DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831, prices available from 015576 8401, ETS 626 8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

Price: Printed Copy \$00
Microfilm \$00

DOE/ID/12869--2

DE91 002363

FINAL REPORT ON PROCESS MODELING OF CUPOLA
FURNACES

Phase I
May 19, 1989 - July 19, 1990

July 1990

Work Performed Under Contract DE-FC07-89ID12869

Prepared for
U. S. Department of Energy
Idaho Operations Office, Idaho Falls, ID
Sponsored by the Office of the Assistant Secretary
for Conservation and Renewable Energy
Office of Industrial Technologies
Washington D.C.

Prepared by
The American Foundrymen's Society
505 State Street
Des Plaines, IL 60016

TABLE OF CONTENTS

Phase I Executive Summary

Phase I Final Report from Modern Equipment Company, Inc.

Phase I Final Report from Massachusetts Institute of Technology

Phase I Final Report from University of Michigan

PROJECT'S EXECUTIVE SUMMARY

This report describes the first phase of the AFS/DOE program on mathematical modeling of cupola behavior, covering the period May 19, 1989 to July 19, 1990. The objective of the program is to develop a comprehensive mathematical model of the cupola furnace for on-line and off-line process control and optimization. The work is being carried out by five organizations: Massachusetts Institute of Technology with responsibility for heat transfer and fluid flow modeling, and incorporation of the chemical models being developed by the University of Michigan team. Modern Equipment Company has the responsibility of compiling information on needed sensors for monitoring operation and providing materials data to be used for cupola input. General Motors, Central Foundry Division, is investigating the potential to augment the mathematical models with artificial intelligence programs. Lastly, General Motors Research Laboratories are charged with providing accurate cupola operational data to test the models being developed.

To date, a one-dimensional steady state model has been developed which considers heat transfer, fluid flow and important chemical processes: combustion, iron composition development, limestone calcination and iron oxidation. The model is based on established physico-chemical principles and data available in the literature. Model predictions compare favorably with data obtained in a production scale cupola, operating under carefully controlled, but realistic, conditions. At the present time, the chemical sub-models are being incorporated into the master program, and a complete working cupola model is expected by September, 1990.

Work on a two-dimensional steady state model is also progressing. At the present time, it includes only fluid flow behavior. However, it will soon be upgraded to include heat transfer and chemical processes. In its current state, the model can demonstrate such effects, as due to, charge inhomogeneity and tuyere angle. The greatest utility will arise once the new features are integrated into the model.

A key aspect of the Phase I program was to determine areas of weakness in the models and to suggest work to be carried out in Phase II that would improve model accuracy. Three principle areas have been identified: 1. Dissolution kinetics of coke-carbon in liquid iron. 2. Oxidation reactions affecting carbon, silicon and manganese levels in the iron. 3. Melting and subsequent droplet behavior of mixed charges having different melting points and size. In addition, there is a need for more experimental data on a wide range of conditions existing inside the cupola.

The goals for Phase II include: perfection on the one-dimensional steady state model, completion of the two-dimensional steady state model, development of a one-dimensional transient model, and rendering of these models user friendly. To accomplish these goals, research in the three areas noted above will be carried out. In addition, extensive efforts will be made to secure needed cupola data, both pertaining to conditions inside the cupola and to input-output type information. These data will be used to more extensively test model sub-routines, and to provide mechanistic information in some cases. To maximize the utility of the programs being developed, a Participants Advisory Group has been formed to formulate the foundry needs and desires with respect to operation of the computer programs, and to develop plans for augmenting the models in their foundries.

INTRODUCTION

This report summarizes the work carried out under Department of Energy Contract # DE-FC07-89ID12889. The work described covers Phase I of a program to develop process models of the cupola melting furnace used for the production of cast iron. The purpose of the modeling effort is to provide a needed means for optimizing cupola operation, with potential annual savings to the foundry industry of \$300 million dollars. The models would also provide the American foundry industry with needed tools to counter foreign competition.

Cast iron is produced by melting steel and cast iron scrap. Current annual U.S. production of liquid cast iron is about 18 million tons, 70% of which is produced in cupola melters. Cupolas produce iron at a lower cost and have better environmental controls than other melting processes, which accounts for its dominance. The cupola process has drawbacks. Thermal and melting rate efficiencies are poor (~30%) and considerable fractions (10-50%) of valuable alloy elements (C, Si and Mn) are oxidized in the melting process. Finally, fluctuations in the fraction of alloy oxidized results in unpredictable changes in iron composition.

The drawbacks of cupola operation can be viewed as real opportunities. The cupola's advantages have already made it the primary melting process. Elimination or reduction of its inefficiencies would make the process more effective while simultaneously reducing the cost of the product.

Conceptually, there are ways to deal with the cupola's shortcomings, however, improvements in one regard frequently reduces the quality in others. This is due to the complex and interactive nature of the cupola's chemical and heat transfer processes and the frequent operation of the furnace in a transient manner with respect to charge size and composition, blast rate and coke rate. Currently, this complexity makes it very difficult to approach optimum operation.

An effective mathematical process model of the cupola offers a solution to cupola operational problems. Such a model would define optimum operating conditions, offer corrective solutions to problem situations, warn of impending difficulties, carry out off-line cost/benefit studies, provide real time status of the operation, serve accounting functions on materials and efficiency, and ultimately automate cupola operation based on inputs from sensors.

The objective of the current AFS/DOE program is to develop the appropriate process models. These are a one-dimensional transient model to represent cupola operation in real time and a two-dimensional steady state model for off-line optimization studies. In order to adequately develop accurate representations of the chemical and physical processes inside the cupola a one-dimensional steady state model had to be developed first.

The modeling program is divided into two phases. The goals of Phase I (a one year project, just completed) were: (1) to develop a one-dimensional steady state model, covering all important chemical and physical processes. The model was to be based on best available data with an assessment of its

accuracy based on comparisons of model predictions and representative cupola operational data. This work would define the experimental and computational studies needed to perfect the model in Phase II (a two year project). (2) Work would be initiated on a two-dimensional model. This would provide the needed, more accurate descriptions of the combustion process and flow maldistribution resulting from charge material non-uniformity. (3) A study of the availability and cost of sensors to provide needed inputs to the process models and the identification of sensors that are needed but not currently available. (4) Examination of the potential use of artificial intelligence to facilitate the models through development of very simple models based on rules extracted from the full models.

This report summarizes the results of three teams' efforts: (1) Gas and heat flow modeling and integration of the model with chemical processes, by the Massachusetts Institute of Technology, (2) development of models of critical chemical processes by the University of Michigan, and (3) assessment of sensor availability and cost by Modern Equipment Corporation. The artificial intelligence work was postponed to Phase II because the models were not well enough advanced at the end of this phase to enable extraction of meaningful general rules of operation.

**PHASE I
FINAL REPORT
ON**

SENSOR DEVELOPMENT FOR THE CUPOLA FURNACE

BY:

MODERN EQUIPMENT COMPANY, INC.

Modern Equipment Company, Inc.

336 South Spring Street

Box 266

Port Washington, WI 53074

(414) 284-9431

TWX 910-260-3642

FAX 414-284-9433

5/29/90

AFS/DOE STUDY FOR ON-LINE MODELING ON A CUPOLA (#757A) - MODERN EQUIPMENT CO. INC. PHASE I SUMMARY REPORT

Sensors for the cupola were categorized in two groups:

1) Sensors normally found on present state-of-the-art cupola melting systems, and 2) available sensors not ordinarily found on present day melting systems. Information concerning sensor operating principles has been collected but summation is being held pending further Phase II Model development and better recognition of specific needs of the model.

It was recognized that all charge materials chemical and physical properties will be required as model inputs. Preliminary lists of these values assumed to be important to the proper functioning of the model were prepared for certain typical charge materials.

Dynamic methods of determining surface to mass characteristics of metallic charge materials suggested in the September 27, 1989, Ann Arbor meeting are still being studied without conclusion. At the moment, a practical approach to this needed model input is to research and compile information of this nature to allow for easy user input to the model. This approach will also require inclusion of proper instructional information, either within the model or in manuals, to allow users to tailor the information for their own site specific reasons. Methods for off line sampling and testing are another option for this need.

Considerable time was spent in transferring information on the Modern-Lillybeck program to, and liaising with, the University Research people.

Our most recent activity relates to a request to determine preliminary sensor costs for implementation of the model on a production cupola. This required a host of assumptions concerning what sensors might be existing for a given user as well as what uses might be desirable for a given operation. Our interim report on this subject is attached.

INTERIM REPORT

AFS DCE STUDY FOR ON-LINE MODELING ON A CUPOLA #757A) - IMPLEMENTATION COST STUDY

GENERAL

Implementation costs for using the subject model, over and above the purchase cost of the model, will vary widely and be dependent on a specific candidate's existing point of departure, plus the uses desired. Accordingly, this Study defines two cases: I, a sophisticated higher production cupola operation, and II, a lower production, less sophisticated operation.

In each case, it was necessary to assume existing equipment and/or existing sensor availability. It was also deemed necessary to define certain uses that would be desirable and practical for the two case conditions. Obviously, any expansion of the uses beyond those identified may impact on implementation costs.

The Study lists manual inputs as well as automatic sensor inputs to the model and, in certain instances, automatic options to manual inputs that may or may not be desirable due to high implementation costs.

It is assumed that some wrap-around or bridge programs will likely be required to achieve the use goals, but the costs of this software have not been estimated in this Study. This was considered beyond the scope of this Study as the comprehensiveness of the model in final form is not presently known, and bridge software costs will vary depending on the source (clients in-house generation from the model or from outside agencies).

Implementation costs were estimated based on equipment or systems presently having some proven track record and include engineering and mark-up costs anticipated for purchase from outside engineering and equipment suppliers. Clients' in-house engineering and direct purchase of sensors from manufacturers would normally reduce costs to some degree.

CASE I - SOPHISTICATED CANDIDATE

A) ASSUMPTIONS

Candidate is operating a hot blast water-cooled cupola with oxygen enrichment or injection, has a holding furnace, uses wet slag granulation, probably is a multi-shift operation, and likely in the 15 tph and up melt rate range.

Existing equipment will include:

- 1) Scales for metallics, coke, flux and alloy adjustment commodities (materials).
- 2) An air weight control device to determine blast air blower output.
- 3) A winddrum pressure recorder.
- 4) A spectrometer in the chemistry lab.
- 5) Hot blast temperature control.
- 6) Oxygen use control.
- 7) Spout metal and furnace metal temperature measuring devices.
- 8) A suitable computer with screen and printer.

A further assumption is that the model will be implemented primarily to instruct the operator, and consideration for "closing the loop", other than for the chemically correct charge use, is looked upon as a future happening.

B) DESIRABLE USES OF THE MODEL

- 1) Least Cost Operating Charge
This calculation would be available on demand and would take into account the desired melt rate, spout metal temperature and chemistry goals, holding furnace temperature and chemistry goals, cost and performance characteristics of all materials, materials availability, oxygen costs and atmospheric humidity.
- 2) Chemically Correct Charges
This would be a dynamic program of recognizing the weights of the metallic charge materials in a given charge and adjusting the batching of the coke and alloy additions for the specific charge to achieve the spout metal goals taking into account the chemistry and performance characteristics of all materials, atmospheric humidity, blast temperature, and oxygen use.

- 3) Materials Purchasing
This program, available on demand, would define desirable amounts and acceptable price information to guide materials purchases, taking into account anticipated production requirements, present inventory, and materials performance characteristics.
- 4) Maintenance Programs
Blast system leakage, refractory repair, and many other maintenance functions relating to hours of operation, tons produced, and other program readouts.
- 5) On Line Operator Instruction
Instructive read-outs to guide operator for achievement of the most efficient melting (quality and cost).
- 6) Other Uses
 - a) New materials performance evaluation.
 - b) Furnace design changes - use of tuyere inserts size and geometry changes etc.
 - c) Operational adjustments for energy cost variables, coke, power, natural gas, and oxygen.
 - d) Perpetual inventory control.

It should be noted that all of the above "uses" will likely require some wrap-around specialty software or bridge programs.

C) REQUIRED INPUTS TO THE MODEL AND/OR BRIDGE PROGRAMS

- 1) Manual Inputs
 - a) Materials chemical and physical (performance characteristics).
 - b) Materials costs.
 - c) Materials delivery lead time.
 - d) Production requirements (short term and long term).
 - e) Required melt chemistry and temperature goals.
 - f) Energy costs - power, natural gas, and oxygen.
 - g) Spout and furnace metal temperature -- could be automatic inputs, depending on type of existing measuring devices.
 - h) Slag chemistry.
 - i) Materials additions to cupola runner or holding furnace -- could be automatic with optional automatic weighings.
 - j) Cupola physical parameters.
 - k) Incoming materials quantity.

2) Automatic Inputs - Sensors

- a) Weights of cupola charge materials from existing scales.
- b) Blower blast rate from existing air weight control device.
- c) "Real" blast rate entering winddrum to account for heater, valve and other system leakage. Will require a special separate air weight control device suitable for use with high temperature air.
Estimated Cost\$ 6,500
- d) Blast air temperature at air heater from existing heater controls.
- e) "Real" blast temperatures in winddrum to account for system heat losses.
Estimated Cost\$ 800
- f) Oxygen flow rate from existing control.
- g) Winddrum pressure from existing instrument.
- h) Side wall and tuyere heat losses to water-cooling from flow meter and in and out temperature measuring devices.
Estimated Cost\$13,500
- i) Atmospheric humidity.
Estimated Cost\$ 1,000
- j) Spout metal chemistry from spectrometer.
- k) Natural gas consumption for externally fired hot blast heater and/or for top gas carbon monoxide combustion pilot burners from gas metering devices.
Estimated Cost\$ 4,400
- l) Top gas temperature from properly located thermocouples protected from charging action.
Estimated Cost\$ 2,300
- m) Holding furnace power input from existing controls.
- * Miscellaneous costs for hardware to automate inputs from existing sensors and to interface with batching controls for chemically correct charge use.
Estimated Cost\$25,000

* Cost will vary widely depending on existing conditions.

3) Optional Sensors

It is assumed that the model will be able to accurately calculate the following:

- a) Metal melt rate from scale inputs and materials characteristics.
- b) Top gas CO and CO₂ levels from carbon and oxygen balances.
- c) Slag production rate from materials characteristics.

While generally representing more major investment requirements, it is possible to use sensors to automate feed-back inputs to the model for the above and certain other inputs previously mentioned as being done manually.

- * a-1) Metal melt rate using load cells under the holding furnace and weighing ladles.
Estimated Cost\$60,000
- a-2) Metal melt rate using refractory weir and laser metal level sensing.
Estimated Cost\$55,000
- b) Instrumentation and sampling systems to measure a representative sample of cupola top gas for CO and CO₂ content.
Estimated Cost\$75,000
- c) Conversion to dry slag handling fitted with conveyors and scales to weigh slag.
Estimated Cost\$125,000
- * d) Scale equipment and material handling automation for input of spout and holding furnace materials addition.
Estimated Cost\$30,000
- e) Spout metal temperature feed-back using automated dipping of emersion thermocouples on programmed basis to minimize probe costs.
Estimated Cost\$ 6,000

* Costs will vary widely depending on existing conditions.

CASE II - LOW TONNAGE CANDIDATE

A) ASSUMPTIONS

Candidate is operating a cold blast cupola with oxygen enrichment melts for 3 to 6 hours per day with melt rate in the 5 to 12 tph range.

Existing equipment will include:

- 1) Scale for weighing all materials but no automatic batching.
- 2) An air weight control device to determine blast air blown output.
- 3) An oxygen control.
- 4) A winddrum pressure indicator.
- 5) A thermal analysis system with CE, C, and Si readout.
- 6) Device for occasional metal temperature measurement.
- 7) A suitable computer, screen and printer.

B) DESIRABLE USES OF THE MODEL

- 1) Least Cost Operating Charge
This calculation would be available on demand and would take into account the desired melt rate, spout metal temperature and chemistry goals, cost and performance characteristics of all materials, oxygen costs and seasonal humidity conditions.
- 2) Materials Purchasing
This program, available on demand, would define desirable amounts and acceptable price information to guide materials purchases, taking into account anticipated production requirements, present inventory, and materials performance characteristics.
- 3) On Line Operator Instruction
Instructive read-outs to guide operator or achievement of the most efficient melting (quality and cost).
- 4) New Materials Evaluation

C) REQUIRED INPUTS TO THE MODEL AND/OR BRIDGE PROGRAMS

1) Manual Inputs

- a) Materials chemical and physical (performance characteristics.
- b) Materials costs and lead time.
- c) Production requirement - short term and long term.
- d) Required melt chemistry and temperature goals.
- e) Oxygen costs.
- f) Cupola physical parameters.
- g) Seasonal (daily) humidity conditions.
- * h) Measured spout metal temperature.
- * i) Measured spout metal chemistry.

