Crystallization of Synthetic Blast Furnace Slags Pertaining to Heat Recovery

by

Shaghayegh Esfahani

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Materials Science and Engineering
University of Toronto

© Copyright by Shaghayegh Esfahani, 2016
Crystallization of Blast Furnace Slags Pertaining to Heat Recovery

Shaghayegh Esfahani
Doctorate
Materials Science and Engineering
University of Toronto
2016

Abstract

Heat recovery from blast furnace slags is often contradicted by another requirement, to generate amorphous slag for its use in cement production. As both the rate and extent of heat recovery and slag structure are determined by its cooling rate, a relation between the crystallization kinetics and the cooling conditions is highly desired.

In this study, CaO-SiO₂-Al₂O₃-MgO (CSAM) slags with different basicities were studied by Single Hot Thermocouple Technique (SHTT) during isothermal treatment and non-isothermal cooling. Their time-temperature-transformation (TTT) and continuous-cooling-transformation (CCT) diagrams were plotted and compared with each other. Furthermore, kinetic parameters such as the Avrami exponent \((n)\), rate coefficient \((K)\) and effective activation energy of crystallization \((E_A)\) were found by analysis of data obtained from in-situ observation of glassy to crystalline transformation and image analysis. Also, the dependence of nucleation and growth rates of crystalline phases were quantified as a function of time, temperature, and slag basicity. Together with the observations of crystallization front, they facilitated establishing the dominant mechanisms of crystallization.

In addition to the experimental work, a mathematical model was developed and validated that predicts the amount of crystallization during cooling. A second mathematical model that
calculates temperature history of slag during its cooling was coupled with the above model, to allow studying the effect of parameters such as the slag/air ratio and granule size on the heat recovery and glass content of slag.
In the Name of God

To my parents, my husband and my brother...
Acknowledgments

First and foremost I offer my sincerest gratitude to my advisor and mentor, Prof. Mansoor Barati, for his full support, patience and immense knowledge. I have been remarkably fortunate to have a supervisor who gave me the freedom to explore on my own and at the same time provide full guidance at any time that was needed.

I am grateful to all the members of my Ph.D. advisory committee, Prof. McLean, Prof. Stavros Argyropoulos, Prof. Ravi Ravindran and Prof. Charles Jia for their constructive suggestions.

I would also like to acknowledge my colleague Dr. Karim Danaei, Daniel Budurea from Dtek Electronics Ltd. and Dr. Sina Mostaghel from Hatch Ltd. for their assistance.

I owe my deepest gratitude to my father and mother whose unwavering support and unconditional love from thousands of miles away made this undertaking possible.

This thesis would not have been possible without my unbelievably supportive, patient and loving husband, Dr. Farshid Bahrami. His continuous encouragement and endless love brightened the most frustrating moments of my work and helped me move on. I would also like to thank my brother, Matin, for being an extra source of inspiration and strength in my life, particularly during the early years of being away from home.

I would like to thank the University of Toronto Open Fellowship, Ontario Government, Natural Sciences and Engineering Research Council of Canada (NSERC) and Hatch Ltd. for their financial support.
# Table of Contents

Acknowledgments...........................................................................................................v

Table of Contents........................................................................................................... vi

List of Figures .......................................................................................................................x

List of Tables ...................................................................................................................... xvi

List of Symbols ................................................................................................................... xix

List of Acronyms ............................................................................................................... xxi

Chapter 1 ..........................................................................................................................1

1 Introduction ....................................................................................................................1

Chapter 2 ..........................................................................................................................5

2 Literature Review ..........................................................................................................5

2.1 Energy recovery from metallurgical slags ...............................................................5

2.1.1 Metallurgical slags ..............................................................................................5

2.1.2 Use of slag as cement feedstock .......................................................................7

2.1.3 Slag Granulation ...............................................................................................8

2.1.4 Energy content of slags ...................................................................................9

2.1.5 Review of energy recovery methods ..................................................................11

2.1.6 Evaluation of energy recovery methods ..............................................................27

2.2 Crystallization of slag .............................................................................................31

2.3 Summary ....................................................................................................................33

Chapter 3 ..........................................................................................................................36

3 Experimental ...............................................................................................................36

3.1 Hot Thermocouple Technique (HTT) .................................................................36
3.1.1 The Development of the hot thermocouple technique .............................................. 37
3.1.2 Description of the hot thermocouple technique (HTT) ........................................... 39
3.1.3 Modified HTT ................................................................................................................. 40
3.1.4 Hardware Controller ....................................................................................................... 43
3.1.5 Power supplies and thermocouple power driver .......................................................... 46
3.1.6 Verification of temperature measurement ....................................................................... 47
3.2 Sample Preparation ........................................................................................................... 49
3.3 Experimental Procedure ................................................................................................... 51
  3.3.1 Isothermal Experiments ............................................................................................... 51
  3.3.2 Continuous cooling experiment .................................................................................... 52
Chapter 4 ................................................................................................................................. 54
  4 Crystallization behavior ...................................................................................................... 54
    4.1 Visualization of Crystallization ....................................................................................... 54
      4.1.1 Slags with high basicity (NBO/T ≥ 1.71) .................................................................. 54
      4.1.2 Slags with low basicity (NBO/T<1.71) .................................................................... 58
    4.2 Determination of the crystalline phases ....................................................................... 60
    4.3 Time-Temperature-Transformation (TTT) diagram ...................................................... 61
    4.4 Continuous Cooling Transformation (CCT) diagram .................................................... 63
Chapter 5 ................................................................................................................................. 65
  5 Prediction of the critical cooling rate ................................................................................... 65
    5.1 Critical Cooling Rate ....................................................................................................... 66
      5.1.1 Relationship between slag composition and critical cooling rate ......................... 68
      5.1.2 Dependence of critical cooling rate on viscosity ..................................................... 69
Chapter 6.................................................................80
  6  Kinetics of crystallization .........................................................80
      6.1 Theoretical treatment of transformation ........................................80
      6.2 Experimental determination of phase change ........................................84
      6.3 Determination of the Avrami exponent \( (n) \) and rate coefficient \( (k) \): ..........86
      6.4 Nucleation .................................................................................89
          6.4.1 Dependence of nucleation rate on temperature .................................89
          6.4.2 Time dependency of nucleation rate .................................................91
      6.5 Growth .......................................................................................92
          6.5.1 Activation energy of growth ..........................................................97
      6.6 Mechanism of slag crystallization ...................................................99
      6.7 Effect of impingement on growth rate ...............................................100
      6.8 Effective activation energy of crystallization .......................................101

Chapter 7......................................................................................110
  7  Mathematical modeling of slag crystallization and heat recovery .................110
      7.1 Modeling the heat recovery process ..................................................110
          7.1.1 Assumptions..............................................................................110
          7.1.2 Enthalpy method ......................................................................112
          7.1.3 Enthalpy method vs. variable time step (VTS) method .......................113
          7.1.4 Numerical solution ......................................................................114
          7.1.5 Analytical alternative of the “heat recovery” mathematical model ..........120
          7.1.6 Temperature profile of slag droplets ..............................................122
      7.2 Modeling the amount of glassy content ..............................................123
      7.3 Effect of operating parameters on heat recovery and slag structure ..........128
7.3.1 Effect of air to slag ratio ................................................................. 128

Chapter 8 ........................................................................................................... 133

8 Contributions and conclusions ....................................................................... 133

8.1 Conclusions ................................................................................................... 133

8.2 Contributions ................................................................................................ 135

8.3 Publications .................................................................................................. 136

9 Future Research Directions ............................................................................ 138

Bibliography ....................................................................................................... 140

Appendix A ......................................................................................................... 152

Appendix B ......................................................................................................... 153
List of Figures

Figure 1.1- Schematic figure of the research plan of the study. .......................................................... 3

Figure 2.1- Temperature dependence of heat content for a typical blast-furnace slag [31]. ........ 11

Figure 2.2 - Temperature history of a 5 mm slag drop in fluidized bed [8]. ................................. 12

Figure 2.3 - Appearance of slag granulation by RCA with cup rotation speed of 3000 rpm [41]. 14

Figure 2.4 - Schematic diagram of Rotary Cup Atomizer [31]. ....................................................... 14

Figure 2.5 - (a) slag atomization on the spinning disc and (b) granulated slag product [23, 50]. 16

Figure 2.6 - Process flow diagram of the rotary–drum granulation–heat recovery system [8]... 17

Figure 2.7 - Plant lay–out of Merotec slag granulation process [55]. ............................................. 18

Figure 2.8 - Schematic diagram of slag air granulation and heat recovery [26]. ......................... 19

Figure 2.9- Schematic of process developed by Paul Wurth [60]. .............................................. 20

Figure 2.10- Schematic of the process developed by JFE [62]..................................................... 21

Figure 2.11 - Process flow diagram for energy recovery through methane reforming [42]. ... 23

Figure 2.12 - Steam reforming of methane using granulated slag heat [64]............................... 24

Figure 2.13 – Coal gasification process [67]. ................................................................................. 26

Figure 2.14 - Steam reforming of methane using granulated slag heat [64]............................... 30

Figure 2.15- TTT diagram of BF slag by Kashiwaya et al. [72]. ............................................... 31

Figure 2.16 – CCT diagram of BF slag by Kashiwaya et al. [72]. ............................................... 31
Figure 2.17 - TTT diagram of BF slag by Qin et al. [73] ................................................. 32

Figure 2.18 - CCT diagram of BF slag by Qin et al. [73] .................................................. 32

Figure 2.19 – TTT diagram of synthetic BF slag with varying Al₂O₃ content by Sun et al. [66], CaO/SiO₂=1.0, A₁=11wt%, A₂=20wt%, A₃=23wt% ................................................................. 33

Figure 3.1 - Basic circuit diagram of the first hot thermocouple apparatus (a) by Ordway [96] (b) by Welch [97]. .................................................................................................................. 38

Figure 3.2 - Comparison of the single and double hot thermocouple setups [77]. ............... 39

Figure 3.3 - Schematic of the thermocouple tip. .................................................................... 40

Figure 3.4 - Schematic view of the HTT setup. ................................................................. 40

Figure 3.5 – Schematic figure showing the principal of AC based HT controller [77]........... 41

Figure 3.6 – Schematic figure showing the principal of the modified DC based HT controller. 41

Figure 3.7 - Simplified block diagram of the new concept target design. ....................... 43

Figure 3.8 - Hot thermocouple controller block diagram. ................................................. 45

Figure 3.9 - Schematic diagram of the timing of the power supply and acquisition ............ 46

Figure 3.10 - Melting temperature measurement for HTT apparatus calibration a) Na₂SO₄ b) CaF₂................................................................................................................................. 48

Figure 3.11 - Derivative of the time-temperature curve for Na₂SO₄ ................................. 48

Figure 3.12 - XRD analysis of slag with C/S=1.18 after water quenching. ...................... 50

Figure 3.13 - Pseudo-ternary diagram of the slag system; MgO-CaO-SiO₂ with 15 wt % Al₂O₃ [103]. ......................................................................................................................... 51
Figure 3.14 - Heat treatment of slag samples: a) isothermal heat treatment b) schematic TTT diagram plotted from isothermal heat treatment experiments c) continuous cooling

Figure 3.15 - Crystallization of slag with C/S=1.31 during continuous cooling (cooling rate=\(~1°C.s^{-1}\)).

Figure 4.1 - Equiaxed growth at 1380°C isotherm (NBO/T=1.94).

Figure 4.2 - Enlarged images showing (a) equiaxed crystals of sample with NBO/T=1.71 at 1300°C (b) elongated crystals of sample with NBO/T=1.94 at 1150°C.

Figure 4.3 - Mixed planar and equiaxed growth at 1320°C isotherm (NBO/T=1.94).

Figure 4.4 - Planar growth at 1300°C isotherm (NBO/T=1.94).

Figure 4.5 - Faceted and planar growth at 1170°C isotherm (NBO/T=1.71).

Figure 4.6 - Elongated crystallization at 1150°C isotherm (NBO/T=1.94).

Figure 4.7 - Crystallization of slag with NBO/T=1.94 at 1100°C isotherm.

Figure 4.8 - Crystallization of slag NBO/T=1.56 at 1250°C isotherm.

Figure 4.9 - Crystallization of slag NBO/T=1.56 at 1150°C isotherm.

Figure 4.10 - TTT Diagram for samples with (a) NBO/T= 1.18 (b) NBO/T = 1.44 (c) NBO/T =1.56 (d) NBO/T=1.71(e) NBO/T = 1.78 (f) NBO/T =1.94.

Figure 4.11 - Start curves of the TTT diagrams.

Figure 4.12 - CCT Diagram for slag samples with (a) NBO/T = 1.44 (b) NBO/T = 1.56 (c) NBO/T = 1.71(d) NBO/T = 1.78 (e) NBO/T = 1.94 (f) Comparison of all CCT diagrams.

Figure 5.1 - $R_c$ from TTT diagram vs. NBO/T and $\Lambda_{corr}$

Figure 5.2 - Relationship between slag composition and critical cooling rate.
Figure 5.3 - $R_C$ and $\eta_{nose}$ Pa.s vs. $\Delta_{corr}$.

Figure 5.4 - Correlation between slag composition and viscosity at liquidus temperature ($\eta_l$).

Figure 5.5 - Log $R_C$ vs. Log ($\eta_{nose}$/Pa.s).

Figure 5.6 - Log $\eta_{nose}$ and log $\eta_L$ vs. Log $R_C$.

Figure 5.7 - Critical cooling rate against $\lambda$.

Figure 5.8 - $R_C$ from TTT vs. $R_C$ predicted.

Figure 6.1 - An illustration of the concept of extended volume ($V_e$). (a) Two precipitate crystals have nucleated together and grown to a finite size in the time $t$. (b) New regions (shown as lighter grey) are formed as the original crystals grow. These regions are no longer available for newer crystals to nucleate from [117].

Figure 6.2 - Crystallization of slag with C/S=1.52 at 1200°C isotherm ($\tau =$ incubation time).

Figure 6.3 - Crystallization of slag with C/S=1.38 at 1200°C isotherm ($\tau =$ incubation time).

Figure 6.4 - Crystallization of slag with C/S=1.31 at 1200°C isotherm ($\tau =$ incubation time).

Figure 6.5 - Crystallization of slag with C/S=1.18 at 1200°C isotherm ($\tau =$ incubation time).

Figure 6.6 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.52.

Figure 6.7 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.38.

Figure 6.8 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.31.

Figure 6.9 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.18.
Figure 6.10 – Dependence of nucleation rate on the temperature range of $T - TL$ [134]...... 90

Figure 6.11 - $\ln N$ rate verses $1/T$ for all samples in the early stage of nucleation. ............... 91

Figure 6.12 - Nucleation in slag with C/S=1.38 at T= 1170°C after (a) 10s (b) 11s. .................... 92

Figure 6.13 - Change of nucleation rate with time for all slags at T=1200°C ......................... 92

Figure 6.14 - Growth rate measurement for sample with C/S=1.38 at T=1250°C (a) $\tau$ – $\tau$=3s .. 93

Figure 6.15 - Crystal thickness verses time (a) C/S=1.52 (b) C/S=1.38 (c) C/S=1.31 (d) C/S=1.18. ................................................................. 94

Figure 6.16 - Dependence of growth rate on basicity. ......................................................... 95

Figure 6.17 - Interface morphology for sample with C/S=1.18 at (a) T=1250°C the interface is fully dendritic (b) T=1200°C semi-dendritic (c) T=1130°C planar........................................... 96

Figure 6.18 - $G$ verses $(1/T)$. .............................................................................................................. 98

Figure 6.19 - Change of activation energy of growth with basicity. ......................................... 99

Figure 6.20 - Effect of impinging on the growth rate for sample with C/S=1.18 at T=1150°C after (a) 10s (b) 70s (c) 80s. ................................................................. 101

Figure 6.21 - Growth rate change with collision of neighboring crystals. ......................... 101

Figure 6.22 - $\ln K$ vs. $1/RT$ (C/S=1.52)................................................................................... 103

Figure 6.23 - $\ln K$ vs. $1/RT$ (C/S=1.38)................................................................................... 104

Figure 6.24 - $\ln K$ vs. $1/RT$ (C/S=1.31)................................................................................... 104

Figure 6.25 - TTT diagram of the slags. .............................................................................. 105

Figure 6.26 - $\ln K$ vs. $1/RT$ (C/S=1.18)................................................................................... 106
Figure 6.27 - XRD spectrums of slag with C/S=1.38 at T=1150°C and T=1250 °C. .......................... 106

Figure 6.28 - XRD spectrums of slag with C/S=1.18 at T=1150°C and T=1250°C. ....................... 107

Figure 6.29 - LnK verses 1/RT for all slag compositions. ................................................................. 108

Figure 7.1 - Schematic diagram of the model principal................................................................. 111

Figure 7.2 - Schematic figure of enthalpy-temperature function for (a) pure crystalline material .......................................................................................................................... 113

Figure 7.3 - H-T relationship for slag with 47% CaO, 33%, SiO₂, 15% Al₂O₃, 5%MgO. ............ 118

Figure 7.4 - Effect of the number of layers (M) on the contact time ............................................. 119

Figure 7.5 - Comparison between the experimental results of [150] and the model outputs for position of the solidification front in a lead droplet. r/R= is the position of the liquid-solid interface from center of lead sphere (cm). ..................................................................................................... 120

Figure 7.6 - Analytical solution compared with modeling result (constant air temperature without phase change)........................................................................................................ 121

Figure 7.7 - Comparing temperature profiles from analytical solution and numerical modeling (constant air temperature with phase change) ............................................................................. 122

Figure 7.8 - Temperature profile of slag droplets at MairMslag = 0.77 and D=5mm. .......... 123

Figure 7.9 - (a) approximation of a continuous cooling curve with a series of isothermals and (b) adding transformed contents at different temperature validation of model. ....................... 125

Figure 7.10 - Validation of the model for predicting phase transformation by using TTT diagram and cooling path. The green points show the results by Agarwal et al. [152] and the smaller blue dots show the results by the existing code. ...................................................................................................................... 126

Figure 7.11 - TTT diagram (C/S=1.31). ......................................................................................... 127
Figure 7.12 - Crystallized fraction during continuous transformation (2°C/s) from experimental measurement and predicted by the code (C/S=1.31). ................................................................. 127

Figure 7.13 - CCT obtained from experimental measurements and modeling calculations (C/S=1.31).................................................................................................................. 128

Figure 7.14 - Heat recovery efficiency, air exit temperature, and amorphous content of slag as a function of $M_{air}/M_{slag}$ for slag with C/S=1.52 and D=8mm. ........................................... 130

Figure 7.15 - Effect of droplet size on the heat recovery efficiency........................................ 131

Figure 7.16 - Effect of droplet size on contact time. ................................................................. 131

Figure 7.17 - Effect of droplet size on air exit temperature.................................................... 132

Figure 9.1 - End time of crystallization for sample with C/S=1 with and without Cr$_2$O$_3$ at T=1100 °C isotherm (repeated 14 times). ........................................................................................................ 138
List of Tables

Table 2.1 - Range of chemical composition and production rate of ferrous slags .................. 5
Table 2.2 - Typical chemical composition and production rate of non–ferrous slags [9-12] ........ 6
Table 2.3 - Estimated production of slag and its energy content (estimates are for year 2013) [3, 9, 10, 12, 29, 30] ........................................................................................................... 9
Table 2.4 - Endothermic reactions for chemical recovery of waste heats [40] ......................... 22
Table 2.5 - Basic parameters of dry granulation–based heat recovery methods ...................... 27
Table 3.1 - Melting point measurement with the modified HTT in the current study ............. 48
Table 3.2 - Composition of the slag samples ........................................................................... 49
Table 4.1 - Summary of crystal morphology for slag compositions at different temperature ranges ........................................................................................................................................... 60
Table 5.1 - Liquidus temperature, $T_L$, calculated using FactSage™ ................................... 67
Table 5.2 - Critical cooling rates estimated using TTT and CCT diagrams ............................. 68
Table 5.3 - $T_{nose}/T_L$ value in the current study and Ref. [92, 105] ................................. 75
Table 5.4 - Critical cooling rate predicted for CSAM slags (current study) ......................... 77
Table 5.5 - Critical cooling rate predicted for CSAM slags from Ref. [105] ......................... 77
Table 5.6 - Critical cooling rate predicted for CAM and CA slags Ref. [92] ......................... 78
Table 6.1 - Values of the Avrami exponent in relation to geometry and mechanism of growth [104] ........................................................................................................................................... 83
Table 6.2 - Avrami exponent ($n$) and $LnK$ ............................................................................. 89
Table 6.3 - Crystal growth rate (µm/s) at different temperatures. ........................................... 95

Table 6.4 - Activation energy of growth (ED) ........................................................................ 99

Table 6.5 - XRD results of the crystalline phases formed at two different temperatures ....... 103

Table 6.6 - Effective activation energy EA .............................................................................. 107

Table 7.1 - Properties of the heat recovery system ................................................................. 117
List of Symbols

- \( n = \) Avrami exponent
- \( K = \) Rate coefficient
- \( E_A = \) Effective activation energy of crystallization
- \( R_C = \) Critical cooling rate
- \( T_L = \) Liquidus temperature
- \( T_n = \) TTT nose Temperature
- \( \Lambda_{corr} = \) Corrected optical basicity
- \( \eta_n = \) TTT nose viscosity
- \( \eta_L = \) Viscosity at liquidus temperature
- \( t_n = \) TTT nose time
- \( \Delta H_M = \) Enthalpy of fusion
- \( B = \) Nucleation barrier
- \( \Delta S_M = \) Entropy of fusion
- \( V_e = \) Extended volume
- \( V_\alpha = \) Volume of transformed phase (\( \alpha \))
- \( V = \) Total volume
- \( \dot{N}(T) = \frac{dN}{dt} \)
- \( \tau = \) Incubation time
- \( G = \) Growth rate
- \( N = \) Nucleation
- \( \dot{N} = \) Nucleation rate
- \( \Delta G^* = \) Nucleation energy barrier
- \( N_0 = \) Pre-exponential constant of nucleation
- \( E_D = \) Barrier to diffusion of molecules across the phase boundary
- \( L_V = \) Latent heat per unit volume
- \( \gamma_{SL} = \) Solid/liquid interfacial free energy
- \( T_{max} = \) Maximum nucleation rate temperature
- \( \Delta T = T - T_L \)
- \( D = \) Diffusion coefficient
- \( D_0 = \) Pre-exponential constant of diffusion
- \( E_D = \) Activation energy of growth
- \( E_A = \) Effective activation energy of crystallization
- \( \Delta T_r = \Delta T / T_L \)
- \( T_r = T / T_L \)
- \( V_{droplet} = \) Droplet velocity
- \( V_t = \) Terminal velocity
\( V_{air} \) = Air velocity
\( Re \) = Reynolds number
\( \rho_{air} \) = Air density
\( \nu_{air} \) = Kinematic viscosity of air
\( D \) = Droplet diameter
\( Pr \) = Prandtl number
\( H(T) \) = Enthalpy function
\( Nu \) = Nusselt number
\( h \) = Heat transfer coefficient
\( K_{Air} \) = Thermal conductivity of air
\( M \) = Number of layers
\( \Delta r \) = Distance between layers
\( \alpha \) = thermal diffusivity
\( H_i^n \) = Enthalpy at layer \( i \) and time step \( n \)
\( T_{air\_outlet} \) = Temperature of air at outlet
\( M_{air} \) = Air flowrate
\( M_{slag} \) = Slag flowrate
\( q \) = Total heat transferred from slag to air
\( q_{max} \) = Total amount of slag enthalpy
List of Acronyms

TTT = Time temperature transformation
CCT = Continuous cooling transformation
HTT = Hot thermocouple technique
CSAM = CaO-SiO$_2$-Al$_2$O$_3$-MgO
C/S = CaO/SiO$_2$
GBFS = Granulated blast furnace slag
RCA = Rotary cup atomizer
ACQ = Acquisition
AC = Alternated current
DC = Direct current
MCU = Microcontroller unit
PC = Personal computer
SW = Software
A/D = Analog to Digital
ADC = Analog to Digital Converter
IC = Integrated circuit
TC = Thermocouple
PWM = Pulse Width Modulation
IA = Instrumentation Amplifier
TRIAC = Triode for Alternating Current
MOSFET = Metal-Oxide Semiconductor Field Effect Transistor
SCR = Silicon controlled rectifier
NBO/T = non-bridging oxygen atoms over tetrahedrally coordinated atoms
JMAK = Johnson-Mehl-Avrami-Kolmogorov
HRE = Heat recovery efficiency
Chapter 1

1 Introduction

Metal manufacturing industry has achieved tremendous improvements in its energy efficiency in the past several decades. The specific energy consumption of steel in the U.S., for instance, has decreased from 48 to 20 MJ/ton in the period 1960–2000 [1]. This accomplishment has been realized by implementing numerous technological advancements such as introduction of continuous and chained operations where the regular cooling–heating cycles between the processing steps are eliminated. In a study, Fruehan et al. [2] estimated the potential energy saving in steel manufacturing and showed that there is an opportunity to further reduce the energy consumption involved in making liquid steel by about 20–30%. With established technologies to recover the thermal and chemical energies of process off–gas, the waste heat of slags presents the last untapped source that may be used for energy conservation in the rather energy–intensive metals industry.

