AN EXPERIMENTAL STUDY OF SMELT-WATER INTERACTION IN THE RECOVERY BOILER DISSOLVING TANK

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ABSTRACT

A laboratory apparatus was constructed to simulate the operating conditions of recovery boiler smelt dissolving tanks and used to systematically study the interaction between molten smelt droplets and water. Experiments were performed on synthetic smelt made of 80 wt% Na_2CO_3 and 20 wt% $NaCl$ at 800^oC, 900^oC and 1000^oC. The results show that upon contact with water, some smelt droplets explode immediately and break into small pieces, some require a delay time to explode and others solidify without exploding. The probability of explosion depends strongly on water temperature and to some extent, smelt temperature. At a given smelt temperature, there exists a water temperature range below which explosion always occurs (the lower critical water temperature) and above which there is no explosion (the upper critical water temperature). The lower critical water temperature decreases with increasing smelt temperature, while the upper critical water temperature remains the same at 82^oC in all cases. Up to this upper critical water temperature, both the explosion delay time and explosion intensity increase with increasing water temperature. The data was used to construct a Smelt-Water Interaction Temperature (SWIT) diagram that can predict if a molten synthetic smelt droplet will explode in water at different smelt and water temperatures.

INTRODUCTION

In kraft pulp mills, black liquor is burned in a recovery boiler to recover the spent pulping chemicals and to produce steam and electrical power for use in various processes. The combustion results in the formation of molten smelt at the bottom of the boiler that consists of mainly Na_2CO_3 and Na_2S, with a small amount of Na_2SO_4, $NaCl$ and potassium salts. Molten smelt flows out of the boiler at 800^oC to 850^oC through several smelt spouts at a flow rate of 0.7 to 1.3 L/s per spout. As the smelt stream emerges from the spout trough, it is shattered by a steam jet into small, discrete droplets before falling into the dissolving tank underneath (Figure 1). The droplets interact with water or weak wash in the dissolving tank and dissolve. The resulting solution (green liquor) is subsequently causticized with lime to produce white liquor for reuse in the pulping process.
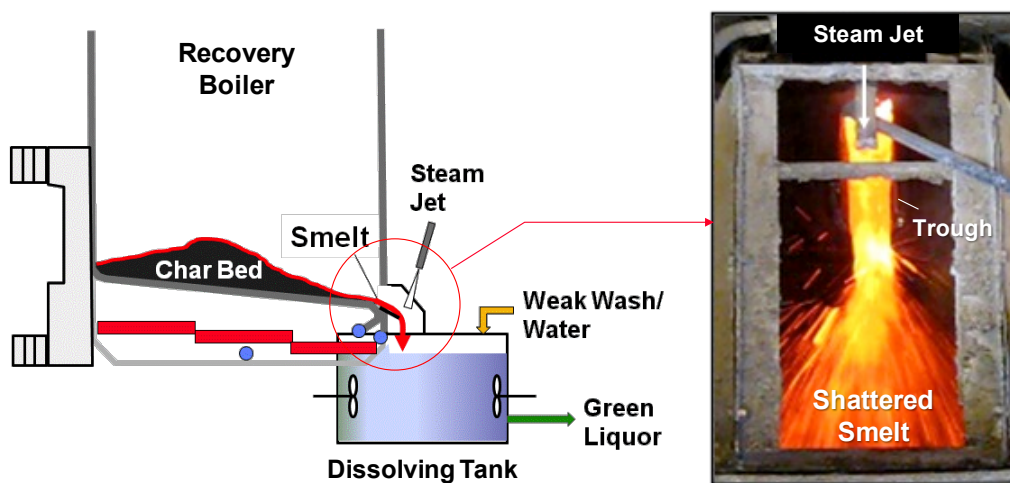

Figure 1. *Molten smelt stream shattered by a steam jet*

While smelt-water interaction is violent and often dangerous, the process is necessary for effective smelt dissolution. Dissolving tank safety has therefore been a priority in recovery boiler operation [1]. Dissolving tanks constantly rumble with loud noise, which at times causes tremors of the ground and buildings nearby. As with the commonly known smelt-water explosions that occur inside the boiler when a large amount of water from leaked tubes comes in contact with a pool of molten smelt in the char bed [2], explosions can also occur in the dissolving tank [3-6], particularly when molten smelt is inadequately shattered by the steam jet, allowing large lumps of molten smelt to pour into the dissolving tank and interact with water. The problem is worse when there is a surge in smelt flow (or run-off). There have been 33 incidents of dissolving tank explosions reported in North America in the past 40 years [3], causing personnel injury, equipment damage and unscheduled boiler shutdowns. Undoubtedly many more dissolving tank explosions have occurred that have not been reported.

Shick and Grace [4] conducted a comprehensive literature review on explosions involving contact of two liquids. They concluded that smelt-water explosions involve basically the same vapor explosion mechanism as other liquid-liquid systems where the high heat from one liquid causes the other liquid to vaporize rapidly. Vapor explosions are known to occur in other industries including the nuclear industry, where during an accident hot fuel may come in contact with water [7]; the metal industry where molten metal comes into contact with water [8], and the liquid natural gas transportation industry where water is in contact with cold liquefied natural gas [9]. Molten volcanic lava flowing into the ocean is another example of vapor explosion [10]. The smelt-water system differs from many other liquid-liquid systems in that the components in smelt are highly soluble in hot water. Although this may not change the basic mechanism, it does imply a possible effect of smelt and green liquor properties on dissolving tank explosions [4].

There have been only two studies on the causes of dissolving tank explosions published to date and they both were in the mid-1950s. Sallack [5] conducted a series of laboratory experiments to investigate explosions in the soda smelt dissolving operation by pouring molten synthetic smelt made of mixtures of Na_2CO_3 and NaCl, and mixtures of Na_2CO_3 and NaOH into steel pans containing water, and observing how they interacted. He concluded that the composition of the smelt (i.e. the NaCl content), the temperature of the water, the composition of the dissolving liquor, and the efficiency of the shatter sprays were important factors influencing explosions in the smelt dissolving tank, while the smelt temperature had no effect on explosions. Nelson and Kennedy [6] performed similar laboratory experiments using both synthetic soda and kraft smelts. They confirmed Sallack's findings and reported further that kraft smelt with a high sulphidity was more violent than soda smelt or kraft smelt with a low sulphidity, and that the higher the smelt reduction efficiency the more explosive was the smelt.

