

The Interaction of Molten Smelt and Water

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Abstract

An effective and safe dissolving tank operation is essential to the proper management of a kraft recovery process. While dissolving tank explosions that lead to equipment damage, personnel injury, and unscheduled shutdowns are thankfully rare, loud and violent dissolving tank operation is a surprisingly common occurrence at many mills. Here we present a study of the interaction of molten smelt droplets falling into water, as a function of the smelt and water temperatures. The results demonstrate that droplets always “explode” either at the water surface or beneath it, as long as the water temperature is below a critical value. As the water temperature rises, explosions become less likely. Beyond a certain temperature, droplets do not explode at all, leaving solid smelt to accumulate on the tank bottom. These droplet explosions, while violent, can be very useful, as they enhance smelt dissolution.

Keywords: vapour explosion, smelt, recovery boiler, dissolving tank

I. INTRODUCTION

In the pulp and paper industry, the kraft pulping process uses a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na₂S) to dissolve wood into fiber, which is used to make paper products. It is the most widely used pulping method because the alkali pulping chemicals can be recovered from the waste stream through a chemical recovery cycle, and in the process, steam power is generated, which can account for most of the total energy consumption of a typical pulp mill.

The recovery boiler is a key unit in the kraft recovery cycle. In the boiler, the spent chemical plus organic waste material is combusted to generate steam, and the chemicals form high temperature molten “smelt”. Smelt consists of mostly Na₂CO₃ and Na₂S with small amounts of Na₂SO₄, NaCl and potassium salts [1]. It accumulates at the bottom of the boiler, flows out through multiple smelt spouts at about 800°C, and falls into the dissolving tank below. In the dissolving tank, smelt interacts with water and dissolves. The resulting solution is

then converted back to fresh pulping chemical by a causticizing process.

As the smelt falls into the dissolving tank, the smelt stream is shattered into droplets by a high pressure steam jet, as shown in Figure 1. While smelt dissolution in water is necessary to process the large amount of molten smelt effectively, this process is violent and dangerous. The dissolving tank constantly rumbles, and at times, causes tremors of the ground and buildings nearby. During severe conditions, a dissolving tank explosion may occur, causing an expensive shutdown and personnel injury. Over the past 30 years, about one explosion incident was being reported annually by mills in North America [2]. Needless to say, one explosion incident is too many when it comes to workplace safety. As regulations on occupational health and safety have become increasingly stringent, effective and safe dissolving tank operation has become a top priority for kraft pulp mills.

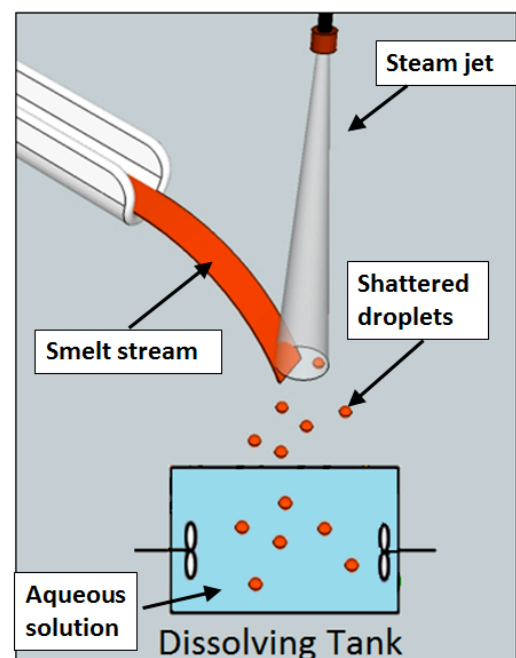


Figure 1: Shattering and dissolution of molten smelt in the dissolving tank.

