

The melting tank is a rectangular refractory box about 3–4 ft high (3). The granular feed materials are charged and mechanically stirred in at one end, where melting and evolution of CO_2 are most concentrated. Much of the length of the tank is devoted to achieving uniformity of the glass temperature and composition. At the opposite end is a constriction or throat, containing a weir under which the glass flows to the refiner section. Homogenizing is completed there, plus removal of any retained CO_2 bubbles, by passing gas in much larger bubbles up through the melt: a process called "fining." The refiner discharges to a forehearth from which the liquid is taken for forming by sheet casting, molding, blowing, fiberizing, etc.

Glass furnace refractories may be subjected to corrosion by several mechanisms. Winder and others (12) explain the corrosion mechanisms associated with the glass-melting furnace. Refractories contacting liquid silicate in the molten glass bath undergo chemical degradation, with several physical mechanisms of material removal being possible. Any glass flow tends to increase contacting refractory corrosion driven by surface tension, temperature, or density differences. Considering application of the same glass-melting temperature in both oxy-fuel and air-fuel cases, the decreased viscosity of glass melt in an oxy-fuel furnace may be expected to increase both convective flow and the diffusion rates of alkali and alkaline-earth species into contacting tank sidewall and bottom refractories. In addition, increased OH^- diffusion into the refractory surface may also cause a degradative effect in the case of refractories containing silicate phases.

According to Winder and others (12), glass tank bottom refractories are generally subjected to relatively minor convective flow, unless situated close to bubblers, stirrers, etc., because of buildup of thick boundary layers. However, tank sidewall refractories are exposed to the three-phase interface at the melt line, where a surface tension-driven convection mechanism, otherwise known as the Marangoni effect, is responsible for relatively rapid material removal. In addition, the three-phase melt line interface usually acts as a heterogeneous nucleation source for exsolution of gaseous phases from the molten glass bath. Surface tension-driven convective forces are associated with the

gas bubbles, which consequently grow at this interface, and these forces tend to cause accelerated refractory corrosion locally. Undercutting immediately below the melt line has also been a common experience, associated with a liquid-corrosion phenomenon called upward drilling (3). By contrast, all refractories above the melt line face a different chemistry, but always coupled with thermal cycling because of the reciprocal operation of the burners and gas flow. If oil is used as fuel, its ash becomes part of the chemical and erosive environment.

Refining

The glass-conditioning operation (refining) occurs in the forehearth and provides molten glass that is uniform in temperature. Temperature sensing is critical in the forehearth and shares problems similar to those encountered in the melt section. Plungers and nozzles used to distribute the molten glass are refractory ceramics or molybdenum, but they experience high wear and erosion resulting from glass flow and corrosion.

Forming

The forming process varies for the type of glass. Freitag and Richerson (4) review the forming process for the different glass industries. Two glass-forming processes are used in the flat glass industry. One developed by Pilkington Brothers (PB) and one developed by PPG Industries, Inc. Major differences between the two processes involve how the glass is introduced into the furnace. A typical float zone furnace is 49 meters long and 9 meters wide and can hold 909 metric tons of glass. In the PPG process, the refined glass flows in a continuous, full-width ribbon onto a molten bath of tin contained in an air-cooled refractory-lined steel shell. In the PB process, the molten glass enters a much narrower region onto a molten bath of tin and takes a very complicated flow path before it reaches its full width. In both processes, glass enters at a temperature of 1040°C and exits at a temperature of 600°C. The tin bath is maintained at a temperature of 815°C, whereas the steel shell air is cooled to 100°C. An atmosphere of N_2 plus 5%–8% H_2 is used to prevent oxidation. Alternate materials considered for replacement of the refractory-lined steel/tin bath shell are either costly, difficult to fabricate into the desired shape, or lack oxidation resistance.

A fused-silica gate called a tweel regulates the flow of glass into the float zone furnace from the refiner. The tweel meters the glass flowing into the float zone furnace and thereby helps control the finished product thickness. Because the life of the tweel is only 10 months, alternate materials are being sought to increase life. In addition to molten glass compatibility, requirements for the tweel include high-thermal shock resistance and load-carrying capability at molten glass temperatures. Replacements for water-cooled materials are also sought because of the high level of maintenance and added cost for corrosion.

