SMELT DROPLET-WATER INTERACTION IN THE KRAFT RECOVERY BOILER DISSOLVING TANK

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

In the dissolving tank of a recovery boiler, violent interaction between smelt droplets and water can cause the tank to rumble and tremor, and in severe cases, a dissolving tank explosion accident. A laboratory apparatus was constructed to visualize smelt droplet-water interaction with high speed imaging, and to examine the effects of various dissolving tank operating parameters on the explosion characteristics of synthetic smelt droplets composed of sodium carbonate and sodium chloride. The results show that smelt droplets are more likely to explode when 1) the water temperature is low, 2) the smelt composition approaches the eutectic composition, 3) the droplet size is large, and 4) there is an external disturbance. Experiments were also conducted using real kraft smelt and green liquor. The results show that real smelt behaves in a similar manner as synthetic smelt, and that replacing water with green liquor promotes droplet explosions. A 1-D heat transfer model of smelt droplet-water interaction was also developed to explain the explosion mechanism. The modeling results suggest that whether a droplet explodes or not depends on the thickness of the solidified layer formed on the smelt
droplet surface at the moment the vapor film around the droplet collapses. Experimental results from this study also show that explosions that occur on the water surface generate less sound and tank vibration than explosions that occur beneath the water surface, and that droplet explosions promote smelt dissolution. To improve dissolving tank safety and efficiency, it is important to avoid accumulation of a large amount of smelt in the dissolving tank.
Acknowledgments

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# Table of Contents

Chapter 1.  INTRODUCTION ........................................................................................................1

  1.1 The Kraft Process ..................................................................................................................2

  1.2 Dissolving Tank Operation and Issues ..................................................................................4

  1.3 Literature Review ..................................................................................................................7

    1.3.1 Vapor explosions .............................................................................................................7

    1.3.2 Smelt-water explosion research .....................................................................................10

    1.3.3 Knowledge gap ................................................................................................................11

  1.4 Objectives ............................................................................................................................12

Chapter 2.  APPARATUS AND METHODOLOGY ..................................................................13

Chapter 3.  VISUALIZATION WITH HIGH SPEED IMAGING ............................................16

  3.1 Three Types of Droplet Behavior .........................................................................................16

  3.2 Smelt Droplet Impingement and Breakup Behavior ............................................................20

  3.3 Bubble and Fragment Dynamics .........................................................................................23

  3.4 External Disturbances ..........................................................................................................28

Chapter 4.  A 1-D HEAT TRANSFER MODEL .................................................................31

  4.1 Model Formulation .............................................................................................................31

  4.2 Model Implementation .........................................................................................................37

    4.2.1 Heat transfer within the droplet .....................................................................................37

    4.2.2 Heat removal at the droplet surface .............................................................................40

    4.2.3 Vapor film collapse criteria ..........................................................................................42

    4.2.4 Vapor film dynamics .....................................................................................................44

  4.3 Verification of the Enthalpy Method .....................................................................................45

  4.4 Model Demonstration .........................................................................................................46

Chapter 5.  RESULTS AND DISCUSSION ............................................................................51
5.1 Effects of Smelt and Water Temperatures .............................................52
5.2 Effect of Smelt Composition ..................................................................54
5.3 Simulation Results and Discussion ..........................................................61
   5.3.1 Vapor film collapse time .................................................................62
   5.3.2 Droplet solidification .....................................................................66
5.4 Effect of External Disturbances ...............................................................70
   5.4.1 Droplet impingement onto the water surface .................................70
   5.4.2 Droplet impact onto the tank bottom .........................................75
   5.4.3 Water agitation ...........................................................................78
Chapter 6. APPLICATION TO DISSOLVING TANK ........................................80
  6.1 Effect of Droplet Size ..........................................................................80
  6.2 Real Kraft Smelt and Green Liquor ....................................................84
  6.3 Explosion Intensity ...........................................................................88
  6.4 Smelt Dissolution ...............................................................................92
     6.4.1 Pre-diffusion stage ......................................................................94
     6.4.2 Diffusion stage ..........................................................................96
Chapter 7. CONCLUSIONS ........................................................................100
  7.1 Summary of Results ..........................................................................100
  7.2 Implications .......................................................................................101
  7.3 Recommendations for Future Work ...................................................103
References ..................................................................................................104
Appendix A ...............................................................................................114
Appendix B ...............................................................................................126
Appendix C ...............................................................................................128
List of Tables

Table 1: Inputs and outputs of the 1-D heat transfer model .......................................................... 37
Table 2 Typical experimental conditions and values of non-dimensional numbers and smelt properties ______51
Table 3: Droplet explosion behavior of various pure salt compounds and mixtures, $T_w = 20$ to $100\degree$C .......................... 60

List of Figures

Figure 1-1: The kraft chemical recovery process [1] ........................................................................... 2
Figure 1-2: A recovery boiler, with the dissolving tank circled [3] .......................................................... 3
Figure 1-3: Smelt flow down a spout, front view (left) and top view (right) ........................................ 4
Figure 1-4: Dissolving tank operation schematics .............................................................................. 5
Figure 1-5: Four stages of a vapor explosion as a hot liquid poured into a cold liquid [42] .................... 8
Figure 2-1: Experimental apparatus for the study of smelt droplet-water interaction ......................... 14
Figure 3-1: An immediate explosion (Phantom v2512 / 512x320 / 100k) ........................................... 17
Figure 3-2: A delayed explosion (Mega Speed MS70KS2 / 200x200 / 10k) ........................................ 18
Figure 3-3: No explosion (Mega Speed MS70KS2 / 512x512 / 1000) .................................................. 19
Figure 3-4: Smelt droplet breakup (Phantom v2512 / 1280x800 / 25k) ................................................ 20
Figure 3-5: Infrared images of smelt droplet impinging on the water surface (Phantom v2512 / 1280x800 / 25k) ............................... 21
Figure 3-6: Infrared images of smelt droplet breakup and coalescence (Phantom v2512 / 1280x800 / 5k) .... 22
Figure 3-7: Bubble dynamics of a droplet explosion on the bottom of the tank (Phantom v2512 / 512x320 / 100k) .............................. 23
Figure 3-8: Infrared images of smelt fragment dynamics during a droplet explosion on the bottom of the tank (Phantom v2512 / 512x320 / 100k) ................................................................. 24
Figure 3-9: Normalized equivalent droplet diameter for the droplet explosion in Figure 3-2 ............... 25
Figure 3-10: Smelt fragment dynamics of the droplet explosion in Figure 3-8 ...................................... 26
Figure 3-11: Two waves of bubble expansion (Phantom v2512 / 1280x800 / 25k) ................................ 27
Figure 3-12: Explosion triggered by droplet impact onto the tank bottom (Mega Speed MS70KS2 / 514x514 / 200) .............. 28
Figure 3-13: Smelt-water interaction with water agitation (Phantom v2512 / 512x320 / 100k) ............... 29
Figure 3-14: A multi-droplet chain explosion (Phantom v2512 / 1280x800 / 25k) ................................. 30
Figure 3-15: Triggering between multiple droplet explosions (Phantom v2512 / 1280x800 / 25k) .......... 30
Figure 4-1: Fate of a molten smelt droplet in water ........................................................................... 32
Figure 4-2: 1-D heat transfer model ................................................................................................... 33
Figure 4-3: Enthalpy-temperature relationship ...................................................................................... 38
Figure 4-4: $T(r)$ predicted by the analytical solution and enthalpy method, no phase change or film boiling ............................................. 46
Figure 4-5: $T(r)$ at different times, assuming the vapor film does not collapse ................................... 47
Figure 4-6: T(t) at the center and surface of the droplet _____________________________ 48
Figure 4-7: Thickness of different layers as a function of time ________________________ 48
Figure 4-8: Vapor film thickness as a function of time ________________________________ 49
Figure 4-9: Heat flux from the droplet surface to the surroundings _____________________ 50
Figure 5-1: Explosion probability at different temperatures, 20% NaCl ______________________ 52
Figure 5-2: Explosion delay time at different temperatures, 20% NaCl ________________ 53
Figure 5-3: Phase diagram of the Na₂CO₃-NaCl system _______________________________ 54
Figure 5-4: Mass and diameter of smelt droplets composed of different amounts of Na₂CO₃ and NaCl __________________________ 55
Figure 5-5: Explosion probability, 0, 20 and 40% NaCl, Tₚ = 800, 900, and 1000°C _____________ 56
Figure 5-6: Explosion delay time at different temperatures, 40% NaCl ____________________ 56
Figure 5-7: Explosion probability, 0 to 40% NaCl content, Tₚ = T_m + 50°C ________________ 57
Figure 5-8: Explosion probability, 40 to 100% NaCl content, Tₚ = T_m + 50°C ____________ 58
Figure 5-9: Comparisons of the explosion probability of smelt droplets with the same T_m __________________________ 59
Figure 5-10: Delay time and predicted t_vfc, 20% NaCl ________________________________ 62
Figure 5-11: Droplet surface temperature at t_vfc, 20% NaCl ____________________________ 63
Figure 5-12: Convective heat transfer coefficient due to film boiling as a function of Tₚ and T_w, 20% NaCl _______ 64
Figure 5-13: Predicted t_vfc, 40% NaCl _____________________________________________ 65
Figure 5-14: Solidified layer thickness at t_vfc, 20% NaCl ______________________________ 66
Figure 5-15: Solidified layer thickness at t_vfc for smelt droplets with different compositions, Tₚ = T_m + 50°C ______ 67
Figure 5-16: Phase diagram of the Na₂CO₃-Na₂S system ___________________________________________ 68
Figure 5-17: Solidified layer thickness at t_vfc as a function of Na₂S in a Na₂CO₃-Na₂S system, Tₚ = T_m + 50°C ____ 69
Figure 5-18: Velocity of a 7 mm diameter smelt droplet falling through air as a function of falling distance _______ 72
Figure 5-19: Explosion probability as a function of falling distance, 20% NaCl, Tₚ = 800°C ______________________ 73
Figure 5-20: Explosion delay time as a function of falling distance, 20% NaCl, Tₚ = 800°C __________________________ 73
Figure 5-21: Solidified layer thickness at t_vfc with different adjusted Tmf, 20% NaCl, Tₚ = T_m + 50°C ___________ 74
Figure 5-22: Velocity profile of a smelt droplet in water, 20% NaCl, Tₚ = 800°C, T_w = 80°C ____________________________ 76
Figure 5-23: Explosion probability as a function of water depth, 20% NaCl, Tₚ = 800°C ________________________ 77
Figure 5-24: Explosion delay time with and without agitation, 20% NaCl, Tₚ = 800°C _______________ 78
Figure 6-1: Solidified layer thickness at t_vfc as a function of droplet size, 20% NaCl, Tₚ = 800°C ________________ 81
Figure 6-2: Droplet breakup and explosion visualized with phenolphthalein ____________________________ 82
Figure 6-3: Predicted t_vfc as a function of droplet size, 20% NaCl, Tₚ = 800°C _________________ 83
Figure 6-4: Normalized solidified layer thickness at t_vfc, 20% NaCl, Tₚ = 800°C __________________________ 84
Figure 6-5: Explosion probability of synthetic (80% Na₂CO₃, 20% NaCl) and real smelt droplets, Tₚ = 800°C ___________ 85
Figure 6-6: Delay time of synthetic (80% Na₂CO₃, 20% NaCl) and real smelt droplets, Tₚ = 800°C _______________ 86
Figure 6-7: Solidified layer thickness of synthetic (80% Na₂CO₃-20% NaCl) and real smelt droplets ____________________________ 87
Figure 6-8: Acoustic sound of smelt droplet explosions as a function of delay time __________________________________________ 88
Figure 6-9 Immediate explosion after droplet breakup (Phantom Miro321S / 1200x1920 / 1.3k) _____________________________ 89
Figure 6-10: Spectrograms of a typical immediate and a typical delayed explosion ___________________________________________ 90
Figure 6-11: Correlation between acoustic and vibration intensities for immediate and delayed explosions ________________ 91
Figure 6-12: Smelt dissolution followed by a droplet explosion __________________________________________________________ 92
Figure 6-13: Smelt dissolution as a result of nucleate boiling __________________________________________________________ 93
Figure 6-14: Smelt particle collected from the tank bottom ______________________________________________________________ 94
Figure 6-15: Particle size distribution after the pre-diffusion stage ______________________________________________________ 95
Figure 6-16: Coalescence of multiple smelt droplets as they contact each other ____________________________________________ 95
Figure 6-17: Experimental apparatus for the study of smelt particle diffusion ____________________________________________ 96
Figure 6-18: Remaining mass of a 0.2 g Na₂CO₃ particle as a function of time _____________________________________________ 97
Figure 6-19: Remaining mass of a 0.2 g Na₂CO₃ particle as a function of time, experiments vs. simulations _____________ 98
Figure 6-20: Dissolution time of 0.25 g particles (80% Na₂CO₃-20% NaCl) under different concentrations and agitation conditions ____________________________________________ 99
Figure A-1: Breakup of pure Na₂CO₃ droplet, T_w = 40°C _____________________________________________________________ 114
Figure A-2: Behavior of a pure NaCl droplet in water at 50°C __________________________________________________________ 115
Figure A-3: Behavior of a pure Li₂CO₃ droplet, T_w = 80°C ____________________________________________________________ 116
Figure A-4: Behavior of a pure Na₂SO₄ droplet in hot water, T_w = 80°C ________________________________________________ 117
Figure A-5: Behavior of a pure NaCl droplet, T_w = 80°C ______________________________________________________________ 118
Figure A-6: Behavior of Li₂CO₃-Na₂CO₃-K₂CO₃ droplet, T_w = 90°C, T_s = 500°C _______________________________________ 119
Figure A-7: Behavior of a Li₂CO₃-Na₂CO₃-K₂CO₃ droplet, T_w = 95°C, T_s = 725°C ______________________________________ 120
Figure A-8: Behavior of a NaCl-CaCl₂ droplet, T_w = 90°C, T_s = 590°C _____________________________________________ 121
Figure A-9: Behavior of a NaCl-CaCl₂ droplet, T_w = 95°C, T_w = 900°C ____________________________________________ 122
Figure A-10: Behavior of a real kraft smelt droplet that undergoes a delayed explosion, T_w = 78°C ____________________ 123
Figure A-11: Behavior of real kraft smelt droplet that undergoes no explosion, T_w = 85°C _____________________________ 124
Figure A-12: Interaction between hot solid smelt and water, T_w = 60°C, T_s = 600°C ___________________________________ 125
Figure B-1: Image processing for bubble dynamics analysis __________________________________________________________ 126
Figure C-1: Comparison of the smelt droplet-water and the water droplet-hot surface systems __________________________ 128
Figure C-2: Experimental apparatus for vapor film stability study ______________________________________________________ 129
Figure C-3: Water drop behavior at different hot crucible temperatures ___________________________________________________ 130
Figure C-4: Droplet life time as a function of hot surface temperature and water droplet temperature _______________ 131
Figure C-5: Droplet life time of different salt concentrations __________________________________________________________ 132
Figure C-6: Droplet impingement behavior from 15 cm above the crucible _____________________________________________ 133
Figure C-7: Vapor film collapse triggered by a disturbance __________________________________________________________ 134
Nomenclature

\begin{itemize}
\item \(A\) \hspace{0.5cm} \text{projected area}
\item \(Bi\) \hspace{0.5cm} \text{Biot number}
\item \(C_p\) \hspace{0.5cm} \text{drag coefficient}
\item \(C_p\) \hspace{0.5cm} \text{specific heat capacity}
\item \(C_s\) \hspace{0.5cm} \text{saturation concentration}
\item \(D\) \hspace{0.5cm} \text{diameter / diffusivity}
\item \(E\) \hspace{0.5cm} \text{Young’s modulus}
\item \(F_o\) \hspace{0.5cm} \text{Fourier modulus}
\item \(g\) \hspace{0.5cm} \text{acceleration due to gravity}
\item \(H\) \hspace{0.5cm} \text{enthalpy}
\item \(h\) \hspace{0.5cm} \text{heat transfer coefficient}
\item \(H_f\) \hspace{0.5cm} \text{enthalpy of fusion}
\item \(H_v\) \hspace{0.5cm} \text{heat of vaporization}
\item \(H_v'\) \hspace{0.5cm} \text{modified heat of vaporization}
\item \(l:\) \hspace{0.5cm} \text{brightness intensity}
\item \(k\) \hspace{0.5cm} \text{thermal conductivity}
\item \(L\) \hspace{0.5cm} \text{characteristic length}
\item \(m\) \hspace{0.5cm} \text{mass}
\item \(n\) \hspace{0.5cm} \text{number of element}
\item \(Nu\) \hspace{0.5cm} \text{Nusselt number}
\item \(Nu_{sat}\) \hspace{0.5cm} \text{Nusselt number for film boiling with water at the boiling point}
\item \(Pr\) \hspace{0.5cm} \text{Prandtl number}
\item \(q_{\text{cond}}\) \hspace{0.5cm} \text{conductive heat flux}
\item \(q_{\text{conv}}\) \hspace{0.5cm} \text{convective heat flux}
\item \(q_{\text{rad}}\) \hspace{0.5cm} \text{radiative heat flux}
\item \(q_{\text{surf}}\) \hspace{0.5cm} \text{heat flux at the droplet surface}
\item \(r\) \hspace{0.5cm} \text{radius}
\item \(Re\) \hspace{0.5cm} \text{Reynolds number}
\item \(Sc\) \hspace{0.5cm} \text{dimensionless degree of subcooling}
\item \(Sp\) \hspace{0.5cm} \text{dimensionless degree of superheat}
\item \(t\) \hspace{0.5cm} \text{time}
\item \(T\) \hspace{0.5cm} \text{temperature}
\item \(T_b\) \hspace{0.5cm} \text{boiling point}
\item \(t_{\text{vfc}}\) \hspace{0.5cm} \text{time of vapor film collapse}
\item \(T_{\text{cr}}\) \hspace{0.5cm} \text{critical temperature}
\item \(T_{\text{crit,w}}\) \hspace{0.5cm} \text{critical water temperature}
\item \(T_f\) \hspace{0.5cm} \text{complete freezing temperature}
\item \(T_i\) \hspace{0.5cm} \text{interface temperature}
\item \(T_m\) \hspace{0.5cm} \text{complete melting temperature}
\item \(T_{\text{mb}}\) \hspace{0.5cm} \text{minimum film boiling temperature}
\item \(T_o\) \hspace{0.5cm} \text{initial temperature}
\item \(t_o\) \hspace{0.5cm} \text{time zero}
\end{itemize}
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<td>$\Delta T_{\text{sub}}$</td>
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</tr>
<tr>
<td>$\Delta T_{\text{sup}}$</td>
<td>degree of superheating</td>
</tr>
<tr>
<td>$T_\infty$</td>
<td>temperature of the bulk liquid</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity of droplet</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number</td>
</tr>
<tr>
<td>$We'$</td>
<td>modified Weber number</td>
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**Greek letters**

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<td>$\alpha$</td>
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<td>$\delta$</td>
<td>thickness</td>
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<tr>
<td>$\varepsilon$</td>
<td>emissivity / temperature range between liquidus and solidus</td>
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<tr>
<td>$\lambda_\alpha$</td>
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<tr>
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<tr>
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<tr>
<td>$\sigma$</td>
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**Subscript**

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<td>original</td>
</tr>
<tr>
<td>$s$</td>
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<td>$v$</td>
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Chapter 1. INTRODUCTION

In the pulp and paper industry, the kraft process is the dominant pulping method: kraft pulp accounts for two-thirds of the world’s virgin pulp production and for over 90% of chemical pulp. It has an advantage economically over other pulping processes, as its chemical recovery process allows reuse of up to 97% of the pulping chemicals, while generating a significant amount of steam and power [1]. The continued advancement of science and technology in the kraft recovery process is of great importance to the industry.