Metallurgical slags constitute the largest by–product of the high temperature operations involved in the extraction and refining of metals. Slags are comparable to molten lava and are generally rich in silica (SiO$_2$), alumina (Al$_2$O$_3$), and lime (CaO). Slag is formed from the refining reactions, remaining gangue of the ore, the erosion of the furnace refractory, and the added fluxes. The molten slag is tapped at temperatures up to 1650°C, carrying a substantial amount of high quality thermal energy. This energy is usually not recovered, as the slag is tapped and cooled in the ambient or rapidly quenched to make glassy granules that are used as feedstock for cement manufacturing. Over the past four decades, several processes have been proposed to recover the waste energy of slag as heat, electricity, and fuel, while none has been commercialized yet. A renewed attempt at evaluation of the proposed processes is critical, as the metals industry is striving for another major step in improving its energy efficiency.
Blast furnace slags constitute over 50% of the total slag produced worldwide, amounting to 320 million tonnes. The thermal energy of these slags is equal to 17 million tonnes of coal, and is currently not recovered [3], in large due to challenge of heat recovery while producing a valuable product from slag. Blast furnace slags are most desired as feedstock for Portland cement production due to the large contents of silica and lime in these slags. For this application blast furnace slag has to be cooled rapidly to form an amorphous structure, as otherwise it will cause swelling of the concrete made from slag cement. Up to now, this is achieved by quenching slag in a process known as wet granulation. However, the use of water does not allow recovery of slag. In order to overcome this problem, dry granulation and heat recovery using air has been suggested. The optimum conditions for such air-based cooling system are not known yet; one on hand, large amounts of air are required to ensure rapid cooling, while on the other hand smaller amount of air is preferred to recovery the thermal energy into air as high grade heat. Therefore, one of the most important parameters to be determined is critical cooling rate which is a cooling rate that is just enough to generate glassy slag without consuming too much air. Further, the effect of slag composition on the critical cooling rate, and how such cooling conditions can be applied to slag are required. The present study was undertaken with the aim of answering these questions (a) understand the crystallization behavior of blast furnace type slags in order to determine the critical cooling rate and its relation to composition, (b) investigate the possibility of manipulating slag chemistry for achieving the desired structure, (c) determining the optimum conditions of a heat recovery process in terms of slag/air ratio, granule size, heat recovery vessel dimensions, and slag composition for highest heat grade, while generating a glassy product. Different chapters of the thesis cover the research approach and the findings as discussed below, and Figure 1.1 illustrates the summary of the research plan in the study. Essentially, we consider a heat recovery duct in which granule slag drops are descending in a counter-current flow of air. The flow rate, temperature, and composition of slag, as well as the flow rate and temperature of air are used in a heat transfer model, to calculate cooling profile of slag granules from their surface to core. In addition, the model predicts the exit temperature of air, as well as the heat transfer efficiency, being measures of heat quality and heat recovery efficiency respectively. The slags of various compositions are studied experimentally using a single hot thermocouple
technique (SHTT) to quantify their crystallization kinetics and obtain their respective time-temperature-transformation (TTT) and continuous cooling transformation (CCT) diagrams. The data from this work, together with the temperature history of slag droplets are used in a second mathematical model that predicts the amorphous content of slag granules under the given conditions.

![Diagram](image)

**Figure 1.1- Schematic figure of the research plan of the study.**

Chapter 2 provides an overview of the energy content of metallurgical slags, and the technologies that have been proposed for recovery of that energy. An evaluation of the methods will be made to suggest the most promising routes towards utilizing the waste heat of slag.

In Chapter 3, the experimental procedures are discussed and the set-up of the hot thermocouple technique (HTT) is presented. Chapter 4 presents findings including the crystallization behavior of CSAM slags at different basicities and also TTT and CCT diagrams as well as the critical
cooling rate. Later, in Chapter 5 the prediction of the critical cooling rate is discussed. The kinetic behavior of crystallization including nucleation and growth and Avrami parameters was also studied and is presented in Chapter 6. Chapter 7 of this thesis provides the details of the two mathematical models that were developed for slag crystallization and heat recovery. Finally in the last chapter the conclusion of the study is provided.
Chapter 2

2 Literature Review

2.1 Energy recovery from metallurgical slags

2.1.1 Metallurgical slags

Metallurgical slags are conventionally divided into ferrous and non–ferrous, based on the metal produced in each process. The typical chemical composition and generation rate of various slags for the major metal manufacturing processes are provided in Table 2.1 and 2.2. As seen from these tables, the relative amount of slag produced per ton of iron/steel is less than the non–ferrous operations. However, the order of magnitude larger metal production capacity in iron and steel plants gives rise to a substantially larger slag volume for individual plants.

Table 2.1 - Range of chemical composition and production rate of ferrous slags.

<table>
<thead>
<tr>
<th>Process*</th>
<th>Slag composition [4-6]</th>
<th>Slag temperature (°C) [7]</th>
<th>Slag rate (t/t. crude steel) [8]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>BF</td>
<td>30-56</td>
<td>28–38</td>
<td>8–2</td>
</tr>
<tr>
<td>BOF</td>
<td>45–60</td>
<td>8-22</td>
<td>1–7</td>
</tr>
<tr>
<td>EAF</td>
<td>35-60</td>
<td>9-20</td>
<td>2-9</td>
</tr>
<tr>
<td>LF</td>
<td>30-60</td>
<td>2-35</td>
<td>5-35</td>
</tr>
</tbody>
</table>

*BF: blast furnace, BOF: basic oxygen furnace, EAF: electric arc furnace, LF: ladle furnace
Table 2.2 - Typical chemical composition and production rate of non–ferrous slags [9-12].

<table>
<thead>
<tr>
<th>Metal / Process</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>FeO</th>
<th>Cr₂O₃</th>
<th>Slag temperature (°C)</th>
<th>Slag rate (t/t. metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper–sulphide ore</td>
<td>2</td>
<td>36</td>
<td>4</td>
<td>1</td>
<td>47</td>
<td>–</td>
<td>1000–1300</td>
<td>2.2</td>
</tr>
<tr>
<td>Nickel–sulphide ore</td>
<td>3</td>
<td>36</td>
<td>6</td>
<td>3</td>
<td>46</td>
<td>–</td>
<td>1300–1550</td>
<td>5.3</td>
</tr>
<tr>
<td>Nickel (oxide ores)/ FeNi</td>
<td>-</td>
<td>54</td>
<td>2</td>
<td>32</td>
<td>11</td>
<td>1</td>
<td>1600</td>
<td>50</td>
</tr>
<tr>
<td>Platinum group metals (PGM)</td>
<td>15</td>
<td>42</td>
<td>5</td>
<td>19</td>
<td>12</td>
<td>2</td>
<td>1350–1600</td>
<td>3700</td>
</tr>
<tr>
<td>Zinc</td>
<td>11</td>
<td>24</td>
<td>3</td>
<td>1</td>
<td>47</td>
<td>–</td>
<td>1200–1300</td>
<td>0.01</td>
</tr>
<tr>
<td>Lead</td>
<td>20</td>
<td>22</td>
<td>4</td>
<td>1</td>
<td>35</td>
<td>–</td>
<td>1200</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Traditionally, molten slag is poured into slag pits and is allowed to cool gradually. This slag is land–filled or crushed and used as a base material for road construction. The ferrous slags, particularly those of blast furnace (BF) are also increasingly used as a cementitious material known as calcium-silicate hydrate due to their high content of calcium silicates [13], although the use of non–ferrous slags for this purpose has also been proposed [14]. For this application, the slag is converted into granules in a process known as slag granulation and subsequently ground and charged to the cement kilns. This application is very advantageous economically and environmentally not for the metals industry alone but also for the cement industry as explained in the following section.
2.1.2 Use of slag as cement feedstock

It has been shown that substituting earth minerals with slag could give rise to up to 50 percent reduction in the CO$_2$ emissions associated with production of Portland cement [15]. Other than reducing CO$_2$ emissions, using slag cement instead of Portland cement has many other benefits, the most important of which is discussed in the following paragraphs.

2.1.2.1 Advantages of using slag cement

A) Environmental benefits

Cement production is an energy intensive partly due to the energy needed for calcination of limestone. Using slag can lower the energy consumption of cement making significantly. Producing an equal volume of slag will require 90% less energy than Portland cement. It has been discussed that substituting 50% of cement feed with slag can reduce the energy consumption up to 34% [16]. In addition, usage of slag cement reduces the “urban heat island” effect by enabling concrete to reflect more light and cooling structures due to the lighter color of slag cement compared with Portland cement [17].

B) Higher quality

Concrete containing slag powder has higher strength and durability as a result of less permeability. In addition, because of the reduced unit volume, concrete will have higher resistance against alkli-silica and sulfate attack which in return extends the life of concrete. Furthermore, slag cement reduces the temperature difference between the surface and the center of concrete in large structures which guards against thermal cracking.

C) Reduced material extraction

Raw materials for Portland cement require mining and processing. For every ton of Portland cement, 1.6 tons of raw materials is extracted. Substitution of raw minerals by slag reduces the need for extraction of raw materials significantly.
2.1.2.2 Demand for slag cement

Currently over 200 Mt/year of granulated blast furnace slag (GBFS) cement is used worldwide which is approximately equal to 62% of the total amount of blast furnace slag that was produced in the year 2013 [18]. Considering 50-80% of this type of cement contains BF slag [19], it is estimated that each year 100-160 Mt of slag is sold to the cement industry. According to the USGS survey, each ton of GBFS was sold for as high as $100 in the year 2011 [20]. Based on these figures, the value of the total amount of BF slag sold to the cement industry would be approximately $10-16 billion. Furthermore, if the total heat of this slag was recovered it would be about 45-70 TWh/y adding a value of $4.5-7 billion. This demonstrates the significance of heat recovery from slags during granulation process which will further be discussed in the following sections.

2.1.3 Slag Granulation

The slag used as a cement feedstock needs to be in amorphous form (i.e. glassy) to avoid subsequent swelling of the concrete. Consequently, the granulation processes use pressurized water, wet granulation, or large quantities of air, dry granulation, to prevent slow cooling and crystallization of the slag during solidification. Cooling rates in excess of 10°C/s [21] are required to form an amorphous slag with sufficiently strong hydraulicity.

Despite the effectiveness of wet granulation in producing a glassy slag, the thermal energy contained in the high temperature slag is not recovered. In addition, the wet process uses a large amount of water for granulation, typically around 10 tonnes of water of which 1–1.5 tonnes evaporates per tonne of slag [22-24]. Leaching of alkaline oxides in water and release of H₂S gas are other environmental problems associated with wet granulation. Dry granulation, on the other hand presents an opportunity to simultaneously generate a glassy slag and recover the sensible heat in the form of hot gases, steam, or chemical energy. As a result, the attempts to recover slag waste heat have been focused on dry granulation.

The attempts for dry granulation of slag date back to 1930 [25], but the research surged in 1970s and 1980s in Europe and Japan, resulting in laboratory and pilot scale testing of several methods.
In Section 2.1.5, the processes that have been proposed for energy recovery from slag, based on the use of dry granulation are described.

### 2.1.4 Energy content of slags

The energy consumed in high temperature processing of metals is distributed between metal, slag, off–gas, and the natural losses to the refractories and atmosphere. The slag thermal energy represents about 10–90% of the output energy depending on the slag/metal ratio and the discharge temperature. For instance, Rodd et al. [26] concluded that for ferro–nickel production, slag represents approximately 80% of the total energy input into the electric smelting furnaces. For steel production, on the other hand, estimated share of slag energy is 10–15% [27, 28]. Nevertheless, on a world basis the total amount of energy contained in slag is substantial for all metals (Table 2.3).

To estimate the energy content of the slags, the generation rates presented above were used together with FactSage™ thermodynamic calculation of slag enthalpy for typical compositions and temperatures given previously. The results are summarized in Table 2.3. The heat value provided in this table represents the heat released from the slag once cooled from its discharge temperature to ambient temperature of 25°C.

---

Table 2.3 - Estimated production of slag and its energy content (estimates are for year 2013) [3, 9, 10, 12, 29, 30 ].
<table>
<thead>
<tr>
<th>Process/Metal</th>
<th>Slag Temp.</th>
<th>Slag Enthalpy</th>
<th>Slag Production</th>
<th>Energy Value</th>
<th>Million t Coal Equiv.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace</td>
<td>1400-1450</td>
<td>1.6</td>
<td>321.3</td>
<td>5.14×10⁸</td>
<td>142.8</td>
</tr>
<tr>
<td>Other ferrous processes</td>
<td>1300-1600</td>
<td>1.3-1.8</td>
<td>292.0</td>
<td>4.37×10⁸</td>
<td>121.5</td>
</tr>
<tr>
<td>Non-ferrous Metals</td>
<td>1000-1600</td>
<td>1.2-1.5</td>
<td>52.0</td>
<td>6.55×10⁸</td>
<td>18.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>665.2</td>
<td>1.02×10⁹</td>
<td>282.5</td>
</tr>
</tbody>
</table>

As it is evident from Table 2.3, ferrous slags account for over 90% of the available energy associated with slags where BF slag alone constitutes ~ 50% of this energy. It is thus not surprising that majority of the investigations in this area have focused on BF slags. It should be noted that the values reported in this table represent the maximum energy content of the slag, when solidified slowly and to crystalline phase. However, as discussed earlier, a growing number of slag treatment operations consider the subsequent use of slag in cement making, and convert molten slag to a glassy phase. This approach comes with a disadvantage though, as the heat released from solidification of slag to amorphous phase is about 17% less than that of a slag forming crystalline structure, Figure 2.1 [31].
Attempts to recover energy from metallurgical slags have faced a fundamental constraint that is the low thermal conductivity of slag, ranging from 1 to 3 W.m\(^{-1}\).K\(^{-1}\) for solid to 0.1–0.3 W.m\(^{-1}\).K\(^{-1}\) for molten slags at 1400–1500°C [7, 32, 33]. Because of this, the core of a slag pot cooled in air may remain liquid for days. Numerical simulations [11] and experimental measurements [8, 34] of temperature distribution inside slag droplet suspended in air point to considerable temperature gradients. As an example, Figure 2.2 shows that in the temperature range of 1100–1300°C, corresponding to the transition temperature of liquid to glassy slag [33], the temperature difference between core and surface of a drop as small as 5 mm, can exceed 200°C. It is thus apparent that for forming a glassy product and also efficient heat recovery, the slag must be broken up into small droplets with a large surface available for heat transfer. Consequently, the earlier attempts [35-38] to recover the heat from slag without granulating it have been gradually abandoned, as the recovery efficiencies have been low and/or the slag is not cooled fast enough to become glassy. As a solution, Donald and Pickles [39] have investigated a method to recover
the thermal energy of slags using molten salts. Their experiments involving pouring a stream of slag into molten salt, measuring the temperature rise of the bath, and relating it to the energy recovery. They found that efficiencies as high as 66% can be achieved while the slag structure was similar to the water–quenched samples (i.e., glassy). However, in this direct heat extraction process, dissolution of slag in the salt and slag–salt separation remain to be addressed. Therefore, practically all active developments in this area are concentrated on granulation of the slag prior to recovering the energy.

The original investigations on the utilization of slag waste heat have focused on thermal energy recovery, i.e., transferring the heat of slag to hot air, steam or molten salts. Recently, the efforts have been directed to producing fuel gas, through an endothermic reaction that exploits the slag heat. Direct generation of electricity from waste heats based on the thermoelectric principle has also been proposed. In this section, these methods are described.

Figure 2.2 - Temperature history of a 5 mm slag drop in fluidized bed [8].
2.1.5.1 Thermal energy recovery

The differences between various methods are in the way slag is fragmented (the use of centrifugal force or impinging jets), the heat transfer medium (air, steam, or salt), and the heat transfer mode (i.e. direct-contact in packed or fluidized bed or indirect heat exchange). In this thesis, the energy recovery methods are categorized based on the method of slag granulation.

A) Rotary cup atomizer (RCA)

The rotary cup atomizer was first designed in Britain by Pickering et al. [31] and has been extensively studied since then. It essentially atomizes the molten slag by combined actions of a rotating cup and air blast, and cools the droplets rapidly to produce a glassy product. The particles are cooled as they travel through air and are later introduced to two successive fluidized beds for heat recovery. The suspension of particles with mean diameter of 2 mm in fluidized bed prevents the slag particles from clustering and at the same time provides rapid cooling to generate slag with over 95% glass content. A schematic diagram of the RCA is presented in Figure 2.4. It has been discussed that while the fast rotation of the RCA at 500–1500 rpm is sufficient to generate and break up the slag film, the annular air jet supplied around the cup facilitates the formation of smaller and more uniform particles. Based on their small scale experiments (0.2–0.5 kg slag per second), Pickering et al. proposed a commercial scale system, that if operated continuously, would yield an energy recovery of 59%. The losses occur because a) the total latent heat is not released when glassy slag is formed b) the solid slag is discharged from the heat recovery vessel at 250°C and c) heat loss in the slag accumulator. On the other hand, the main advantages of RCA are claimed to be high productivity and controllable slag grain diameter Figure 2.3. It has also been proposed by Akiyama and his co–workers [40-42] that by impinging reactive gas such as mixture of methane and stream, the sensible heat of the slag can be efficiently recovered as chemical energy as will be explained later.

Influence of operating conditions such as cup shape, rotating speed, slag viscosity and gas flow rate on grain size was later investigated by Mizuochi et al. [41] Their results indicated that the diameter and shape of the slag droplets was strongly dependent on the rotation speed of the cup
with higher rotating speeds resulting in smaller and more uniform spherical particles. In another work by Yu et al., [43] it has been found that when exceeding 1000 rpm, the decrease in the granule diameter becomes less significant and also the temperature of the slag does not have a considerable effect on the slag granule diameter.

Figure 2.3 - Appearance of slag granulation by RCA with cup rotation speed of 3000 rpm [41].

Figure 2.4 - Schematic diagram of Rotary Cup Atomizer [31].

The granulation efforts using a rotating cup were continued in 1990s by Siemens VAI (formerly VAI–UK) and Davy McKee [16, 44, 45], although heat recovery was not practiced in these trials. Commercialization of the technology has not been realized due to technical challenges
such as formation of slag wool and degradation of the atomizer cup. Recently, rotary cylinder has been tested in the laboratory scale [46], anticipating a higher efficiency of the granulation energy due to the reduced slip between slag and metal in this design. The experiments have shown that spherical glassy slag of various sizes can be produced, however, heat recovery tests have not been performed.

B) Granulation by spinning disk

The early works involved the use of spinning disks for slag granulation were carried out in Japan by Sumitomo Metal Industries in 1980s [8], aiming to form a BF glassy slag. Recent developments in spinning disk granulation method include the works of Akiyama and co–workers at Hokkaido University, Japan, [40, 41, 47], and those of Xie, et al. [23, 24, 48-50] at CSIRO, Australia. The former group however have proposed the recovery of the slag heat into chemical energy, as will be explained later.

In spinning disk granulation, a stream of slag is delivered onto the disk rotating at 1000–3000 rpm. The liquid steam is fragmented due to the impact with the disk and the centrifugal force. The droplets are scattered radially and collected in the heat recovery chamber where slag is cooled in fluidized or packed bed.