In the container glass industry, after conditioning to the desired temperature and uniformity, the molten glass is transferred to the forming operation through the gob feeder. The gob feeder is an integral part of the forehearth and includes a mixer, plunger, orifice, and shears. The materials of construction for the gob feeder include water-cooled metals (cut-off blades), precious metals (stirrer), and refractories (plunger) to accommodate glass gob temperatures approaching 1100°C.

With the exception of coatings, no advanced ceramic materials are used in the forming of glass containers. Opportunities for their use exist, however, because of the increasing emphasis on lightweight glass containers, continuous production, and improved energy efficiency as competition increases from abroad. Specific opportunities include replacement of graphite in areas of hot handling, with alternate materials providing higher toughness, greater hardness, and improved oxidative ability. Lower-cost materials are sought to replace precious metals used in the forehearth and gob feeder. Materials with higher thermal diffusivity and hot hardness are sought for the molds to extend life and reduce cycle time without external cooling. Higher-temperature-capable materials are desired throughout the mold machine for reduced maintenance and improved quality.

In the fiberglass industry, molten glass leaves the hearth and enters the fiberization process directly or after an intermediate marbleizing process. Marbleizing is commonly used for textile fiber production when the forming process is not located in close proximity to the melter. Fiberization occurs by attenuating a melt stream with air, steam, or combustion gas (for wool) or by drawing molten glass through precious metal bushings. For the wool processing, a single stream of molten glass falls into a rapidly rotating cylinder (centrifuge) made of high-temperature base metal alloy. The cylinder contains 10,000 to 30,000 laser-drilled holes having diameters 0.1–0.015 inches. Operating conditions include steady-state temperatures of 1093°C while exposed to air. Typical lifetime is 40–100 heats. Alternate materials are sought with increased creep strength, resistance to corrosion (sulfidation) and oxidation, and reduced cost. As the molten glass is driven through the perforated cylinder, downwardly directed high-velocity gas jets attenuate the flow and form fibers of varying lengths.

In the continuous textile forming process, glass marbles are fed through orifices in an electrically heated platinum alloy bushing. Bushing life is about 6 months, at which time the bushing is recycled because of the high cost of raw material. Life is limited by hole wear and sag. Operating conditions include steady-state temperatures of 1200°C in air. Forced convection-air cooling is used prior to the sizing application to increase productivity. A winding drum collects the filaments and applies a traction force to stretch the fibers as they are pulled through a mechanical device that applies an organic sizing and twists multiple filaments into a single strand. Materials used to handle and guide hot filaments are carbon-based. Alumina and silicon nitride guides are used for sizing application and twisting where high wear can occur. Alternate materials are sought for fiber handling that exhibit many of the characteristics of monolithic ceramics but have improved toughness for increased reliability.

The specialty glass market segment is a catchall for glass products not contained in the flat glass, container glass, and fiberglass market segment. An important difference is that the specialty glass producers, unlike the other glass producers, work with higher-temperature glasses, aluminosilicates, and borosilicates, as opposed to soda-lime glass. Because of the high temperatures, refractories and thermocouple sheaths are a problem. A range of high-temperature base metal alloys and precious metals are used throughout the melt and forming steps. After the melting process, the glass goes in different directions for forming, depending on the final product. During the forming operation, molds are generally superalloys. Ceramic molds were considered but shown to increase the presence of stones in the finished glass. Opportunities common among the different glass market

segments also exist, but operating conditions both above and below the melt are much harsher in specialty glass.

Combustion-Heated Furnaces

There are 600 glass furnaces in North America. The life of a glass-melting furnace between rebuilds varies, but 7–8 years is not uncommon. The cost of rebuilding a furnace can easily exceed $1 million and is very time consuming. Glass-melting furnaces can be divided into those heated electrically and those heated primarily by combustion.

Freitag and Richerson (4) explain that combustion-heated glass furnaces can be further divided according to the method used to recover exhaust heat and the way the fuel is burned (with air or pure oxygen). Recovery of exhaust waste heat is performed with a regenerator or recuperator. Regenerator furnace designs represent one of the oldest and most universal devices for saving energy in the glass industry.