The recovery boiler is a key unit in the kraft recovery process, in which a molten salt mixture, called smelt, is produced. Molten smelt flows out from the bottom of the boiler, and it is shattered by steam jets into droplets, which then fall into a dissolving tank. In the dissolving tank, smelt mixes with water to produce an aqueous solution called green liquor. The interaction between smelt droplets and green liquor can lead to a violent dissolving tank, and in rare instances, a dissolving tank explosion accident. Fundamentally, this interaction is a vapor explosion phenomenon caused by the rapid vaporization of water in the green liquor when it contacts the high temperature molten smelt. To understand the interaction of smelt and green liquor in a recovery boiler dissolving tank, this thesis examines smelt droplet-water interaction both experimentally and by model simulations. This chapter presents a brief overview of the kraft process, dissolving tank operation and issues, a literature review, and finally a list of thesis objectives.
1.1 The Kraft Process

A typical kraft chemical recovery process consists of a series of unit operations, as shown in Figure 1-1. In a digester, wood chips are cooked into pulp with pulping chemicals called white liquor, which is a solution of sodium hydroxide (NaOH) and sodium sulphide (Na₂S). The pulp produced is separated from the liquid stream by washing. The remaining stream, called weak black liquor, is a mixture of water, spent pulping chemicals, and organic wood residue. It has about 85% water and 15% dry solids by weight, and so is concentrated in a series of evaporators to heavy black liquor with 65 to 85% dry solids, before being sent to the recovery boiler [2].

Heavy black liquor is sprayed into the recovery boiler. Some of the liquor burns in flight; the rest falls onto a porous char bed at the bottom of the boiler and burns in a reducing atmosphere. The combustion of the organic material in the liquor produces a significant amount of energy, which heats the cooling water around the boiler to generate steam for use in various processes in the mill. The inorganic component in the liquor is converted to molten smelt, which accumulates at the bottom of the recovery boiler. Molten smelt continuously flows out from the bottom of the recovery boiler through multiple smelt spouts, falls into a dissolving tank, and mixes with water.

Figure 1-1: The kraft chemical recovery process [1]
to generate green liquor. Figure 1-2 shows a schematic of a recovery boiler with the dissolving tank circled. The green liquor is subsequently sent to a causticizing plant, where white liquor is regenerated through a causticizing reaction with lime (calcium oxide). The lime mud (calcium carbonate), a byproduct of the causticizing reaction, is calcined back to lime in a lime kiln.

Figure 1-2: A recovery boiler, with the dissolving tank circled [3]
1.2 Dissolving Tank Operation and Issues

Smelt is a salt mixture composed of sodium carbonate ($\text{Na}_2\text{CO}_3$) and sodium sulphide ($\text{Na}_2\text{S}$), and small amounts of sodium sulphate ($\text{Na}_2\text{SO}_4$), sodium chloride ($\text{NaCl}$) and potassium salts [4]. Smelt sulphidity, calculated as $\frac{[\text{Na}_2\text{S}]}{[\text{Na}_2\text{S}]+[\text{Na}_2\text{CO}_3]+[\text{NaOH}]} \%$, is a measure of $\text{Na}_2\text{S}$ content in the smelt. It typically ranges between 25 to 45%. Molten smelt continuously flows out of the boiler at about 800°C with a flow rate of about 1 liter per second per smelt spout [5]. These smelt streams are broken up into droplets by steam shatter jets, located in front of each spout. For safety reasons, the spouts are usually covered by a hood. An operator can observe the smelt flow by lifting up a hatch on the dissolving tank hood. Figure 1-3 shows two pictures of a smelt flow, one from the front, and the other from above.

![Figure 1-3: Smelt flow down a spout, front view (left) and top view (right)](image-url)
Figure 1-4 illustrates the dissolving tank operation. Based on previous studies of smelt shattering, shattered smelt droplets are on the order of a few millimeters [5,6]. Therefore, under normal operation conditions, tens of thousands of smelt droplets per second per spout fall into the dissolving tank. The dissolving tank is located 2 to 3 meters below the smelt spouts. It is usually round or elliptical, with a diameter roughly the width of the recovery boiler wall, and 3 to 4 meters in height. The process water, called weak wash, enters the dissolving tank at about 60°C. The retention time of smelt in the dissolving tank is about 30 minutes, and agitators are installed to facilitate smelt dissolution.

![Dissolving tank operation schematics](image)

**Figure 1-4: Dissolving tank operation schematics**

The resulting green liquor leaves the dissolving tank at around 90°C. The smelt concentration in green liquor is described in terms of the by Total Titratable Alkali (TTA), which is calculated as $[Na_2S] + [Na_2CO_3] + [NaOH]$, usually around 120 g/L Na₂O equivalent. A smelt concentration too close to the saturation concentration may lead to the precipitation of pirssonite ($Na_2Ca(CO_3)_2·2H_2O$), causing scaling problems in the tank. The weak wash flow rate, and the
temperature, density, liquid level, and TTA of the green liquor are closely monitored to ensure the quality of the green liquor provided to the processes downstream. The steam and gas generated as a result of the interaction between the high temperature smelt and green liquor pass through a scrubber to reduce particulates and odors, before being vented to atmosphere, or are recycled back into the recovery boiler.

The interaction between smelt droplets and green liquor in the dissolving tank can be violent, causing the tank to rumble and vibrate. Under abnormal operating conditions, the noise and tank vibration become excessive, and at times, the ground and buildings nearby can shake. This happens especially when smelt is not well shattered due to recovery boiler operation upsets. For example, the smelt flow may suddenly increase during unplugging of a clogged smelt spout, which is called “smelt runoff” [7,8]. Also, at low smelt sulphidity, the smelt stream may freeze due to a higher melting temperature, which may lead to so-called “jellyroll smelt” that is highly viscous and difficult to shatter [9]. The interaction of smelt and green liquor cannot be seen from outside of the enclosed tank; operators often rely on the level of noise and tank vibration to assess the dissolving tank operation, and take action before the tank becomes too violent.

Highly violent interaction between smelt and green liquor may produce a large amount of steam that surges out from the dissolving tank hood, as well as loud explosions, leading to an evacuation of the area. In extreme cases, a dissolving tank explosion results in property damage, personnel injury and costly boiler shutdowns. In North America, 37 dissolving tank explosion incidents have been reported since 1974 [10,11]. Many less severe incidents have likely occurred but were not reported. As regulations on occupational health and safety have become increasingly stringent in recent years, safe dissolving tank operation has become a top priority for kraft pulp mills.

In addition to the safety issue, effective smelt dissolution is important to avoid smelt accumulation at the bottom of the dissolving tank, and to generate high quality green liquor. However, there is a lack of information on the dissolution of smelt droplets [7]. Fundamental knowledge of how smelt droplet interacts with green liquor/water is needed for safer and more effective dissolving tank design and operation.
1.3 Literature Review

Smelt-water interaction is a physical vapor explosion phenomenon, which results from rapid liquid vaporization and over-pressurization within inertial constraints [12–15]. Vapor explosions occur when a “hot” liquid interacts with a “cold, more volatile” liquid, and the heat transfer is so rapid that it can lead to instantaneous vaporization of the cold liquid, resulting in explosion shockwaves. In the pulp and paper industry, smelt-water interaction has been mainly studied in the context of smelt-water explosion accidents in the recovery boiler, and previous studies have shown that smelt composition plays a role in recovery boiler explosions [12]. In the context of smelt-water interaction in the dissolving tank, very few studies have been conducted. This literature review section presents 1) an overview of the vapor explosion phenomenon, focusing on the interaction between a single hot liquid droplet and a pool of cold liquid, and the effect of material composition, 2) past studies of recovery boiler explosions and dissolving tank explosions, and 3) the knowledge gap.

1.3.1 Vapor explosions

Vapor explosions are a common safety concern in several industries including nuclear, metal processing, liquefied natural gas, and pulp and paper [12–17], as well as in domestic cooking [18] and sub-marine volcano eruptions [19–21]. The majority of research on vapor explosions has been conducted by the nuclear industry, in which vapor explosions occur when a jet of molten nuclear fuel (e.g. uranium-235) falls into cold cooling water during a reactor failure.

Vapor explosions have been studied extensively by conducting experiments with molten metal and water (e.g. [22–26]), and by running computer simulations (e.g. [27–31]). Vapor explosion studies can be categorized based on the mode of contact between the hot and cold liquids: a) hot liquid poured into cold liquid, b) cold liquid poured into hot liquid, c) a layer of cold liquid on top of hot liquid, and d) a layer of hot liquid on top of cold liquid. Experiments on vapor explosions can also be categorized based on the experimental scale: small-scale single droplet experiments (e.g. [22,25,32–34]) and large-scale experiments (e.g. [35–38]). Since the explosion
process is somewhat stochastic, experimental results are often specified in terms of qualitative behaviors and explosion probability [22,39–41].

It is well accepted that a vapor explosion event occurs in four distinct stages: premixing, triggering, propagation, and expansion [13,16]. Figure 1-5 is a graphical representation of the stages of a vapor explosion, when a hot liquid is poured into a cold liquid.

![Figure 1-5: Four stages of a vapor explosion as a hot liquid poured into a cold liquid](image)

In the premixing stage, after the hot liquid falls into the cold one, a vapor film forms around the hot liquid due to film boiling of the cold liquid. The vapor film separates the two liquids, and the system is in a metastable state. In the nuclear industry, since the liquid fuel jets into water, research has focused on the jet flow characteristics and jet breakup mechanism [23,29,35,43,44], and film boiling phenomena using high temperature solid metals immersed into water [45–49]. Fauske proposed that film boiling is necessary for a vapor explosion to occur, and so that the cold liquid must be heated to above its spontaneous nucleation temperature to form a vapor film [50]

In the triggering stage, somewhere in the system, the vapor film destabilizes and collapses, resulting in a small droplet-scale explosion. The vapor film collapse may occur either spontaneously, or can be triggered by an external disturbance. Studies of single molten droplet explosions showed that fragmentation plays a key role in a small-scale droplet explosion [22,33,34,51–53]. Fragmentation of the hot liquid dramatically increases the interface area and heat transfer rate between the hot and cold liquids. The cold liquid then vaporizes in a fraction of a millisecond, rapidly enough to cause a pressure build up and explosion shockwave. The detailed fragmentation mechanism itself is a field of study, which usually involves high speed
imaging visualization [25,32,54–58]. In general, the fragmentation mechanisms can be classified into either thermal fragmentation, driven by heat transfer and rapid vaporization effects, or hydrodynamic fragmentation, driven by the relative velocity between the hot and cold liquid. An example of thermal fragmentation is the liquid jet mechanism: when the vapor film collapses, small jets of the cold liquid shoot toward the hot liquid and penetrate into the hot liquid. The subsequent sudden vaporization of the cold liquid from inside the hot liquid breaks the hot liquid into fine fragments.

In the propagation stage, Board and Hall proposed a detonation theory that the explosion shockwave propagates through the mixture, similar to a chemical detonation [59]. The classical ZND detonation model suggests the existence of equilibrium downstream the Chapman-Jouquet plane with sonic flow relative to the wave front. Since the difference in pressure behind and ahead of the front is significant, more hot liquid is fragmented as a result of hydrodynamic instability as the shockwave passes through. This leads to larger heat transfer and more cold liquid vaporized, causing the explosion to escalate. In a case that a propagating wave passes through a series of dispersed melt droplets, the wave is a non-linear wave, and the phenomenon is more similar to bubble detonation [60,61].

Finally, in the expansion stage, the expansion of the high pressure mixture behind the shockwave front against the inertial constraints imposed by the surroundings can cause potential damages. Research on the propagation and expansion stages has focused on pressure buildup, energy release mechanism, and energy conversion efficiency by examining the explosion pressure peak and the metal debris that remains after experiments [38,62–66].

Most studies on vapor explosions have been conducted using pure metal or metal oxide [26,33,40,52,67]. Some studies have found that the properties of the hot liquid play a role in vapor explosions. For example, under the same conditions, alumina (Al₂O₃) tends to explode, whereas uranium dioxide (UO₂) only interacts mildly with water [36,68]. It has been proposed that the solidification of the hot material may prevent it from fragmentation, and thus, an explosion [69,70]. A few studies also examined the role of composition in a binary molten metal system [68,70–72]. They found that mixtures of uranium dioxide and zirconium dioxide (ZrO₂) of 80% - 20% and 50% - 50% by weight did not explode, whereas those of 70% - 30% did. The
current view is that the UO$_2$-ZrO$_2$ mixture with non-eutectic compositions may form a partially solid, or “mushy” layer, during cooling. This layer can resist against external forces and prevent droplet fragmentation. However, it is recognized by the scientific community that the lack of data limits the understanding of the effect of multi-component materials on vapor explosions [44,72].

1.3.2 Smelt-water explosion research

In the pulp and paper industry, smelt-water interaction has been mostly studied in the context of smelt-water explosion accidents in recovery boilers, which can occur when cooling water from a leaking tube comes in contact with the molten smelt pool at the bottom of the boiler. In 1962, as a result of concerns about the frequency and severity of recovery boiler explosions, the Black Liquor Recovery Boiler Advisory Committee was formed to share knowledge on recovery boiler explosions, and to provide guidelines for the industry on recovery boiler operation safety. In 1963, the Smelt-Water Research Group was formed to carry out smelt-water explosion research. Experiments were mainly conducted by dropping or injecting a small amount of water into a pool of molten smelt [12,39]. It was the results from these experiments led to the conclusion that smelt-water explosion was not a chemical explosion, but rather a physical vapor explosion; and so some theories from vapor explosion might be applicable to smelt-water explosions.

Research has also shown that the composition of smelt plays a significant role in smelt-water explosions. It was found that pure molten Na$_2$CO$_3$ did not explode, but adding components such as NaCl, Na$_2$S, and NaOH made the molten mixtures “explosive”. These components were thus referred to as “sensitizers”; however, the reason behind the effect of composition was not well understood. Different smelt compositions were then tested for the purpose of identifying possible additives that could be used to prevent smelt-water explosions in the recovery boiler; however, no conclusive result was found. As a result of these research efforts and the industry attention to promote good inspection and maintenance practices, the likelihood of smelt-water contact in the boiler was minimized. As recovery boiler explosions have become rare, the industry began shifting its attention to dissolving tank safety.
Only two studies on dissolving tank explosions were conducted, in the mid-1950s. Sallack [73] conducted a series of laboratory experiments by pouring more than 100 g of synthetic smelt, composed of Na$_2$CO$_3$ and NaCl, into a steel pan containing water. He found that the smelt explosion behavior was affected by water temperature, smelt composition, and dissolving liquid composition. Also, pure Na$_2$CO$_3$ did not explode under any circumstances, but became explosive if sensitizers were added. Nelson and Kennedy [74] performed similar laboratory experiments using both synthetic smelt and real kraft smelt. They confirmed Sallack’s findings and reported further that kraft smelt with a high sulphidity behaves more violently than kraft smelt with a low sulphidity.

1.3.3 Knowledge gap

There is a large body of literature on vapor explosions in the nuclear industry, and in the context of recovery boiler explosions; however, smelt droplet-water interaction in the dissolving tank has several unique characteristics that warrant further study. First, the relative quantity between smelt and water in the dissolving tank is very different from that in the recovery boiler. Second, the material properties of molten smelt are very different from those of molten metals studied by the nuclear industry, including lower density, thermal conductivity, surface tension, and viscosity, and a higher heat capacity. Thirdly, vapor explosions in all other scenarios have been studied in the context of an accident, where contact between the hot and cold liquids must be avoided; in the dissolving tank, smelt is purposefully brought into contact with water, and small droplet explosions presumably have implications on smelt dissolution.

The experiments conducted in the two dissolving tank explosion studies by Sallack and by Nelson and Kennedy used smelt of over 100 g instead of a single smelt droplet. Furthermore, the lack of information on material properties in the 1950s limited the interpretation of their results.

Recently, a laboratory study of the interaction between single smelt droplets and water was conducted by Jin [75], in which synthetic smelt droplets composed of 80 wt% Na$_2$CO$_3$ and 20 wt% NaCl were dropped into water at different smelt and water temperatures. The interaction was observed with a regular camera. It was found that water temperature plays a critical role in smelt
droplet-water interaction, and that smelt temperature has less influence. This study established a foundation for understanding smelt droplet-water interaction; however, it just scratched the surface of this subject. The following questions remain unanswered, and more research is needed to address them:

- Is the behavior of smelt droplet-water interaction in the dissolving tank similar to other small-scale vapor explosion phenomena?
- How to explain the effects of smelt and water temperatures on smelt droplet-water interaction characteristics?
- How does smelt composition affect smelt droplet-water interaction, and why?
- How do other parameters in the dissolving tank affect smelt droplet-water interaction?
- What are the implications of smelt droplet-water interaction on dissolving tank safety and dissolution efficiency?