Despite the importance of dissolving tank safety, the interaction behavior of smelt droplets in the dissolving tank is not well understood because one cannot see inside the tank, and few laboratory studies have been conducted. Shick and Grace compiled a comprehensive literature review on liquid-liquid explosions in the early 1980's [3], and suggested that smelt-water explosions involve the same vapor explosion mechanism as other liquid-liquid systems, where high heat transfer from one liquid causes the other liquid to vaporize rapidly. However, the interaction between smelt and water in the dissolving tank differs from other liquid-liquid systems in that one liquid (molten smelt) is highly soluble in the other (water). The composition of smelt and the smelt concentration in the water may vary, and this can affect dissolving tank operation. While liquid-liquid explosions have been extensively studied by the nuclear, metal processing, and liquefied natural gas industries [3-9], as well as in the context of oceanic volcano science [10], only two studies of smelt-water interaction in the dissolving tank have been published, both in the mid-1950s [11,12]. These studies were crudely carried out; the results obtained were insufficient to draw quantitative conclusions.

Here we present the interaction of molten smelt droplets falling into water, as a function of the smelt and water temperatures, building on our previous work [13, 14].

II. EXPERIMENTAL SETUP

A schematic of the experimental apparatus used in the study of smelt-water interaction is shown in Figure 2. A cylindrical furnace sits on a stainless steel table, and the temperature inside the furnace is constantly measured. A 220mm long cylindrical alumina crucible, tapered at the bottom as shown on the right, is installed in the furnace; the 3mm hole on the bottom is partially plugged by an alumina rod. When conducting experiments, a smelt sample is fed into the crucible from the top. As the crucible is heated up to a desired temperature, molten smelt begins to leak out from the hole on the bottom, one drop at a time, into a 20-liter tank located under the furnace.

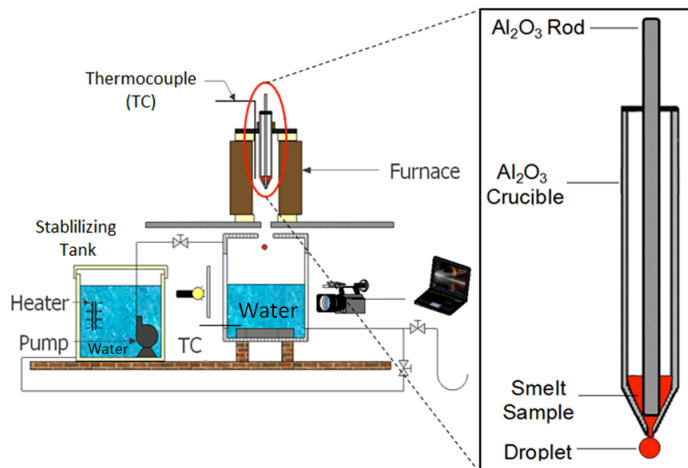


Figure 2: Experimental apparatus for the smelt-water interaction experiments.

The tank is made of stainless steel sheets on the side walls and transparent polycarbonate sheets on the front and back walls for observation of the smelt-water interaction. Water is heated by a temperature-controlled heater in a 40-liter stabilizing tank, and is circulated between the two tanks with a pump. A video camera is used to record the smelt-water interaction at a frame rate of 25 fps.

In this study, synthetic smelt composed of 80wt% Na_2CO_3 and 20wt% NaCl was used, and the diameter of the droplets was around 7mm. The droplets fell 700mm into 120mm of water. Experiments were carried out at three smelt temperatures (T_s): 800°C, 900°C and 1000°C, and the water temperature (T_w) was varied between 25°C and 100°C. For each condition, the experiment was repeated over 30 times.

III. RESULTS AND DISCUSSION

The behavior of a molten smelt droplet in water depends on the smelt temperature and water temperature. Series of photos recorded by the video camera show three distinct interactions, shown in Figure 3. Some droplets disintegrate immediately at the water surface (*Immediate Explosion*). Some sink beneath the water surface and explode either in the middle of the water tank or after settling on the tank floor (*Delayed Explosion*). Finally, some droplets sink to the bottom of the tank, solidify, and never explode (*No Explosion*). To quantify the effects of T_s and T_w on the interaction, the “explosion probability” and “explosion delay time” (dt) were investigated.