CSIRO has been working on the design, development and scale up of the method since 2002 [48]. The early works involved optimization of the granulation method that was later integrated with heat recovery. Their concept is based on a two–step process; in the first step, molten slag is granulated using the spinning disk. Through contact with an uprising air flow, the slag droplets freeze and their temperature drops to about 900°C, forming an amorphous phase. This slag is then charged to a packed bed heat exchanger where counter–current flow of secondary air cools the slag to about 50°C. The hot air of both steps is at temperatures above 600°C and may be used to generate steam or be used for preheating/drying.

Figure 2.5 shows still images of the slag atomization and the final product. As seen, the granules are comparatively uniform and within the range of 1–1.5 mm. The smaller particle size in this
technology offers several advantages, including faster cooling, higher glassy content, shorter flight time, and ease of grinding for subsequent use.

Figure 2.5 - (a) slag atomization on the spinning disc and (b) granulated slag product [23, 50].

Their process has been successfully tested on blast furnace slag at rates up to 10 kg/min. Further developments are underway to first test slag rates up to 100 kg/min and later 1000–2000 kg/min.

C) Granulation using rotating drum

In early 80s, Japanese companies Ishikawajima–Harima Heavy Industries and Sumitomo Metal developed a process in which a stream of blast furnace slag breaks up as it is impinged onto a rotating drum [13, 51-53]. The slag particles then fall into a fluidized bed where the heat was recovered. The process was later modified to lubricate the drum surface with a thin film of water or oil, giving rise to smaller heat loss and reduction in the particles scattering [8]. Further, pulverized cool slag was injected into the fluidized bed to accelerate the slag cooling, in order to decrease the required flight time for the droplets and make the plant smaller [8]. It also reduces the agglomeration of slag particles at high temperature. This process was tested in full scale of 40 t/hr at Wakayama Steel Works [8, 13] with a reported 50–60 % recovery of the slag sensible heat into hot air. A flowsheet of the process is provided in Figure 2.6.
Another attempt to granulate and recover heat of BF slag using a twin–drum technique was made by NKK in 1980s [54]. In this method, the slag is poured into the space between two drums. A film of slag is dragged and frozen on the drums as they rotate outwards. Heat is transferred to a coolant inside the drums, which is later transferred to a boiler to generate steam. Large scale trials were conducted at NKK Fukuyama Works, yielding relatively low 40% heat recovery. The slag glassy content also reached a maximum of 80%, making the product unsuitable for substituting with cement.

D) Granulation by solid slag impingement

Between 1979 and 1981, Swedish group Merotec (a subsidiary of the State Steel Company), developed a process for dry slag granulation based on mechanical disintegration of a liquid slag film by impinging particles [55, 56]. The method involves striking the slag stream with previously solidified slag particles, to break up the slag into granules that together with the recycled particles are charged to a multi–stage fluidized bed, Figure 2.7. The slag temperature is adjusted to 500–800°C in the fluidized bed by controlling the ratio of recycled to liquid slag. The heat is primarily (65%) recovered into high pressure steam while it is claimed that about 10% additional heat may be recovered from the fluidizing hot air, that is otherwise exhausted [55].
The slag granulates are typically below 6 mm where the –3 mm particles are recycled to the granulator.

![Diagram of Merotec slag granulation process](image)

**Figure 2.7 - Plant lay-out of Merotec slag granulation process [55].**

E) **Granulation by air blasts**

Air blast granulation technique was first developed by Mitsubishi Heavy Industries and Nippon Kokan KK (now JFE) [54, 57-59]. The early works began in 1977 leading to pilot testing in mid 80s, and operating at commercial scale of 80 t/hr until early 90s [26]. In this method, the slag is first pre-treated to optimize the flow and to adjust the viscosity. The slag is poured to a gutter under which the main air nozzle breaks up the stream of slag spread to a falling film (Figure 2.8). Other nozzles are also used to avoid scattering upward and sideward. The air velocity, flow rate, position of the gutter, and the nozzle size are carefully controlled to achieve acceptable size distribution of the droplets. The heat of the flying droplets is partially extracted to a waste heat boiler tubes suspended downwards by radiation and convection. The remainder of the heat is exchanged through a second boiler located at the bottom of the unit and embedded in the slag granules. The steam from the two boilers is collected into a steam drum while the slag granules (< 3mm) are discharged at temperatures around 200–300°C. A design for air blast granulation of BOF slag in the Mitsubishi Heavy Industries which discharges slag from BOF at intervals of 30
min has included slag granulating capacity of maximum 80t/h with steam generation rate of 15 t/h. An energy balance of the system has shown that ~41% of the heat is recovered in steam, another 39% is carried by the hot air exhausted at 500°C and could potentially be recovered [59]. The reasons for ceasing the operation of this process are not clear, although low recovery rate, scattering of the droplets, and energy intensiveness of the granulation process have been considered as the shortcomings [23].

Figure 2.8 - Schematic diagram of slag air granulation and heat recovery [26].

In an experimental study by Liu et al. [21], the efficiency of an embedded boiler has been measured by flowing a bed of slag down between boiler tubes. According to them, under optimum conditions, heat recovery can reach a substantial 90%. However, oven–heated slag granules were used in their work and the overall efficiency of a granulation–heat recovery system is not clear.
F) Paul Wurth’s process

Figure 2.9 and 2.10 illustrate examples of the processes that have been proposed recently. In Figure 2.9-(a), developed by Paul Wurth [60], steel balls are mixed with slag to quench the slag below its glass formation temperature so that it remains a glassy phase, while the heat is transferred to the steel balls and later recovered in an air-blown heat exchanger.

![Schematic of process developed by Paul Wurth [60].](image)

G) JFE Steel Corporation process

In Figure 2.10, developed by JFE [61, 62], the slag is cast into a sheet <10 mm thick using a twin-drum solidification process, and then crushed into slabs that are transferred to a heat recovery unit where air flows through the bed and is then used for steam and subsequent power generation.
Recovery as chemical energy

Generation of fuels based on the utilization of the slag thermal energy in endothermic reactions has been recently studied. Through this method, the thermal energy facilitates such endothermic reactions as phase change (such as melting of material) or other heat consuming reactions (for example decomposition of limestone, \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \) or melting), that could be later reversed to release heat. Also, as a way of producing fuel gas, the following reactions have been proposed \([40]\): gasification of coal (Reactions (1)–(2)), reforming of hydrocarbons (Reactions (3)–(5)), and decomposition of methanol, Reaction (6). In addition, the use of hot slag as a medium for heat storage and carrier has been proposed \([46, 63]\).
Table 2.4- Endothermic reactions for chemical recovery of waste heats [40].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy (kJ/mol)</th>
<th>Exergy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $C + CO_2 \rightarrow 2CO$</td>
<td>172</td>
<td>122</td>
</tr>
<tr>
<td>(2) $C + H_2O \rightarrow CO + H_2$</td>
<td>131</td>
<td>91</td>
</tr>
<tr>
<td>(3) $CH_4 + CO_2 \rightarrow 2CO + 2H_2$</td>
<td>247</td>
<td>171</td>
</tr>
<tr>
<td>(4) $CH_4 + H_2O \rightarrow CO + 3H_2$</td>
<td>206</td>
<td>142</td>
</tr>
<tr>
<td>(5) $CH_8 + H_2O \rightarrow CO + 5H_2$</td>
<td>498</td>
<td>298</td>
</tr>
<tr>
<td>(6) $CH_3OH \rightarrow CO + 2H_2$</td>
<td>90</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 2.4 summarizes the proposed endothermic reactions and their thermodynamic data. An analysis [40] of the reactions has shown that decomposition of limestone, reforming of methane, and gasification of carbon are the most promising heat absorbing reactions, as they present the least exergy loss among all the reactions studied. The latter two processes have received more attention due to their potential to generate fuel that is easy to transport and be used for various applications.

A) Energy recovery by methane reforming

In 1997 Kasai et al. [42] proposed the use of hot BF slag for promoting water reforming of methane (i.e. Reaction (4)). Figure 2.11 depicts the scheme of this concept. As shown, part of the slag sensible heat is transferred to the reactants (methane and steam), generating CO and H₂. The still molten slag (~ 1500 K) is transferred to the granulation step, in which steam is generated by extracting the remainder of the sensible and latent heat. The steam is fed back to the reformer, thereby increasing the overall efficiency of the process. The sensible heat of the high temperature reducing gases is recovered through a heat exchanger that produces steam for power generation. The chemical energy of the gases is partially recovered in the methanation reactor where the reverse reaction generates methane and steam. Water vapor is condensed in a second heat
exchanger and CH$_4$ is directed back to the reformer. The feasibility of the reforming process using hot slag surface [42] and the effect of slag composition on the reaction rate [41] were examined in two separate studies. It was shown that larger CaO content in the slag gives rise to higher reaction rates while FeO and sulphur have inhibiting effects. The apparent rate of reforming was found to be $10^{-3} - 10^{-1}$ mol.cm$^{-2}$.s$^{-1}$. The experimental work provided limited insight into the energy recovery efficiency, as they involved only examination of the reaction rate over a small slag surface at a fixed temperature. The heat recovery steps were not included, thus the overall energy recovery efficiency is not known.

![Process flow diagram](image)

Figure 2.11 - Process flow diagram for energy recovery through methane reforming [42].

Maruoka et al. [64] designed a new system in which the slag is first granulated using a rotary cup and is then accumulated in a packed bed shown in Figure 2.12. The steam reforming of methane takes place with the aid of a Ni–based catalyst. The thermal energy required for the reaction is recovered by direct heat exchange between gas mixture and the slag granules in the slag bed. In their materials and energy balance analysis, they assumed that per tonne of hot metal, 299 kg of blast furnace slag is generated at 1250°C. This slag, if cooled to 250°C through the proposed system, can generate as much as 106 Nm$^3$ of CO+H$_2$ (molar ratio of H$_2$: CO = 3:1) exiting the reactor at 1100°C. This would represent chemical energy recovery of 0.24 GJ/ton hot metal (0.81
GJ/ton slag) or 51% of the slag thermal energy. The gas also has an additional 0.155 GJ/ton hot metal (0.52 GJ/ton slag), which if recovered fully, would increase the total recovery to ~ 83%. Although this proposed system appears promising, it remains to be tested. In addition, technical issues such as clustering of slag granules at temperatures as high as 1100°C, as well as the structure of the granulated slag for subsequent use should be investigated.

Figure 2.12 - Steam reforming of methane using granulated slag heat [64].

In a more recent experimental work, reforming of methane by CO₂ has been investigated by Purwanto and Akiyama [65]. They purged a mixture of CO₂–CH₄ through a packed bed of slag granules ~ 2 mm diameter at a temperature range of 973–1273 K. Analysis of the exhaust has revealed that increasing the temperature has a substantial effect on the methane conversion extent, which reached a maximum of 96%. Again, since the focus of this research was only on the conversion kinetics, no information may be obtained regarding the energy recovery efficiency.
Converting the thermal energy to chemical energy, particularly in the form of a fuel, offers advantages such as a higher energy density (compared to steam/hot air), possibility of transporting energy, and the potential of re-generating the thermal energy at much greater temperatures. However, an analysis by the author shows that the rate of heat extraction from slag by such reactions as methane reforming is far from being enough to prevent the slag from crystallization. According to Sun et al.[66], this can be addressed by converting the thermal energy of slag to chemical energy only when the slag temperature is below the glass formation temperature, so that extended periods do not result in crystallization of slag. In other words, the energy recovery process will consist of at least two steps, one for the high temperature range, where slag needs to be cooled rapidly, perhaps using air, and the second step in which slag is cooled through endothermic reactions. For this purpose, the crystallization behavior of the slag at different temperatures needs to be established.

B) Energy recovery by coal gasification

In a study by Li et al. [40], recovering slag heat through coal gasification was evaluated by using a materials–energy balance. In the proposed coal gasification system, CO$_2$ is injected together with coal into a molten BF slag bath, generating carbon monoxide through Reaction (1). The thermal energy of off–gas is recovered in a heat exchanger to make steam while the cleaned gas is used as fuel. According to this analysis, a steel mill generating 10 Mt of steel would also produce 3 Mt slag, from which 0.132 Mt of CO is generated. Based on energy content of 1.6 GJ/ton slag, this represents thermal–to–chemical conversion efficiency of 35%. However, the total energy recovery is greater, because a non–quantified amount of heat is recovered as steam.

Figure 2.13 shows a schematic diagram of a coal gasification process proposed by Hong-xiong L. et al. [67] which uses a rotary cup atomizer. Li et al. analyzed this concept further through detailed kinetic study on the effect of different parameters such as the heating rate and molten blast furnace slag on the coal gasification reaction rate [68].
C) Energy recovery through PCB (Printed Circuit Boards)

In a recent investigation by Qin et al. [67] a new technique was proposed which recovers the heat of BF slag by first granulating slag using rotary a multinozzle cup atomizer and later pyrolyzing printed circuited boards.

2.1.5.3 Direct electricity generation

Direct conversion of waste heat to thermoelectric power has been recently reviewed by Rowe [69]. The method presents an environmentally friendly, safe and reliable technology which can convert unused heat into electricity. With the emergence of modern semiconductors with Seebeck coefficient in the order of several hundred microvolts per degree, the technology appears promising, particularly for high quality heat such as that of slag. Low temperature trials have been successfully demonstrated on a laboratory scale and in prototype commercial systems. As an example, an investigation on steel plant heat recovery has been carried out where large amounts of cooling water are discharged at constant temperatures of around 90°C. It has been estimated that total electrical power of around 8 MW would be produced employing currently available modules fabricated using bismuth telluride material technology.
The thermoelectric technology is an emerging area, particularly for high temperature applications. The choice of thermoelectric materials with large Seebeck coefficient for high temperature systems is rather limited. However, the slag waste heat may be stored in phase change materials (PCMs) as proposed by Nomura et al.[63], in a temperature range of ~150–1000°C, coinciding well with the operating temperature for a range of thermoelectric materials that may suitably be used for energy conversion.

2.1.6 Evaluation of energy recovery methods

Among the various routes of energy recovery from high temperature slags, the thermal methods have been developed most, and are gradually reaching commercial testing and acceptance. Dry granulation followed by recovery of heat into steam or hot gases (air) has been practiced in several pilot and plant trials, although none has been established for long term commercial use.

Table 2.5 presents a summary of the basic parameters for the thermal recovery methods. As can be seen, the heat recovery efficiency for these processes is within the range of 40–65%.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CSIRO</td>
<td>Australia</td>
<td>Pilot</td>
<td>Spinning disk</td>
<td>Hot air</td>
<td>–</td>
<td>600</td>
<td>[23]</td>
</tr>
<tr>
<td>British Steel Corporation – University of Nottingham</td>
<td>England</td>
<td>Pilot</td>
<td>RCA</td>
<td>Hot air</td>
<td>59</td>
<td>430–520</td>
<td>[31]</td>
</tr>
<tr>
<td>Ishikawajima – Harima Heavy Industries &amp; Sumitomo Metal</td>
<td>Japan</td>
<td>Plant</td>
<td>Single rotating drum</td>
<td>Hot air</td>
<td>50–60</td>
<td>600</td>
<td>[8]</td>
</tr>
<tr>
<td>Merotec</td>
<td>Sweden</td>
<td>Pilot</td>
<td>Slag particle impingement</td>
<td>Steam</td>
<td>65</td>
<td>Steam, 40 bar, 250°C</td>
<td>[55]</td>
</tr>
<tr>
<td>NKK–Mitsubishi</td>
<td>Japan</td>
<td>Pilot/ Plant</td>
<td>Air blast</td>
<td>Steam</td>
<td>41</td>
<td>Steam, 250°C</td>
<td>[59]</td>
</tr>
<tr>
<td>NKK</td>
<td>Japan</td>
<td>Plant</td>
<td>Twin rotating drums</td>
<td>Steam</td>
<td>40</td>
<td>–</td>
<td>[54]</td>
</tr>
</tbody>
</table>
The requirement for forming a glassy product while recovering the heat poses a fundamental challenge in efficient heat recovery. While large quantities of air are required for rapid quenching of solidifying slag, the temperature (and heat quality) of the heat carrier, steam/air, is reduced at higher flow rate. The lower gas temperature in turn reduces the recovery of energy utilization as steam or heat source in the subsequent steps, leading to lower overall efficiency. As a result, the trend in the slag treatment processes is towards controlled granulation so that small and uniform slag grains are generated. The larger contact area promotes heat transfer for a given air flow rate, and also facilitates fluidization of the grains, as well as their subsequent use as cement feedstock. In addition, Bisio [70] has shown that where the use for hot air exists, such as blast furnace, generation of hot air is more energy efficient than steam.

The recovery of heat from dry–granulated slag grains conventionally takes place in fluidized bed for improved heat transfer and also preventing agglomeration of the particles. However, the disadvantage of fluid–bed is that slag is discharged at a temperature typically above 200°C, causing energy loss. An optimum design may include a two–step heat recovery, in which initially the slag is rapidly cooled in a fluidized bed below the clustering temperature (800–900°C). Subsequently, the remainder of the heat is recovered in a packed bed, through embedded boiler tubes or direct contact of air–slag. Within this context, the proposed process by CSIRO [23, 48, 50] appears very promising, as the slag discharge temperature (50°C) is considerably lower than the previous methods (~200–300°C). Such difference in the slag temperature could result in increasing the recovery efficiency by additional 10–15% compared to those presented in Table 2.5.

Conversion of slag waste heat into chemical energy offers several advantages over the thermal technologies:

1. The fuel may be transported over long distances without a loss in the energy content.
2. Metallurgical industry may be linked to the chemical and energy sectors.
3. Fuels have a substantially larger energy density compared to steam or hot air, making their transportation and storage more economically attractive. As an example, the energy density of saturated steam at 250°C (40 bar) is 44 MJ/m³, whereas that of CO–H₂ gas
mixtures generated through reactions (1)–(6) and compressed to the same pressure is an order of magnitude larger (450–500 MJ/m$^3$).

4. The energy of the fuels may be considered of high quality, as the fuels may be combusted to generate temperatures exceeding 2000°C, if necessary, whereas the use temperature for air/steam is limited by their discharge temperature (typically 600°C or below).

Despite these advantages, the recovery of slag waste heat into chemical energy is still in its early development stages and has not developed beyond laboratory testing of only reforming step. There is no data on the integrated system consisting of combined heat recovery–reforming, thus a comparison with thermal energy methods is not possible. A major challenge in effective conversion of thermal to chemical energy appears to be the low volume of gas that is generated compared to the slag mass. As an example, a thermodynamic evaluation shows that at 60% heat recovery, each tonne of gas mixture (stoichiometric mixture of methane at 25°C and steam at 200°C) would require about 10 tonnes of slag to reach appropriate reforming temperature of 900°C. This amount of gas is clearly not sufficient for quenching the slag fast enough so that a glassy phase is formed. In addition, the long contact time required for such amount of heat transfer would result in a prohibitively large reactor. As a result, it is apparent that the process must consist of two steps; in quenching step, the slag is granulated and cooled rapidly to a temperature below its crystallization temperature (~ 1000–1100°C [71]) using air. The slag is then charged to a second vessel, where the remaining heat is transferred to the reactants (e.g. methane and steam/CO$_2$). The heat recovered in the first step may be utilized to generate the steam needed for reforming. A schematic diagram of this concept is shown in Figure 2.14.
Thermoelectric power generation from slag waste heat is a very attractive alternative to thermal and chemical energy forms, although this technology is still in its infancy. Currently there are several challenges against direct conversion of slag heat to electricity, (a) the operating temperature of the existing thermoelectric materials is significantly lower than the molten slag, (b) high melting point of slags limits the temperature range at which the heat can be extracted effectively, while molten, and (c) the slags are extremely corrosive, thus interfacing slag and thermoelectric materials would pose technical difficulties. For these reasons, it appears that a potential thermoelectric technology can benefit from PCMs as heat carriers. Recovering the heat of high temperature slags, the PCMs then provide a continuous supply of thermal energy to the thermoelectric system at lower temperatures. The type of PCM and its operating temperature range should be matched to the type of the thermoelectric material selected (typically below 1000°C). Extensive research is required to answer such questions as coupling of the intermittent slag supply to the power system, conversion efficiency, and cost.

Figure 2.14 - Steam reforming of methane using granulated slag heat [64].
2.2 Crystallization of slag

Time-temperature-transformation (TTT) diagram of slag which represents the relationship between the time required for crystallization and the temperature, provides essential information for determining the optimum cooling path during slag granulation. A few studies have been carried out on the determination of TTT [72, 73] and CCT [74] diagrams for BF slags Figure 2.15 and 2.16. Kashiwaya et al. [72] studied the crystallization behavior of a fixed slag composition, with emphasis on the mineralogy of the crystalline phases.

![In situ observation: tentative TTT](image1)

**Figure 2.15- TTT diagram of BF slag by Kashiwaya et al. [72].**

![TTT and CCT](image2)

**Figure 2.16 – CCT diagram of BF slag by Kashiwaya et al. [72].**
Lei et al. [74] on the other hand, measured the crystalline content of continuously cooled slag of given composition. In a more recent study by Qin et al. [73], the TTT and CCT diagrams, shown in Figure 2.17 and 2.18, along with the crystallization behavior and transformation kinetics of a single blast furnace slag composition during isothermal and non-isothermal experiments was studied.

![TTT diagram of BF slag by Qin et al. [73].](image1)

Figure 2.17- TTT diagram of BF slag by Qin et al. [73].

![CCT diagram of BF slag by Qin et al. [73].](image2)

Figure 2.18- CCT diagram of BF slag by Qin et al. [73].

In a study by Sun et.al [75] the effect of Al₂O₃ on the crystallization properties such as the glass formability of slag compositions with similar CaO/SiO₂ content was studied.
In another article by Sun et al. [66], the TTT diagrams of similar slag compositions were studied and the potential of heat recovery was investigated.

![TTT diagram of synthetic BF slag with varying Al₂O₃ content by Sun et al. [66]. CaO/SiO₂=1.0, A1=11wt%, A2=20wt%, A3=23wt%](image)

Although these works provide essential data on crystallization behavior of slag, their application is limited to the slag compositions studied; a systematic study on the effect of slag composition on its crystallization behavior is lacking. This is of particular interest when the slag composition changes due to operational parameters or feed composition. Also, it might present options for adjusting the slag chemistry so that its crystallization behavior can be manipulated based on the needs.

