Sponsor TBD Report No.: _____

AISI/DOE Technology Roadmap Program

Final Report

**Development Of An Oxygen-enriched Furnace
System For Reduced CO₂ and NO_x Emissions For
The Steel Industry**

by

Edward W. Grandmaison, David J. Poirier, and Eric Boyd

January 20, 2003

Work Performed under Cooperative Agreement

No. DE-FC07-97ID13554

Prepared for

U.S. Department of Energy

Prepared by

American Iron and Steel Institute

Technology Roadmap Program Office

Pittsburgh, PA 15220

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Number of pages in this report: 138

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$$1\% \text{ stack oxygen: } (m_L/A)^2 = 2.72 t - 4.14$$

$$2\% \text{ stack oxygen: } (m_L/A)^2 = 2.87 t - 2.10$$

$$5\% \text{ stack oxygen: } (m_L/A)^2 = 2.45 t - 0.023$$

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$$0\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.285 t - 0.245$$

$$25\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.316 t - 0.260$$

$$50\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.310 t - 0.285$$

$$90\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.281 t - 0.0770$$

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$$0\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.55 t - 2.02$$

$$\begin{aligned}
&25\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.87 t - 2.86 \\
&50\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.77 t - 2.61 \\
&90\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.54 t - 1.14
\end{aligned}$$

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$$\begin{aligned}
&1\% \text{ stack oxygen: } (m_G/A)^2 = 0.176 t - 0.105 \\
&2\% \text{ stack oxygen: } (m_G/A)^2 = 0.192 t - 0.128 \\
&5\% \text{ stack oxygen: } (m_G/A)^2 = 0.196 t - 0.112
\end{aligned}$$

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$$\begin{aligned} 1\% \text{ stack oxygen: } (m_L/A)^2 &= 1.94 t - 4.54 \\ 2\% \text{ stack oxygen: } (m_L/A)^2 &= 1.86 t - 1.96 \\ 5\% \text{ stack oxygen: } (m_L/A)^2 &= 2.13 t - 0.436 \end{aligned}$$

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$$\begin{aligned} 0\% \text{ oxygen enrichment: } (m_G/A)^2 &= 0.134 t + 0.321 \\ 25\% \text{ oxygen enrichment: } (m_G/A)^2 &= 0.192 t - 0.280 \\ 50\% \text{ oxygen enrichment: } (m_G/A)^2 &= 0.184 t - 0.086 \\ 75\% \text{ oxygen enrichment: } (m_G/A)^2 &= 0.207 t - 0.351 \\ 90\% \text{ oxygen enrichment: } (m_G/A)^2 &= 0.234 t - 0.366 \end{aligned}$$

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$$\begin{aligned} 0\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.73 t - 2.08 \\ 25\% \text{ oxygen enrichment: } (m_L/A)^2 &= 2.09 t - 3.41 \\ 50\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.97 t - 1.90 \\ 75\% \text{ oxygen enrichment: } (m_L/A)^2 &= 2.21 t - 5.56 \\ 90\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.98 t - 0.556 \end{aligned}$$

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Executive summary

The steel industry is faced with the challenge of meeting stricter environmental legislation that allows only very low emissions of primary pollutants, NO_x and CO_2 from furnaces. This work has involved the development of a technology that will reduce combustion emissions from steel furnaces and reduce cost of producing steel.

The purpose of this work was to develop an O_2 -enriched furnace system that will reduce CO_2 and NO_x emissions under typical steel industry operating conditions. The combination of the latest burner technology for air-fuel combustion with O_2 -enrichment should result in both lower NO_x emissions and reduced CO_2 emissions. The issues that were addressed by this work include: (i) the optimum configuration of the ultra-low- NO_x burner for high energy efficiency (low CO_2), low NO_x emissions and uniform heat flux distribution, (ii) the effect of air infiltration on furnace performance during O_2 -enriched combustion, and (iii) the effect of O_2 -enrichment combustion on scale formation in steel reheat furnaces.

To achieve these goals, a modification to an ultra-low- NO_x burner (developed by Canadian Gas Research Institute, CGRI) design to accommodate O_2 -enriched combustion was made and installed in a pilot reheat furnace. The burner was tested and optimized within its range of operating configurations. Steel reheat scale formation rates and the furnace temperature distribution were measured. The primary conclusions drawn from this work are outlined in the following paragraphs.

The CGRI low NO_x burner relies on injection of fuel and oxidant streams through a series of ports normally arranged on a circumferential ring on the primary axis of the burner. These ports are set at an angle to the burner axis, leading to entrainment of combustion product gases into the resulting jets and a confluence of the feed streams downstream from the burner source. In normal operation, and the mode employed in this work, seven fuel and oxidant jets were used. In order to incorporate the use of oxygen enrichment, the oxidant stream (a combination of air and/or oxygen in this case) was supplied through a series of concentric jets, the oxygen feeding through the center jet and the air being supplied through the annular jet. This allowed for independent control for a full range of oxygen enrichment levels. The oxidant nozzles were set at a constant angle of 10° to the burner axis and two oxygen nozzle sizes were tested with a diameter of 5.31 mm (0.209 in.) finally chosen for "best" burner operation. Four fuel nozzle angles were tested and an angle of 20° relative to the burner axis appeared to give slightly better performance. The choice for these "best" conditions was based on assessment of NO_x emission levels and combustion stability. One should expect the optimization of the burner configuration to be dependent on the furnace geometry, burner orientation and to some extent, firing rate. Fuel usage and NO_x level optimization should be less dependent on these factors.

The single CGRI burner used in this work was designed to operate at a maximum firing rate of 400 kW (1.4 MBtu/h). In order to compare furnace performance under the different operating conditions proposed in this work, the furnace was operated at a constant target temperature of 1100°C , corresponding to firing rates of 325 -- 365 kW at 0% oxygen enrichment, depending on the stack oxygen concentration. The firing rate required to maintain this furnace temperature decreased linearly with the level of oxygen enrichment. At 100% oxygen enrichment firing rates in the range of 200 -- 220

kW were required to maintain furnace temperature. This represents potential savings of 40 – 45% in fuel usage and a corresponding reduction in CO₂ emissions. At constant levels of oxygen enrichment, the firing rate was expected to increase with increased stack O₂ (excess oxidant). This behavior was observed at low oxygen enrichment levels, < ~30%, but within the scatter of the present data, it was less evident at higher enrichment levels.

NO_x emissions up to ~12 mg NO_x/MJ were observed in this work. Oxygen enrichment had little effect on NO_x emission up to an enrichment level of ~60%. At higher O₂-enrichment, emission levels decreased but not to zero because of fuel nitrogen (1.6%) present in the natural gas supply. NO_x emission increased with increasing stack oxygen concentration (up to ~6% O₂ w.b. in the present work) at all oxygen enrichment levels. Effects of furnace temperature and firing rate could not be investigated due to limited firing capacity with one-burner operation.

The roof and blind sidewall refractory surface-temperatures in the furnace were monitored during all experimental runs to determine the temperature uniformity. Temperature uniformity was expressed in terms of the standard deviation about the average value as well as the minimum and maximum variation about this average. Oxygen enrichment level had the most significant effect on this temperature variation. The standard deviation of the temperature variation was in the range, 19 -- 27 °C with no oxygen enrichment and 31--34 °C with 90% oxygen enrichment. This corresponded to a range between the minimum and maximum temperatures of about ~70 °C with no oxygen enrichment and ~115 °C with 90% oxygen enrichment.

With oxygen enrichment, there is substantial reduction in the gas flow rate through the furnace due to lower nitrogen content in the oxidant feed and a reduction in firing rate. The single burner operation demonstrated in this work tends to amplify the temperature variations with higher temperatures in the burner region of the furnace and lower temperatures near the exhaust plenum. Multi-burner operation would reduce the temperature variations noted above. As with conventional burner systems, some attention would have to be focused on optimizing furnace temperature and heat transfer profiles for oxygen enriched combustion systems.

The effect of air infiltration on the refractory temperature distribution in the furnace was similar in magnitude to a reduction in firing rate equivalent to that required to heat the infiltration air to the furnace temperature. Air infiltration also had an effect on NO_x levels leading to emissions similar to those observed with no air infiltration but with similar stack oxygen concentrations. It was discovered that the premixed pilot burner accounts for about 1 – 2% of the energy input to the furnace, but contributes a disproportionate amount of the NO_x emissions on an energy input basis.

Steel scaling tests were performed as an integral part of this study. Oxygen enrichment leads to different combustion product environments with significantly larger proportions of CO₂ and H₂O along

with the excess oxygen commonly present in combustion systems. The effect of employing oxygen enrichment, compared with more traditional combustion environments, was assessed in terms of

- Scale surface habit (ranked on a scale of 0 → 5 for a smooth → porous surface),
- Scale intactness (ranked on a scale of 0 → 6 for an intact → heavily detached scale),
- Scale adhesion (ranked on a scale of 0 → 4 for little effort for removal → difficult to remove), and
- Scaling rates

Five steel grades [designated as DC (low carbon steel), DS (Mn-Si-Cb HSLA steel), SB (50 Ksi Weathering steel), SF (70 Ksi Weathering steel) and SJ (70 Ksi Line Pipe steel)] in this work were evaluated and ranked. These rankings were based on visual observation and physical tests over a wide range of operating conditions. Photomicrographs with 0% and 90% oxygen enrichment conditions were also produced to provide supporting evidence for these tests.

The only factor affecting scale habit and intactness was the steel grade; the stack oxygen and oxygen enrichment levels did not significantly affect these properties. Based on physical tests, supported by photomicrography, the steel grades were ranked from a smooth, intact scale to a rough and cracked/separated scale in the order:

$$DS > DC > SF > SJ > SB$$

Smooth → Rough

The steel grade was also the most important factor affecting scale adhesion with the order of scale removal effort:

$$SF > SB > SJ > DC$$

More adherent → Less adherent

(the DS grade was not tested for this characteristic). This adhesion ranking corresponds most significantly with the composition of the steel samples – e.g. the SF, SB and SJ grades had somewhat more elevated levels of Ni, Cu, Cr and/or Mo. Photomicrographs also indicated that the more adherent samples had a porous scale and/or rough steel/scale interface. Those scales that were easily removed had a clearly defined separation at the steel/scale interface.

The scale appeared to be less adherent with increasing stack oxygen concentrations and the effort for scale removal appeared to decrease slightly with increasing oxygen enrichment and increasing sample exposure times. These effects were much smaller than the difference observed between sample grades. The implication of these results are that oxygen enrichment has far less effect on the scale properties than that accounted for by differences due to the steel grade/composition.

Scaling rate data, expressed in terms of the mass gain (oxygen uptake) and steel mass loss (Fe loss) were obtained for the DC and SB steel grades at 3 stack oxygen concentrations (1, 2 and 5%) and 4 oxygen enrichment levels (0, 25, 50 and 90%). The scaling rate for the SB grade (a more adherent and porous scale) was lower and the data exhibited more scatter than the DC samples. The oxidation rates followed a parabolic behavior at 5% stack oxygen. At lower stack oxygen concentrations (1% and 2%), a lower initial oxidation rate was observed, followed by a parabolic behavior after the first 0.5 h of exposure to the furnace atmosphere. Within the tests for each grade, the

parabolic oxidation rate was most strongly affected by the stack oxygen concentration and the oxygen enrichment level only had a small effect on the parabolic oxidation rates.

Scaling rate data for the SF and SJ grades were obtained at 2% stack oxygen and 0% oxygen enrichment as part of a series of replicate tests for the scaling rates. The parabolic oxidation rate parameters for steel mass loss at these conditions could be ranked in the order:

$$\text{SJ, SB} < \text{SF} < \text{DC}$$

Low mass loss $\leftarrow$ High mass loss

The steel mass loss after 4 h could be ranked in the order:

$$\text{SJ} < \text{SB} < \text{SF} < \text{DC}$$

Low mass loss $\leftarrow$ High mass loss

The difference between the SJ, SB and SF scaling rates in each case was not large, but these three grades had significantly lower scaling rates than the DC grade. This ranking of the scaling rates also corresponds to the other scale properties i.e. (i) a rough and cracked/separated scale $\rightarrow$ smooth intact scale, and (ii) a decrease in the scale adhesion characteristics.

1. Introduction

This is the final report on all work conducted under the subject contract. This report contains a summary of progress made toward the objects, including a full account of the work carried out with detailed presentation and analysis of results as well as explanations of challenges encountered.

This section provides an overview of the impetus for the work, an outline of the objectives and the tasks involved in achieving them.

1.1. Overview

Until recently, the focus on CO₂ and NO_x reduction in steel furnace applications has been on burner design and modification. Successful advances have included air staging and causing air to swirl as it mixes with fuel. The attractiveness of new burner designs or modifications to existing burners is the relatively low cost associated with the improvements, relative to the high capital costs of post furnace clean-up equipment. Burner modifications typically reduce NO_x emissions to 100 -- 300 ppm, a significant reduction, but not to levels considered acceptable in the present environmentally protective climate.

Recent burner developments (Besik et al, 1996, Cain et al, 1997) have been able to reduce NO_x emissions to 10 -- 30 ppm while maintaining combustion efficiency, by modifying the circulation patterns within the furnace. In essence, combustion products are entrained into air and fuel jets, prior to the air and fuel mixing and combusting. This is accomplished solely through burner generated product gas circulation patterns. Entrainment of combustion products into the fuel and air streams reduces the maximum temperatures reached during combustion. This reduces peak temperatures, resulting in much lower NO_x production (NO_x production is very temperature sensitive in the range used in many furnace applications). Burners operating on similar principles have been developed by North American Manufacturing (in conjunction with Tokyo Gas) for natural gas/air combustion.

Another approach to reducing NO_x emissions and at the same time increasing furnace efficiency or throughput, involves the use of oxygen-enriched air. Adding oxygen and reducing the air requirement for combustion results in less nitrogen entering the furnace (with air) making less nitrogen available to be converted to NO_x. As well, by reducing the amount of nitrogen passing through the furnace, less energy is lost out the stack by the unnecessary heating of that nitrogen. Significant fuel savings (up 50% reduction) are achievable. Fuel savings are offset to some extent by the cost of the oxygen; however, O₂ production technologies are becoming more economical as time passes. Steel industries already use significant quantities of oxygen and so have the facilities to handle and supply oxygen to their processes.

1.2. The contract

“Development of an O₂-enriched furnace for reduced CO₂ and NO_x emissions for the steel industry” is a research project funded by a contract obtained from the American Iron and Steel Institute

in Jan 2000. The project was one year in duration. It involved studies of natural gas/air/oxygen combustion in a pilot scale furnace using a novel ultra-low-NO_x burner.

1.3. Objectives

The purpose of this work was to develop an O₂-enriched furnace system that will reduce CO₂ and NO_x emissions under typical steel industry operating conditions. The combination of the latest burner technology for air-fuel combustion with O₂-enrichment should result in both lower NO_x emissions and reduced CO₂ emissions. The issues that are addressed by this work include: (i) the optimum configuration of the ultra-low-NO_x burner for high energy efficiency (low CO₂), low NO_x emissions and uniform heat flux distribution, (ii) the effect of air infiltration on furnace performance during O₂-enriched combustion, and (iii) the effect of O₂-enrichment combustion on scale formation in steel reheat furnaces.

This project should produce a burner and combustion technology that results in much lower NO_x and CO₂ emissions than current technologies and practical experience and measurements on the use for O₂-enriched combustion under conditions applicable to the steel industry. The acquired measurements should also serve to develop rules of thumb and empirical correlations that allow NO_x and CO₂ emissions and scale buildup to be predicted from furnace operating conditions.

1.4. Tasks and scheduling

The project entailed the following major tasks:

1. Burner design, fabrication and installation
2. Furnace control system modifications
3. Gas analysis system modifications and additions
4. Oxygen storage and flow control system design, installation and testing
5. Furnace, burner and control systems hazard analysis and preliminary testing
6. Experiments
7. Data analysis
8. Progress and final report preparation

Table 1.1 shows time scheduled for the major project tasks. Information regarding tasks 1 -- 5 is presented in Sec. 2 of this report. A description of experimental design and methods is given in Sec. 3, while presentation, analysis and discussion of results appear in Sec. 4.

2. Development of an O₂-enriched furnace system

Testing and development of the O₂-enriched furnace system were conducted at the Centre for Advanced Gas Combustion Technology (CAGCT), Research Furnace Laboratory, Queen's University in Kingston, Ontario, Canada. The Research Furnace, a pilot scale facility, was initially built for a project with the steel industry in Canada, and closely simulates steel reheat furnaces. While large for a research facility, it features extensive probing facilities and is well instrumented for conducting many kinds of combustion related measurements.

The interior of the furnace, Fig. 2.1, is divided into two unequal size chambers by a checker-work brick end-wall. The first chamber is the furnace cavity or combustion chamber which has the internal dimensions 4.5 m long, 3 m wide and 1 m high (177 in. x 118 in. x 39 in.). The second chamber serves as an exhaust plenum and has interior dimensions of 0.6 m long, 3 m wide and 1 m high (24 in. x 118 in. x 39 in.). The checker wall, 215 mm thick (8.5 in.), with an 8 x 3 arrangement of small openings, 75 mm x 115 mm (3 in. x 4.5 in.), separates these two chambers. One side-wall of the furnace cavity is the so-called fired side-wall, with three burners located at positions B1, B2 and B3 as shown in Fig. 2.1. In the present work, a single burner in the B1 position was used for all experimental measurements. The refractory linings for the furnace walls and roof are fabricated from ceramic fibre modules, 305 mm (12 in.) thick; the furnace wall structure and refractory is 362 mm (14 in.) as shown in Fig. 2.1.

The entire floor of the furnace was made up of 34 water-cooled steel panels as shown in Fig. 2.2. These panels are instrumented to permit the measurement of heat flux to the floor, based on measurements of the cooling water flow rate and of the temperature difference between the outlet and inlet of each panel. Smaller panels, 500 mm x 500 mm (19.7 in. x 19.7 in.), are used in the area near the burner side-wall, panels 4-5, 8-9, 12-13, 16-17, 20-21, 24-25, and 28-29, as shown in Fig. 2.2. Larger panels 500 mm x 1000 mm (19.7 in. x 39.5 in.), cover the rest of the floor area in the combustion chamber; additional panels (not shown in Fig. 2.2) serve as protective cooling surfaces for the furnace structure.

The furnace is equipped with probe ports located at positions P1 – P33, Fig. 2.3, permitting access for measurement of local gas temperature, gas composition, heat flux, etc. A larger port, 0.5 x 1.0 m (19.7 in. x 39.5 in.), not shown in Fig. 2.3, is located adjacent to the B1 burner position allowing for traversable probing in the nearfield region of this burner.