1.4 Objectives

To address dissolving tank safety and operation issues, and to expand the fundamental knowledge of vapor explosions, this thesis examines the interaction behavior between single smelt droplets and water in the context of recovery boiler dissolving tank operation, with the following objectives:

1. To gain a qualitative understanding of smelt droplet-water interaction by visualizing the interaction behavior with high speed imaging (Chapter 3);

2. To develop a heat transfer model that explains the smelt droplet explosion mechanism (Chapter 4);

3. To quantitatively study the effects of smelt and water temperatures, smelt composition, and external disturbances on smelt droplet-water interaction characteristics (Chapter 5);

4. To examine the application of this laboratory study to actual dissolving tank operation, by considering droplet size, real smelt and green liquor composition, smelt droplet explosion violence, and smelt dissolution (Chapter 6).
Chapter 2. APPARATUS AND METHODOLOGY

In the majority of the experiments in this study, synthetic smelt made of a mixture of Na$_2$CO$_3$ and NaCl was used instead of real smelt with Na$_2$S, and water was used instead of green liquor. This is because real kraft smelt and green liquor contains Na$_2$S which is highly corrosive and readily oxidizes when exposed to air. The synthetic smelt with NaCl has similar properties to real kraft smelt, and is easier to handle. Real smelt and green liquor collected from a Canadian kraft mill, and other salts including Na$_2$SO$_4$, lithium sulphate (Li$_2$CO$_3$), potassium sulphate (K$_2$CO$_3$), and calcium chloride (CaCl$_2$) were also tested to examine how well the Na$_2$CO$_3$-NaCl smelt-water system represents other systems.

The apparatus built for this study is illustrated in Figure 2-1. The crucible (100 mm long, 25 mm ID) is made of Inconel to withstand the high corrosivity of the molten smelt at high temperature, and is tapered at the bottom with a 5 mm hole at the bottom tip. An Inconel plunger (150 mm long and 13 mm in diameter) is mounted in the center of the crucible to seal the hole at the bottom. The crucible is placed in a vertical tubular furnace, and smelt sample is loaded into the crucible from the top, with its temperature measured using a K-type thermocouple. The smelt melts in the crucible and is ejected through the hole at the bottom, one drop at a time, by lifting the plunger. The height of the furnace above the water tank can be adjusted to control the falling distance of the droplet from 55 to 85 cm.
Figure 2-1: Experimental apparatus for the study of smelt droplet-water interaction

Beneath the furnace sits a 20 L stainless steel tank in which the smelt droplet interacts with water. A 40L polypropylene tank sits beside the stainless steel tank as a hot water reservoir, and a submersible pump sends water from the reservoir tank to the stainless steel tank. Both tanks are insulated, and immersion heaters and digital thermometers are installed to control the water temperature. A stirrer powered by a Fisher Scientific motor (115 V, 50 W, and 60 Hz) in the tank agitates the water. After a set of experiments, water is discharged through a drain. The stainless steel tank has transparent polycarbonate windows on the front and back walls. A camera is placed in front of the stainless steel tank to document the interaction behavior, and a 50 watt spot light with a light diffuser is placed at the back of the tank to provide illumination. An external microphone placed near the tank records the sounds of the interactions, and a vibrometer attached to the tank measures the tank vibration. A computer is used to store the video images, audio data, and vibration data of smelt droplet-water interactions.

The cameras used in this study include a Canon Rebel T3i/ EOS 600D and three high speed cameras: a Mega Speed MS70KS2 (up to 5000 fps at a maximum resolution of 512 x 512), a
Phantom v2512 (up to 25600 fps at a maximum resolution of 1280 x 800, 28 Micron pixel, 12 bits), and a Phantom Miro321s (up to 1380 fps at a maximum resolution of 1920 x 1200, with color). Sometimes, an infrared filter (0.75 mm wavelength) was attached to the high speed video camera to filter out the background and visualize the high temperature smelt droplet only. The dissolution behavior of the smelt droplets was visualized with the aid of phenolphthalein, a pH indicator that turns pink when Na₂CO₃ dissolves in water as the pH of water changes from neutral to basic.

The videos recorded from the experiments were processed using Visualdub, and the videos recorded by the Phantom high speed cameras were generated with Phantom CineViewer software. To quantitatively analyze the video images of smelt droplet-water interaction, ImageJ was used for image processing. Audio and vibration data recorded by the microphone and vibrometer were processed using the Audacity audio editing software. The smelt droplet-water interaction characteristics investigated in this study include the explosion probability, explosion delay time, and explosion intensity, defined as

- **Explosion probability**: the number of exploded droplets, indicated by a large vapor bubble expansion and an explosion sound, divided by the total number of tests, which are usually more than 15 for each experimental condition.
- **Explosion delay time**: the time from the first contact of smelt droplet and water to a droplet explosion, usually on the order of seconds.
- **Explosion intensity**: the peak acoustic energy and tank vibration measured by the microphone and vibrometer in decibels, and determined using MATLAB algorithms.

The variability of the explosion probability results was tested by conducting experiments for smelt composed of 80 wt% Na₂CO₃ and 20 wt% NaCl at 800°C with water temperatures ranging between 20 and 100 °C on three different days. The variability of the explosion delay time and the explosion intensity data were often large due to the stochastic nature of the smelt droplet-water interaction. To mitigate this, median and median absolute deviations were used to quantify the data variability because they are more robust to outliers as compared to the mean and standard deviations.
Chapter 3. VISUALIZATION WITH HIGH SPEED IMAGING

This study provides the first ever visualization of the interaction between smelt droplets and water, using high speed imaging, and more discussion and analysis will be presented in Chapter 5. The video images presented in this chapter were taken with several different cameras, and the camera model, image resolution and frame rate are specified in the figure captions as (camera model / resolution / frame rate). The smelt droplets used in these experiments were composed of 80% Na₂CO₃ and 20% NaCl by weight, approximately 7.1 mm in diameter. Behaviors of other molten salt mixtures and real kraft smelt are presented in Appendix A, and they are similar to those presented here with 80% Na₂CO₃ and 20% NaCl smelt. Topics included in this chapter are: 1) the general types of smelt droplet-water interaction, 2) smelt droplet impingement and breakup behavior, 3) the behavior of the vapor bubble and fragments of smelt resulting from a droplet explosion, and 4) smelt droplet-water interaction that is triggered by an external disturbance.

3.1 Three Types of Droplet Behavior

There are three typical types of smelt droplet-water interaction behaviors. When the synthetic smelt droplets fall into water, some smelt droplets explode quickly on the water surface, referred to as “immediate explosions”; some submerge beneath the water surface and explode in the water after a short delay, referred to as “delayed explosions”; and others do not explode.
Figure 3-1 shows an example of an immediate explosion. At $t = 0$ ms, the droplet impacts on the water surface. A big splash is observed above the water surface ($t = 0.22$ ms), and at the same time, a vapor bubble expands downward, creating a large bubble dome ($t = 0.85$ ms). The entire bubble expansion process takes less than 1 ms. The explosion bubble shrinks back for at about $t = 10$ ms. Afterward, the smelt droplet can no longer be observed, as it has dissolved in water. Immediate explosions usually generate a high pitched sound.

Figure 3-1: An immediate explosion (Phantom v2512 / 512x320 / 100k)
Figure 3-2 shows an example of a delayed explosion, which takes place in a much longer time frame. When the droplet contacts the water surface, it rapidly vaporizes the water around it, creating a small vapor pocket ($t = 44$ ms). The entire impingement process is quiet, and the droplet subsequently submerges beneath the water surface surrounded by a thin layer of vapor film ($t = 117$ ms). After a short delay time, the droplet is suddenly disturbed ($t = 159$ ms), and soon after a large vapor bubble is created ($t = 163$ ms). Afterward, what is left is a cloud of smelt dust that quickly dissolves in water. Delayed explosions usually generate a low pitched sound.

![Figure 3-2: A delayed explosion](image-url)
Figure 3-3 shows a smelt droplet that does not explode, and the interaction may take up to a few seconds. Similar to the delayed explosion, the droplet first submerges into water quietly with a vapor film around it. After a short period of time, the vapor film collapses, causing a disturbance to the droplet ($t = 12.6$ s). This time, however, the droplet does not explode, and it dissolves into water much more slowly than the droplets that explode.

**Figure 3-3: No explosion** *(Mega Speed MS70KS2 / 512x512 / 1000)*
3.2 Smelt Droplet Impingement and Breakup Behavior

When a smelt droplet impinges onto the water surface, it sometimes breaks up into many smaller droplets, each surrounded by its own vapor film, as shown in Figure 3-4.

Figure 3-4: Smelt droplet breakup (Phantom v2512 / 1280x800 / 25k)
Since the vapor film can impede the view, direct observation of the smelt droplet is difficult, and has been a challenge in the field of vapor explosion research [76]. To understand the behavior of smelt droplet impingement, an infrared filter was placed in front of a high speed camera to visualize the high temperature smelt droplet only. An example of smelt droplet impingement behavior is shown in Figure 3-5. When the smelt droplet impinges onto the water surface, it first spreads out (t = 11.2 ms) and afterward recoils back to roughly a spherical shape without breaking up (t = 29.2 ms). The effect of smelt droplet impingement on the characteristics of smelt droplet-water interaction will be presented in more detail in Chapter 5.

Figure 3-5: Infrared images of smelt droplet impinging on the water surface (Phantom v2512 / 1280x800 / 25k)
Figure 3-6 shows an example of droplet breakup behavior in water, and afterward coalescence in water. The droplet impinges onto the water surface ($t = 0$ ms), submerges beneath the water surface, and recoils ($t = 40$ ms). Then, the droplet breaks into two droplets ($t = 82$ ms). After the first droplet bounced off on the tank bottom, the second one catches up with the first one, and the two droplets coalesce ($t = 368$ ms). The droplet eventually cools, indicated by the fading of its brightness in the image ($t = 2.41$ s).

Figure 3-6: Infrared images of smelt droplet breakup and coalescence (Phantom v2512 / 1280x800 / 5k)
3.3 Bubble and Fragment Dynamics

When a droplet explodes \((t = 1.5 \text{ ms})\), the resulting vapor bubble expands to a few times its diameter \((t = 4.6 \text{ ms})\), as shown in Figure 3-7. It can be seen that some relatively large pieces of smelt have not yet fragmented, and they travel with the edge of the bubble. Subsequently, the bubble quickly collapses \((t = 5.6 \text{ ms})\), and the intermixing between water and the smelt pieces leads to a second wave of explosion burst within tenths of a millisecond \((t = 5.8 \text{ ms})\). After the vapor bubble collapses, a cloud of very fine particles spreads outwards \((t = 8.1 \text{ ms})\).

Figure 3-7: Bubble dynamics of a droplet explosion on the bottom of the tank \((Phantom \, v2512 / 512x320 / 100k)\)
Infrared imaging was also used to observe the dynamics of the smelt fragments, and an example is shown in Figure 3-8. A droplet sits at the bottom of the tank (t = 0 ms) before it explodes (t = 0.03 ms). The smelt fragments expand within the expanding vapor bubble, and the smelt front reaches its maximum size at t = 3.3 ms. Within tenths of a millisecond, the fragments vanish because they cool quickly after the vapor bubble collapses and water mixes with the smelt fragments.

![Figure 3-8: Infrared images of smelt fragment dynamics during a droplet explosion on the bottom of the tank](Phantom v2512 / 512x320 / 100k)

The bubble and fragment dynamics can be quantitatively examined by image processing with ImageJ, and the methodology is presented in Appendix B. The dynamic of the vapor bubble is indicated by the equivalent bubble diameter normalized by the initial droplet diameter, $\frac{D_b}{D_o}$. Figure 3-9 shows $\frac{D_b}{D_o}$ as a function of time for the droplet explosion presented in Figure 3-2. The vapor bubble first expands to over five times the original droplet diameter, and then shrinks back. The diameter after 6 ms can no longer be determined, as the cloud of smelt fragments begins to spread out and impede the view of the bubble.
Similar to $\frac{D_b}{D_o}$, the dynamics of smelt fragments can be examined from the infrared images by the equivalent diameter normalized by the initial droplet diameter, $\frac{D_f}{D_o}$. In addition, the dynamics of thermal energy distribution during the explosion is quantified by the normalized weighted intensity of the smelt fragments, $\frac{I_f}{I_o}$. Figure 3-10 shows $\frac{D_f}{D_o}$ and $\frac{I_f}{I_o}$ of the droplet explosion presented in Figure 3-8; both $\frac{D_f}{D_o}$ and $\frac{I_f}{I_o}$ first increase, and then decrease after $t = 3.5$ ms as the vapor bubble begins to collapse. Note that $\frac{I_f}{I_o}$ decreases more rapidly than $\frac{D_f}{D_o}$, indicating that all the hot smelt fragments suddenly cool off when the water mixes with the smelt fragments.
Occasionally, it was observed that after the vapor bubble collapses, a second wave of vapor bubble expansion is formed, as shown in Figure 3-11. These results suggest that during the initial smelt-water contact, only part of the smelt droplet broke into fine fragments, and a portion of the thermal energy stored in the droplet is released. The hydrodynamic force created by the collapse of the first vapor bubble further fragments the rest of the smelt, and the release of the remaining thermal energy causes a second vapor bubble expansion.
Vapor explosions have been observed using molten metal and water in the past (e.g. [24,57]), including the cyclic bubble expansion and collapse behavior first observed by Ciccarelli using flash simultaneous X-ray radiography and regular photography [26], and later by others [24,57,77]. The observations from this study agree well with these previous studies, and confirm that smelt droplet-water interaction is a small-scale vapor explosion phenomenon. However, some differences are apparent between smelt droplet-water interaction and a molten metal droplet explosion. First, explosions caused by molten metal droplets often result in multiple waves of vapor bubble expansion and collapse, whereas explosions caused by molten smelt droplets rarely result in a second bubble expansion. Second, after the initial droplet-water contact, a significant amount of the molten metal remains at the center of the vapor bubble, whereas the molten smelt breaks up into much smaller fragments. These differences suggest that molten smelt is easier to fragment than molten metal, likely because smelt has a lower density,
viscosity, and especially surface tension at its molten state, and lower mechanical strength in its solid state, than the metal counterparts.

3.4 **External Disturbances**

The smelt droplet explosions presented so far were caused by a vapor film collapse resulting from cooling of the droplet, referred to as spontaneous explosions. However, droplet explosions can also be triggered by external disturbances. For example, immediate explosions are likely a result of triggered vapor film collapse caused by the impact of droplet impingement. Also, delayed explosions often occur when droplets hit the tank bottom, as shown in Figure 3-12. The droplet is surrounded by a vapor film as it falls through water (t = 0.20 s). It hits the tank bottom (t = 0.28 s) and explodes (t = 0.29 s) right away. This kind of explosion, referred to as a “base-triggered” explosion, has also been observed with molten tin and water [53].

![Figure 3-12: Explosion triggered by droplet impact onto the tank bottom](Mega Speed MS70KS2 / 514x514 / 200)
Figure 3-13 shows an experiment with water agitation, to promote contact between the smelt droplet and water. It was observed that small amounts of smelt burst out from the droplet as the water constantly interacts with the smelt droplet surface. The droplet does not explode from the less intense interactions (t = 69 ms, 109 ms, and 141 ms), until a more intense interaction triggers the droplet explosion at t = 132 ms. On the contrary, without agitation, the smelt droplet would stay stable within the vapor film until the vapor film collapses, as illustrated in Figure 3-2.

Figure 3-13: Smelt-water interaction with water agitation (Phantom v2512 / 512x320 / 100k)
It was also observed that the explosion of one droplet often triggers the explosion of other droplets nearby, creating a multi-droplet chain explosion, as shown in Figure 3-14. Initially, there are multiple droplets in the water. The droplets at the bottom of the tank first explode (t = 12.4 ms), triggering the explosions of small droplets in the middle (t = 17.2 ms), and subsequently the tiny droplets floating on the water surface (t = 17.3 ms). The propagation velocity is about 10 - 20 m/s.

![Image 1](image1.png)

**Figure 3-14: A multi-droplet chain explosion (Phantom v2512 / 1280x800 / 25k)**

A closer look at the video shows that triggering also occurred in a fraction of a millisecond between the droplets near the tank bottom. Figure 3-15 shows the three droplets initially at the tank bottom (t = 0 s). As the small droplet on the left hits the tank bottom, it explodes (t = 1.6 ms). This disturbs the vapor film of the larger droplet in the middle, indicated by the ripple of the vapor film. The triggered vapor film collapse causes the large droplet to explode (t = 2 ms).

![Image 2](image2.png)

**Figure 3-15: Triggering between multiple droplet explosions (Phantom v2512 / 1280x800 / 25k)**
Chapter 4. A 1-D HEAT TRANSFER MODEL

An explosion is a rapid increase in volume and release of energy in an extreme manner [78]. When the smelt droplet contacts water, fragmentation of the hot liquid dramatically increases the interface area and heat transfer rate between the hot and cold liquid. The cold liquid vaporizes rapidly enough to cause a pressure build up and explosion shockwave.

The hypothesis proposed in this thesis is that whether or not a smelt droplet explodes depends on the thickness of the solidified layer formed on the smelt surface at the moment of vapor film collapse. When the vapor film collapses, if the droplet is completely molten or has only a thin solidified layer on its surface, the disturbance introduced by the vapor film collapse can cause the droplet to readily deform and fragment, leading to a small-scale vapor explosion. On the other hand, if the droplet has formed a thick solidified layer, the protective layer will have a higher physical strength to withstand the force of the external disturbance, and the droplet will not deform or fragment, and thus not explode. Since it is not possible to experimentally track the temperature distribution within a droplet, as well as the solidified layer thickness in the smelt droplet-water interaction experiments, a heat transfer model was developed to analyze and interpret the experimental results that will be presented in later chapters.

4.1 Model Formulation

Earlier studies [54,55,79,80] and the experimental observations presented here suggest that heat transfer plays an important role in smelt droplet-water interaction. The two key aspects are film boiling of the water, and solidification characteristics of the droplet. Figure 4-1 proposes a model of the fate of a molten smelt droplet in water. At time zero, \( t_c \), the droplet contacts water, and a vapor film immediately forms around the droplet due to the high surface temperature. For a short period of time, the vapor film separates the droplet from the water. As heat is released from the droplet to its surroundings, the droplet cools and begins to form a solidified layer on its surface. The solidified layer consists of a completely solid layer and a partially solid layer. It grows thicker inward with time. As the droplet cools, the rate of vapor generation decreases and the
vapor film becomes unstable, and eventually collapses at time $t_{vfc}$. A 1-D mathematical model was developed to describe the heat transfer between the droplet and water, from $t_o$ to $t_{vfc}$.