* Assuming use of a personal palm top computer for transmitting information to the model.

Estimated Cost\$ 1,000

2) Automatic Inputs - Sensors

- a) Blast air from air weight control.
- b) Oxygen use Estimated Cost\$ 2,500
- c) Materials weights - load cell in steel
yard rod of existing scale(s).
Estimated Cost\$ 2,800
- d) PLC or industrial computer to accomplish
the above. Estimated Cost\$15,000

**PHASE I
FINAL REPORT
ON**

**MATHEMATICAL MODELING OF GAS AND HEAT FLOW
IN CUPOLA FURNACES**

BY:

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

EXECUTIVE SUMMARY

The objective of this research program is to develop a comprehensive mathematical model of the cupola furnaces for on-line process control and optimization. This report describes the progress on the mathematical modeling of gas flow and heat transfer in cupolas that was made during the period of July 1, 1989 to July 1, 1990. The whole research program is a joint effort with the University of Michigan and the American foundry community, with the MIT group focusing on the heat flow, fluid flow and mass transfer aspects of the cupola operations. The project is supported by the Department of Energy under contract number: DE-FC07-89ID12869.

The research program was initiated in July, 1989 and the objectives of Phase I (i.e., for July 1989 to July 1990) have been accomplished. In addition, a multi-solid stream model has been developed to enhance our understanding of heat transfer phenomena in cupolas. During the course of our research work, good, continuing contact has been established and is being maintained between our research effort and the foundry community to ensure that the model is realistic and on the right track.

More specifically, a working one dimensional model describing the fluid flow and heat and mass transfer has been established. The model's predictions agree well with operational experience. The model has been integrated with the chemical model of iron oxidation in cupolas that was developed by the University of Michigan team and is being integrated with other chemical models.

A multi-solid stream model that treats charge materials as separate entities has been developed. This better represents the fact that the solid temperatures are likely to be different for different solid materials and the chemical processes undergone by each solid stream are also different because these materials differ greatly in physical and chemical properties. This specific approach was not considered at the outset; but its development was a result of extensive discussions with the foundry community on a better representation of melting processes.

Work on the two-dimensional model has been initiated and good progress is continuing. The model development has progressed to the point where the model now enables the prediction of gas flow as a function of operating conditions such as cupola bed structure, tuyere angles, etc. The heat transfer phenomena and chemical reactions are now being incorporated into the model.

The next phase of the research effort is to extensively test our one dimensional model against experimental measurements; to extend the model to represent transient behavior; to complete developing and to test the two dimensional mathematical representation of the cupola

operations; and to carry out an experimental study of the melting process in a small scale model system so as to refine the description of the mathematical models. The above models, having been tested against experimental measurements, will be made user-friendly and ultimately delivered to the foundry community at the end of this program for implementation in an on-line process control.

1. INTRODUCTION

The principal task of the research team at the Massachusetts Institute of Technology (MIT) is the development of a comprehensive mathematical representation of cupola operations. The main emphasis is on the heat flow, mass transfer and fluid flow phenomena and on the integration of this transport model with the thermochemical model which is being developed at the University of Michigan (UM). This work is closely tied to the extensive practical data base provided by General Motors Research Laboratories (GMRL) and Modern Equipment Corporation (Modern). Ultimately, a comprehensive model will be developed and will be used for process optimization, process control and new process development by the U.S. foundry industry. The main motivation for this work is derived from the fact that there is a considerable potential for improving the thermal efficiency of cupolas, through a better understanding of the interrelationships between the key process parameters and the quantification of these through modeling. More specifically, there is a potential saving of 625,000 tons of metallurgical coke, 44,000 tons of oxygen, and 60,000 tons of silicon annually. Together with other potential savings, these could amount to a dollar value of about \$300 million per annum.

This program of research, projected for a three year period, is to be carried out in two phases. The first phase, covering the period of July of 1989 to July of 1990, is in essence a feasibility study, while the second phase, of two years duration, will involve the realization and testing of the model and its delivery to the industrial community.

During Phase 1, the principle tasks for the MIT group may be summarized as follows: *

- (i) Preparation of a comprehensive survey of both the cupola and blast furnace modeling literature.
- (ii) The development of a conceptual picture of the cupola process.
- (iii) The quantification of this picture in terms of a simple one dimensional model that includes the thermochemical relationships (which are being developed by the UM team) and the testing of this model against existing information in the literature.
- (iv) Extensive discussions with both the UM team and the foundry community to ensure that the model development is realistic and is fully interfaced with the corresponding thermochemical modeling work.

* These represent a more concise statement of tasks and subtasks 1, 2, 6, 7, 9, 11, 12 and 13 listed in the original proposal.

- (v) Initiation of a two dimensional model development.
- (vi) Development of the proposal for Phase 2.

The above tasks have been accomplished. In addition, a multi-solid stream model has been developed to better represent the heat transfer between the rising hot gas and individual solid streams. More specifically, a working one dimensional model describing the fluid flow and heat and mass transfer has been established. The model has been integrated with the chemical model of iron oxidation developed by the UM team; it is ready to be integrated with other chemical models under development at the UM. The predictions of the model agree reasonably well with cupola experience.

One distinctive feature in cupola operations is that the charged materials melt at different temperatures and undergo different chemical processes because the materials differ in physical and chemical properties. Towards the end of better representing this complex melting phenomena and of enhancing our understanding of the chemical processes involved in different solid materials, a multi-solid stream mode has been developed. This model enables keeping track of the temperature rise in each of the solid streams and allows the study of the chemical processes undergone by each stream. The development of this model was not one of the original proposed tasks and its development results from the needs of the foundry community.

A good start has been made on the development of two-dimensional mathematical model and the work is progressing rapidly. The modeling work has reached the point where, with the model, one can predict gas flow as a function of operating conditions such as cupola bed structure, tuyere angles with respect to the vertical wall, etc. Other considerations such as heat transfer, chemical reactions and melting processes are now being incorporated into the two-dimensional model.

The important aspects that need to be studied for the second phase are also identified and are described as major tasks in the proposal for the second phase, which has been submitted earlier.

During the course of our research work, close contact with the U.S. foundry industry has been maintained to ensure that our model development is in the best interest of the foundry community.

This report describes in detail the work on the development of the mathematical models. These models represent the fluid flow, heat flow and mass transfer in cupolas that was completed at MIT during the last year. The material to be presented is organized as follows:

- Critical review of the literature on blast furnaces and cupolas

- Development of one dimensional mathematical model
- Description of one dimensional multi-solid stream model
- Initiation of two-dimensional mathematical model

2. CRITICAL REVIEW OF LITERATURE

A comprehensive literature review has been carried out to investigate previous modeling work on cupolas and blast furnaces. While extensive literature exists on the blast furnace modeling, only limited sources are available on the cupola. In what follows, our review will focus on the published work concerning the dynamic aspects (e.g., fluid flow, heat and mass transfer) of both cupolas and blast furnaces because they are of direct relevance to our modeling effort.

The dynamics of the iron blast furnace has received considerable attention over the past few decades. Elliott [1] made early contributions, for example, on blast furnace raceways and on temperature distributions in beds with counter-current flow. That temperature was found to be very sensitive to the ratio of gas flow to the solid flow--a first indication of the significance of gas maldistribution. Many investigations were carried out subsequently on the flow of gases in packed beds, most notably by Szekely and coworkers [2-10]. Their work may be summarized by stating that the way various bed materials pack together can have a considerable influence on the flow paths of gas through a packed bed. Of particular importance are variations in packing size and void fraction. Both can lead to non-uniformity of flow and subsequently of temperature and reaction rates. Furthermore, sharp changes in particle size, such as produced by the layering of materials fed to the bed, result in interfaces of low permeability that impeded gas flow.

These publications provide a basic methodology for tackling flow problems in packed bed systems, however, in case of blast furnaces and cupolas, further complications will arise because of the melting processes and more complex packing structures. This came to light for the case of blast furnaces. With the careful dissection of quenched furnaces, Sasaki et al. [11] illustrated the formation of zones of low gas permeability due to the softening of ore layers as the burden moves down through the furnace. The softening of the ore layers has been well described by Yamoka et al. [12]. These investigators found that both sinter and pellets undergo a sharp drop in permeability starting at about 1000°C. Because the 1000°C isotherm within the furnace is a surface of approximately conical shape with its rounded apex at the center of the burden five-ten meters above the base of the cone, softening starts at the center of the burden and extends outwards. At temperatures above 1400°C the reduction of iron oxides proceeds rapidly. The iron and slag produced are molten and percolate down through the remaining coke. Below this isotherm the only solid

present is coke. The 1000°C and 1400°C isotherms define the limits of this zone, which has become known as the cohesive zone. Here softening ore tends to force gas to flow horizontally through coke slits.

These experimental observations have stimulated many significant studies of flow, temperature distribution and reaction within the blast furnace; they also provided a vast data base for comparison. Because of the near impossibility of performing meaningful laboratory studies, most of these investigations have relied on mathematical models [13-26]. Strictly speaking, a mathematical model describing blast furnace operations should contain the following equations:

- (i) Equations describing flow of gas, solids and liquids
- (ii) Equations describing the conservation of heat in each phase
- (iii) Equations describing chemical reaction rates in terms of local temperature, gas composition, etc.
- (iv) Auxiliary relationships such as those between gas density and composition and temperature, dependence of permeability on extent of reaction/temperature, boundary conditions, etc.

In fact, no model as rigorous as this has appeared in the literature. Fortunately, however, the main features of blast furnace behavior can be represented by models which entail simplifying assumptions. For example, iron oxide reduction reactions usually go to completion in the furnace with the results that the real blast furnace (and any satisfactory mathematical model) is insensitive to changes in reaction rate. This implies that gross simplifications can be made in setting up the equations listed above.

Koump et al. [13] were probably among the first to mathematically model the process dynamics of blast furnaces. Their model was developed for the shaft region of a blast furnace under steady state operation. Such process variables as gas and solid temperature distributions as well as gas concentration distributions were considered.

More sophisticated one dimensional models of blast furnaces were developed subsequently by Muchi and coworkers [15-20]. Their models were based on the numerical solution of a set of simultaneous differential equations that describe the conservation of energy, mass and momentum. With the models, they studied the dynamics of blast furnaces for the region from the top to the tuyere level. Process variables such as gas concentration and temperature distribution, etc. were used. The predictions of the models compared reasonably well with the experimental results.

Hatano and Kurita [23] developed a mathematical model to include also the radial variation of process variables. Most of the equations (i) through (iv) are present in their model. The solid and liquid motions are treated in a simplified (but creditable) fashion. The model does not contain a rigorous treatment of the fact that the burden is made up of alternate layers of ore and coke of different permeabilities. Instead the burden is approximated as a continuum of anisotropic permeability.

Yagi and co-workers [24] conducted a study of heat and gas flow in blast furnaces. Using the finite element method, they were able to represent rigorously the complex packed structure in a real blast furnace, e.g., the alternating coke and ore layers. The details regarding mass transfer phenomena such as chemical reactions and species distribution, however, were not included in their model.

Shimoda and co-workers [25] recently described softening tests on three kinds of sinter and showed that increase in gas flow resistance correlated well with the degree of shrinkage (compaction) of the sinter in their test. These authors went on to examine the effect of gas permeability in the cohesive zone on gas flow in the burden using a mathematical model.

Recently, Burke and Burgess [26] presented a two dimensional (axisymmetric) mathematical model of blast furnaces. Their model consists of fourteen partial differential equations that describe the phenomena of gas flow, liquid flow, solids flow, heat and mass transfer and major chemical reactions in the blast furnaces. The results compare reasonably well with the experimental results available. One of the interesting features in their model development is that those highly nonlinear equations were solved using a commercially available package, PHEONICS; thereby greatly speeding up the programming effort.

Flow of the solids within the furnace is important in the correct formulation of mathematical models. A recent interesting investigation of this phenomenon is that of Takahashi et al [27]. These investigators studied the flow of solids (sand and glass beads) in a cold physical model of blast furnace. The model is a vertical slice of the furnace. The model included injection of air and continuous removal of solids from the bottom. Three regions of solids motion were evident: fast moving, slowing moving and stagnant.

The dynamics of the other regions of the blast furnace have also been studied by both mathematical and physical models. Interesting work has been performed by Yamaguchi, et al [28] and Burgess [29] on the blast furnace raceway. Flooding of the bosh region of the furnace

has also been studied, notably by Szekely and Mendrikowski [30], Kuwano et al [31], Standish and Drinkwater [32].

While there exists voluminous literature on blast furnaces, only very limited work is available on the modeling of the heat transfer and fluid flow phenomena in the cupola furnaces. Furthermore, almost all the published models addressed the issues of thermochemical reactions and species distributions based on the chemical equilibrium principles. These thermochemical models [33-37], will not be discussed here as they are irrelevant to the modeling of gas flow and heat transfer. Exceptions are those in references [38-40], however.

Breen[38] was probably among the first to study the heat transfer phenomena in cupolas. Assuming constant physical properties, he analytically calculated the averaged temperature distributions of gas, coke and scrap at various levels. He also conducted experiments to measure these quantities at 51mm from the inside wall in an experiment cupola of 457 mm diameter. His work showed a good agreement between the calculated and experimental results. Petroveski [39] experimentally measured the composition and temperature distribution of gases in the combustion zone in a pilot plant cupola of 610mm in diameter. Draper and Nymekye [40] recently conducted theoretical and experimental work to determine the temperatures of gas and solids and the gas composition in the combustion zone in a cupola of 610 mm diameter. While their work can be of value to understand some of the basics of the cupola operations, it is quite primitive and far from useful for the process control since many important process aspects such as flow maldistribution, phase change, heat transfer between the molten metal and slag drops and hot gas, etc. are not addressed at all.

The main points that can be drawn from the above discussion on the literature of both cupolas and blast furnaces may be summarized as follows:

- While useful work has been done on the thermochemical aspects of cupola operations (33-37), the heat flow, fluid flow and mass transfer aspects of the problem have received very little attention up to the present. References (38-40) represent an exception to this rule, but none of this work is suitable for performing process optimization and control studies.
- In contrast to the cupola operations, blast furnaces have been very extensively modeled and this literature is quite voluminous.
- When this project was initiated, it was hoped that the way heat flow, fluid flow and mass transfer problems have been treated in the blast furnace would be of direct, immediate help in the present study. Unfortunately, this turned out to be only partially true. While there are

many similarities between ironmaking in the blast furnace and scrap melting in the cupola, in that both obtain molten iron (and slag) as the liquid products, rely on coke as the fuel and involve the counter-current interactions between an ascending hot gas stream, consisting principally of N_2 , CO and CO_2 , with solids, there are also major differences. The most important of these is that the reduction of the iron oxides in the stack region is of the principal interest in ironmaking and this aspect of the problem has received by far the most attention, together with factors that influence the permeability of the burden. The solution loss, or Boudouard reaction is of importance, but the CO thus generated is used for the reduction of the iron oxides. The problems involving the melting of the charge and the smelting reduction have been very much less studied. In contrast, in cupola practice the actual melting process, the interaction of the molten metal with the coke and the superheating of the metal are issues of paramount importance. In this regard the blast furnace literature is not of great help. Indeed, study of the prior blast furnace literature provides an excellent basis for representing heat flow, fluid flow and mass transfer phenomena in the stack region (i.e., in the region where the solids are in contact with a gas); however, the modeling of the actual melting process and the interaction of the molten phases with the gas and the solid streams will require additional fundamental input. These issues will be examined in the second phase of this program, by both the MIT team (to study the melting process experimentally) and the UM team (to study the iron-coke interactions and alloy oxidation experimentally).

3. DEVELOPMENT OF ONE-D MODEL

The first step in the establishment of a mathematical model is to develop a conceptual picture of the cupola process, compatible with the statement of the governing equations. Such a conceptual picture has been developed as a result of extensive discussions with Dr. S. Katz, Mr. C. Landefeld, both of GMRL, Mr. N. Lillybeck of Deere & Company (Deere) and Mr. R. Schueller of Modern; and is sketched in Fig. 1. This conceptual picture represents the basis of the model. Moving from the top down, heat exchange between the gas and solids takes place in the preheating zone, together with the calcination of limestone and some of the Boudouard reaction. In the following region the reaction between the carbon dioxide and the coke takes place also, but this is the area where the scrap iron and the scrap steel melt. In the subsequent region the molten metal (and slag) streams interact with the coke and also receive their superheating from the gas and from the coke. In the zone immediately below, combustion of the coke takes place. The actual combustion profiles are definitely two dimensional. In the following zone, molten streams lose heat through the cupola wall and molten metal picks up carbon while

percolating through the coke bed. Finally, in the slag-metal reaction zone the final adjustment of the metal composition will take place.