Refractories commonly used in regenerative glass melt furnaces are AZS, silica, and zirconia silicate. AZS is the material of choice for the sidewall, with zirconia content ranging from 33% to 41%. Various chrome-containing refractories are commonly used in the fiberglass industry because of their superior erosion resistance but are gradually being replaced because of environmental concerns about chrome. Even though superior in performance, chrome-containing refractories are not used in the flat, container, and specialty glass industries because chrome impurities result in glass discoloration.

At the front of the furnace where the charge is introduced, erosion and thermally induced damage are the most severe and limit furnace life. Materials that are more corrosion-resistant are sought for the sidewalls. AZS electrodes and burner blocks are located on the sidewall below the melt line. These blocks support the electric boost heat electrodes and burner nozzles, both of which experience high local temperatures and thermal stresses that result in reduced life.

The main refractory problems occur above the glass melt where temperatures are the hottest and products of combustion reside. Superstructure refractories can experience temperatures approaching 1600°C when air-fuel fired, and much hotter when oxy-fuel fired. Silica is the material of choice for the crown in soda-lime glass furnaces because of its low cost ($642/m^2) and its ability to dissolve into the melt if dislodged. However, silica does not perform well under the increasingly harsh environment of oxy-fuel firing. Muysenberg and others (11) describe the corrosion mechanism for silica refractory exposed to oxy-fuel atmosphere in flint container glass furnace at 1510°C. NaOH from the furnace atmosphere dissolves in FeCaO-silicate grain boundary liquid phase at exposed refractory surfaces. Because of higher flame temperature and lack of diluting nitrogen, the concentration of NaOH vapor is much higher in an oxy-fuel system than in one heated with an air-fuel flame. The resulting lower viscosity liquid penetrates the open porosity (~24%) by capillary action. The refractory structure is unstable in the presence of this liquid, and the crystalline SiO_2 refractory skeleton is dissolved.

Hot face corrosion and ratholing have proven to be very aggressive in oxy-fuel furnaces (13). It is extremely important to seal an area that begins to rathole. The time frame is a matter of hours and days, not weeks, before a significant amount of refractory material disappears and structural and operational integrity become a concern (14).The rate of corrosion is more dependent on the position in the furnace and concentration of alkali than the temperature (13). The corrosion normally does not occur on the hot face of the refractory, but in a joint or other fissure. The hot flux migrates up into an opening in the crown or superstructure wall, cools, and condenses. The flux then attacks the surrounding silica to form a glassy phase that drains out of the fissure. This often forms a void as large or larger than a baseball before it is discovered on the cold face of the refractory or from observations on the hot face (15).

Mullite has been used for the crown in processing higher-temperature glasses but can create inclusions in the glass (4). Although mullite appears to perform slightly better than silica, it is thermodynamically unstable against NaOH, KOH, etc., in oxy-fuel environments and also does not represent the optimum choice for extended refractory service life (8).

Materials such as fused AZS have been considered for the crown, but the cost is much higher ($\$10{,}764/m^2$) and the weight is much greater (4, 14). AZS samples exposed to oxy-fuel glass melting atmospheres exhibit more corrosion than material exposed to air-fuel, but this product is considerably less affected than the porous silica and mullite refractories (8). Muysenberg and others (11) explain the corrosion mechanism responsible for the degradation of AZS refractory in oxy-fuel atmosphere of a flint container glass furnace at 1510°C. NaOH from the furnace atmosphere dissolves in NaAlO-silicate grain boundary phase at exposed refractory surfaces. The refractories' alumina structure is unstable in the presence of this liquid and is dissolved. This effect causes an expanding liquid-phase volume on the refractory surface. The aluminosilicate liquid contains both dissolved and crystalline zirconia so that run-down and drip contaminates the glass bath with a potent source of defects. Defects resulting from corrosion by-products dripping onto the glass surface currently cause a 2% reduction in yield, and total energy loss for the entire U.S. glass industry because of defects is approximately 6×10^{12} Btu/yr (9).