The model is based on the following assumptions:

- The droplet is spherical;
- The heat transfer within the droplet is by conduction only;
- The cooling of the droplet prior to its full immersion in the water is negligible;
- No air is entrained in the vapor film when the droplet enters the water (the vapor film contains water vapor only);
- The droplet falls through water at a constant velocity;
- The density of the molten smelt is the same as that of the solid smelt ($\rho_l = \rho_s$);
- Thermophysical properties of smelt are assumed to be constant;
- The heat transfer across the vapor film is by conduction only;
- No external disturbance is considered.

*Figure 4-1: Fate of a molten smelt droplet in water*
The model takes into account the following aspects of heat transfer, as illustrated in Figure 4-2:

- Conductive heat flux within the droplet ($q_{cond}$)
- Convective heat flux from the droplet to the surroundings ($q_{conv}$)
- Radiative heat flux from the droplet surface to water ($q_{rad}$)
- Heat conduction across the vapor film ($q_{cond,v}$)
- Heat flux from the vapor film to the bulk water ($q_{conv,v}$)
- Phase change of the droplet from liquid to partially solid, and then to solid
- Vaporization and condensation at the vapor-water interface
The governing energy equation in spherical coordinates is

\[ \rho C_p \frac{\partial T}{\partial t} = k \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) \right) \]  

Eqn. 1

where \( C_p \) and \( k \) are the heat capacity and thermal conductivity, \( T \) is temperature, and \( r \) is radial position. The initial condition and boundary conditions are

\[ T(r)|_{t=0} = T_o \]  

Eqn. 2

\[ \frac{\partial T}{\partial r}|_{r=0} = 0 \]  

Eqn. 3

\[ -k \frac{\partial T}{\partial r}|_{r=R} = q_{surf} \]  

Eqn. 4

where \( T_o \) is the initial droplet temperature. \( q_{surf} \) is the total heat flux from the surface of the droplet to the surroundings, which consists of a radiative heat flux and a convective heat flux due to film boiling, that must be prescribed.

If the material solidify at a fixed temperature, without considering the partially liquid phase, the position of the solid-liquid phase boundary, \( R' \) changes with time, and the heat balance at the solid-liquid boundary depends on the heat fluxes in both the solid and liquid phases, as

\[ -k \frac{\partial T}{\partial r}|_{r=R'(t), s} - k \frac{\partial T}{\partial r}|_{r=R'(t), l} = \rho H_f \frac{dR'(t)}{dt} \]  

Eqn. 5

where \( H_f \) is the latent heat of fusion. This moving phase change boundary problem is difficult to solve analytically [81], especially for a system where a partially liquid phase also exists; but it can be solved numerically.
To non-dimensionalize the above equations, let \( r^* \), the Fourier number \( Fo \), \( T^* \), and \( R'^* \) be the non-dimensionalized radius, time, temperature, and position of the phase change boundary layer, expressed as

\[
\begin{align*}
    r^* &= \frac{r}{R} & \text{Eqn. 6} \\
    Fo &= \frac{\alpha t}{R^2} & \text{Eqn. 7} \\
    T^* &= \frac{T(r, t) - T_w}{T_i - T_w} & \text{Eqn. 8} \\
    R'^* &= \frac{R'}{R} & \text{Eqn. 9}
\end{align*}
\]

Substituting these quantities into Eqn. 1 to 5 yields the following non-dimensional equations:

\[
\begin{align*}
    \frac{\partial T^*}{\partial Fo} &= \frac{2}{r^*} \frac{\partial}{\partial r^*} \left( r^{*2} \frac{\partial T^*}{\partial r^*} \right) & \text{Eqn. 10} \\
    T^*(r^*) \bigg|_{Fo=0} &= 1 & \text{Eqn. 11} \\
    \frac{\partial T^*}{\partial r^*} \bigg|_{r^*=0} &= 0 & \text{Eqn. 12} \\
    \frac{\partial T^*}{\partial r^*} \bigg|_{r^*=1} &= -Bi & \text{Eqn. 13} \\
    \frac{\partial T^*}{\partial r^*} \bigg|_{r^*=R'^*,s} - \frac{\partial T^*}{\partial r^*} \bigg|_{r^*=R'^*,l} &= -\frac{1}{Ja} \frac{dR'^*}{dFo^*} & \text{Eqn. 14}
\end{align*}
\]

where \( Bi \) is the Biot number, and \( Ja \) is the Jakob number, defined as

\[
\begin{align*}
    Bi &= \frac{Lh}{k} & \text{Eqn. 15} \\
    Ja &= \frac{C_p \Delta T}{H_f} & \text{Eqn. 16}
\end{align*}
\]
\( \alpha \) is the thermal diffusivity, \( L \) is a characteristic length, \( h \) is the heat transfer coefficient between the droplet and its surroundings, \( k \) is thermal conductivity within the droplet, \( C_p \) is the heat capacity of the droplet, \( \Delta T \) is the difference between the droplet temperature and the melting temperature, and \( H_f \) is the latent heat of fusion of the droplet.

Examining the non-dimensionalized equations, \( Fo \) and the governing equation show that the characteristic time increases with \( R^2 \), and decreases when \( \alpha \) increases. This suggests heat transfer occurs more slowly as the droplet size increases and as thermal diffusivity decreases. Similarly, \( Ja \) and the phase change boundary condition suggest that a larger sensible heat to latent heat ratio leads to a more rapid formation of the solidified layer. \( Bi \) characterizes the temperature distribution within the droplet. For \( Bi < 0.1 \), the temperature within the droplet can be assumed uniform. For the typical values of \( h \) for water between 20 and 100°C, which will be presented later in this chapter, \( 0.08 < Bi < 0.8 \). Thus, the temperature within the droplet cannot be assumed uniform.

The vapor film will collapse after a finite time. To examine the status of the droplet at \( t_{vfc} \), a vapor film collapse criterion is required as part of the model.

In addition to the heat transfer between the droplet and water, the vapor film may grow or shrink in thickness as a result of vaporization or condensation at the water-vapor interface. This depends on the difference between the heat input from the droplet surface, \( q_{conv,d} \), and heat output to the bulk water, \( q_{conv,v} \), and can be modeled as

$$ \rho H_v' \frac{d\delta_v}{dt} = q_{conv,v} - q_{cond,v} \quad Eqn. 17 $$

where \( \delta_v \) is the thickness of the vapor film, and \( H_v' \) is the adjusted enthalpy of vaporization taking into account the sensible heat due to temperature change in the vapor film.
The inputs and outputs of the 1-D heat transfer model are listed in Table 1.

<table>
<thead>
<tr>
<th>Model Inputs</th>
<th>Model Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Initial smelt temperature</td>
<td>At any time step until ( t_{vc} ):</td>
</tr>
<tr>
<td>• Water temperature</td>
<td>• Time elapsed</td>
</tr>
<tr>
<td>• Properties of smelt (a function of smelt composition)</td>
<td>• Heat fluxes</td>
</tr>
<tr>
<td>• Droplet size</td>
<td>• Temperature profile</td>
</tr>
<tr>
<td>• Properties of the cold liquid (water)</td>
<td>• Thicknesses of the solid layer, partially solid layer, and the sum of the two, referred to as the solidified layer</td>
</tr>
</tbody>
</table>
<pre><code>                                                                  | • Liquid fraction in the partially liquid layer as a function of radial position |
                                                                  | • Thickness of the vapor film                                                  |
</code></pre>

### 4.2 Model Implementation

This section describes the implementation of the model by presenting the enthalpy method that is used to model the heat transfer within the droplet, the heat removal at the droplet surface implemented as a boundary condition, the vapor film collapse criterion, and a model for the vapor film dynamics. The model was solved in MATLAB.

#### 4.2.1 Heat transfer within the droplet

Solidification of the molten smelt droplet is a phase change problem with moving phase boundaries, known as a Stefan problem [82–84]. It can be solved using the enthalpy method [85,86], in which the transient part of the energy equation is written in terms of enthalpy, \( H \), instead of temperature using the relationship

\[
\frac{dH}{dT} = C_p dT \tag{Eqn. 18}
\]
The enthalpy method is advantageous because it does not require tracking the phase change boundary, and a partially liquid phase can be easily introduced.

With a phase change, the enthalpy can be calculated as sensible heat, according to the temperature difference from a reference temperature, plus the latent heat of fusion, if phase change occurred. Figure 4-3 shows the relationship between enthalpy and temperature, using a reference level of the solid material at its complete freezing temperature, $T_f$, assuming the heat capacity is constant. The solid line represents the case pure substances or mixtures at the eutectic composition, for which freezing occurs at a fixed temperature. The dashed line represents mixtures at a non-eutectic composition, for which the latent heat is assumed to be absorbed or released proportionally during a temperature interval, $\varepsilon$, between $T_f$ and the complete melting temperature, $T_m$.

![Figure 4-3: Enthalpy-temperature relationship](image-url)
To numerically solve Eqn. 1 subject to its initial and boundary conditions, the droplet radius is divided into small elements with an element size of $\Delta r$. The enthalpy of each element at the initial temperature in the liquid phase can be calculated using

$$H = C_p(T - T_f) + H_f \quad \text{Eqn. 19}$$

The enthalpy change of each element during a heat transfer process is then calculated based on heat fluxes from adjacent elements due to temperature differences and the boundary conditions. Let $n - 1$, $n$, and $n + 1$ denote the timesteps, and $i - 1, i, \text{ and } i + 1$ represent adjacent element numbers, then

$$H_i^{n+1} = H_i^n + \frac{k_s \Delta t}{\rho} \left( \frac{T_{i-1}^n - 2T_i^n + T_{i+1}^n}{(\Delta r)^2} + \frac{T_{i+1}^n - T_{i-1}^n}{r_i \Delta r} \right) \quad \text{Eqn. 20}$$

The temperature of each element at the next timestep can be obtained by

$$T = \begin{cases} 
T_f + \frac{H}{C_p} & H \leq 0 \ (\text{solid}) \\
T_f + \epsilon \left( \frac{H}{H_f + C_p \epsilon} \right) & 0 \leq H \leq H_f \ (\text{partially solid}) \\
T_f + \frac{H - H_f}{C_p} & H \geq H_f \ (\text{liquid}) 
\end{cases} \quad \text{Eqn. 21}$$

Thus, the temperature and the phase of each element at any position and time can be computed. The phase change boundary can be identified by determining the element with a temperature closest to the phase change temperature, which also defines the thicknesses of the solid and partially solid layers.

To ensure convergence, the following criterion must be met [85]:

$$\frac{\Delta t}{(\Delta r)^2} < \frac{\rho C_p}{2k} \approx 10^6 \ (s/m^2) \quad \text{Eqn. 22}$$

Therefore, increasing spatial resolution by a factor of 10 requires an increase of time resolution by a factor of 100, which dramatically increases the computational time. In most simulations, $\Delta t$ was chosen to be 1 ms, and $\Delta r$ to be $\frac{R}{100}$ or 35 µm for a typical droplet 7 mm in diameter. A
series of simulations were run to confirm that the results in the thesis are mesh and timestep independent.

4.2.2 Heat removal at the droplet surface

The boundary condition at the droplet surface remains to be specified. Since the droplet surface temperature can be as high as 1000°C, heat transfer can occur both via convection and radiation. The total heat flux leaving the droplet surface is then

\[ q_{\text{surf}} = q_{\text{conv}} + q_{\text{rad}} \]  

Eqn. 23

where \( q_{\text{conv}} \) is the convective heat flux and \( q_{\text{rad}} \) is the radiative heat flux. For a hot surface emitting radiation, which is absorbed by the water at the water-vapor interface, the heat flux can be expressed as

\[ q_{\text{rad}} = \varepsilon\sigma(T_h^4 - T_b^4) \]  

Eqn. 24

where \( \varepsilon \) is the emissivity that is equal to 0.96 for water, \( \sigma \) is the Stefan-Boltzmann constant, \( T_h \) is the hot droplet surface temperature and \( T_b \) is the boiling point of water.

Convective heat flux due to film boiling, \( q_{\text{conv}} \), can be expressed as

\[ q_{\text{conv}} = h_{fb}(T_h - T_w) \]  

Eqn. 25

where \( T_w \) is the temperature of the bulk water, and \( h_{fb} \) is the convective heat transfer coefficient due to film boiling that must be specified. To assess the relative roles of natural convection (convection due to a fluid density difference) and forced convection (due to fluid movement), one calculates \( \frac{Gr}{Re^2} \) where \( Gr \) is the Grashof number and \( Re \) is the Reynolds number, defined as

\[ Gr = \frac{g\beta(T_h - T_w)D^3}{v^2} \]  

Eqn. 26

\[ Re = \frac{\rho v L}{\mu} \]  

Eqn. 27
where $g$ is the acceleration due to gravity, $D$ is the droplet diameter, $\beta$, $\nu$, $\rho$, and $\mu$ are respectively the volumetric thermal expansion coefficient, kinetic viscosity, density, and dynamic viscosity of the fluid that the droplet travels through, and $\nu$ is the velocity of the droplet. Since $\frac{Gr}{Re^2} \ll 1$, the effect of natural convection is negligible, and forced convection must be considered [81]. Liu and Theofanous proposed a Nusselt number correlation for forced convection with film boiling in subcooled water flows [45]:

$$Nu = \frac{h_{fb}L}{k} = Nu_{sat} + CRe^nPr_t^{\frac{1}{2}} \left( \frac{\mu_t}{\mu_v} \right) \left( \frac{Sc}{Sp} \right)$$  \hspace{1cm} Eqn. 28

$$Nu_{sat} = 0.5Re^{\frac{1}{2}} \left( \frac{\mu_t}{\mu_v} \right) \left( \frac{r^4}{Sp} \right)^{\frac{1}{4}}$$  \hspace{1cm} Eqn. 29

$$Sc = \frac{C_{p,t} \Delta T_{sub}}{H_v' Pr_t}$$  \hspace{1cm} Eqn. 30

$$Sp = \frac{C_{p,v} \Delta T_{sup}}{H_v' Pr_v}$$  \hspace{1cm} Eqn. 31

$$H_v' = H_v + 0.68 C_{p,v} \Delta T_{sup}$$  \hspace{1cm} Eqn. 32

where

$Nu$: Nusselt number
$L$: characteristic length (diameter of the spherical droplet)
$k$: thermal conductivity of the droplet
$\mu_t$ and $\mu_v$: viscosity of water and vapor
$Pr$: Prandtl number
$Sc$: dimensionless subcooling
$Sp$: dimensionless superheat
$\Delta T_{sub}$: degree of subcooling
$\Delta T_{sup}$: degree of superheating
$H_v'$: modified heat of vaporization of water taking account the sensible heat [87]
The constants \( C \) and \( n \) in Eqn. 28 are 0.072 and 0.77 based on studies of submerging metal spheres into water [45]. Therefore, the convective heat transfer due to film boiling, \( h_{fb} \), can be calculated as a function of the water temperature and droplet surface temperature.

### 4.2.3 Vapor film collapse criteria

Studies on film boiling have shown that vapor film collapse criteria depend on many parameters including the properties of the hot solid and cold liquid, the shape of the hot solid, subcooling of the cold liquid, wettability of the surface, and system pressure [47–49, 88–90]. Correlations are usually developed for different systems based on experimental results; none have been developed for film boiling on a molten surface.

There are two well-accepted approaches to develop a vapor film collapse criterion. The first views vapor film collapse as heat flux-controlled, backed by Taylor’s instability theory. It states that the film will collapse if the vapor being generated cannot sustain the natural growth rate of unstable disturbances [91–93]. The second theory views vapor film collapse as temperature-controlled, backed by the thermodynamic superheat limit theory. At a constant pressure and composition, the superheat limit represents the highest temperature a liquid can attain without undergoing homogeneous nucleation [94,95]. When water comes into contact with the hot droplet surface, according to Carslaw and Jaeger, the interface temperature between the two materials, \( T_i \), is calculated as [96]

\[
T_i = \frac{T_w + \alpha T_h}{1 + \alpha} \tag{Eqn. 33}
\]

where

\[
\alpha = \frac{k_h \rho_h c_{p.h}}{\sqrt{k_w \rho_w c_{p,w}}} \tag{Eqn. 34}
\]

\( T_w \) is the temperature of the water and \( T_h \) is the temperature of the hot surface. If \( T_i \) is above the superheat limit temperature, water will immediately vaporize to form a vapor film. Therefore,
vapor film collapse is only possible when $T_i$ falls below the superheat limit, and this temperature threshold is called the minimum film boiling temperature, $T_{mfb}$.

The maximum possible value for $T_{mfb}$ is the critical temperature of water, $T_{cr} = 374^\circ$C, above which water must vaporize. Spiegler computed $T_{mfb}$ based on the Van der Waals equation of state, and obtained a superheat limit of 0.844 of $T_{cr}$ [95]. Other equations of state, including the Redlich-Kwong, Soave, and Peng-Robinson, yield other values, 0.895, 0.919, and 0.921 of $T_{cr}$, respectively [97,98]. The effect of water subcooling on $T_{mfb}$ is not fully understood, and results from different experimental studies vary widely depending on the experimental conditions [47–49,99,100]. Studies of film boiling with a hot metal sphere in subcooled water have correlated $T_{mfb}$ linearly with the degree of subcooling plus a base constant [49,99,101,102].

In this work, the temperature-controlled approach is used. The constants in the $T_{mfb}$ correlation fall in the middle of the range of values in the literature, and the vapor film collapse criterion implemented in the model is expressed as

$$T_i < T_{mfb} = 0.92T_{cr} + 3\Delta T_{sub} \quad \textbf{Eqn. 35}$$

Note that this criterion assumes a smooth droplet surface with no nuclei to create heterogeneous nucleation. Thus, the vapor film is assumed to be composed of steam only, and that with no air is entrained during droplet impingement onto the water surface. Relaxing these assumptions would result in a vapor film that is more likely to collapse, and a lower value of $T_{mfb}$. Although these assumptions, and the coefficients in Eqn. 35, affect the exact value of the model outputs (i.e. the solidified layer thickness at $t_{vfc}$), the model nevertheless provides important information on the effect of different parameters on the relative solidification rate of the droplet.