Instrumentation for the furnace also includes fixed thermocouples, static pressure taps, orifice meters for gas and air and flow meters for the cooling water panels. Refractory wall surface-thermocouples are located at positions T1 – T41 as shown in Fig. 2.4. These thermocouples, 0.254 mm (.01 in.) dia. Pt/Pt-10%/Rh, are embedded about 5 mm (.2 in.) into the refractory walls (small resistance between the refractory body and thermocouple bead). The size and positioning of these thermocouples help minimize measurement error.

Development of an O₂-enriched furnace system from the existing facility required the completion of the tasks outlined in Sec. 1.4 and listed in Table 1.1. The following sections will describe in moderate detail what was required to complete these tasks.

Fig. 2.1. The CAGCT research furnace. Section views including the internal flow pattern occurring with a sidewall mounted burner configuration (all dimensions in mm).

Fig. 2.2. Cooling panel layout in furnace floor (all dimensions in mm) of the CAGCT Research Furnace. Panels are normally covered with an insulating blanket, but can be exposed to simulate a heat transfer load to various parts of the furnace floor. Metered cooling water runs through 9 parallel circuits (panels 3, 2 & 1 constitute one line; panels 7, 6, 5 & 4 constitute another line, etc.). The water temperature is measured at the input and output of each panel.

Fig. 2.3. Probing port location in the roof and blind sidewall of the CAGCT Research Furnace. A larger port for traversable probes is located in the sidewall adjacent to burner B1.

Fig. 2.4. Location of refractory-wall thermocouples in the CAGCT Research Furnace.

2.1. Burner design

In the mid 1990's, CAGCT along with the Canadian Gas Research Institute (CGRI) developed an ultra-low NO_x burner (< 25 ppm) for use with natural gas and air (Besik et al., 1996), hereafter referred to as the CGRI burner. The burner aerodynamics produces a dilute combustion zone with low peak temperatures resulting in ultra-low NO_x production. The aim of this project is to develop and test a burner of a similar design for use in oxygen-enriched natural gas combustion.

The design, assembly view and section of the O_2 -enriched CGRI burner are shown in Fig. 2.5. The burner consists of a ring-array of alternating fuel and oxidant nozzles directed at different angles to the burner axis.

It was decided that the oxygen supply tubes and jets (parts J & K) should run coaxial to the air supply tube and jets (parts I & R). Premixing of the air and oxygen was not considered because of concerns about the cleanliness of the air supply system. The oxygen nozzle diameter and the air nozzle annulus were sized so that the momentum of the combined oxidant stream would remain constant with changing O_2 -enrichment level for a constant firing rate. Between trials, when the furnace is cool, it is possible to change the fuel nozzle size and angle and the oxygen nozzle size to examine the effects of these changes on burner performance.

The burner was designed for a maximum firing rate of 400 kW (1.4 MBtu/h). The material of construction for the entire burner was 304 stainless steel, chosen for its strength, corrosion resistance and compatibility with oxygen under the operating conditions investigated. Sizing of oxygen-wetted passages was done to maintain oxygen pressure and velocity within limits compatible with 304 stainless steel.

Fig. 2.5. Assembly drawing for the O₂-enriched CGRI Burner.

2.2. Furnace control system

Changes to the furnace control system were necessitated by the addition of a third stream (oxygen) to the two existing streams (natural gas and air). Items in the original furnace control-system to be replaced included the four-loop controller for Air-to-fuel ratio control and a temperature/firing rate controller.

Additions to the furnace system for the use of oxygen included: integrated natural gas, air and oxygen flow and safety shutdown control using PC based DAQ control system, O₂ valve train, and O₂ storage and supply system.

A PC-based controller and O₂ valve train were used to monitor and regulate the flow and shutdown of O₂ flow based on a flow sensing device, limit switches and relays.

Specialized control and data acquisition software was developed, using National Instruments' LabVIEW software.

2.3. Hazard analysis and safety considerations

Hazard analysis is important when working with potentially dangerous equipment or materials. These analyses helped to insure the safe design and operation of the new and modified systems. Hazards analysis help to ensure that the system behaves in a safe manner in every instance of failure of any single component. It should require the simultaneous failure of more than one component in order for a dangerous situation to arise. Hazard analysis tables were prepared for various scenarios..

All O₂ wetted parts of the system are made from materials that are O₂-compatible at the pressure, flow and temperatures used; in most cases this meant copper and nickel alloys and stainless steel for certain components. The design range of oxygen pressure, temperature and flow rate encountered in this project is such that ignition and flammability hazards for O₂ wetted components should not be an issue.

Good housekeeping practices were maintained in order to lessen hazards related to oxygen enrichment of the ambient environment. No other experiments or activities were permitted in the furnace lab during experiments using oxygen enrichment.

Development and adherence to standard operating procedures (SOP's) and emergency responses is important when operating complex systems to avoid damaging equipment and/or creating potentially dangerous situations. SOP's and SOP checklists for furnace startup, operation, shutdown, etc. that are required in the course of a typical experiment were developed including emergency response procedures to follow in case of the development of a hazardous situation.

Before the first tests using oxygen, dry runs and simulations of system failures were performed on furnace systems. Nitrogen was used to test the oxygen valve train operation. Emergency and standard operating procedures were studied by all operators prior to working with the O₂-enriched furnace system.

All staff at CAGCT Furnace laboratory have access to MSDS's (Material Safety Data Sheets) for all hazardous materials handled at the laboratory and have received training in the proper use of the devices that they are required to operate. The furnace system was only operated when Authorized Personnel were present.

2.4. Equipment cleaning for O₂ service and supply and storage of oxygen

When convenient, parts were purchased pre-cleaned for O₂ service by the manufacturer. When this was not possible, parts were disassembled, if possible and cleaned according to the method developed in-house.

Equipment cleaning for oxygen service is a prime safety consideration for any project in which oxygen is to be used. Several good references have been utilized to establish a method for the cleaning of oxygen-wetted metallic equipment in this project. The method used here should not be applied to any other project where the O₂ supply pressure, temperature and flow may be substantially different.

The oxygen valve train for flow control was designed and assembled by North American Manufacturing (Canada) Inc. It is similar in most respects to the natural gas valve train in terms of the number and type of regulators, actuators and valves used. The exception being that all equipment was O₂ compatible and cleaned for oxygen service.

The oxygen storage system was set up by Air Liquide. Oxygen was stored and supplied to the valve train from a trailer based storage tank/evaporator system. The storage tank held approximately 2300 litres of liquid oxygen at 150 psi and was capable of supplying the required 2000 SCFH maximum flow of gaseous O₂.

3. Experimental design and methods

There were six major objectives of the experimental work. These involved furnace trials with various O₂ enrichment and stack O₂ levels to study: (i) burner optimization, (ii) fuel savings/CO₂ reduction, (iii) NO_x emission levels, (iv) temperature distribution within the furnace and the effect of a cooling load on furnace performance, (v) effects of air infiltration on furnace performance and (vi) steel reheat scale formation and scale morphology.

The experimental plan developed to examine these effects is shown in Table 3.1.

Table 3.1. Experimental design for the project – Development of an O₂-enriched furnace system for reduced CO₂ and NO_x emissions for the steel industry

Test No. ¹	Run No. ¹	Test Objective	O ₂ Nozzle Dia.	Fuel Nozzle Angle	Firing Rate ²	Cooling Panel Exposure	Stack O ₂ %vol.	O ₂ Enrichment
1 & 2	001020 & 001024	Effect of O ₂ nozzle size and O ₂ enrichment on Fuel savings and NO _x levels.	0.277"	15°	Max ²	0.0%	2%	0 to 100%
3 & 4	001027 & 001031		0.209"	15°	"	0.0%	2%	0 to 100%
5 & 6	001102 & 001103	Effect of Fuel nozzle angle and O ₂ enrichment on Fuel savings and NO _x levels.	optimum	0°	"	0.0%	2%	0 to 100%
7 & 8	001107		optimum	10°	"	0.0%	2%	0 to 100%
9 & 10	001109		optimum	20°	"	0.0%	2%	0 to 100%
11 & 12	001113		optimum	optimum	"	3.25% (7)	2%	0 to 100%
13 & 14	001115	Effect of Firing rate/Cooling load and O ₂ enrichment on Fuel savings and NO _x levels.	optimum	optimum	"	7.5% (7, 11)	2%	0 to 100%
15 & 16	001120		optimum	optimum	"	7.5% (7, 11)*	2%	0 to 100%
17 & 18	001122		optimum	optimum	"	7.5% (6, 7)*	2%	0 to 100%
19 & 20	001201		optimum	optimum	"	0.0%	1%	0 to 100%
21 & 22	001204	Effect of Excess O ₂ level and O ₂ enrichment on Fuel savings and NO _x levels.	optimum	optimum	"	0.0%	3%	0 to 100%
23 & 24	001206		optimum	optimum	"	0.0%	5%	0 to 100%
25 & 26	010103	Effect of Air Infiltration on NO _x levels at maximum O ₂ enrichment. ³	optimum	optimum	"	0.0%	2%	High
27 & 28	010111		optimum	optimum	"	0.0%	5%	High
29	010122	Steel Scale Tests ⁴ Steel scaling rate tests: two grades of steel, each grade over 5 time periods: 30, 60, 120, 180, and 240 min. (10 samples for each steel scale trial). The CAGCT will conduct measurements of mass gain/loss due to scaling. Additionally, heating of steel scale test samples will be conducted for 5 grades of steel, 1 sample for each grade, over 240 min. period. These samples will be used to examine steel scale morphology. Morphology assessment will be done by another facility.	optimum	optimum	"	0.0%	2%	0%
30	010117		"	"	"	"	"	25%
31	010124		"	"	"	"	"	50%
32	010214		"	"	"	"	"	90%
33	010124		optimum	optimum	"	0.0%	5%	0%
34	010125		"	"	"	"	"	25%
35	010129		"	"	"	"	"	50%
36	010215		"	"	"	"	"	90%
37	010201		optimum	optimum	"	0.0%	1%	0%
38	010131		"	"	"	"	"	25%
39	010212		"	"	"	"	"	50%
40	010221		"	"	"	"	"	90%
41	001127	Preliminary steel scale test	optimum	optimum	"	0.0%	2%	0%
42	010213	Steel scaling at 75% Oxygen enrichment	optimum	optimum	"	0.0%	2%	75%
43	010222	Extended high-O ₂ enrichment trial	optimum	optimum	"	0.0%	1 to 5%	100%
R1 & 2	010704	Steel reheat scale replicate tests	optimum	optimum	"	0.0%	2%	0%
R3 & 4	010718	Steel reheat scale replicate tests	optimum	optimum	"	0.0%	2%	0%

¹ Each run number represents a day worth of furnace operation at the conditions noted. Two or three runs per week can be completed during the experimental period. The exact number of runs required to complete the desired set of operating conditions is not precisely known at this time since it will depend largely on the time required for the furnace to equilibrate after changing the O₂ enrichment level. However, based on past experience this experimental plan should account for an adequate number trial days.

² Firing rate will be adjusted (lowered) to maintain constant furnace temperature as O₂ enrichment increases. This will demonstrate fuel savings to be gained by O₂ enrichment and will also provide a better basis for comparison of NO_x levels.

³ Air will be introduced to the furnace away from the nearfield of the burner.

⁴ Samples will be quenched in a nitrogen bath.

* "Uncovered" cooling panels actually covered with 1/8" thick fibre refractory paper to help maintain furnace operating temperature.

Burner settings to remain constant for all trials include: air and O₂ nozzle angle (10°), air nozzle annulus size, and fuel nozzle diameter (1/4 in.).

Note: This table is a guideline for the experimental program. Actual operating conditions used may vary depending on operating characteristics and limits of equipment. Experimental plans may be altered based on results of preceding experiments.

The experiments that make up the design follow a logical sequence. The first experiments (tests 1 -- 10) were aimed at optimizing burner configuration for "best" performance (low NO_x, fuel savings, and combustion stability). These tests were performed first so that the remaining tests could be conducted with the "optimum" burner configuration.

Tests 11 -- 24 were designed to examine effects of furnace operating settings, including excess oxidant, O₂ enrichment level and furnace load, on NO_x emission. Tests 25 -- 28 were designed to examine the effect of air infiltration on furnace performance. The final tests, 29 -- 40, were tailored to examine steel reheat scale rate behaviour for a range of relevant operating conditions. Additional experiments (tests 41 -- 43) were performed to provide some replicate data, verify methodology and to otherwise enhance and supplement the data set.

Each run number represents one day worth of furnace operation (typically 8 hours) at the conditions noted. On average two runs per week were completed during the experimental phase of the project.

3.1. Burner optimization and NO_x emission tests

Some burner parameters that remained constant for all trials included air and O₂ nozzle angle ($\beta_a = \beta_{O_2} = 10^\circ$), air-nozzle annulus size, and fuel nozzle diameter $D_f = 6.4$ mm (1/4 in.). These values have been observed to be "good" in natural-gas/air burner-development tests. Some floor sink panels operated bare, the rest were covered with 1-inch thick ceramic-blanket insulation. No air preheat was used.

Furnace temperature control set point was 1100 °C for all trials. This was necessitated in part due to the limited operating range with the single burner used. Multi-burner operation would allow for higher furnace temperatures as well as the exploration of the effects of burner turndown on furnace performance.

Concentrations of O₂, CO₂, CO, NO_x and CH₄ in the exhaust gases were continuously measured. Refractory surface temperatures of the furnace walls and ceiling and heat flux to water-cooled floor panels are also continuously monitored. Quasi-steady-state furnace conditions for gas composition measurements were assumed once the furnace control temperature reached the operator set point (1100 °C in these trials) and gas analysis readings stabilized.

Firing rate was adjusted to maintain constant furnace temperature as O₂ enrichment and excess oxidant was varied. This helped to clearly demonstrate fuel savings gained by O₂ enrichment and provided a better basis for comparison of other data including NO_x levels.

In some runs "uncovered" cooling panels had to be covered with 1/8 in. thick fibre-refractory paper to help maintain furnace temperature.

3.2. Air infiltration tests

Infiltration air typically enters an industrial furnace in one of two ways. The furnace may experience a periodic influx of air when a furnace door is temporarily opened as part of the normal operating procedure; the amount of air infiltration can be quite large in magnitude and sudden in its

introduction. In the other case, the furnace may be operated under slightly negative pressure, in which case, air will infiltrate wherever it is able, but typically at a lower rate and in a more uniform manner. In both cases, the air that is introduced into the furnace does not follow the same entry path as the air that is supplied to the burner for combustion, i.e. air infiltration cannot be simply simulated by increasing the excess air level for the burner. In these trials, infiltration air was supplied and controlled by running the furnace under varying degrees of negative pressure. This resulted in air leaking through furnace sample and probe ports, resulting in a somewhat uniform distribution of air infiltration supply. Furnace operating conditions were monitored before and after infiltration in order to facilitate meaningful comparisons of NO_x emission levels.

3.3. Temperature distribution and steel scale formation

3.3.1. Temperature distribution

Refractory temperature profile, from the interior face to the exterior, takes a considerable time to go through its transient phase to near-steady state. The “best” data for examining temperature profiles and fuel savings are taken from the later part of the steel reheat scale tests. In these tests, operating conditions were maintained constant for long periods of time (approx. 4 hours) after the furnace operating set points had been achieved. This was deemed close to a minimum acceptable period, from past experience, for the operating conditions used.

3.3.2. Steel scale formation

The participating steel companies provided samples of five steel grades for the testing program. These grades are denoted as DC (low carbon), DS (C-Mn-Si-Cb HSLA), SB (50 ksi weathering), SF (70 ksi weathering) and SJ (70 ksi line pipe). The compositions of these grades are noted in Table 3.2.

The steel samples were exposed to the furnace combustion product atmosphere by hanging them through specimen ports (~10 cm diameter) in the roof of the furnace adjacent to the exhaust plenum as shown in Fig. 3.1. Roof thermocouples (T1 --- T3, Fig. 3.1; T21 --- T23, Fig. 2.4) and the primary furnace thermocouple are located near these specimen ports to provide an accurate estimate of the furnace temperature near these samples. In order to perform the complete set of experiments outlined below, it was necessary to suspend a series of up to 4 samples at one time through each port. The samples were supported in this fashion with 1/8 in. dia. stainless steel wire (a preliminary series of experiments was performed to establish this experimental procedure). Based on previous experiments in this furnace, the temperature profile in the furnace gas through the 1.0 m, vertical span (Fig. 3.1) was relatively steady within $\pm 10^{\circ}\text{C}$. This temperature variation is similar in magnitude to that observed in the furnace roof in this section of the furnace.

The scaling experiments were performed at a target temperature of 1100°C for prescribed periods of time to monitor scaling rates for different grades of steel as outlined below:

1. Two grades of steel, DC and SB, were examined over the full range of oxygen enrichment levels (0%, 25%, 50% and 90%), stack oxygen concentrations (nominally 1%, 2% and 5%) and oxidation times ranging from 1.8 ks (30 minutes) to 14.4 ks (4 hours).

2. Two additional grades, SF and SJ, were tested at 2% stack oxygen concentration, 0% oxygen enrichment and oxidation times ranging from 1.8 ks to 14.4 ks. Replicate tests were performed for these conditions to provide an estimate of the experimental error in this work.

Fig. 3.1. Drawing of the CAGCT research furnace showing the location of the specimen ports, S1 --- S4, and roof thermocouples, T1 --- T3, adjacent to the ports.

Table 3.2. Compositions of the five steel grades provided by the participating steel companies.

	Low Carbon	0.4% Si HSLA	50WT (CAN/CSA G40.21 Gr. 50WT)	70ksi Weathering Steel (CAN/CSA G40.21 Gr. 70A)	X70 Linepipe Steel (API 5LX70)
	DC	DS	SB	SF	SJ
	Percent by Mass				
C	0.060	0.060	0.190	0.150	0.050
Mn	0.270	0.650	1.300	0.280	1.420
P			0.007	0.010	0.009
S			0.008	0.008	0.002
Si		0.400	0.260	0.270	0.290
Cu			0.009	0.300	0.014
Ni			0.008	0.350	0.019
Cr			0.031	0.260	0.170
Mo			0.002	0.006	0.240
V			0.030	0.050	0.002
Cb		0.030	0.002	0.033	0.076
B					0.0002
Ti			0.014	0.013	0.011
Al			0.035	0.022	0.036
Sn			0.002	0.002	0.002
Ce					0.002
N			0.006	0.005	0.007
Ca					0.0004

3. All five grades of steel were tested for a 14.4 ks period, over the full range of oxygen enrichment (0%, 25%, 50% and 90%) and stack oxygen level (1%, 2% and 5%) with the scale layer preserved for later morphology analysis.