### 2.3 Summary

Driven by energy crisis of 1970s, numerous investigations were made in 1970–1980s to develop a method of heat recovery from slag, while generating a slag suitable for other applications. These attempts however diminished with the ease of the energy prices in 1990s. A renewed interest in this area has resulted in experimental and pilot trials of several technologies, although none has yet been established industrially. The following are the major findings from a thorough review of the past and state–of–the–art in waste heat recovery from slags.
1. The world production of slag represents a heat content of 282 TWh per year (2013), with blast furnace slag accounting for about 50% of this energy.

2. Driven by a demand to produce amorphous slag as substitute to cement and limited by the low thermal conductivity of slag, majority of the methods for energy recovery from slag are relying on dry granulation of slag.

3. Being investigated for over three decades, the thermal energy recovery methods are most developed among the various schemes proposed for energy recovery from slags.

4. Compared to rotary drum or air jet granulation, the techniques employing spinning disks or rotary cups offer the advantage of generating uniform and small grains at a lower energy consumption rate. Smaller droplets are quenched faster and require less coolant, resulting in recovery of more heat and at higher temperature.

5. Because of the cooling rate requirements, a two–step heat recovery consisting of a fluidized bed, followed by a packed bed would yield higher energy recovery efficiency, as both high outlet gas temperature and low slag discharge temperature are achieved.

6. The chemical energy recovery methods offer the advantage of high energy density and zero loss in the energy content during transportation. These methods are under investigation, with methane reforming and coal gasification receiving more attention as the feasible routes.

7. An optimum chemical energy recovery system consists of two vessels, where in one the slag is cooled to below the crystallization temperature, and in the other fuel generation takes place.

8. Thermoelectric power generation based on the slag waste heat appears to be the next emerging technology in this area. The use of PCMs as heat carriers appears to address the major challenges that the technology is currently facing.

9. Currently, substituting Portland cement with slag cement is one of the most desirable uses of slags. For this application, high cooling rates are required to form an amorphous (glassy) slag. However, it is crucial to develop an ideal cooling path that prevents crystal formation and at the same time allows efficient recovery of high quality heat from slag.
10. TTT and CCT diagrams are useful tools which can help control and predict the microstructure of slags and therefore enhance the recycle and reuse of slags. These findings will not only be interesting from fundamental point of view, they also lead to possible optimization of the slag chemistry for dictating its crystallization behavior, and expanding heat recovery options from slag.

11. Although there have been studies on the crystallization behavior of BF slag, their application is limited to only those slag compositions studied; a systematic study on the effect of slag composition on its crystallization behavior is lacking.
Chapter 3

3 Experimental

Experiments to study the crystallization behavior of slag were performed by the hot thermocouple technique. In this chapter first the details of the device functions and the set-up will be discussed and later the experiments will be explained.

3.1 Hot Thermocouple Technique (HTT)

The hot thermocouple technique (HTT) is an experimental method that allows heating, cooling, or isothermal treatment of materials with precise control of temperature and cooling/heating rates. The technique relies on the use of a thermocouple wire as both a temperature sensing device, and a heating element. The specimen under investigation is placed on the tip of the thermocouple and undergoes the desired thermal treatment. Small sample size allows thermal homogeneity within the material, also direct contact between the specimen and thermocouple reduces temperature difference. Further, the specimen can be visualized in-situ throughout the process, allowing observation of high temperature interactions and phenomena. Rapid temperature readings followed by current injection to the material in between allow precise control of the temperature and heating rate.

The hot thermocouple technique has been widely used in studying the effect of composition and cooling rate on the glass formability and kinetics of crystallization of mold flux. For example, Kashiwaya et al. [76, 77] and Orrling et al. have studied the crystallization behavior [78, 79] and the effect of water vapor [80] on the crystallization of mold flux. In two other studies by Klug et al. [81, 82] the effect of Na₂O on fluorine-free mold flux was investigated by plotting the TTT diagram of the material. Similar studies on mold flux using this technique include the works reported in References [83-91]. In addition to mold flux, the technique has been employed by Prapakorn et al. [92] and Valdez et al. [93] to evaluate crystallization behavior of metallurgical slags. Another example is the research by Jing et al. on Ti-bearing blast furnace slags [94] and the study by Qin et al. on crystallization behavior and construction of time-temperature-
transformation (TTT) and continuous cooling transformation (CCT) diagrams of blast furnace slags [73, 95].

3.1.1 The Development of the hot thermocouple technique

The Single Hot Thermocouple Technique (SHTT) equipment was invented by Ordway [96] in the 1950’s for studying the growth of single crystals in a small droplet of melt at temperatures up to 1600°C. Before the introduction of this method, investigations of this type were performed using the hot-wire apparatus which consisted of a 0.3mm platinum wire bent to a V-shape and heated by current from a 6.3V transformer. The voltage of the transformer was supplied by a continuously variable autotransformer or a manual rheostat used in operating sewing machines. Since the measurement of temperature was not possible with this device, attempts were made to measure the temperature by a thermocouple, a difficult procedure as it extracted heat from the sample. Therefore, the idea of having a separate heat source for the thermocouple was considered by Ordway et al. [96]. However, he later discovered a more suitable solution which was using a high-frequency alternating current for heating. Consequently, the direct current electromotive force produced by the thermocouple was separated out by a filter and measured independently. The specimen was placed on a 0.25mm Type-S thermocouple wire and held in place by capillarity forces at the thermocouple junction. A schematic diagram of the circuit is shown in Figure 3.1-a.

Welch et al. [97] later modified the electrical arrangements for a less expensive apparatus. In their design, instead of using 5 kHz oscillator and 30W power amplifier, a half-wave rectified current of mains frequency was used. The thermocouple was connected to the power supply or to the temperature measuring circuit by a high-speed polarized relay with single-pole changeover contacts. The oscillation of the mains frequency allowed the heating current to be applied only during alternate half-cycles and the measuring circuit during the intermediate half-cycles. The basic circuit diagram of the device is shown in Figure 3.1-b.
In the 1970’s this technique gained more interest and other researchers reported new progress on this method and its application. For example Ohta et al. [98] used the method to measure the liquidus temperature of cryolite systems and Noguchi et al. [99] studied slag reactions using the same technique [99]. HTT was also employed by Yanagase et al. [86] to investigate the effect of slag composition on matt-slag separation in copper smelting, and Asayama et al. [100] to measure the critical cooling rate of silicate glasses.

In 1998, the Double Hot Thermocouple Technique (DHTT) was developed by Kashiwaya et al. [77] which consisted of two thermocouples instead of one (Figure 3.2). This type of hot thermocouple technique is suitable for studies where the phenomenon of interest (e.g. solidification, mass transport, reactions, etc.) needs to be investigated under a defined thermal gradient. For example, in the case of studies concerned with the crystallization of mold slags, DHTT allowed the simulation of the transient conditions which can occur in the slag film that forms between the mold of a continuous casting machine and the solidifying shell. Later this technique was further developed by Kashiwaya et al. [101] for measurement of thermal diffusivity by laser flash analysis.
3.1.2 Description of the hot thermocouple technique (HTT)

The main component of a HTT device which controls the heating and cooling rate is the “thermocouple driver”. In all of the previous HTT setups, similar thermocouple drivers based on the use of AC power have been employed. Here, as will be discussed in the following section, a new thermocouple driver design based on DC power is introduced which is more accurate and simpler to make.

The device consists of a type-B thermocouple (Pt–6%Rh / Pt–30%Rh) wire with the diameter of 0.5 mm that acts as the main heating source. A small piece of the specimen (about 5 mm in diameter) is placed on the tip of the thermocouple which itself is held by copper tubes Figure 3.3. This thermocouple setup is housed inside a machined aluminum chamber with a glass lid which enables direct observation of the specimen by a microscope (as shown in Figure 3.4). A CMOS camera is placed on top of the microscope which enables capturing videos and still images with high resolution (1280 × 1024 pixels).

![Figure 3.2 - Comparison of the single and double hot thermocouple setups [77].](image-url)
3.1.3 Modified HTT

In the new HTT apparatus, the overall concept remains similar to the previous setups with the main difference that the thermocouple driver was redesigned with the aim of improving the accuracy of temperature control. In order to achieve the functional requirements and improve on previous implementations of this type of controller, the following key aspects of the design were addressed: synchronized thermocouple reading, relay switching noise, thermocouple supply
control, and switching/chopping frequency. Each of these improvements will be discussed in the following sections.

### 3.1.3.1 Using a DC power supply with variable voltage

Instead of using an AC power source switched on and off with a TRIAC (Triode for Alternating Current), the new HTT system uses a variable voltage DC power supply (4.8-11V) and produces a pulsed current by a MOSFET (metal–oxide–semiconductor field-effect transistor) switch resulting in higher frequency (480Hz) of heating pulses applied to the thermocouple. This higher switching frequency decreases thermocouple temperature sampling time with 2 ms time interval between the measurements compared to 16.6 ms in the previous thermocouple drivers. The principle of the previous controller proposed by Kashiwaya et al. [77] is shown in Figure 3.5. A silicon controlled rectifier (SCR), rectifies the AC current into half-wave. In one half, the thermocouple is heated and in the other the temperature is measured by powering off the current and using the relay circuit. The maximum duration of each of these cycles is 1/120 s. Figure 3.6 shows the difference between the new controller operated by DC current resulting in a square-wave which will be explained further in the following sections.

![Figure 3.5](image1.png)  
**Figure 3.5** – Schematic figure showing the principal of AC based HT controller [77].  

![Figure 3.6](image2.png)  
**Figure 3.6** – Schematic figure showing the principal of the modified DC based HT controller.
3.1.3.2 Synchronized TC reading

Another modification of the device is that a synchronous analog to digital conversion is employed. Previously designed controllers operate asynchronously and a separate asynchronous acquisition system was used to read the thermocouple temperature. A large capacitor was used to smooth out the ripples caused by relay switching on and off and voltage sagging when disconnected from the thermocouple. It has been reported [77] that a capacitor adds noise into the system allowing the temperature measurement during only one–third of the half wave. If the acquisition is synchronized with the thermocouple power control (the thermocouple temperature is recorded only when power is off in between the pulses that heat up the thermocouple) the capacitor is not required. In addition, the noise can be eliminated and the accuracy of temperature readings can be improved.

3.1.3.3 Relay switching noise

The relays used in previous controllers to connect the acquisition system to the thermocouple are subject to contact bouncing in addition to fast relay closing/opening frequency (60 Hz) that will wear in a short period of time. The solution that was implemented in the current design was to have both power and acquisition connected to the thermocouple. Then the thermocouple is powered with a voltage as demanded, and a clamping circuit is used to protect the acquisition circuit input from excessive voltage.

3.1.3.4 Thermocouple power control

Other previously used controllers use a fixed voltage AC power supply. The need for variable power provoked the idea of using a variable voltage DC power supply. An electronic switching power supply is able to regulate the power applied to the thermocouple, resulting in a better power control. Essentially, the thermocouple power will be derived with a square wave and a variable duty cycle. Also the amplitude of the square wave can be adjusted to accommodate distinct loads (thermocouple wire gauge, sample size, thermocouple).
3.1.3.5 Switching frequency

Because the thermocouple is not powered constantly but in successive power pulses, the voltage generated by the thermocouple will be subject to some fluctuation in between power pulses (thermocouple voltage will slightly drop/sag in between the pulses, during temperature reading). The smaller the system mass and the higher the energy exchange with the ambient, the larger this voltages dip/sag will be. This is not a significant problem in particular because in both the new and old design the target temperature is reached by powering the thermocouple sufficiently but in the new system because of the smaller interval between pulses the heat loss from the sample will be lower and so will be the voltage dip/sag. A simplified block diagram of the new concept target design is shown in Figure 3.7.

![Simplified block diagram of the new concept target design](image)

*ACQ: Acquisition, TC: Thermocouple

3.1.4 Hardware Controller

HTT controller was designed at its core with a powerful ARM7 microcontroller (model: LPC2361) from NXP Ltd. In order to achieve the timing requirements, the acquisition circuits were controlled each by their own microcontroller (ARM Cortex M0 – LPC1111) and in turn by the main MCU.
The hot thermocouple driver in this study was initially intended for use in SHTT mode but was designed so that it is also suitable for tests that require a thermal gradient (i.e. used as a DHTT). Therefore, two separate variable DC power supplies were used to allow applying an external differential voltage between the two thermocouples. In order to connect the acquisition circuit input directly to the thermocouple and still have the two channels separated for DHTT applications, the two channels (power supplies and acquisition circuits) are completely isolated from each other and from the main MCU. Therefore, the presence of the isolation block in the diagram provides galvanic isolation between the two channels and main MCU. A complete block diagram of the controller is shown in Figure 3.8.
Figure 3.8 - Hot thermocouple controller block diagram.


The power is applied to the thermocouple in pulses and controlled by the duty cycle and amplitude. The maximum duty cycle is 0.5 s because the acquisition needs to take place in between pulses, as depicted in Figure 3.9.
To achieve the synchronous acquisition, each falling edge of the power pulse will trigger the acquisition on the corresponding channel. The Analog to Digital Converter (ADC) resolution determines the accuracy of the measurements and therefore a 16 bit resolution ADC was used. There is a small delay after the power is switched off and the actual ADC conversion takes place. This is to avoid the inherent switching noise and allow the acquisition input to settle properly at the correct thermocouple voltage output. Acquisition needs to be completed before the next power pulse and therefore is limited to \(~0.4\) of the PWM (Pulse Width Modulation) cycle.

### 3.1.5 Power supplies and thermocouple power driver

The power supplies are basically DC-DC switching regulators. In order to minimize the ripples of the DC output voltage, a two-phase buck topology was used. The output voltage can be adjusted between 5 and 11 V and the peak output current can be up to 40A. Considering that the load is switching on and off at the PWM maximum duty cycle of 0.5, the RMS (Root Mean Square) current that these power supplies can provide is up to \(40/\sqrt{2}=28\)A.

The power can be controlled independently on each of the channels (voltage and PWM duty cycle) but they will still operate in synchronization with each other since they are driven from the same timer at different PWM duty cycles or different output voltages. In order to control the power to the thermocouple, a MOSFET switch is used. The advantages of using MOSFETs are the low power dissipation (low internal resistance) and fast on/off switching.

Four low R\(_{DS}\) (drain-source resistance) p-channel MOSFETs are used to implement the thermocouple power driver switching. They have a rated maximum current of 60A each.
3.1.6 Verification of temperature measurement

For verifying the temperature measurements of the device, the melting point of four different materials with known melting points were measured. Samples with 3-4 mg were placed on the tip of the thermocouple and heated at 5°C/s.

The melting point was determined by plotting the derivative of the time-temperature curve \( \frac{dT}{dt} \) (Figure 3.11) of the time-temperature curve (Figure 3.10-a). In Figure 3.11, the dotted line shows the actual melting point and the dashed line is the first dip that is defined as the melting point. This was repeated five times for each material. After each test the thermocouple was detached from the device and cleaned by water and acetic acid in an ultrasonic bath for fifteen minutes. The results of these measurements are presented in Table 3.1, with the error representing 95% confidence interval. The accuracy of the measurements was compared with a study by Klug et al. [82], in which a similar measurement was performed. A comparison of the results is presented in the same table.

![Graphs](image-url)
Figure 3.10 - Melting temperature measurement for HTT apparatus calibration a) Na$_2$SO$_4$ b) CaF$_2$

![Graph showing melting point measurement for HTT apparatus calibration]

Figure 3.11 - Derivative of the time-temperature curve for Na$_2$SO$_4$.

Table 3.1 - Melting point measurement with the modified HTT in the current study.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Avg. of 5 measurements $T_M$ (°C) – this work</th>
<th>Avg. measurements $T_M$ (°C) – Ref. [82]</th>
<th>Actual $T_M$ (°C) [102]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>1420±5.6</td>
<td>1420±21.2</td>
<td>1418</td>
</tr>
<tr>
<td>BaCl</td>
<td>966±6.2</td>
<td>–</td>
<td>963</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>884±8.6</td>
<td>884±13.2</td>
<td>884</td>
</tr>
<tr>
<td>NaCl</td>
<td>802±8.0</td>
<td>–</td>
<td>801</td>
</tr>
</tbody>
</table>
3.2 Sample Preparation

Seven CSAM (CaO, SiO$_2$, Al$_2$O$_3$, MgO) slag samples with different basicities defined as the molar ratio of CaO/SiO$_2$ (C/S) ratio were prepared. The composition of each sample is shown in Table 3.2 and also superimposed on the corresponding phase diagram presented in Figure 3.13. The degree of depolymerization of the network, quantified by the number of non-bridging oxygen atoms over tetrahedrally coordinated atoms (NBO/T, calculated from Eq. 3.1-Appendix A) is also presented in Table 3.2.

Table 3.2 for all the compositions. Optical basicity ($\Lambda_{corr}$- Appendix B) is another measure of the slag depolymerization (mainly used in Chapter 5) is also included in Table 3.2.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>47</td>
<td>45</td>
<td>44</td>
<td>42</td>
<td>40</td>
<td>36</td>
<td>27</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>33</td>
<td>35</td>
<td>36</td>
<td>38</td>
<td>40</td>
<td>44</td>
<td>53</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>MgO</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>C/S</td>
<td>1.52</td>
<td>1.38</td>
<td>1.31</td>
<td>1.18</td>
<td>1.07</td>
<td>0.86</td>
<td>0.53</td>
</tr>
<tr>
<td>NBO/T</td>
<td>1.94</td>
<td>1.78</td>
<td>1.71</td>
<td>1.56</td>
<td>1.44</td>
<td>1.18</td>
<td>0.77</td>
</tr>
<tr>
<td>$\Lambda_{corr}$</td>
<td>0.671</td>
<td>0.661</td>
<td>0.656</td>
<td>0.645</td>
<td>0.636</td>
<td>0.616</td>
<td>0.579</td>
</tr>
</tbody>
</table>
To prepare the synthetic slags, 10 g of oxide powders were blended and melted in a graphite crucible (D=4cm, h=4cm) and heated to approximately 50°C above the slag melting temperature under argon atmosphere. After holding at the temperature for 4 hours, the material was quenched in water, resulting in a glassy homogenous slag which was confirmed by XRD (X-Ray Diffraction) analysis as shown for one of the prepared slags with C/S=1.18 (Figure 3.12).

Figure 3.12 - XRD analysis of slag with C/S=1.18 after water quenching.

\[
\frac{NBO}{T} = \frac{2x_{CaO} - 2x_{Al_2O_3} + 2x_{MgO}}{x_{SiO_2} + 2x_{Al_2O_3}} \quad [7]
\]

Eq. 3.1
3.3 Experimental Procedure

In each run, 3-5 mg of sample was placed on the tip of the thermocouple of the SHTT device. For each sample, a new thermocouple was used and was cleaned prior to the test, first with water followed by acetone in an ultrasound device for 5-10 minutes.

3.3.1 Isothermal Experiments

The sample was heated to 1600°C and held for 1 minute then cooled at approximately 70°C.s⁻¹ to different temperatures at which an isothermal investigation of crystallization is carried out. During each isothermal dwell, the crystallization process was recorded and the start and end times of crystallization were determined as schematically depicted in Figure 3.14-a and b. The crystals appear as an opaque phase in the transparent glassy matrix and are easily identified by using a microscope. The beginning of the transformation was defined as the time at which the
amount of crystallization is less than 1 vol%. To increase the image resolution, an additional light source was placed underneath the thermocouple (the bright ring seen in Figure 3.15).

![Diagram](image)

(a) (b) (c)

Figure 3.14 - Heat treatment of slag samples: a) isothermal heat treatment b) schematic TTT diagram plotted from isothermal heat treatment experiments c) continuous cooling

### 3.3.2 Continuous cooling experiment

The continuous cooling experiments were carried out by first heating the slag to 1600°C and later cooling the slag sample at a certain rate from 1600°C (Figure 3.14-c). The onset and completion times of crystallization at all cooling rates were recorded and the CCT diagrams were then plotted (Section 4.4).

![Images](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1300°C</th>
<th>1280°C</th>
<th>1260°C</th>
<th>1240°C</th>
</tr>
</thead>
</table>

Figure 3.15 - Crystallization of slag with C/S=1.31 during continuous cooling (cooling rate= ~1°C.s⁻¹).
Chapter 4

4 Crystallization behavior

The discussions in this chapter and the following requires comparisons with slag compositions in other studies and since C/S is not a sufficient criteria to distinguish the slag structure, NBO/T is used as an alternative measure of the slag structure in this chapter and the following.

4.1 Visualization of Crystallization

The crystallization behavior of the slag samples at different temperature ranges were observed and will be described in this section. Two different crystallization modes could be identified for the slags with NBO/T=1.71-1.94 and NBO/T<1.71.

4.1.1 Slags with high basicity (NBO/T ≥ 1.71)

At temperatures between 1380-1450°C the nucleation and growth of crystalline phase appeared to lead to equiaxed crystallites, as shown in Figure 4.1. This is believed to be caused by the low viscosity and convection in the slags that arises from the temperature differences between the sample bulk and thermocouple/slag interface. The convection results in the nucleated particles eventually being removed from the thermocouple surface and continuing to grow as equiaxed crystals within the bulk of the sample. At very high temperatures (>1380°C) these crystals were not stable and broke apart because of the extensive fluid flow. This phenomenon did not happen in the case of slags with lower basicities due to the higher viscosity.

Figure 4.2 contains enlarged images of samples with NBO/T=1.71 and 1.94 at different temperatures demonstrating the distinction between elongated and equiaxed crystals.
Figure 4.1 - Equiaxed growth at 1380°C isotherm (NBO/T=1.94).

Figure 4.2- Enlarged images showing (a) equiaxed crystals of sample with NBO/T=1.71 at 1300°C (b) elongated crystals of sample with NBO/T=1.94 at 1150°C.

As the temperature decreases to about 1300°C, in addition to the equiaxed crystals, planar crystallization is also seen where a few crystals tend to grow and cover a large area of slag; thus, a combination of small and large crystals are formed, (Figure 4.3). With further decrease in the temperature, the small equiaxed crystals begin to disappear so that only planar crystals are present (Figure 4.4). One would expect that lower temperatures promote nucleation and result in large number of small crystals which is not the case for this temperature range. It is believed that
at these temperatures, the driving force, \textit{i.e.} undercooling is still insufficient for homogeneous nucleation, as evidenced by the formation of crystals only from the thermocouple surface. Therefore, the number of crystals is dictated by how easily they can be detached from the thermocouple by fluid flow forces. At lower temperatures, due to the higher viscosity of slag, this phenomenon is hindered, resulting in the planar crystallization. However, at low enough temperatures, nucleation can dominate the crystallization process as discussed below.