While these above studies provided good insights into the causes of dissolving tank explosions, the investigations were not systematically carried out. The experiment scale was large; over 100 grams of molten smelt was poured into green liquor manually. The extent of explosion (or explosion intensity) in each experiment was reported as "dud", "mild", "moderately violent", "violent" or "very violent", arbitrarily determined based on visual observations and noise generated during the experiment. The data obtained were not sufficient to draw any quantitative conclusions. Furthermore, since there was no sufficient information on thermal properties of molten smelt (i.e. melting temperatures, viscosity, surface tension, etc.) at the time, it was difficult for the researchers to properly interpret their results. Furthermore, the theories on these types of vapor explosions were in a very early stage when the experiments were done, which affected how these researchers interpreted their data.

The objective of this research project was to construct a laboratory apparatus to simulate the operating conditions of recovery boiler smelt dissolving tanks and use it to systematically study the interaction between molten smelt droplets and water under various operating conditions, and to quantify the effects of each condition. This paper describes the experimental setup and procedures, and the results of experiments performed to date using a synthetic smelt mixture of 80 wt% Na_2CO_3 and 20 wt% NaCl.

EXPERIMENTAL SETUP AND PROCEDURES

The Apparatus

Figure 2a shows the experimental apparatus used in this study. It consists of three main components: i) a smelt droplet generator, ii) a water control system, and iii) a data acquisition system. The entire apparatus is enclosed in an isolation booth to ensure the safety of the researchers in an unlikely event of catastrophic explosion.

The smelt droplet generator is a tubular electrical furnace which houses a 220mm long cast alumina (Al_2O_3) tube crucible with a 30mm ID open top end and a 3mm ID hole at the tapered bottom end (Figure 2b). A cast Al_2O_3 rod, 10mm in diameter, is inserted vertically into the crucible from the top, to seal the hole at the tapered bottom end. Pulverized smelt is fed into the crucible from the top and piles up on the bottom in the space between the crucible and the rod. As the crucible is heated up in the furnace to a desired temperature above the complete melting temperature of the sample, molten smelt begins to seep out from the crucible through the rod seal, forming a molten droplet at the crucible tip. As the droplet grows larger, its weight continues to increase until it reaches a point where gravity overcomes the surface tension. The droplet then breaks away from the crucible tip and falls into the water tank below, while allowing a new droplet to form at the crucible tip. By adjusting the position of the rod, the amount and temperature of the smelt sample in the crucible, and the pressure in the crucible, it is possible to produce molten smelt droplets of a desired size and flow rate, one droplet at a time. Fresh smelt is added to the crucible from the top as required to generate a constant flow of molten droplets. The molten smelt temperature can be measured with a thermocouple (T1), but this is done only occasionally due to the high corrosivity of the molten smelt. However, a correlation between molten smelt temperature and furnace temperature was pre-established so that it can be used to estimate molten smelt temperature based on the furnace temperature.
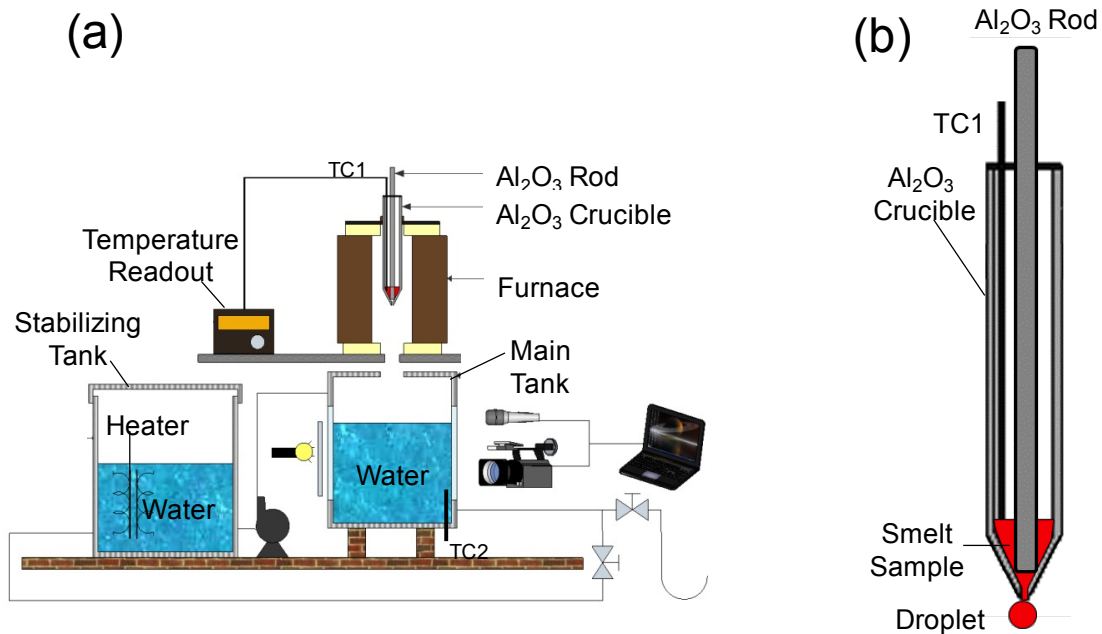

Figure 2: *Experimental apparatus for smelt-water interaction*

The water control system consists of two water tanks. The main tank, located directly under the furnace, is a 22-liter rectangular container (250mm x 250mm x 350mm) made of stainless steel sheets on the side walls and transparent polycarbonate sheets on the front and back walls so that the behavior of smelt droplets can be observed. The water is heated in a larger 40-liter stabilizing tank using a temperature-controlled coiled heater. A pump is used to circulate the water between the two tanks. The water level in the main tank is controlled by adjusting the water inlet and outlet valves, and its temperature is constantly monitored using a thermocouple.

