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A MODEL TO EXPLAIN COMPOSITION EFFECTS IN SMELT-WATER EXPLOSIONS

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ABSTRACT

A salt bridge model, which takes into account mass transfer of components between the two fluids, was developed and proved successful in interpreting the effects of composition on explosiveness in the smelt-water system. The model is based on the fact that the main smelt constituent, sodium carbonate, is not soluble in water at temperatures approaching the critical point, while certain other constituents are soluble. The soluble substances allow a substantial increase in the critical temperature of the solution, which in turn shifts the range of contact interface temperatures at which spontaneous explosions can occur (between the spontaneous nucleation temperature and the critical temperature of the coolant) to higher values. The model was able to provide an explanation of why sodium chloride, sodium hydroxide, and sodium sulfide act as smelt sensitizers and a semiquantitative definition of the concentration ranges in smelt and in the quench solution where spontaneous explosions are likely.

INTRODUCTION AND BACKGROUND

Smelt-water explosions have been a problem in the kraft pulp industry for a long time. It has also long been recognized that smelt composition can have a pronounced effect on explosiveness. Sallack (1) found dissolving tank violence to be correlated to the NaCl content in the normally Na_2CO_3 smelt. He

confirmed this sensitivity in laboratory tests. Nelson and Kennedy (2) also found that smelt composition could have a pronounced effect on explosivity in laboratory experiments.

Following some major explosions in recovery boilers, a Smelt-Water Research Group was set up under the auspices of the Fourdrinier Kraft Institute. The initial study was conducted by Babcock & Wilcox and Combustion Engineering under coordination by The Institute of Paper Chemistry (3). Subsequently work was sponsored at Arthur D. Little and Battelle-Columbus (4). In addition to conclusively showing that smelt-water explosions were noncombustible in nature, laboratory explosivity tests demonstrated a marked dependence on composition of both smelt and the quench liquid. NaCl, NaOH and Na₂S were shown to be sensitizers for Na₂CO₃ smelts, while Na₂SO₄ and Na₂CO₃ themselves did not give explosions. No satisfactory explanation of composition effects was developed, although Battelle did note that sensitizers were compounds whose solubility in water increased with temperature as the critical temperature of water was approached. Thus their saturated solutions could be heated above the critical temperature of water without reaching a critical point.

Shick (5) extended the Battelle concepts by proposing a concentration gradient mechanism for smelt-water explosions. He stated that at the smelt-water contact interface it is necessary to consider the mutual solubilities of the two liquids in each other. Instead of a sharp interface between smelt and water, there are concentration gradients on both sides with water present in smelt and smelt dissolved in water. These concentration gradients form a "salt-bridge" at the interface. Shick's concept provided a commonality for sensitizers that no other theory was able to give. However, he was unable to use it to make quantitative predictions on the effects of smelt composition on explosivity.

Explosion Theories

Work on explosions in LNG-water systems led to the homogeneous nucleation theory of explosions. Enger and Hartman (6) found that a necessary condition for explosions was that the hot liquid temperature exceeds the homogeneous nucleation temperature (also called the limit of superheat temperature, T_{s1}) of the cold liquid. This was confirmed by Porteus and Reid (7) in LNG-water and by Henry and Fauske (8) in Freon-water and Freon-mineral oil systems. This condition provides a lower bound for explosions. At 1 atm pressure, the superheat limit temperature for hydrocarbons is about 0.89-0.9 times the critical temperature. For hydrocarbon mixtures, the T_{s1} is closely approximated by a mole fraction average of the T_{s1} of the pure components.

Spiegler, et al. (8a) computed the Leidenfrost temperature (which is almost the same as the limit of superheat temperature) by using the Van der Waals equation of state. For simple cryogenic fluids they obtained a value of 0.844 times the critical temperature. We have calculated the limit of superheat for water at low pressure from several equations of state and obtained values of $0.895 T_c$, $0.919 T_c$ and $0.922 T_c$ from the Redlich-Kwong, Soave, and Peng-Robinson equations, respectively. Apfel (8b) has shown that the limit of superheat for many liquids is from 0.85 to 0.9 times the critical temperature. In this paper we have used $0.89 T_c$ as the limit of superheat temperature for water and for aqueous salt solutions.

There is also an upper limit to the hot fluid temperature above which explosions are not probable and stable film boiling occurs instead. This limit is less definite, but data from laboratory scale experiments indicate that a value equal to $1.1 * T_{s1}$ is a reasonable approximation.