10s 12s 16s 27s

Figure 4.3 - Mixed planar and equiaxed growth at 1320ºC isotherm (NBO/T=1.94).

14s 16s 20s 23s

Figure 4.4 - Planar growth at 1300ºC isotherm (NBO/T=1.94).

The growth mechanism remains planar down to 1250ºC but as the temperature is further decreased, elongated crystals begin to form and grow in the bulk of the slag, away from the thermocouple.
The difference between sample with NBO/T=1.94 and the other two samples in this group (NBO/T=1.71 and NBO/T=1.78) is the temperature range in which the crystals appear faceted and elongated which is much greater in the former (1120-1200°C). Also the elongated crystals are considerably smaller and with higher density. This is evident by a comparison between Figure 4.5 and 4.6.

Figure 4.5 - Faceted and planar growth at 1170°C isotherm (NBO/T=1.71).

When the temperature reaches about 1150-1170°C, the crystals are elongated and much smaller (Figure 4.6). At temperatures below 1100°C the crystals become very fine and their density increased to a level where a “cloud” of crystals appeared to have formed (Figure 4.7). This change in crystallization behavior is consistent with the transformation theory that at large enough undercooling, massive nucleation can take place, leaving limited space for growth of each crystal [104].
Figure 4.6 – Elongated crystallization at 1150°C isotherm (NBO/T=1.94).

Figure 4.7 - Crystallization of slag with NBO/T=1.94 at 1100°C isotherm.

4.1.2 Slags with low basicity (NBO/T<1.71)

The slags with NBO/T lower than 1.71, showed a different crystallization behavior. The crystallization was translucent instead of opaque, because of higher silica content in these slags. Due to this difference, the crystallization could not be observed without the aid of an additional light source. The crystallization starts from the thermocouple wire and appears as arrays of dendrites forming a planar front in temperature ranges above 1100°C (Figure 4.8 – 4.9). At temperatures below ~1100°C, crystallization is very slow and starts from the bulk of the sample with very small and cloud-like crystals. At NBO/T=1.18 the crystallization takes place only at
one temperature (1100°C). Table 4.1 summarizes crystal morphology of the slag compositions in this study at the different temperature ranges.

Figure 4.8- Crystallization of slag NBO/T=1.56 at 1250°C isotherm.

Figure 4.9 - Crystallization of slag NBO/T=1.56 at 1150°C isotherm.
Table 4.1 - Summary of crystal morphology for slag compositions at different temperature ranges.

<table>
<thead>
<tr>
<th>NBO/T</th>
<th>1100°C</th>
<th>1150-1170°C</th>
<th>1170-1250°C</th>
<th>1250-1300°C</th>
<th>1300-1380°C</th>
<th>1380-1450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.94</td>
<td>cloud-like</td>
<td>elongated</td>
<td>planar</td>
<td>planar-equiaxed</td>
<td>equiaxed</td>
<td></td>
</tr>
<tr>
<td>1.71-1.78</td>
<td>cloud-like</td>
<td>elongated</td>
<td>faceted-planar</td>
<td>planar-equiaxed</td>
<td>equiaxed</td>
<td></td>
</tr>
<tr>
<td>1.44-1.56</td>
<td>cloud-like</td>
<td>planar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.18</td>
<td>planar</td>
<td>no crystallization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.77</td>
<td>no crystallization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2 Determination of the crystalline phases

X-ray Diffraction (XRD) analysis was used to determine the crystalline phases that form during crystallization. For each slag composition, the crystalline phases at two different temperatures (1150°C and 1250°C) were analyzed. The samples were prepared by placing 3-5mg slag sample on the tip of the HTT and quenched to isothermal temperatures (i.e. 1150°C and 1250°C) until fully crystalline.

Based on these results, two crystalline phases are present in these slags: Melilite (a solid solution comprised of Akermanite=Ca$_2$MgSi$_2$O$_7$ and Gehlenite=Ca$_2$Al$_2$Si$_2$O$_7$) and Merwinite=Ca$_3$MgSi$_2$O$_8$ slags with NBO/T<1.56 crystallized as Melilite at both 1150°C and 1250°C while slags with higher basicity contain Merwinite as well as Melilite at 1250°C but only Melilite at 1150°C. These results are almost consistent when compared with the phase diagram (Figure 3.13). In two other studies by Rocabois et al. [105] and Kashiwaya et al. [19] XRD and SEM analysis was performed on slag compositions similar to this study. In the study by Kashiwaya et al. a blast furnace slag composition of C/S=1.28 was analyzed and two main crystalline phases of Merwinite and Gehlenite were observed. It was found that Merwinite precipitated faster than Gehlenite which can be attributed to the difference of the diffusivity of Mg and Al since Si and Ca are present in both phases. For slags with higher basicity, since Al acts as an acidic oxide and
forms AlO₄⁻ five tetrahedron in the silicate structure, it is more difficult for it to migrate compared to Mg. In addition, since Merwinite has lower Gibbs free energy of formation, it has higher driving force to form.

### 4.3 Time-Temperature-Transformation (TTT) diagram

The TTT diagrams of different slag compositions are shown in Figure 4.10. The sample with a NBO/T=0.77 did not crystallize at any temperature. Also, the sample with NBO/T=1.18 only crystallized at a single temperature (shown as a point in Figure 4.10 - a). The start curve of TTT diagrams of six slag samples are shown in Figure 4.11.
Figure 4.10 - TTT Diagram for samples with (a) NBO/T= 1.18 (b) NBO/T = 1.44 (c) NBO/T =1.56 (d) NBO/T=1.71(e) NBO/T = 1.78 (f) NBO/T =1.94.
As evident from Figure 4.11, with increasing basicity expressed as NBO/T, the TTT curves of glassy to crystalline transformation shift to the left indicating higher tendency for crystallization. This agrees with the fact that with the increase of basicity, a greater number of Si-O bonds are broken, which in turn facilitates the re-ordering of the silicate structure, i.e. faster crystallization. Higher basicity also shifts the TTT diagrams to higher temperatures since the liquidus temperatures increase with an increase in the basicity.

4.4 Continuous Cooling Transformation (CCT) diagram

The CCT diagrams of the slag were obtained by continuously cooling the samples at different rates and recording the start time of the crystallization. The CCT diagrams for the five slag compositions (NBO/T=1.44-1.94) are presented in Figure 6.14 (a)–(e). The slag with NBO/T<1.44 did not crystallize when cooled even as slow as 0.2 °C.s⁻¹. The summary of all CCT diagrams is shown in Figure 4.12 (f) for comparison.
Figure 4.12 - CCT Diagram for slag samples with (a) NBO/T = 1.44 (b) NBO/T = 1.56 (c) NBO/T = 1.71 (d) NBO/T = 1.78 (e) NBO/T = 1.94 (f) Comparison of all CCT diagrams.
Chapter 5

5 Prediction of the critical cooling rate

The application of ironmaking blast furnace slag in cement or glass making materials requires knowledge of its crystallization kinetics. As cement feedstock for example, the slag is suitable if it is highly amorphous, necessitating a certain cooling rate that prevents crystallization. On the other hand, in the process of energy recovery from slag, a smaller amount of coolant (e.g. air), thus a low cooling rate, is desired to allow producing a high grade heat. The compromise between these two constraining requirements on the cooling rate is to cool the slag, at a rate that is just sufficient to prevent crystallization, but not greater. Defined as critical cooling rate $R_C$, this parameter is highly dependent on the composition of the material being cooled.

Previously, many studies have been performed to both compute and predict $R_C$ for glasses [76, 100, 106-113]. Some of these methods are based on generating time-temperature curves either at a constant temperature (isothermal treatment) or at a constant rate (continuous cooling). For example, in a study by Baradarian et al. [114] a theoretical expression was found for determination of $R_C$ based on non-isothermal equations derived from isothermal Avrami equations. The expression was later validated based on DSC measurements. Macfarlane et al. [108] used growth and nucleation theories together with the additivity principle to calculate the critical cooling rate. Another method based on DTA has also been proposed by Ray et al. [115].

Numerical methods have been developed which are relatively accurate but are very time consuming and require knowledge of fundamental kinetic and thermodynamic parameters. Among these, the most practical method is the experimentally based “nose method” in which the critical cooling rate is obtained from the Time-Temperature-Transformation (TTT) diagram by essentially determining the tangent to the TTT diagram at its nose. In a recent study by Qin et al. [73] the critical cooling rate of a single synthetic blast furnace slag composition was found to be equal to 10°C/s by this method. In another study by Sun et al. [66, 75] similar technique was used to find the effect of the alumina content on the cooling rate and glass formability of three synthetic CSAM slag compositions. In order to understand the relation between $R_C$ and the slag composition, and seek the possibility of establishing an empirical correlation, the current study
was conducted. Seven CaO-SiO$_2$-Al$_2$O$_3$-MgO (CSAM) slags were prepared and their crystallization behaviors were observed visually, and quantified by determining their TTT/CCT (Continuous-Cooling-Transformation) diagrams, as described in the previous chapter. In this chapter, those results together with data from 5 other studies, encompassing 44 slag compositions were evaluated to investigate a possible relationship between slag composition and $R_c$. Further, the data were fitted to a model by Uhlmann and his co–workers [106, 116] to establish a semi–empirical expression for estimating $R_c$ from the slag liquidus temperature and viscosity.

5.1 Critical Cooling Rate

The critical cooling rate is the minimum cooling rate that results in a completely glassy slag (i.e. no crystalline content) and can be found from Eq. 5.1.

$$R_{C(TTT)} = \frac{T_L - T_{nose}}{t_{nose}}$$  \hspace{1cm} \text{Eq. 5.1}

where $T_L$ is the liquidus temperature, $T_{nose}$ and $t_{nose}$ are the temperature and time corresponding to the nose of the TTT or CCT diagrams, respectively. The nose of the diagram represents a temperature at which the kinetics of transformation is the fastest, as a result of opposite dependence of nucleation and growth to undercooling [117]. A tangent to the nose, originated from the liquidus temperature ($T_L$) yields $R_c$. From the TTT diagrams of the above slags, $T_{nose}$ and $t_{nose}$ were obtained. Also, the liquidus temperature of each slag was determined using FactSage™ thermodynamic package [118] (Table 5.1) which was also verified experimentally by HTT. The results yielded the critical cooling rates of the slags, plotted against NBO/T in Figure 5.1.
Table 5.1 - Liquidus temperature, $T_L$, calculated using FactSage™

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_L$ (°C)</td>
<td>1578</td>
<td>1444</td>
<td>1430</td>
<td>1396</td>
<td>1360</td>
<td>1290</td>
<td>1225</td>
</tr>
<tr>
<td>$T_L$ (°C)</td>
<td>1519</td>
<td>1483</td>
<td>1461</td>
<td>1400</td>
<td>1321</td>
<td>1294</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 5.1 - $R_C$ from TTT diagram vs. NBO/T and $\Lambda_{corr}$.

The critical cooling rates obtained from CCT diagram are in the range of 0.3–21°C.s$^{-1}$ for slags with NBO/T of 1.56 to 1.94, as shown in Table 5.2. It is evident that $R_C$ from TTT diagram is larger than the value obtained from CCT diagram. The difference between the $R_C$ values agrees with the critical cooling rates reported for glass formation in other studies [110]. The reason for this difference is when calculating $R_C$ from Eq. 5.1, it is assumed that the crystallization rate is as rapid as that at the nose of the TTT diagram thus the critical cooling rate obtained from the TTT diagram overestimates the cooling rate required for the transformation under continuous cooling.
conditions [112]. For practical purposes and when amorphous product is desired, the larger of the two, *i.e.* from TTT diagram is more useful as it reduces the possibility of crystallization.

### Table 5.2 - Critical cooling rates estimated using TTT and CCT diagrams.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_C$ from CCT diagram</td>
<td>21</td>
<td>12</td>
<td>8</td>
<td>0.3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$R_C$ from TTT diagram</td>
<td>56</td>
<td>30</td>
<td>23</td>
<td>9</td>
<td>6</td>
<td>0.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>

#### 5.1.1 Relationship between slag composition and critical cooling rate

In order to establish a correlation between composition and critical cooling rate, data from five other references [92, 105, 107, 119, 120] were compared to the results of the current study, with 51 compositions in total. The compositions in these studies ranged from CA (CaO, Al$_2$O$_3$) [92], CAM (CaO, Al$_2$O$_3$, MgO) [92] and CSAM slags containing various other types of oxide including FeO, TiO$_2$, Na$_2$O, K$_2$O etc. [107, 119, 120]. As a simple basicity measure such as C/S, would not represent the slag chemistry for this wide range of compositions, the results are presented against two more inclusive indices, NBO/T and corrected optical basicity ($\Lambda_{corr}$) [121] in Figure 5.2. The results indicate that the coefficient of variation (CV) was equal to 0.58 for Figure 5.2-a as compared to a value of 0.70 for Figure 5.2-b. This is due to the wide range of alumina content in these samples. Since alumina has amphoteric behavior in slag structure, it can act as both network-modifier or network-former depending on its concentration and availability of the charge-balancing cations in the slag composition [121]. Corrected optical basicity accounts for this behavior and therefore using this parameter is highly suggested when comparing the critical cooling rate for different slag compositions especially when the alumina content changes significantly.
As seen in Figure 5.2-b, the scatterplot is demonstrated by three parallel trend lines. The compositions of the samples following each trend line belong to a specific group of slags with a few exceptions. The line on the right belongs to CAM and CA slag system. The line in the middle represents CSAM slag and finally the line on the left denotes slags containing oxides such SiO₂, CaO, Al₂O₃, MgO as well as TiO₂, FeO, MnO, K₂O, Na₂O etc. It is believed that the addition of these oxides contributes to the formation of inclusions which act as nucleating sites and therefore increase of \( R_C \). Also, as will be discussed later, various studies are not necessarily consistent in their method of \( R_C \) determination, hence additional deviations in the values.

### 5.1.2 Dependence of critical cooling rate on viscosity

The relationship between the critical cooling rate and composition hinted the possibility of relating \( R_C \) to viscosity as both viscous flow and crystallization are dependent on the slag structure and composition. The viscosity at \( T_{\text{nose}} \) was calculated using Factsage™ by first calculating the viscosity at a temperature range above the liquidus and then extrapolating the data to \( T_{\text{nose}} \). The calculated viscosity of the slags at liquidus temperature was compared to measured viscosity of similar slag compositions which resulted in similar values. Figure 5.3 shows the dependence of both viscosity and \( R_C \) on \( \Lambda_{\text{corr}} \). As evident from this figure, the two form a mirror image of each other, showing an opposite dependence on the slag basicity.
Figure 5.3 - $R_C$ and $\eta_{nose}$ (Pa. s) vs. $\Lambda_{corr}$.

A similar relation between viscosity at $T_L$ and $R_C$ could be seen (Figure 5.4), which is not surprising, noting that the ratio of $\frac{T_{nose}}{T_L}$ is constant as explained below. In this figure, NBO/T is again compared with optical basicity and it is shown that the correlation is stronger when using $\Lambda_{corr}$ (evident from CV value of 0.69 in Figure 5.4-a compared to 0.88 in Figure 5.4-b).
Figure 5.4 - Correlation between slag composition and viscosity at liquidus temperature ($\eta_L$).

The $R_c$ values of the current study were compared with those in two other publications by Prapakorn et al. (for CA and CAM slags) [92] and Rocabois et al. (CSAM) [105]; it was found that there is a linear relationship between Log $R_c$ and Log $\eta_{nose}$ ($\eta_{nose}$ = viscosity at $T_{nose}$), Figure 5.5. This finding is in agreement with the earlier studies carried out on different binary silicate systems [100, 122].
Figure 5.5 - Log $R_c$ vs. Log ($\eta_{nose}$/Pa.s).

The same plot was found for $\eta_L$ and the correlation was compared. Based on Figure 5.6, both $\eta_L$ and $\eta_{nose}$ correlate very well with $R_C$. This trend is in agreement with the results reported by Asayama et al. [100] which show a similar trend between the liquidus viscosity of six alkaline and alkaline earth silicate systems.
5.2 Prediction of the critical cooling rate

According to Eq. 5.1, $T_L$, $T_{nose}$, and $t_{nose}$ are required to calculate the critical cooling rate. The liquidus temperature of slag, $T_L$, can be obtained from the phase diagram or thermodynamic packages containing slag chemistry models. Also, Uhlmann and Yinnon [116] have shown that $T_{nose}$ is directly related to the liquidus melting temperature through Eq. 5.2. Therefore, if the time at the nose of the TTT diagram ($t_{nose}$) is known $R_C$, can be predicted.

$$T_{nose} = 0.77T_L \quad \text{Eq. 5.2}$$

$t_{nose}$ can be calculated using the simplest form of the theory of transformation kinetics correlation Eq. 5.3.

$$X_c = \left(\frac{\pi}{3}\right) \hat{N} G^3 t^4 \quad \text{Eq. 5.3}$$
In this equation, \( \hat{N} \) is the nucleation rate, \( G \) is the growth rate, \( t \) is transformation time and \( X_c \) is the minimum detectable transformed volume fraction, conventionally taken as 0.01.

\[
R_c = \frac{(T_L - T_{nose})[\frac{\pi}{3} \times \hat{N} \times G^3]^{1/4}}{X_c^{1/4}} \tag{Eq. 5.4}
\]

\( G \) and \( \hat{N} \) can be calculated using Eq. 5.5 and Eq. 5.6 [106].

\[
\hat{N} = \frac{K'}{\eta} \exp\left(\frac{0.0205B}{\Delta T_r^2 T_r^3}\right) \tag{Eq. 5.5}
\]

\[
G = K'' \frac{T_L}{\eta} \left[1 - \exp\left(-\frac{\Delta H_M \Delta T_r}{RT_{nose}}\right)\right] \tag{Eq. 5.6}
\]

where \( \Delta T_r = \frac{\Delta T_{nose}}{T_L} \) and \( T_r = \frac{T_{nose}}{T_L} \) and \( R \) is gas constant.

The predictive expression for \( R_c \), Eq. 5.7, is obtained by substituting Eq. 5.5 and Eq. 5.6 into Eq. 5.4. This equation shows that \( R_c \) can be calculated by only having three parameters (i.e. \( \eta_{nose} \), \( T_M \) and \( \Delta H_M = \) heat of fusion).

\[
R_c = \frac{AT_L^2}{\eta_{nose}} \exp(-0.212B) \left[1 - \exp\left(-\frac{0.3 \Delta H_M}{RT_L}\right)\right]^{3/4} \tag{Eq. 5.7}
\]

In Eq. 5.7, \( B \) is the nucleation barrier and can be found by plotting \( R_c \) against \( \lambda = \frac{AT_L^2}{\eta_{nose}} \left[1 - \exp\left(-\frac{0.3 \Delta H_M}{RT_L}\right)\right]^{3/4} \) for a set of measurements, with the slope of the line representing \( \exp(-0.212B) \). In order to estimate the value of \( B \), the required parameters \( (T_L, \eta_{nose}, \) and \( \Delta H_M) \) were obtained by thermodynamic calculations for the slag compositions of the current study. The ratios of \( T_{nose}/T_L \) for the present work and earlier reports [92, 105] are shown in
Table 5.3. As seen, the average value for $T_{nose}$ is 0.82$T_L$ which is greater than the value suggested by Uhlmann et al. 0.77$T_L$.

Table 5.3 - $T_{nose}/T_L$ value in the current study and Ref. [92, 105]

<table>
<thead>
<tr>
<th>Reference</th>
<th>No. of measurements</th>
<th>Avg. $T_{nose}/T_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>6</td>
<td>0.80 ± 0.03</td>
</tr>
<tr>
<td>Rocabois et al. [105]</td>
<td>14</td>
<td>0.85± 0.07</td>
</tr>
<tr>
<td>Prapakorn et al. [92]</td>
<td>6</td>
<td>0.81 ± 0.03</td>
</tr>
<tr>
<td>Total</td>
<td>20</td>
<td>0.83 ±0.06</td>
</tr>
</tbody>
</table>

Based on thermodynamic calculations it was concluded that $\Delta H_M$ can be assumed constant and the critical cooling rate for the slags in this study was not dependent on this parameter. A plot of the data (Figure 5.7) yields a value of $B=103$. According to Uhlmann [123], the nucleation barrier may also be estimated from Eq. 5.8, yielding a value of $B\approx108$. It should be noted that this equation can only be used in the case of materials with large entropies of fusion ($\Delta S_M>33$ J.mol$^{-1}.K^{-1}$) [124]. This criterion holds for the slag compositions in the current study ($\Delta S_M\approx75$ J.mol$^{-1}.K^{-1}$).
Figure 5.7 – Critical cooling rate against $\lambda$

\[ B \approx 12.6 \Delta H_M / R T_L \]  

Eq. 5.8

Using a value of $B = 103$, the critical cooling rate expression can be presented as:

\[ R_c = \left(1.23 \times 10^{-5}\right) \left(T_E^2 / \eta_{nose}\right) \]  

Eq. 5.9

The validity of the correlation was tested against the data presented in Ref. [92, 105], as well as those of this study. The expression would clearly best reproduce the $R_c$ values of slag compositions investigated in the present work, as the correlation constants were based on its experimental data. There is also a good agreement between the predicted critical cooling rates and the reported values by Prapakorn [92]. The differences are believed to be primarily due to the uncertainties in accurately locating the nose of the TTT diagram, as the nose is rather wide in their measurements. A consistent trend can also be found between calculated $R_c$ and the reported values by Rocabois et al. [105]. The differences between measured and calculated critical cooling rates in this case are larger by a factor of 0.5–10. This is believed to be caused by their method of obtaining the TTT diagrams, which involves containing the slag sample in a sealed
steel crucible, holding at the desired temperature, and then quenching the sample, and measuring the glass content by microscopic observation. This approach would entail several errors; temperature measurement, as the slag is not in direct contact with thermocouple; cooling of slag during its transfer from furnace until quenching (reported to take 5–10 s), and limitations in the number of slag samples that can be processed for each isotherm. The SHTT technique used in the current study eliminates all these limitations by direct measurement of slag temperature, and also providing essentially numerous images with microsecond intervals, while crystallization is taking place. Therefore, the expression is believed to be valid for providing a reasonable estimate of the critical cooling rate of slags.