The data acquisition system consists of a video camera, a microphone, two temperature indicators and a laptop computer. The video camera (25 frames per second) is placed in front of the tank to record the behavior of the smelt droplet as it enters the water tank and interacts with water. Two 120-watt light bulbs with a light diffuser are mounted vertically behind the back wall to illuminate the experiment. The microphone is placed near the tank wall to record the sound of the smelt-water interaction. The temperature indicators are used to monitor the molten smelt and water temperatures.

Procedures

Synthetic smelt was used in this study. It was prepared by melting a well-mixed mixture of 80 wt% Na_2CO_3 and 20 wt% NaCl directly in the droplet generator. This composition was chosen mainly because the sample would be completely molten and fluid in the crucible at the temperatures examined, but also because it has a complete melting temperature of 750^oC, which is close to that of the typical kraft smelt from softwood mills with a liquor sulphidity of about 33% on TTA (total titratable alkali), or from hardwood mills with a sulphidity of about 25% on TTA. The size of the droplets generated in each experiment was measured by comparing their video images against the nearby reference, a ruler taped on the front window of the tank.

Experiments were carried out at three smelt temperatures (T_s): 800^oC, 900^oC and 1000^oC. The water level in the tank was set at 120 mm, and the water temperature (T_w) was varied between 25^oC and 100^oC. For each condition, the experiment was repeated over 30 times. Median values and median absolute deviations were used to quantify the variability of the data, as they are more robust to outliers that resulted from the randomness in smelt-water interaction behavior.

RESULTS AND DISCUSSION

Droplet Size

At the given experimental conditions, the droplet size was found to vary only slightly from experiment to experiment. An example of the size distribution for 41 droplets produced at 800^oC is shown in Figure 3. The diameter varied from 6.5 to 9 mm, with the majority between 7.5 and 8 mm.
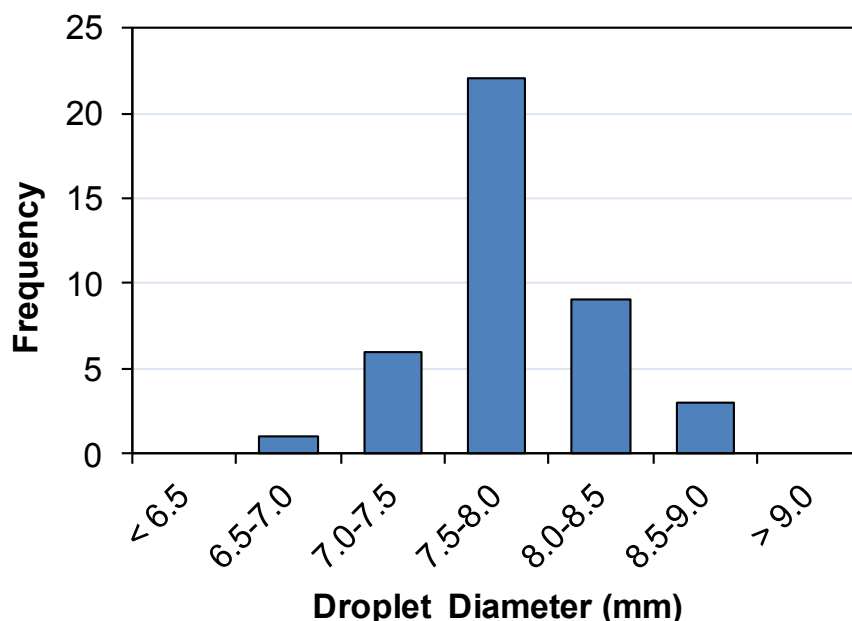

Figure 3: *Size Distribution of Synthetic Smelt Droplets Produced at 800^oC (n=41)*

Types of Interaction

Video images of molten smelt droplets as they entered the water tank and contacted with water showed three clear types of interaction. As shown in Figure 4, some droplets broke into small pieces upon contact with water and exploded immediately at the water surface (Immediate Explosion), some sank and then exploded with a short delay either in the middle of the water tank or after settling on the bottom floor (Delayed Explosion), while others sank to the bottom of the tank and solidified without exploding (No Explosion).

The type of interaction that a molten smelt droplet may follow depends on both smelt temperature (T_s) and water temperature (T_w). In order to quantify the effects of T_s and T_w on interaction, the following three characteristics are used: explosion probability, explosion delay time, and explosion intensity. It was also observed that vapor bubbles constantly formed, and detached away from the smelt droplet (Delayed Explosion and No explosion).
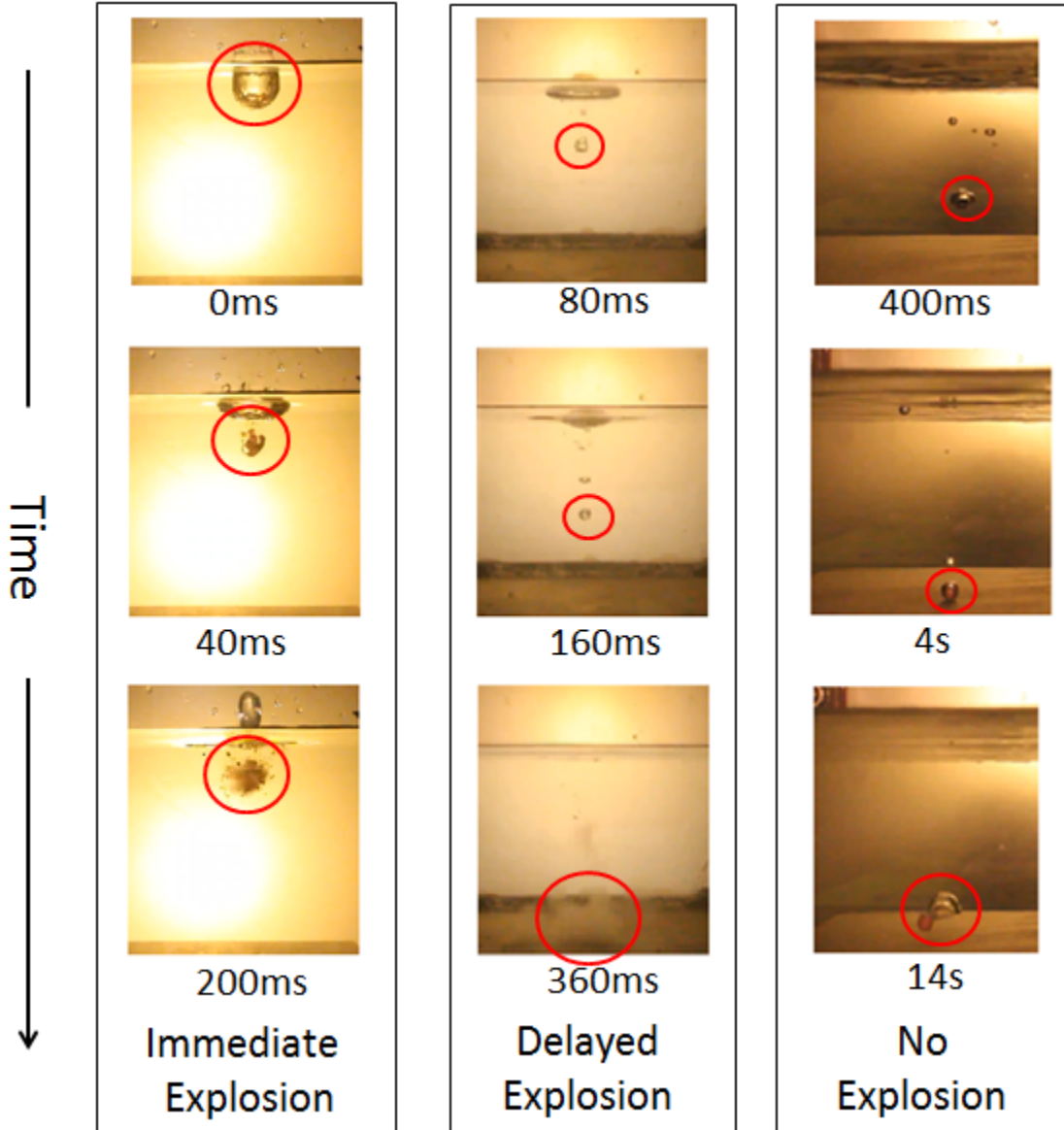