The steel specimens were nominally 12.7 x 63.5 x 100 mm (0.5" x 2.5" x 4") and 630 g. The mass and surface area for each specimen were estimated by direct measurement prior to exposure to the furnace atmosphere. Following the desired oxidation period, the samples were removed from the furnace, quickly quenched in a N₂ atmosphere and weighed with the accumulated scale retained on the sample. For samples tested under conditions (1) and (2) above, the scale layer was removed and the sample was again weighed to provide an estimate of the steel mass loss. The scaling results were then expressed in terms of the mass gain (oxygen uptake) or steel mass loss per unit area of the steel samples. A full range of steel mass loss measurements were obtained for the conditions noted above. The scale from most samples could be de-scaled easily but the scale from some sample grades required extra "persuasion" with a hammer and scraper. The mass gain measurements were not as complete since there was some scale loss (inside the furnace) for some grades when the samples were removed from the furnace.

3.3.3. Steel scale morphology

Scale morphology work included samples of the 5 steel grades. Each sample was exposed to furnace atmospheres for a 4 hour period at 1100°C at one of four oxygen enrichment levels (0, 25, 50 and 90%) and one of 3 stack oxygen levels (nominally 1, 2 and 5%). This resulted in a total of 5 (grades) × 4 (O₂ enrichments) × 3 (O₂ stack levels) = 60 samples. Some scale morphology information was also attained from samples used for determining scale formation rates.

Four different morphology analyses were conducted:

1. Non-magnified visual observations of the surface habit characteristics were made for each morphology sample. The scale surface was ranked from 0 to 5 corresponding to the following surface characteristic observations:
  - 0 – smooth
  - 1 – a few nodules along as-cast edge
  - 2 – a few nodules randomly distributed
  - 3 – slightly mottled with blisters and nodules
  - 4 – heavily mottled
  - 5 – porous
2. Scale "intactness" was ranked between 0 and 6 corresponding to:
  - 0 – intact
  - 1 – few fine cracks
  - 2 – few fine flakes from outer surface of scale
  - 3 – some fine flakes from outer surface of scale
  - 4 – loss of small bits of thick scale from sides after cooling

- 5 – loss of large sections of thick scale from sides after cooling
- 6 – loss of thick scale from sides and main faces after cooling

3. Scale adhesion was ranked according to the effort required for removal from the steel substrate. This analysis was done on the steel samples used to determine steel mass loss, since it was necessary to remove the scale from those samples. A ranking of 1 to 4 was used, corresponding to qualitative observations:
  - 1 – scale falls off with very little effort
  - 2 – removed with little effort
  - 3 – removed with some effort
  - 4 – difficult to remove
4. Characteristics of subsurface scale and the scale/steel interface were examined by photomicrography. Selected morphology samples were encased in epoxy, sectioned (cut perpendicular to the sample face, straight through), mounted and photographed under an optical microscope. Photomicrographs for a subset of the full 60 samples at 50x magnification were obtained for:
  1. Each grade at 0% oxygen enrichment and three stack oxygen levels (a “base” case intended to show “conventional” operation effects) – total of 15 samples
  2. Each grade at 90% oxygen enrichment and 2% stack oxygen – total of 5 samples.

4. Results and discussion

Results from the experiments that directly address the project objectives are presented and discussed in this section of the report. Definitions for all symbols and terms used are given in the Notation section at the end of this report.

In addition to designing the burner and modifying the furnace control system, there were six major objectives of the experimental work. Presentation and discussion of the results of the O₂-enriched combustion experiments are presented in the following subsections:

- Burner optimization
- Fuel savings/CO₂ reduction
- NO_x emissions
- Temperature distribution
- Air infiltration
- Steel scale formation

4.1. Burner optimization

Burner optimization trials were conducted first so that the optimum configuration could be used in the remaining tests. Oxygen nozzle diameter and fuel nozzle-angle were the two burner parameters tested. The criteria used to determine “best” burner configuration was NO_x emission levels and combustion stability. No discernable differences were seen with regard to fuel savings/CO₂ reduction between the various configurations tested.

The use of NO_x emission levels, as a performance criterion, was straightforward. A complete quantitative presentation and explanation of NO_x emission results appears in Sec. 4.3 of this report.

Comparing combustion stability levels was a subjective, but relatively simple task. Stability was assessed by visual observation of the space in front of the burner, viewable through an observation port opposite the burner face. Dilute combustion technologies produce a dilute combustion zone, when viewed inside a hot furnace there is not sufficient difference in temperature between the refractory and the reacting gases to produce a visible flame. Only the glow from the hot refractory walls is visible. An intermittent flickering or constant visible flame is an indication of non-ideal mixing in the furnace. It is usually accompanied by a slight fluctuation in furnace pressure coinciding with the appearance or intensity of any visual flame.

Two oxygen nozzle sizes, $D_{O_2} = 7.0$ mm (0.277 in.) and 5.3 mm (0.209 in.), were tested. Both nozzles performed well over most conditions tested. The larger diameter nozzle appeared to give slightly worse NO_x emission and combustion stability performance for oxygen enrichment levels in the range $\psi_{O_2} = 60$ -- 90%. Oxygen enrichment level, ψ_{O_2} , is defined as $\psi_{O_2} \equiv \left(\frac{\dot{m}_{O_2}}{\dot{m}_{O_2} + \dot{m}_{O_{2,a}}} \right) \times 100$, the percentage of total oxygen supplied to the furnace as pure oxygen. Although differences in the NO_x

levels between the two nozzles were not statistically significant, the smaller diameter nozzle was chosen for use in the remaining trials because of the stability observations.

Four fuel nozzle angles were tested, $\beta_f = 0, 10, 15$ and 20° , where β_f is the angle formed between the axis of the fuel nozzle outlet and the main axis of the burner. Again, the differences in NO_x emission levels between the various fuel nozzle angles used were statistically insignificant. However, there appeared to be slightly better performance in the upper O_2 enrichment range for the 20° nozzles. Additionally, combustion stability observations indicated that the 20° fuel nozzles were superior to the other nozzles used.

Based on the observations stated above, it was decided to continue the combustion tests using the smaller of the two O_2 nozzles, $D_{\text{O}_2} = 5.3 \text{ mm}$ (0.209 in.) and the $\beta_f = 20^\circ$ fuel-nozzle. It should be noted that in the course of the remaining trials, combustion stability was observed to be good in all cases except where very high excess-oxidant levels were used. Further testing might reveal a configuration that performs well over a broader operating range; however, this was outside the scope of the present project.

4.2. Fuel savings/ CO_2 reduction

One of the primary objectives of the current work with the CGRI O_2 -enriched burner is the determination of the reduction in fuel usage and CO_2 emissions that can be expected. The reduction in fuel usage and hence CO_2 emissions is a significant benefit of employing O_2 -enriched combustion. Less energy is lost out of the stack by the unnecessary heating of nitrogen. Significant reductions in fuel consumption (up 50% reduction for some applications) are achievable in most applications.

Reduction of fuel usage and CO_2 emissions was determined by monitoring the firing rate required to maintain constant furnace load and stack O_2 level for various levels of O_2 enrichment.

Figure 4.2.1 shows firing rate versus oxygen enrichment level for various stack oxygen levels at constant furnace load. The plot shows that fuel usage (firing rate) decreases in a linear fashion with increasing O_2 enrichment level. The reduction in fuel usage shown, and hence CO_2 emissions, is on the order of 40 -- 45% for 100% oxygen enrichment. The figure also demonstrates the effect of excess oxidant level (stack O_2 level) on the required firing rate. As expected, the required firing rate tends to increase with increased stack O_2 (excess oxidant level), but this trend was only evident at lower values of oxygen enrichment, $\psi_{\text{O}_2} < \sim 30\%$. At higher oxygen enrichment levels this trend was not evident within the experimental error associated with these measurements.

Fig. 4.2.1. Firing rate vs. oxygen enrichment level for various stack oxygen levels. Furnace temperature between 1080 and 1120 °C. No exposed cooling panels. No air infiltration. $D_{O_2} = 5.31$ mm.

4.3. NO_x emissions

A large portion of the experimental work was dedicated to examining effects of furnace operating settings, including excess oxidant, O₂ enrichment level and furnace load, on NO_x emissions.

The NO_x emissions for the CGRI burner with no oxygen enrichment were typically 8 – 10 ppm (w.b.) at 1100°C. Pollutant emission levels are normally expressed on a volume-basis corrected for excess air level, which is fine for comparison purposes when one fuel and one oxidant are used. When employing oxygen enrichment, the volume of the exhaust gases produced is reduced significantly as

oxygen enrichment increases. Therefore, pollutant emissions are better presented and compared on a mass basis.

Mass-basis results can be normalized in various ways for more meaningful comparisons. Published results for pollutant emissions are often reported with units of mg/MJ. These are the units used to present the results in this report. These units provide a measure of the mass of pollutant emitted per unit energy consumed.

Firing rate was adjusted to maintain constant furnace temperature as O₂ enrichment and excess oxidant was varied. This provided a good basis for comparison of NO_x levels across the data set.

Figures 4.3.1 and 4.3.2 display the same data in two slightly different, but revealing ways. Figure 4.3.1 permits one to examine the effects of oxygen enrichment on NO_x production, while effects of excess oxidant level on NO_x emissions can be more clearly seen in Fig. 4.3.2. Furnace conditions were near steady state with an average refractory temperature in the range $\langle T_r \rangle = 1080$ -- 1120 °C, no cooling panels were exposed and no air infiltration was permitted.

Figure 4.3.1 shows how NO_x emissions varied with O₂ enrichment levels for various ranges of stack oxygen level. The graph demonstrates that there is no dramatic increase in NO_x emissions with increasing O₂ enrichment. NO_x emissions, in fact, appear to remain relatively constant in the O₂ enrichment range of 0 – 60 %. This is somewhat different from the case with conventional O₂-enriched burners, where a sharp increase in NO_x emissions are encountered. Conventional oxygen-enriched burners produce a much hotter flame than conventional air-only burners. Emissions of NO_x are sensitive to temperature and although nitrogen available for conversion to NO_x decreases with increased O₂ enrichment, NO_x emissions rise due to the increased peak temperature. The CGRI O₂-enriched burner is a dilute combustion technology which, as previously explained, exhibits much lower peak temperatures than typical O₂-enriched burners. The relatively low NO_x emission levels observed for the CGRI O₂-enriched burner with 0 -- 60 % O₂ enrichment are due to these lower peak “flame” temperatures.

As O₂ enrichment levels increase beyond 60 % enrichment, Fig. 4.3.1 shows that NO_x emissions decrease for all levels of excess oxidant. This is expected since, as even with conventional burners, when firing with nearly pure oxygen, nitrogen available for conversion to NO_x is significantly reduced, resulting in lower NO_x production. One expects NO_x production to drop to zero when pure O₂ (100 % O₂ enrichment) is the only oxidant used. This is not the case for the results displayed in Fig. 4.3.1. Although no nitrogen from air is available for conversion to NO_x, there is nitrogen entering the furnace from the fuel, natural gas. In our case, approximately 1.6 % of the fuel is nitrogen. This fuel-nitrogen is sufficient for production of the NO_x levels observed at 100 % O₂ enrichment.

Fig. 4.3.1. NO_x production vs. oxygen enrichment level for various stack oxygen levels. Furnace temperature between 1080 and 1120 °C. No exposed cooling panels. No air infiltration. $D_{O_2} = 5.31$ mm.

Although there is no pronounced trend in NO_x production with O_2 enrichment level, the difference in the NO_x levels between different excess oxidant levels is evident. Higher levels of NO_x emissions are observed as the stack oxygen level increases. This trend is clearly demonstrated in Fig. 4.3.2.

Figure 4.3.2 shows the same data set as in Fig. 4.3.1, displayed in a different format. Figure 4.3.2 shows NO_x emissions versus stack oxygen level for various ranges of O_2 enrichment.

Fig. 4.3.2. NO_x production vs. stack oxygen level for various oxygen enrichment levels. Furnace temperature between 1080 and 1120 °C. No exposed cooling panels. No air infiltration. D_{O₂} = 5.31 mm.

This figure clearly shows the relative effects of excess oxidant and O₂ enrichment on NO_x emission levels. It is evident that excess oxidant is influential for all levels of O₂ enrichment, while O₂ enrichment is only influential at levels above 60 % enrichment.

Fig. 4.3.3. NO_x production vs. stack N₂ level for various stack oxygen levels.
Furnace temperature between 1080 and 1120 °C. No exposed cooling panels.
No air infiltration. D_{O₂} = 5.31 mm.

The NO_x production rate as a function of the stack N₂ levels is shown in Fig. 4.3.3. Riley et al., (2000) reported results of an oxygen enrichment study with dilute oxygen combustion. They suggested that an increase of 10% nitrogen in the furnace gas leads to an increase of about 60% in NO_x emissions. In the present work this trend appears to be valid up to nitrogen concentrations of about 50% N₂ w.b. after which the NO_x levels remain relatively constant or decrease slightly. The increase in NO_x emissions with increasing stack oxygen levels is also evident in Fig. 4.3.3.

Due to the limited firing capacity of the furnace in single-burner operation mode, effects of furnace temperature on emission levels could not be extensively investigated. Although the data outside of the furnace temperature range $\langle T_f \rangle = 1080 \text{ -- } 1120 \text{ }^\circ\text{C}$ is sparse, there is enough to get a general impression of the relative effects of furnace temperature on NO_x emissions. Figure 4.3.4 shows how NO_x emission levels varied with furnace temperature for various levels of O_2 enrichment.

Fig. 4.3.4. NO_x production vs. furnace temperature (arithmetic mean refractory temperature) for various oxygen enrichment levels. Stack oxygen level between 1.5 and 2.0 %w.b. No air infiltration. $D_{\text{O}_2} = 5.31 \text{ mm}$.

Although the data are concentrated around the furnace-temperature set point used for all the experiments (1100 $^\circ\text{C}$), and is quite sparse on either side of 1100 $^\circ\text{C}$, two clear trends are evident. As expected, emissions of NO_x increase dramatically with increasing furnace temperature and, as before, O_2 enrichment level is strongly influential for enrichment levels above 60 %.

It is possible to develop a correlation to predict NO_x emissions based on O₂ enrichment and excess oxidant levels. The data are well fitted to the following power-law correlation:

$$[\text{NO}_x] = 4.15[\text{O}_2]^{0.574} \left(1 - \frac{\psi_{\text{O}_2}}{100} \right)^{0.488} + 1.17 \quad (4.3.1)$$

where [NO_x] has units of g/h, [O₂] is the percentage of oxygen in the stack gas on a volume wet-basis and ψ_{O_2} is the percentage of oxygen enrichment employed. Unfortunately, due to the limited scope of the experimental plan, effects of firing rate and furnace temperature cannot be included in a statistically significant way.

The degree of correlation between the data set and Eqn. 4.3.1 is high with residual errors that are small and appear to be randomly distributed. The relative influence of oxygen enrichment level and the partial pressure of O₂ inside the furnace can be determined to some extent by comparing the magnitude of the exponents for the related terms. Based on the magnitude of the two exponents, one would conclude that the two variables have roughly the same degree of influence over the range of values investigated.

Equation 4.3.1, although adequate for the system and conditions used, does not provide a fundamental explanation of the results. The number of variables examined and the operating range of variables used are not sufficient to make a comprehensive model for NO_x emissions that could be applied with confidence to other systems. However, it does demonstrate the relative effects of the two main variables investigated and should provide reasonable predictive accuracy within the data range investigated.

4.4. Temperature distribution

Temperature distribution is an important aspect of furnace performance and is of particular interest here, since oxygen-enriched combustion typically results in intensified (hotter) combustion zones.

The best of the current data set available for studying the effects of oxygen enrichment on furnace temperature distribution are the trials that involved steel reheat scale measurements. Operating conditions were maintained at constant levels for extended periods during these trials, thus giving the best steady-state readings for making comparisons.

The main furnace cavity is a box nominally 3m wide by 4m long and 1m high (177 in. x 118 in. x 39 in.). Refractory surface-temperatures (43 thermocouples) were continually logged throughout each trial for the furnace roof and blind sidewall (opposite the burner sidewall), Fig. 2.4.

Figure 4.4.1 shows a schematic of the major flow patterns of gas within the main furnace chamber. These play an essential role in the determination of temperature distribution inside the furnace.

Effects of O₂ enrichment on temperature distribution in the furnace can be determined by examining Figs. 4.4.2 to 4.4.4. Each figure contains a furnace schematic showing the difference in local interior refractory surface temperature from the mean value for four levels of oxygen enrichment ($\psi = 0$,

25, 50 and 90%) at a single stack oxygen level. Data are positioned in the figure at the approximate corresponding furnace location. The results at each furnace location are listed in the same order as the tabular data (i.e. top reading corresponds to 0% O₂ enrichment, bottom reading is at 90% O₂ enrichment). A table containing information corresponding to the series of temperature measurements is displayed at the top of each figure. Included in the tables are values for the oxygen enrichment level, ψ , the arithmetic area-mean temperature

Fig. 4.4.1. Schematic of major gas flow features inside the CAGCT Research Furnace.

Trial No.	Clock time	γ , %	$\langle T_{\text{ref}} \rangle_{\text{arith.}}$ °C	$\langle T_{\text{ref}} \rangle_{\text{ref.}}$ °C	$\Delta T_{\text{ref.}}$ °C
010201	14:20	0.0	1099	1099	23.0
010131	12:29	24.6	1100	1101	28.2
010212	14:23	51.6	1106	1107	33.0
010221	15:46	91.1	1118	1119	31.9

Fig. 4.4.2a. Difference in local temperature from the arithmetic mean, for the interior surface of the furnace roof refractory (plan view) for various levels of oxygen enrichment. Stack oxygen level 1 % w.b.. No exposed cooling panels. No air infiltration. Temperature units, °C. Readings from inoperative thermocouples are omitted.

Notes:

- (i) Data are positioned in the figure at the approximate corresponding furnace location.
- (ii) The results at each furnace location in the figure are listed in the same order as the tabular data (i.e. top reading corresponds to 0% O_2 enrichment, bottom reading is at 90% O_2 enrichment).

Trial No.	Clock time	w, %	$\langle T_{\text{furnace sidewall}} \rangle_{\text{amb}}$, °C	$\langle T_{\text{furnace sidewall}} \rangle_{\text{ref}}$, °C	$\langle T_{\text{furnace sidewall}} \rangle_{\text{ref}}$, °C
010201	14.20	0.0	1106	1107	27.2
010131	12.29	24.6	1108	1109	29.8
010212	14.23	51.6	1110	1111	33.9
010221	15.46	91.1	1123	1124	33.0

Fig. 4.4.2b. Difference in local temperature from the arithmetic mean for the interior surface of the furnace blind sidewall refractory (elevation) for various levels of oxygen enrichment. Stack oxygen level 1 % w.b. No exposed cooling panels. No air infiltration. Temperature units, °C. Readings from inoperative thermocouples are omitted.