It is to be re-emphasized that the principal issues that the modeling effort will have to address are the coke consumption, the melting rate, the final metal composition and temperature and the relationship between these quantities and the operating parameters.

On the basis of the physical picture shown in Fig. 1. We developed a simple one dimensional model, representing the heat exchange and composition changes within the system. This one dimensional model consists of a set of nonlinear ordinary differential equations, which were derived from the first principles governing the conservation of momentum, materials and energy, over a horizontal differential slice of a cupola furnace, as shown in Fig. 2. For the sake of simplicity, these governing mathematical equations are listed in Appendix I, along with other auxiliary equations for the overall heat and mass balances.

The independent variable in the one dimensional model was the vertical distance along the furnace, while a total of 13 dependent variables were utilized at the present. More specifically:

- In the solid stream, the temperature, the coke content, the iron content and the limestone.
- In the gas stream, the temperature, carbon monoxide, carbon dioxide, hydrogen, nitrogen and water vapor.
- In the liquid stream, the temperature, iron and carbon content. (The iron and carbon content shall be calculated from the chemical models under development at the UM.)
- Other variables describing the behavior of silicon, manganese and sulfur can be readily added.

In developing the one dimensional mathematical representation, the following assumptions have been made:

- Heat and mass transfer in the axial direction is convectively predominant.
- The thermal conductivity within individual particles in the bed is high and particles have a uniform internal temperature.
- An averaged particle size is evaluated following the procedure described in [41] and is used for heat transfer calculations while the particle size of individual solids is used for the chemical reaction rate calculations.

- Heat generated by the chemical reactions is partitioned between the gas and solid phases.
- Melting is included through use of the equivalent heat capacity method [42].
- Slag and molten metal are assumed well mixed after melting and thus are at the same temperature. The liquid drops are assumed to be 5mm in diameter for the calculation of heat transfer between the gas and liquid.

The resultant simultaneous differential equations were integrated numerically using the Runge-Kutta integrator. Since this is a two point boundary value problem [43], this integration had to be carried out in an iterative fashion. The methodology adopted in developing the model is a self-consistent approach. The overall heat and mass balance is first made for the whole furnace starting from the tap hole up to the top. (The equations describing the overall heat and mass balance are provided in Appendix I.) This calculation gives the first guess of the boundary conditions needed for solving the differential equations, and it provides the first estimate of the bounds for the physical quantities such as temperature and gas composition from the numerical blow-up (a numerical instability common to a two point boundary value problem). Having been so pre-conditioned, the governing differential equations are then integrated from the top to the bottom and from the bottom back up to the top until the bounds set previously are satisfied.

The core part of the program is the numerical integration. To be sure that this part is coded correctly, the calculations by the program are compared with those obtained analytically for a simple counter-current system in which only the heat exchange between the gas and solids takes place without chemical reactions and melting processes. (The system is the only ideal case for which the analytical solution is possible.) The results are shown in Fig. 3, where it can be seen that the match between the numerical results and the analytical ones is remarkably good, indicating this central part of the program is correctly written.

Figs. 4 and 5 show a selection of the computed temperature and gas concentration profiles for a set of operating conditions for a General Motors (GM) cupola. The theoretical predictions were found to be in good agreement with measurements which were made in a cupola of production size and provided by Dr. Katz of GMRL, as seen in Table 1, indicating that the computational approach is on fundamentally correct.

That the numerical model is realistic is further evidenced by the comparison of the model with the experimental results, as can be seen in Fig. 6. The numerical results were found to in reasonably good agreement with the measured ones for the solid temperature distribution. The experimental data were obtained in a cupola of production size at GM, operated in a conventional mannar. The cupola, 1.5 meter in diameter and refractory-lined, uses oxygen enriched hot blast. The measurement of solid temperatures was made using a thermocouple encased in a steel cube having 1.25 cm walls.

Computed temperature profiles for other sets of operating conditions are provided in Figs 7 and 8; and their corresponding gas composition distributions along the furnace are shown in Figs. 9 and 10. The results show that gas concentrations undergo rapid changes a short distance above the tuyere level. Afterward the concentrations remain unchanged, suggesting that this is the region where only heat transfer between the gas and solids is significant. The results of the gas compositions are consistent with the temperature profiles (see Figs. 9 and 10). A sharp change in temperature occurs correspondingly in the region right above the tuyere level within which the chemical reactions proceed rapidly and hence the gas composition changes drastically.

An important aspect of the computational work is that one may make predictions regarding the effect of changing the process parameters. This predictive ability is sketched in Figs. 11 and 12, showing the gas composition profiles corresponding to changes in the coke size. It is seen that the results do reflect the correct trends, in that an increase in the coke size would diminish the extent of the Boudouard reaction, while a decrease in the coke size would increase the carbon monoxide in the exit gas stream. The corresponding temperature distributions are shown in Figs. 13 and 14. Fig. 15 also shows the gradual superheating of the liquid stream (metal and slag are assumed at the same temperature in the present model) for the cases in Figs. 13 and 14, respectively. It can be seen that the superheating of the liquid stream is higher when the coke size is increased by 50% than that when the coke size is reduced by 50%. These predictions are as expected because the reduction in the extent of the endothermic Boudouard reaction results in high superheating and vice versa. They are also fully consistent with cupola practice.

4. DEVELOPMENT OF ONE-D MULTIPLE SOLID STREAM MODEL

One of the distinctive features in the cupola operations is that the solid materials making up the charge differ in physical properties such as thermal conductivity, heat capacity, particle sizes and also melting points (for example, cast iron melts at about 1150 °C and steel melts at around 1500°C). With mixtures of these materials

charged into a cupola, different materials may experience different thermal histories when traveling downward. For instance, the temperature changes in coke and steel will not be the same. This process is further complicated by the fact that the material of lower melting point starts melting earlier, forming liquid stream while the material of higher melting point remains solid. Moreover, the compositions of various charge materials are considerably different; these in combination with the temperature difference in solid streams will have a strong effect on the chemical reactions involved. To better represent the above heat and mass transfer and melting phenomena for each type of solid material, a mathematical model, which entails evaluating the temperature distribution in each solid stream, is established.

The development of this model serves a dual purpose. On the one hand, it quantifies the thermal history of each solid stream for given operating conditions, thereby enabling a more accurate prediction of the subsequent melting of separate metal streams and hence their final compositions. On the other hand, it serves as a guideline to identify the critical areas of relevance to the melting process where experimental work is needed to further our understanding.

Although the scientific principles regarding the energy conservation in this system are similar to those in other counter-current systems (see Appendix II), the model development entails different considerations and input of different parameters. Partly because of the unavailability of such data as the mutual heat transfer coefficients between the solid streams, no publications were found on the subject of treating the solids as separate streams in a counter-current system.

The critical and yet fundamental issue that has to be addressed, before any other complications, such as melting, liquid flow, chemical reactions, etc., are added, is how the energy transfer takes place between each solid stream and hot gas as well as that between the individual solid streams. Our model development at this stage is directed at meeting this end.

Let's first consider a counter-current system where different types of solid materials (e.g., coke, limestone, cast iron and steel for the case of cupolas), as in Fig. 1, but with each being treated as a single stream depending on its intrinsic thermal properties, flow into the system from one end and hot gas into from the other. The heat transfer occurring in the system may be described by a set of ordinary differential equations that are derived from the conservation principles. These equations are different from the ones in the previous section in that they contain heat transfer coefficients characterizing the energy exchange between the solid species. These

equations are then solved numerically using the eigenvalue techniques based on the matrix theory. For brevity here, the governing equations and the solution procedures are given in Appendix II.

One of the gross simplifications one would make to start with, at the first glance of the problem, would be the neglecting of heat transfer between the solid streams in comparison with that between them and gas phase. For not only does this make the system numerically stable (much of the stability here has to do with the mathematical theory of eigenvalues encountered in our systems, elaboration of which is beyond the scope of this report) but also the coefficients characterizing the energy exchange between the solid and gas are well documented. Physically, this assumption corresponds to a situation where only a few particles, having no contact between each other, are immersed in a stream of hot gas.

Shown in Fig 16 are the results computed by neglecting the heat transfer between solid streams. The input conditions correspond to one of operating conditions for a GM cupola, except that the incoming hot gas temperature and solid temperature are assumed at 1200K and 298K, respectively. As revealed in Fig. 16, the difference in the temperature distributions of solid streams is clearly indicated by the computed results. Indeed, to the extreme degree, the solid temperatures at the outlet would be 400K different, say for cast iron and steel. Similar results were also obtained for the cases corresponding to other operating conditions (see below). These results, however, are a bit suspicious or, more correctly, unphysical from the point of view of cupola operations because, with such a drastic temperature difference, there exists a significant heat transfer, say, through conduction mode, between the cast iron stream and steel stream. Clearly, this assumption is too idealized to represent the real cupola system; and a mechanism regarding the heat exchange between the solids should be taken into account.

To our knowledge, up to the present, there has been neither experimental nor theoretical work on the issue of mutual heat transfer coefficients between the solid streams and also the interfacial surface areas involved. These values are evaluated as follows, based on our experience with cupola operations. A rough estimate of the heat transfer coefficients may be obtained by assuming that heat transfer between the solid streams is through conduction. Having obtained the heat transfer coefficients, we made a rough estimate of the interfacial surface areas involved to start calculations. These values were subsequently adjusted until the temperature difference between two metallic solid streams was within 50K. The results calculated following this procedure are presented in Fig. 17. In comparison with Fig. 16, it can be seen that the mutual heat transfer between the solid streams indeed plays a significant role. It is felt that these results are more realistic than those in Fig. 16 in the case of cupola operations.

To serve a further comparison, the results calculated by lumping all solid streams as one solid stream are shown in Fig. 18.

The similar behavior has also been found in the results obtained for other operating conditions, as shown in Figs. 19-24. The significance of the interfacial heat transfer between the solid streams is again clearly indicated by the results in Figs. 19 and 20. In comparison, the corresponding results computed by neglecting the heat transfer between the solid streams are provided in Figs. 21 and 22, where it can be seen that the unphysically big difference in temperatures of solid streams exist, and those by lumping all the solid streams as one stream are presented in Figs. 23 and 24. These results further suggest that a better understanding of the heat transfer between the solid streams is needed if an accurate representation of heat transfer phenomena in cupolas is to be established.

To accurately predict the temperature distributions of the multiple solid streams, more accurate estimation of the mutual heat transfer coefficients and hence the associated interfacial surface areas must be devised, preferably by experiments. Obviously, this is an area that warrants much experimental undertaking and genuine theoretical inputs as well as the interactions between them. An experimental study of these has been proposed in the second phase of this program using a small scale system. Also, GM will attempt to measure temperatures in different materials in the large cupola used for the other data provided.

One important point should be stressed here. Although much work has been done on the transport phenomena in counter-current systems, into the category of which the present work falls also, no publications were found on the subject of treating solids as individual streams. Hence, this work may be not only of significance to the cupola studies but also of fundamental value to the study of counter-current systems in general.

5. DEVELOPMENT OF TWO-D MODEL

The two dimensional (more correctly, axisymmetric) mathematical model is developed to represent the variation of process variables in both radial and axial directions, such as maldistribution of gas flow and its effect on the heat transfer between the gas phase and condensed phases, melting processes and chemical reactions.

Preliminary developments have been included in this model; in fact, the model has been developed to the point where the gas maldistribution can be studied as a function of operating conditions such as tuyere angles and packed bed structures. The heat transfer

and chemical reactions such as coke combustion and gasification are being incorporated.

A schematic representation of the cupola to be modeled is given in Fig. 25. The mathematical formulation that describes the gas flow, heat flow and mass transfer phenomena in multi-dimensions is composed of a set of highly nonlinear, coupled partial differential equations. These equations represent the conservation of energy, momentum and materials together with the chemical reactions; and are provided in Appendix III.

These equations are being solved numerically by a finite difference code, PHOENICS. The PHOENICS program is a commercially available software designed to solve the partial differential equations arising from the conservation of mass, momentum and energy. Modifications are needed when it is used to solve specific problems. Because the Ergun's equation which describes fluid flow in packed beds does not belong to the generalized transport equation solvable by PHOENICS, an alternative formulation must be used. The generic formulation governing fluid flow behavior of any kind is the Navier-Stokes equation. Starting with this equation, an averaging process is taken over a differential control volume of a packed bed, resulting in a modified Navier-Stokes equation describing the fluid flow through a packed bed. The equation may be reduced to the multidimensional Ergun equation when the viscous and inertial terms are negligible compared to the resistance due to the packing media.

It needs be pointed out that because the two dimensional model consists of a set of highly nonlinear, coupled partial differential equations, it is much more complex than the one dimensional. Hence, a good strategy is essential for successfully solving simultaneously the set of coupled governing partial differential equations. The natural step to start with in our model building is to decouple the part of the equation set that describes the fluid flow from the rest and solve it first; having made sure about fluid flow, other complexities such as heat transfer, chemical reactions and melting processes can then be added.

The two dimensional representation of the gas flow in cupolas has now been established, with which one can study gas flow through a packed cupola bed. Figs. 26-29 show some of the results, obtained from the two dimensional model, regarding the fluid flow behavior for a given bed structure and inflow conditions.

The computed results of the gas flow velocity field are shown in Fig. 26. In the calculation, the particle size and porosity of the cupola bed are assumed to follow radial distributions given by $D_p = 0.1 + 0.06 \cdot R$ and $\epsilon = 0.35 + 0.1 \cdot R$, respectively, where D_p is the particle diameter, ϵ

the bed porosity and R the dimensionless radius, $0 < R < 1$. The flow pattern is as expected. Strong flow occurs near the tuyere front where the gas experiences a sudden expansion from the tuyere outlet to the hearth of the cupola. A short distance above the tuyere level, the flow becomes fully developed. As a result of the bed being packed densely at the center and gradually loosely towards the wall, the gas encounters the largest resistance around the center and the resistance decreases radially outward toward the wall. This effect is shown by the computed results, that is, less gas flow occurs around the center and the gas velocity increases gradually towards the wall.

It is generally accepted that gas maldistribution is caused by the non-uniform packing structure. This is further illustrated by the computed results, as shown in Fig. 27, where the particle size distribution and packing pattern follow a loose packing at the center ($D_p = 0.1 - 0.06 \cdot R$ and $\epsilon = 0.35 - 0.1 \cdot R$, respectively). Again, the effect of tuyere (or inflow) is seen in the near-tuyere region and the gas flow becomes fully developed a short distance above it. In response to the loosing packing at the center, the flow of gas varies radially from the highest velocity to the lowest velocity from the vertical axis of the furnace.

The gas maldistribution has a detrimental effect on the cupola operations, particularly in the region away from the wall, because it likewise affects the heat exchange, hence chemical reactions and melting process. To avoid this effect, a cupola must be packed uniformly. This is confirmed by the results computed by our present two dimensional model of gas flow, as illustrated in Fig. 27. In comparison with Figs. 26 and 27, Fig. 28 shows that a fairly uniform flow may be obtained (except in the near tuyere region) by assuring uniformity in packing.

It is noted that the above remarks have been made based only on the gas flow behavior in cupolas. A full assessment of the effect of gas maldistribution on cupola operations needs be examined along with the heat and mass transfer phenomena, which will be done in the next phase of the research program.

The angles at which gas is injected into cupolas also have an influence on the gas flow, in particular in the region near the tuyere front. This influence is important in cupola operations as it has a direct influence on the coke combustion and melt superheating. The computed results regarding the effect of tuyere angles on the gas flow are shown in Figs 26, and 29 where the angles are 30° and 90° from the vertical axis, respectively. It can be seen that the effects of tuyere angles are felt primarily in a small region near the tuyere and are smeared away by the strong mixing due to the porous packing a short distance from it.

As shown above, the gas maldistributions in the context of cupolas are within the expectation from the first principles and predicted reasonably well as a function of inflow conditions and bed structure. Other effects such as heat transfer and chemical reactions are now being added to complete the model development.

6. SUMMARY OF THE WORK THAT HAS BEEN DONE

The modeling work on the fluid flow, heat and mass transfer in cupolas, specified in the first phase of the program, has been well accomplished. Our model development has been made sure, through extensive communications with the foundry community, to be in the best interest of the U.S. foundry industry and to be on the right track. More specifically:

- A one dimensional model describing the fluid flow and heat and mass transfer has been developed and is working reasonably well. The integration of the model with the chemical model of iron oxidation developed by the UM team has been completed and that with other chemical models that are under development at UM is being undertaken.