Figure 4: *Three distinct types of smelt-water interaction with the droplet circled*

Explosion Probability

For each experimental condition, the probability of explosion was calculated by dividing the number of droplets that exploded by the total number of droplets tested (about 30). As shown in Figure 5, at a given T_s, there appears to be a water temperature range below which the explosion probability was 100% (i.e. always exploded) and above which the explosion probability was 0% (i.e. did not explode at all). The low end of this temperature range is referred to as the lower critical water temperature, $T_{crit,w}$, and the high end as the upper critical water temperature ($T_{crit,w}$). The

results clearly show that the lower $T_{crit,w}$ decreased with increasing smelt temperature: 72°C for T_S= 800°C, 65°C for T_S= 900°C and 50°C for T_S=1000°C. The upper $T_{crit,w}$, on the other hand, remained the same at 82°C in all cases.

Figure 5 also shows the explosion probability for an actual kraft smelt at 800°C. The results were almost the same as those obtained for synthetic smelt at 900°C with its lower $T_{crit,w}$ at 65°C and upper $T_{crit,w}$, at 82°C. At present, it is not known why this lower $T_{crit,w}$ was lower than that of the synthetic smelt at 800°C.
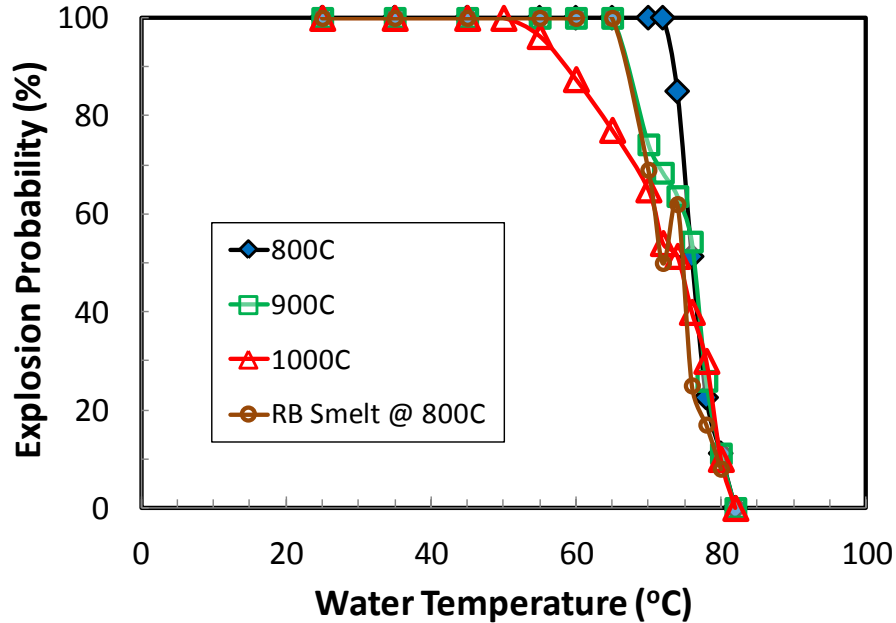
Figure 5: *Explosion probability of molten smelt at different water and smelt temperatures (each data point is based on about 30 experiments)*

The results are consistent with those of Sallack [5] and Nelson [6], although the data obtained in this study are more quantitative, showing that smelt temperature did have an effect. It is also worth noting that the upper $T_{crit,w}$ of 82°C found for all cases in this study is also the same as that of Sallack's [5].

Using the data in Figure 5, a Smelt-Water Interaction Temperature (SWIT) diagram was constructed to show the combined effect of T_S and T_W on the explosion probability of molten synthetic smelt droplets (Figure 6). The diagram predicts how molten smelt and water interact at different temperatures. Below the lower $T_{crit,w}$ curve, explosion will occur; above the upper $T_{crit,w}$ line of 82°C, explosion will not occur; between the lower and upper critical water temperatures, an explosion may or may not occur. The left boundary of this SWIT diagram is conveniently set at the freezing temperature of the synthetic smelt, 750°C, although it is likely to be at a lower temperature due to either supercooling or the interaction between water and partially frozen smelt. This SWIT diagram resembles the diagram created by Dullforce et al. [7], based on their study of the interaction between molten Sn (tin) droplets in water.