Table 5.4 - Critical cooling rate predicted for CSAM slags (current study).

<table>
<thead>
<tr>
<th>NBO/T</th>
<th>( \Lambda_{corr} )</th>
<th>( T_L (^\circ C) )</th>
<th>( t_{nose} (s) )</th>
<th>( \eta_{nose} (\text{Pa.s}) )</th>
<th>( T_{nose} (^\circ C) )</th>
<th>RC ((^{\circ C}.s^{-1}))</th>
<th>TTT</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.94</td>
<td>0.671</td>
<td>1578</td>
<td>8</td>
<td>0.7</td>
<td>1165</td>
<td>56</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>1.78</td>
<td>0.661</td>
<td>1444</td>
<td>9</td>
<td>1.8</td>
<td>1175</td>
<td>30</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>1.71</td>
<td>0.656</td>
<td>1430</td>
<td>12</td>
<td>2.1</td>
<td>1140</td>
<td>23</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>1.56</td>
<td>0.645</td>
<td>1396</td>
<td>32</td>
<td>3.4</td>
<td>1100</td>
<td>9</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>1.44</td>
<td>0.636</td>
<td>1360</td>
<td>40</td>
<td>5.6</td>
<td>1100</td>
<td>6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1.18</td>
<td>0.616</td>
<td>1290</td>
<td>528</td>
<td>19.0</td>
<td>1100</td>
<td>0.4</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5 - Critical cooling rate predicted for CSAM slags from Ref. [105].
<table>
<thead>
<tr>
<th>NBO/T</th>
<th>$\Lambda_{corr}$</th>
<th>$T_L$ (°C)</th>
<th>$t_{nose}$ (s)</th>
<th>$\eta_{nose}$ (Pa.s)</th>
<th>$T_{nose}$ (°C)</th>
<th>$R_L$ (°C.s$^{-1}$)</th>
<th>$R_C$ (°C.s$^{-1}$)</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.12</td>
<td>0.618</td>
<td>1408</td>
<td>300</td>
<td>4.2</td>
<td>1025</td>
<td>1.3</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>1.04</td>
<td>0.615</td>
<td>1396</td>
<td>600</td>
<td>6.7</td>
<td>1025</td>
<td>0.6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1.01</td>
<td>0.613</td>
<td>1403</td>
<td>330</td>
<td>15.2</td>
<td>1175</td>
<td>0.7</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>0.99</td>
<td>0.612</td>
<td>1387</td>
<td>900</td>
<td>9.3</td>
<td>1050</td>
<td>0.4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>0.89</td>
<td>0.599</td>
<td>1376</td>
<td>390</td>
<td>32.2</td>
<td>1300</td>
<td>0.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.86</td>
<td>0.598</td>
<td>1343</td>
<td>300</td>
<td>21.4</td>
<td>1100</td>
<td>0.8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.81</td>
<td>0.603</td>
<td>1408</td>
<td>300</td>
<td>4.2</td>
<td>1025</td>
<td>1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>0.78</td>
<td>0.601</td>
<td>1396</td>
<td>600</td>
<td>6.7</td>
<td>1025</td>
<td>0.1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.72</td>
<td>0.571</td>
<td>1403</td>
<td>330</td>
<td>15.2</td>
<td>1175</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>0.64</td>
<td>0.567</td>
<td>1387</td>
<td>900</td>
<td>9.3</td>
<td>1050</td>
<td>1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>0.63</td>
<td>0.592</td>
<td>1376</td>
<td>390</td>
<td>32.2</td>
<td>1300</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.62</td>
<td>0.612</td>
<td>1343</td>
<td>300</td>
<td>21.4</td>
<td>1100</td>
<td>0.12</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>0.52</td>
<td>0.559</td>
<td>1380</td>
<td>300</td>
<td>12.4</td>
<td>1200</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>0.543</td>
<td>1305</td>
<td>900</td>
<td>43.4</td>
<td>1200</td>
<td>0.003</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.6 - Critical cooling rate predicted for CAM and CA slags Ref. [92].
<table>
<thead>
<tr>
<th>NBO/T</th>
<th>$\Lambda_{corr}$</th>
<th>$T_L(°C)$</th>
<th>$t_{nose}$ (s)</th>
<th>$\eta_{nose}$ (Pa.s)</th>
<th>$T_{nose}$ (°C)</th>
<th>TTT</th>
<th>$R_C (°C.s^{-1})$</th>
<th>$R_C (°C.s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.27</td>
<td>0.704</td>
<td>1500</td>
<td>6</td>
<td>0.6</td>
<td>1140</td>
<td>59</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>1.13</td>
<td>0.698</td>
<td>1400</td>
<td>8</td>
<td>1.1</td>
<td>1120</td>
<td>37</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1.07</td>
<td>0.705</td>
<td>1470</td>
<td>5</td>
<td>0.7</td>
<td>1200</td>
<td>54</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>0.92</td>
<td>0.689</td>
<td>1383</td>
<td>8</td>
<td>1.2</td>
<td>1160</td>
<td>28</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>0.84</td>
<td>0.687</td>
<td>1365</td>
<td>18</td>
<td>1.3</td>
<td>1080</td>
<td>16</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>0.66</td>
<td>0.672</td>
<td>1428</td>
<td>5</td>
<td>1</td>
<td>1200</td>
<td>46</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.8 - $R_C$ from TTT vs. $R_C$ predicted.
Chapter 6

6 Kinetics of crystallization

There have been several studies on crystallization kinetics of mold fluxes [3, 76, 77, 81, 112, 125, 126] due to their important role in controlling the heat transfer and lubrication in the steel continuous casting mold. However, similar investigations for metallurgical slags are scarce [73, 105, 127, 128]. In a recent study [73] the transformation kinetics of a slag with composition close to the BF slags has been studied but to this date, a comprehensive study on the effect of composition on the rate and extent of crystallization is lacking. This chapter will present the results of the kinetic study on CASM slags.

6.1 Theoretical treatment of transformation

Quantifying the transformed volume fraction during isothermal transformation requires the understanding of the effect of impingement between two growing domains (i.e. crystals/grains) of the new phase. The theoretical treatment was carried out through the extended volume fraction concept, proposed by Johnson, Mehl, Kolmogrorov, and Avrami [129-132], and known as the “Avrami theory”.

Supposing that two crystals of the new phase co–exist at time \( t \), after a small time interval new regions have formed (Figure 6.1-b). However, only those crystals that have formed in the previously untransformed regions can contribute to a change in the real volume of the product phase \( \alpha \).

\[
dV^\alpha = \left(1 - \frac{V_\alpha}{V}\right) dV_e^\alpha
\]

Eq. 6.1

In the above equation, \( V^\alpha \) is the volume of the phase that is being transformed (\( \alpha \)), \( V \) is the total volume and \( V_e^\alpha \) is the extended volume, which is the space that new regions are able to grow in unrestrictedly. Multiplying the change in extended volume by the probability of the formation of the untransformed regions is basically excluding regions which clearly cannot contribute to the real change in volume of the product [117].
For a random distribution of precipitated crystals, this equation can easily be integrated to obtain the transformed volume fraction (Eq. 6.2):

$$\frac{V_{\alpha}}{V} = 1 - \exp\left(-\frac{V_{e\alpha}}{V}\right)$$

Eq. 6.2

$V_{e\alpha}$ can be calculated by using nucleation and growth models and completely neglecting any impingement effects. For an isothermal transformation with isotropic growth at a constant rate $G$ and a nucleation rate per unit volume, $\dot{N}(t) = dN/dt$, the volume of a spherical crystal nucleated at time $t = \tau$ is given by:

$$v_{\tau} = \frac{4\pi}{3} r^3 = \frac{4\pi}{3} G^3 (t - \tau)^3$$

Eq. 6.3

The number of nuclei that form in a time increment $d\tau$ will be $\dot{N}(t) \times d\tau$ per unit volume of untransformed $\alpha$ and thus the change in the extended volume between the time intervals of $\tau$ and $\tau + d\tau$ is determined through Eq. 6.4.

$$dV_{e\alpha} = \frac{4}{3\pi} V \dot{N}(t) G^3 (t - \tau)^3 d\tau$$

Eq. 6.4

By substituting the above equation into Eq. 6.1, the following is obtained for $V_{\alpha}$:
\[ dV^a = \left(\frac{4}{3\pi}\right)\left(1 - \frac{V_a}{V}\right)V N(t) G^3(t - \tau)^3 d\tau \]  
Eq. 6.5

considering, \( X = \frac{v^a}{V} \), is obtained:

\[-\ln(1 - X) = \frac{4\pi}{3} G^3 \dot{N}(t) \int_0^t (t - \tau)^3 d\tau = \frac{\pi}{3} \dot{N}(t) G^3 t^4 \]  
Eq. 6.6

and therefore at a constant nucleation rate we have:

\[ X = 1 - \exp\left[-\frac{\pi}{3} \dot{N}(t) G^3 t^4\right] \]  
Eq. 6.7

This equation (Eq. 6.7) is known as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation.

A simplified form of the above equation is often used (Eq. 6.8).

\[ X = 1 - \exp[-(kt)^n] \]  
Eq. 6.8

This expression describes the relationship between the transformed volume fraction and time as a sigmoidal curve. The coefficient \( K \) is a kinetic parameter which includes both nucleation and growth rates. The Avrami exponent, \( n \), can provide useful information on the mechanism of transformation. In the following paragraphs, the relationship between \( n \) and the mechanism of nucleation and growth will be described.

In the case of transient nucleation rate, if \( N(t) \) is considered a simple function of time, at an isothermal temperature \( N(t) = N_0 t^a \) and thus, \( \dot{N}(t) = aN_0 t^{a-1} \).

The growth mechanism can be either diffusion-controlled or interface-controlled. The former involves short or long-term diffusion of atoms so that the formation of new phase involves compositional changes. The interface-controlled growth on the other hand takes place through local rearrangement of the atoms. In the case of diffusion controlled growth, \( G \) can be considered a function of diffusion coefficient and time, \( G = k (D/t)^{1/2} \). By substituting \( \dot{N}(t) \) and \( G \) into Eq. 6.7 and comparing with Eq. 6.8, we can find:
- if $a>1$, i.e. nucleation rate is increasing with time, $n>2.5$
- if $1>a>0$, i.e. nucleation rate is decreasing with time, $2.5>n>1.5$
- if $a=1$, i.e. nucleation rate is constant with time and $n=2.5$
- if $a=0$, i.e. nucleation rate is zero and $n=1.5$

However, if the growth is interface-controlled, the growth rate, $G$, is constant with time, therefore:

- if $a>1$, i.e. nucleation rate is increasing with time, $n>4$
- if $1>a>0$, i.e. nucleation rate is decreasing with time, $n=4$
- if $a=1$, i.e. nucleation rate is constant with time and $3>n>4$
- if $a=0$, i.e. nucleation rate is zero and $n=3$

The above is summarized in relation to the Avrami exponent in Table 6.1.

<table>
<thead>
<tr>
<th>Diffusion-controlled growth</th>
<th>$n$</th>
<th>Interface-controlled growth</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All shapes growing from small dimensions, increasing nucleation rate</td>
<td>&gt;2.5</td>
<td>Increasing nucleation rate</td>
<td>&gt;4</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, constant nucleation rate</td>
<td>2.5</td>
<td>Constant nucleation rate</td>
<td>4</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, decreasing nucleation rate</td>
<td>1.5-2.5</td>
<td>Decreasing nucleation rate</td>
<td>3-4</td>
</tr>
<tr>
<td>All shapes growing from small dimensions, zero nucleation rate</td>
<td>1.5</td>
<td>Zero nucleation rate (Saturation of point sites)</td>
<td>3</td>
</tr>
<tr>
<td>Growth of crystals of appreciable initial volume</td>
<td>1-1.5</td>
<td>Grain edge nucleation after saturation</td>
<td>2</td>
</tr>
<tr>
<td>Needles and plates of finite long dimensions, small in comparison with their separation</td>
<td>1</td>
<td>Grain boundary nucleation after saturation</td>
<td>1</td>
</tr>
<tr>
<td>Thickening of long cylinders (needles)</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickening of very large plates</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 6.2 Experimental determination of phase change

Using image analysis techniques, the crystallized fraction of each slag was determined for 9-10 different isothermal temperatures ranging from 1100 to 1300ºC. The crystallized fraction during isothermal transformation for all slag samples at 1170ºC is shown in Figure 6.2 – 6.5. In these figures, the light regions are opaque crystals, which form in the transparent amorphous slag matrix. The bright ring appearing in the middle of some of these figures is due to the additional light source used below the thermocouple to increase the image resolution.
Figure 6.2 - Crystallization of slag with C/S=1.52 at 1200°C isotherm (τ = incubation time).

Figure 6.3 - Crystallization of slag with C/S=1.38 at 1200°C isotherm (τ = incubation time).

Figure 6.4 - Crystallization of slag with C/S=1.31 at 1200°C isotherm (τ = incubation time).
6.3 Determination of the Avrami exponent \((n)\) and rate coefficient \((k)\):

The crystallized fraction from the isothermal treatments were found to follow a sigmoidal form Figure 6.6 – 6.9, described by the JMAK equation (Eq. 6.7). Constants \(n\) and \(Lnk\) could be obtained by plotting \(Ln[-Ln(1-X)]\) verses \(Ln(t-\tau)\) (Eq. 6.9) with values presented in Table 6.2

\[
Ln[-Ln(1-X)] = nLn(k) + nLn(t-\tau) \tag{Eq. 6.9}
\]
Figure 6.6 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.52.

Figure 6.7 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.38.
Figure 6.8 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.31

Figure 6.9 - (a) Crystallized fraction as a function of time (b) JMAK plots for the slag with C/S=1.18
Table 6.2- Avrami exponent \((n)\) and \(LnK\).

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>(n)</th>
<th>(LnK)</th>
<th>(n)</th>
<th>(LnK)</th>
<th>(n)</th>
<th>(LnK)</th>
<th>(n)</th>
<th>(LnK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>–</td>
<td>–</td>
<td>1.9</td>
<td>-1.8</td>
<td>2.0</td>
<td>-1.8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1120</td>
<td>3.1</td>
<td>-0.8</td>
<td>1.4</td>
<td>-2.3</td>
<td>1.5</td>
<td>-1.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1130</td>
<td>–</td>
<td>–</td>
<td>1.3</td>
<td>-2.7</td>
<td>1.6</td>
<td>-2.0</td>
<td>1.5</td>
<td>-5.3</td>
</tr>
<tr>
<td>1140</td>
<td>2.9</td>
<td>-1.1</td>
<td>1.3</td>
<td>-2.7</td>
<td>1.7</td>
<td>-2.1</td>
<td>1.5</td>
<td>-5.4</td>
</tr>
<tr>
<td>1150</td>
<td>2.7</td>
<td>-1.4</td>
<td>2.0</td>
<td>-2.8</td>
<td>1.9</td>
<td>-2.2</td>
<td>1.4</td>
<td>-4.9</td>
</tr>
<tr>
<td>1160</td>
<td>3.9</td>
<td>-1.3</td>
<td>1.4</td>
<td>-2.1</td>
<td>1.4</td>
<td>-2.3</td>
<td>2.0</td>
<td>-5.0</td>
</tr>
<tr>
<td>1170</td>
<td>3.1</td>
<td>-1.2</td>
<td>1.7</td>
<td>-2.0</td>
<td>1.8</td>
<td>-2.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1180</td>
<td>2.8</td>
<td>-1.3</td>
<td>1.6</td>
<td>-2.0</td>
<td>1.9</td>
<td>-2.2</td>
<td>1.9</td>
<td>-4.7</td>
</tr>
<tr>
<td>1200</td>
<td>4.0</td>
<td>-1.9</td>
<td>1.7</td>
<td>-2.4</td>
<td>1.9</td>
<td>-2.2</td>
<td>2.2</td>
<td>-4.7</td>
</tr>
<tr>
<td>1250</td>
<td>3.8</td>
<td>-2.2</td>
<td>2.1</td>
<td>-3.0</td>
<td>1.7</td>
<td>-2.2</td>
<td>2.0</td>
<td>-5.1</td>
</tr>
<tr>
<td>1270</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.0</td>
<td>-5.3</td>
</tr>
<tr>
<td>1300</td>
<td>4.0</td>
<td>-2.6</td>
<td>1.6</td>
<td>-2.9</td>
<td>1.8</td>
<td>-2.9</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

6.4 Nucleation

6.4.1 Dependence of nucleation rate on temperature

Nucleation rate can be expressed as Eq. 6.10 [133, 134].

\[
\dot{N}(T) = N_0 \exp\left(-\frac{\Delta G^*}{RT}\right) \exp\left(-\frac{E_D}{RT}\right) \tag{Eq. 6.10}
\]

where, \(
\dot{N}(T) = dN/dt\) is the nucleation rate, \(N_0\) is the pre-exponential constant and \(E_D\) is the barrier to diffusion of molecules across the phase boundary. \(\Delta G^*\), which is the nucleation energy barrier, is highly dependent on undercooling, \(\Delta T\) (Eq. 6.11), whose magnitude depends on the temperature. At large undercoolings (i.e. lower temperature), \(\Delta G^*\) can be considered very small compared to \(RT\) and thus the term \(\exp\left(-\frac{\Delta G^*}{RT}\right)\) can be neglected in Eq. 6.10. However, at low
undercoolings the barrier to diffusion is very small and the term \( \exp\left(-\frac{E_D}{RT}\right) \) can be neglected. The two–fold dependence of nucleation rate on temperature, Figure 6.10, implies that at a certain temperature, \( T_{\text{max}} \), nucleation rate reaches a maximum value.

\[
\Delta G^* = \left( \frac{16\pi \gamma_{SL}^3 T_M^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2}
\]

Eq. 6.11

where, \( \gamma_{SL} \) is the solid/liquid interfacial free energy, \( L_v \) is the latent heat of fusion per volume.

Figure 6.10 – Dependence of nucleation rate on the temperature range of \( T - T_L \) [134].

To find \( T_{\text{max}} \) from the experimental data, the nucleation rate was measured at the early stage of nucleation (where separate crystals could be identified) and plotted against \( 1/T \) (Figure 6.11). The nucleation rate, defined as the number of nuclei per unit time and volume, was found from image analysis and the volume was estimated from the area and thickness of the slag sample. As shown in this figure, \( T_{\text{max}} \) is in the range of 1140-1160°C, which is close to the nose temperature (\( T_{\text{nose}} \)) of the TTT diagram obtained as 1100 - 1165°C as shown in Figure 6.25. In a study by James [127], \( T_{\text{max}} \) was approximated for a few simple binary silicate systems as \( T_{\text{max}}/T_L=0.54-0.59 \) with \( T_L \) being the liquidus temperature of slag. Based on the liquidus temperatures, this results in values of 782-884°C for the current slag compositions which is
significantly smaller than 1150°C. This is not unexpected, as the nose temperature represents the temperature at which a minimum, measurable amount of transformation has taken place that is determined by a combination of nucleation and growth rates. However, since nucleation is the primary mode of phase transformation in early stages in the current system, $T_{max}$ is very close to $T_{nose}$.

![Graph showingLn (N/s^-1 mm^-3) vs 1/T for C/S values ranging from 1.18 to 1.52 at 1150°C](image)

Figure 6.11 - Ln $\dot{N}$ rate verses $1/T$ for all samples in the early stage of nucleation.

### 6.4.2 Time dependency of nucleation rate

Depending on the nucleation mechanism, the nucleation rate may increase, decrease or remain constant with time. The dependence of nucleation rate on time was investigated by image analysis as shown in Figure 6.12 for the slag with C/S=1.38. The resulting nucleation rates for all slag compositions at T=1200°C are presented in Figure 6.13. As seen, the slag with C/S=1.52 experiences a significant increase in the nucleation rate with time. On the other hand, for the slag with C/S=1.31 and 1.38, the nucleation rate decreases with time. As the basicity is further decreased (C/S=1.18), the nucleation rate becomes close to zero.
Figure 6.12 - Nucleation in slag with C/S=1.38 at T= 1170°C after (a) 10s (b) 11s.

Figure 6.13 - Change of nucleation rate with time for all slags at T=1200°C.

6.5 Growth

The growth rate can also be determined by measuring the thickness of the crystals at different times, using image analysis, as shown in Figure 6.14. For each slag, the measurements were made for three temperatures (1150°C, 1200°C, 1250°C) and the growth rate was measured until the crystal under study grows independently and before colliding with any neighboring crystals. The result of this analysis is presented in Figure 6.15
Figure 6.15 (a)-(d). The slope of these curves corresponds to the growth rate of individual crystals, presented in Table 6.3 and Figure 6.16. For all slags the slopes is constant with time (i.e. constant growth rate). Figure 6.16 shows that the growth rate increases with the increase of basicity which can be attributed to the decrease of viscosity and consequently the higher mobility at the crystal/glass interface. Also, with the increase of temperature (decrease of undercooling) the growth rate increases due to the higher mobility of atoms at higher temperatures [135]. Interestingly, this effect becomes more pronounced as the basicity is increased.

Figure 6.14 - Growth rate measurement for sample with C/S=1.38 at T=1250°C (a) $t - \tau = 3s$
(b) $t - \tau = 6s$. 
Figure 6.15 - Crystal thickness verses time (a) C/S=1.52 (b) C/S=1.38 (c) C/S=1.31 (d) C/S=1.18.
Table 6.3 - Crystal growth rate (\(\mu\text{m/s}\)) at different temperatures.

<table>
<thead>
<tr>
<th>Basicity (C/S)</th>
<th>Growth rate ((\mu\text{m/s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1250°C</td>
</tr>
<tr>
<td>1.52</td>
<td>68</td>
</tr>
<tr>
<td>1.38</td>
<td>58</td>
</tr>
<tr>
<td>1.31</td>
<td>38</td>
</tr>
<tr>
<td>1.18</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 6.16 - Dependence of growth rate on basicity.