Notes:

- Data are positioned in the figure at the approximate corresponding furnace location.
- The results at each furnace location in the figure are listed in the same order as the tabular data (i.e. top reading corresponds to 0% O₂ enrichment, bottom reading is at 90% O₂ enrichment).

Trial No	Clock time	ψ , %	$T_{\text{ref}}^{\text{rad}}$, °C	$T_{\text{ref}}^{\text{air}}$, °C	$T_{\text{ref}}^{\text{rad}}$, °C	$T_{\text{ref}}^{\text{air}}$, °C
010122	17.02	0.0	1100	1100	1100	22.1
010117	14.02	24.4	1103	1104	1104	28.1
010124	13.13	49.8	1108	1110	1110	30.5
010214	14.11	90.0	1113	1115	1115	32.0

Fig. 4.4.3a. Difference in local temperature from the arithmetic mean for the interior surface of the furnace roof refractory (plan view) for various levels of oxygen enrichment. Stack oxygen level 2 % w.b. No exposed cooling panels. No air infiltration. Temperature units, °C. Readings from inactive thermocouples are omitted.

Notes:
(i) Data are positioned in the figure at the approximate corresponding furnace location.
(ii) The results at each furnace location in the figure are listed in the same order as the tabular data (ie. top reading corresponds to 0% O₂ enrichment; bottom reading is at 90% O₂ enrichment).

Trial No.	Clock time	ψ , %	$\langle T_{\text{blind sidewall}} \rangle_{\text{arithmetic}} \text{ } ^\circ\text{C}$	$\langle T_{\text{blind sidewall}} \rangle_{\text{rad.}} \text{ } ^\circ\text{C}$	$\langle T_{\text{blind sidewall}} \rangle \text{ } ^\circ\text{C}$
010122	17.02	0.0	1107	1107	24.6
010117	14.02	24.4	1108	1108	33.0
010124	13.13	49.6	1116	1117	31.4
010214	14.11	90.0	1117	1118	33.9

Fig. 4.4.3b. Difference in local temperature from the arithmetic mean for the interior surface of the furnace blind sidewall refractory (elevation) for various levels of oxygen enrichment. Stack oxygen level 2 % w.b. No exposed cooling panels. No air infiltration. Temperature units, $^{\circ}\text{C}$. Readings from inoperative thermocouples are omitted.

Notes:

- Data are positioned in the figure at the approximate corresponding furnace location.
- The results at each furnace location in the figure are listed in the same order as the tabular data (i.e. top reading corresponds to 0% O_2 enrichment, bottom reading is at 90% O_2 enrichment).

Trial No.	Clock time	γ , %	$\langle T_{\text{roof}} \rangle_{\text{airb}}$, °C	$\langle T_{\text{roof}} \rangle_{\text{red}}$, °C	$\sigma_{T_{\text{roof}}}$, °C
010124	17:19	0.0	1083	1084	19.4
010125	14:55	24.7	1101	1101	23.1
010129	15:46	49.8	1108	1109	27.3
010215	13:59	90.1	1103	1104	31.1

Fig. 4.4.4a. Difference in local temperature from the arithmetic mean for the interior surface of the furnace roof refractory (plan view) for various levels of oxygen enrichment. Stack oxygen level 4 % w.b.. No exposed cooling panels. No air infiltration. Temperature units, °C. Readings from inoperative thermocouples are omitted.

Notes:

- Data are positioned in the figure at the approximate corresponding furnace location.
- The results at each furnace location in the figure are listed in the same order as the tabular data (i.e. top reading corresponds to 0% O₂ enrichment, bottom reading is at 90% O₂ enrichment).

Trial No	Clock time	%	T _{max} internal °C	T _{min} internal °C	T _{max} external °C	T _{min} external °C
010124	17:19	0.0	1091	1092	22.8	22.8
010125	14:55	24.7	1108	1108	26.8	26.8
010126	15:46	49.8	1114	1115	29.5	29.5
010215	13:59	50.1	1081	1090	30.8	30.8

Fig. 4.4b. Difference in local temperature from the arithmetic mean for the interior surface of the furnace blind sidewall refractory (elevation) for various levels of oxygen enrichment. Stack oxygen level 4 % w.b. No exposed cooling panels. No air infiltration. Temperature units, °C. Readings from inoperative thermocouples are omitted.

Notes:

- (i) Data are positioned in the figure at the approximate corresponding furnace location.
 (ii) The results at each furnace location in the figure are listed in the same order as the tabular data (ie. top reading corresponds to 0% O₂ enrichment, bottom reading is at 50% O₂ enrichment).

$$\langle T_r \rangle_{\text{arith}} = \langle T_r \rangle = (1/S) \int_S T_r dS \quad (4.4.1)$$

and the radiative area-mean temperature

$$\langle T_r \rangle_{\text{rad}} = \left((1/S) \int_S T_r^4 dS \right)^{1/4} \quad (4.4.2)$$

The first average is appropriate for the calculation of conductive heat loss through the roof or wall, and the second is appropriate for crude calculations of radiant transfer within the furnace cavity. We see that there is little difference between the arithmetic and radiative means, due to the relative uniformity of temperature within the furnace. The sidewall and roof averages appear to be nearly the same, with the sidewall slightly hotter in most cases.

The last columns in the tables contain σ_T , the standard deviations of surface temperature measurements. This provides a simple indication of the relative non-uniformity in refractory temperature, the lower the value the more uniform the refractory temperature. The data follow a consistent pattern. The standard deviation of the refractory surface temperatures increases from 22 to 32 °C in going from no O₂ enrichment ($\psi = 0\%$) to high enrichment levels ($\psi = 90\%$), for all stack O₂ levels.

However, σ_T provides no details regarding any other characteristics of the temperature distribution. The refractory temperature distribution is not random or normally distributed. It is a function of furnace geometry, burner design, operating conditions, etc. The best means of examining changes in the temperature distribution is by examining the data in the furnace diagram portion of Figs. 4.4.2 to 4.4.4. The temperature difference values on the furnace diagrams show precisely where and by how much local refractory temperature deviated from the average.

Figure 4.4.2a shows that for the case with no O₂ enrichment, the temperature in the hottest locations are roughly 30 °C above the average while the coolest locations are nearly 40 °C below the average. As O₂ enrichment increases, local maximums reach 60 °C above the average in a seemingly more localized fashion, while cooler areas are 60 °C below the average temperature value.

Understanding the factors influencing combustion reaction rate, gas residence-time and flow patterns of gas within the furnace is essential to comprehending changes in temperature distributions with O₂ enrichment.

Combustion rate is a function of both the local concentration and temperature of the reactants (fuel and oxidant). As O₂ enrichment increases, O₂ concentration in the oxidant feed stream increases due to the reduction in N₂ with reduced airflow. However, it is the concentration of both reactants when mixed that determines the reaction rate, since no reaction can occur until fuel and oxidant meet. Although the concentration of pure O₂ is five times that in air of the same pressure, the O₂-enriched CGRI burner jet design causes the O₂ to be diluted to roughly 1/50th its original concentration before it mixes with significant levels of fuel. This dilution process is responsible for the much-improved temperature distribution results over conventional burners.

A factor that further compounds the poor temperature distribution seen in many O₂-enriched systems, is the large reduction in volumetric flow rate of gas as O₂ enrichment increases. The air

replaced by O_2 eliminates a large volume of N_2 from the system and the reduced firing rate requirement further reduces volumetric flow. Going from air-only to pure O_2 -fired with a 50% reduction in firing rate, results in an 86% reduction in volumetric flow. This change in flow rate tends to amplify variations in temperature distribution. When the flow rate of gas within the furnace is slower, in areas of combustion, the hot gas generated has more time to transfer energy to its immediate surroundings, creating a hot-spot. Slower gas flow in areas of the furnace where cooling loads are present and little or no combustion takes place result in cool spots. Conversely, if gas flow rate is higher, as in air-only combustion, energy released by combustion is more effectively distributed throughout the furnace, resulting in uniform temperature distribution.

The temperature distribution results in Figs. 4.4.2 to 4.4.4 can be interpreted with these factors in mind.

The natural gas, air and oxygen that enter the furnace emanate from the burner face. These gases are introduced into the furnace as jets of gas with momentum sufficient to entrain large amounts of surrounding products of combustion. Very near the burner face, the combination of cool feed materials and products of combustion that have previously transferred energy to refractory and cooling loads make for a relatively cool region of the furnace. The effect of O_2 enrichment is relatively small near the burner face since little to no combustion occurs in this region.

As feed gases and entrained products flow toward the opposite wall, the expanding jets with their entrained furnace gases begin to mix and combustion of fuel with available oxidant begins. Oxygen enrichment has the effect of intensifying reaction, and hence, localizing energy released in combustion systems. As previously stated, the O_2 -Enriched CGRI Burner substantially mutes this effect because reactants are highly diluted with combustion products before combustion occurs. However, there is still a measurable effect with refractory temperatures exhibiting somewhat higher levels in this region with increased O_2 enrichment. Although dilution of the oxidant jet takes place in the same manner as with air-only combustion, the oxidant remains more concentrated in the case of O_2 -enriched combustion because of the significant reduction of N_2 in the oxidant feed.

Before gas flow impinges on the opposite wall (blind sidewall), combustion of the fuel is virtually complete and a major portion of the flow diverts along the face of the blind sidewall. A much smaller portion returns along the face of the front wall (nearfield port wall) toward the burner wall. These are areas where the hot products of combustion transfer a significant portion of the energy to the surroundings and so is a slightly warmer region of the furnace. Some elevation in refractory temperatures with O_2 enrichment is seen in this region as well. This is due to the aforementioned residence time effect caused by reduced volumetric flow in the O_2 -enriched cases.

Figure 4.4.2b shows temperature distribution along the blind sidewall of the furnace. When combustion products reach the back portion of the furnace (near the exhaust plenum wall), significant levels of energy have been transferred from the gas to previously encountered refractory, more so for O_2 -enriched because of the slower flow rate (higher residence time). Temperatures toward the exhaust plenum wall reflect this somewhat, being relatively cooler than most other parts of the furnace and more so for the O_2 -enriched cases.

Some of the combustion products pass through openings in the back wall to the exhaust plenum, but a portion, depending on the volumetric flow at this point, forms a return flow along the burner sidewall toward the burner. The flow rate will be less and the gases cooler for the O₂-enriched cases than for air-only cases. The result can be seen in the temperature profiles observed along the burner sidewall and the central part of the furnace cavity.

Generally, interior refractory surface-temperature-distribution was more uniform than expected for an oxygen-enriched combustion application. The maximum not exceeding the average by more than 100 °C and usually by less, once the refractory was on average above 800 °C.

A series of tests were performed to measure the heat flux to floor panels #7 and/or #11, Fig. 2.2, and to investigate the effect that this load would have on the furnace performance. However, with a single panel exposed, the furnace temperature could not be maintained at 1100 °C with oxygen enrichment levels below 40% (e.g. $T_f \approx 1030$ °C with $\psi = 0\%$ and a firing rate of 370 kW). With two panels exposed a furnace temperature of only $T_f \approx 1010$ °C was obtained with $\psi = 100\%$ and a firing rate of 330 kW. Thus these tests did not yield data which could be used to make a fair comparison between different operating conditions. Some of the NO_x emission results at the lower temperatures noted in Fig. 4.3.4 were obtained as part of these experiments.

4.5. Air infiltration

In these trials, infiltration air was supplied and controlled by running the furnace under varying degrees of negative pressure. The air leakage through furnace sample and probe ports resulted in a somewhat uniform distribution of entry points. Furnace operating conditions were monitored before and after infiltration in order to facilitate meaningful comparisons of NO_x emission levels.

Effects of air infiltration on NO_x emissions and temperature distribution in the furnace are shown in Figs. 4.5.1 and 4.5.2. Both figures contain a furnace schematic showing local interior refractory surface temperatures for various levels of air infiltration at a single excess O₂ level and 100% oxygen enrichment ($\psi = 100\%$). Data are positioned in the figure at the approximate corresponding furnace location. The results at each furnace location are listed in the same order as the tabular data (i.e. top reading corresponds to highest furnace pressure, bottom reading, lowest furnace pressure). A table containing information corresponding to the series of temperature measurements is displayed at the top of each figure. Included in the tables are values for the furnace pressure, firing rate, oxygen enrichment level, stack O₂ and NO_x levels and the arithmetic area-mean temperature of the refractory interior surface.

Figure 4.5.1 shows results for three furnace operating pressures (levels of air infiltration) for a single firing rate, excess burner feed oxidant level (10%) and oxygen enrichment level, $\psi = 100\%$. The first row of data corresponds to the no-air-infiltration case, since the furnace pressure is positive (0.05 in. of water column). This can be regarded as the base case. The second row of data corresponds to the same furnace settings as the first set with the exception that the furnace pressure was reduced to -0.05 in.w.c. This resulted in air infiltration, which can be quantified by comparing O₂ levels in the exhaust gases. An increase in stack O₂ from 5.5 to 7.5% by volume corresponds to an air infiltration rate equal to 20% of the volumetric burner feed. The third row of data corresponds to a furnace

operating pressure of -0.10 in w.c. The difference in stack O₂ levels between this and the base case indicate an infiltration rate equal to 43% of the burner volumetric feeds.

Test No	P. w.c.	Pilot burner	m ³ -A/h ² KW	w. %	O ₂ % w.b	NO _x mg/M ³ < T _{amb} °C	CO ₂ % w.b
010103	0.05	On	212	100.0	5.5	5.7	1117
010103	-0.05	On	211	100.0	7.5	7.2	1115
010103	-0.10	On	211	100.0	9.0	10.2	1113

Fig. 4.5.1. Interior surface temperature of furnace roof refractory (plan view) for various air infiltration levels. Excess oxidant level of 10%. Oxygen enrichment level of 100%. No exposed pooling panels. Temperature units: °C

Notes: (i) Temperature readings are positioned in the figure at the approximate corresponding furnace location.

(ii) The three temperature readings at each furnace location in the figure are listed in the same order as the tabular data (ie. Top reading corresponds to furnace pressure of 0.05 in. w.c., bottom reading is at -0.10 in.w.c.)

Trial No.	P, in.w.c.	Pilot burner	$m(\Delta H_c)$, kW	η , %	O ₂ , % w.b.	NO _x , mg/MJ	$\langle T_{ref} \rangle_{arm}$, °C
010103	0.05	On	206	100.0	1.4	1.2	1109
010103	0.05	Off	206	100.0	1.9	0.8	1106
010103	-0.10	Off	206	100.0	4.1	1.1	1102

Fig. 4.5.2. Interior surface temperature of furnace roof refractory (plan view) for various air infiltration levels. Excess oxidant level of 3%. Oxygen enrichment level of 100%. No exposed cooling panels. Temperature units, °C.

Notes:

- Temperature readings are positioned in the figure at the approximate corresponding furnace location.
- The three temperature readings at each furnace location in the figure are listed in the same order as the tabular data (i.e. Top reading corresponds to furnace pressure of 0.05 in. w.c., bottom reading is at -0.10 in. w.c.).

The magnitude of effect that air infiltration has on furnace temperature should be similar to the fraction of the furnace input energy, $m(-\Delta h_c)$, required to heat the infiltration air to furnace temperature. In the case with high air infiltration, the air requires approximately 5% of the energy released from combustion of the fuel to heat it to furnace temperature. This should result in roughly the same effect as reducing the firing rate by 5%. The table values and furnace temperature schematic in Fig. 4.5.1 show a very modest effect of air infiltration on the furnace refractory temperature, similar to the effect of a 5% reduction in firing rate, perhaps somewhat less. Insufficient transition time to achieve thermal steady state accounts for the slight difference from the expected result.

Table values for NO_x emissions in Fig. 4.5.1 show emissions increase, nearly doubling as air infiltration levels increase from 0% to 43% of the burner volumetric feed. The increase in NO_x from no air infiltration to the maximum shown in the table corresponds well with those data collected for similar stack O_2 levels and effective O_2 enrichment levels without air infiltration for the O_2 -enriched CGRI Burner, previously shown in Fig. 4.3.1. This is the expected result, since the air supplied as infiltration air would have, in most cases, been substantially diluted with furnace product gases before coming into contact with any significant concentration of fuel, much the same as the burner supplied oxidant.

Figure 4.5.2, in addition to showing effects of air infiltration at a lower excess oxidant level (3%), also demonstrates the effect of shutting off the continuous pilot burner on furnace temperature and NO_x emission. Results for two furnace operating pressures (levels of air infiltration) for a single firing rate, excess burner feed oxidant level (3%) and oxygen enrichment level, $\psi = 100\%$. The first row of data corresponds to no air infiltration. The second row of data corresponds to the same furnace settings as the first set with the exception that the continuous pilot burner was shut off. The pilot burner is an air/natural gas premixed burner design that accounts for approximately 1--2% of the energy input to the furnace. The temperature profiles reflect this reduction in energy input. The interesting result is the large reduction in NO_x emission when the pilot burner is shut off. The emission level drops by 25%. This means that on an energy input basis, the pre-mixed pilot burner is emitting roughly 20 times the NO_x of the O_2 -enriched CGRI Burner. This is not a great surprise since premixed burners typically emit much higher levels of NO_x than most low- NO_x diffusion-type burners. The third row of data in Fig. 4.5.2 shows results for high air infiltration rate, also without the pilot burner on. Results from these conditions should be compared to the second row of data, also without the pilot burner on. As expected the NO_x level increases, by approximately 20% over the case without air infiltration.

Generally, the effect of air infiltration on furnace temperature distribution and NO_x emissions was as expected. The refractory temperature effect of air infiltration was similar in magnitude to a reduction in firing rate corresponding to the amount of energy required to heat the infiltration air to furnace temperature. NO_x emissions were affected by air infiltration. The air infiltration NO_x emission levels corresponded to levels seen without air infiltration but with similar stack oxygen concentrations. An interesting bit of information was obtained regarding the NO_x emissions produced by the pre-mixed pilot burner. Apparently, the pre-mixed pilot burner accounts for a disproportionate amount of the NO_x emissions on an energy input basis, roughly 20 times the O_2 -enriched CGRI Burner.

4.6. Steel scaling program

This section of the report describes results of a series of steel scaling trials performed in conjunction with the oxygen enrichment tests described earlier in this report. The objective of these tests was to investigate the impact that O₂-enriched combustion product atmospheres would have on scale morphology and scaling rates.

4.6.1. Overview

The problem of steel scaling has received considerable attention through publications in the research literature and textbooks, e.g. Birks and Meier (1983) and Kofstad (1988). Recent work of Abuluwefa et al. (1996a – 1996c, 1997a, 1997b) provides a good background for current research activities in this field.