In summary, the simple homogeneous nucleation theory indicates explosions may occur if

$$1.00 < T_{\text{hot}}/T_{\text{sl,cold}} < 1.10$$

An equivalent statement for light hydrocarbons is

$$0.89 < T_{\text{hot}}/T_{\text{crit,cold}} < 0.98$$

It is interesting to note that the upper bound for explosions is almost the same as the critical temperature of the cold fluid. Ochiai and Bankoff (9) showed that film boiling becomes quite stable at temperatures higher than the critical temperature because wetting is not possible. Swift (10) and Henry (8) also considered the critical temperature of the coolant as the maximum value of the surface temperature. The coolant critical temperature as an upper bound of explosions was confirmed in many systems - light hydrocarbon-water (7), Freon-mineral oil (8), tin-water (11) - and is consistent with experimental results in aluminum-water (12,13) and steel-water (13).

A very different theory of these types of explosions is the detonation model of Board (14). He applied the classical theory of detonation to the one-dimensional case of a plane explosion front propagating through a coarsely mixed region of hot and cold fluids. This concept has been refined into the 4-stage model of explosions now commonly accepted. The four stages are coarse intermixing, triggering, escalation/propagation, and expansion. Versions of the 4-stage model have the potential of predicting energy conversion ratios and details of the blast wave. This is not possible with the homogeneous nucleation model which only predicts the boundaries of the explosive region.

Fauske (15) has proposed a criterion which can serve as a tie between the homogeneous nucleation concepts and the 4-stage model. He suggested that large-scale explosions only occur if the interface temperature on contact is above the superheat limit temperature of the cold liquid. This was rationalized as a necessary condition for film boiling, which stabilized the system while coarse intermixing proceeded. Large scale explosions could only occur if there was extensive intermixing before triggering.

The simple homogeneous nucleation theory has been most successful in predicting explosive boundaries in weakly explosive systems that are self-triggered. It is likely that the criterion is most germane to the triggering step. Many systems which are nonexplosive in simple contact modes have reacted violently in shock tube experiments or when a sufficiently energetic detonator was used as a trigger.

In this paper we will show that the effects of smelt composition on explosiveness in laboratory scale experiments can be explained by using the simple homogeneous nucleation theory in conjunction with Shick's salt-bridge concepts.

FORMULATION OF SALT-BRIDGE MODEL

Keevil (16) presents data on the vapor pressure of aqueous solutions at high temperature. The vapor pressure of the sodium carbonate and sulfate solutions approaches that of pure water as the temperature is increased. On the other hand, the vapor pressure of more soluble salts such as sodium chloride and sodium sulfide (16) and potassium carbonate (17) remains below that of water as the critical temperature of water is approached. Furthermore, their solubilities increase with temperature so that their saturated solutions could be heated well above the critical temperature of water without reaching a critical point. Keevil

(16) indicated that the intermolecular forces for NaCl-water may be strong enough to prevent critical conditions even at temperatures as high as 800°C and pressures of 400 atm.

Since the upper bound for explosiveness is the critical temperature of the cold fluid, it is important to find data on the critical temperature as a function of salt concentration. Marshall (18) compared his critical temperature-composition measurements for NaCl-water with those obtained previously by Olander (19), Sourirajan (20), and Schroer (20a). The critical temperature increases from 374°C for pure water to 388°C for a 1% (by weight) NaCl solution, to 424°C for a 5% solution and to 467°C for a 10% NaCl solution. Sourirajan (20) showed critical temperatures at higher concentrations to be 600°C at 19.6% and 700°C at 26.4% NaCl.

Urusova (21) investigated the vapor pressure of NaOH-water and NaCl-water solutions at 350-550°C. The critical temperature of NaOH solutions increases to 450°C at 10.3 % (by weight) NaOH, 500°C at 15.3%, and 550°C at 20%. We could not find similar data in the literature for Na₂S, possibly because it may be chemically unstable. The sodium sulfide could form sodium hydroxide by hydrolysis or react with water to form hydrogen and sodium sulfate at high temperature.