The dependence of growth rate on time may provide some indications to the mechanism of growth. In most cases, linear dependence corresponds to interface-controlled growth whereas when growth is proportional to the square root of time, it can be considered to be diffusion-controlled. However, in the former case, it has been suggested that a constant growth rate does not always translate to interface-controlled growth. For example, Uhlmann [136] has discussed that in most multicomponent systems the growth rate is controlled by diffusion even though the growth is not of function the square root of time. This is due to the dendritic growth morphology
in which the scale of diffusion field can be unvaried resulting in a constant growth rate. This behavior is consistent with the results observed by Swift [137] in his study on crystallization of soda-lime-silica glasses. In other studies by Schurer and Uhmlann [138], it was observed that in such growth behavior, arrays of dendrites with a planar front is formed. In other words, measurements of growth rate are based on observations that are not detailed enough to distinguish between a flat interface, and a growth front composed of many dendrites advancing simultaneously. Accordingly, for determining the mechanism of growth it is best to examine the morphology of the interface in atomic scale. In general, when faceted interface is observed, the rate-controlling step is the interface reaction. However, when the interface is rough and cellular, such as dendritic growth, the rate limiting mechanism for growth is diffusion [139].

In the case of the compositions in the current study, the morphology of the interface was not examined in near atomic scale but an observation through a microscope clearly shows that the interface is not faceted which confirms a dendritic growth. With the decrease of basicity, the interface becomes rougher and the dendrites become coarser to a point where they can easily be observed through the microscope for a sample with C/S=1.18 (Figure 6.17). An interesting behavior seen for this slag is that the growth becomes more dendritic as the undercooling is decreased as depicted in Figure 6.17 (a)-(c).

![Figure 6.17](image_url)

(a) (b) (c)

Figure 6.17 - Interface morphology for sample with C/S=1.18 at (a) T=1250°C the interface is fully dendritic (b) T=1200°C semi-dendritic (c) T=1130°C planar.
6.5.1 Activation energy of growth

In the case of diffusion-controlled growth, crystal thickness ($X$) is proportional to the square root of the diffusion coefficient, $D(T)$, through Eq. 6.12. Thus, the growth rate ($dX/dt$) and the diffusion coefficient are related through Eq. 6.12 and the activation energy of growth, $(E_D)$, can be obtained from Eq. 6.13.

$$X = k \sqrt{D(T) \times t} \quad \text{Eq. 6.12}$$

$$\frac{dX}{dt} = \frac{1}{2} k \sqrt{\frac{D(T)}{t}} \quad \text{Eq. 6.13}$$

$$G(T) = \frac{1}{2} k \sqrt{D_0 \exp \left( -\frac{E_D}{RT} \right)} \quad \text{Eq. 6.14}$$

where $D_0$ is the pre-exponential constant.

For determining the activation energy of growth, the growth rates presented in the previous section were plotted against $(1/T)$ at three temperatures ($1150^\circ\text{C}$, $1200^\circ\text{C}$, $1250^\circ\text{C}$), as shown in Figure 6.18. The slope of these lines is equal to $-\frac{1}{2} \frac{E_D}{RT}$, giving the approximate activation energy of growth (Eq. 6.15), which should also be equal to the activation energy of diffusion of species, Table 6.4.
\[
\ln G = \ln \left( \frac{1}{2} k - \frac{1}{2} \ln T + \frac{1}{2} \ln D_0 - \frac{1}{2} \frac{E_D}{RT} \right)
\]  

Eq. 6.15

As depicted in Figure 6.19, \( E_D \) decreases with the decrease of basicity from \( C/S = 1.52 \) to \( C/S = 1.31 \). However, for the sample with \( C/S = 1.18 \), the activation energy for growth is the highest. It should be noted that this activation energy is for the entire growth phenomena, and may represent diffusion barrier for several species, rather than one. In other world, as short or long range diffusion of several different atoms are required to transform an amorphous structure to a crystalline one, the activation energy obtained here is likely a composite effect of diffusion of all participating atoms. On the other hand, if diffusion of only one specific atom was slowest among diffusing atoms, the activation energy could be attributed to that atom. The diffusion activation energy of oxygen, which has the smallest value compared to the other components, was found from Ref. [140] and compared to the values in Table 6.4. The values fall between 142-167 \( \text{kJ.mole}^{-1} \) for a slag system of \( \text{CaO}, \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) which is in good agreement with the values found in this study.
6.6 Mechanism of slag crystallization

In this section, the $n$ values will be compared with theoretical values for various nucleation and growth modes, to determine the crystallization mechanism pertaining to the slags of the present study. As discussed earlier, the growth for slags appear to involve a diffusion-controlled process. According to the $n$ values suggested by Christian [104], for slag C/S=1.52, the nucleation rate is increasing, indicating that based on the theoretical treatment, $n$ must be above 2.5. This is consistent with the measured value of $4.0 > n > 2.8$ presented in Table 6.2. However, for the
slag with C/S=1.31 and C/S=1.38, the nucleation rate is decreasing which would suggest $n$ values between 1.5-2.5. This is also in agreement with the measured values of $n$ which falls within the same range as demonstrated in Table 6.2. For the sample with C/S=1.1 the nucleation rate is close to zero which again shows a match between the measured $n$ values and the those suggested according to Christian [104] for temperatures below 1160°C ($n=1.5$). The only existing discrepancy is for sample with C/S=1.18 at temperatures above 1160°C which is attributed to the difficulty in defining the starting point of nucleation of this sample due to the transparency of the formed crystals at high temperatures, resulting in lower contrast between the matrix and the crystals.

### 6.7 Effect of impingement on growth rate

In a separate analysis, the effect of impingement on the growth rate of crystals was studied. The results show after a crystal collides with another crystal, the growth appears to halt for a short period and once the two crystal fronts merged, continue to grow at the same rate as before. As an example, for the slag with C/S=1.18 at T=1150°C (Figure 6.20), a crystal (crystal no. 1) forms from the wire with a constant growth rate until it collides with a second crystal (crystal no. 2). At this point, as depicted in Figure 6.21, the growth is first paused for about 10 seconds, and then resumes for another 25 seconds until a third crystal (crystal no. 3) hits crystal no. 1. The growth rate is again paused for approximately 10 seconds. When all the three crystals merge together the growth continues at its initial rate. The uncertainty of the measurements is $4.7\mu m$ (212 pixels per 1 mm).
Figure 6.20 - Effect of impinging on the growth rate for sample with C/S=1.18 at T=1150°C after (a) 10s (b) 70s (c) 80s.

Figure 6.21 - Growth rate change with collision of neighboring crystals.

6.8 Effective activation energy of crystallization

The $K$ parameter in the JMAK equation (Eq. 6.7) is the kinetic term which encompasses the rates of nucleation and growth. An Arrhenius-type dependence with temperature (Eq. 6.16) was
sought, with the slope of $\ln K$ versus $1/T$ yielding the effective activation energy ($E_A$), as depicted in Figure 6.22 - 6.24 and 6.26. The $E_A$ values obtained from these figures are presented in Table 6.6. A positive slope for the line implies negative effect of temperature on $K$, i.e. negative values for the effective activation energy. The following analysis discusses the reason for this unconventional dependence of $K$ on temperature.

$$K = K_0 \exp\left(-\frac{E_A}{RT}\right)$$  \hspace{1cm} \text{Eq. 6.16}

Based on the Avrami exponent and observation of the kinetics of transformation, the growth of slag crystals is controlled by diffusion, thus a similar dependence on temperature between diffusion coefficient and growth rate is expected (Eq. 6.13) [141].

Eq. 6.9 was applied to the transformation data of the current study and the corresponding plots were drawn. For the slags with C/S > 1.18 (Figure 6.22 – 6.24) the overall rate constant increases linearly with the decrease of temperature due to the increase of $\Delta T$, an apparent indication that the extent of transformation is dominated by nucleation rather than growth of crystals. However, at $T \approx 1150^\circ$C, corresponding to the nose temperature of the TTT diagram (Figure 6.25) [142], the rate constant has a sudden drop, followed by continued increase with temperature. This change can be related to the different phases that form in the two different temperature ranges (i.e. 1100$^\circ$C to $\sim 1150^\circ$C and 1160$^\circ$C to $\sim 1300^\circ$C). X-Ray Diffraction (XRD) analysis was performed on the slags at $T=1150^\circ$C and $T=1250^\circ$C and the results are summarized in Table 6.5. As evident from this table, for slag compositions with C/S > 1.18, the crystalline phases are different at the two temperatures (e.g. Figure 6.27) but for the slag of C/S=1.18 Melilite, is the stable phase at both temperatures (Figure 6.28).
Table 6.5- XRD results of the crystalline phases formed at two different temperatures
(Melilit= Ca$_4$Al$_2$MgSi$_3$O$_{14}$, Merwinite=Ca$_3$MgSi$_2$O$_8$)

<table>
<thead>
<tr>
<th>Basicity (C/S)</th>
<th>1150°C</th>
<th>1250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.52</td>
<td>Melilit</td>
<td>Melilit, Merwinite</td>
</tr>
<tr>
<td>1.38</td>
<td>Melilit</td>
<td>Melilit, Merwinite</td>
</tr>
<tr>
<td>1.31</td>
<td>Melilit</td>
<td>Melilit, Merwinite</td>
</tr>
<tr>
<td>1.18</td>
<td>Melilit</td>
<td>Melilit</td>
</tr>
</tbody>
</table>

Figure 6.22 - $\ln K$ vs. $1/RT$ (C/S=1.52).
Figure 6.23 - $\ln K$ vs. $1/RT$ (C/S=1.38).

Figure 6.24 - $\ln K$ vs. $1/RT$ (C/S=1.31).
For the slag with C/S=1.18 (Figure 6.26) the rate constant goes through a maximum at ~1160°C. This can be attributed to a shift from a growth-dominated crystallization at higher temperatures to a nucleation-dominated crystallization at temperatures below these maxima. This hypothesis is in agreement with the results of the activation energies of growth ($E_D$) for this slag, which is the highest as presented in Table 6.6. The higher activation energy of this slag could result in very low growth rates and consequently a growth-restricted mechanism. The viscosity of the slag with C/S=1.18 is significantly greater than the other three as was shown in Chapter 5 leading to lower mobility of the species, which in turn slows down the growth. This would create conditions under which the extent of crystallization is determined primarily by generation of new crystals.
Figure 6.26 - \( \ln K \) vs. \( 1/RT \) (C/S=1.18).

Figure 6.27 - XRD spectrums of slag with C/S=1.38 at T=1150°C and T=1250°C.
The $K - T$ plots of all slags has been summarized in Figure 6.29. As shown in this figure, at a constant temperature the rate constant increases with the increase of C/S. This is due to the oxide structure becoming depolymerized and the bonds weakened as the C/S increases resulting in lower viscosities. With the decrease of viscosity the ionic mobility increases and it becomes easier for the structure to rearrange and accommodate the changes induced by crystallization. This can also be explained by the nucleation rate having an inverse relationship with viscosity ($\eta$) (Eq. 6.17) at a constant $\Delta T$ [107].
\[ \dot{N}(T) = \frac{K'}{\eta} \exp \left( \frac{0.0205B}{\Delta T_r^2 T_r^3} \right) \]

Eq. 6.17

where \( \Delta T_r = \frac{\Delta \tau}{T_L} \) and \( T_r = \frac{T}{T_L} \) and \( B \) and \( K' \) are constants.

Figure 6.29 also points to another interesting observation; that with the increase of basicity, the diagrams shift from an inverse cup shape (C/S=1.18) to a partially curved shape followed by a segment of increase for the sample with C/S=1.31 to a sluggish increase for the sample with C/S=1.38, to a clear increase for the sample with C/S=1.52 (all with the decrease of temperature). In other words, if we consider each slag independently, there is a break close to 1160°C, which is because of a change in the type of crystalline phases formed as discussed earlier. However, when comparing all the curves together, there is another trend which shows gradual shift from nucleation dominated regime (for the slags of C/S= 1.31, 1.38, 1.52) to a regime where both nucleation and growth control the process (hence the curved shape at C/S=1.18). The observed trend between various basicities can be related to the viscosity and its impact on mobility of atoms.

Figure 6.29 - \( \ln K \) verses \( \frac{1}{RT} \) for all slag compositions.
Based on the discussion above, the composite effect of the different dependence of nucleation and growth on temperature results in the decrease in $K$ with temperature, the way seen in Figure 6.22 – 6.24 and 6.26. In other words, fitting the data to an Arrhenius type correlation yields an effective activation energy that is only a fitting parameter, and not a true indicator of an intrinsic energy barrier for phase transformation.
Chapter 7

7 Mathematical modeling of slag crystallization and heat recovery

Two mathematical models were developed and employed in combination with experimental data to calculate the extent of heat recovery and slag crystallization, two parameters of foremost importance, in a simplified slag processing unit. The first model was developed to calculate the temperature history of slag during its cooling to allow optimizing the air/slag ratio for both heat recovery and slag glass content. This model was later combined with the second which was aimed to predict the amount of crystallization during cooling. The results were validated by experiments involving non-isothermal crystallization of slag particles that represent a real slag cooling scenario.

7.1 Modeling the heat recovery process

In the heat recovery model, it is assumed that slag droplets of known size are released into a vertical heat recovery vessel/duct. While descending, the counter–current air flow cools the droplets and receives their thermal energy. The purpose of the model is to (a) obtain cooling rate of slag particles which will be used in the second model to predict glass content, (b) calculate the amount of heat recovered into hot air, as a function of parameters such as air/slag ratio and slag granule size.

7.1.1 Assumptions

The key assumptions in the existing code are the following:

1. The heat is transferred from the center of the liquid slag droplet to the slag surface by conduction and later by convection and radiation to air (Figure 7.1).

2. Air temperature is assumed uniform but the droplets are considered to have a temperature gradient.
3. Heat loss from the vessel walls is negligible.

4. Droplets are spherical and retain their size during the process.

5. Droplets fall at $V_{\text{droplet}} = V_t - V_{air}$; where $V_t$ is the terminal velocity found through Eq. 7.1. $V_{air}$ is the velocity of air determined from the duct area, air flow rate and temperature.

$$V_t = \sqrt{\frac{4}{3} \left( D g \rho_{slag} / C_d \rho_{air} \right)}$$  \hspace{1cm} \text{Eq. 7.1}

Figure 7.1 - Schematic diagram of the model principal.

The heat transfer coefficient is calculated using Eq. 7.2 Eq. 7.4. Eq. 7.2 is valid for $Re < 10^5$ [143] which is in the range of Reynolds number in the current study. Eq. 7.3 is known as the Ranz-Marshall equation [144] and is used for calculating the Nusselt number for falling droplets.
\[
Re = V_t \times D \times \frac{\rho_{air}}{v_{air}} \\
\text{Eq. 7.2}
\]

\[
Nu = 2 + 0.6 \left( Re^{1/2} \times Pr^{1/3} \right) \\
\text{Eq. 7.3}
\]

\[
h = Nu \times \frac{K_{air}}{D} \\
\text{Eq. 7.4}
\]

In the above equations, \( D \) is the droplet diameter, \( \rho_{air}, v_{air} \) and \( Pr \) are the air density, kinematic viscosity and Prandtl number respectively.

### 7.1.2 Enthalpy method

The enthalpy method was adapted for the calculations of phase change and heat transfer in moving boundary problems especially in situations in which the material does not have a distinct solid/liquid interface such as glassy substances (Figure 7.2 - a). In such systems, the melting or solidification takes place over an extended range of temperatures (Figure 7.2 - b) and the solid and liquid are separated by a two-phase moving region. In this approach, an enthalpy function, \( H(T) \), which represents the total heat content of the substance, is used as a dependant variable, being a function of temperature for the given material.

The enthalpy formulation of this phase change problem is given by Eq. 7.5 which is considered valid over the entire solution domain including the solid and liquid phases as well as the interface.

\[
\rho \frac{\partial H(T)}{\partial t} = \nabla \cdot (k \nabla T) \\
\text{Eq. 7.5}
\]
Figure 7.2 - Schematic figure of enthalpy-temperature function for (a) pure crystalline material (b) glassy material [145].

7.1.3 Enthalpy method vs. variable time step (VTS) method

In the enthalpy method, the phase change problem is reduced to the solution of a single equation in terms of enthalpy. There are no boundary conditions to be satisfied at the solid-liquid interface which is used in other techniques such as the Variable Time Step approach (VTS). Also, there is no need to accurately track the phase boundary and to consider liquid and solid regions separately [145].

In the present model, one dimensional solidification of a liquid having a melting temperature range is considered. Initially the liquid is at a uniform temperature, $T_o$, higher than the melting temperature range. For times, $t > 0$, the boundary is kept at a temperature $T_\infty$ which is lower than the liquidus temperature range of slag. The enthalpy formulation for a spherical geometry is given by:

$$\rho \frac{\partial H (r, t)}{\partial t} = k \left( \frac{\partial^2 T}{\partial r^2} + \frac{2 \partial T}{r \partial r} \right), \quad 0 < r < R \tag{Eq. 7.6}$$

$$\rho \frac{\partial H (r, t)}{\partial t} = 3k \frac{\partial^2 T}{\partial r^2}, \quad r = 0 \tag{Eq. 7.7}$$
\[
k \frac{\partial T}{\partial r} = h(T_\infty - T) + \varepsilon \sigma (T_\infty^4 - T_M^4), \quad r = R \tag{Eq. 7.8}
\]

where, \(\rho\) is the density, \(k\) is the thermal conductivity, \(H\) is the enthalpy and \(r\) is the radius of the sphere, \(h\) is the heat transfer coefficient, and \(\varepsilon\) is the emissivity of the slag. The boundary condition at \(r = 0\), Eq. 7.7, satisfies the symmetry requirement.

### 7.1.4 Numerical solution

A computer code was developed in MATLAB that calculates heat exchange between a flow of molten slag droplets discharged at \(T_S = 1600^\circ C\) and descending at velocity \((V)\), into a duct and a counter current flow of air. Initially, the operating parameters of the system are set. These include the slag droplets (charging rate, diameter, emissivity, density, temperature-enthalpy relationship, thermal conductivity, and discharge temperature), vessel diameter, and air properties (flow rate, exit temperature, kinematic viscosity, heat capacity and thermal conductivity). Some of these parameters that do not vary significantly with temperature are assumed constant but for others the relationship with temperature is used in the model (Table 7.1). The calculation then follows, through Finite Difference approach, as explained below.

#### 7.1.4.1 Finite difference approximation

The heat transfer equations were discretized into finite difference relations. The region \(0 \leq r \leq R\) is subdivided into \(M\) equal layers each of width \(\Delta r = R/M\) and the simple central explicit method was implemented:

\[
p \frac{H_{i+1}^n - H_i^n}{\Delta t} = k \left[ \frac{T_{i-1}^n - 2T_i^n + T_{i+1}^n}{(\Delta r)^2} + \frac{2}{i\Delta r} \frac{T_{i+1}^n - T_{i-1}^n}{2\Delta r} \right], \text{for } i = 1, 2, \ldots, M - 1 \tag{Eq. 7.9}
\]

\[
\rho \frac{H_0^{n+1} - H_0^n}{\Delta t} = \frac{k}{(\Delta r)^2} \left[ 6(T_1^n - T_0^n) \right], \text{ for } i = 0 \text{ (Since } \frac{\partial^2 T}{\partial r^2} \bigg|_{r=0} = \frac{2(T_1 - T_0)}{\Delta r^2}) \tag{Eq. 7.10}
\]

\[
k \frac{T_{M+1}^n - T_{M-1}^n}{2\Delta r} = h \left( T_\infty^n - T_M^n \right) + \varepsilon \sigma \left( T_\infty^4 - T_M^4 \right), \text{ for } i = R \tag{Eq. 7.11}
\]
The simple explicit method is very simple computationally, but the maximum size of the time step is restricted by stability considerations (Eq. 7.12). If calculations are to be performed over a large period of time, the number of steps, therefore the number of calculations needed may become prohibitively large. To mitigate this difficulty, finite difference schemes that do not impose such restrictions but are computationally more complicated such as simple implicit method, can be used.

\[ \Delta t \leq \frac{\Delta r^2}{6\alpha} \]  

Eq. 7.12

where \( \alpha \) the thermal diffusivity (W/mK), \( \alpha = k/\rho C_p \).

### 7.1.4.2 Numerical procedure

In the present model, the contact time (the duct height) is not fixed and is allowed to vary so the core temperature of slag particles is at 1100°C at the discharge point. In other words, the input and output temperatures of slag are fixed, on that basis the duct height is calculated. The algorithm used in the model is as follows:

1. Input air and slag properties.
2. Define the initial and final temperature for slag as 1600°C and 1100°C respectively.
3. Define the initial temperature for air as 25°C and assume a final temperature of \( T_{\text{air,outlet}} \).
4. Fix the numerical values of \( T_i^n \) and \( H_i^n \) (0\( \leq i \leq R \)) at the initial time level \( i.e., n=0 \).
5. Find Reynolds number, terminal velocity and drag coefficient.
6. Find the heat transfer coefficient (\( h \)) through Eq. 7.4.
7. Compute \( H_i^{n+1} \) for \( i = 1,2, ..., M - 1 \) from Eq. 7.9.
8. Compute the corresponding \( T_i^{n+1} \) from the \( H - T \) relation, \( i.e., \) Figure 7.3.
9. Determine \( T_M^{n+1} \) for the surface boundary condition at \( r = R \), by finite difference representation of Eq. 7.11.

By the end of this step, heat transfer by conduction from the slag core to surface at time level \( n+1 \) is completed.

10. Calculate the total heat transferred from the slag droplets to air by convection and radiation during time interval \( n \) to \( n + 1 \) by the heat balance equation and update the air temperature.

11. Repeat the above steps until the air inlet temperature reaches 25°C.

12. Find the slag core temperature. If the temperature is higher or lower than 1100°C, increase or decrease the \( T_{\text{air,outlet}} \) respectively.

13. Repeat step 1-11 until \( T_{\text{air,outlet}} \) results in a slag core temperature of 1100°C.

As a base case, the following parameters were used, and varied when applicable to investigate the effect of each parameter on the heat transfer efficiency.