- Additional work has been done on the modeling of solid charges as separate streams; more specifically, a multi-solid stream model has been developed to represent the temperature distribution in each of solid streams (the chemical processes undergone by each stream are being incorporated).

- The two-dimensional modeling work has been well started and good progress is being made. The modeling work on the representation of gas flow in cupolas has been completed. The predictions of the gas flow maldistributions as a function of operating conditions such as cupola bed structure, tuyere angles, etc., in the context of cupolas are well within the expectations from the first principles. Other effects such as heat transfer, chemical reactions and melting processes are currently being incorporated.

7. THE WORK TO BE DONE

The feasibility of developing a mathematical model of the cupola process having been well demonstrated, during the first phase of the program, the key components of the Phase 2 work, to be completed in the next two years, are the following:

- (i) The development of a fully tested and refined one dimensional model, where the transport phenomena and the

thermochemical aspects of the problem are fully integrated and critically tested against experimental measurements.

- (ii) The extension of this model to represent transient behavior (in one dimension) so as to describe start-up, shut-down and the response of the system to changes in the operating conditions; the testing of this transient model against experimental data.
- (iii) The continuation of developing the two dimensional representation, with a full integration of the transport phenomena and thermochemical aspects of the cupola process; the extensive testing of the model against experimental measurements and the corresponding refining and updating of the model.
- (iv) The study of the melting of materials possessing different melting temperatures using a small scale experimental set up, which consists of a small PYREX column packed with quartz and low melting point alloys, and the corresponding refinement of the description of the above mathematical models.

In the development of the model, particular attention will be paid to representing the melting process, with due allowance for the different melting characteristics of the iron and the steel and of scrap particles of differing size. The molten iron and steel streams will be treated as separate entities while descending through the cupola. They will, of course, be combined in the molten metal pool and the stream existing the taphole. These will entail combining the multi-stream model with the other process models. Furthermore, attention will be paid to the superheating process, resulting from the contact between the molten iron and steel streams and the hot ascending gases and to the heat loss through the cupola wall.

Finally, the models will represent a full integration of the transport (i.e., heat flow, fluid flow and mass transfer) and the thermochemical (i.e., thermodynamic equilibrium) aspects of the problem.

REFERENCES

1. J.F. Elliott, Trans. Metal. Soc., AIME, Vol. 227, p802, 1964
2. J. Szekely and R.G. Carr, Trans. Metal. Soc., AIME, Vol 242, p918, 1968
3. V. Stanek and J. Szekely, *ibid*, Vol 245, p1185, 1969
4. V. Stanek and J. Szekely, Can. J. Chem. Eng., Vol 50, p9, 1972
5. V. Stanek and J. Szekely, AIChE J., Vol 20, p974, 1974
6. J. Szekely and J. Poveromo, AIChE J., Vol 21, p769, 1975
7. J. Szekely and M. A. Propster, AIChE J., Trans ISIJ, Vol 19, p11, 1979
8. J. Yagi and J. Szekely, Trans. ISIJ, p569, 1977
9. J. Yagi and J. Szekely, Trans. ISIJ, p576, 1977
10. J. Yagi and Szekely, AIChE J., Vol. 25, p800, 1979
11. K. Sasaki et al., *ibid*, Vol 17, p252, 1977
12. Y. Yamaoka, H. Hotta and S. Kajikawa, Trans. ISIJ, Vol. 22, p164, 1982
13. V. Koump, R.H. Tien, R.G.Olsson and T.F. Perzak, Process Simulation and Control in Iron and Steelmaking, edited by J.M. Uye and H.L. Bishop, AIME Publications, New York, 1966
14. I. Muchi, J. Yagi, K. Tamura and A. Moriyama, Journal of The Japan Institute of Metals, Vol 30, p826, 1966
15. I. Muchi, K. Tamura, J. Yagi and A. Moriyama, *ibid*, p1115
16. J. Yagi, K. Tamura and A. Moriyama, *ibid*, Vol 31, p103, 1967
17. J. Yagi, H. Nishio, K. Sakasi and I. Muchi, *ibid*, p771
18. I. Muchi and J. Higuchi, Trans. ISIJ, Vol. 12, p54, 1971
19. I. Muchi, Trans. ISIJ, Vol 7, p223, 1967
20. J. Yagi and I. Muchi, Trans. ISIJ, Vol 10, p392, 1970
21. M. Cross et al., "Control '84", SME, AIME, New York, p348, 1984

22. Y. Togino, M. Sugata, and K. Yamaguchi, Trans., Vol. 20, p639, 1982
23. M. Hatano and K. Kurita, Trans. ISIJ, Vol 22, p448, 1982
24. J. Yagi, K. Tekeda and Y. Omori, *ibid*, Vol 22, p884, 1982
25. T. Shimoda, K. Kurita and Y. Iwanaga, Trans, ISIJ, Vol 27, p780, 1987
26. P.D. Burke and J.M. Burgess, 1989 Ironmaking Conference Proceedings, p773
27. H. Takahashi, K. Kushima and T. Takeuchi, ISIJ International, Vol 29, p117, 1989
28. K. Yamaguchi, Trans. ISIJ, Vol 25, p371, 1985
29. J.M. Burgess, International Hearth and Raceway Symposium, Newcastle, Australia, Aust. Inst. Min. and Met., 1981
30. J. Sekely and J. Mendrykowski, Chem. Eng. Sci., Vol 27, p959, 1972
31. Y. Kuwano, Trans. ISIJ, Suppl. VII. p125, 1971
32. N. Standish and J.B. Drinkwater, JOM, Vol 22, p355, 1982
33. R.D. Pehlke, AFS Trans. p.806, 1976
34. J. Briggs, The british Foundrymen, Vol 65, p340, 1972
35. N. Meysson, Fonderie No.343, p165, 1975
36. W.J. Evans, R.G. Hurley, and R.C. Creese, AFS Trans., p411, 1980
37. R. W. Shields, K.W. Roessing and H.L Bishop, in Process Simulation and Control in Iron and Steel making, ed. J.M. Uys and H.L Bishop, p.167, 1966
38. J.G. Breen, Australasian Institute of Mining and Metallurgical proceedings, No. 208, p25 (1963)
39. I.J. Petrovski, AFS International Cast Metals Journal, p10, 1981
40. A.B. Draper and K. Nymekye, AFS Transactions, p615, 1982
41. J. Szekely, J.W. Evans and H.Y. Sohn, Gas Solid Reactions, Academic Press, New York, 1976.

42. J. Szekely and N.J. Themelis, Rate Phenomena in Process Metallurgy, Wiley, New York, 1971.
43. W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, Numerical Recipes, Cambridge University Press, 1986.

LIST OF SYMBOLS FOR ONE-D MODEL

A. SYMBOLS FOR APPENDIX I

$a_{s,i}$	Interfacial surface area per unit volume of bed between the gas and solids or between the gas and liquid stream (m^2/m^3)
C_i	Concentration of gaseous species i , (moles/ Nm^3)
C_g	Heat capacity of gas (Joule/mole)
C_s	Heat capacity of solids (Joule/mole)
C_l	Heat capacity of liquid stream (Joule/mole)
D_i	Diameter of solid particles or liquid drops (m)
d_i	Size of solid species i , $i=C$:Coke, $i=L$:Limestone, $i=Fe$:Fe, (m)
ΔH_i	Heat release due to chemical reaction i (Joule/mole)
f_i	Fraction of solids consumed due to reactions, $i=c$: Coke, $i=L$:limestone, $i=Fe$:FeO
F_1, F_2	Parameters characterizing the resistance of the packed bed to the gas flow (see their definitions in Appendix III)
G	Superficial mass flowrate of gas (Kg/sec m^2)
G_i	Superficial mass flowrate of solid, $i=L$:Limestone, $i=C$: Coke, $i=s$: Solids, $i=l$: Liquid (Kg/sec m^2)
h_p	Heat transfer coefficients between gas and solids, (Joule/ m^2 sec)
h_{ps}	Heat transfer coefficients between gas and solids in the liquid flow zone (Joule/ m^2 sec)
h_{pl}	Heat transfer coefficients between the gas and liquid in the liquid flow zone (Joule/ m^2 sec)
k_g	Thermal conductivity of gas (Joule/m K sec)
m_i	Weight change per mole of species i due to chemical reaction i , $i=C$: Carbon in Boudouard reaction, $i=L$: Limestone in limestone decomposition reaction, $i=Fe$: Fe in iron oxidation
N_i	Number of particles of solid species i per unit volume ($\#/m^3$)
P	Pressure (Pa)
P_i	Rate of production of liquid materials (Kg/sec)
Pr	Prandtl number for the gas
Re	Reynolds number
R_i	Reaction rates of chemical reaction i , (moles/sec m^3)
Sc	Schmidt Number
T_g	Temperature of gas (K)
t	Temperature of solid (K)
$t_{s,l}$	Temperature of solid and liquid in the liquid flow zone (K)
t_i	Temperature of solid species i , $i=C$: Coke, $i=L$:limestone, $i=Fe$: Fe (K)
Y_i	Mole fraction of gas species i
C_i	Charge rate of solid i , $i=m$ for steel, $i=C$ for casting iron, $i=A$ for ferro-alloys, $i=P$ for pig iron, $i=k$ for Coke (kg/sec m^3) (Used in overall mass balance only)
$V_{i,u}$	Weight fraction of element u contained in solid charge i

	$u=1:\text{Fe}, u=2:\text{C}, u=3:\text{Si}, u=7:\text{FeO}, u=8:\text{Fe}_2\text{O}_3, u=12:\text{CaO}, u=13:\text{MnCO}_3, u=14:\text{CaCO}_3$
$U_{i,u}$	Weight fraction of element u contained in liquid materials
$Y_{i,0}$	Off gas composition of species i , (mole fraction)
G_0	Total moles of off gas
G_b	Total moles of incoming blast
X_{o2}	Mole fraction of oxygen enrichment in the blast
T_b	Blast temperature (K)
X_{H_2O}	Mole fraction of moisture in the blast
T_{H_2O}	Temperature of steam in the blast (K)
G_s	Charge rate of solids (Kg/sec m^2)
T_s	Temperature of solid charges (K)
M_i	Molecular weight of species i (Kg/mole)
t_{slag}	Slag temperature (K)
t_m	Metal tapping temperature (K)
$T_{g,0}$	Off gas temperature (K)
L_{fe}	Latent heat for melting of Fe (Joule/Kg)
z	Radial and axial direction (m)
ϵ	Porosity
μ	Molecular viscosity (Kg/m sec)
ρ	Density of gas (Kg/ Nm^3)

B. SYMBOLS FOR APPENDIX II

a_i	Interfacial surface area per unit volume of bed between the gas and solid liquid stream i (m^2/m^3)
a_{ij}	Interfacial surface area per unit volume of bed between solid streams i and j (m^2/m^3)
A	Characteristic matrix used to determine eigenvalues
C_{gp}	Heat capacity of gas (Joule/ mole K)
C_{ip}	Heat capacity of solid stream i (Joule/mole K)
f	Unknown vector containing the temperatures of gas and solids to be determined
G_i	Superficial mass flowrate of solid stream i (Kg/sec m^2)
h_i	Heat transfer coefficients between gas and solid stream i (Joule/ m^2 sec)
h_{ij}	Heat transfer coefficients between solid streams i and j (Joule/ m^2 sec)
I	Unit matrix
m_{ik}	Weight change of species i due to chemical reaction k (Kg/mole)
t_i	Temperature of solid stream i (K)
ϕ_{ik}	Factor partitioning the chemical reaction heat between the i -th solid stream and gas
λ	Eigenvalues of matrix A

C. SYMBOLS FOR APPENDIX III

A_{gs}	Interfacial surface area per unit volume of bed between the gas and solids (m^2/m^3)
C_g	Heat capacity of gas (Joule/mole K)
C_i	Concentration of gaseous species i (moles/ Nm^3)
C_s	Heat capacity of solid stream i (Joule/mole K)
D_i	Diffusion coefficients of gaseous species i through packed bed (m^2/sec)
h_{gs}	Heat transfer coefficients between gas and solids (Joule/ m^2 sec K)
K_g	Thermal conductivity of gas in packed bed (Joule/K-m sec)
K_s	Thermal conductivity of solid in packed bed (Joule/K-m sec)
u, v	Axial and radial components of gas velocity (m/sec)
u_s, v_s	Axial and radial components of solid velocity (m/sec)
χ_i	weight change contributed to gaseous species i due to chemical reactions
x, r	Axial and radial direction

APPENDIX I

MATHEMATICAL FORMULATION OF ONE-DIMENSIONAL GAS FLOW, HEAT AND MASS TRANSFER PROBLEMS

1. Governing equations

mass balance on gas (continuity equation):

$$\frac{dG}{dz} = -m_C R_{CO} - m_{CO_2} R_L + m_{F_e} R_{F_e} \quad (1)$$

mass balance on carbon dioxide:

$$G \frac{d}{dz} \left(\frac{C_{CO_2}}{\rho} \right) = -R_L + R_{CO} - \frac{C_{CO_2}}{\rho} \frac{dG}{dz} \quad (2)$$

mass balance on carbon monoxide:

$$G \frac{d}{dz} \left(\frac{C_{CO}}{\rho} \right) = -2R_{CO} - \frac{C_{CO}}{\rho} \frac{dG}{dz} \quad (3)$$

mass balance on water vapor:

$$G \frac{d}{dz} \left(\frac{C_{H_2O}}{\rho} \right) = R_{H_2O} - \frac{C_{H_2O}}{\rho} \frac{dG}{dz} \quad (4)$$

heat balance on gas:

$$\frac{dT}{dz} = \frac{\left\{ h_p a_s (T - t) - \sum \psi_i R_i (-\Delta H_i) + C_s T \left[m_C (R_C + R_{CO} + R_{H_2O}) + m_{CO_2} R_L - m_{F_e} R_{F_e} \right] \right\}}{G \left(C_s + T \frac{dC_s}{dT} \right)} \quad (5)$$

one-dimensional Ergun equation:

$$-\frac{dP}{dz} = G(F_1 + F_2 + G) \quad (6)$$

heat balance on Solids:

$$\frac{dt}{dz} = \frac{\{h_p a_s (T - t) + \sum (1 - \psi_i) R_i (-\Delta H_i)\}}{G_s \left(C_s + t \frac{dC_s}{dt} \right)} \quad (7)$$

coke fraction consumed due to coke related reactions:

$$\frac{df_c}{dz} = -m_c R_{CO} / G_c \quad (8)$$

limestone fraction consumed due to limestone decomposition:

$$\frac{df_L}{dz} = -m_{CaO} R_L / G_L \quad (9)$$

Iron fraction that is oxidized:

$$\frac{df_{Fe}}{dz} = -m_{Fe} R_{Fe} / G_{Fe} \quad (10)$$

in liquid flow zone:

The above mathematical representations apply to the region up to the end of the melting zone. The separation of liquid phase (slag+molten metal) from the solid phase is considered occurring after melting is finished. Temperatures of liquid, solid and gas are then described by the following equations:

$$\frac{dT}{dz} = \frac{\{h_{ps} a_s (T - t_s) + h_{pl} a_l (T - t_l) - \sum \psi_i R_i (-\Delta H_i) + C_s T [m_c R_{CO} + m_{CaO} R_L]\}}{G \left(C_s + T \frac{dC_s}{dT} \right)} \quad (6')$$

$$\frac{dt_s}{dz} = \frac{\{h_{ps}a_s(T-t_s) - \sum (1-\psi_i)R_i(-\Delta H_i)\psi_{si}\}}{G_s\left(C_s + t_s \frac{dC_s}{dt_s}\right)} \quad (11)$$

$$\frac{dt_l}{dz} = \frac{\{h_{pl}a_l(T-t_l) + \sum (1-\psi_i)R_i(-\Delta H_i)\psi_{sl}\}}{G_l\left(C_l + t_l \frac{dC_l}{dt_l}\right)} \quad (12)$$

where h_i is determined by the following formula:

$$h_i = (2 + 1.1\text{Pr}^{1/3} \text{Re}^{0.6})k_g/D_i \quad (13)$$

2. Rate expressions for chemical reactions

1. Reaction rate for $\text{CO}_2 + \text{C} = 2\text{CO}$:

$$R_{\text{CO}}^* = \frac{\pi d_c^2 \phi_c^{-1} N_c 273 P' y_{\text{CO}} / 22.4 t_c}{1/k_{cf} + 6/d_c \rho_c E_f k_c}$$

where

$$k_{cf} = (2 + 1.1\text{Re}_c^{1/3} \text{Sc}^{0.6})D_{\text{CO}_2}/d_c$$

$$\text{Re}_c = d_c G / \mu_s \varepsilon$$

$$\text{Sc} = \mu_s / \rho D_{\text{CO}_2}$$

$$D_{\text{CO}_2} = 2.236 \times 10^{-6} T^{1.78} / P'$$

$$k_c = 2.99 \times 10^{13} \exp(-30261.7/t_c)$$

$$E_f = 3(m \coth m - 1)/m^2$$

$$m = \frac{d}{2} \sqrt{\rho_c k_c / D_{\text{S2}}}$$

$$D_{\text{S2}} = D_{\text{CO}_2} \xi_c \varepsilon_c, \quad \xi_c = \varepsilon_c^2, \quad \varepsilon_c = 0.45$$

2. Reaction rate for $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$:

$$R_L^* = \frac{\pi d_L^2 \phi_L^{-1} N_L (t_L - t^*)}{(-\Delta H_L) \left[\frac{1}{h_p} + \frac{d_L}{2k_s} \left((1 - f_L)^{-1/3} - 1 \right) \right] + \frac{(1 - f_L)^{-1/3}}{k_L} \left[\frac{1 + 4 P_{\text{CO}_2} / P_d}{1 - P_{\text{CO}_2} / P_d} \right]}$$

where

$$t^* = 1053^\circ \text{K}$$

$$(-\Delta H_L) = 45400 - 4.5 t_L$$

$$P_d = \exp \left(20.3 \times 10^3 \left(\frac{1}{1170} - \frac{1}{t_L} \right) \right)$$

$$k_L = 2.25 \times 10^{-3}$$

$$k_s = 0.680$$

$$P_{\text{CO}_2} = 22.4 y_{\text{CO}_2} \rho P'$$

3. Reaction rate for iron oxidation is given by the chemical model by Dr. Pehlke's group.

3. Mass balance over the whole furnace

The overall mass balance is made over the whole furnace to determine a first estimate of the off-gas composition, thus providing the composition boundary conditions for the gas phase.