The homogeneous nucleation theory predicts that explosions occur only when the temperature at the fluid-fluid interface is between the homogeneous nucleation temperature and the critical temperature of the coolant. The interface temperature is commonly calculated from the equation in Carslaw and Jaeger (22) for the time-independent contact temperature between two infinite slabs of material, each initially at a uniform temperature.

$$T_1 = (r_1 * T_h + T_c) / (1 + r_1)$$

where

$$r_1 = \left[\frac{k_h \rho_h C_{vh}}{k_c \rho_c C_{vc}} \right]^{1/2}$$

k, ρ , and Cv are the thermal conductivity, density and specific heat capacity. Subscripts h, c refer to hot and cold phases, respectively.

When dealing with fluids which are soluble in each other, there will be concentration gradients as well as temperature gradients, and an interfacial concentration will be established. We define T_* as the critical temperature for the coolant at the interfacial concentration, C_1 . It is assumed that the interface temperature can be calculated from the conduction equation with constant properties (the effect of mass transfer on the heat transfer is neglected). It is further assumed that the homogeneous nucleation temperature for solutions is also given by 0.89 times the critical temperature. Then the explosion criterion can be written as

$$0.89 T_* < T_1 < T_*$$

For a given interface temperature, T_1 , the explosive range will be bounded between two interface concentrations. One boundary will be the concentration corresponding to $T_* = T_1$. This would be the lowest interfacial concentration at which explosions would occur. The upper bound on interface concentration would be that corresponding to $T_* = T_1/0.89$. Thus the criteria can be written as

$$C(\text{low}) < C_1 \leq C(\text{high})$$

where C_1 is the smelt-water interface concentration.

$C(\text{low})$ is the salt concentration corresponding to T_1 .

$C(\text{high})$ is the concentration corresponding to $T_1/0.89$.

The interface concentration can be calculated in a manner directly analogous to that used for calculating the interface temperature. The equation is

$$C_i = (r_2 * C_h + C_c)/(1 + r_2)$$

where $r_2 = (D_h/D_c)^{1/2}$

C_h = salt concentration in the smelt.

C_c = salt concentration in the bulk water.

D_c = diffusion coefficient of salt in water.

D_h = diffusion coefficient of water in salt if salt concentration is dominant in the smelt, or diffusion coefficient of salt in Na_2CO_3 if salt concentration is low.

For smelt at 800°C contacting boiling water, the interface temperature is estimated to be 440°C. The system will be within the explosive region for solutions having critical temperatures between 440 and 528°C [(440 + 273)/0.89 - 273]. The salt concentrations that correspond to these temperatures are 7 and 12% by weight, respectively.

Diffusion coefficients are needed to calculate the interfacial salt concentration. The diffusion coefficient for NaCl in water is 1.35E-5 cm²/sec at 18.5°C. At 150°C, the diffusivity of NaCl in water is estimated at 1.17E-4 using the Nernst-Haskell equation (23). The self-diffusivities of sodium and chloride ion in molten NaCl at the melting point are 7.38E-5 and 5.82E-5, respectively and increase with increasing temperature (24). The diffusivity of water in molten LiCl-KCl eutectic mixtures was found by Melendres (25) to be 3.1E-5 and 8.0E-5 at 390 and 480°C, respectively. All of the relevant diffusivities are of the same general magnitude. If they were equal, the interface

concentration would be a simple numerical average of the salt concentrations in the hot and cold fluids. If the hot fluid diffusivity were 1/2 of the cold fluid diffusivity, the interface concentration would be given by $C_i = 0.414 \times C_h + 0.586 \times C_c$. If the hot fluid diffusivity were twice that of the cold, the interface concentration would be given by $C_i = 0.585 \times C_h + 0.414 \times C_c$. The arithmetic average is a reasonable approximation and is used as an estimate of the interface concentration in this paper.

COMPARISON OF SALT BRIDGE MODEL WITH DATA - EFFECTS OF SMELT COMPOSITION

The effects of smelt composition on explosivity tests under laboratory conditions were summarized by Battelle (4) as follows:

- * The major smelt constituent, Na_2CO_3 , was not in itself explosive.
- * The likelihood of an explosion increased with increasing amounts of Na_2S in the smelt.
- * Smelt containing relatively small amounts of Na_2S were more easily sensitized by the minor smelt constituents, NaCl and NaOH .
- * Other minor smelt components, K_2CO_3 , Na_2SO_4 , and Na_2SO_3 , in descending order, were minor sensitizers.

All of these results were obtained in experiments in which the explosions were self-triggered. The same is true of the dissolving tank experiments of Sallack (1) and Nelson (2). Composition effects are much less marked when external triggers are used. Bergman and Laufke (26) obtained explosions with all tested smelt compositions, including pure Na_2CO_3 , by using detonators with a high ignition impulse.