A schematic of the steel scaling process encountered with exposure of a steel surface to an oxidizing gas phase is shown in Fig. 4.6.1. The scaling rate of steel can be measured in terms of the thickness of the scale layer, w , or the mass gain of steel sample, m_G , per unit area, A , of the steel substrate. The scaling rate can then be described by the relation,

$$\rho_{\text{scale}} \frac{dw}{dt} = \frac{d}{dt} \left(\frac{m_G}{A} \right) \quad (4.6.1)$$

Fig. 4.6.1. Schematic diagram of the classic idealized steel scaling process with exposure of a steel surface to an oxidizing gas phase.

The oxidation rate can depend on a number of mechanisms including:

- (1) transport of the oxidant gas from the bulk phase to the gas/scale surface,
- (2) phase boundary reactions at the gas/scale interface, and
- (3) diffusion of a species (anion or cation) through the scale layer.

The first two mechanisms do not depend on the scale thickness, w , and these mechanisms lead to a linear growth rate,

$$\rho_{\text{scale}} \frac{dw}{dt} = \frac{d}{dt} \left(\frac{m_G}{A} \right) = \text{Constant} \quad (4.6.2)$$

$$w = k_L' t + C_1 \quad \text{or} \quad \frac{m_G}{A} = k_L' t + C_2 \quad (4.6.3)$$

where k_L' and k_L'' are linear rate constants expressed in terms of scale thickness or mass units respectively. The integration constants, C_1 and C_2 , may be close to zero if the linear growth rate starts from time $t \approx 0$.

The third oxidation mechanism above commonly applies after an initial layer of oxide film has been established and leads to a parabolic oxidation rate. For iron and steel oxidation, this process is based on cation transport through the oxide film. This diffusion rate determining step is inversely proportional to the oxide film thickness, w , (integrated form of Fick's law of diffusion),

$$\rho_{\text{scale}} \frac{dw}{dt} = \frac{d}{dt} \left(\frac{m_G}{A} \right) = \frac{\text{Constant}}{w} \quad (4.6.4)$$

$$w^2 = k_p' t + C_3 \quad \text{or} \quad \left(\frac{\Delta m}{A} \right)^2 = k_p'' t + C_4 \quad (4.6.5)$$

where k_p' and k_p'' are parabolic rate constants expressed in terms of scale thickness or mass units respectively. The integration constants, C_3 and C_4 , may be close to zero if the parabolic growth rate starts from time $t \approx 0$.

In the current project, the effect of the combustion product atmosphere on the scaling rate and scale morphology for several steel grades was of interest. The combustion product atmosphere was dictated by the level of excess oxidant and oxygen enrichment conditions employed in the experimental program.

4.6.2. Steel scale morphology

Scale morphology work included samples of the 5 steel grades. Each sample was exposed to furnace atmospheres for a 4-hour period at 1100°C at one of four oxygen enrichment levels (0, 25, 50 and 90%) and one of 3 stack oxygen levels (nominally 1, 2 and 5%). This resulted in a total of 5 (grades) $\times$ 4 (O_2 enrichments) $\times$ 3 (O_2 stack levels) = 60 samples. Some scale morphology information was also attained from samples used for determining scale formation rates.

Four different analyses were conducted:

- Scale surface habit
- Scale intactness
- Scale adhesion

- Photomicrography

Scale surface habit and intactness

Non-magnified visual observations of surface habit characteristics were made for each morphology sample. The scale surface was ranked from 0 to 5 corresponding to the following surface characteristics:

- 0 – smooth
- 1 – a few nodules along as-cast edge
- 2 – a few nodules randomly distributed
- 3 – slightly mottled with blisters and nodules
- 4 – heavily mottled with blisters and nodules
- 5 – porous surface scale

Scale “intactness” for each steel sample was ranked between 0 and 6, corresponding to:

- 0 – intact
- 1 – a few fine cracks
- 2 – a few fine flakes from outer surface of scale
- 3 – some fine flakes from outer surface of scale
- 4 – loss of small bits of thick scale from sides after cooling
- 5 – loss of large sections of thick scale from sides after cooling
- 6 – loss of thick scale from sides and main faces after cooling

Figure 4.6.2 shows an example of a steel test sample before furnace exposure. Figures 4.6.3 to 4.6.9 show cooled steel test samples after removal from the furnace. Each figure exhibits a different combination of surface habit and scale intactness characteristics. The only factor appearing to significantly affect steel scale habit and intactness was the steel grade tested. Furnace O₂ level and O₂ enrichment levels were not statistically significant factors for this data set.

The order of the steel grades in going from a smooth, intact scale to rough and cracked/separated scale was: DS, DC, SF, SJ, and SB. Composition of the steels was presented previously in Table 3.2. The outward scale surface characteristics do not appear to be linked to the steel chemical composition in any obvious way. It appears that perhaps steel carbon content may have some influence on scale habit and intactness, becoming less smooth and intact as carbon content rises and the formation and escape of CO₂ from the steel/scale interface increases. More will be said about steel composition and scale morphology later in this section.

Fig. 4.6.2. Steel sample before furnace exposure.

Fig. 4.6.3. Steel scale surface for steel grade DS at 50% oxygen enrichment and 1.7% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 0 (smooth) and Scale Intactness = 0 (intact).

Fig. 4.6.4. Steel scale surface for steel grade DS at 90% oxygen enrichment and 0.82% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 1 (a few nodules along as cast edge) and Scale Intactness = 0 (intact).

Fig. 4.6.5. Steel scale surface for steel grade DC at 50% oxygen enrichment and 4.3% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 2 (a few nodules randomly distributed) and Scale Intactness = 1 (a few fine cracks).

Fig. 4.6.6. Steel scale surface for steel grade SF at 25% oxygen enrichment and 1.7% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 3 (slightly mottled) and Scale Intactness = 2 (a few fine flakes from outer surface of scale).

Fig. 4.6.7. Steel scale surface for steel grade SB at 50% oxygen enrichment and 1.7% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 4 (heavily mottled) and Scale Intactness = 4 (loss of small bits of thick scale from sides after cooling).

Fig. 4.6.8. Steel scale surface for steel grade SB at 25% oxygen enrichment and 4.3% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 4 (heavily mottled) and Scale Intactness = 5 (loss of large sections of thick scale from sides after cooling).

Fig. 4.6.9. Steel scale surface for steel grade SB at 50% oxygen enrichment and 4.3% stack oxygen. Exposed for 4 hours at 1100 °C. Surface Characteristic = 4 (heavily mottled) and Scale Intactness = 6 (loss of thick scale from sides and main faces after cooling).

Scale adhesion

Scale adhesion was ranked according to the effort required for scale removal from the steel substrate. This analysis was done on the steel samples used to determine steel mass loss, since it was necessary to remove the scale from those samples. A ranking of 1 to 4 was used, corresponding to qualitative observations:

- 1 – scale falls off with very little effort
- 2 – removed with little effort
- 3 – removed with some effort
- 4 – difficult to remove

Figure 4.6.10 demonstrates the appearance of a de-scaled test sample where the scale has come completely off with little effort. Figure 4.6.11 shows an example of a sample that has been de-scaled with much greater effort and evidence of a residual porous scale remains attached to portions of the steel surface.

Factors appearing to affect steel scale adhesion, from most dominate to least dominate, were: Steel grade > Furnace oxygen concentration level > Oxygen enrichment level > Furnace exposure time. The effect of steel grade was much more pronounced than for any of the other factors listed.

The order of scale removal effort, from high to low effort, for the various grades of steel tested was SF>SB>SJ>DC. The scale adhesion results can, in part, be related to the composition of the steels, Table 3.2. Surface enrichment of elements, especially Ni, can result in surface enrichment and metal/scale entanglement, Sachs and Tucker (1968). The SF steel grade is highest in Ni content and possesses the most tenacious scale. Other metal components, such as Cu, can also influence scale characteristics. Steel grades SF, SB and SJ all have somewhat elevated levels of Cu, Cr and Mo.

As previously mentioned, effects of oxygen concentration inside the furnace, oxygen enrichment level, and sample exposure time on scale adhesion were of much smaller magnitude than the effect of steel grade. However, effects were discernable and trends were consistent across all grades tested.

Scale adhesion was observed to decrease with increasing oxygen concentration. More will be said about this based on observations made in the following section discussing steel scale photomicrographs.

Effort required for scale removal appeared to decrease with increasing oxygen enrichment. This effect was the smallest of those observed and it can be said that for these steel grades, the effect of oxygen enrichment on scale adhesion is minimal

Lastly, scale adhesion tended to decrease with increasing furnace exposure time. This may be a result of a relatively adherent layer of wustite being the primary scale component during the initial phases of steel oxidation. It can be speculated that later formation of a more porous scale containing the three iron oxides, wustite, magnetite and hematite, may be less difficult to remove.

Fig. 4.6.10. “Clean” de-scaled steel sample.

Fig. 4.6.11. De-scaled steel sample showing residual porous "subscale".

Photomicrography

Scale and the scale/steel interface for the as-cast face of steel samples were examined by photomicrography. Selected morphology samples were encased in epoxy, sectioned (cut perpendicular to the sample face, straight through), mounted and photographed under an optical microscope. Photomicrographs for a subset of the full 60 samples at 50x magnification were obtained for:

1. Each grade at 0% oxygen enrichment and three stack oxygen levels (a “base” case intended to show “conventional” operation effects) – total of 15 samples
2. Each grade at 90% oxygen enrichment and 2% stack oxygen – total of 5 samples.

Additionally, some SEM (scanning electron microscopy) work was performed on a subset of the above noted samples. The attraction of using SEM for some of the samples was the improved depth of field focus and, more importantly, in backscatter-mode, to distinguish the boundaries, thickness and morphology of iron oxide phases through the scale profile.

Photomicrography results are presented in two configurations. Figures 4.6.12 to 4.6.15 facilitate scale morphology comparison between steel grades at individual sets of operating conditions, while Figs. 4.6.16 to 4.6.20 aid comparisons of operating variable effects on scale morphology for individual steel grades.

Each photomicrograph shows a full section profile of the entire scale thickness (shown here scaled to 30x magnification) with a portion of the metal substrate (light region) shown at the bottom of each photo. The dark region at the top of each photo is part of the epoxy that encapsulates the sample. The epoxy, which is softer than the scale and metal substrate, typically can be seen to have striations, artifacts from the sanding and polishing done as part of the sample mounting process. Similarly shaded and textured areas within the photo are likely epoxy filled cracks or pores. The photos are well suited to qualitative evaluation of porosity and discontinuities (fissures, gaps, etc.) in the scale profile. Additionally, the photomicrographs produced from SEM analysis show greater depth of field and in backscatter mode show the distribution of the different iron oxide phases present.

The degree of overall porosity of the sectioned scale seems to follow the order observed for scale intactness presented earlier in this section. The order of the steel grades, from a smooth, intact scale to rough and cracked/separated scale, was: DS, DC, SF, SJ, and SB. Figure 4.6.13. most clearly shows this same order for least porous to most porous steel grade. Figures 4.6.12, 4.6.14 and 4.6.15 also show the same general trend, though less definitively.

These same figures (4.6.12 to 4.6.15) corroborate, to a large extent, the scale adhesion results reported earlier in this section. The order of scale removal effort, from high to low effort, for the various grades of steel tested was SF>SB>SJ>DC. Looking at the steel/scale interfaces in Figs. 4.6.12 to 4.6.15, it can be generally seen that porous scale and/or rough steel surface structure exists at the steel surface interface for the steels with adherent scales while the steels with easily removed scale have a gap (epoxy filled) at the steel/scale interface in most cases. Figure 4.6.21(a) consists of a pair of 400x photomicrographs showing the steel surface interface representing the least (DC) and most (SF)

tenacious scales. The DC sample has only epoxy present near the steel substrate interface, while the SF sample has substantial amounts of scale present with some evidence of metal/scale entanglement, perhaps due to surface enrichment of Ni. As previously noted, the SF grade had relatively more Ni and other noble metals than the other steel grades. Figure 4.6.21(b) shows similar behaviour depicted in 250x SEM photomicrographs for the DS and SF steel/scale interface.

Figures 4.6.16 to 4.6.20 each show a series of photomicrographs taken for an individual steel grade for stack oxygen levels of 0.82 %, 1.7% and 4.25% all at 0% oxygen enrichment and another sample exposed at 1.7% stack oxygen with 90% oxygen enrichment. Photomicrographs A, B and C in each figure can be used to evaluate the effect of oxygen concentration in the furnace on the scale morphology while photos B and D can be compared to evaluate the effect of oxygen enrichment on scale morphology.

Figure 4.6.16 shows a series of photos for steel grade DC. Photos A, B and C show that the scale appears relatively unchanged over the range of oxygen concentrations used, exhibiting the same overall level of porosity and fissures and a large epoxy-filled separation gap between the steel substrate and the main portion of scale. Comparing photos B and D in Fig. 4.6.16, shows that the oxygen enriched case, D, appears to have somewhat less porous scale in the outer 2/3 of the scale, but possesses a porous layer of scale close to the steel interface, though a clearly visible thin layer of epoxy occurs along the entire steel interface. This small but clearly defined separation further supports the observations of easily removable scale noted previously in this section.

Examining results for the other steel grades, Figs. 4.6.17 to 4.6.20, it is evident that under the range of conditions studied, stack oxygen level and oxygen enrichment had much less influence on scale morphology than the steel grade. Although effects of oxygen concentration and enrichment levels were small, there does appear to be a discernible pattern of somewhat consistent effects. As in the case for the DC steel grade, it appears that the oxygen enriched cases, D, appear to have somewhat less porous scales in the outer 2/3 of the scale and possess a porous layer of scale closer to the steel interface, though a clear thin layer of epoxy is clearly visible along the entire steel interface in most cases for all steel grades. The effect of furnace oxygen concentration level on scale morphology is less consistent, although it does follow similar trends in most cases. It appears that overall porosity of the scale increases slightly with increased furnace oxygen concentration, though there are a few exceptions to this observation. In these cases, it is possible that some anomalous effect, such as the loss of a portion of scale during furnace exposure may have significantly affected scale formation. But, since mass gain and loss measurements (discussed in sections that follow) indicate that loss of scale inside the furnace was likely minimal, this is probably not the case.

Fig. 4.6.12. Photomicrographs (30x) of the steel/scale interface for five sample grades at 0.82% stack oxygen and 0% oxygen enrichment. Samples exposed for 4 hours at 1100 °C.

DC

DS

SJ

SB

SF

Fig. 4.6.13a. Photomicrographs (30x) of the steel/scale interface for five sample grades at 1.7% stack oxygen and 0% oxygen enrichment. Samples exposed for 4 hours at 1100 °C.

Fig. 4.6.13b. SEM (50x) of DS, DC, SJ, SB, and SF steel grades at 0% oxygen enrichment and 1.7% stack oxygen. Samples exposed for 4 hours at 1100 °C.

DS

DC

SJ

SB

SF

Fig. 4.6.13c. SEM (Backscatter, 15x) of DS, DC, SJ, SB, and SF steel grades at 0% oxygen enrichment and 1.7% stack oxygen. Samples exposed for 4 hours at 1100 °C.

DC

DS

SJ

SB

SF

Fig. 4.6.14. Photomicrographs (30x) of the steel/scale interface for five sample grades at 4.25% stack oxygen and 0% oxygen enrichment. Samples exposed for 4 hours at 1100 °C.

DC

DS

SJ

SB

SF

Fig. 4.6.15. Photomicrographs (30x) of the steel/scale interface for five sample grades at 1.7% stack oxygen and 90% oxygen enrichment. Samples exposed for 4 hours at 1100 °C.

Fig. 4.6.16. Photomicrographs (30x) of the scale/steel interface for the DC steel grade. Samples exposed for 4 hours at 1100 °C:

- A: 0.82% stack oxygen, 0% oxygen enrichment
- B: 1.7% stack oxygen, 0% oxygen enrichment
- C: 4.25% stack oxygen, 0% oxygen enrichment
- D: 1.7% stack oxygen, 90% oxygen enrichment

Fig. 4.6.17. Photomicrographs (30x) of the scale/steel interface for the DS steel grade. Samples exposed for 4 hours at 1100 °C:

- A: 0.82% stack oxygen, 0% oxygen enrichment
- B: 1.7% stack oxygen, 0% oxygen enrichment
- C: 4.25% stack oxygen, 0% oxygen enrichment
- D: 1.7% stack oxygen, 90% oxygen enrichment

Fig. 4.6.18. Photomicrographs (30x) of the scale/steel interface for the SB steel grade. Samples exposed for 4 hours at 1100 °C:

- A: 0.82% stack oxygen, 0% oxygen enrichment
- B: 1.7% stack oxygen, 0% oxygen enrichment
- C: 4.25% stack oxygen, 0% oxygen enrichment
- D: 1.7% stack oxygen, 90% oxygen enrichment

Fig. 4.6.19. Photomicrographs (30x) of the scale/steel interface for the SF steel grade. Samples exposed for 4 hours at 1100 °C:

- A: 0.82% stack oxygen, 0% oxygen enrichment
- B: 1.7% stack oxygen, 0% oxygen enrichment
- C: 4.25% stack oxygen, 0% oxygen enrichment
- D: 1.7% stack oxygen, 90% oxygen enrichment

Fig. 4.6.20. Photomicrographs (30x) of the scale/steel interface for the SJ steel grade. Samples exposed for 4 hours at 1100 °C:

- A: 0.82% stack oxygen, 0% oxygen enrichment
- B: 1.7% stack oxygen, 0% oxygen enrichment
- C: 4.25% stack oxygen, 0% oxygen enrichment
- D: 1.7% stack oxygen, 90% oxygen enrichment

DC

SF

Fig. 4.6.21a. Photomicrographs (400x) of the scale/steel interface for least (DC) and most (SF) adherent scales. Both samples exposed for 4 hours at 1100 °C, 0% oxygen enrichment, and 1.7% stack oxygen.

Fig. 4.6.21b. SEM (250x) of the steel/scale interface for steel grades DS (upper photo) and SF (lower photo) steel grade at 0% oxygen enrichment and 1.7% stack oxygen. Exposed for 4 hours at 1100 °C.

4.6.3. Scaling rate tests, DC and SB grades

The primary series of scaling tests were performed with two steel grades, DC and SB (steel compositions were given in Table 3.2). For these tests, steel specimens were exposed to a complete range of operating variables associated with the overall oxygen enrichment studies. These included the oxygen enrichment level (0%, 25%, 50% and 90%) and the stack oxygen concentration (nominal levels of 1%, 2% and 5%). The furnace operating temperature was maintained at 1100°C, consistent with the other trials performed in this work. Each sample was pre-weighed and a surface area was estimated by direct measurement. The samples were then exposed to the furnace atmosphere for times ranging from 1.8 ks (0.5 h) to 14.4 ks (4.0 h). The samples were then removed from the furnace, cooled in a N₂ atmosphere, weighed with the scale attached and weighed again with the scale removed. The steel mass gain (a measure of the oxygen uptake in the oxide) and the steel mass loss (oxide material removed) were estimated from these measurements.