Explosion Delay Time

The explosion delay time of a molten smelt droplet is defined as the time it takes for the droplet to explode after contacting water. In this study, the delay time was obtained by counting the number of frames recorded by the video camera starting from when the smelt droplet first touched the water to when it exploded. The exact explosion time was determined with the help of the acoustic spectrum registered by the camera. An example of this is shown in Figure 7. The droplet appeared in the camera window at Frame 415, struck the water surface at Frame 416 and exploded at Frame 437, as also confirmed by the sound spectrum below. Since the droplet was in water for 21 frames and the video was recorded at 25 frames per second, the explosion delay time in this case was estimated to be 0.84 seconds.
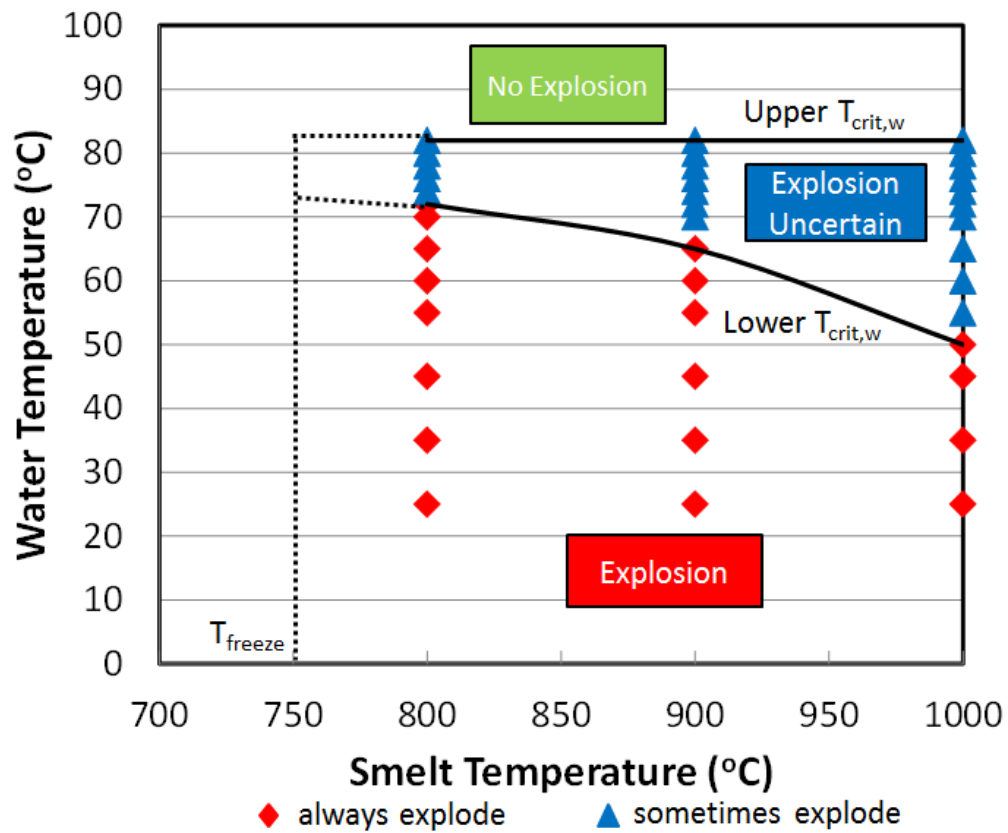
Figure 6: *Smelt-Water Interaction Temperature (SWIT) diagram (80% Na$_2$CO$_3$ and 20% NaCl)*
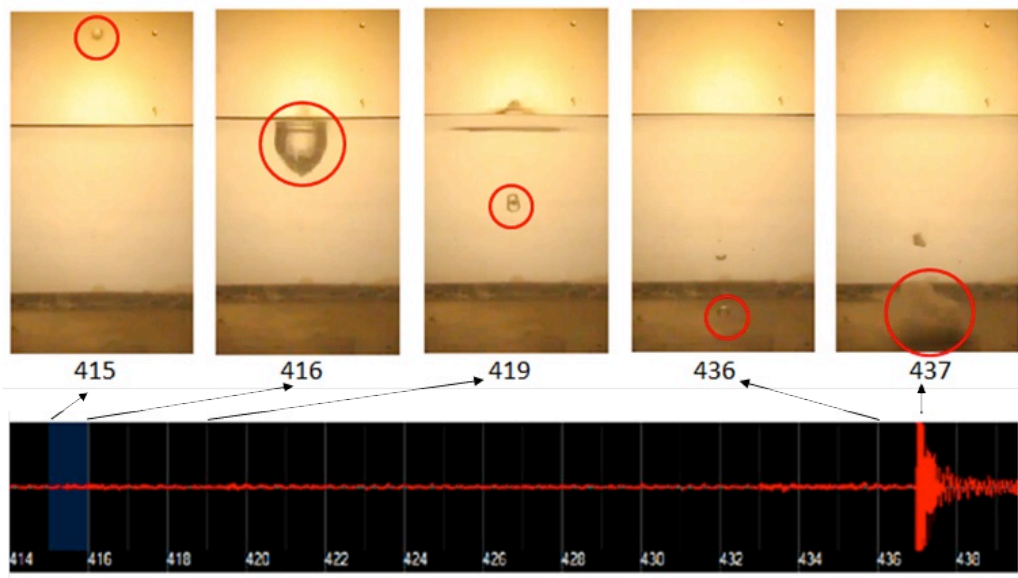

Figure 7: Smelt droplet explosion images (upper) and corresponding audio waveform (lower)