To implement the vapor film collapse criterion in the heat transfer model, the model calculates $T_i$ using Eqn. 33 at each timestep based on the droplet surface temperatures, $T_h$. As $T_h$ decreases over time and $T_i$ eventually falls below $T_{mfb}$, the simulation stops at $t_{vfc}$, and information including the vapor film collapse time and solidified layer thickness at $t_{vfc}$ is generated.
4.2.4 Vapor film dynamics

The vapor film may grow or shrink in thickness as a result of vaporization or condensation at the water-vapor interface. The change in vapor film thickness is modeled numerically by Eqn. 17, given an assumed initial vapor film thickness at \( t_0 \). The heat flux across the vapor film towards the vapor-water interface is assumed to be heat conduction only due to the small thickness of the film, calculated as

\[
q_{\text{cond},v} = k_v \frac{(T_h - T_b)}{\delta_v} \quad \text{Eqn. 36}
\]

where \( k_v \) is the thermal conductivity of the vapor film. The heat removed from the water-vapor interface by the convection of the bulk water, \( q_{\text{cond},v} \), can be represented as

\[
q_{\text{conv},v} = h_{vw}(T_b - T_w) \quad \text{Eqn. 37}
\]

where \( h_{vw} \) is the convective heat transfer coefficient for heat flow from the thin vapor film to the bulk water, that can be determined from a correlation for the Nusselt number for flow around a free falling drop,

\[
Nu = 2 + 0.6Re^{\frac{1}{2}}Pr^{\frac{1}{3}} \quad \text{Eqn. 38}
\]

Given the assumption of a constant falling velocity, this equation yields a heat transfer coefficient of about 4800 W/(m\(^2\)K), for the typical conditions of the smelt droplet-water interaction experiments presented in this thesis.
4.3 Verification of the Enthalpy Method

To verify the implementation of the enthalpy method, the numerical solution was validated against an analytical solution of a simple scenario: the transient cooling of a solid sphere upon submerging into a liquid medium at a constant temperature. The corresponding analytical solution [103] is

\[
\theta = \frac{1}{R} \sum_{n=1}^{\infty} \frac{4[\sin(\lambda_n) - \lambda_n \cos(\lambda_n)]}{\lambda_n[2\lambda_n - \sin(2\lambda_n)]} \sin(\lambda_n R) e^{-\lambda_n^2 F_o} \quad \text{Eqn. 39}
\]

where \(\theta\) is the normalized temperature \(\frac{T - T_\infty}{T_0 - T_\infty}\), \(T_0\) is the initial droplet temperature, and \(T_\infty\) is the temperature of the bulk liquid. \(R\) is the radial position, \(r\), normalized by the radius of the sphere \(r_0\). \(F_o\) is the Fourier modulus defined as \(F_0 = \frac{k}{\rho C_p r_0^2 t}\). \(\lambda_n\) are the roots of the transcendental equation

\[
1 - \lambda_n \cot \lambda_n = Bi \quad \text{Eqn. 40}
\]

which must be obtained numerically. Figure 4-4 shows temperature profiles for an 800°C smelt sphere of 7 mm diameter, submerged into 80°C water. The analytical solution and the numerical solution using the enthalpy method match very well, showing that the model was implemented in MATLAB correctly.
Figure 4-4: $T(r)$ predicted by the analytical solution and enthalpy method, no phase change or film boiling

4.4 Model Demonstration

This section presents a sample simulation result, for a particular smelt droplet-water interaction: a synthetic smelt droplet 7 mm in diameter, composed of 80% Na$_2$CO$_3$ and 20% NaCl at an initial temperature of 800°C, entering water at 80°C. For this condition, the modeling result should yield a vapor film collapse time of 3.8 s, but for this specific simulation, the vapor film is assumed not to collapse.
Figure 4-5 shows the predicted temperature profile within the droplet at times $t = 0$, $5$, and $10$ s. At $t=0$, the temperature of the droplet is $800^\circ$C. The droplet cools over time, with the temperature of the droplet surface decreasing faster than that at the center of the droplet.

![Temperature profile graph](image)

**Figure 4-5: $T(r)$ at different times, assuming the vapor film does not collapse**

Figure 4-6 shows the variation of temperature with time at the center and surface of the droplet, and Figure 4-7 shows the predicted thicknesses of the solid, partially solid, and total solidified layers. At time A, the droplet surface begins to solidify. At B, the droplet surface becomes completely solid. At C, the center of the droplet begins to solidify. At D, the center of the droplet becomes completely solid. The partially solid layer first grows, and later decreases in thickness once the liquid-partially solid boundary reaches the center of the droplet, and as the solid-partially solid boundary moves toward the center of the droplet. The liquid fraction within the partially solid layer varies depending on the radial position, and can be calculated using the Lever rule.
Figure 4-6: $T(t)$ at the center and surface of the droplet

Figure 4-7: Thickness of different layers as a function of time
Figure 4-8 shows the vapor film dynamics, with an initial vapor film thickness of 100 µm. Initially, the thickness of the vapor film increases dramatically to about 145 µm due to the extremely high heat flux across a very thin vapor film, leading to vaporization of water at the vapor-water interface. As the vapor film thickness increases and the droplet surface temperature decreases, the heat flux from the droplet surface across the vapor film decreases. As a result, the vapor film thickness reaches a peak value, after which the vapor film begins to shrink.

![Vapor Film Thickness vs Time](image)

**Figure 4-8: Vapor film thickness as a function of time**

Note that the vapor film thickness at the first few timesteps is affected by the assumed initial thickness. A lower initial thickness leads to a higher initial heat flux from the droplet surface to the water-vapor interface, causing a more rapid growth of the thickness and a higher peak thickness value. However, a sensitivity study with initial thicknesses ranging from 1 to 500 µm showed that the vapor film dynamics quickly stabilize as time elapses, and become independent
of the initial assumed thickness after 40 ms. Once stabilized, the vapor film thicknesses predicted by the model is on the order of tens to less than 200 µm, which agrees with the observations from other film boiling studies (e.g. [46,48]).

Figure 4-9 shows the convective and radiative heat flux from the droplet surface to the surroundings. As the droplet temperature decreases, film boiling around the droplet, which impedes the heat transfer, becomes less stable. This leads to an increase of the convective heat transfer coefficient as expressed in Eqn. 28, and thus an increase of the convective heat flux. The radiative heat flux, by comparison, is small and decreases with time as the droplet surface cools.

Figure 4-9: Heat flux from the droplet surface to the surroundings
Chapter 5. RESULTS AND DISCUSSION

To study the effect of different dissolving tank operating parameters on smelt droplet-water interaction characteristics, synthetic smelt droplets were dropped into a tank of water at different conditions using the experimental apparatus presented in Chapter 2. The experimental results of the effects of smelt temperature, $T_s$, water temperature, $T_w$, and smelt composition on droplet explosion probability and delay time are presented in Section 5.1 and 5.2. Then the results are discussed with the help of the heat transfer model in Section 5.3. The effects of external disturbances including droplet impingement onto the water surface, droplet impact onto the tank bottom, and water agitation are also examined in Section 5.4. Table 1 summarizes the typical experimental conditions and the values of non-dimensional numbers and smelt properties in these conditions, unless stated otherwise.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Value</th>
<th>Smelt Properties Value</th>
<th>Non-dimensional Numbers Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelt Temperature</td>
<td>800°C</td>
<td>$H_f$ 320 kJ/kg</td>
<td>$Re$ 1500</td>
</tr>
<tr>
<td>Water Temperature</td>
<td>20 ~ 100°C</td>
<td>$\rho$ 1885 kg/m$^3$</td>
<td>$We$ 670</td>
</tr>
<tr>
<td>Smelt Composition</td>
<td>80 wt% Na$_2$CO$_3$ + 20 wt% NaCl</td>
<td>$C_p$ 1696 J/kg°C</td>
<td>$Gr$ 37000</td>
</tr>
<tr>
<td>Droplet Diameter</td>
<td>7.1 ± 0.2 mm</td>
<td>$k$ 1.58 W/m°C</td>
<td>$Fo$ 0.04</td>
</tr>
<tr>
<td>Falling Distance</td>
<td>55 cm</td>
<td>$\sigma$ 0.19 N/m</td>
<td>$Bi$ 0.08 ~ 0.8</td>
</tr>
<tr>
<td>Water Depth</td>
<td>10 cm</td>
<td>$\mu$ 0.005 Pas</td>
<td>$Ja$ 0.1</td>
</tr>
</tbody>
</table>
5.1 Effects of Smelt and Water Temperatures

In dissolving tank operation, $T_s$ depends on the operating conditions of the recovery boiler, and $T_w$ may fluctuate during the process startup and when the water flow is adjusted to ensure steady green liquor concentration. Figure 5-1 shows the explosion probability of a smelt droplet at different $T_s$ and $T_w$. At each temperature condition, more than 15 tests were conducted to calculate the explosion probability.

Figure 5-1 shows that the explosion probability is a strong function of $T_w$: increasing $T_w$ leads to a transition of the interaction behavior from immediate explosion to delayed explosion and then to no explosion. Below a lower critical water temperature (lower $T_{crit,w}$), droplets always explode. Above an upper critical water temperature (upper $T_{crit,w}$) of 82°C, droplets do not explode. In between, increasing $T_w$ leads to decreased likelihood of a droplet explosion. $T_s$, on the other hand, plays a minor role in decreasing the lower $T_{crit,w}$. 

![Figure 5-1: Explosion probability at different temperatures, 20% NaCl](image-url)
Explosion delay time, defined as the time from the first contact of the smelt droplet and water to a droplet explosion, is shown in Figure 5-2. It increases with increasing $T_s$ and $T_w$ up to 2.5 s near the upper $T_{\text{crit},w}$, with $T_w$ being the more dominant factor of the two.

Figure 5-2: Explosion delay time at different temperatures, 20% NaCl
5.2 Effect of Smelt Composition

The effect of smelt composition on smelt droplet-water interaction was studied with synthetic smelt of Na$_2$CO$_3$-NaCl mixtures of different compositions. Figure 5-3 shows the phase diagram of the Na$_2$CO$_3$-NaCl system. For pure Na$_2$CO$_3$, pure NaCl, and the mixture at the eutectic composition of 40% NaCl, the phase transition occurs at single temperatures of 858, 801, and 633°C, respectively. For a mixture, the phase change occurs over a range of temperatures, bounded by the liquidus (complete melting temperature, $T_m$), and the solidus (complete freezing temperature, $T_f$). Above $T_m$, the mixture is completely liquid. Solidification begins to occur when the temperature falls below $T_m$, and the liquid content in the mixture decreases as the temperature decreases. The mixture becomes completely solid when the temperature falls below $T_f$.

![Phase diagram of the Na$_2$CO$_3$-NaCl system](image)

For the Na$_2$CO$_3$-NaCl system, $T_f$ is equal to the eutectic temperature of 633°C. $T_m$ is a function of the composition of the mixture, and decreases as the composition approaches the eutectic composition. The thermophysical properties of the mixture are also a function of smelt composition. Increasing the NaCl content from 0 to 100% changes the thermophysical properties...
of the material from those of Na$_2$CO$_3$ to those of NaCl. Real kraft smelt is composed mainly of Na$_2$CO$_3$ and Na$_2$S, which exhibits similar phase change characteristics.

To investigate the effect of smelt composition on smelt droplet explosion behavior, synthetic smelt droplets composed of various amounts of Na$_2$CO$_3$ and NaCl were dropped into water. Figure 5-4 shows the mass and diameter of the droplets generated from the crucible. The result show that increasing NaCl content leads to a decrease in the droplet mass, but has no effect on the droplet diameter, because of the lower density of NaCl than Na$_2$CO$_3$.

![Figure 5-4: Mass and diameter of smelt droplets composed of different amounts of Na$_2$CO$_3$ and NaCl](image)

Experiments were first conducted with 0 (pure Na$_2$CO$_3$), 20 and 40% NaCl smelt at constant temperatures of 800, 900, and 1000°C. Pure Na$_2$CO$_3$ was not tested at 800°C, which is below its melting temperature (858°C). Figure 5-5 shows the explosion probability of the smelt droplets at different temperatures and compositions. Pure Na$_2$CO$_3$ droplets never explode. Increasing the NaCl content from 0% to 40% increases the likelihood of a droplet explosion at the same temperatures, and 40% NaCl droplets still explode at $T_w$ close to the boiling point.
For the 40% NaCl droplets, the explosion delay time increases with both $T_s$ and $T_w$, as shown in Figure 5-6. Compared to the results for 20% NaCl droplets shown in Figure 5-2, increasing NaCl content shifts the curves to the right.
For a given $T_s$, the difference between a constant $T_s$ and $T_m$ varies as the composition changes. To eliminate the effect of this difference from the result, experiments were conducted at $T_s = T_m + 50^\circ C$, with smelt compositions ranging from 0 to 100% NaCl content. Figure 5-7 shows the explosion probability of smelt droplets below the eutectic composition of 40% NaCl content. Pure $Na_2CO_3$ droplets and droplets with 10% NaCl never explode, regardless of $T_w$. At 20% NaCl, droplets always explode in water up to about 70°C, and at 30% NaCl, droplets always explode in water up to about 80°C. At the eutectic composition of 40% NaCl, droplets always explode regardless of $T_w$.

![Figure 5-7: Explosion probability, 0 to 40% NaCl content, $T_s = T_m + 50^\circ C$]
The explosion probability of smelt droplets above the eutectic composition of 40% NaCl content is shown in Figure 5-8. Increasing the NaCl content above the eutectic composition has the opposite effect than that below the eutectic composition, resulting in less likelihood of a droplet explosion. These results clearly indicate that the likelihood of a droplet explosion increases as the composition approaches the eutectic composition with a lower $T_m$. 

Figure 5-8: Explosion probability, 40 to 100% NaCl content, $T_i = T_m + 50^\circ C$
Figure 5-9 shows that for droplet compositions with the same $T_m$ on either side of the eutectic composition, droplets are more likely to explode when the NaCl content is higher: for 10 and 100% NaCl droplets of $T_m = 800^\circ C$, 100% NaCl droplets explode for $T_w < 50^\circ C$, but 10% NaCl droplets do not; for 20 and 80% droplets of $T_m = 745^\circ C$, 80% NaCl droplets are more likely to explode than 20% NaCl droplets. This suggests that in addition to $T_m$, the likelihood of a droplet explosion also depends on the thermophysical properties of the smelt, which are also affected by smelt composition.

![Figure 5-9: Comparisons of the explosion probability of smelt droplets with the same $T_m$](image)

This set of experiments also reveals another difference in interaction behavior at different smelt compositions. At low NaCl contents, delayed explosions occur in between a certain water temperature range. When the NaCl content is high, immediate explosions are mostly observed, and if the droplet does not explode, it more often breaks up upon impinging onto the water surface into smaller droplets. An analysis of droplet impingement behavior will be presented in Section 5.4.
To determine whether these effects of composition are applicable beyond the Na$_2$CO$_3$-NaCl system, experiments were conducted with other molten salts over a wide range of $T_w$ and $T_s$. Table 3 summarizes the results of various pure compounds and salt mixtures at their eutectic compositions, listed in order of decreasing $T_m$. These molten salts were selected to test a wide range of $T_m$ and thermophysical properties.

Table 3: Droplet explosion behavior of various pure salt compounds and mixtures, $T_w = 20$ to 100°C

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_m$ (°C)</th>
<th>$T_s$ (°C)</th>
<th>Explosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$CO$_3$</td>
<td>891</td>
<td>940</td>
<td>No</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>884</td>
<td>935</td>
<td>No</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>858</td>
<td>900</td>
<td>No</td>
</tr>
<tr>
<td>Na$_2$CO$_3$-Na$_2$SO$_4$ (57%-43%)</td>
<td>826</td>
<td>875</td>
<td>No</td>
</tr>
<tr>
<td>NaCl</td>
<td>801</td>
<td>850</td>
<td>Yes/No</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>772</td>
<td>820</td>
<td>Yes</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>723</td>
<td>775</td>
<td>No</td>
</tr>
<tr>
<td>Na$_2$SO$_4$-NaCl (86%-14%)</td>
<td>626</td>
<td>675</td>
<td>Yes</td>
</tr>
<tr>
<td>NaCl-CaCl$_2$ (33%-67%)</td>
<td>504</td>
<td>550 ~ 900</td>
<td>Yes</td>
</tr>
<tr>
<td>Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ (32%-33%-35%)</td>
<td>400</td>
<td>500 ~ 800</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The results show that, in general, droplets of salt mixtures with low $T_m$ tend to explode, and those with high $T_m$ tend not to explode. Also, similar to the results with the Na$_2$CO$_3$-NaCl system, chloride salts are more likely to explode than carbonate salts. For example, CaCl$_2$ droplets explode whereas Li$_2$CO$_3$ droplets do not despite the fact that CaCl$_2$ has a slightly higher $T_m$. 

60
5.3 Simulation Results and Discussion

The key conclusions of the experimental work on the effect of smelt temperature, water temperature, and smelt composition on smelt droplet-water interaction are:

- Increasing $T_w$ decreases the likelihood of a droplet explosion, and increases explosion delay time.
- $T_s$ has less influence on the likelihood of a droplet explosion, but increasing $T_s$ increases explosion delay time.
- As the smelt composition approaches the eutectic composition with a lower $T_m$, droplets are more likely to explode.
- At the same $T_m$, droplets with high NaCl content are more likely to explode.

To explain these experimental results, and to verify the hypothesis proposed that whether a droplet explodes or not depends on the thickness of the solidified layer formed on the smelt droplet surface at the moment of vapor film collapse, simulations were run with the heat transfer model with different input parameters. Molten salts properties including thermal conductivity, heat capacity, density, and latent heat of fusion were obtained from [104–106].

There are two outputs of the model that are the most relevant to smelt droplet explosion behavior. The first one is the vapor film collapse time, $t_{vfc}$, which corresponds to the delay time of the exploded droplets in the experiments. The second one is the extent of droplet solidification at $t_{vfc}$, which dictates how well the solidified layers can prevent fragmentation and explosion of the droplet. Determination of how thick the solid and partially solid layer is enough to prevent a droplet explosion requires knowledge of the mechanical properties of the solid and partially solid smelt, which are not available. Therefore, in this study, the sum of the solid and partially solid layer thicknesses, denoted as the solidified layer thickness, is used to serve as a measure of the extent of droplet solidification.
5.3.1 Vapor film collapse time

Figure 5-10 shows a comparison of explosion delay time and the predicted $t_{vfc}$ for 20% NaCl droplets at different temperature conditions. In this and subsequent plots, the lines that represent the modeling results are curve fits of discrete points, 2°C apart in $T_w$. Also, $t_{vfc}$ results for $T_w$ above the upper $T_{crit,w}$ are excluded from the graph as the droplets do not explode.