Steel grade DC

The test conditions employed for the DC steel samples are shown in Table 4.6.1. This table also indicates the data successfully obtained for the mass gain, m_G/A , and mass loss, m_L/A , as indicated by the “X” symbol for each scaling time. A complete set of mass loss data was obtained for these conditions and all but 4 samples successfully produced mass gain results.

The scaling rate data for the DC grade generally followed a parabolic oxidation rate beyond the initial oxidation time of 1.8 ks. The data were fitted to linear models of the form:

$$\text{Steel mass gain:} \quad (m_G/A)^2 = \beta_0 + \beta_1 t \quad (4.6.6)$$

$$\text{Steel mass loss:} \quad (m_L/A)^2 = \gamma_0 + \gamma_1 t \quad (4.6.7)$$

The parameter estimates, β_0 , β_1 , γ_0 , and γ_1 , at each operating condition are shown in Table 4.6.2. The scaling rates in this report are expressed in terms of kg/m² for m_G/A and m_L/A with the exposure time expressed in ks (kiloseconds). The stoichiometric coefficient, α , for the Fe/O ratio, i.e. Fe _{α} O, was also estimated from the mass loss (Fe) and mass gain (O) data at large oxidation time ($t \approx 14.4$ ks) for each operating condition noted in Table 4.6.2.

The oxidation rates for the complete set of operating conditions noted in Table 4.6.1 are shown graphically in Figs. 4.6.22 and 4.6.23. These results are expressed in terms of the mass gain and the square of the mass gain as a function of oxidation time in Fig. 4.6.22; the results for the mass loss and square of the mass loss are shown in Fig. 4.6.23. The complete set of data appear to be well described by parabolic relations for $t \geq 1.8$ ks,

$$\text{DC grade, steel mass gain:} \quad (m_G/A)^2 = 0.298 t - 0.211 \quad (4.6.8)$$

DC grade, steel mass gain: $(m_L/A)^2 = 2.68 t - 2.16$ (4.6.9)

with $\alpha \approx 0.856$ at large time

Table 4.6.1. Furnace operating conditions employed for the scaling tests with the DC steel samples. Scaling times noted with the “X” symbol indicate successful mass gain or loss measurements for the corresponding experimental operating condition.

Stack oxygen	O2 enrichment	Steel mass gain, m_G/A				Steel mass loss, m_L/A			
		1.8 ks	3.6 ks	7.2 ks	14.4 ks	1.8 ks	3.6 ks	7.2 ks	14.4 ks
1%	0%	X	X	X	X	X	X	X	X
1%	25%	X	X	X	X	X	X	X	X
1%	50%	X	X	X	X	X	X	X	X
1%	90%	X	X	X	X	X	X	X	X
2%	0%	X			X	X	X	X	X
2%	25%	X	X		X	X	X	X	X
2%	50%	X		X	X	X	X	X	X
2%	90%	X	X	X	X	X	X	X	X
5%	0%	X	X	X	X	X	X	X	X
5%	25%	X	X	X	X	X	X	X	X
5%	50%	X	X	X	X	X	X	X	X
5%	90%	X	X	X	X	X	X	X	X

Table 4.6.2. Parameter estimates for the parabolic oxidation rates of the DC steel samples.

Stack oxygen	O ₂ enrichment	$(m_G/A)^2$		$(m_L/A)^2$		α
		$\beta_0, \text{kg}^2/\text{m}^4$	$\beta_1, \text{kg}^2/\text{ks-m}^4$	$\gamma_0, \text{kg}^2/\text{m}^4$	$\gamma_1, \text{kg}^2/\text{ks-m}^4$	
1%	0%	-0.381	0.299	-3.43	2.70	0.861
1%	25%	-0.321	0.292	-4.23	2.74	0.863
1%	50%	-0.354	0.300	-5.76	2.81	0.847
1%	90%	-0.363	0.310	-3.13	2.63	0.834
2%	0%	-	-	-2.10	2.86	-
2%	25%	-0.282	0.349	-3.53	3.19	0.857
2%	50%	-0.384	0.324	-1.47	2.76	0.857
2%	90%	-0.114	0.300	-1.32	2.67	0.851
5%	0%	-0.048	0.239	-0.52	2.08	0.844
5%	25%	-0.129	0.309	-0.83	2.67	0.845
5%	50%	-0.135	0.308	-0.58	2.75	0.863
5%	90%	0.246	0.233	1.02	2.31	0.883

$$(m_G/A)^2 = \beta_0 + \beta_1 t$$

$$(m_L/A)^2 = \gamma_0 + \gamma_1 t$$

Fig. 4.6.22. Scaling rates for the DC steel grade at different operating conditions of stack oxygen concentration and oxygen enrichment levels. The results are expressed in terms of the steel mass gain in the left graph and the square of the mass gain (testing for parabolic growth rates) in the right graph. The solid line in the right graph is the parabolic fit for the experimental data based on the relationship, $(m_G/A)^2 = 0.298 t - 0.211$. The dashed line in the left graph is the same relation expressed in terms of the mass gain per unit area.

Fig. 4.6.23. Scaling rates for the DC steel grade at different operating conditions of stack oxygen concentration and oxygen enrichment levels. The results are expressed in terms of the steel mass loss in the left graph and the square of the mass loss (testing for parabolic growth rates) in the right graph. The solid line in the right graph is the parabolic fit for the experimental data based on the relationship, $(m_L/A)^2 = 2.68 t - 2.16$. The dashed line in the left graph is the same relation expressed in terms of the mass loss per unit area.

While these relations give a broad picture of the scaling kinetics, some caution must be used since the scatter in the data shown in Figs. 4.6.22 and 4.6.23 may conceal effects of different operating conditions and reaction mechanisms. These effects can be revealed by examining the data for each set of operating conditions in more detail, Table 4.6.2 and Figs. 4.6.24 – 4.6.31.

The effect of the stack oxygen concentration with oxygen enrichment levels as a parameter is shown in Figs. 4.6.24 – 4.6.27. For oxidation times, $t \geq 1.8$ ks, these results are described by the parabolic relations:

1% stack oxygen:

$$(m_G/A)^2 = 0.300 t - 0.355 \quad (4.6.10)$$

$$(m_L/A)^2 = 2.72 t - 4.14 \quad (4.6.11)$$

and $\alpha \approx 0.856$ (Fe_αO) at large t

2% stack oxygen:

$$(m_G/A)^2 = 0.320 t - 0.232 \quad (4.6.12)$$

$$(m_L/A)^2 = 2.87 t - 2.10 \quad (4.6.13)$$

and $\alpha \approx 0.858$ (Fe_αO) at large t

5% stack oxygen:

$$(m_G/A)^2 = 0.272 t - 0.016 \quad (4.6.14)$$

$$(m_L/A)^2 = 2.45 t - 0.023 \quad (4.6.15)$$

and $\alpha \approx 0.861$ (Fe_αO) at large t

For a full parabolic behavior, we would expect a zero intercept in these relationships and this is indeed observed for the 5% stack oxygen concentrations where the intercepts, -0.016 for the mass gain squared and -0.023 for the mass loss squared, are not significantly different from zero. This type of mechanism would occur when there is a high oxygen concentration with diffusion control based on the finite scale layer formed early in the oxidation process. At the lower stack oxygen concentrations, there is a delay in the start of the parabolic scale growth, with the largest delay at the 1% stack oxygen level. This is consistent with an initial oxidation mechanism controlled, to some degree, by the phase boundary reactions associated with CO_2 and H_2O . The present experimental techniques cannot confirm whether these processes dominate the initial oxidation process – more accurate data would be required for oxidation times under 1.8 ks.

There is another phenomenon we can observe from these oxidation rates for the DC samples. The parabolic rate constants (slopes in above relations) are highest for the 2% stack oxygen and the steel mass gain or loss at oxidation times of $t \approx 14.4$ ks depicted in Figs. 4.6.25 and 4.6.27 confirm this

behavior with $(m_G/A)^2 \approx 4.0, 4.4$ and $3.9 \text{ kg}^2/\text{m}^4$ and $(m_L/A)^2 \approx 35.0, 39.0$ and $35.0 \text{ kg}^2/\text{m}^4$ at stack oxygen concentrations of 1%, 2% and 5% respectively. The lower oxidation rate in moving from 2% to 1% stack oxygen is due to a slight change in the slope of the parabolic rate, but also a shift in the intercept due to the initial oxidation mechanism at shorter oxidation times. The parabolic oxidation rate constant at 5% stack oxygen is the lowest of the three values, but the net initial oxidation rate is higher, leading to a mass gain/loss at larger oxidation times, $t \approx 14.4 \text{ ks}$, comparable to that observed at 1% stack oxygen, but still lower than at 2%. Hence there appears to be different phenomena occurring as the stack oxygen level is changed for this steel grade with some changes in the oxidation rate constants but also some change in the mechanism for the initial oxidation process.

The effect of the oxygen enrichment levels with the stack oxygen concentration as a parameter is shown in Figs. 4.6.28 – 4.6.31. For oxidation times, $t \geq 1.8 \text{ ks}$, these results are described by the parabolic relations:

0% oxygen enrichment:

$$(m_G/A)^2 = 0.285 t - 0.245 \quad (4.6.16)$$

$$(m_L/A)^2 = 2.55 t - 2.02 \quad (4.6.17)$$

and $\alpha \approx 0.859 (\text{Fe}_\alpha\text{O})$ at large t

25% oxygen enrichment:

$$(m_G/A)^2 = 0.316 t - 0.260 \quad (4.6.18)$$

$$(m_L/A)^2 = 2.87 t - 2.86 \quad (4.6.19)$$

and $\alpha \approx 0.858 (\text{Fe}_\alpha\text{O})$ at large t

50% oxygen enrichment:

$$(m_G/A)^2 = 0.310 t - 0.285 \quad (4.6.20)$$

$$(m_L/A)^2 = 2.77 t - 2.61 \quad (4.6.21)$$

and $\alpha \approx 0.856 (\text{Fe}_\alpha\text{O})$ at large t

90% oxygen enrichment:

$$(m_G/A)^2 = 0.281 t - 0.0770 \quad (4.6.22)$$

$$(m_L/A)^2 = 2.54 t - 1.14 \quad (4.6.23)$$

and $\alpha \approx 0.856 (\text{Fe}_\alpha\text{O})$ at large t

Fig. 4.6.24. Scaling rates for the DC steel grade shown for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the steel mass gain (testing for linear growth rates), the dashed lines show the regression relation developed from the parabolic rate expression for each stack oxygen concentration.

Fig. 4.6.25. Scaling rates for the DC steel grade shown for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the square of the mass gain (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expression for each stack oxygen concentration:

$$1\% \text{ stack oxygen: } (m_G/A)^2 = 0.300 t - 0.355$$

$$2\% \text{ stack oxygen: } (m_G/A)^2 = 0.320 t - 0.232$$

$$5\% \text{ stack oxygen: } (m_G/A)^2 = 0.272 t - 0.016$$

Fig. 4.6.26. Scaling rates for the DC steel grade shown for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the mass loss (testing for linear growth rates); the dashed lines show the regression relation developed from the parabolic rate expression for each stack oxygen concentration.

Fig. 4.6.27. Scaling rates for the DC steel grade shown for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the square of the mass loss (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expression for each stack oxygen concentration:

$$1\% \text{ stack oxygen: } (m_L/A)^2 = 2.72 t - 4.14$$

$$2\% \text{ stack oxygen: } (m_L/A)^2 = 2.87 t - 2.10$$

$$5\% \text{ stack oxygen: } (m_L/A)^2 = 2.45 t - 0.023$$

Fig. 4.6.28. Scaling rates for the DC steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the mass gain (testing for linear growth rates); the dashed lines show the regression relation developed from the parabolic rate expression for each oxygen enrichment level.

Fig. 4.6.29. Scaling rates for the DC steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the square of the mass gain (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expression for each oxygen enrichment level:

$$0\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.285 t - 0.245$$

$$25\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.316 t - 0.260$$

$$50\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.310 t - 0.285$$

$$90\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.281 t - 0.0770$$

Fig. 4.6.30. Scaling rates for the DC steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the steel mass loss (testing for linear growth rates); the dashed lines show the regression relations developed from the parabolic rate expression for each oxygen enrichment level.

Fig. 4.6.31. Scaling rates for the DC steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the square of the mass loss (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expression for each oxygen enrichment level:

$$0\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.55 t - 2.02$$

$$25\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.87 t - 2.86$$

$$50\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.77 t - 2.61$$

$$90\% \text{ oxygen enrichment: } (m_L/A)^2 = 2.54 t - 1.14$$

The parabolic rate constants (slopes in above relations) are highest for the 25% oxygen enrichment case and the steel mass gain or loss at oxidation times of $t = 14.4$ ks depicted in Figs. 4.6.29 and 4.6.31 indicate that $(m_G/A)^2 \approx 3.9, 4.3, 4.2$ and $4.0 \text{ kg}^2/\text{m}^4$ and $(m_L/A)^2 \approx 35.0, 38.0, 37.0$ and $35.0 \text{ kg}^2/\text{m}^4$ at oxygen enrichment levels of 0%, 25%, 50% and 90% respectively. At each enrichment level there is some delay in the onset of the parabolic behavior as indicated by the intercepts observed in these rate expressions. In general we can also observe a slightly higher oxidation rate under oxygen enrichment conditions but this effect does not appear to be large. Further work would have to be performed to observe this effect in more detail.

The steel scaling tests performed for the DC steel samples indicate that there is only a small effect of stack oxygen concentration on the oxidation process. A slightly lower oxidation rate with a low stack oxygen concentration ($\sim 1\%$) was observed compared with a 2% stack oxygen level. At higher stack oxygen concentrations (5%) a full parabolic oxidation mechanism was observed during the scaling process and this led to overall oxidation rates comparable to those observed at 1% stack oxygen. The steel scaling rates observed with oxygen enriched combustion conditions was slightly higher than those observed, but this effect was not large and further work would be needed to assess the best overall operating conditions with respect to this variable.

Steel grade SB

The test conditions employed for the SB steel samples are shown in Table 4.6.3. There were sufficient SB steel samples to perform scaling tests at 5 exposures times - a time of 10.8 ks (3.0 h) was added for these tests compared to the DC tests. In addition, a test was also performed at 2% stack oxygen and 75% oxygen enrichment. As shown in Table 4.6.3, a complete set of mass loss data was obtained for these conditions and all but 8 of the samples successfully produced mass gain results.

The scaling rate data for the SB grade generally followed a parabolic oxidation rate beyond the initial oxidation time of 1.8 ks. As in the previous analysis, the data were fitted to linear models of the form:

$$\text{Steel mass gain:} \quad (m_G/A)^2 = \beta_0 + \beta_1 t \quad (4.6.6)$$

$$\text{Steel mass loss:} \quad (m_L/A)^2 = \gamma_0 + \gamma_1 t \quad (4.6.7)$$

and the parameter estimates, β_0 , β_1 , γ_0 , and γ_1 , at each operating condition are shown in Table 4.6.4. The stoichiometric coefficient, α , for the Fe/O ratio, i.e. Fe_αO , is also estimated at large oxidation time ($t \approx 14.4$ ks) for each operating condition noted in Table 4.6.4.

The SB scaling data are shown graphically in Figs. 4.6.32 and 4.6.33 in terms of the mass gain (Fig. 4.6.32) and steel mass loss (Fig. 4.6.33). The complete set of data in these graphs are described by parabolic relations for $t \geq 1.8$ ks,

$$\text{SB grade, steel mass gain:} \quad (m_G/A)^2 = 0.188 t - 0.118 \quad (4.6.24)$$

$$\text{SB grade, steel mass loss:} \quad (m_L/A)^2 = 1.93 t - 1.93 \quad (4.6.25)$$

with $\alpha \approx 0.905$ at large time ($t \approx 14.4$ ks)

These results indicate that the SB grade has about a 30-40% lower scaling rate than the DC grade (expressed in terms of the slopes for the corresponding mass gain/mass loss parabolic expressions). The results in Figs. 4.6.32 and 4.6.33 also indicate that there is a larger degree of scatter in the data for the SB grade compared to the DC tests (Figs. 4.6.22 and 4.6.23). This is in part due to a larger random scatter in the data about the regression lines describing the parabolic relations, but there was also a larger variation between operating conditions. These effects can be revealed by examining the data for each set of operating conditions in more detail. The estimates of the scaling rate parameters for the SB grade at each operating condition are shown in Table 4.6.4, along with graphical presentations in Figs. 4.6.34 – 4.6.41.

Table. 4.6.3. Furnace operating conditions employed for the scaling tests with the SB steel samples. Scaling times noted with the “X” symbol indicate successful mass gain or mass loss measurements for the corresponding experimental operating condition.

Stack oxygen	O ₂ enrichment	Steel mass gain, m _G /A					Steel mass loss, m _L /A				
		1.8 ks	3.6 ks	7.2 ks	10.8 ks	14.4 ks	1.8 ks	3.6 ks	7.2 ks	10.8 ks	14.4 ks
1%	0%	X	X	X	X	X	X	X	X	X	X
1%	25%	X	X	X	X	X	X	X	X	X	X
1%	50%	X	X	X	X	X	X	X	X	X	X
1%	90%	X	X	X	X	X	X	X	X	X	X
2%	0%	X			X	X	X	X	X	X	X
2%	25%	X	X		X		X	X	X	X	X
2%	50%	X		X		X	X	X	X	X	X
2%	90%	X	X	X	X	X	X	X	X	X	X
5%	0%	X	X	X	X	X	X	X	X	X	X
5%	25%	X	X		X	X	X	X	X	X	X
5%	50%	X	X		X	X	X	X	X	X	X
5%	90%	X	X	X	X	X	X	X	X	X	X
2%	75%	X	X	X	X	X	X	X	X	X	X

Table 4.6.4. Parameter estimates for the parabolic oxidation rates of the SB steel samples.