Figure 8 shows the droplet explosion delay time at different smelt and water temperatures. Higher T_s resulted in a longer delay time. At a given T_s, the delay time increased with an increase in T_w, up to the upper $T_{crit,w}$ of 82°C when explosion could no longer occur (or the delay time was "indefinitely" long). The data seemed to deviate more as the delay time increased, reflecting the randomness of the smelt explosion behavior or the low explosion probability.
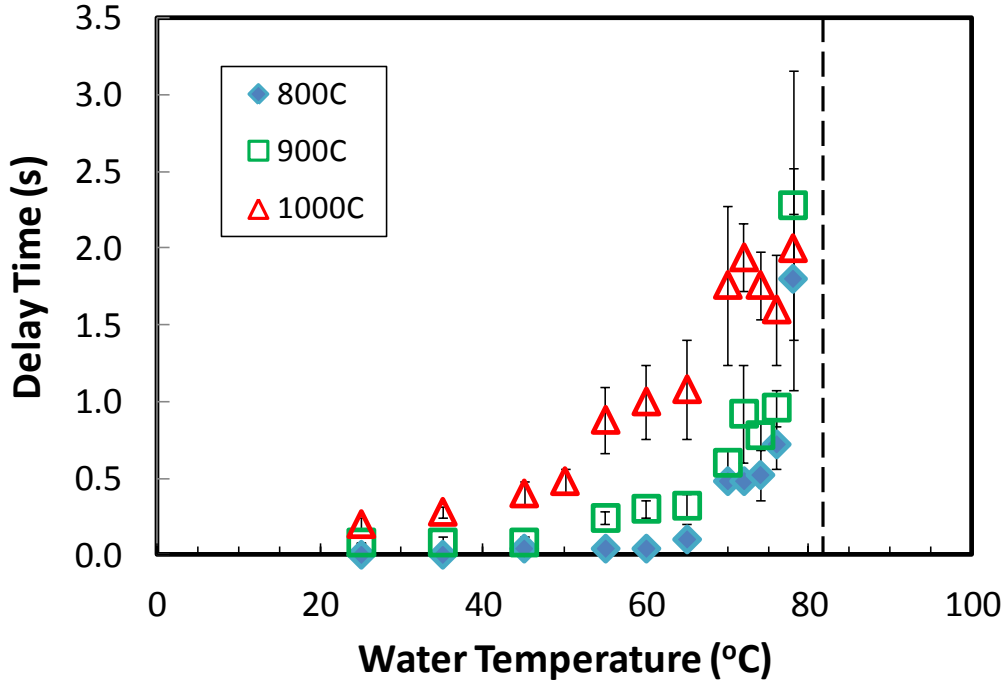

Figure 8: *Droplet explosion delay time at different smelt and water temperatures*

Explosion Intensity

The explosion intensity of each explosion event was determined by analyzing the level of noise recorded by the microphone placed near the water tank. The acoustic data was processed and then imported into MATLAB to identify the acoustic peak of each explosion. Figure 9, for example, shows the acoustic data of four continuous explosions recorded by the microphone. The first explosion peak was observed two seconds after the microphone starts to collect data. As the explosion occurred, the noise level increased from the background value of 0-10dB to about 80dBs.

Figure 10 shows the explosion intensity of a molten smelt droplet falling into water, as a function of water temperature (T_w) and smelt temperature (T_s). As in the case of the delay time, the explosion intensity increased as T_W increased up to the upper $T_{crit,w}$ of 82°C. Beyond this temperature, data was not available since there was no explosion. T_s, on the other hand, did not appear to have an effect on explosion intensity. This conclusion, however, is difficult to draw due to the large deviation of the data especially at low T_W. Nonetheless, this was probably the reason why Sallack [5] reported that T_S appeared to have no effect on explosion.
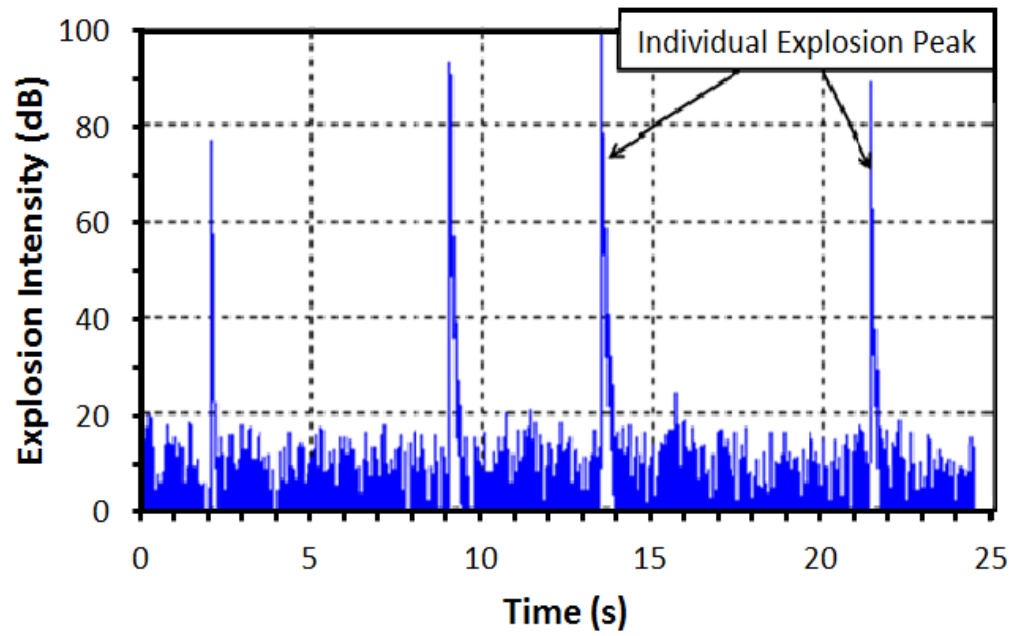
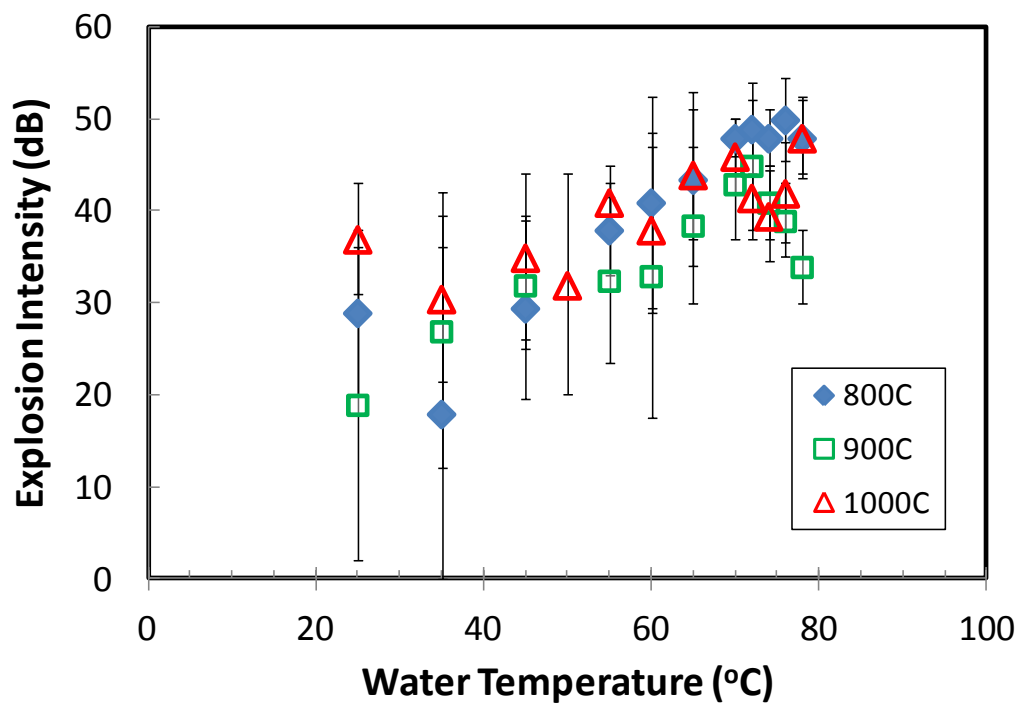**Figure 9**: *Explosion peak intensities*