![Figure 5-10: Delay time and predicted $t_{vfc}$, 20% NaCl](image)

The simulation results are in good agreement with the experimental data in showing the trend that increasing $T_s$ and $T_w$ leads to longer $t_{vfc}$, with $T_w$ being the more dominant factor. This is because of two reasons: 1) the total amount of sensible heat released from the droplet before the vapor film collapse, and 2) the rate of heat transfer.
The sensible heat release from the droplet is proportional to the difference between the initial and the final droplet temperature at $t_{vfc}$. The initial droplet temperature is $T_s$, and although the final droplet temperature varies across the droplet radius, an indication is provided by the droplet surface temperature, shown in Figure 5-11. For the most part, the droplet surface temperature at $t_{vfc}$ is independent of $T_s$, except when the vapor film collapses immediately upon smelt-water contact ($T_w < 48^\circ C$ for 800°C smelt, and $T_w < 30^\circ C$ for 900°C smelt). Therefore, higher $T_s$ results in a larger amount of heat release before $t_{vfc}$.

Figure 5-11 also shows that the droplet surface temperature at $t_{vfc}$ decreases as $T_w$ increases. This is because water vaporizes more easily as its temperature approaches the boiling point, resulting in a higher $T_i$ and a lower $T_{mf}$, as per Eqn. 33 and Eqn. 35. Thus, a lower droplet surface temperature, $T_h$, in Eqn. 33 is required to sustain the vapor film. As a result, increasing $T_w$ also implies a larger amount of heat release before $t_{vfc}$.
The second reason that delay time and $t_{vfc}$ increase with increasing $T_s$ and $T_w$ is related to the rate of heat transfer. Figure 5-12 shows that the convective heat transfer coefficient due to film boiling in Eqn. 28 decreases with increasing $T_s$ and $T_w$, and approaches zero as $T_w$ approaches the boiling point, which leads to a lower heat transfer rate. Therefore, the combined effect of a larger amount of heat release before the vapor film collapses and a lower heat transfer rate leads to an increase in the delay time and predicted $t_{vfc}$.

![Figure 5-12: Convective heat transfer coefficient due to film boiling as a function of $T_s$ and $T_w$, 20% NaCl](image-url)
Figure 5-13 shows the predicted $t_{vfc}$ for 40% NaCl droplets. Compared to the results for 20% NaCl droplets shown in Figure 5-10, increasing NaCl content shifts the curves to the right, which agrees with the experimental results.

Figure 5-13: Predicted $t_{vfc}$, 40% NaCl
5.3.2 Droplet solidification

Figure 5-14 presents the solidified layer thickness formed on the surface of a 20% NaCl droplet, 7 mm in diameter, at \( t_{vfc} \). For \( T_w < 60^\circ C \), regardless of \( T_s \), the droplet has no solidified layer at \( t_{vfc} \). For \( T_w > 60^\circ C \), a solidified layer forms on the surface of the droplet before \( t_{vfc} \). Increasing \( T_w \) results in more droplet solidification at \( t_{vfc} \), and for \( T_w > 80^\circ C \), the entire droplet is solidified (solidified layer thickness = \( \frac{D}{2} \)).

![Solidified Layer Thickness vs. Water Temperature](image)

Figure 5-14: Solidified layer thickness at \( t_{vfc} \), 20% NaCl

The solidified layer thickness predicted by the model can explain the effect of \( T_s \) and \( T_w \) on smelt droplet explosion probability shown in Section 5.1. At low \( T_w \), the smelt droplet is completely molten, and readily fragments and explodes when the vapor film collapses. Increasing \( T_w \) leads to a higher \( T_i \) and a lower \( T_{mblf} \), indicating a more stable vapor film that provides more time for a droplet to solidify, as shown in Figure 5-10. As a result, a thicker solidified layer is formed on the droplet surface, and the droplet becomes less likely to fragment and explode. Increasing \( T_s \) also leads to a longer \( t_{vfc} \), but at the same time, the smelt droplet has more sensible heat to release and so takes longer to solidify. Therefore, \( T_s \) has less influence on the solidified layer thickness.
and the likelihood of a droplet explosion. Increasing $T_i$ leads to a decrease of the lower $T_{\text{crit,w}}$, shown in Figure 5-1. This is due to smelt droplet impingement upon the water surface, which will be discussed in Section 5.4.1.

Simulations were also run to examine the effect of smelt composition on the solidified layer thickness at the moment of vapor film collapse. As shown in Figure 5-15, pure Na$_2$CO$_3$ droplets solidify even at a low water temperature (35°C) in which the vapor film is unstable and so collapses quickly. Increasing the NaCl content up to the eutectic composition of 40% NaCl decreases $T_m$, making the droplets more difficult to solidify. The droplets then only solidify at a high $T_w$, when more time is provided for solidification due to a more stable vapor film. This shifts the curve to the right until the eutectic composition is reached, corresponding to smelt droplets with the lowest $T_m$ that is the most difficult to solidify. Increasing NaCl content beyond the eutectic composition leads to an increase in $T_m$, and so 80% and 100% NaCl droplets solidify more at the same $T_w$.

![Figure 5-15: Solidified layer thickness at $t_{vfc}$ for smelt droplets with different compositions, $T_i = T_m + 50°C$](image-url)
For droplet compositions with the same $T_m$ (i.e. 10 vs. 100% NaCl, and 20 vs. 80% NaCl), droplets with higher NaCl content are predicted to form a thinner solidified layer at $t_{vfc}$. This is because droplet solidification is not only affected by $T_m$, but also by the thermophysical properties of the droplet. NaCl has a lower density (1553 kg/m$^3$), thermal conductivity (1.00 W/mK), and heat capacity (855 J/kg°C) than Na$_2$CO$_3$ (1968 kg/m$^3$, 1.72 W/mK, and 1059 J/kg°C). As the NaCl content increases from 0 to 100%, $\alpha$, the ratio of thermophysical properties of the droplet relative to that of water defined by Eqn. 34, decreases from 1.48 to 0.82. Thus, $T_i$ in Eqn. 33 becomes lower. A lower $T_i$ resulting from higher NaCl content makes the vapor film collapse sooner and at a higher droplet surface temperature given the same the minimum film boiling temperature, $T_{mf\beta}$. As a result, the droplet solidifies less, and so is more likely to explode. Simulations were also run for the other molten salt systems in Table 3. The results are in good agreement with the experimental results.

In kraft pulp mills, smelt is composed mainly of Na$_2$CO$_3$ and Na$_2$S. The effect of Na$_2$S content in a Na$_2$CO$_3$-Na$_2$S mixture on droplet solidification was examined using the model. $T_m$ and $T_f$ of the system were obtained from the Na$_2$CO$_3$-Na$_2$S phase diagram shown in Figure 5-16 [107].

![Figure 5-16: Phase diagram of the Na$_2$CO$_3$-Na$_2$S system](image-url)
Figure 5-17 shows that, similar to the Na$_2$CO$_3$-NaCl mixture, as the composition approaches the eutectic composition of 32.9% Na$_2$S, the droplets solidify less, and so are more likely to explode. The effect of Na$_2$S above the eutectic composition is more significant than below the eutectic composition because $T_m$ changes more as a function of composition.

![Graph showing solidified layer thickness as a function of Na$_2$S content](image)

**Figure 5-17: Solidified layer thickness at $t_{vfc}$ as a function of Na$_2$S in a Na$_2$CO$_3$-Na$_2$S system, $T_s = T_m + 50^\circ$C**

Previous recovery boiler explosion research [12] suggested that components such as NaCl and Na$_2$S have a sensitizing effect when added to Na$_2$CO$_3$, and so make the mixture explosive, but the reason for such an effect was not understood. This study answers that question: pure Na$_2$CO$_3$ does not explode readily due to its high $T_m$ and high values of thermophysical properties. It therefore solidifies easily before $t_{vfc}$, forming a protective solidified layer on its surface that prevents fragmentation of smelt, and thus an explosion. The addition of NaCl lowers $T_m$ and the values of thermophysical properties, resulting in less solidification at $t_{vfc}$ that increases the likelihood of an explosion.
5.4 Effect of External Disturbances

Results in Chapter 3 show that vapor film collapse can be caused by external disturbances, resulting in a smelt droplet explosion. This section presents experimental results and analysis of the effects of external disturbances, including droplet impingement onto the water surface, droplet impact onto the tank bottom, and water agitation, on smelt droplet-water interaction characteristics.

5.4.1 Droplet impingement onto the water surface

There is no fundamental study on the behavior of a liquid drop impinging onto a liquid surface with a vapor film in between. However, the behavior of a liquid drop impinging onto a hot solid surface with film boiling [108–115], and of a liquid drop onto a liquid surface without film boiling [116,117] have been studied. These studies have shown the droplet spreading and recoil behavior, to which the smelt droplet impingement onto the water surface (Figure 3-5) resembles.

Droplet impingement behavior is affected significantly by two parameters: the Weber number, $We$, which characterizes breakup of a fluid, and the interface temperature, $T_i$, which gives an indications of the stability of film boiling. $We$ is defined as

\[
We = \frac{\rho v^2 D}{\sigma}
\]

Eqn. 41

where $\rho$, $v$, $D$, and $\sigma$ are the density, velocity, diameter, and surface tension of the droplet. As $We$ increases, the disturbance caused by droplet impingement increases due to the higher kinetic energy of the droplet, creating a more intense droplet breakup. A threshold value of $We$, or critical Weber number above which the droplet will break up, is usually developed for different systems. For a droplet traveling in an inviscid fluid, the critical Weber number for droplet breakup is about 12 [118]. The critical Weber number for droplet impingement onto a solid surface is difficult to determine because considerations of surface properties are needed [113,119], and that for droplet impingement onto a liquid surface are even less understood [117].
The effect of film boiling on droplet impingement behavior has been recently studied by dropping a water droplet onto a hot solid surface [90,120,121]. It was found that the vapor film acts as a cushion to reduce the disturbance created by droplet impingement. When the vapor film becomes more stable with a higher $T_i$, a higher $We$ is required for the droplet to break up. Also, a higher $We$ can create a greater disturbance that leads to a vapor film that is easier to collapse, and thus a higher $T_{mfb}$. In this study, the effect of $We$ and $T_i$ on droplet breakup was further confirmed in a separate set of experiments by dropping water drops onto a hot stainless steel crucible. The results agree well with the studies by others, and are presented in Appendix C.

The effect of droplet impingement on smelt droplet-water interaction was examined by varying the droplet falling distance. Considering gravity and air resistance, the velocity of a free falling droplet can be calculated by

$$m \frac{dv}{dt} = \frac{1}{2} \rho_a C_D A v^2 - mg \quad \text{Eqn. 42}$$

$$v_\infty = \sqrt{\frac{2mg}{\rho_a C_D A}} \quad \text{Eqn. 43}$$

$$v(t) = -v_\infty \tanh \left( \frac{gt}{v_\infty} \right) \quad \text{Eqn. 44}$$

where $m$ is the droplet mass, $\rho_a$ is the density of air, $A$ is the projected area of the droplet, $v_\infty$ is the terminal velocity, and $C_D$ is the drag coefficient equal to 0.47 for a spherical droplet with a $Re$ of about 1500 in the experimental conditions. The distance traveled by the droplet as a function of time can then be calculated numerically. The velocity of a 7 mm diameter smelt droplet falling through air as a function of falling distance, is shown in Figure 5-18.
In this study, experiments were conducted by dropping synthetic smelt (80% Na₂CO₃-20% NaCl) droplets into water from 55, 70, and 85 cm above the water surface, to alter the droplet impingement velocity and thus $We$. Based on calculations, increasing falling distance from 55 to 85 cm, increases the droplet impingement velocity from 3.3 to 4.2 m/s, and the $We$ from 670 to 1250. The impingement velocities were also measured experimentally from consecutive frames of high speed videos, which yielded 3.1 and 4.0 m/s for a falling distance of 55 and 85 cm.

Figure 5-19 shows the experimental result of explosion probability as a function of falling distance at different $T_w$. For $T_w \leq 70^\circ C$, explosions occur immediately upon droplet impingement regardless of the falling distance. For $72^\circ C \leq T_w \leq 80^\circ C$, increasing falling distance leads to more explosions. For $T_w \geq 85^\circ C$, no explosion occurs regardless of the falling distance. The temperature range between which the falling distance has an effect corresponds to the a similar range between the lower and upper $T_{crit,w}$. Also, the explosion delay time decreases as the falling distance increases, as shown in Figure 5-20.
Figure 5-19: Explosion probability as a function of falling distance, 20% NaCl, $T_s = 800^\circ C$

Figure 5-20: Explosion delay time as a function of falling distance, 20% NaCl, $T_s = 800^\circ C$
These results suggest that for $T_w < \text{lower } T_{\text{crit},w}$, the vapor film collapses due to the disturbance of droplet impingement from a 55 cm fall, and the droplets always explode immediately on the surface. For lower $T_{\text{crit},w} < T_w < \text{upper } T_{\text{crit},w}$, increasing droplet velocity leads to a higher $We$, and a more intense disturbance of droplet impingement with a higher chance to trigger a vapor film collapse. This results in an increase in the probability of immediate explosions with short delay time. Above the upper $T_{\text{crit},w}$, the vapor film is stable, and the smelt droplets do not explode regardless of the variation of disturbance in this study.

The effect of an external disturbance such as the impingement onto the water surface can be simulated using the heat transfer model. To reflect a less stable vapor film in the model, the vapor film collapse criterion, $T_i < T_{mfb}$, was arbitrarily adjusted by increasing $T_{mfb}$. Figure 5-21 shows the predicted solidified layer thickness at $t_{vfc}$ with adjusted $T_{mfb}$ that are 0, 80, 100, and 200°C above the default value defined by Eqn. 35.

![Figure 5-21: Solidified layer thickness at $t_{vfc}$ with different adjusted $T_{mfb}$, 20% NaCl, $T_s = T_m + 50°C$](image_url)

The modeling result shows that increasing $T_{mfb}$ by 0, and 80 and 100°C, the water temperature threshold, below which the droplet is completely molten, increases from 60 to 72, and to 80°C.
This suggests that within a certain $T_w$ range, increasing the level of disturbance as a result of increasing falling distance can lead to less droplet solidification, and thus a higher likelihood of a droplet explosion. When $T_{mf_b}$ is increased by 200°C, the droplet is always molten regardless of $T_w$, suggesting that if the falling distance is high enough, a droplet explosion may always be triggered by the droplet impingement.

Smelt droplet impingement can also be used to explain why increasing $T_s$ leads to a decrease of the lower $T_{crit,w}$, as shown in Section 5.1. When $T_w$ is slightly below the lower $T_{crit,w}$, increasing $T_s$ leads to a more stable vapor film that can better withstand the disturbance of droplet impingement. This makes the droplets less likely to explode, and as a result, the lower $T_{crit,w}$ shifts to the left.

Finally, as described previously in Section 5.2, increasing NaCl leads to more immediate explosions when the droplets do explode and droplet breakup when they do not. This can also be explained by considering $We$ and $T_i$. For the typical experimental conditions, $We$ is equal to 720 for a pure Na$_2$CO$_3$ droplet, and 1570 for a pure NaCl droplet, mainly due to the difference in droplet surface tension, which is 110 mN/m for NaCl, and 220 mN/m for Na$_2$CO$_3$. In addition, increasing NaCl content leads to a lower $\alpha$ due to lower values of thermophysical properties of NaCl than Na$_2$CO$_3$, and thus a lower $T_i$. The increase of $We$ implies a stronger disturbance at the moment of droplet impingement, and the decrease of $T_i$ a less stable vapor film to cushion the droplet impingement. The combined effect leads to more immediate explosions and droplet breakup.

### 5.4.2 Droplet impact onto the tank bottom

Smelt droplet explosions were often triggered when the droplets impacted onto the tank bottom, as shown in Figure 3-12, and therefore, the effect of droplet impact onto the tank bottom on droplet explosion behavior was studied. Figure 5-22 presents the velocity profile of an 800°C smelt droplet in 85°C water, without a breakup or an explosion. The velocity was determined by measuring the distance the droplet traveled between video frames.
Upon impinging onto the water surface (t = 0 s) the droplet velocity is about 3 m/s. It decelerates rapidly, and within 40 ms reaches a terminal velocity of about 0.3 m/s as a result of a balance of forces: gravity, drag and buoyancy, acting on a droplet, with a surrounding vapor film. Without the vapor film, the terminal velocity of a droplet can be calculated as

$$u_\infty = \sqrt{\frac{4gd(\rho_s - \rho_w)}{3Cd\rho_w}}$$

Eqn. 45

where $d$ and $\rho_s$ are the diameter and density of the smelt droplet, and $\rho_w$ is the density of water. The density of a molten mixture of 80% Na$_2$CO$_3$ and 20% NaCl is 1.88 g/cm$^3$, and for the typical droplet diameter of 7 mm, the calculated terminal velocity is 0.41 m/s. The value is larger than the terminal velocity measured experimentally due to the vapor film around the droplet.

Since the droplet quickly reaches a terminal velocity, it can be assumed that the magnitude of the disturbance due to impact onto the tank bottom is independent of water depth, but the time at
which the disturbance occurs varies linearly with the water depth. To study the effect of droplet impact onto the tank bottom on smelt droplet-water interaction, smelt droplets were dropped into water of different depths: 5, 10, 15, and 20 cm; the corresponding travel times to the tank bottom are 0.18, 0.35, 0.53, and 0.70 s, respectively.

Figure 5-23 shows the explosion probability as a function of water depth in the tank. Only for $T_w > \text{lower } T_{\text{crit,w}}$, the vapor film is stable enough to allow the droplet to withstand the disturbance of droplet impingement onto the water surface. For lower $T_{\text{crit,w}} < T_w < \text{upper } T_{\text{crit,w}}$, the explosion probability increases with increasing water depth because, as the droplet falls through water and cools, the vapor film around the droplet becomes less stable and more susceptible to the disturbance of droplet impact onto the tank bottom. For $T_w > \text{upper } T_{\text{crit,w}}$, the vapor film is so stable that no explosions occur regardless of disturbance of droplet impact. This upper $T_{\text{crit,w}}$ value may be valid only for the specific magnitude of disturbance in this study, and a droplet explosion may be triggered at higher $T_w$ if a disturbance is strong enough.