Two fused-cast alumina refractories (α-*β* alumina, *β*-alumina) are also considered acceptable in areas where batch carryover and subsequent contamination by silicate is not an issue (8). Experience with these alumina refractories after use has shown the presence of an α-alumina layer. Considerable experience in application of these refractories in glass-melting furnaces suggests that this effect passivates over the long term. This layer represents a stable phase in application and as such is not considered a problem. However, since the *β*-alumina refractory undergoes less transformation, which creates less new porosity, this is considered the optimum choice for above-glass application in most (low alkali) glass-melting environments (8).

Electrically Heated Furnaces

Electrical heating is used exclusively in many smaller specialty and fiberglass melting furnaces because of its lower initial cost and low emissions, even though energy costs remain high. Key disadvantages of all electric furnaces are the high-energy cost and short furnace life. Electric furnaces are rebuilt as often as every 6 months, but because of their small size, down time is limited to only

about 2 days. An example of an electric furnace is a bottom entry electrode furnace. The melt exits through a submerged throat into a separate temperature-conditioning chamber. Bubblers and stirrers are frequently used to improve homogeneity of the melt and eliminate bubbles. Materials used in the construction of small specialty glass and fiberglass furnaces include precious metals (for bubblers, stirrers, plungers) and molybdenum (for electrodes and flow control hardware). Replacement materials are sought that are lower in cost and provide longer life.

Refractory Recycling

When refractory linings are inadequate for continued use, the spent lining is demolished and discarded, and a new one is put in place. Depending on the particular application, refractory material may last only a few hours or as long as several years. Spent refractory materials are disposed of in a landfill or recycled. Many issues must be considered for the successful recycling and reuse of spent refractory material. These include the type; users and producers of refractories; local, state, and federal regulations; health concerns; contamination; value of materials including worth of components and cost associated with disposal; and economics of separation and beneficiation.

Many factors are driving the interest in recycling and/or reuse of spent refractory materials. Foremost is the need to develop pollution prevention technologies that will improve competitiveness, efficiency, and compliance with environmental regulations. Other incentives include more stringent environmental regulations and rising costs of landfill space, landfill bans on hazardous materials, and changing regulations that ban disposal of spent refractories with slag and waste both mineral-and fuel-related natural resources. Refractory recycling is complicated by the presence of varying amounts and types of impurities within the used refractories, problems sorting and removing unwanted refractories, and problems with foreign objects being transported with the refractories of interest.

Controlled Atmosphere Dynamic Corrosion Application Furnace (CADCAF)

The EERC currently has the capability to test the corrosion resistance of refractories or other materials by flowing slag in an air environment. However, the literature survey of the needs of the steel and glass industry and the known needs of coal gasification systems indicate the need for a bench-scale flowing corrodent reactor capable of operating in a variety of atmospheres other than air. Under Task 6.4, the CADCAF was designed and is being built to simulate conditions of dynamic corrosion on the vertical wall of a refractory-lined glass, steel, or coal gasification system under controlled atmospheric conditions. The CADCAF is an electrically heated bench-scale box furnace with a removable top, made of stainless steel. Approximate external dimensions are 40 by 30 by 40-in. deep, and internal working area, 18- by 16- by 18-in. deep. It is illustrated in Figures 1 and 2. It has the capability of testing two refractory test samples simultaneously, up to a maximum of 1600°C.

It uses 12 molybdenum disilicide ($MoSi_2$) heating elements, which are located on all four sides of the furnace in an 18-in. square. The insulated walls are 7 in. thick with high-temperature grade, vacuum-cast ceramic fiber insulation. The furnace has a sealed cylindrical inner chamber where the test samples are located. This inner chamber has a 12-in. diameter by 12-in. height, made of