Mass balance on Fe to calculate molten metal production rate:

$$\begin{aligned} & (C_m V_{m,1} + C_C V_{C,1} + C_A V_{A,1} + C_P V_{P,1}) \\ & + (C_m V_{m,7} + C_C V_{C,7} + C_A V_{A,7} + C_P V_{P,7}) 56 / 72 \\ & + (C_m V_{m,8} + C_C V_{C,8} + C_A V_{A,8} + C_P V_{P,8}) 112 / 160 \\ & = P_m (U_{m,1} + U_{m,7} 56 / 72 + U_{m,8} 112 / 160) + P_s (U_{s,1} + U_{s,2} 56 / 72 + U_{s,8} 112 / 160) \end{aligned}$$

Mass balance on CaO to calculate slag production rate:

$$P_s = C_{L,12}(V_{L,12} + V_{L,13}56/100)/U_{s,12}$$

The following mass balance equations are used to calculate off-gas compositions:

Mass balance on N_2 :

$$Y_{N_2,0}G_0 = 0.79G_b$$

Mass balance on water vapor in blast:

$$Y_{H_2O,0}G_0 = X_{H_2O}G_b$$

Mass balance on moisture in solid input:

$$Y_{H_2O,0}G_0 = (C_m V_{m,H_2O} + C_C V_{C,H_2O} + C_A V_{A,H_2O} + C_P V_{P,H_2O} + C_k V_{k,H_2O} + C_L V_{L,H_2O}) / 18$$

Mass balance on O_2 :

$$G_0(0.5Y_{H_2O,0} + 0.5Y_{CO,0} + Y_{CO_2,0}) = (0.21 + X_{O_2})G_b + C_L(V_{L,13}/84 + V_{L,14}/100) + (C_m V_{m,3} + C_C V_{C,3} + C_A V_{A,3} + C_P V_{P,3} - P_m U_{m,3}) / 28$$

Mass balance on C:

$$\begin{aligned} G_0(Y_{CO} + Y_{CO_2}) = & (C_m V_{m,2} + C_C V_{C,2} + C_A V_{A,2} + C_P V_{P,2} + C_k V_{k,2}) / 12 \\ & + (C_m V_{m,13} + C_C V_{C,13} + C_A V_{A,13} + C_P V_{P,13} + C_L V_{L,13}) / 84 \\ & + (C_m V_{m,14} + C_C V_{C,14} + C_A V_{A,14} + C_P V_{P,14} + C_L V_{L,14}) / 100 \\ & - (P_m U_{m,2} + P_{s,2} U_{s,2}) / 12 \end{aligned}$$

4. Heat balance over the whole furnace

The heat balance is made over the whole furnace to provide a first estimate of the boundary condition for the off gas temperature.

Heat input:

1. Sensible heat from blast

$$H_{in,1} = G_b((C_{p,air} + C_{p,O_2}X_{O_2})T_b + C_{p,H_2O}X_{H_2O}T_H)$$

2. Sensible heat from solids

$$H_{in,2} = G_S C_{p,S} T_S$$

3. Heat released due to reaction ($C + CO_2 = CO$):

$$H_{in,3} = Y_{CO,0} G_0 (-\Delta H_{CO}^{\circ}) / 2$$

4. Limestone decomposition:

$$H_{in,4} = G_L (-\Delta H_L^{\circ}) / M_{CaCO_3}$$

5. Magnesia decomposition:

$$H_{in,5} = G_{MgCO_3} (-\Delta H_{MgCO_3}^{\circ}) / M_{MgCO_3}$$

6. Heat released due to combustion:

$$H_{in,6} = G_b (0.21 + X_{O_2}) (-\Delta H)$$

7. Plasma boasting heat:

$$H_{in,7} = H_{plasma}$$

8. Heat in slag formation:

$$H_{out,5} = P_{slag} (1.8 t_{slag} - 520) / 4.184$$

Heat output:

1. Sensible heat in molten metal:

$$H_{out,1} = 0.203 P_m t_m$$

2. Sensible heat in off-gas:

$$\dot{Q}_{\text{in},2} = G_0 C_{p,g} T_{g,0}$$

3. Heat loss through the wall:

$$\dot{Q}_{\text{in},3} = \omega (H_{\text{in},3} + H_{\text{in},4} + H_{\text{in},5})$$

4. Heat for melting of metal:

$$\dot{Q}_{\text{in},4} = L_F P_m / 56.0$$

The off-gas temperature is then calculated as follows:

$$T_g = \left(\sum_{i=1}^3 H_{\text{in},i} - \sum_{i=1,3,4} H_{\text{out},i} \right) / G_0 C_{p,g}$$

APPENDIX II

MATHEMATICAL FORMULATION OF MULTI-SOLID STREAM MODEL

heat balance on gas:

$$G \frac{d}{dz} (C_{gp} T) = - \sum h_i a_i (T - t_i) - \sum \sum m_{ik} C_{gp} T R_k - \sum \sum \phi_{ik} (-\Delta H_k) R_k \quad (1)$$

heat balance on each of solid streams:

$$G_i \frac{d}{dz} (C_{ip} t_i) = h_i a_i (T - t_i) + \sum (1 - \phi_{ik}) (-\Delta H_k) R_k - \sum m_{ik} C_{ip} t_i R_k + \sum h_{ij} a_{ij} (t_j - t_i) \\ i=1,2,\dots,\text{number of solid streams} \quad (2)$$

where R_k is the rate of chemical reactions, h_i and a_i the heat transfer coefficient between gas and solid streams and the surface areas involved, and h_{ij} and a_{ij} the mutual heat transfer coefficients between solid streams and the associated surface areas.

When the chemical reactions are ignored, the above equations can be cast in matrix form by substituting $f_i = f_{i0} \exp(r_i z)$ ($f_i = T, t_i, \dots$) into the ordinary differential equations,

$$A f = r I f$$

Hence, the eigenvalues of this system can be calculated by setting the determinant of the above matrix to zero:

$$|A - rI| = 0$$

With each eigenvalue so calculated, we can obtain an associated eigenvector. The linear combination of all eigenvectors gives the solution of the original ordinary differential equations, which is expressed as a set of algebraic equations containing the same number of constants as that of the ODE's. These constants are then solved for by satisfying the solution with the boundary conditions at the boundaries.

APPENDIX III

MATHEMATICAL FORMULATION OF GAS FLOW, HEAT FLOW AND SPECIES DISTRIBUTIONS IN TWO DIMENSIONS

1. Equations describing gas flow in a packed bed:

$$\frac{\partial(\rho u)}{\partial x} + \frac{1}{r} \frac{\partial(\rho r v)}{\partial r} = 0$$

$$\frac{\partial(\rho u^2)}{\partial x} + \frac{1}{r} \frac{\partial(\rho r u v)}{\partial r} = -\frac{\partial P}{\partial x} + 2 \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left[\mu r \left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x} \right) \right] - (F_1 + F_2 |u|) u$$

$$\frac{\partial(\rho u v)}{\partial x} + \frac{1}{r} \frac{\partial(\rho r v^2)}{\partial r} = -\frac{\partial P}{\partial r} + \frac{\partial}{\partial x} \left[\mu \left(\frac{\partial u}{\partial r} + \frac{\partial v}{\partial x} \right) \right] + \frac{2}{r} \frac{\partial}{\partial r} \left(\mu r \frac{\partial v}{\partial r} \right) + \mu \frac{2v}{r^2} - (F_1 + F_2 |v|) v$$

where u and v are superficial velocities in axial and radial directions, respectively; and F_1 and F_2 are parameters characterizing the resistance to the gas flow by the packed materials,

$$F_1 = \frac{150 \mu (1 - \epsilon)^2}{\epsilon^3 \rho (\phi d)^2}$$

$$F_2 = \frac{1.75 \rho (1 - \epsilon)}{\epsilon^3 \rho \phi d}$$

2. Equations describing temperature distributions of solids and gas:

$$\frac{\partial(\rho u C_s T_s)}{\partial x} + \frac{1}{r} \frac{\partial(\rho r v C_s T_s)}{\partial r} = \frac{\partial}{\partial x} \left(K_s \frac{\partial T_s}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r K_s \frac{\partial T_s}{\partial r} \right) - h_{gs} A_{gs} (T_s - T_g) + \sum_{i=1}^N \psi_i \Delta H_i R_i$$

$$\frac{\partial(\rho u_g C_g T_g)}{\partial x} + \frac{1}{r} \frac{\partial(\rho r v_g C_g T_g)}{\partial r} = \frac{\partial}{\partial x} \left(K_g \frac{\partial T_g}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r K_g \frac{\partial T_g}{\partial r} \right) - h_{gs} A_{gs} (T_s - T_g) + \sum_{i=1}^N (1 - \psi_i) \Delta H_i R_i$$

3. Equations describing the gas species distributions:

$$\frac{\partial(\rho u C_i)}{\partial x} + \frac{1}{r} \frac{\partial(\rho v r C_i)}{\partial r} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(r D_i \frac{\partial C_i}{\partial r} \right) + \sum_{i=1}^N \chi_i R_i$$

Figure 1. Schematic representation of cupola melting processes.

Figure 2 Diagram showing the control volume used in deriving the governing ordinary differential equations for one dimensional mathematical models.

Figure 2 Diagram showing the control volume used in deriving the governing ordinary differential equations for one dimensional mathematical models.

Figure 3 Comparison of temperature distributions calculated by the iterative Runge-Kutta numerical method and by analytical method. Analytical solutions are given by curves and numerical values are represented by discrete points.

Figure 4. Computed temperature distribution in a GM cupola furnace (Run #7). The operating conditions are: blast rate=1.311(scms), enriched oxygen=0.034(scms), blast temperature=9220K, cast iron charge rate=2.192(kg/s), steel charge rate=0.731(kg/s), coke charge rate=0.303(kg/s) and limestone charge rate=0.091(kg/s). Lump sizes of limestone and coke are 0.04(m) and 0.11(m), respectively.

Figure 5. Computed gas composition distribution in the GM cupola furnace (Run #7). The operating conditions are the same as those in the previous figure, i.e., Figure 4. It can be seen that gas composition changes drastically a short distance up from the tuyere level and afterwards it remains unchanged.

Figure 6. Comparison of computed and measured temperature distributions for a GM cupola. Curves are calculated results and points marked by $\diamond$ are measured results for solids. The operating conditions are: blast rate=1.157(scms), enriched oxygen=0.035(scms), blast temperature=9220K, cast iron charge rate=1.361(kg/s), steel charge rate=1.361(kg/s), coke charge rate=0.282(kg/s) and limestone charge rate=0.144(kg/s). Lump sizes of limestone and coke are 0.04(m) and 0.11(m), respectively.

Figure 7. Gas composition distribution in the GM cupola furnace(Ruh #8). The operating conditions are: blast rate=1.317(scms), enriched oxygen 0.034(c.c.ms), blast temperature 922°K, cast iron charge rate=0.932(kg/s), steel charge rate=2.051(kg/s), coke charge rate=0.310(kg/s) and limestone charge rate=0.093(kg/s). Lump sizes of limestone and coke are 0.04(m) and 0.114(m), respectively.

Figure 8. Gas composition distribution in the GM cupola furnace(Run #9). The operating conditions are: blast rate=1.340(scms), enriched oxygen=0.035(scms), blast temperature=922oK, cast iron charge rate=1.452(kg/s), steel charge rate=1.452(kg/s), coke charge rate=0.301(kg/s) and limestone charge rate=0.0907(kg/s). Lump sizes of limestone and coke are 0.04(m) and 0.11(m), respectively.

Figure 9. Temperature distribution corresponding to the conditions in Figure 7.

Figure 10. Temperature distribution corresponding to the conditions in Figure 8.

Figure 11. Calculated gas composition distribution in the GM cupola furnace when the coke size is doubled with other operating conditions kept the same as those in Figure 4. As a consequence of doubling the coke size, the mole fraction of CO in the exit gas stream is decreased while that of CO₂ is increased.

Figure 12. Calculated gas composition distribution in the GM cupola furnace when the coke size is reduced by 50%. Other operating conditions are the same as those in Figure 4. In comparison with the previous figure, i.e., Figure 11, this figure shows that the ratio (CO/CO_2) in the off gas stream is greatly increased, which is expected as the Boudouard reaction is promoted when the coke size is reduced.

Figure 13. Predicted temperature distribution in the GM cupola furnace when coke size is doubled while other operating conditions are kept the same as those in Figure 4. Notice that the exit gas attains a higher temperature as do coke and liquid streams, which is expected as increasing the coke size diminishes the extent of the endothermic Boudouard reaction.

Figure 14. Predicted temperature distribution in the GM cupola furnace when coke size is reduced by 50% while other operating conditions are kept the same as in Figure 4. Notice also the drop in the off-gas temperature as a result of reducing the coke size.

Figure 15. Enlarged view of predicted variation in the superheating of molten streams with changing coke sizes: (a) coke size is 5.5cm in diameter and (b) coke size 22cm in diameter. Comparison of (a) with (b) reveals that an increase in coke size increases the superheat in the liquid streams, which is consistent with cupola practice.

Figure 16. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola. The mutual heat transfer coefficients between the solid streams are ignored; as a result, artificially high solid temperature difference exists among the solid streams. The input conditions such as particle sizes and gas flow correspond to Run #8.

Figure 17. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola with the mutual heat transfer coefficients between the solid streams taken into account. The input conditions such as particle sizes and gas flow correspond to Run #8.

Figure 18. Temperature distribution computed using the multi-solid stream model for the shaft region of a GM cupola with solids lumped as one stream. The input conditions such as particle sizes and gas flow correspond to Run #8.

Figure 19. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola with the mutual heat transfer coefficients between the solid streams taken into account. The input conditions such as particle sizes and gas flow correspond to Run #7.

Figure 20. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola with the mutual heat transfer coefficients between the solid streams taken into account. The input conditions such as particle sizes and gas flow correspond to Run #9.

Figure 21. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola without the mutual heat transfer coefficients between the solid streams taken into account. The input conditions such as particle sizes and gas flow correspond to Run #7.

Figure 22. Temperature distribution computed by the multi-solid stream model for the shaft region of a GM cupola without the mutual heat transfer coefficients between the solid streams taken into account. The input conditions such as particle sizes and gas flow correspond to Run #9.

Figure 23. Temperature distribution computed using the multi solid stream model for the shaft region of a GIM cupola with solids lumped as one stream. The input conditions such as particle sizes and gas flow correspond to Run #7.

Figure 24. Temperature distribution computed using the multi-solid stream model for the shaft region of a GM cupola with solids lumped as one stream. The input conditions such as particle sizes and gas flow correspond to Run #9.