![Figure 5-23: Explosion probability as a function of water depth, 20% NaCl, $T_s = 800^\circ\text{C}$](image)
5.4.3 **Water agitation**

In actual dissolving tanks, the green liquor is constantly agitated to facilitate smelt dissolution. The water flow can be affected by many parameters including size and shape of the tank, and the power output and arrangement of the agitators. In this thesis work, the effect of agitation on smelt droplet-water interaction was investigated by dropping smelt droplets into a water, with and without an agitator (115 V, 50 W, and 60 Hz) stirring the water. The explosion probability and delay time results are shown in Figure 5-24 and Figure 5-25.

![Figure 5-24: Explosion probability with and without agitation, 20% NaCl, $T_s = 800^\circ C$](image-url)

```
Figure 5-24: Explosion probability with and without agitation, 20% NaCl, $T_s = 800^\circ C$
```
The results show that agitation slightly promotes droplet explosions for lower $T_{crit,w} < T_w < upper T_{crit,w}$, and clearly reduces explosion delay time. This is due to both more disturbance and increased heat transfer rate as a result of the agitation. Similar findings were found in a cryogenic study [122], in which the film boiling around a water droplet collapsed sooner in the stirred liquid nitrogen than in the calm condition without stirring.
Chapter 6. APPLICATION TO DISSOLVING TANK

Conditions in an actual dissolving tank are much more complex than those in the laboratory experiments described in Chapter 5. The smelt droplet size distribution that falls into the dissolving tank depends on smelt flow conditions and shatter jets performance, and may range from millimeters to centimeters [5,6]. Also, the actual dissolving tank operation involves real kraft smelt and green liquor, which are more complex in composition than synthetic smelt and water. Furthermore, safe and effective dissolving tank operation requires knowledge of not only how often smelt droplets explode (explosion probability) and how long it takes for them to explode (explosion delay time), but also how smelt droplet-water interaction affects the tank violence and smelt dissolution.

6.1 Effect of Droplet Size

Smelt droplets generated in this study were about 7 mm in diameter. Due to the limitation of the apparatus and the method used, the effect of smelt droplet size was not studied experimentally, but examined using model simulations. The vapor film collapse criterion was assumed to be independent of the droplet size, and the possibility of droplet breakup as a result of increasing $We$ was not considered. The convective heat transfer coefficient in Eqn. 28 was re-evaluated, as $Re$ is a function of the droplet diameter and droplet terminal velocity; the calculation shows that $h$ is proportional to $D^{1.1}$.

Simulations were run for smelt droplets of diameter $D = 1.75, 3.5, 7, 14, \text{ and } 28 \text{ mm}$, corresponding to $1/4, 1/2, 1, 2, \text{ and } 4$ times the size of the 7 mm droplets in the experiments. To analyze the effect of droplet size on droplet solidification, two metrics were considered: the solidified layer thickness, and solidified layer thickness normalized by the droplet radius.

For the case of a single droplet explosion, the absolute thickness metric is presumably more appropriate than the normalized thickness for assessing how well the layer prevents a droplet from fragmentation caused by a vapor film collapse. Figure 6-1 shows the solidified layer thickness at $t_{vfc}$ for smelt droplets of different sizes. Increasing droplet size leads to a solidified layer that is the same or thinner depending on $T_w$, except for when the entire droplet is solidified.
This is because increasing droplet size leads to a decrease of the surface to volume ratio, and as shown by Eqn. 20, a decrease of the rate of heat conduction in the droplet near the droplet surface. Given the same rate of heat removal from the droplet surface, with a smaller rate of heat conduction within the droplet, the droplet solidifies less before its surface temperature becomes too low to sustain the vapor film.

Figure 6-1: Solidified layer thickness at $t_{vk}$ as a function of droplet size, 20% NaCl, $T_i = 800^\circ C$
Some experimental videos also show that small smelt droplets breaking away from a main droplet upon impinging onto the water surface do not explode, when the main droplet does. An example is shown Figure 6-2, with phenolphthalein added to the water to visualize the small smelt droplets. Shortly after a droplet impinges onto the water surface (t = 0 s), a large droplet lands on the tank bottom surrounded by a vapor film (t = 2.4 s), and then subsequently explodes (t = 3.7 s). Many smaller smelt droplets form as a result of droplet impingement and float back to the water surface. As soon as their vapor films collapse, these small droplets sink quickly to the tank bottom, leaving a pink trail behind.

![Figure 6-2: Droplet breakup and explosion visualized with phenolphthalein](image-url)
Figure 6-3 shows the predicted $t_{vfc}$ as a function of droplet size. For $T_w < 55^\circ C$, the vapor film always collapses at $t = 0$. For $T_w > 55^\circ C$, increasing smelt droplet size leads to longer $t_{vfc}$ due to a lower heat transfer rate resulting from two factors. The first one is a smaller surface area to volume ratio. The second one is a longer time before the temperature of the center of the droplet begins to decrease. As a result of the decrease in temperature gradient across the droplet, the rate of heat conduction within the droplet becomes lower, and droplet surface temperature decreases faster with the same heat removal rate by the surroundings.

In the case of a multi-droplet chain explosion, the normalized thickness metric is more appropriate than the absolute thickness because it takes into account the size of the droplet when a shockwave passes by to fragment the droplet. Ursic et al. suggest that the fragmentation of molten droplets in the propagation stage can be described by a modified Weber number [80]

$$
We' = \frac{\rho u^2 D^3}{E \delta^3} (1 - \mu^2)
$$

Eqn. 46
where $E$ is the Young’s modulus, $\mu$ is the Poisson’s ratio (neither of which are available for solid smelt), and $\delta$ is the crust thickness. Notice that $We’$ contains the ratio, $\frac{\delta}{D}$, suggesting that the normalized solidified layer thickness is important in the case of a multi-droplet chain explosion.

Figure 6-4 shows the normalized solidified layer thickness at $t_{vc}$ for smelt droplets of different sizes. For $T_w < 55^\circ C$, the droplets always explode, as a stable vapor film does not form. For $T_w > 55^\circ C$, increasing droplet size leads to significantly thinner thickness, and the droplets are more likely to fragment and explode.

![Graph showing normalized solidified layer thickness at $t_{vc}$ for different water temperatures and droplet diameters.](image)

**Figure 6-4: Normalized solidified layer thickness at $t_{vc}$, 20% NaCl, $T_s = 800^\circ C$**

### 6.2 Real Kraft Smelt and Green Liquor

Real kraft smelt and green liquor are very difficult to handle in the laboratory due to their corrosivity and tendency to oxidize. To confirm that the interaction of real kraft smelt with green liquor is similar to the interaction of synthetic smelt and water described in this study,
experiments were conducted with samples collected from a Canadian kraft pulp mill. The real smelt is composed of 74% Na$_2$CO$_3$, 17% Na$_2$S, and other minor components. Using the software FactSage database (by CRCT-ThermFact Inc. & GTT-Technologies), the complete freezing temperature, $T_f$, was calculated to be 510°C, and the complete melting temperature, $T_m$, 750°C. The green liquor was composed of 17.2 g/L NaOH, 137.8 g/L Na$_2$CO$_3$, and 42.4 g/L Na$_2$S, with a sulphidity of 26.4%, density of 1.22 g/ml, and boiling point of 107°C.

Figure 6-5 and Figure 6-6 show the explosion probability and explosion delay time obtained from experiments with real kraft smelt droplets and green liquor, compared with those of synthetic smelt (80% Na$_2$CO$_3$-20% NaCl) and water. The results show that real kraft smelt behaves in a similar manner as the synthetic smelt in water. Replacing water with green liquor increases the explosion probability and decreases the delay time. The droplet explosion behavior is also more stochastic with green liquor, and immediate explosions are sometimes observed even at $T_w$ close to the boiling point.

Figure 6-5: Explosion probability of synthetic (80% Na$_2$CO$_3$-20% NaCl) and real smelt droplets, $T_e = 800°C$
Figure 6-6: Delay time of synthetic (80% Na₂CO₃-20% NaCl) and real smelt droplets, $T_s = 800^\circ$C

Discussed in Section 5.2, the smelt droplet explosion behavior depends heavily on the complete melting temperature, $T_m$, and thermophysical properties of the smelt. The real smelt tested behaves in a similar manner to the synthetic smelt (80% Na₂CO₃ and 20% NaCl) because they both have similar $T_m$ (746 vs. 750°C), and similar thermophysical properties (calculated $\alpha$ of 1.34 vs. 1.37). Therefore, the solidified layer thickness before $t_{vfc}$ is similar for the synthetic smelt and real kraft smelt, resulting in similar explosion behavior.

Green liquor may promote droplet explosions by its higher boiling point and density, both of which cause the vapor film to collapse sooner: a higher boiling point increases the heat transfer rate from the droplet to the surroundings, described in Eqn. 25, and $T_{mfh}$ in Eqn. 35; a higher density lowers $\alpha$ and $T_i$ in Eqn. 34 and 33.

The effect of salt concentration on film boiling was also examined experimentally in a different configuration, by dropping Na₂CO₃ solutions and green liquor droplets on a hot stainless steel surface. It was found that for this configuration, salt concentration also has a significant effect on
disrupting film boiling, which agrees with studies by others on the effect of salt concentration on film boiling [88,123–126]. The details of this study are presented in Appendix C.

The effects of real kraft smelt and green liquor were also studied with the heat transfer model, by changing $T_m$, $T_f$, and the thermophysical properties of the droplet, and the density and boiling point of the surrounding liquid. The modeling result, as shown in Figure 6-7, is consistent with the experimental result. The model predicts that real smelt behaves in a similar manner as synthetic smelt, and replacing water with green liquor results in a thinner solidified layer that results in more droplet explosions.

![Graph showing solidified layer thickness against water temperature for synthetic smelt-water, real smelt-water, and real smelt-green liquor](image)

Figure 6-7: Solidified layer thickness of synthetic (80% Na$_2$CO$_3$-20% NaCl) and real smelt droplets
6.3 Explosion Intensity

A violent dissolving tank is characterized by loud noise and intense vibration. Therefore, in this study, smelt droplet explosion violence was examined by measuring the acoustic sound (via a microphone) and tank vibration (via a vibrometer) resulting from smelt droplet explosions.

Figure 6-8 shows the intensity data in dB as a function of delay time, obtained from 770 droplet (80% Na₂CO₃ - 20% NaCl) explosions. The result suggests that the explosion sound depends on the type of interaction. Immediate explosions with short delay time usually generate stochastic sounds; explosions with long delay time usually generate more predictable sounds.

![Figure 6-8: Acoustic sound of smelt droplet explosions as a function of delay time](image.png)
The scatter in the acoustic intensity of immediate explosions may be explained by the stochastic nature of smelt droplet impingement behavior, which was also reported by other droplet impingement studies [118,127,128]. Some droplets explode instantaneously in a coherent way, as shown in Figure 3-1, releasing the thermal energy from the whole droplet at the same time. Other droplets break up into smaller droplets upon impingement, and each then explodes individually. Figure 6-9 shows an example of a large droplet that first breaks up into smaller ones (t = 22.3 ms), and these droplets then explode on the water surface (t = 60.8 ms).

![Immediate explosion after droplet breakup](Phantom Miro321S / 1200x1920 / 1.3k)

This explosion is categorized as an immediate explosion since the droplet explodes without submerging beneath the water surface, and the explosion generates a high-pitched sound. However, with the same amount of energy, sound generated from multiple sources is less loud than that generated from a single source. Also, some small fragments that result from droplet breakup quench instead of participating in the explosion, resulting in lower sound intensity. On the contrary, in a delayed explosion, the entire droplet always explodes instantaneously when the vapor film collapses, resulting in higher and more consistent sound intensity.
Previous dissolving tank explosion research [73,74] reported louder sound at low $T_w$, which contradicts the results of this study. This may be due to the difference in frequency spectrum of the sounds of an immediate explosion and a delayed explosion. Figure 6-10 shows the spectrograms of a typical immediate explosion and a typical delayed explosion of similar intensity. The sound intensity of the immediate explosion is of higher frequency than that of the delayed explosion. Human hearing is most sensitive around 2000 to 5000 Hz [129], and thus can detect immediate explosions more easily.

Figure 6-10: Spectrograms of a typical immediate and a typical delayed explosion
Figure 6-11 shows the relationship between tank vibration, measured by a vibrometer attached to the tank wall, and explosion sound for immediate and delayed explosions. It suggests that tank vibration also depends on the type of droplet explosion and where the explosion occurs. For immediate explosions, the acoustic and vibration intensities show little correlation. For delayed explosions, the vibration intensity is generally higher than that of immediate explosions, and it increases with increasing acoustic intensity. This is because when the droplet explodes on the water surface, a significant amount of mechanical energy is released to the air and not converted to tank vibration. When the droplet explodes completely beneath the water surface, the mechanical energy transmits to the tank wall through water, causing the tank to vibrate more.
6.4 **Smelt Dissolution**

Smelt droplet-water interaction was examined from the perspective of smelt dissolution. Figure 6-12 shows smelt dissolution resulting from a droplet explosion. The smelt droplet enters water (t = 0 s), and explodes when its vapor film collapses (t = 0.34 s). At the same time, a pink cloud quickly forms, suggesting that smelt (Na₂CO₃) dissolves quickly into water.

![Figure 6-12: Smelt dissolution followed by a droplet explosion](image)

If a droplet does not explode, it will solidify into a solid particle that takes a much longer time to dissolve. In this study, the dissolution behavior of unexploded solid smelt particles was examined. Section 4.2 showed that the small droplets may break away from the main droplet upon impinging onto the water surface, resulting in a smaller mass to be dissolved. In addition,
nucleate boiling after the vapor film collapse may lead to rapid smelt dissolution. Figure 6-13 shows that after the vapor film collapses, vigorous contact between smelt and water on the solidified droplet surface leads to rapid release of a pink cloud ($t = 7.3$ s). This indicates that a significant amount of smelt dissolves in water during nucleate boiling, after which the smelt particle remains at the tank bottom and dissolve slowly.

Figure 6-13: Smelt dissolution as a result of nucleate boiling
Figure 6-14 shows a smelt particle collected from the tank bottom immediately after nucleate boiling. It has a puck-like shape with a hole in the middle, as a result of cavitation when vapor bubbles detach from the top of the molten droplet.

![Smelt particle collected from the tank bottom](image)

**Figure 6-14: Smelt particle collected from the tank bottom**

From the above observations, the entire smelt dissolution process can be divided into two stages: a pre-diffusion stage and a diffusion stage. The pre-diffusion stage is defined as the smelt droplet-water interaction from the moment of droplet impingement up to the end of nucleate boiling. The diffusion stage describes the subsequent dissolution of the smelt particle by mass diffusion.

### 6.4.1 Pre-diffusion stage

Generated from the crucible in the apparatus, the initial mass of a typical 7 mm diameter smelt droplet is about 0.4 g. The mass of the smelt particle after the pre-diffusion stage can be determined by drying and weighing the particles collected from the tank bottom. The smelt droplet-water interaction is stochastic, with respect to droplet impingement, hydrodynamics in water, vapor film collapse, and nucleate boiling, and so the particles vary in size. Figure 6-15 shows the percentage of the original mass of 149 particles remaining after the pre-diffusion stage,
and this data set has a median of 51%. The conclusion is that a significant amount of mass is either broken away or dissolved due to nucleate boiling during the pre-diffusion stage.

![Figure 6-15: Particle size distribution after the pre-diffusion stage](image)

Also note that the pre-diffusion stage not only results in smaller smelt particles, but also larger particles in certain conditions. Figure 6-16 shows that if multiple molten smelt droplets surrounded by vapor films contact each other, they may coalesce into a larger droplet.

![Figure 6-16: Coalescence of multiple smelt droplets as they contact each other](image)
6.4.2 Diffusion stage

The diffusion of a solid smelt particle was studied experimentally by dissolving smelt particles in water and Na₂CO₃ solutions, with the apparatus shown in Figure 6-17. The particle is placed inside a beaker of water or solution with a magnetic stirrer in it. A hot plate provides heat and a magnetic field to control the temperature, and to agitate the solution in the beaker. The temperature and conductivity of the solution are constantly measured by a thermometer and electrical conductivity meter (YSI Model 3200) as the particle dissolves. The relationship between the concentration and the conductivity of the solution was obtained by calibrating the conductivity meter with known Na₂CO₃ concentrations. The solution concentration measured in the experiments was used to calculate the dissolved and residual particle mass at any given time.

![Figure 6-17: Experimental apparatus for the study of smelt particle diffusion](image)

The dissolution kinetics was first examined by dissolving a pure 0.2 g Na₂CO₃ droplet in 100 ml of water at 60°C, agitated by the stirrer spinning at 220 rpm. Figure 6-18 shows the mass of the Na₂CO₃ droplet as it dissolves.
The dissolution behavior of a smelt particle was modeled, based on the idea that a diffusion layer exists between the particle surface and the bulk liquid. It can be described as

$$\frac{dm}{dt} = A \frac{D}{\delta_{dt}} (C_s - C_b)$$  \hspace{1cm} \text{Eqn. 47}

where $C_s$ is the saturation concentration, $C_b$ is the bulk concentration of the solution in the beaker, $A$ is the particle surface area, $D$ is the diffusivity and $\delta_{dt}$ is the thickness of the diffusion layer. For pure Na$_2$CO$_3$, the saturation concentration is 410 g/L for $T_w = 60^\circ$C [130], and the diffusivity is about $10^{-9}$ m$^2$/s [131]. The boundary layer thickness depends on the agitation conditions including the agitation speed, location of the particle, and geometry of the container. It is usually on the order of tens to hundreds of micrometers when a solution is well agitated, but a more accurate value needs to be determined experimentally. The model assumes that the particle is spherical, and suspended in water so that the solute can diffuse radially in all directions.

Figure 6-18: Remaining mass of a 0.2 g Na$_2$CO$_3$ particle as a function of time
Figure 6-19 shows dissolution kinetics for a 0.2 g pure Na₂CO₃ particle predicted by the diffusion layer model with a diffusion layer thickness of 50, 100, and 200 µm, compared with the experimental data. The result shows that the dissolution kinetics of a smelt particle follows the diffusion layer model with a boundary layer thickness of about 100 µm.