Figure 10: *Droplet explosion intensity at different water and smelt temperatures*

Images of droplet fragmentation and explosion in the water suggest that explosion intensity is likely related to the way the droplet breaks up upon impacting the water surface. As shown in Figure 11, at low T_w, the droplet broke up into small fragments; some of which subsequently exploded while others did not, thus reducing the overall intensity of the explosion and leading to the high variability of the intensity data. Variation in the extent of fragmentation was another factor contributing to data variability. At high T_w, however, the entire droplet participated in the explosion at once, generating a much larger amount of vapor in a confined space, and hence, a louder noise.
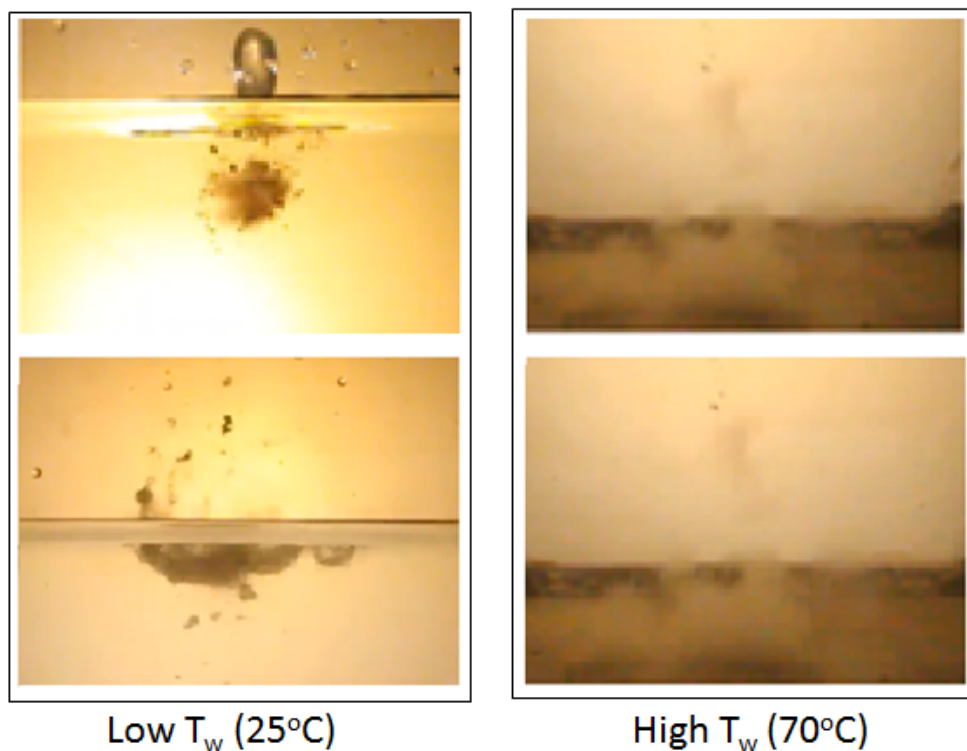

Low T_w (25°C)　　　　High T_w (70°C)

Figure 11: Fragmentation and explosion of droplets at low and high water temperatures.

EXPLOSION MECHANISM

Results of this study support the vapor explosion mechanism proposed by Sallack [5] and endorsed by Nelson and Kennedy [6], which is basically the same mechanism for other liquid-liquid systems where the heat from one liquid (hot) causes the other liquid (cold) to vaporize rapidly [4, 11, 12, and 13].