Figure 25. Schematic representation of geometry of a cupola furnace.

Figure 26. 2-D velocity field showing the gas flow through a packed cupola. The bed structure is assumed following the dense-packing at the center: $\epsilon = 0.35 + 0.1 \cdot R$ and $D_p = 0.1 + 0.06 \cdot R$ where ϵ is the bed porosity, D_p particle diameter and $0 \leq R \leq 1$. Injection velocity is 6.74 (m/s), which corresponds to the inflow condition in Run #7, as given by Dr. Katz. The injecting gas is air and its physical properties are evaluated at $T=500^\circ\text{C}$. The tuyer is at 90° to the wall.

Figure 27. 2-D velocity field showing the gas flow through a packed cupola. The bed structure is assumed following the loose-packing at the center: $\epsilon = 0.35 - 0.1 \cdot R$ and $D_p = 0.1 - 0.06 \cdot R$ where ϵ is the bed porosity, D_p particle diameter and $0 \leq R \leq 1$. Other conditions are the same as in Figure 26.

Figure 28. Effect of bed structure on the gas flow through the packed cupola. The bed is assumed to have a uniform porosity of 0.43 and solids are .11 m in diameter. Other conditions are the same as in Figure 26. In comparison with the previous two cases, (i.e., Figures 26 and 27), the flow in this case is rather uniform, as expected.

Figure 29. 2-D velocity field showing the gas flow through a packed cupola. The bed structure is assumed following the dense-packing at the center: $\epsilon = 0.35 + 0.1 \cdot R$ and $D_p = 0.1 + 0.06 \cdot R$ where ϵ is the bed porosity, D_p particle diameter and $0 \leq R \leq 1$. Injection velocity is 6.74 (m/s), which corresponds to the inflow condition in Run #7, as given by Dr. Katz. The injecting gas is air and its physical properties are evaluated at $T=500$ °C. The tuyer is at 30° to the wall.

Table 1. Comparison of calculated and experimental results for some important process variables in the GM cupola furnace.

	Off Gas Temp. (°K)		CO ₂ %		CO%	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Run #7	588	559	11	9.8	21	22.2
Run #8	498	515	9.5	10.8	20	20.4
Run #9	627	587	9.3	9.9	22.5	21.6
Run #10	529	597	18.0	17.3	13.4	14.1

**PHASE I
FINAL REPORT
ON**

**MATHEMATICAL MODELING OF CHEMICAL REACTIONS
IN CUPOLA FURNACES**

BY:

UNIVERSITY OF MICHIGAN

INTRODUCTION

The present report summarizes the work that has been conducted at the University of Michigan (UM) during the past year on development of an on-line process model for a cupola furnace. UM contracted to provide models of key chemical processes governing the compositions of iron and slag be developed on the basis of physical chemical fundamentals and the best available data. The modeling results were also to establish areas that required further research to perfect the mathematical models.

A schematic view of a conventional cupola furnace is presented in Figure 1 which also lists the key chemical processes modeled during the initial year of this research program. The processes considered include:

- oxidation of solid steel and cast iron
- carbon pickup
- oxidation of C, Si and Mn by CO_2 and FeO
- sulfidation of liquid and solid steel and cast iron
- desulfurization of liquid steel and cast iron in the slag layer

In the following sections of this report, the numerous modeling attempts are outlined, and the most complete and accurate algorithms are described. The results of the models are used to predict the extent of silicon and manganese losses and carbon pickup, and in the cases of silicon and carbon, are compared with carefully documented experimental cupola melting data taken on a large pilot scale furnace.

These modeling efforts have made clear the specific nature of experimental information which was limited or lacking to suggest required further experimental work. These cases are cited in the following sections of the report which document the modeling efforts for the chemical processes noted above.

Figure 1: Outline of Conventional Cupola Showing Major Parts.
Key Cupola Reactions Modeled are indicated (bold face).

OVERVIEW OF CHEMICAL PROCESSES

The development of models for each of the key chemical processes requires consideration of a series of reactions; some occurring simultaneously, others occurring in series. In general, the chemical potentials (thermodynamic activities) of the reacting species are changing as the reactions proceed, and are further altered with position in the furnace by phase or material movement, e.g. melting or gas flow, and by temperature changes. Consequently, separate reaction strings must be described in terms of thermodynamic characteristics and transport mechanisms which are applicable throughout the cupola. It is in this latter area where additional information is required. The research goals of Phase II of this project are focused on transport phenomena in the cupola melting process.

Utilizing the best fundamental information available, the chemical processes outlined in the previous section have been modeled. The results of these modeling efforts have been compared with carefully documented industrial data, specifically fully documented experiments on a full-scale pilot operation conducted at Marquette by General Motors.

In modeling these chemical processes, the reaction strings leading to the final metal composition have been combined as follows:

Silicon

The reactions investigated include CO_2 desiliconization of liquid metal and silicon oxidation from the liquid metal by iron oxide in the slag layer.

Manganese

The reactions investigated include the oxidation of manganese in the liquid metal by CO_2 in the gas phase and by iron oxide in the slag phase.

Carbon

The reactions investigated include CO_2 decarburization of solid iron, CO_2 decarburization of liquid iron droplets, coke-carbon dissolution in iron and steel droplets, and decarburization of the droplets by FeO in the slag.

Sulfur

The reactions involving sulfur transfer in the cupola are, the sulfur pick up by the solid charge and molten metal droplets from SO_2 present in the gas phase and sulfur distribution between slag and metal due to slag/metal reactions in the hearth of the furnace.

Multi-Stream Model

As noted in the above section on Carbon, it is apparent that the carbon contents of the cast iron and steel charge materials are substantially different, and therefore each will react differently in their movement down through the furnace. Furthermore, other charge materials, e.g. ferroalloys will also behave differently with respect to chemical interactions with the gas phase.

Also, each will melt at different levels in the furnace, and a general mixing of these metallic streams will not occur until reaching the well of the furnace. Consequently, a multi-stream model for the metallic charges will be utilized. The viability of this approach has been documented^{1,2}.

I. MATHEMATICAL MODELING OF IRON OXIDE FORMATION AND REDUCTION BY COKE

In this study the oxidation phenomenon in the stack of the cupola has been investigated. The main objective of this work was to develop a mechanism for the oxidation of the charge, to build a mathematical model on the basis of the mechanism, and to predict the amount of iron oxide formed in the solid stack. The predictions of the model developed can then be used to estimate the amount of silicon, manganese and carbon loss that takes place in an operating cupola, due to oxidation.

Oxidation of Solid Iron

The oxidation mechanism depends on the thickness of the oxide layer on the surface of the solid charge. In the case of pure iron, the oxidation in a CO-CO_2 atmosphere with a small thickness of oxide layer (less than 10^{-3}cm) is controlled by the rate of dissociation of CO_2 to CO and O^- ions^{3,4}, with the rate law being linear. However, at higher film thicknesses the flux of iron through the oxide layer is inversely proportional to the oxide thickness. The diffusion of iron through the oxide layer will eventually become the rate-

controlling step. This occurs when the oxide thickness becomes greater than about 10^{-3} cm.

All metallic charges in the cupola have a thin layer of oxide on them. The thickness of this oxide layer has been assumed to be 0.01 cm, and hence the diffusion of iron through the oxide layer will be the rate controlling process. Iron ions diffuse through the oxide layer and reach the surface where they combine with the oxygen of CO_2 instantaneously. This is schematically illustrated in Figure 2.

Figure 2: Schematic Diagram of the Oxidation Phenomenon indicating Diffusion of Iron Ion through the Oxide Layer via Cation Vacancies.

The oxidation of iron leads to the formation of wustite, which is normally the major constituent of the oxide scales formed on iron at temperatures above approximately 570°C⁵. Moreover, kinetically the oxidation rate is not significant below this temperature. Very recently, N. Lillybeck has measured the scale thicknesses on hot rolled steel and reported them to be on the order of 0.002 cm⁶.

As will be shown later, the oxide layer present on the charge material accounts for an appreciable fraction of the total amount of iron oxide in the slag layer. Hence, it is essential to characterize experimentally the thickness of the oxide layer with the nature of the charge material. Thus, more experimental data on initial oxide layer characterization would improve the accuracy of the mathematical model.

As the coke and iron-base charge materials are heated in the stack of the furnace, the Boudouard reaction between the gases and the coke:

and the oxidation of the iron-base charge materials may occur:

The range of CO to CO₂ ratios in the stack of the cupola is 0.7 to 4, with typical values falling between 1.5 and 2.5

The conditions under which these reactions can occur are indicated in Figure 3.

Figure 3: Equilibrium of Iron-Oxygen-Carbon Systems at 1 atm.⁷ The mole %CO is the percentage of CO in the CO + CO₂ portion of the gas phase. For the Boudouard reaction, the curve is shown for a CO + CO₂ gas mixture.

Under conditions above the tuyeres where the gases are oxidizing to the iron surfaces and the temperature is high enough for formation of wustite, oxidation of the solid charge will occur.

The kinetic model developed for the oxidation phenomenon has considered the thermodynamic limitations for the formation of wustite in terms of the partial pressure ratios of CO₂ and CO, and the temperature boundaries for stability of this phase.

For a PCO/PCO₂ ratio of 1.5 the wustite formation begins at approximately 700°C. At temperatures below 700°C, the oxidation rate is

slow. At PCO/PCO_2 ratios greater than 1.5, the minimum temperature at which stable iron oxide can form is given by:

$$T(^{\circ}\text{F}) = 317.4R + 228.25 = T(^{\circ}\text{C})$$

where $R = \text{PCO}/\text{PCO}_2$

The above equation indicates that at a ratio of $\text{PCO}/\text{PCO}_2 = 2.5$, the oxidation begins at approximately 1000°C . This is also the temperature at which the oxidation kinetics reach a significant rate.

Model Development for Oxidation of the Solid Charge

The scaling constant, that is the rate at which the iron oxide thickness grows as a function of time at a given temperature, has been used in the present oxidation model. The scaling function was obtained from the oxidation studies conducted by Himmel et al.⁵

Under isothermal conditions, if the time spent by the charge at temperature is known, then the amount of oxide grown at that temperature can be calculated as:

$$\Delta = (K/\rho)t^{0.5}$$

where:

Δ is the thickness grown at that particular temperature, cm

K is the scaling constant for iron oxide ($\text{gms}/\text{cm}^2 \text{ s}^{0.5}$) which is a function of temperature, $K = 0.9603\exp(-8930.8/T^{\circ}\text{K})$

ρ is the density of iron oxide,

t is the net time spent at that particular temperature.

The above equation assumes that the total time spent by the material is at one fixed temperature. To overcome that problem for the present situation in which the charge goes through a series of temperatures in the stack of a cupola, the following procedure was adopted.

1. The thermodynamic conditions for formation of wustite are determined by the model based on gas composition and temperature.
2. At each particular temperature (given favorable conditions for wustite formation), the oxide thickness of the incoming charge is converted to an

equivalent time value at the new temperature level using the equation given above.

3. Then to the above time value, the time spent by the charge at that temperature level is added to give the total equivalent time spent by the charge at that temperature.

4. The net equivalent time is then used in combination with the above equation to calculate the oxide thickness which exists after exposure at this new temperature.

5. The oxide thickness formed is then converted to an equivalent time for the next temperature and the procedure is repeated until the maximum temperature is reached.

Hence, the amount of iron oxidized in passage through the cupola stack can be evaluated. The heat evolved from the formation of iron oxide in each zone can be calculated, once the amount of iron oxide formed is specified.

An initial thickness of 0.01 cm of oxide has been assumed for all metallic charges. The model requires the user to specify an equivalent diameter for each kind of charge. Based on the equivalent diameter, a percentage of iron that gets oxidized is calculated using the procedure described above. Thus, for any charge mixture, containing cast iron and/or steel and based on their sizes, shapes and relative amounts, the total weight of iron oxide formed can be determined.

The amount of iron oxide generated relative to the weight of the metal charged has been tabulated below, along with the equivalent diameters of cast iron and steel, respectively.

Equivalent Diameter

Cast Iron = 9.9568cm

Steel = 0.378cm

<u>Run #</u>	<u>Iron to Steel Ratio</u>	<u>Iron oxide generated(wt %)</u>
7	3	8.1
8	0.45	14.7
10	1	11.0

It should be noted that as the iron to steel ratio decreases, i.e. the relative amount of steel in the charge increases the higher relative surface area results in a substantial increase in the amount of iron oxide formed.

COKE-SLAG REACTION

To investigate the extent of the reaction between coke lumps and the slag in the hearth of the cupola, the data from a study conducted by Cramb and Fruehan⁸ has been used. The authors measured the rate of the reaction between slags containing iron oxide and solid carbon.

They placed a rotating carbon rod in slags containing iron oxide and calculated the rate of reaction from the pressure change in the system. They also conducted experiments with a stationary rod, and results from these studies were used. These experiments were conducted in the temperature range 1300-1500°C.

Their kinetic data were applied to the coke-slag reaction in the hearth of the cupola. The rate constant for the reaction of FeO in slag with graphite is 4×10^{-6} mol/cm²sec. The parameters required to calculate the amount of iron oxide reacting with coke are given below:

Area of contact = 2×10^4 cm²

(assuming a coke lump with a diameter of 11 cm; for the GM Cupola).

Time = 2500 sec.⁶

Amount of iron oxide reaction = 15 kg (approx.)

The above amount of iron oxide accounts for approximately 3% or less of the total amount of iron oxide in the slag. Hence, the fraction of iron oxide consumed due to the reaction with coke can be neglected for these conditions.

This reaction must be further investigated to confirm the above findings. Since the work described above has been conducted with graphite, the kinetics may be different for coke, and hence experimental work is necessary to determine accurately the amount of iron oxide reacting with coke.

The model must account for the fact that as iron temperature increases the silicon loss decreases. This could be due to a more aggressive reaction between coke and FeO at higher temperatures or carbon

dissolved in iron may react more vigorously with FeO at higher temperatures. The coke-FeO reaction requires further study.

2. MATHEMATICAL MODELING OF SILICON BEHAVIOR IN THE CUPOLA

Silicon losses from the metal can occur in the cupola by several reaction steps. CO₂ desiliconization of solid iron has not been considered, and the quenched cupola experiments have shown this mechanism to be unimportant⁹.

Silicon loss in the cupola also could occur via oxidation by the gas phase, when the molten metal droplets fall through the coke bed. In a study conducted by Heine¹⁰, the author found that if silicon and carbon were present simultaneously, then carbon would preferentially get oxidized above a temperature of 1470°C, this corresponds to the temperature above which carbon is preferentially oxidized compared to silicon. This will be discussed in greater detail in a later section. It suffices to note at this stage that silicon oxidation by the gas phase corresponds to a zone in the temperature range from the melting point of cast iron to 1470°C. This accounts for a small distance in the cupola, and hence the time available for silicon oxidation is relatively small. Experimental work must be conducted to investigate the silicon oxidation kinetics, to determine the amount of silicon lost via oxidation from the metal droplets in the oxidizing gaseous mixture. However, for the current model liquid phase silicon oxidation by the oxidizing gas has been neglected.

Siliconization by Si-S(g) or SiO(g) from coke reactions could occur, although measurements by General Motors on coke in the tuyere area has shown no evidence that these reactions occurred to an appreciable extent.

The major zone of the furnace where silicon oxidation takes place is in the slag layer. In modeling oxidation of silicon in the slag, the droplet size was not considered because reaction with FeO approaches completion. However, there is competition among the silicon, carbon and manganese in the liquid iron for reaction with the FeO. This is illustrated schematically in Figure 4. Further experimental work is needed to determine the kinetics of alloy oxidation in the slag layer.

Figure 4: Schematic Diagram of the Slag Layer in the Hearth of the Cupola

To estimate the amount of silicon lost due to oxidation in the slag layer, the results from a kinetic study conducted by Narita et al.¹¹ have been used. The authors investigated the kinetics of oxidation of alloying elements in liquid iron with an iron oxide-bearing slag. Their results for slags containing more than 40% FeO, at a temperature of 1450°C, was used. In this case, they found that the rate of silicon oxidation was controlled by silicon transfer in the metal phase.

The data from the study conducted by Narita et al.¹¹, which has been used to compute the silicon loss in the slag layer has been incorporated in the model on the basis of assumption that in the slag layer a homogeneous metal stream exists. This assumption was made

since the kinetic study was only conducted for metal with high carbon and silicon contents.