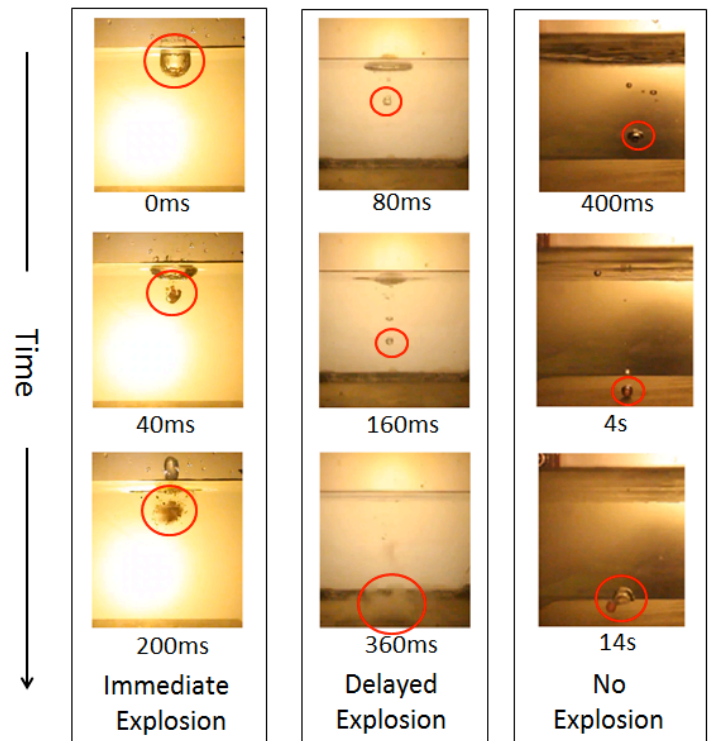


Figure 3: Three regimes of smelt-water interaction (the red circles highlight the droplets).

The explosion probability was calculated by dividing the number of exploded droplets over the total number of trials. The explosion probability as a function of water and smelt temperature is shown in Figure 4. For an 800°C smelt droplet, when water temperature is below 72°C, which we refer to as the lower critical water temperature (lower $T_{w,crit}$), the droplet always explodes. Above 72°C, the probability begins to decrease, and drops to zero at 82°C, which we refer to as the upper critical water temperature (upper $T_{w,crit}$). With the increase of smelt temperature from 800°C, to 900°C, and to 1000°C, the lower $T_{w,crit}$ shifts to the left while the upper $T_{w,crit}$ remains the same. Results also show that the behavior of real smelt, which is indicated by the brown curve, is similar to that of the synthetic smelt.

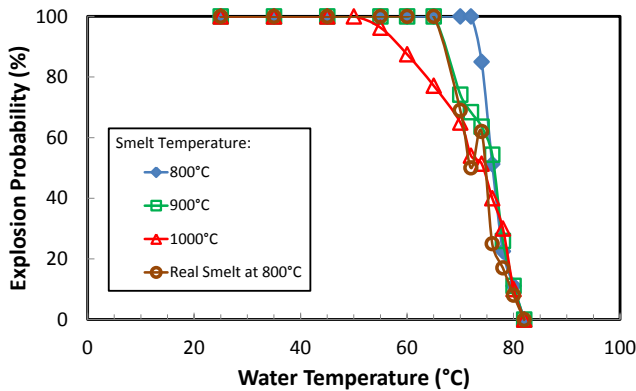


Figure 4: Explosion probability at different water and smelt temperatures.

Using the lower and upper $T_{w,crit}$, a Smelt-Water Interaction Temperature diagram, or SWIT diagram, can be constructed to show the combined effect of T_s and T_w on the explosion probability, as shown in Figure 5. Under the lower critical water temperature curve, explosions always occur. Above this curve, explosions occur sometimes. Above the upper $T_{w,crit}$ line, no explosion is observed. The left boundary of the diagram is the freezing temperature of smelt, which is around 750°C.