Figure 6-19: Remaining mass of a 0.2 g Na₂CO₃ particle as function of time, experiments vs. simulations

In actual dissolving tank operation, the concentration of Na₂CO₃ is usually maintained at about 200 g/L. To study the effect of smelt concentration on the diffusion of a smelt particle, particles made of 80% Na₂CO₃ and 20% NaCl, with a mass of 0.25 g, were placed into solutions with different Na₂CO₃ concentrations, with and without a 220 rpm agitation. The concentration of Na₂CO₃ in water was varied between 0 and 300 g/L, and the time for the smelt particle to completely dissolve was measured. The mass diffusion of a pure Na₂CO₃ particle was also modeled with a diffusion layer thickness of 50 and 100 µm. The simulated particles were assumed to have dissolved when the residual mass fell below 1% of the original mass.
Figure 6-20 presents experimental and modeling results of smelt particle diffusion. Increasing Na$_2$CO$_3$ concentration in water increases the dissolution time, and agitation reduces the amount and variability of the dissolution time. The result also shows that the diffusion layer model with $\delta_{dl} = 50$ µm predicts the results reasonably well; in general $\delta_{dl} = 100$ µm over-predicts the dissolution time. This may be because the diffusion layer model does not consider the effect of NaCl in the particle. NaCl dissolves faster in water than Na$_2$CO$_3$, creating pores in the particle, which increases the smelt surface area, and thus the dissolution rate. The diffusion layer model, with either of the diffusion layer thickness values, under-predicts the dissolution time when the Na$_2$CO$_3$ concentration is at 300 g/L. This may be because of the formation of sodium monohydrate (Na$_2$CO$_3$·H$_2$O) on the particle surface as a result of high Na$_2$CO$_3$ concentration, inhibiting the mass diffusion and resulting in a much longer dissolution time.

Figure 6-20: Dissolution time of 0.25 g particles (80% Na$_2$CO$_3$, 20% NaCl) under different concentrations and agitation conditions.
Chapter 7. CONCLUSIONS

7.1 Summary of Results

This thesis presents a fundamental study of smelt droplet-water interaction in the dissolving tank of a kraft recovery boiler. The interaction behavior was, for the first time, visualized with high speed imaging, and observations confirm that smelt droplet explosions are in many ways similar to other small-scale vapor explosion phenomena. The effects of various dissolving tank parameters on smelt droplet explosion characteristics were investigated both by conducting experiments with synthetic smelt (a Na$_2$CO$_3$-NaCl mixture) and by simulations with a 1-D heat transfer model. Real kraft smelt and green liquor were also tested to assess the applicability of the results of this study to actual dissolving tank conditions. Finally, the role of smelt droplet explosions on dissolving tank safety and efficiency was analyzed based on smelt droplet explosion intensity and dissolution rate. The main conclusions of this study are the following:

- Whether a smelt droplet explodes depends on the thickness of the solidified layer formed on the smelt droplet surface when the vapor film collapses.
- Increasing water temperature decreases the likelihood of a droplet explosion, and increases the explosion delay time.
- Smelt temperature has less influence on the likelihood of a droplet explosion, but increasing smelt temperature increases the explosion delay time.
- As the smelt composition approaches the eutectic composition with a lower complete melting temperature, smelt droplets become more likely to explode.
- With similar complete melting temperature, smelt droplets with lower values of thermophysical properties (thermal conductivity, density, and heat capacity) are more likely to explode.
- Increasing droplet size increases the likelihood of a droplet explosion.
- Between the lower and upper critical water temperatures, droplet explosions are affected by external disturbances including droplet impingement onto the water surface, droplet impact onto the tank bottom, and water agitation.
- Real kraft smelt behaves in a similar manner as synthetic smelt made of 80% Na$_2$CO$_3$ and 20% NaCl. Replacing water with green liquor promotes droplet explosions.
• The explosion sounds and tank vibration depend on the type of droplet explosion: immediate explosions generate less sound and tank vibration than delayed explosions.

• Exploded smelt droplets dissolve in water quickly, whereas unexploded droplets take a much longer time to dissolve.

### 7.2 Implications

Actual dissolving tank operation is much more complex than the conditions in this laboratory study. For example, water temperature in the dissolving tank is not uniform; smelt composition is much more complex than a binary salt mixture; the falling distance in a dissolving tank is 2-3 meters, resulting in a much higher droplet impingement velocity; agitation characteristics in the dissolving tank are not well monitored; and smelt droplet size distribution are affected by the shatter jets performance and breakup and coalescence behavior of the smelt droplets in water. Therefore, the data obtained from this study should be interpreted carefully. Nonetheless, this study provides fundamental information of smelt droplet-water interaction that can be used to develop improved guidelines for safe and effective dissolving tank operation, characterized by rapid smelt dissolution, minimal dissolving tank violence, and prevention of a dissolving tank explosion accident.

From the smelt dissolution point of view, smelt droplet explosions can significantly promote smelt dissolution. The retention time in the dissolving tank is on the order of 30 minutes, which is a similar time frame as the dissolution time of the smelt particles tested in this study. This suggests that smelt dissolution could become an issue when the tank is not operated under normal conditions, including larger droplet size, high local smelt concentration, or agitator failures.

From the dissolving tank safety point of view, a large-scale vapor explosion should be avoided. Due to the large number of droplets falling into the dissolving tank every second, and the complexity of dissolving tank operation, it is not plausible to prevent all droplets from exploding. Therefore, instead of preventing droplet explosions, dissolving tank safety may be best promoted by controlling the smelt droplet explosion behavior.
Although smelt droplet explosions cause some tank noise and vibration, it is likely that dissolving tank explosion accidents are the result of multi-droplet chain explosions of large amount of smelt in the tank. Therefore, dissolving tank operation should focus on avoiding the accumulation of molten smelt that can potentially be triggered to explode. This study shows that immediate explosions generate less sound and tank vibration than delayed explosions, and more importantly, they have a shorter delay time that ensures a smaller amount of molten smelt in the tank.

Therefore, dissolving tank operation should aim to promote droplet explosions and reduce explosion delay time. The following are operational strategies that could be considered:

- Keep water temperature low and away from the boiling point;
- Keep the smelt temperature low, but not so low that allows jelly-roll smelt formation;
- Keep the smelt composition close to the eutectic composition, to prevent droplet solidification;
- Orient the steam shatter jet downward to add momentum to the smelt droplet and increase the droplet impingement velocity;
- Keep the smelt concentration in green liquor high to promote droplet explosions with shorter delay time;
- Promote tank agitation for both safety and dissolution purposes;
- Ensure proper smelt shattering to distribute the droplets over a large area of the tank to minimize triggered explosions.
7.3 Recommendations for Future Work

This thesis has examined the interaction of a single smelt droplet and water. To take this study a step further, the following recommendations are made for future work:

- Since dissolving tank noise and vibration are the only parameters that can be detected from outside of the tank, the effect of multi-droplet explosions on explosion sound and vibration intensity should be investigated, as the basis of a monitoring system for dissolving tank operation.

- The heat transfer model developed in this study should be improved by coupling with knowledge of mechanical properties of smelt, to quantitatively predict the extent of droplet solidification that can prevent a droplet explosion.

- The results and insights presented in this thesis should be applied to the interaction between water and the smelt pool in the recovery boiler, to improve recovery boiler safety.
References


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Appendix A

Selected Molten Salt Droplet-Water Interactions

This section presents selected video images of salt droplet-water interaction. The salt composition and water temperature is specified, and the salt temperature is 50°C above its complete melting temperature, unless stated otherwise. Other experimental conditions are the same as the default conditions stated in Chapter 5.

Pure Na₂CO₃, $T_w = 40°C$

Figure A-1 shows that pure Na₂CO₃ droplet breakup into large fragments, which then quench in water.

![Figure A-1: Breakup of pure Na₂CO₃ droplet, $T_w = 40°C$](image)
Pure NaCl, $T_w = 55^\circ$C

Figure A-2 shows that the droplet breaks up into fragments upon impinging onto the water surface. As compared to the case of a Na$_2$CO$_3$ droplet, the fragment dissolves in water much faster, as NaCl has higher solubility in water than Na$_2$CO$_3$.

Figure A-2: Behavior of a pure NaCl droplet in water at 50°C
Pure Li$_2$CO$_3$, $T_w = 80^\circ$C

Figure A-3 shows a pure Li$_2$CO$_3$ that was droplet dropped into water at 80°C and did not explode. The vapor film around a Li$_2$CO$_3$ droplet generally lasts a longer period of time before it collapses, than that around a 80% Na$_2$CO$_3$ and 20% droplet, due to high values of thermophysical properties.

Figure A-3: Behavior of a pure Li$_2$CO$_3$ droplet, $T_w = 80^\circ$C
Pure Na$_2$SO$_4$, $T_w = 80°C$

Figure A-4 shows a pure Na$_2$SO$_4$ droplet in water at 80°C, that did not explode.
Pure NaCl, $T_w = 85^\circ$C

Figure A-5 shows a pure NaCl droplet in water at 85°C, that did not explode. Due to the low density of NaCl as compared to that of Na$_2$CO$_3$, the lifting force due to film boiling may overcome gravity, causing the droplet to float to the water surface ($t = 6$ s). The droplet falls to the tank bottom after the vapor film collapses.

Figure A-5: Behavior of a pure NaCl droplet, $T_w = 80^\circ$C
Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$, $T_w = 90^\circ$C, $T_s = 500^\circ$C

Figure A-6 shows a 500°C Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ droplet at its eutectic composition that is dropped into water at 85°C. Due to the low complete melting temperature, the droplet explodes even though it is hot. The droplet exploded immediately due to the absence of a stable vapor film as a result of the low salt temperature.

Figure A-6: Behavior of Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ droplet, $T_w = 90^\circ$C, $T_s = 500^\circ$C
Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$, $T_w = 95^\circ$C, $T_s = 725^\circ$C

Figure A-7 shows a 900°C Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ droplet at its eutectic composition that is dropped into water at 95°C. Due to the low complete melting temperature, the droplet explodes even though the water is hot. This was a delayed explosion due to the presence of a stable vapor film, as a result of the high salt temperature.

Figure A-7: Behavior of a Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ droplet, $T_w = 95^\circ$C, $T_s = 725^\circ$C
NaCl-CaCl$_2$, $T_w = 90^\circ$C, $T_s = 590^\circ$C

Figure A-8 shows an immediate explosion of a 590°C NaCl-CaCl$_2$ droplet in water at 90°C.

Figure A-8: Behavior of a NaCl-CaCl$_2$ droplet, $T_w = 90^\circ$C, $T_s = 590^\circ$C
**NaCl-CaCl₂, \( T_w = 95°C, T_s = 900°C \)**

Figure A-9 shows the delayed explosion of a 900°C NaCl-CaCl₂ droplet at its eutectic composition dropped into water at 95°C.

![Figure A-9: Behavior of a NaCl-CaCl₂ droplet, \( T_w = 95°C, T_s = 900°C \)](image)
Real kraft Smelt, $T_w = 78^\circ$C

Figure A-10 shows a real kraft smelt droplet dropped into water at $78^\circ$C. Similar to the behavior of a synthetic smelt droplet with 80% $\text{Na}_2\text{CO}_3$ and 20% $\text{NaCl}$, the real smelt droplet explodes after a period of time. Due to the amount of char in the real kraft smelt, a black cloud appears after the droplet explodes.

Figure A-10: Behavior of a real kraft smelt droplet that undergoes a delayed explosion, $T_w = 78^\circ$C
Real kraft smelt, $T_w = 85^\circ C$

Figure A-11 shows a real kraft smelt droplet in water at 85°C that did not explode. Due to the amount of char in the real kraft smelt, a black cloud appears as the droplet begins to dissolves in water after the vapor film collapse.

Figure A-11: Behavior of real kraft smelt droplet that undergoes no explosion, $T_w = 85^\circ C$
Solid Smelt, 80% Na₂CO₃-20% NaCl, $T_w = 60^\circ$C, $T_s = 600^\circ$C

2 grams of synthetic smelt composed of 80% Na₂CO₃ and 20% NaCl was placed in an alumina crucible, melted in an oven, re-solidified, and heated up to 600°C. The hot solid smelt particle is then dropped into water at 60°C, as shown in Figure A-12. The solid smelt quenches in water without any violent interaction.

Figure A-12: Interaction between hot solid smelt and water, $T_w = 60^\circ$C, $T_s = 600^\circ$C
Figure B-1 shows how bubble dynamics of a droplet explosion are analyzed, using the explosion in Figure 3-2 as an example, processed in ImageJ. Each image is first converted to a binary image, with a threshold automatically determined by ImageJ based on its analysis of the histogram. The smaller droplets that break away from the main droplet as a result of droplet impingement are excluded. The black pixels, which indicate the projected area of the vapor bubble, are counted. The equivalent diameter of the bubble is obtained by converting the ragged area into a spherical one, which is then normalized by the initial droplet diameter to calculate a normalized equivalent diameter, $\frac{D_B}{D_o}$.

Figure B-1: Image processing for bubble dynamics analysis
The dynamics of smelt fragments are examined quantitatively in the same way, but from infrared images. The spreading of the smelt fragments, also quantified by the equivalent diameter normalized by the initial diameter of the droplet, $\frac{D_f}{D_0}$, is obtained from the total area of the pixels above a certain threshold of brightness. In the case of the images shown in Figure 3-8, 30 was chosen to be the threshold below which the thermal energy is too low to be differentiated from the background. In addition to the area occupied by the fragments, the distribution of thermal energy is also quantified by a combination of the area occupied by smelt and the level of brightness of the pixels in the infrared images. The normalized weighted intensity, $\frac{I_f}{I_o}$, is calculated by summing the brightness value of each pixel in the explosion area, normalized by the initial weighted brightness of the smelt droplet.
Appendix C

Film Boiling of Liquid Drops on a Stainless Steel Crucible

Introduction

Film boiling plays an important role in smelt droplet-water interaction. Since it was difficult to examine film boiling between water and a hot smelt droplet surface via the experimental apparatus described in Chapter 2, a systematic study of film boiling of a water droplet on a hot stainless steel surface was conducted. The analogy of the smelt droplet-water system and the water droplet-hot surface system is shown in Figure C-1. In this study, experiments were conducted by dropping a droplet of water or of an aqueous solution onto a hot stainless steel substrate at different conditions.

Figure C-1: Comparison of the smelt droplet-water and the water droplet-hot surface systems
Experimental Apparatus

The apparatus is shown in Figure C-2. The stainless steel crucible is slightly deeper in the center so that the water droplet can be contained. The crucible was placed on a hot plate to be controlled at a constant temperature up to 420°C. A thermocouple was inserted into a hole at the bottom of the crucible to monitor its temperature. A water bath was used to control the temperature of the solution for the experiments. A camera (Canon Rebel T3i/ EOS 600D) was used to document the behavior of the droplet as it contacted the crucible. Variables examined include the crucible temperature, droplet temperature, droplet falling distance, and salt concentration in water. For each experimental condition, the experiments were repeated three times.

Figure C-2: Experimental apparatus for vapor film stability study
Effect of Surface Temperature, Water Temperature, and Concentration

The typical interaction behavior between a water droplet at room temperature and a hot stainless steel surface at different surface temperatures is shown in Figure C-3. When the surface temperature is low, at 150°C, the droplet undergoes nucleate boiling after contacting the surface. When the surface temperature is at 220°C, the water droplet interact violently with the hot surface, and vanishes instantly; when the surface temperature is very high, at 300°C, the droplet recovers to its original spherical shape soon after landing onto the surface, and the droplet can last for a few seconds due to the vapor film that is more stable.

Figure C-3: Water drop behavior at different hot crucible temperatures
The droplet life time, which is the time it takes for the droplet to completely vaporize, is determined from video recordings. The droplet life times of 30, 55, and 80°C water droplets falling from 2 cm above the surface are shown in Figure C-4, and the results agree with a typical boiling curve. When the hot surface temperature is just above the boiling point of water, nucleate boiling of the droplet is observed. When the surface becomes sufficiently hot, a vapor film forms between the water droplet and surface, and this inhibits the heat transfer rate, leading to a longer droplet life time. In between, transition boiling is observed, where the droplet reacts violently with the hot surface. The results also show the stochastic nature of the boiling behavior, especially in the transition boiling regime.

![Figure C-4: Droplet life time as a function of hot surface temperature and water droplet temperature](image)

While the temperature of the surface has a great effect on the boiling behavior, the effect of water droplet temperature is small. This is because the amount of water is small, and the water droplet quickly heats to the boiling point upon landing on the hot surface.
The effect of salt concentration on film boiling was also studied by dropping Na$_2$CO$_3$ solution and green liquor onto the hot stainless steel surface. As shown in Figure C-5, the addition of Na$_2$CO$_3$ into the water droplet makes film boiling more difficult, because film boiling occurs at a higher surface temperature, and so the droplet life time becomes shorter.

![Figure C-5: Droplet life time of different salt concentrations](image-url)
Effect of Falling Distance and Droplet Impingement

To investigate the effect of falling distance on the droplet breakup behavior in the presence of a vapor film, water droplets at 30°C were dropped onto the stainless steel surface at 220 and 410°C, from 15 cm above, as shown in Figure C-6. Similar to the behavior in Figure C-3, the droplet interacts violently with the surface when the surface temperature is 220°C. However, when surface temperature is higher, increasing the falling distance leads to the breakup of the water droplet upon impingement.

Figure C-6: Droplet impingement behavior from 15 cm above the crucible
Effect of External Disturbance

The effect of a disturbance on vapor film boiling was also examined. A stable vapor film was established between a water pool and hot stainless steel surface. As shown in Figure C-7, the addition of a small drop of water to the water pool introduces a small disturbance to the system, collapsing the vapor film. This leads to direct contact between the water and the hot stainless steel surface, resulting in a violent interaction.

Figure C-7: Vapor film collapse triggered by a disturbance
Experiments with Smelt Surface

Experiments were also conducted by dropping a water droplet onto a synthetic smelt surface. In this set of experiments, a mixture of 80% Na₂CO₃ and 20% NaCl powder was placed on the stainless steel crucible, which was heated in a furnace up to 1000°C. After the mixture had reached a desired temperature, the crucible was taken out of the furnace, and a water droplet was dropped onto the surface of the molten or solid smelt. The recorded video showed that film boiling can occur both on the molten and solid surfaces, as long as the surface temperature is high enough and the placement of the droplet is gentle enough. Also, when the surface is completely molten, and the temperature of the surface is relatively low, violent splashing occurs. These results show that the solidification of smelt is critical in preventing a violent interaction.

Summary

The conclusions from this film boiling study include the following:

- When dropping a water droplet onto a stainless steel surface, the boiling behavior is mainly a function of the hot surface temperature;
- Increasing salt concentration in a water droplet increases the temperature at which film boiling can occur, and decreases the droplet lifetime;
- Film boiling can also occur on both solid and molten smelt surfaces;
- If the temperature of a molten smelt surface is not high enough to create film boiling, a violent splash will occur;
- Vapor film collapse can be triggered by an external disturbance.