They found that the iron oxide reacted with C, Si and Mn at a certain fixed ratio, which is 37%, 48%, and 15% of the total oxidation, respectively. The numbers indicate the relative mole percent of the particular element getting oxidized per unit time. Unfortunately, their results are not universal, and hence more experimental work is needed in this area. Important variables that need to be examined in these experiments are the metal composition, temperature and slag basicity. They assumed that the following reactions took place:

Model Verification

The model developed in this study was tested against industrial data made available by General Motors from an experimental investigation on a refractory lined cupola at Marquette MI. The dimensions of this cupola are given below.

Distance from charge door to metal tap hole = 7.8 m.

Distance from the lower tuyere row to the metal tap hole = 1.15 m.

External diameter of the cupola = 1.8 m.

Average internal diameter of the cupola = 1.5 m.

The cupola was operated with a 600°C blast temperature and the air was enriched with 2% O₂.

The charge materials were carefully characterized with regard to their dimensions and chemical composition. They have also measured the time-temperature profile along the cupola length. This information is required by the present model as an input. The time-temperature profile will be computer generated in the final model. The output metal also was characterized in terms of its chemical composition. This information was

then used to make comparisons with the model predictions. The model was run for the two types of charge material as separate streams.

The actual percentage silicon in the tapped metal along with that predicted by the model have been tabulated below for the three different runs.

<u>Run #</u>	<u>Iron to Steel</u> <u>Ratio</u>	<u>%Si (actual)</u>	<u>%Si (predicted)</u> <u>(Narita et al.¹¹)</u>	<u>%Si (predicted)</u> <u>(proportional)</u>
7	3	1.4	1.12	1.52
8	0.45	0.5	-0.55	0.53
10	1	0.7	0.18	0.88

Hence, experimental data is needed to ascertain the extent of silicon loss in the slag layer. Future work should be conducted in which metal droplets could be dropped through a slag layer and parameters such as height of slag layer, metal composition, etc. could be varied to ascertain their influence on silicon loss.

An initial layer of iron oxide is assumed to exist on the cast iron and steel charge materials. This initial layer represents an amount of iron oxide over and above that formed by gaseous oxidation of the solid charge. The magnitude of the contribution of this initial layer to the total iron oxide on the solid metallic charge materials is on the order of 40% of the total FeO.

This parameter of initial oxide thickness is a key variable in the reaction processes, and therefore it is imperative that a suitable test or method be developed to characterize the initial oxidation state of cupola charge materials.

Finally, with the multi-stream model, the metallic streams mix in the well of the cupola. At this point, it is necessary to consider heats of mixing of alloying elements, particularly significant is the heat of mixing of silicon due to ferrosilicon additions. The heats of solution in iron for silicon and carbon are:¹²

$$\text{Si(l)} = \underline{\text{Si}}(\%) \quad \Delta H^m = -28,500 \text{ cal/g-mole}$$

$$\text{C(gr)} = \underline{\text{C}}(\%) \quad \Delta H^m = 5,100 \text{ cal/g-mole}$$

3. MATHEMATICAL MODELING OF MANGANESE LOSS IN THE CUPOLA

Manganese loss in the cupola is assumed to be due to the reaction at the slag/metal interface when metal droplets fall through the slag layer by the reaction:

As discussed earlier, iron oxide formed in the stack of the cupola forms a part of the slag layer and oxidizes carbon, silicon and manganese, the relative rates of which were obtained from the work conducted by Narita et al.¹⁰. The manganese loss calculated using the kinetic data from the study conducted by Narita et al.¹¹ has been tabulated below, wherein manganese was assumed to be oxidized at a fixed relative ratio as described earlier. This manganese loss model, assumes homogeneous metal streams; due to the limitation of the kinetic data available.

The manganese loss has also been calculated assuming that manganese reacts with iron oxide in the slag layer, in proportion to its composition in the charge material. In this manganese loss model dual stream assumption has been made. The results have been tabulated below.

<u>Run #</u>	<u>% Mn (actual)</u>	<u>% Mn (predicted)</u> <u>(Narita et al.¹¹)</u>	<u>% Mn (predicted)</u> <u>(proportional)</u>
7	0.44	-0.41	0.42
8	0.22	-1.27	0.20
10	0.25	-0.90	0.26

The extent of manganese oxidation by the gas phase is negligible, since the temperature range over which manganese oxide is stable relative to carbon monoxide is relatively small⁷, and hence has been neglected in the current model. However, experimental work on oxidation kinetics in the slag is needed to verify the assumptions that have been made in this area; since data on the kinetics of manganese oxidation in the presence of iron oxide-bearing slags is scarce.

The data from General Motors for all the runs are currently unavailable. Hence, additional comparisons of the model with the manganese data will be conducted later when these data become available.

4. MATHEMATICAL MODELING OF CARBON BEHAVIOR IN THE CUPOLA

The extent of carbon transfer reactions in the solid stack is negligible, this has been discussed in greater detail in the next section. The metal in the cupola picks up carbon when the molten droplets are in direct contact with the coke lumps. As the different types of metallic charges reach their melting points in the stack of the cupola, the metal droplets thus formed drip through the coke bed, coming in direct contact with the coke. A major fraction of their residence times in the coke bed is spent in contact with coke. The free fall time is a small fraction of the total residence time. This has been confirmed by Shu-sen et al.¹³ They found that 93% of the total residence time of the metal droplets in the coke bed, is spent in contact with coke and only 7% of the total time accounts for free fall. The molten droplets also lose carbon simultaneously due to the oxidizing atmosphere in the cupola and also due to the reaction at the slag/metal interface. The various reactions affecting carbon concentration have been examined to determine their pertinence to the model.

Carburization/Decarburization in the Solid Stack

The saturation carbon level at the eutectoid temperature of 738°C is 0.02%. The charge materials, both cast iron and steel enter the cupola with carbon contents greater than 0.02%. Hence, up to the eutectoid temperature, no carbon pickup by the solid charge material is possible. Moreover, the diffusivity of carbon in irons at the eutectoid temperature is of the order of 10^{-15} cm²/sec, and hence no significant decarburization is possible. At higher temperatures where the diffusion coefficient increases in magnitude, and thus may lead to appreciable carbon transport in the solid charge; the variation of carbon concentration with distance from the surface of the charge material, can be expressed as follows:

$$\frac{C - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left[\frac{x}{2\sqrt{Dt}}\right]$$

where:

C_0 = Initial uniform carbon concentration

C_s = Equilibrium carbon concentration at the surface (as dictated by the ratio P_{CO}/P_{CO_2})

x = distance from the surface

C = carbon concentration at the distance x from the surface

D = diffusivity of carbon in iron at a particular temperature.

t = time

Model predictions indicated that the carbon content of the charge material decreased by around 0.02%, for a charge with 75% cast iron. This model assumed that separate streams of cast iron and steel were present in the cupola, that is dual stream assumption was made. These predictions were made in the absence of an oxide layer, which would significantly limit the extent of carbon transport.

The extent of carburization/decarburization of the solid charge in the stack of the cupola appears to be negligible and hence it has been ignored in the carbon pickup model.

Carbon Dissolution Mechanism

The cast iron and steel charges melt at different heights in the cupola, cast iron with a melting point of around 1150°C melts higher up compared to steel which has a melting point near 1500°C . The model assumes that the droplets of cast iron and steel fall through the cupola separately, that is, they do not mix until the very last stage in the cupola melting. The cast iron droplets fall through a greater height of the coke bed compared to the steel droplets, and hence their residence time in the coke bed is proportionately larger.

The carbon pickup is governed by the diffusion of carbon from the coke/metal interface to the bulk through a boundary layer while the molten metal droplet is in direct contact with the coke lump. The driving force for diffusion is the difference in the carbon saturation level for the particular type of charge and the bulk carbon content. The nature of the driving force for carbon pickup justifies the consideration of two separate metallic streams of cast iron and steel, respectively, since the carbon saturation and bulk levels are significantly different for the two materials, and do not permit the calculation of the driving force on an average basis. Besides, as pointed out earlier, the residence time for the two types of charges is not the same, due to the difference in their melting points, and hence taking an average time is also not acceptable, since it would not represent the physical phenomenon correctly.

In the slag layer, the coke lumps are covered with slag which occupies a major fraction of the volume of the hearth of the cupola. Hence, the metal droplets rarely come in contact with coke, and hence carbon

pickup in the slag layer cannot occur to any appreciable extent. This has been observed by Selby and Coon¹⁴, who studied the increase in carbon pickup due to an increase in the well-depth.

Model Development

The carbon pickup can be represented by the following equation¹³:

$$V \frac{d(\%C)}{dt} = -(D/\delta) \cdot A \cdot [\%C - \%C(\text{sat})]$$

where:

V is the volume of the droplet,

%C is the carbon level at any time t,

%C(sat) is the saturation carbon level which is a function of composition of the charge material and temperature,

D is the Diffusivity of carbon in the liquid metal,

δ is the boundary layer thickness,

A is the area of contact over which carbon pickup occurs.

The method by which the size of the metal droplet was calculated has been elaborated upon later. The droplet in contact with a coke lump is assumed to have a hemispherical shape, hence the contact area with coke over which carbon pickup occurs, is essentially the area of the base of the hemisphere, which can be estimated once the volume of the droplet is calculated. This is shown schematically in Figure 5. At this time the carbon level is expressed as concentration; at a later stage the model will be modified to express these transfer reactions in terms of thermodynamic activity¹.

Figure 5: Schematic Diagram of a Molten Metal Droplet on a Coke Lump indicating the Carbon Transfer Reactions.

The boundary layer thickness has been calculated from the correlation, that has been graphically represented in the work done by Olsson et al.¹⁵. The authors studied the rate of dissolution of carbon in molten Fe-C alloys by rotating cylindrical graphite samples in a stationary crucible containing the melt. Their correlation is:

$$D/\delta = (\text{const}) V^{0.7}$$

where V is the velocity of the droplet. From their plot, assuming a velocity of about 100 cm/s (This relatively large value was selected because of the presence of internal turbulence in the droplets as they move over the coke), the D/δ value obtained was of the order of 0.05 cm/s. The value of D ~

$5 \times 10^{-5} \text{ m}^2/\text{s}$. This gives a value of δ equal to 0.001cm, which is approximately 0.2% of the radius of the metal droplet.

Integrating the carbon pickup equation between the limits of the initial and final carbon levels in a time period 't' leads to,

$$n[\%C(\text{sat}) - \%C(\text{ini})]/[\%C(\text{sat}) - \%C(\text{fin})] = (D/\delta) \cdot (A/V) \cdot t$$

where:

$\%C(\text{ini})$ is the initial carbon level at time $t=0$,

$\%C(\text{fin})$ is the final carbon level at time $t=t$,

t is the time period over which carbon pickup occurs.

The mathematical model discretizes the cupola into different temperature zones in which the carbon pickup takes place. The temperature distribution over the height of the cupola was made available by General Motors for three different runs. The temperature profile in the cupola was made available by General Motors up to around 1300°C. Beyond that the temperature values were obtained by extrapolation of the data to the tuyeres. In the well zone, the temperature was extrapolated on the basis of the known top temperature; and the assumption that there is approximately a 750°C drop in the well zone because of incomplete combustion at the tuyere level and below that (down to the tapchase due to heat losses through the walls. These assumptions must be experimentally verified. Hence, it is essential that temperature profile measurements in the cupola be conducted, down to the slag layer, if accurate model predictions are to be made.

The first temperature zone is located at the melting point of the charge materials, and the last temperature zone is located immediately above the slag layer. The model calculates the carbon pickup for the two different types of charges, cast iron and steel.

The steps involved in the modeling procedure are outlined below:

1. The molten droplet enters the first carbon pickup zone at its melting point, with its carbon level equal to the carbon present in the input charge, which is the $\%C(\text{ini})$ for this particular zone. The droplet spends a given amount of time in the zone during which carbon diffuses into the bulk, since the bulk carbon content is less than the saturation level. At the end of the

time period the carbon level, which is the %C(fin), is greater than the initial level.

2. The droplet now exits from this temperature zone and moves into the next zone, during which it comes in contact with other coke lumps.

3. Thus in the next zone the initial carbon level is the final carbon content of the previous zone, and the carbon picked up in this zone can then be estimated. Hence, in this manner the carbon level at the end of each zone can be calculated.

4. The %C(fin) of the last zone thus represents the final carbon level of the metal. This is not the carbon content of the tapped metal since the droplet loses carbon due to oxidation as mentioned earlier.

To determine the carbon pickup accurately, the parameters involved in the modeling had to be calculated. The following sections describe the technique used to estimate each of the parameters.

Size of the metal droplet

The maximum stable size of the metal droplet was estimated from first principles. A force balance was conducted, equating the force due to the weight of the droplet and the surface tension forces, as illustrated in Figure 6. The force balances can be expressed as:

$$mg = \gamma \ 2\pi r$$

$$\frac{4\pi r^3}{3} \rho g = \gamma \ 2\pi r$$

where:

r is the radius of the particular droplet, that is either cast iron or steel,
 ρ is the respective density,
 g is the acceleration due to gravity,
 γ is the surface tension of the metal.

Figure 6: Schematic Diagram indicating the Forces acting on a Falling Metal Droplet.

The values of surface tension and density for cast iron and steel were determined from reference¹². They are shown below along with the radius of the droplet. It is recognized that surface tension varies markedly with sulfur content, and therefore it is important to establish the sulfur concentration of iron and steel droplets as they move downward through the cupola.

<u>Droplet</u>	<u>Density(gms/cm³)</u>	<u>Surface tension(dynes/cm)</u>	<u>Radius(cm)</u>
Cast iron	6.5	620	0.382
Steel	7.15	1590	0.583

Carbon Saturation level

The solubility limit of carbon in iron is a function of temperature and its composition, and is given by the following¹⁶,

$$\%C(\text{sat}) = 1.3 + 0.00257T - 0.31\%Si - 0.33\%P - 0.45\%S + 0.28\%Mn$$

where:

- T is the temperature in °C,
- %Si is the percentage of silicon in the charge,
- %P is the percentage of phosphorus in the charge,
- %S is the percentage of sulfur in the charge,
- %Mn is the percentage of manganese in the charge.

Contact time

The total residence time of the droplet in the coke bed is estimated from the equation presented in the study conducted by Tsuchiya et al.¹⁷, which is a function of the distance through which the droplets fall, the volume velocity of iron and the dynamic hold-up of iron. The dynamic hold-up can be estimated by the empirical correlation developed by Ohtake and Okada¹⁸. The dynamic hold-up of iron is a function of several variables, such as surface area of the coke per unit volume and hence the diameter of the coke lumps, mass velocity of the liquid, viscosity and density of the droplets. The total residence time thus obtained was divided by the number of temperature zones, to obtain the time spent by the droplets in each zone.

The residence time was calculated as follows:

$$t = \frac{h \cdot H_d}{U_L}$$

where:

- h = distance through which the metal droplets fall in the cupola (m)
- U_L = volume velocity of iron ($\text{m}^3/\text{h-m}^2$)

H_d = dynamic hold-up of iron (m^3/m^3)

where:

$$H_d = 21.2 \left(\frac{D_p N}{\mu_L} \right)^{0.51} \left(\frac{D_p^3 g \rho_L^2}{\mu_L^2} \right)^{-0.44} (a_s D_p)^{-0.60}$$

where:

D_p = diameter of coke lumps

N = mass velocity of liquid iron

μ_L = viscosity of liquid

ρ_L = density of liquid

a_s = surface area of coke per unit volume

g = acceleration due to gravity

Some typical residence times in seconds are given below.

<u>Run #</u>	<u>Cast iron</u>	<u>Steel</u>
7	34	30
8	29	18
10	24	18

Slag-layer height determination

It is important to estimate the height of the slag layer in the hearth of the cupola. Since it is essentially one of the determining factors of the total distance over which the carbon pickup occurs. The molten metal droplets are in contact with the incandescent coke from their melting point onwards until the slag layer. Hence, the height of the slag layer is crucial if the distance over which carbon pickup occurs has to be calculated.

The height of the slag layer can be calculated as follows¹⁹:

$$S(\text{cm}) = y(\text{cm}) - 7.71 P_c (\text{gms})$$

where:

S is the depth of the slag above the top of the slag taphole,

Y is the height of the slag dam above the top of the slag hole,

Pc is the pressure inside the cupola.

Results of the Carbon Dissolution Model

The results of the carbon pickup model have been presented in this section. As mentioned earlier, these carbon contents are not that of the tapped metal, since the carbon lost due to oxidation has to be accounted for before the final carbon content is predicted. Thus, the values shown in the table below, are greater than the final carbon content.