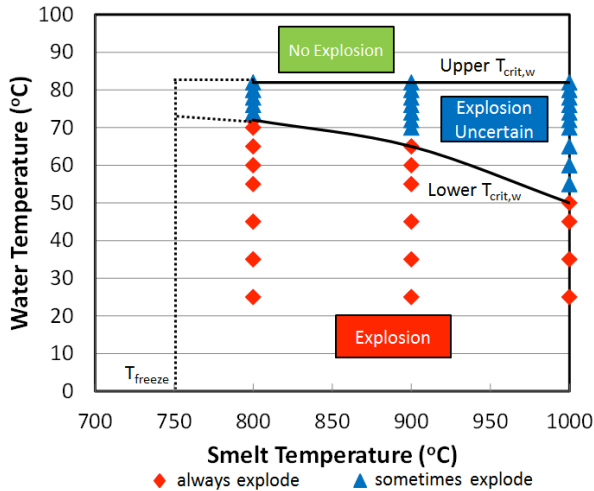


Figure 5: Smelt-Water Interaction Temperature diagram (80% Na_2CO_3 and 20% NaCl).

We define the explosion delay time as the time between the first contact with water and when the droplet explodes. The contact time was determined from the video recordings, and the explosion time was obtained from the acoustic signal recorded by the camera. Figure 6 illustrates the droplet explosion delay time at different smelt and water temperatures. At a given T_s , dt increases with increasing T_w ; dt also increases as T_s increases.

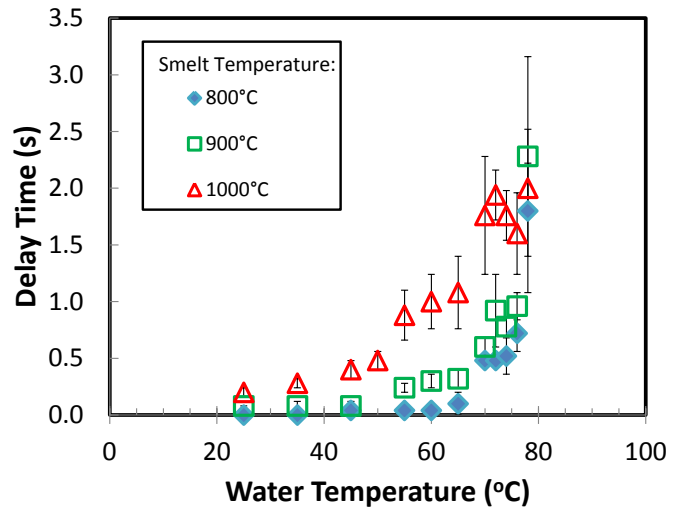


Figure 6: Droplet explosion delay time at different smelt and water temperatures.

The explosion delay time offers insight into the effect of the tank bottom on the droplet behavior. With 120mm of water in the tank, droplets take about 0.4s to impact the tank bottom for the first time; if they bounce and don't explode, the second impact usually occurs at $dt=0.8s$. Figure 7 superimposes the data of Figures 4 and 6: explosion probability and delay time at different T_w . Notice that the delay time curves plateau at about 0.4s for all three smelt temperatures, and towards the end of each plateau, the corresponding explosion probability begins to decrease. This suggests that the impact on the tank bottom can trigger some droplet explosions, and that it is only an incremental rise in T_w that can overcome the effect of the tank bottom, so that dt begins to rise again. The droplets that survive the first impact may not explode. The second plateau appears at $dt=0.8s$ for $T_s=900^\circ\text{C}$ and 1000°C , and corresponds to droplets that survived the first impact, bounced up, and impacted the tank bottom a second time. In a sense, the existence of the tank bottom shifts the explosion probability curve upwards. The delay time asymptotes towards infinity when the upper $T_{w,crit}$ is reached, and the smelt droplets no longer explode. The data is more scattered as the delay time increases, reflecting the stochastic nature of smelt explosions, and/or the low probability of explosions at high water temperature.

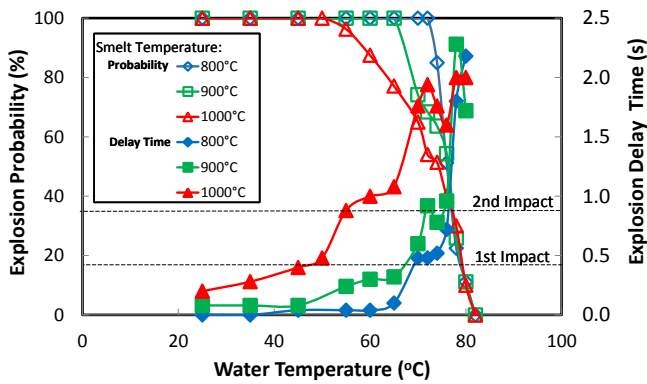


Figure 7: Explosion probability and delay time at different smelt and water temperatures.