1. The target core temperature of 1100°C temperature is based on the slag clustering temperature. As explained in Chapter 2, in a two-step heat recovery process which is considered the most efficient method for heat recovery [29], the slag granules are discharged from a fluidized bed to a packed bed after reaching the clustering temperature which is typically 900 °C-1100°C. When the slag reaches 900°C on the surface, the core temperature will be about 1100°C. This would ensure the slag granules will not stick to each other. Another reason for choosing 1100°C as the target temperature is that it is close to the nose temperature of a typical BF slag time–temperature–transformation (TTT) diagram which is the temperature that the slag experiences the highest crystallization rate. In other words, if the core reaches this temperature and does not crystalize we can be certain that it will not crystallize after this point in any of the other layers.
2. The duct diameter was fixed at 4 m.

3. Slag and air properties that were used in this case study are depicted in Table 7.1.

Table 7.1 - Properties of the heat recovery system.

<table>
<thead>
<tr>
<th></th>
<th>Slag</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temp</td>
<td>1600°C</td>
<td>Initial temperature 25°C</td>
</tr>
<tr>
<td>Final core temp</td>
<td>1100°C</td>
<td>Final temperature $T_{air_exit}$</td>
</tr>
<tr>
<td>Discharge rate</td>
<td>140 t/h</td>
<td>Thermal Conductivity Variable [146]</td>
</tr>
<tr>
<td>Droplet size</td>
<td>5, 8 mm</td>
<td>Density Variable [146]</td>
</tr>
<tr>
<td>Density</td>
<td>2800 kg/m$^3$ [147]</td>
<td>Specific heat capacity Variable [146]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>Variable [148]</td>
<td>Kinematic viscosity Variable [146]</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Factsage™ [149] (Figure 7.3)</td>
<td>Prantl Number Constant [146]</td>
</tr>
</tbody>
</table>

7.1.4.3 Enthalpy-temperature function

In order to use the enthalpy method, the enthalpy-temperature relationship is required. Thermodynamic data of FactSage™ were used for this purpose. For example the enthalpy-temperature function of a slag composition used in the calculations is shown in Figure 7.3.
Figure 7.3 - H-T relationship for slag with 47% CaO, 33% SiO$_2$, 15% Al$_2$O$_3$, 5%MgO.

7.1.4.4 Finding the mesh size

Since the required time to run the code significantly increases with the mesh size (i.e. number of imaginary layers), it is important to find the minimum number of layers that can be used for stable execution of the code without any error introduced because of numerical calculations. This was done by assuming different number of layers and finding the required contact time for the droplet to reach a certain temperature at a constant $M_{air}/M_{slag}$. It was found that when $M \geq 15$, the contact time does not change significantly as presented in Figure 7.4; thus, the sufficient number of layers was chosen as $M = 15$. 
Validation of the numerical method

The model was first validated against experimental results of Milanez et al. [150]. In their research, an experimental rig was designed to simulate the process of radial solidification of a pure lead sphere of 1 cm radius in air. The movement of the solidification interface was measured by means of thermocouples evenly spaced within the sphere.

The $H - T$ relationship of pure lead was calculated by Factsage™ and the data were fed to the present model. The movements of the interface and the temperature profile were calculated. Figure 7.5 compares the experimental and calculated results for the position of the solid/liquid interface in the lead droplet. As seen, there is a good agreement between the two, pointing to the validity of the model.
7.1.5 Analytical alternative of the “heat recovery” mathematical model

For further validation of the code, the analytical solution for one-dimensional transient heat conduction in a sphere (radius = $r_0$) subjected to convection from all surfaces was applied.

$$
\theta = \sum_{n=1}^{\infty} \frac{4 (\sin \lambda_n - \lambda_n \cos \lambda_n)}{2 \lambda_n - \sin (2 \lambda_n)} \left( e^{-\lambda_n r / r_0} \right) \frac{\sin (\lambda_n r / r_0)}{\lambda_n r / r_0} \left( 1 - \lambda_n \cot \lambda_n \right) = Bi
$$

Eq. 7.13

where, $\theta = \frac{T_l - T_\infty}{T - T_\infty}$.

In the above equation, the heat transfer coefficient and the temperature of the surroundings ($T_\infty$) are considered to have constant values. Therefore, to be able to compare the code (numerical model) results with the results of the above equation, the average heat transfer coefficient ($h_{Avg} = 200$) was applied. The temperature of the surrounding was also considered to be constant. The result of the code without considering phase change is presented in Figure 7.6.
Figure 7.6 - Analytical solution compared with modeling result (constant air temperature without phase change).

Considering phase change occurring by applying the enthalpy-temperature function of the slag results in the cooling path shown in Figure 7.7. The red dashed line and the black dotted line are the cooling paths found by the analytical method and the mathematical model respectively. The reason for the mismatch of the two cooling paths is that in the analytical solution phase change has not been considered. Therefore, the use of the analytical model is limited to cooling below the solidification temperature of slag.
Figure 7.7 - Comparing temperature profiles from analytical solution and numerical modeling (constant air temperature with phase change).

7.1.6 Temperature profile of slag droplets

The temperature profile of slag droplets at all layers can be found at different $M_{\text{air}}/M_{\text{slag}}$ ratios. As an example, the temperature profiles in a 5 mm slag granule at $M_{\text{air}}/M_{\text{slag}} = 0.77$ are shown in Figure 7.8.
Figure 7.8 - Temperature profile of slag droplets at $\frac{M_{\text{air}}}{M_{\text{slag}}} = 0.77$ and D=5mm.

7.2 Modeling the amount of glassy content

The results of the heat transfer model, i.e. cooling curves at numerous imaginary layers within the droplet were fed to the slag crystallization model discussed below, to yield the glass content of slag granules. The energy balance between the slag and gas also provides the essential data to calculate the heat recovery efficiency.

The crystallization model consists of two parts. In the first part, the incubation time is calculated using Schei’s principal of additivity [151]. According to this rule, the time spent at a particular temperature, $\Delta t_i$, divided by the isothermal time required for the transformation to start at that temperature, $t_0^i$, can be considered as the fraction of the total incubation time spent at that temperature. Scheil proposed that for a non-isothermal treatment, the transformation will start when the sum of fractional incubation time reaches unity (Eq. 7.14).

$$\sum_{i=1}^{n} \frac{\Delta t_i}{t_0^i} = 1$$  \hspace{1cm} \text{Eq. 7.14}
In this equation, \( n \) is the number of increments assumed during a continuous cooling between the equilibrium temperature and the temperature at which the transformation starts.

The second part of the model involves breaking down the continuous cooling curve into a series of isothermals [152] (Figure 7.9 - a). Using the additivity rule in a non-reversible process, the total crystalline content can be determined by adding the amount in each isotherm, as depicted in Figure 7.9 - b. From the fraction of phase \( V_i \) formed up to the end of the preceding time step, an “effective” time \( t_{i+1}^* \) can be calculated using the JMAK equation (Eq. 7.15):

\[
t_{i+1}^* = \frac{1}{K(T_{i+1})} \ln \left( \frac{1}{1 - V_i} \right)^{1/n_{i+1}}
\]

where \( K(T_{i+1}) \) and \( n_{i+1} \) are kinetic constants of each isotherm found from the TTT diagram of these slags [142].

The effective time can be used to calculate the volume percentage of transformation after a time increment of \( \Delta t \) (Eq. 7.16):

\[
V_{i+1} = 1 - \exp \left[ -K(T_{i+1})(t_{i+1}^* + \Delta t)^{n_{i+1}} \right]
\]

Eq. 7.15

Eq. 7.16
Figure 7.9 - (a) approximation of a continuous cooling curve with a series of isothermals and (b) adding transformed contents at different temperature validation of model.

7.2.1.1 Validation against similar models

The code was initially validated with the mathematical results by Agarwal and Brimacombe [152] developed for pearlite-austenite transformation on the TTT diagram for a eutectoid carbon steel. The cooling rate and the TTT diagram used in their calculation was fed into the existing code. The code calculates the fraction of the transformed austenite with time (Figure 7.10). The solid symbols show the results by Agarwal and Brimacombe and the dotted line show the results found by the existing code.
Figure 7.10 - Validation of the model for predicting phase transformation by using TTT diagram and cooling path. The green points show the results by Agarwal et al. [152] and the smaller blue dots show the results by the existing code.

7.2.1.2 Validation against experiments

A second validation was done by using the experimental results. The transformed fraction for the slag with C/S=1.31 was measured from SHTT runs carried out under various cooling rates, followed by image analysis. This produced the CCT diagram of such slag. The TTT diagram and kinetic parameters pertaining to isothermal crystallization of the same slag were also obtained from separate runs (Figure 7.11). The parameters were then fed to the crystallization model described earlier, to predict the extent of crystallization for various cooling rates. Figure 7.12 compares the calculated and measured crystalline fraction of slag for a given set of conditions, showing a good agreement between the two.
By applying the same procedure for different cooling rates, the CCT diagram was constructed and compared with the model results, Figure 7.13. As seen, the two curves match well, validating the modeling approach and the concept of extending TTT data to continuous cooling. In essence,
this provides a tool for predicting crystallization rate and extent of slag under various cooling rates, from isothermal treatment data. Coupled with the first model that estimates cooling profiles of a slag during a process such as air or water granulation, it yields the evolution of slag phases with time, so that parameters such as flow of the atomization media, slag pouring temperature, etc. can be optimized for the desired glass content and possible heat recovery during the granulation process.

Figure 7.13 - CCT obtained from experimental measurements and modeling calculations (C/S=1.31).

7.3 Effect of operating parameters on heat recovery and slag structure

The mathematical models described above in combination with data from TTT diagrams can be used to predict the efficiency of heat recovery and slag structure (i.e. amorphous content) under a range of conditions. In this section, effect of two process variables are investigated.

7.3.1 Effect of air to slag ratio

The heat recovery efficiency is defined by the following equation (Eq. 7.17):

\[
\text{Efficiency} = \frac{\text{Heat Recovered}}{\text{Heat Input}} = \frac{\text{C}/\text{S}}{1.31}
\]
\[ HRE = \frac{q}{q_{max}} \]  \hspace{1em} \text{Eq. 7.17}

where \( q \) is the total heat transferred from slag to air (Eq. 7.18) and \( q_{max} \) is the total amount of slag enthalpy with reference to 25°C just before pouring (Eq. 7.19).

\[ q = M_{air} \int_{T_{inlet}}^{T_{outlet}} C_{p_{air}} dT \]  \hspace{1em} \text{Eq. 7.18}

\[ q_{max} = M_{slag} \Delta H_{slag, 25-1600°C} \]  \hspace{1em} \text{Eq. 7.19}

The calculations were made for a slag with C/S=1.52 and D=8mm and the results are shown in Figure 7.14. As seen, with the increase of \( M_{air}/M_{slag} \), both the heat recovery efficiency and the glass content increases. This figure shows at air/slag ratios of about 1.2, slag with 100% glass content can be achieved with 83% heat recovery efficiency. Another parameter shown in this figure is the temperature of the air at the duct exit, which may be used as an indicator of the heat quality. As evident from this figure, the heat quality decreases with the increase of heat recovery efficiency.
Figure 7.14 - Heat recovery efficiency, air exit temperature, and amorphous content of slag as a function of $M_{air}/M_{slag}$ for slag with C/S=1.52 and D=8mm.

### 7.3.1.1 Effect of droplet size

The same conditions in the previous section were repeated for slag droplet of size D=5mm and the heat recovery efficiency and glass content, and contact time were obtained and compared. The minimum cooling rate at the droplet core is 25°C/s which results in 100% glassy slag at all the $M_{air}/M_{slag}$ values covered in the previous section.

As seen in Figure 7.15 – 7.16, contact time and heat recovery efficiency both decrease with the decrease of droplet size. This is because the slag core temperature is the key factor determining the contact time and consequently the heat recovery efficiency. In other words, larger droplet would need longer contact time to reach a certain temperature (i.e. 1100°C) at its core, hence greater heat recovery efficiency. The decrease of the air outlet temperature with the decrease of droplet size (Figure 7.17) can also be explained by the longer contact time that is needed for larger droplets.
Figure 7.15 - Effect of droplet size on the heat recovery efficiency.

Figure 7.16 - Effect of droplet size on contact time.
Figure 7.17 - Effect of droplet size on air exit temperature.
Chapter 8

8 Contributions and conclusions

8.1 Conclusions

The main conclusions of this work can be summarized in three sections:

A) Simultaneous temperature measurement and in-situ observation of slag in a SHTT device allowed derivation of TTT and CCT diagrams for several slags with NBO/T ratios in the range of 0.77 to 1.94. It was found that:

1. With an increase in basicity, the TTT and CCT diagrams of glassy to crystalline transformation shift to the left (shorter time) and to higher temperatures.
2. The dependence of slag crystallization behavior on the slag composition changes at NBO/T ≈1.6. Crystallization features at higher basicity are faster crystallization and opaque crystalline phases, whereas for lower basicity the crystals are translucent.
3. For slags with NBO/T ≥1.6, equiaxed crystals are formed at high temperatures. As the temperature drops, first planar, and then again fine equiaxed crystals become the predominant morphology.
4. For slags with NBO/T <1.6, crystallization involves the growth of very few crystals that grow to complete the process.
5. The $R_c$ values obtained from CCT diagrams are lower than those from TTT diagrams which agrees with the fact that TTT diagrams present an overestimation of transformation rate when slag is cooled continuously.
6. The correlation between the optical basicity ($\Lambda_{corr}$) and $R_c$ is stronger than NBO/T with $R_c$. This is mainly because corrected optical basicity differentiates between the charge-balancing cations and therefore using this parameter is highly suggested when comparing the critical cooling rate for different slag compositions especially when the alumina content changes significantly.
7. The critical cooling rate is inversely proportional to the viscosity.
8. A correlation was developed based on theories of nucleation and growth during slag crystallization to allow prediction of the critical cooling rate using only two parameters: liquidus temperature \((T_L)\) and viscosity at nose temperature \((\eta_{nose})\):

\[ R_c = (1.23 \times 10^{-5}) \left( \frac{T_L^2}{\eta_{nose}} \right) \]

B) The transformation kinetics of four slags with varying C/S values were studied using SHTT. Through image analysis of the samples it was found that the transformation of all samples followed a sigmoidal form and obeyed the JMAK equation.

1. The Avrami exponent was found and compared with the direct observation during transformation for four slag compositions. Due to the higher value of \(n\) (=3-4) for the slag with C/S=1.52, it was concluded that the crystallization of this sample is diffusion-controlled growth with increasing nucleation rate. For the samples with C/S=1.31 and 1.38 with \(n=1.5-2\), the growth is controlled by diffusion but the nucleation rate is decreasing with time. For the slag with the lowest basicity \((i.e.\ C/S=1.18)\), the \(n\) value is 2 at higher temperatures which translates to zero nucleation rate.

2. The mechanism of the growth was found to be diffusion-controlled for all the samples although the growth has a linear dependence with time. This is in accordance with the crystals having a dendritic morphology rather than faceted.

3. The overall rate coefficient \((K)\) has the highest value for C/S=1.52 and the smallest for C/S=1.18. This indicates that the combination of nucleation and growth leads to faster transformation at higher basicity.

C) A mathematical model was developed to find the effect of droplet size and slag to air ratio on the required height of a duct in a counter-current heat recovery process. By using the model the temperature profile of the slag droplets, temperature profile of the air and the cooling rate of the slag droplets were calculated. The effects of the slag droplet size and slag to air ratio on the slag exit temperature, the heat recovery efficiency and the height required were investigated.
This model also leads to design of the duct (diameter and height) so that the desired slag discharge temperature at core, e.g. 1100°C, is reached. The contact time can be used as a reference to predict the required duct height.

8.2 Contributions

This is the most comprehensive research conducted on crystallization behavior of metallurgical slags to date. Each year more than 650 Mt of slag is produced worldwide containing over 282 TWh worth of energy. This energy is not recovered, as the slag is tapped and cooled slowly in the slag dumps or is rapidly quenched by water to make amorphous granules that are used as feedstock for cement manufacturing. The original goal of the study was to investigate the possibility of recovering the energy from molten slags, while controlling the slag structure so that it can be used as valuable product.

As the first part of this research, an extensive literature review was conducted which resulted in a review paper [153] published in the journal *Energy* and became the “most read article in press” in the year 2011. Later, experimental and modeling work was performed with focus on the crystallization behavior of blast furnace slags which is of great interest for generating value-added products from slag, such as cement feedstock. The main contributions can be explained in three main sections which is discussed briefly in the following paragraphs.

From practical point of view, this study provided a large set of data on the CCR of slag which allows a slag processor to determine the proper conditions for obtaining amorphous slag. Further, a semi-empirical model was developed that enables us to calculate the CCR for a slag, without a need to do any experiment. This again is a valuable tool for predicting optimum cooling conditions of slag in an industrial setting.

From scientific point of view, for the first time we have established quantitative and consistent relationships between crystallization parameters of slag and its chemical composition. The mechanism and rate of crystallization and their dependence on the composition and temperature were established. Further, mathematical models were developed and validated that enable calculations of the most important parameters of a heat recovery process (heat recovery
efficiency, amorphous content of slag, and heat quality) as a function of variables such as slag granule size, air/slag ratio, chamber dimensions, etc. Last, but not least, the HTT method used in crystallization studies was improved by a new design that is more accurate and easier to set up.

8.3 Publications

From this Ph.D. work, 6 journal manuscripts have been submitted or are in preparation which are presented below.

Journal articles:


Conference articles:
1. **S. Esfahani, M. Barati**, “Crystallization kinetics of CaO-SiO$_2$-Al$_2$O$_3$-MgO slags,”, to be submitted to the Symposium of Molten Slags, Fluxes and Salts, Seattle 2016


9 Future Research Directions

1. Effect of nucleants on the crystallization behavior of synthetic slags

Many liquid slags contain refractory compounds that can affect crystallization by acting as nucleation agents. In order to determine the effect of such nucleants, i.e. fine crystals in the glassy slag, on the crystallization behavior, a preliminary study was conducted. A slag with C/S=1.18 and 0.3wt % Cr$_2$O$_3$ was prepared and the crystallization behavior was compared with a similar slag containing no Cr$_2$O$_3$. The start of crystallization could not be easily identified for the sample with Cr$_2$O$_3$ addition due to the different optical properties with the nucleant-free slag. To be able to conduct a fair comparison between the crystallization rates of these two samples, the end time of crystallization was compared. The results showed a much faster crystallization (about two orders of magnitude) at all temperatures. However, an interesting observation was made that for this slag, with repeated melting and crystallization, this effect diminished so that after 14 cycles, the crystallization time was close to Cr$_2$O$_3$–free slag, as shown in Figure 9.1. Such behavior was not seen for the latter slag; the crystallization time was in essence independent of the number of cycles.

![Figure 9.1 - End time of crystallization for sample with C/S=1 with and without Cr$_2$O$_3$ at T=1100 °C isotherm (repeated 14 times).](image)
Based on this finding, two hypotheses were put forward (1) Cr₂O₃ containing crystals act as a nucleant in the first few cycles but later it dissolves in the slag and therefore the crystallization occurs much slower, or (2) Cr₂O₃ or Cr₂O₃ spinel particles agglomerate (or dissolve and precipitate as larger particles) during each melting-cooling cycle, leading to fewer particles (i.e. fewer nucleation sites). As the industrial slags often contain such refractory compounds that would influence crystallization, better understanding of the extent and mechanism of such nucleation agents is desired.

2. Sintering properties of slag particles

As discussed in Chapter 2 of this thesis, a promising heat recovery system would consist of two steps, a fluid bed type vessel and a packed bed. The optimum discharge temperature of slag from the first heat recovery unit to the second would depend on the sintering (sticking) temperature of the slag particles, as such clustering of particles should be avoided in the packed bed. Although some have suggested temperatures in the range of 800-1100°C, there is no scientific study to verify this. Therefore, it is recommended that a study be carried out to develop test procedures and measure sintering properties of slag as a function of composition. Also, it would be anticipated that there might be relationships between the sintering temperature and melting or nose temperature of slag, which can be explored.
Bibliography


Appendix A

Calculation of NBO/T for a four component slag composition of SiO$_2$, CaO, Al$_2$O$_3$, MgO [7]:

1) Find the mole fraction of each component: e.g. $X_{\text{CaO}}$, $X_{\text{SiO}_2}$, $X_{\text{Al}_2\text{O}_3}$, $X_{\text{MgO}}$

2) Multiply mole fraction by the number of cations: e.g. $2X_{\text{Al}_2\text{O}_3}$, $X_{\text{CaO}}$, $X_{\text{SiO}_2}$, $X_{\text{MgO}}$

3) Sum all the network formers: e.g. $A = X_{\text{SiO}_2} + 2X_{\text{Al}_2\text{O}_3}$

4) Find the total charge on network-breaking cations: e.g. $B = 2\left[X_{\text{CaO}} + X_{\text{MgO}}\right]$

5) Determine C, by allowing for the electrical charge balance of AlO$_4^{3-}$: e.g. $C = B - 2X_{\text{Al}_2\text{O}_3}$

6) NBO/T = C/A
Appendix B

Calculation of optical basicity ($\Lambda$) [7]:

$$\Lambda = \frac{\sum x_1 n_1 \Lambda_1 + x_2 n_2 \Lambda_2 + x_3 n_3 \Lambda_3 + \cdots}{x_1 n_1 + x_2 n_2}$$

where $n$ is the number of oxygens in the oxide, e.g. 3 for $\text{Al}_2\text{O}_3$, 2 for $\text{SiO}_2$ and $x$ is the mole fraction.

Values of $\Lambda$ in the above equation are:

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO2</th>
<th>MgO</th>
<th>$\text{Al}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.48</td>
<td>0.78</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>

2) Calculation of and corrected optical basicity ($\Lambda_{corr}$) [121]:

Considering a slag composition of 0.5$\text{SiO}_2$, 0.15$\text{Al}_2\text{O}_3$, 0.05$\text{CaO}$, 0.2$\text{MgO}$, the $\text{Al}_2\text{O}_4^-$ units are charge balanced by cations with higher optical basicity (i.e. $\text{CaO} > \text{MgO}$). Therefore, 0.15 (oxide) will be required to charge balance 0.15 $\text{Al}_2\text{O}_3$ (i.e. 0.05$\text{CaO} + 0.1\text{MgO}$). These cations do not contribute to the depolymerization of the silicate network, thus $\Lambda_{corr}$ will be calculated for the composition 0.5$\text{SiO}_2$, 0.15$\text{Al}_2\text{O}_3$, 0.1$\text{MgO}$.