<u>Run #</u>	<u>%C (actual)</u>	<u>%C(predicted)</u> <u>(cast iron)</u>	<u>%C(predicted)</u> <u>(steel)</u>	<u>%C(predicted)</u> <u>(average)</u>
7	3.57	4.70	4.89	4.75
8	2.75	4.68	4.73	4.71
10	3.43	4.77	5.27	5.02

Carbon loss due to oxidation at the metal/gas interface

The elements present in the molten iron that could get oxidized by CO₂ are C, Si and Mn. It had to be first established whether their oxidation occurred simultaneously or whether each of these elements had certain temperature ranges in which they were preferentially oxidized. As indicated earlier, in a study conducted by Heine¹⁰, the author found that there were limiting temperature ranges in which a particular oxide was formed. Considering carbon and silicon, they found that carbon was oxidized compared to silicon at temperatures greater than 1470°C, but below this temperature silicon was oxidized preferentially. (The oxidation experiments were conducted for over an hour.) This temperature also corresponds to the equilibrium temperature for the reaction indicated below:

Thus carbon oxidation starts only above a temperature of 1470°C and terminates at the tuyeres due to lack of oxygen below the tuyere level²⁰. Hence the residence time was calculated as explained before, from the height in the cupola at which this temperature was achieved upto the tuyere level.

The rate of oxidation of carbon was obtained from the work conducted by Fruehan and Martonik²¹. The rate depends on the time of exposure, the partial pressure of CO₂ and the surface area to volume ratio available. They examined the rate of decarburization of liquid iron in CO-CO₂ mixtures and hydrogen at 1800°K. The rate of decarburization in CO-CO₂ mixtures at high carbon contents was seen to be controlled primarily by diffusion in the gas film boundary layer near the surface of the liquid. The presence of 0.3 wt pct sulfur was seen to reduce the rate of decarburization in CO-CO₂ mixtures by about 10%, indicating that a slow chemical reaction on the surface affects the rate slightly when the surface is covered with sulfur atoms.

This carbon loss model is a dual stream model; that is it assumes that cast iron and steel droplets descend through the coke bed in separate streams and do not mix until they reach the hearth of the cupola. The tabulated values of carbon loss thus represent the total amount of carbon lost from cast iron and steel, respectively.

The parameters required to calculate the amount of carbon lost due to oxidation are given below for cast iron and steel, along with the time period over which oxidation occurs. The droplet shape on the coke lump is assumed to be hemispherical hence the surface of the hemisphere is the area over which carbon loss due to oxidation occurs.

The total surface area of exposure for the various runs was obtained by taking the weight of one charge as the basis for all the calculations. The area to volume ratios for the cast iron and steel were taken as 6.23/cm and 4.087/cm, respectively.

The rate of reaction of carbon from the study conducted by Fruehan and Martonik²¹ is 6×10^{-3} gms/cm² min. The total carbon lost due to oxidation has been tabulated below.

Run #	Total Surface Area, cm ²		Reaction Time, min.		C loss %
	Cast Iron	Steel	Cast Iron	Steel	
7	5.7×10^6	1.1×10^6	0.284	0.290	0.146
8	2.0×10^6	2.6×10^6	0.120	0.089	0.042
10	3.5×10^6	2.1×10^6	0.056	0.041	0.023

These results show that carbon oxidation by the gas phase is significant.

Carbon loss due to oxidation in the slag layer

The carbon present in the molten iron is oxidized by the iron oxide present in the slag layer as the metal droplets fall through the the slag at the bottom of the cupola. As mentioned earlier, the kinetic data for the oxidation of the metal was taken from the study conducted by Narita et al.¹¹.

Since the carbon loss model in the slag layer due to reaction with iron oxide, used the kinetic data from the study conducted by Narita et al.¹¹, as explained earlier, similar to the silicon loss model in the slag layer, a homogeneous metal stream assumption had to be made, due to the nature of the kinetic data and the limitations encountered in its applicability. The carbon loss due to oxidation in the slag layer also has been calculated on the basis of the proportional weight method described earlier.

The weight of carbon lost due to oxidation is tabulated below:

<u>Rur #</u>	<u>C loss % (Narita et al¹¹)</u>	<u>C loss % (Proportional)</u>
7	0.50	1.01
8	0.90	2.14
10	0.67	1.53

Prediction of final Carbon

Thus, the carbon content of the tapped metal can be calculated by taking the difference between the carbon pickup as predicted by the model, and the carbon lost due to oxidation at the metal/gas interface and at the metal/slag interface. The reactions that have in effect been considered are given below.

Carbon dissolution

$$C(gr) = \underline{C}$$

Carbon loss due to oxidation by the gas phase

Carbon loss due to oxidation in the slag layer

The carbon content of the tapped metal as calculated and that observed in practice is shown in the table below.

<u>Run #</u>	<u>%C(actual)</u>	<u>%C(predicted)</u> <u>(Narita et al¹¹)</u>	<u>%C (predicted)</u> <u>(Proportional)</u>
7	3.57	4.10	3.59
8	2.75	3.77	2.53
10	3.43	4.33	3.47

The underestimated values of the predicted carbon content can be attributed to several factors, including a lower estimated temperature in region of liquid metal-coke contact, an underestimation of residence time, and an overestimation of the boundary layer thickness. Further work is needed to specify these parameters with greater accuracy.

5. MATHEMATICAL MODELING OF SULFUR BEHAVIOR IN THE CUPOLA

The reactions involving sulfur transfer in the cupola occur in three stages, they are: the sulfidation of the solid charge in the stack of the cupola, the sulfur absorption by the molten metal droplet and sulfur transfer by the slag/metal reaction in the hearth of the furnace.

Sulfidation of the solid charge in the cupola stack

The kinetic data for the formation of iron sulfide can be obtained from the study conducted by McKee and Druschel²², in which they measured the sulfidation rates of iron over the sulfur pressure range of 1-10³ Pa. The data for iron sulfidation is available but it may not be applicable in the present situation. Since in the cupola simultaneous oxidation and sulfidation occur in the stack and hence experimental studies have to be conducted to ascertain the sulfidation rate in the presence of an oxide layer. The data compiled by Lillybeck⁶ demonstrates that the surface area to volume ratio is an important variable in determining the extent of sulfur pickup by the metal. Due to lack of kinetic data, the empirical correlation developed by Lillybeck⁶ will be used in the initial modeling stages. The empirical correlation developed by Lillybeck is based on the results of Carter and Carlson²³. The equation is of the following form:

$$y = 1 - e^{-J(S_{\text{coke}} + S_{\text{metal}})}$$

where:

y = % of total coke sulfur reacting with metallic charge materials

S_{coke} = surface area per unit weight of coke

S_{metal} = surface area per unit weight of metal

J = constant

This equation estimates the percentage of sulfur in the coke that is transferred to the metal and slag and/or off-gases as a function of the surface area of the charge materials.

The factors governing the rate of iron sulfide formation are, the surface area of the charge, the temperature distribution in the cupola, the exposure time and the partial pressure of sulfur dioxide gas. The iron oxide layer will provide resistance to the sulfidation in the solid stack. The model for the sulfidation of the solid charge will be developed on a similar basis as the previous models. The height of the cupola will be discretized into several temperature zones. The first temperature zone that will be considered is the zone with the highest temperature at which sulfide formation is thermodynamically possible. This zone will have the largest concentration of SO₂ gas which will successively decrease as the height of the cupola increases, as greater quantities of metal sulfide are formed.

Sulfur absorption by molten metal droplet

In a study conducted by Abe²⁴, the author found that an appreciable amount of sulfur was absorbed by the metal in the liquid state depending on the partial pressure of sulfur in the gas phase. In the experimental work, specimens with cast iron composition were heated in a ceramic tubular furnace. The furnace was held at a predetermined temperature, and SO₂ gas was blown in at the rate of 200cc/min for 20 min. They found that at a temperature of 1200°C the sulfur increased by 5%. The results of Abe²⁴ have been used to estimate the final S level in the tapped metal.

<u>Run #</u>	<u>Input %S</u> <u>(in metallic charge)</u>	<u>Predicted Tapped %S</u> <u>(in tapped metal)</u>
7	.087	.0914
8	.042	.044
10	.0725	.076

The sulfur transfer in the gas phase could be eliminated as being the rate controlling step. This can be suggested from the study conducted by Carter and Carlson²³, who found that the sulfur pickup did not change with a significant variation in the blast rate. Thus the sulfur transfer is apparently limited by transport in the liquid/solid phases.

This limited experience should be further expanded, and experimental work is needed to ascertain further the rate and mechanism of sulfur pickup by the charge in the liquid state.

Reaction at the slag/metal interface

The iron sulfide formed in the stack of the cupola melts and forms a part of the slag layer. The desulfurization reaction in the slag layer has been shown to approach equilibrium²⁵, hence once the amount of iron sulfide in the slag has been determined accurately, the sulfur level in the metal can be predicted. Sulfur can be transferred from the iron to slag through the reactions given below²⁵.

which would be accounted for by the following reactions²⁵:

Data on the chemical composition of the metal droplets just before entering the slag layer and the tapped metal composition, along with the

relevant slag composition and temperature, could be used to evaluate the importance of each of these reactions, and to establish an improved model for this chemical process.

6. THERMOCHEMICAL DATA FOR RELEVANT REACTIONS IN THE CUPOLA

A summary of thermochemical data for relevant reactions in the cupola is presented in this section. (The free energy is in cal/mole and the standard states are 1 wt% in Fe. for the dissolved elements).

In the well zone, silicon loss takes place by the following reaction²⁶:

Also note that:

Manganese transfer in the slag layer takes place by the following reaction²⁷ :

Sulfur transfer reactions in the slag layer, which approach equilibrium, are given below^{28,29}:

$$\Delta G^\circ = -5,380 + 7.06T$$

$$\Delta G^\circ = -46,030 + 25.5T$$

$$\Delta G^\circ = -46,130 + 21.33T$$

The reactions involving carbon are given below:

$$\Delta G^\circ = -94,755 + 0.02T$$

$$\Delta G^\circ = -28,200 - 20.16T$$

$$\Delta G^\circ = 38,355 - 40.34T$$

$$\Delta G^\circ = 5,100 - 10.0T$$

The heat of formation of iron oxide as a function of temperature is given below:

For $T < 1033^\circ\text{K}$

$$\Delta H = 5.25T - 3.33 \times 10^{-3}T^2 - 1.07 \times 10^5/T - 894$$

For $1033^\circ\text{K} < T < 1179^\circ\text{K}$

$$\Delta H = -1.78T + 0.22 \times 10^{-3}T^2 - 1.55 \times 10^5/T + 2210$$

For $T > 1179^\circ\text{K}$

$$\Delta H = 3.77T - 1.28 \times 10^{-3}T^2 - 1.55 \times 10^5/T - 2460$$

7. KINETIC DATA

The scaling constant data for iron oxide was obtained from the oxidation studies conducted by Himmel et al.⁵, as given below:

$$K \text{ (gms/cm}^2 \text{ s}^{0.5}) = 0.9603 \exp(-8930.8/T^\circ\text{K})$$

The diffusivity of carbon in liquid metal does not vary significantly with temperature; the data used are given below¹²:

For cast iron: $D = 6.7 \times 10^{-5} \text{ cm}^2/\text{s}$

For steel: $D = 7.2 \times 10^{-5} \text{ cm}^2/\text{s}$

The diffusivity of sulfur in liquid iron-carbon alloys, at 1400°C , is³⁰:

$D = 3.5 \times 10^{-5} \text{ cm}^2/\text{s}$

8. REQUIREMENTS FOR FURTHER RESEARCH

Comparisons of the modeled reactions with the results of three well documented cupola trial periods have met with reasonable success. However, it is clear that some assumptions made in the modeling effort require additional assessment and evaluation. In particular, the residence time, transport parameters and other rate controlling properties important in the carbon pick-up model require direct experimentation. This effort will be a key aspect of the phase II portion of the research project.

In addition, the kinetic aspects of oxidation of metal droplets in the tuyere zone and slag/metal reactions in the well of the cupola furnace have been studied and reported in the literature for various experimental conditions. An extensive assessment of these data will be made in phase II of the project, and additional specific experimental studies would be undertaken as required to support these aspects of the modeling effort.

Finally, the need for further research in all the various aspects of the work has been pointed out at various locations in this report, along with specific comments in each case, pointing out the nature of data that is required to complete the modeling study more accurately.

SUMMARY

Mathematical models have been developed in this study to predict the composition of the tapped metal. Compositions could be predicted by the various models with reasonable accuracy compared to experimental data for runs conducted by General Motors. Hence, these models can be used to predict the final composition of the metal tapped from a cupola, and are being included in the dynamic computer model of the cupola melting furnace.

References

1. C. Landefeld and S. Katz: "A dual stream model of Carbon pickup based on carbon activity". General Motors Research Laboratories, Research report No. MR-1005.
2. C. Landefeld: "Chemical Processes and Heat Loss in Cupolas", Foundry Processes: Their Chemistry and Physics, Plenum Press, New York, 1988.
3. F.S. Pettit and J.B. Wagner, Jr.: "Transition from the Linear to the Parabolic Rate Law during the Oxidation of Iron to Wustite in CO-CO₂ Mixtures", Acta Metallurgica, Vol.12, 1964, pp.35-40.
4. F.S. Pettit, R. Yinger and J.B. Wagner, Jr.: "The Mechanism of Oxidation of Iron in CO-CO₂ Mixtures", Acta Metallurgica, Vol.8, 1960, pp.617-623.
5. L. Himmel, R. F. Mehl and C. E. Birchenall: "Self-Diffusion of Iron in Iron Oxides and The Wagner Theory of Oxidation", Trans AIME, Vol. 197, 1953, pp. 827-843.
6. N. P. Lillybeck: John Deere Technical Center, Personal Communication.
7. Kun Li, "Equilibrium of Iron-Oxygen-Carbon Systems at 1 atm", Proc. Blast Furn. Conf. AIME, 1960, Vol. 19, p. 162.
8. B. Sarma, A. W. Cramb and R. J. Fruehan: "Reduction of FeO in Smelting Slags by solid Carbon", CISR Progress Report, April 5, 1990.
9. Lownie, H.W., Jr. D.E. Krause and C.T. Greenidge: AFS Transactions, Vol. 68, pp. 766-774.
10. R. W. Heine: Trans. AFS., Vol. 59, 1951, pp. 121-138.
11. K. Narita, T. Makino, H. Matsumoto, A. Hikosaka and J. Katsuda: Tetsu-to-Hagane, 1983, pp. 1722-1729.
12. J. F. Elliott, M. Gleiser and V. Ramakrishna: "Thermochemistry for Steelmaking", Vol.2, 1963, Addison-Wesley.

13. W. Shu-sen, W. Li-biao and Z. Chen-fu: Cast Metals, Vol. 2, No 1, 1989, pp. 46-51.
14. M.J. Selby and P.M. Coon, BCIRA Report 1289, in BCIRA Journal, 26, No. 1, Jan. 1978.
15. R. G. Olsson, V. Koump and T. F. Perzak: Trans. Met. Soc. AIME, Vol. 236, April 1966, pp. 426-429.
16. F. Neumann, H. Schenck and W. Patterson: Giesserei, Vol. 47, 1960, pp. 25-32.
17. N. Tsuchiya, M. Tokuda and M. Ohtani: Metall. Trans. B, Vol 7B, 1976, pp. 315-320.
18. T. Ohtake and K. Okada: Kagaku Kogaku, Vol. 17, 1953, pp. 176.
19. H. A. Edge, Jr: Cupola Handbook, Des Plaines II, 1984, pp. 235-239.
20. S. Katz: General Motors Research Laboratories, Personal Communication.
21. R. J. Fruehan and L. J. Martonik: Metall. Trans., Vol. 5, 1974, pp. 1027-1032.
22. R. A. McKee and R. E. Druschel: Journal of the Electrochemical Society: Solid State Science and Technology, April 1984, pp. 853-857.
23. S. Carter and R. Carlsson: Trans. AFS, Vol. 62, 1954, pp. 267-281.
24. K. Abe: 43rd International Foundry Congress, No. 12, Bucharest, Romania, 1976.
25. S. Katz: Cupola Handbook, Des Plaines II, 1984, pp. 351-363.
26. S. Katz and V. R. Spironello: AFS Trans., Vol. 92, 1984, pp. 161-172.
27. E. T. Turkdogan: Metall. Trans. B., Vol. 9B, 1978, pp. 163-179.
28. J. F. Elliott and M. Gleiser : "Thermochemistry for Steelmaking", Vol.1, 1961, Addison-Wesley.

29. R. D. Pehlke: "Unit Processes in Extractive Metallurgy", American Elsevier Publishing Co., 1973.
30. Y. Kawai: Journal of the Japan Institute of Metals, Vol. 20, No. 9, 1956, pp. 517-520.

END

DATE FILMED

12 / 12 / 90