Stack oxygen	O ₂ enrichment	(m _G /A) ²		(m _L /A) ²		α
		β ₀ , kg ² /m ⁴	β ₁ , kg ² /ks-m ⁴	γ ₀ , kg ² /m ⁴	γ ₁ , kg ² /ks-m ⁴	
1%	0%	0.0925	0.151	-2.92	1.54	0.835
1%	25%	-0.0548	0.139	-3.79	1.73	0.944
1%	50%	-0.208	0.197	-3.39	1.91	0.868
1%	90%	-0.249	0.219	-3.44	2.17	0.886
2%	0%	-0.0962	0.171	-1.71	1.61	0.863
2%	25%	-0.147	0.189	-2.08	1.81	0.874
2%	50%	-0.143	0.188	-1.04	1.80	0.892
2%	75%	-0.257	0.198	-4.24	2.09	0.904
2%	90%	-0.0440	0.204	-0.717	1.97	0.886
5%	0%	0.170	0.149	0.284	1.87	0.982
5%	25%	-0.345	0.230	-1.78	2.50	0.973
5%	50%	0.0850	0.168	-0.781	2.17	0.999
5%	90%	-0.359	0.239	0.526	1.97	0.877

$$(m_G/A)^2 = \beta_0 + \beta_1 t$$

$$(m_L/A)^2 = \gamma_0 + \gamma_1 t$$

Fig. 4.6.32. Scaling rates for the SB steel grade at different operating conditions of stack oxygen concentration and oxygen enrichment levels. The results are expressed in terms of the steel mass gain in the left graph and the square of the mass gain (testing for parabolic growth rates) in the right graph. The solid line in the right graph is the parabolic fit for the experimental data based on the relationship, $(m_G/A)^2 = 0.188 t - 0.118$. The dashed line in the left graph is the same relationship expressed in terms of the mass gain per unit area.

Fig. 4.6.33. Scaling rates for the SB steel grade at different operating conditions of stack oxygen concentration and oxygen enrichment levels. The results are expressed in terms of the steel mass loss in the left graph and the square of the mass loss (testing for parabolic growth rates) in the right graph. The solid line in the right graph is the parabolic fit for the experimental data based on the relationship, $(m/A)^2 = 1.93 t - 1.93$. The dashed line in the left graph is the same relationship expressed in terms of the mass gain per unit area.

Fig. 4.6.34. Scaling rates for the SB steel grade for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the steel mass gain (testing for linear growth rates), the dashed lines show the regression relation developed from the parabolic rate expressions for each stack oxygen concentration.

Fig. 4.6.35. Scaling rates for the SB steel grade for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the square of the mass gain (testing for parabolic growth rates), the solid lines show the regression relation developed from the parabolic rate expressions for each stack oxygen concentration:

1% stack oxygen: $(m_G/A)^2 = 0.176 t - 0.105$

2% stack oxygen: $(m_G/A)^2 = 0.192 t - 0.128$

5% stack oxygen: $(m_G/A)^2 = 0.196 t - 0.112$

Fig. 4.6.36. Scaling rates for the SB steel grade for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the steel mass loss (testing for linear growth rates), the dashed lines show the regression relation developed from the parabolic rate expressions for each stack oxygen concentration.

Fig. 4.6.37. Scaling rates for the SB steel grade for different stack oxygen concentrations with the oxygen enrichment level as a parameter for each operating condition. The results are expressed in terms of the square of the mass loss (testing for parabolic growth rates), the solid lines show the regression relation developed from the parabolic rate expressions for each stack oxygen concentration:

$$\begin{aligned}
 \text{1\% stack oxygen:} \quad & (m_L/A)^2 = 1.94 t - 4.54 \\
 \text{2\% stack oxygen:} \quad & (m_L/A)^2 = 1.86 t - 1.96 \\
 \text{5\% stack oxygen:} \quad & (m_L/A)^2 = 2.13 t - 0.436
 \end{aligned}$$

Fig. 4.6.38. Scaling rates for the SB steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the mass gain (testing for linear growth rates); the dashed lines show the regression relation developed from the parabolic rate expressions for each oxygen enrichment level.

Fig. 4.6.39. Scaling rates for the SB steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the square of the mass gain (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expressions for each oxygen enrichment level:

$$\begin{aligned}
 &0\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.134 t + 0.321 \\
 &25\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.192 t - 0.280 \\
 &50\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.184 t - 0.086 \\
 &75\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.207 t - 0.351 \\
 &90\% \text{ oxygen enrichment: } (m_G/A)^2 = 0.234 t - 0.366
 \end{aligned}$$

Fig. 4.6.40. Scaling rates for the SB steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the steel mass loss (testing for linear growth rates); the dashed lines show the regression relation developed from the parabolic rate expressions for each oxygen enrichment level.

Fig. 4.6.41. Scaling rates for the SB steel grade shown at different oxygen enrichment levels with the stack oxygen concentration as a parameter for each operating condition. The results are expressed in terms of the square of the mass loss (testing for parabolic growth rates); the solid lines show the regression relation developed from the parabolic rate expressions for each oxygen enrichment level:

$$\begin{aligned}
 0\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.73 t - 2.08 \\
 25\% \text{ oxygen enrichment: } (m_L/A)^2 &= 2.09 t - 3.41 \\
 50\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.97 t - 1.90 \\
 75\% \text{ oxygen enrichment: } (m_L/A)^2 &= 2.21 t - 5.56 \\
 90\% \text{ oxygen enrichment: } (m_L/A)^2 &= 1.98 t - 0.556
 \end{aligned}$$

The effect of the stack oxygen concentration with oxygen enrichment levels as a parameter is shown in Figs. 4.6.34 – 4.6.37. For oxidation times, $t \geq 1.8$ ks, these results are described by the parabolic relations:

1% stack oxygen:

$$(m_G/A)^2 = 0.176 t - 0.105 \quad (4.6.26)$$

$$(m_L/A)^2 = 1.94 t - 4.54 \quad (4.6.27)$$

and $\alpha \approx 0.889$ ($\text{Fe}_{\alpha}\text{O}$) at large t

2% stack oxygen:

$$(m_G/A)^2 = 0.192 t - 0.128 \quad (4.6.28)$$

$$(m_L/A)^2 = 1.86 t - 1.96 \quad (4.6.29)$$

and $\alpha \approx 0.879$ ($\text{Fe}_{\alpha}\text{O}$) at large t

5% stack oxygen:

$$(m_G/A)^2 = 0.196 t - 0.112 \quad (4.6.30)$$

$$(m_L/A)^2 = 2.13 t - 0.436 \quad (4.6.31)$$

and $\alpha \approx 0.957$ ($\text{Fe}_{\alpha}\text{O}$) at large t

The parabolic results based on mass gain data, $(m_G/A)^2$, suggest that there is a lower scaling rate at the 1% stack oxygen level. While this might be an expected result, it should be noted that the data in Fig. 4.6.35 from which this observation is deduced, exhibit considerable scatter. The mass loss data, Fig. 4.6.37, also indicate this trend but within the scatter in this data, we can only say that the mass loss at 5% stack oxygen and a large time ($t \approx 14.4$ ks) is significantly higher at a 90% confidence level (the 1% and 2% stack oxygen levels are not statistically different, but pooling these results and comparing them with the 5% stack oxygen data, we find a difference at a 90% confidence level). The intercepts in the mass loss relationships also decrease with increasing stack oxygen concentration – this is characteristic of a full parabolic form under these conditions. The stoichiometric coefficient, α , was also higher for the scaling conditions at a 5% stack oxygen level. While this is a very crude measure of the scale stoichiometry, the variation observed for this steel grade is in contrast to the relatively constant values observed for the DC scaling tests. This might suggest that there is some difference in the scale composition at the higher stack oxygen levels for the SB steel.

The effect of the oxygen enrichment levels with the stack oxygen concentration as a parameter is shown in Figs. 4.6.38 – 4.6.41. For oxidation times, $t \geq 1.8$ ks, these results are described by the parabolic relations:

0% oxygen enrichment:

$$(m_G/A)^2 = 0.134 t + 0.321 \quad (4.6.32)$$

$$(m_L/A)^2 = 1.73 t - 2.08 \quad (4.6.33)$$

and $\alpha \approx 0.912$ ($Fe_{\alpha}O$) at large t

25% oxygen enrichment:

$$(m_G/A)^2 = 0.192 t - 0.280 \quad (4.6.34)$$

$$(m_L/A)^2 = 2.09 t - 3.41 \quad (4.6.35)$$

and $\alpha \approx 0.939$ ($Fe_{\alpha}O$) at large t

50% oxygen enrichment:

$$(m_G/A)^2 = 0.184 t - 0.086 \quad (4.6.36)$$

$$(m_L/A)^2 = 1.97 t - 1.90 \quad (4.6.37)$$

and $\alpha \approx 0.920$ ($Fe_{\alpha}O$) at large t

75% oxygen enrichment:

$$(m_G/A)^2 = 0.207 t - 0.351 \quad (4.6.38)$$

$$(m_L/A)^2 = 2.21 t - 5.56 \quad (4.6.39)$$

and $\alpha \approx 0.905$ ($Fe_{\alpha}O$) at large t

90% oxygen enrichment:

$$(m_G/A)^2 = 0.234 t - 0.366 \quad (4.6.40)$$

$$(m_L/A)^2 = 1.98 t - 0.556 \quad (4.6.41)$$

and $\alpha \approx 0.874$ ($Fe_{\alpha}O$) at large t

These relations and the data in Figs. 4.6.37 – 4.6.41 indicate that there is a slight increase in the oxidation rate with oxygen enrichment, i.e. at $t = 14.4$ ks, $m_L/A \approx \sim 4.9$ kg/m² at 0% oxygen enrichment and ~ 5.2 kg/m² with oxygen enrichment (average of all conditions).

4.6.4. Replicate scaling rate tests with error analysis, SF and SJ grades

Replicate tests were performed by exposing two grades of steel samples, SF and SJ, to the combustion gas atmosphere with 2% O₂ stack gas and 0% oxygen enrichment at 1100°C. Four samples from each grade were tested at exposure times of 1.8, 3.6, 7.2 and 14.4 ks (corresponding to 0.5, 1, 2 and 4 h). The samples were analyzed for mass gain, m_G/A , and steel mass loss, m_L/A ,

according to the methodology outlined previously. These results served to provide estimates of the scaling rates for these steel grades at this one operating condition and an estimate of the experimental error based on the replicate results – in this section the interpretation of these results are presented in the context of these two objectives.

Experiments with DC and SB grades were also performed to estimate scaling rates at four exposure times in different furnace conditions - these results are described in subsequent sections. Additional samples for these grades were subjected to exposure times of 14.4 ks and these samples were saved for morphology analysis – the scaling rate in terms of the mass gain, m_G/A , were estimated for these samples. These results then provided an estimate of the experimental error at this exposure time (14.4 ks), for different furnace operating conditions, i.e. stack gas oxygen concentration and oxygen enrichment levels.

A summary of the pure error variance arising from these tests is presented later in this section.

Scaling results for steel grades SF and SJ

From these tests, we can observe some features of the oxidation mechanism based on results for the SF grade, Fig. 4.6.42, and the SJ grade, Fig. 4.6.43. These data indicate that at larger exposure times, $t > 1.8$ ks (0.5 h), the oxidation mechanism for these experimental conditions can be adequately described by a parabolic process,

SF grade:

$$\text{mass gain (Fig. 4.6.42, top right graph): } (m_G/A)^2 = 0.227 t - 0.142 \quad (4.6.42)$$

$$\text{mass loss (Fig. 4.6.42, bottom right graph): } (m_L/A)^2 = 2.04 t - 1.64 \quad (4.6.43)$$

Fig. 4.6.42. Oxidation test results for the SF steel grade samples with replication of the experiments (four tests for each exposure time). The solid lines on the right graphs are the parabolic oxidation rates, $(m_G/A)^2$ and $(m_L/A)^2$, Eqns. 4.6.42 and 4.6.43. The dashed lines on the left graphs are the parabolic relations expressed in terms of mass gain and mass loss, m_G/A and m_L/A .

At large exposure times ($t \approx 14.4$ ks), Eqns. 4.6.42 and 4.6.43 give $m_L/m_G \approx 2.98$ indicating a scale stoichiometry of $Fe_\alpha O$ with $\alpha \approx 0.853$.

SJ grade:

$$\text{mass gain (Fig. 4.6.23, top right graph): } (m_G/A)^2 = 0.180 t - 0.0956 \quad (4.6.44)$$

$$\text{mass loss (Fig. 4.6.23, bottom right graph): } (m_L/A)^2 = 1.62 t - 1.05 \quad (4.6.45)$$

At large exposure times ($t \approx 14.4$ ks), Eqns. 4.6.44 and 4.6.45 give $m_L/m_G \approx 2.99$ indicating a scale stoichiometry of $Fe_\alpha O$ with $\alpha \approx 0.855$. A complete set of mass gain estimates could not be obtained for all of the SJ samples because some of scale fell off during the cooling and handling operations in some of the tests (there are fewer points plotted on the mass gain graphs in Fig. 4.6.43).

The onset of the parabolic oxidation rate for the SF and SJ samples appeared to be delayed as indicated by the intercepts in Eqns. 4.6.42 -- 4.6.45. The present results and the experimental methods used in this program do not afford a reliable method to assess this initial oxidation period.

Replicate test results

From the detailed analysis of experimental errors associated with these tests, several points are worth noting in relation to the SF and SJ scaling data shown in Figs. 4.6.42 and 4.6.43. The replicate data indicate that the mean square pure error for the mass gain and mass loss data were relatively constant,

$$\text{mass gain, } m_G/A: \quad s_i^2 = 0.00289 \quad (\text{based on } n = 31 \text{ degrees of freedom})^*$$

$$\text{mass loss, } m_L/A: \quad s_i^2 = 0.00856 \quad (\text{based on } n = 24 \text{ degrees of freedom})$$

*(The mass gain data were augmented by some tests, yielding 14 degrees of freedom, with the DC and SB grades at 14.4 ks, the mass gain data for the SF and SJ grades provided 17 degrees of freedom. The mass loss results are based only on 24 degrees of freedom from the SF and SJ tests)

The experimental error for the data expressed in terms of $(m_G/A)^2$ and $(m_L/A)^2$ depended on the level of the independent variable, i.e. a linear increase with time and this behavior is suggested by the spread of the data in Figs. 4.6.42 and 4.6.43. The 95% confidence region for the linear slopes in Figs. 4.6.42 and 4.6.43 are summarized below:

Fig. 4.6.43. Oxidation test results for the SJ steel grade samples with replication of the experiments (four tests for each exposure time). The solid lines on the right graphs are the parabolic oxidation rates, $(m_G/A)^2$ and $(m_L/A)^2$, Eqns. 4.6.44 and 4.6.45. The dashed lines on the left graphs are the parabolic relations expressed in terms of mass gain and mass loss, m_G/A and m_L/A .

Fig. 4.6.44. A comparison of the oxidation rates for the SF and SJ steel grades showing typical scatter in the data for steel scaling tests in the CAGCT research furnace. The solid lines on the right graphs are the parabolic oxidation rates, $(m_G/A)^2$ and $(m_L/A)^2$, Eqns. 4.6.42 -- 4.6.45. The dashed lines on the left graphs are the parabolic relations expressed in terms of mass gain and mass loss, m_G/A and m_L/A .

mass gain squared, $(m_g/A)^2$:

SF grade: slope = 0.227 ± 0.013

SJ grade: slope = 0.180 ± 0.018

mass loss squared, $(m_l/A)^2$:

SF grade: slope = 2.04 ± 0.08

SJ grade: slope = 1.62 ± 0.08

The results shown in Figs. 4.6.42 and 4.6.43 are also plotted in Fig. 4.6.44 with both sets of data on similar graphs. From the above estimates of the experimental error and confidence regions, we can note that there is a significant difference between the oxidation rates of the two steel grades – this effect is not large and the spread in the data indicated in Fig. 4.6.42 provide a useful measure to compare data for other cases discussed later in this report.

The results of the replicate tests with DC and SB grades at 14.4 ks oxidation times included the extra samples exposed to different furnace operating conditions for morphology analysis. The mass gain for these samples was measured and compared with the samples tested primarily for oxidation rate analysis. The samples tested in this manner permitted a comparison of the mean square pure error at different furnace operating conditions such as stack oxygen concentrations and oxygen enrichment levels. The results of this analysis showed that the experimental error did not depend significantly on these operating conditions.

4.6.5. Analysis and discussion of steel scaling rate results

The scaling rate data for each steel grade were measured at exposure times ranging from 1.8 – 14.4 ks. The results of the steel mass loss (or mass gain) at the extreme times of 1.8 ks and 14.4 ks provide an estimate of the initial oxidation rate (1.8 ks tests) and the scaling rate for the full oxidation period typically experienced in a reheat furnace (14.4 ks). The results of the steel mass loss at 1.8 ks for each steel grade at the different levels of stack oxygen concentration and oxygen enrichment levels are shown in Table 4.6.5; the corresponding results for steel mass loss at 14.4 ks are shown in Table 4.6.6. The data for the DC and SB steel grades can be analyzed in terms of a two-way analysis of variance (ANOVA) to detect any effect of the stack oxygen or oxygen enrichment levels. A variation of the standard ANOVA procedure called Dunnett's test can be used for this purpose.

Steel scaling rates at 0.5 and 4.0 hours

The data for 1.8 ks exposure times indicate that the stack oxygen level has an effect on the initial oxidation rate for both the DC and SB grades. For the DC grade, the average steel mass loss at 1% stack oxygen was 1.23 kg/m^2 and this was significantly lower than the values observed at 2% and 5% stack oxygen (1.84 and 2.04 kg/m^2); there was no significant difference in the data at 2% and 5% stack oxygen for the DC samples. A similar trend was indicated by the data for the SB grade where the initial oxidation rate increased with the stack oxygen concentration, 0.92 , 1.17 and 1.82 kg/m^2 at 1%, 2% and 5% stack oxygen respectively. The oxygen enrichment level did not have a significant effect on the initial oxidation rate for either steel grade. The complete set of data permitting a comparison between

the four steel grades was obtained at 2% stack oxygen. The lowest initial scaling rate at these conditions was observed for the SB grade (average of 1.17 kg/m²), the SJ and SF were not significantly different (1.40 and 1.50 kg/m² respectively) and the highest scaling rate was observed for the DC grade (average of 1.84 kg/m²).

Abuluwefa et al. (1996) examined the initial scaling rate of low carbon steel samples in O₂/N₂ gas mixtures in the temperature range of 1000-1250°C. In the oxygen concentration range of 1-12%, their experimental data for the linear rate constant at 1100°C (temperature for the present work) can be described by a linear increase with oxygen concentration (see the data in Table II of Abuluwefa et al., 1996),

$$k_L'' \approx 1.26 \times 10^{-4} \times \{\%O_2\}$$

where the linear rate constant k_L'' is expressed in units of kg (oxygen uptake)/m²-s. In terms of steel mass loss with a stoichiometric coefficient, $\alpha \approx 0.90$, and a steel exposure time of 1.8 ks, we can convert this rate constant to $k_L'' \approx 0.712 \times \{\%O_2\}$, kg Fe loss/m²-s. Based on this model we would expect to observe steel mass losses of 0.712 kg/m², 1.42 kg/m² and 3.56 kg/m² at 1%, 2% and 5% stack oxygen concentrations, respectively. The present results at 1% and 2% stack oxygen are reasonably close to these values (particularly for the SB, SF and SJ grades), but the results at 5% stack oxygen concentrations are consistently lower. The lower oxidation rate arises at the higher stack oxygen concentrations because the parabolic mechanism appears to dominate the scaling process even at lower oxidation times.