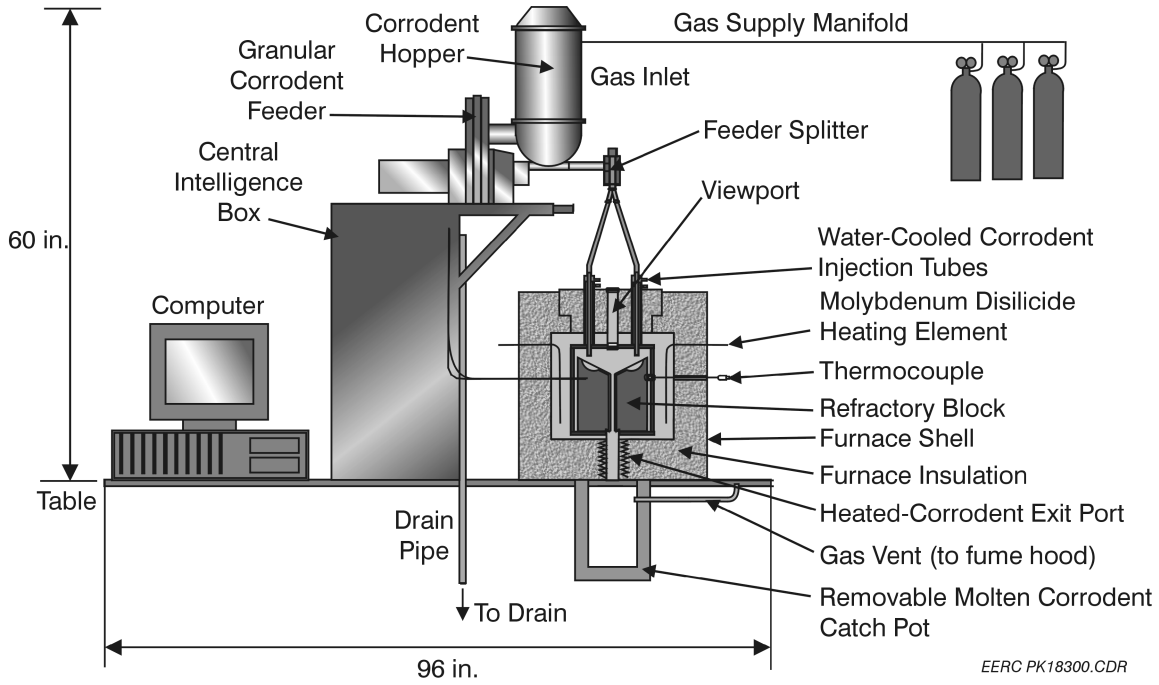

Figure 1. Schematic of the CADCAF.