In this study, the hot liquid is molten smelt made of a mixture of Na_2CO_3 and $NaCl$ with a freezing temperature of 750°C, and the cold liquid is water which boils at 100°C. As a molten smelt droplet at 800°C to 1000°C falls into water at 25 to 100°C, it vaporizes the water forming a vapour film around it. At the same time, depending on the temperature, the droplet may freeze forming a thin frozen layer (or crust) on the surface. The vapor film and solid crust establish a quasi-stable system where the vapor film prevents the water from directly contacting the smelt droplet while the crust keeps the molten smelt core in place (Figure 12a).
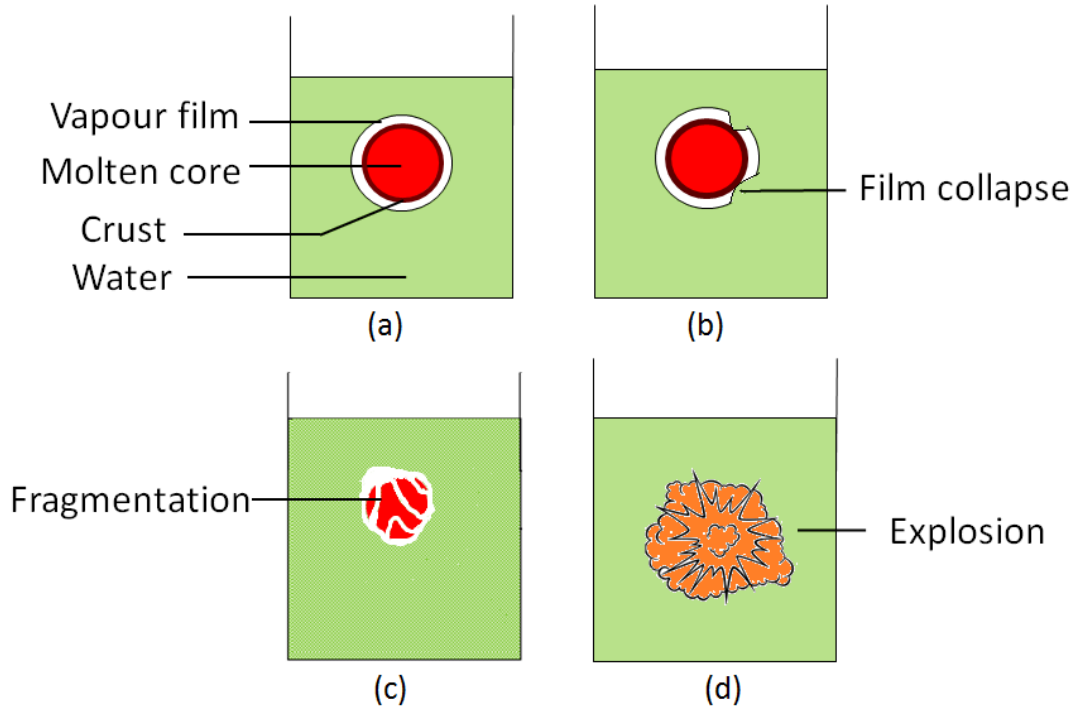
Figure 12: *Probable explosion mechanism of a smelt droplet in water*

Whether or not the molten smelt droplet will explode depends on how long this quasi-stable system lasts. The vapor film can condense due to the cooling effect of the surrounding water and collapse, or can drift away from the droplet due to various hydrodynamic disturbances around it, such as the gravitational movement of the droplet, the impact of the droplet on the tank floor, the convective flow of the water, or a shockwave felt from an exploded molten droplet nearby. As the vapor film collapses, the surrounding water reaches the molten droplet directly (Figure 12b), or if there is a frozen smelt crust present on the surface, the water can cause it to fracture either by thermal shock or by increasing the locally generated vapor pressure, or both. Crust fractures expose the molten smelt core to water (Figure 12c), generating a much larger volume of vapor. This, in turn, rapidly increases the pressure in the confined space between the smelt droplet and water, resulting in an explosion (Figure 12d).

At a water temperature below the lower $T_{crit,w}$, the water cannot vaporize quickly enough to form a sufficient protective vapor film, causing the molten droplet to explode either instantly as it strikes the water surface or with a very short delay. The explosion probability in this case is 100%. At T_w above the lower $T_{crit,w}$, the water can vaporize more readily and form a thicker vapor film, making it more difficult to collapse. Explosion will still occur but with a longer delay. The longer the delay, the thicker the frozen crust becomes making it harder (and longer) to crack. As a result of the thicker vapor film and thicker frozen crust, the explosion probability is no longer 100% but decreases with increasing T_w. At T_W above the upper critical water temperature of 82°C, there is sufficient vapor film to protect the droplet. The frozen crust becomes sufficiently thick and hard that it no longer fractures. The droplet can thus cool and completely solidify without exploding.

Increasing smelt temperature T_s provides more heat to the system, vaporizing more water at the same T_w or the same amount of water at a lower T_w. Above the upper $T_{crit,w}$ of 82°C, there is sufficient heat in the system already for the water to produce a stable vapor film without the additional heat from increasing T_s. In essence, increasing T_s lowers only the lower $T_{crit,w}$ and has no significant effect on the upper $T_{crit,w}$.

PRACTICAL IMPLICATIONS

While the results obtained from this laboratory study have provided much insight into the behaviour of a molten smelt droplet in water, they are far from being sufficient for dissolving tank application. Questions listed below need to be addressed before any meaningful conclusions can be drawn:

- What are the effects of weakwash and green liquor properties (TTA, sulfidity, reduction efficiency, etc.), smelt properties (composition, melting/freezing temperature, etc.) and boiling point rise? Does the smelt-water interaction temperature (SWIT) diagram change for actual smelt?

- What are the effects of smelt flow rate, droplet size and distribution, and distance between smelt spout and liquor level in the dissolving tank?

- Does smelt dissolution play a role in explosion?

- Are there any synergetic effects between droplets? Preliminary results obtained from multiple droplet experiments show that the explosion of one droplet could trigger other droplets to explode.

These are all good topics for future research projects which we hope will provide a better understanding of how molten smelt intacts with water in the dissolving tank, and help devise a viable means for improving dissolving tank safety and operation.

CONCLUSIONS

A fundamental study was conducted to examine how molten smelt droplets interact with water at different temperatures in the dissolving tank. Experiments were performed on synthetic smelt droplets made of a molten mixture of 80 wt% Na_2CO_3 and 20 wt% NaCl, at 800^oC, 900^oC and 1000^oC. The results show that:

- Upon contact with water, some smelt droplets explode immediately and break into small pieces, some require a delay time to explode and others solidify without exploding. The probability of explosion depends strongly on smelt and water temperatures.

- At a given smelt temperature, there appears to be a water temperature range below which explosion always occurs (the lower critical water temperature) and above which there is no explosion (the upper critical water temperature). The lower critical water temperature decreases with increasing smelt temperature, while the upper critical water temperature remains the same at 82^oC in all cases.

- Up to this upper critical water temperature of 82^oC, both the explosion delay time and explosion intensity (noise level) increase with an increase in water temperature.

- The data obtained allowed for the construction of a smelt-water interaction temperature (SWIT) diagram that predicts if a 6.5 to 9 mm molten synthetic smelt droplet will explode in water at different smelt and water temperatures. Such a diagram could be useful if it can be applied to the actual conditions in a dissolving tank.

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