IV. 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 80wt% Na_2CO_3 and 20wt% NaCl , at 800°C, 900°C and 1000°C. The results show that:

- Upon contact with water, some smelt droplets explode immediately and break into small pieces, some explode after a delay time, and others solidify without exploding. The probability of explosion depends strongly on smelt and water temperatures.
- At a given smelt temperature, there is a water temperature range below which an 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°C in all cases.
- Up to this upper critical water temperature of 82°C, the explosion delay time increases with an increase in water temperature.

V. FUTURE WORK

The experimental work on smelt-water interaction will continue. The experimental apparatus is currently being rebuilt to allow us to vary parameters including smelt droplet size, smelt composition, green liquor concentration, and the distance that a droplet falls before reaching the tank. Acoustic and vibration data will be collected to analyze the intensity of droplet explosions. Questions for future research include: How does the explosion probability vary with smelt droplet size and distribution? Do partially molten smelt droplets explode? Does the distance between the smelt spout and liquor level in the dissolving tank affect the tendency for immediate explosions? How does one exploding droplet affect the tendency for other droplets to explode? Can we quantify synergetic effects

between exploding droplets? How do green liquor composition and concentration affect the tendency for droplets to explode? How can our lab-scale results be applied to mill conditions?

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REFERENCES

1. Grace T.M., “Chapter 11 - Recovery Boiler Safety”, in Kraft Recovery Boilers, T.N. Adams, Editor, TAPPI Press, Atlanta, p. 333 (1997).
2. Lien S. and DeMartini N. “Dissolving Tank Explosions: A Review of Incidents between 1973 and 2008”. Unpublished report to BLRBAC and AF&PA, sponsored by the American Forest & Paper Association, New York (2008).
3. Shick P.E. and Grace T.M. “Review of smelt water explosions”, Proceedings of the International Chemical Recovery Conference, p. 155-164, Sponsored by the Technical Section of CPPA and TAPPI, Vancouver, September 22-25, 1981.
4. Dullforce T.A., Buchanan D.J. and Peckover R.S., “Self-triggering of small scale fuel-coolant interaction: I. Experiments”, Journal of Physics D: Applied Physics, 9: 1295-1303 (1976).
5. Buchanan D.J. and Dullforce T.A., “Mechanism of vapor explosions”, Nature, 245, 32-34 (1973).
6. Reid R.C., “Rapid phase transitions from liquid to vapour”, Advances in Chemical Engineering, 12, 105-208, (1983).
7. Epstein S.G., “Molten Aluminum-Water Explosions: An Update”, In Light Metals 1993 (S. K. Das, ed.), Metallurgical Society of AIME, 845-853 (1992).
8. Katz D.L. and Slipevich C.M., “Liquefied Natural Gas/Water Explosions: Cause and Effect”, Hydrocarbon Process, 50, 240-244 (1971).
9. Corradini M.L., Kim B.J. and Oh M.D., “Vapor explosions in light water reactors: A review of theory and modeling”, Progress in Nuclear Energy, 22(1), 1-117 (1988).
10. Francis P. and Self S. “The Eruption of Krakatau”, Scientific American, 249, 149-159 (1983).

11. Sallack J.A., "An investigation of explosions in the soda smelt dissolving operation", Pulp Paper Canada Magazine, 56(10): 114-118 (1955).
12. Nelson W. and Kennedy E.H., "What causes kraft dissolving tank explosions, I. Laboratory Experiments", Paper Trade Journal, 140(29): 50-56 (1956).
13. Jin E., "Interaction between a Molten Smelt Droplet and Water", M.A.Sc. thesis, University of Toronto (2013).
14. Jin E., Bussmann M. and Tran H.N., "An experimental study of smelt-water interaction in the recovery boiler dissolving tank," Proceedings of TAPPI PEERS, Green Bay, WI (2013).