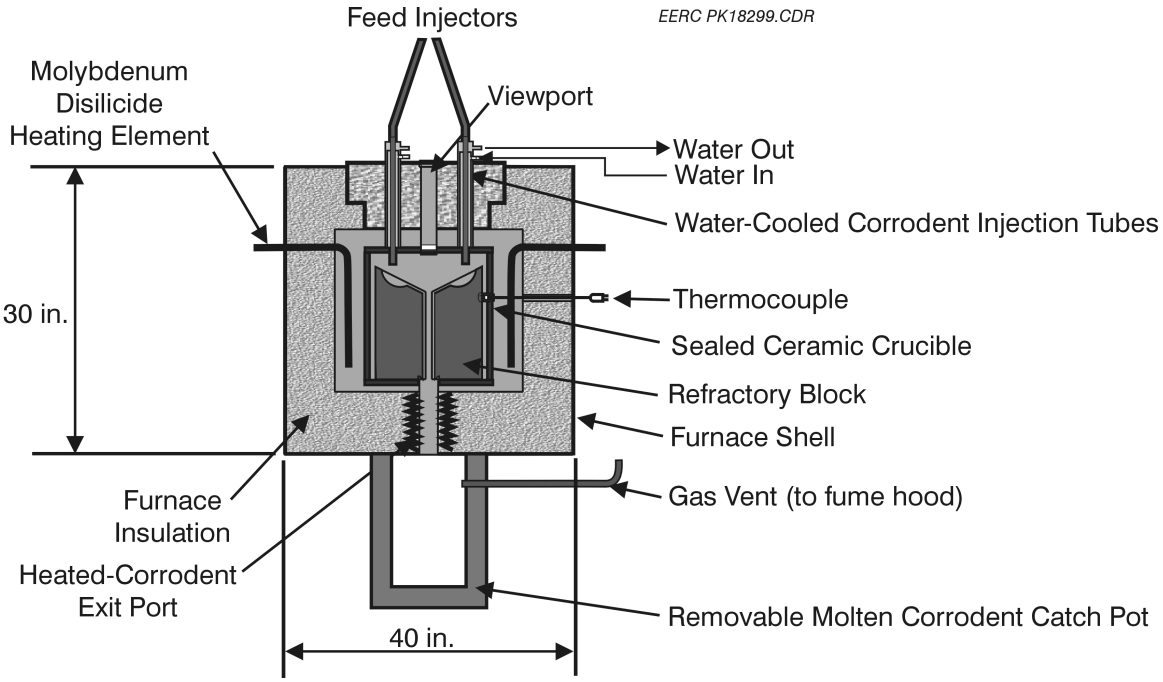

Figure 2. Schematic showing close-up of interior of the CADCAF.

vibration-cast alumina refractory. The walls are approximately 7/8 in. thick, including the removable top and bottom plates.

Two-corrodent injector feed ports and a single view port are located on the removable portion of the top of the furnace. The view port is 99.8% dense recrystallized alumina ceramic tube with a Vycor™ window at the cold junction and a sapphire window at the high-temperature junction. The injector feed tubes are water-cooled stainless steel tubing inside insulated sleeves which hang 2 in. into the inner sample containment vessel within the furnace. The containment vessel container is being constructed from 96% alumina castable refractory in three pieces. The pieces consist of a flat circular top through which the injector tubes pass, a cylindrical body which will hold the samples, and a flat circular bottom which will be cemented to the bottom of the body with ceramic glue.

An exit port for the spent corrodent material will be glued into and project from the bottom of the inner sample container. It is made of the same material as the view port. The molten spent corrodent material will drip through the ceramic tube and be collected in a removable refractory-lined catch pot. A stand with rollers was built to hold the catch pot – for easy removal. When the furnace is in operation, the catch pot will be clamped in place to prevent gas leaks.

The corrodent granules will be introduced into the inner containment vessel by a Hethon™ feeder. The Hethon™ feeder is a precise low-rate volumetric feeder with an internal flexible hopper that allows the use of "massaging paddles" which distort the walls of the hopper to keep the granular corrodent material flowing smoothly. The Hethon™ feeder is operated by means of a tachometrically controlled impulse regulator. The transfer of the corrodent granules from the feeder is controlled by a single 4-mm-diameter feedscrew with center shaft. At the end of the transfer tube is a custom-designed feeder splitter to perform a 1-to-2 way split of the corrodent granules into the two feed injector entry ports, which are connected by high-temperature Tygon™ tubing to the water-cooled stainless steel feed injectors. Corrodents used in this system will include molten slag, steel, and glass.

The sample containment system will be gastight from the top of the corrodent hopper to the gas exit from the corrodent catch pot. The preselected gas mixture will be controlled using a gas manifold and flowmeters. The gas mixture will be introduced through a gas inlet valve located on the side of the corrodent hopper. The gas will mix with the corrodent material, then enter the containment vessel within the furnace through the feed injectors. It will exit the system through a gas outlet vent located on one side of the catch pot and then exhaust through the fume hood. A positive pressure will be maintained in the system by bubbling the gas out of the catch pot through several inches of water head.

The refractory test blocks are 4 by 4 by 9 in. tall with a 30-degree incline on the top surface. On this inclined surface is a well, 1 1/4 by 1/8 in. deep, which is drained by a ½-in.-wide by 1/4-in.-deep open vertical channel. The blocks are cast in rubber molds, cured, then prefired in the furnace before corrodent material is introduced.

As of the end of Task 6.4 at the end of May 2001, the furnace and corrodent feed systems had been purchased, and a stand to hold the furnace and the corrodent catch pot had been built. In addition, the inner containment vessel had been cast, but will not be fired until the furnace is fully

operational. Operational status for the furnace has been delayed because several of the molybdenum disilicide heating elements were broken during shipping of the furnace system, and we are awaiting their replacement.

FUTURE WORK

Over the next year, construction and shakedown of the CADCAF system will be completed under Activity 2 of the new Subtask 6.6 (base cooperative agreement) entitled High-Temperature Materials.

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