The oxidation rates for the four steel grades at 2% stack oxygen concentrations can be ranked in the order:

$$SB (1.17 \text{ kg/m}^2) < SJ (1.40 \text{ kg/m}^2) < SF (1.50 \text{ kg/m}^2) < DC (1.84 \text{ kg/m}^2)$$

The pairwise difference between the SB, SJ and SF grades is not significantly different (95% confidence level), but the DC grade is significantly higher than the other three grades.

Table 4.6.5. Steel mass loss (kg/m^2) at 1.8 ks exposure times for different steel grades at different operating conditions. The data are arranged with results shown for three stack oxygen concentrations in columns and oxygen enrichment levels in rows. Data for the SJ and SF steel grades are based on replicate tests at 0% oxygen enrichment.

	O ₂ enrichment	1% stack O ₂	2% stack O ₂	5% stack O ₂	Averages (at each O ₂ enrichment level)
SJ	0%	-	1.45, 1.33, 1.37, 1.47	-	1.40
SF	0%	-	1.57, 1.56, 1.48, 1.38	-	1.50
DC	0%	1.54	1.89	1.87	1.77
	25%	1.20	1.79	2.02	1.67
	50%	0.72	1.93	2.06	1.57
	90%	1.45	1.75	2.19	1.80
	averages (at each stack O ₂ level)	1.23	1.84	2.04	1.70
SB	0%	1.00	1.21	1.94	1.38
	25%	0.94	1.19	1.73	1.29
	50%	0.79	1.41	1.78	1.33
	75%	-	0.77	-	0.77
	90%	0.94	1.28	1.81	1.34
	averages (at each stack O ₂ level)	0.92	1.17	1.82	1.29

The data for exposure times of 14.4 ks, Table 4.6.5, indicate that the stack oxygen level did not have a significant effect on the scaling rate for the DC steel grade. The parabolic oxidation rate at the higher oxidation times clearly wipes out the initial effect of a lower scaling rate at the lower stack oxygen levels for this grade of steel. For the SB grade, the scaling rate at 1% and 2% stack oxygen levels were not significantly different, but the rate observed at 5% was significantly higher. The effect of oxygen enrichment was not significant for either the DC or SB steel grades. The oxidation rates for the four steel grades at 2% stack oxygen concentrations can be ranked in the order:

$$\text{SJ (4.70 kg/m}^2\text{)} < \text{SB (4.94 kg/m}^2\text{)} < \text{SF (5.26 kg/m}^2\text{)} < \text{DC (6.28 kg/m}^2\text{)}$$

but the difference between the pairs of SJ and SB grades is not significantly different (95% confidence level), while the other pairs in this sequence are significantly different.

Table 4.6.6. Steel mass loss (kg/m²) at 14.4 ks exposure times for different steel grades at different operating conditions. The data are arranged with results shown for three stack oxygen concentrations in columns and oxygen enrichment levels in rows. Data for the SJ and SF steel grades are based on replicate tests at 0% oxygen enrichment.

	O ₂ enrichment	1% stack O ₂	2% stack O ₂	5% stack O ₂	Averages (at each O ₂ enrichment level)
SJ	0%	-	4.72, 4.56, 4.74, 4.77	-	4.70
SF	0%	-	5.24, 5.09, 5.32, 5.38	-	5.26
DC	0%	5.98	6.26	5.45	5.90
	25%	5.95	6.54	6.17	6.22
	50%	5.88	6.21	6.26	6.12
	90%	5.94	6.09	5.84	5.96
	averages (at each stack O ₂ level)	5.94	6.28	5.93	6.05
SB	0%	4.64	4.67	5.26	4.86
	25%	4.85	4.85	5.84	5.18
	50%	4.90	4.85	5.46	5.07
	75%	-	5.24	-	5.24
	90%	5.33	5.07	5.24	5.21
	averages (at each stack O ₂ level)	4.93	4.94	5.45	5.09

Comparison with Previous Scaling Rate Results

There are a number of previous studies of steel scaling available to provide a comparison with the present work. These include:

(1) Sachs and Tuck (1970):

These authors examined the scaling rates for low carbon steel samples in atmospheres of 100% oxygen, air and synthetic combustion product gases. Parabolic oxidation rates were observed for these results over a temperature range of 700 – 1200°C.

(2) Abuluwefa et al (1996, 1997b):

In one series of tests, parabolic oxidation rates were measured with low carbon steels over a temperature range of 1000 – 1200°C in atmospheres with 6% oxygen (balance N₂, Abuluwefa, 1996b). In the other series of tests, parabolic oxidation rates were measured with combustion product atmospheres with 1% O₂ (10% CO₂, 3% H₂O,

balance N₂) and 6% O₂ (6% CO₂, 3% H₂O, balance N₂) over a temperature range of 900-1150°C (Abuluwefa, 1997b).

(3) Ormerod et al. (1997):

In this work a series of experiments were performed to examine the effect of different operating variables on the parabolic scaling rate of low and medium carbon-content steel grades at 850°C and 1150°C. Different combustion product atmospheres were examined – in particular oxygen concentrations of ~2% and ~12% were studied.

The present results on steel scaling were obtained at a single target temperature of 1100°C with steel scaling rates measured from $t \approx 1800$ s. This precludes a fair comparison with the initial, linear oxidation rates observed by some of the above authors, but parabolic oxidation rate data are reported in all of these literature sources. In order to provide a fair comparison with these results, these parabolic rate constants can be presented in the form of an Arrhenius plot (rate constant as a function of the inverse of the absolute temperature) as shown in Fig. 4.6.45. Consistent trends are typically observed for each data set but there are some differences between some of these results. In particular, the results observed by Sachs and Tuck (1970) for oxidation in pure air fall significantly below other data observed for other operating conditions. The present results at 1100°C fall within a range consistent with the trends observed in these previous studies. Considering that these data are obtained for different steel grades (typically low-medium carbon content, mild steels), the overall trends observed in the present work show good agreement with the work of Sachs and Tuck (1970), Abuluwefa et al. (1996, 1997b) and Ormerod et al. (1997).

Fig. 4.6.45. Arrhenius plot of the parabolic rate constant oxidation of steel in various high temperature oxidation atmospheres.

5. Conclusion

5.1 Introduction

The objective of this project was to test a modified version of the CGRI low NO_x burner with O_2 -enriched combustion. This technology has potential to reduce energy costs and emissions of CO_2 and NO_x for the steel industry. The reduction in CO_2 emissions arises directly from the expected savings in fuel with O_2 -enrichment. The behaviour of this burner with O_2 -enrichment suitable for application in the steel industry was an unknown at the outset of this work. Lower flow rates of combustion product gases in the furnace can result in different heat transfer characteristic to the furnace refractory and load. The effect of O_2 -enriched combustion products on the scaling properties of industrial steel grades supplied by the participating steel companies was also unknown. The primary conclusions drawn from this work are outlined in the following sections.

5.2 Burner optimization

The CGRI low NO_x burner relies on injection of fuel and oxidant streams through a series of ports normally arranged on a circumferential ring on the primary axis of the burner. These ports are set at an angle to the burner axis, leading to entrainment of combustion product gases into the resulting jets and a confluence of the feed streams downstream from the burner source. In normal operation (Besik et al., 1995), and the mode employed in this work, seven fuel and oxidant jets were used. In order to incorporate the use of oxygen enrichment, the oxidant stream (a combination of air and/or oxygen in this case) was supplied through a series of concentric jets, the oxygen feeding through the centre jet and the air being supplied through the annular jet. This allowed for independent control for a full range of oxygen enrichment levels. The oxidant nozzles were set at a constant angle of 10° to the burner axis and two oxygen nozzle sizes were tested with a diameter of 5.31 mm (0.209 in.) finally chosen for “best” burner operation. Four fuel nozzle angles were tested and an angle of 20° relative to the burner axis appeared to give slightly better performance. The choice for these “best” conditions was based on assessment of NO_x emission levels and combustion stability. One should expect the optimization of the burner configuration to be dependent on the furnace geometry, burner orientation and to some extent, firing rate. Fuel usage and NO_x level optimization should be less dependent on these factors.

5.3 Fuel savings/ CO_2 reduction

The CGRI burner used in this work was designed to operate at a maximum firing rate of 400 kW (1.4 MBtu/h). In order to compare furnace performance under the different operating conditions proposed in this work, the furnace was operated at a constant target temperature of 1100°C , corresponding to firing rates of 325 -- 365 kW at 0% oxygen enrichment, depending on the stack oxygen concentration. The firing rate required to maintain this furnace temperature decreased linearly with the level of oxygen enrichment. At 100% oxygen enrichment firing rates in the range of 200 -- 220 kW were required to maintain furnace temperature. This represents potential savings of 40 – 45% in fuel usage and a corresponding reduction in CO_2 emissions. At constant levels of oxygen enrichment,

the firing rate was expected to increase with increased stack O_2 (excess oxidant). This behaviour was observed at low oxygen enrichment levels, $\psi_{O_2} < \sim 30\%$, but within the scatter of the present data, it was less evident at higher enrichment levels.

5.4 NO_x emissions

NO_x emissions up to ~ 12 mg NO_x /MJ were observed in this work. Oxygen enrichment had little effect on NO_x emission up to an enrichment level of $\sim 60\%$. At higher O_2 -enrichment, emission levels decreased but not to zero because of fuel nitrogen (1.6%) present in the natural gas supply. NO_x emission increased with increasing stack oxygen concentration (up to $\sim 6\%$ O_2 w.b. in the present work) at all oxygen enrichment levels.

A correlation was developed for NO_x emission ($[NO_x]$ in g/h) based on the percentage of oxygen in the stack gas on a volume wet-basis, $[O_2]$, and the percentage of oxygen enrichment employed, ψ_{O_2} :

$$[NO_x] = 4.15 [O_2]^{0.574} \left(1 - \frac{\psi_{O_2}}{100} \right)^{0.488} + 1.17$$

Effects of furnace temperature and firing rate could not be investigated due to limited firing capacity with one-burner operation.

5.5 Temperature distribution

The roof and blind sidewall refractory surface-temperatures in the furnace were monitored at 43 locations during all experimental runs. Data obtained during steel scaling experiments were most informative since these tests were performed over 4-hour periods at constant operating conditions yielding results more representative of steady state behaviour for the furnace. Temperature uniformity was expressed in terms of the standard deviation about the average value as well as the minimum and maximum variation about this average. Oxygen enrichment level had the most significant effect on this temperature variation. The standard deviation of the temperature variation was in the range, 19 -- 27 °C with no oxygen enrichment and 31--34 °C with 90% oxygen enrichment. This corresponded to a range between the minimum and maximum temperatures of about ~ 70 °C with no oxygen enrichment and ~ 115 °C with 90% oxygen enrichment.

With oxygen enrichment, there is substantial reduction in the gas flow rate through the furnace due to lower nitrogen content in the oxidant feed and a reduction in firing rate. The single burner operation demonstrated in this work tends to amplify the temperature variations with higher temperatures in the burner region of the furnace and lower temperatures near the exhaust plenum. Multi-burner operation would reduce the temperature variations noted above. As with conventional burner systems, some attention would have to be focussed on optimizing furnace temperature and heat transfer profiles for oxygen enriched combustion systems.

5.6 Effect of air infiltration

The effect of air infiltration on the refractory temperature distribution in the furnace was similar in magnitude to a reduction in firing rate equivalent to that required to heat the infiltration air to the furnace temperature. Air infiltration also had an effect on NO_x levels leading to emissions similar to those observed with no air infiltration but with similar stack oxygen concentrations. It was discovered that the premixed pilot burner accounts for about 1 – 2% of the energy input to the furnace, but contributes a disproportionate amount of the NO_x emissions on an energy input basis.

5.7 Scale formation

Steel scaling tests were performed as an integral part of this study. Oxygen enrichment leads to different combustion product environments with significantly larger proportions of CO₂ and H₂O along with the excess oxygen commonly present in combustion systems. The effect of employing oxygen enrichment, compared with more traditional combustion environments, was assessed in terms of

- Scale surface habit (ranked on a scale of 0 → 5 for a smooth → porous surface),
- Scale intactness (ranked on a scale of 0 → 6 for an intact → heavily detached scale),
- Scale adhesion (ranked on a scale of 0 → 4 for little effort for removal → difficult to remove), and
- Scaling rates.

Five steel grades (designated as DC, DS, SB, SF and SJ in this work), with the compositions and common names noted in Table 3.2, were supplied by the participating steel companies for this program. These rankings were based on visual observation and physical tests over a wide range of operating conditions. Photomicrographs with 0% and 90% oxygen enrichment conditions were also performed to provide supporting evidence for these tests.

The only factor affecting scale habit and intactness was the steel grade; the stack oxygen and oxygen enrichment levels did not significantly affect these properties. Based on physical tests, supported by photomicrography, the steel grades were ranked from a smooth, intact scale to a rough and cracked/separated scale in the order:

$$DS > DC > SF > SJ > SB$$

Smooth → Rough

The steel grade was also the most important factor affecting scale adhesion with the order of scale removal effort:

$$SF > SB > SJ > DC$$

More adherent → Less adherent

(the DS grade was not tested for this characteristic). This adhesion ranking corresponds most significantly with the composition of the steel samples – e.g. the SF, SB and SJ grades had somewhat more elevated levels of Ni, Cu, Cr and/or Mo. Photomicrographs also indicated that the more adherent

samples had a porous scale and/or rough steel/scale interface. Those scales that were easily removed had a clearly defined separation at the steel/scale interface.

The scale appeared to be less adherent with increasing stack oxygen concentrations and the effort for scale removal appeared to decrease slightly with increasing oxygen enrichment and increasing sample exposure times. These effects were much smaller than the difference observed between sample grades. The implication of these results are that oxygen enrichment has far less effect on the scale properties than that accounted for by differences due to the steel grade.

Scaling rate data, expressed in terms of the mass gain (oxygen uptake) and steel mass loss (Fe loss) were obtained for the DC and SB steel grades at 3 stack oxygen concentrations (1, 2 and 5%) and 4 oxygen enrichment levels (0, 25, 50 and 90%). The scaling rate for the SB grade (a more adherent and porous scale) was lower and the data exhibited more scatter than the DC samples. The oxidation rates followed a parabolic behaviour at 5% stack oxygen. At lower stack oxygen concentrations (1% and 2%), a lower initial oxidation rate was observed, followed by a parabolic behaviour after the first 0.5 h of exposure to the furnace atmosphere. Within the tests for each grade, the parabolic oxidation rate was most strongly affected by the stack oxygen concentration and the oxygen enrichment level only had a small effect on the parabolic oxidation rates.

Scaling rate data for the SF and SJ grades were obtained at 2% stack oxygen and 0% oxygen enrichment as part of a series of replicate tests for the scaling rates. The parabolic oxidation rate parameters for steel mass loss at these conditions could be ranked in the order:

$$SJ, SB < SF < DC$$

Low mass loss $\leftarrow$ High mass loss

The steel mass loss after 4 h could be ranked in the order:

$$SJ < SB < SF < DC$$

Low mass loss $\leftarrow$ High mass loss

The difference between the SJ, SB and SF scaling rates in each case was not large, but these three grades had significantly lower scaling rates than the DC grade. This ranking of the scaling rates also corresponds to the other scale properties i.e. (i) a rough and cracked/separated scale $\rightarrow$ smooth intact scale, and (ii) a decrease in the scale adhesion characteristics.

Notation

A	steel sample area, m ²
CAGCT	Centre for Advanced Gas Combustion Technology at Queen's University, Kingston, Canada
CGRI	Canadian Gas Research Institute
d.b.	dry basis, composition presented on a moisture-free basis
DAQ	Data acquisition
D _f	fuel nozzle opening diameter, m (in.)
D _a	air nozzle opening diameter, m (in.)
D _{O₂}	oxygen nozzle opening diameter, m (in.)
Δh _c	standard specific enthalpy of combustion of the fuel with product water in vapour form (lower heating value), J/kg
k _p	parabolic rate constant for steel scaling, m ² /ks or kg/m ² -ks
$\dot{m}_f$	mass flow of the fuel jet, kg/s
$\dot{m}_f(-\Delta h_c)$	standard rate of combustion heat release, W
$\dot{m}_a$	mass flow of the air jet, kg/s
$\dot{m}_{O_2}$	mass flow of the oxygen jet, kg/s
$\dot{m}_{x,y}$	mass flow of species x with stream y, e.g.: $\dot{m}_{O_2,a}$ mass flow of oxygen with the air jet, kg/s
m _G	steel sample mass gain, kg
m _L	steel sample mass loss, kg
MSDS	material safety data sheet
SCFH	standard cubic feet per hour
SOP	standard operating procedure
S1, S2, ...	CAGCT Research Furnace sample port 1, 2, ...
t	time, ks
$\langle T_r \rangle$	$\langle T_r \rangle = (1/S) \int_S T_r dS$, arithmetic average temperature of refractory surface S, K
$\langle T_r \rangle_{arith}$	$\langle T_r \rangle_{arith} = \langle T_r \rangle = (1/S) \int_S T_r dS$, arithmetic average temperature of refractory surface S, K
$\langle T_r \rangle_{rad}$	$\langle T_r \rangle_{rad} = (1/S) \int_S T_r^4 dS$, radiative average temperature of refractory surface S, K

w.b.	wet basis, composition reported on a wet or as sampled basis
w	steel scale thickness, mm
α	stoichiometric coefficient, Fe/O ratio, dimensionless
β_0	empirical constant for mass gain parabolic oxidation expression, kg^2/m^2
β_1	empirical constant for mass gain parabolic oxidation expression, $\text{kg}^2/\text{m}^2\text{-ks}$
β_f	angle between the fuel nozzle axis and the burner axis, degrees
β_a	angle between the air nozzle axis and the burner axis, degrees
β_{O_2}	angle between the oxygen nozzle axis and the burner axis, degrees
γ_0	empirical constant for mass loss parabolic oxidation expression, kg^2/m^2
γ_1	empirical constant for mass loss parabolic oxidation expression, $\text{kg}^2/\text{m}^2\text{-ks}$
ψ_{O_2}	$\equiv \left(\frac{\dot{m}_{\text{O}_2}}{\dot{m}_{\text{O}_2} + \dot{m}_{\text{O}_2,\text{a}}} \right) \times 100$, oxygen enrichment level, the percentage of total oxygen supplied to the furnace as pure oxygen, %
ρ	density, kg/m^3

Subscripts

1	stream 1, the fuel jet
2	stream 2, the air (annular) jet
3	stream 3, the oxygen (inner) jet

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