Na₂CO₃ - NaCl System

a. Pure Sodium Carbonate

The lowest interface temperature for this system is calculated to be 524°C for sodium carbonate at its melting point of 851°C in contact with water at 25°C. Since this lowest interface temperature is far above the critical temperature of water (374°C), pure sodium carbonate will not explode spontaneously and needs a strong external trigger.

b. Sodium Carbonate-Sodium Chloride Mixtures

The data of Sallack (1), covering the entire NaCl-Na₂CO₃ concentration range are shown in Table 1. Soda smelt (without sulfide), at temperatures ranging from 1600 to 1700°F, was poured into water at 170-180°F. With smelt containing 6% NaCl, explosions occurred in 1/3 of the tests. With smelt containing 8% or more NaCl, explosions occurred in all tests. The heaviest explosions were produced with smelt containing from 8 to 20% NaCl. Explosions with smelt containing more than 20% NaCl were light, amounting to no more than the shattering of the smelt.

The interface NaCl concentrations for the heaviest explosions are estimated to range between 4 and 10%. This range agrees reasonably well with the 7 to 12% range predicted by the salt bridge theory, especially when considering the uncertainty in the interface concentrations due to the lack of good diffusivity data. It is also consistent with data from the Smelt-Water Research Project (3) which showed no explosions at 5% NaCl and violent explosions at both 15 and 20% NaCl.

(Table 1)

c. Pure Sodium Chloride

Nelson (2) observed violent surface interactions for pure sodium chloride dumped into quench water. Hohmann (27) found that explosions did not occur in flooding mode experiments without an external trigger but did occur in pouring mode experiments with coolant temperatures higher than 50°C. At coolant temperatures of 20°C, violent surface interactions prevented the penetration of large melt masses into the coolant.

Anderson and Bova (28) did extensive experiments injecting small amounts of water into molten NaCl at temperatures between 880 and 980°C. Tests with water at high velocity (50 ft/sec) generated mild interactions which splashed the smelt out of the crucible, but no large explosions. Later tests, run at lower injection velocity, produced several violent interactions.

Anderson and Armstrong (29) found two types of behavior in their tests. In some cases with subsurface injection and in all cases in which glass spheres filled with water were broken beneath the molten salt surface, the water boiled harmlessly to the surface, causing some splashing of the salt but no explosion. Other subsurface injection tests in the same equipment gave explosions from equivalent water masses and geometries. Subsurface movies showed that every explosive case was initiated by an external force which tended to drive the two liquids across the insulating vapor film into contact with each other.

The experimental evidence indicates that the NaCl-water system is not explosive without external triggering. This is in agreement with the salt-bridge model, since the interface concentration (estimated at 50%) is well above the upper boundary.

Na₂S-Na₂CO₃ System

The effect of sodium sulfide concentration on smelt-water explosions is summarized in Table 2. In general, there are only mild explosions or none at all at sulfide concentrations below 20% by weight. Battelle (4) found that the explosion probability ranged from 100% for smelt containing 30% Na₂S down to 10% for a melt containing 20% Na₂S.

(Table 2 here)

After comparing concentration ranges in Table 2 with those in Table 1, it appears that 1% Na₂S is equivalent to about 0.36% NaCl in sensitizing explosions. If so, the upper concentration boundary for Na₂S should be about 35%. Battelle (4) found that pure Na₂S is very reactive with water with explosions occurring in more than 90% of the tests. The high probability does not necessarily mean severe explosions. The behavior of pure Na₂S may be analogous to what Sallack found with NaCl-Na₂CO₃ at very high NaCl concentrations. Another factor, that could be an influence at the upper boundary, is that with pure or mostly pure sensitizers the diffusion coefficient for water into smelt is the relevant parameter in determining the interface concentration and not the diffusion coefficient of the sensitizer within the molten smelt.

NaOH-Na₂CO₃ System

Sallack (1) found that smelt composed of NaOH and Na₂CO₃ exploded with 100% probability when the NaOH content was above 10% by weight. Nelson (2) obtained consistent results in laboratory quenching tests in which there were no explosions at 5% NaOH and violent explosions at 10 and 15% NaOH. These results are summarized in Table 3.

(Table 3 here)

After comparing Table 3 with Table 1 it appears that 1% NaOH is equivalent to 0.7% NaCl in sensitizing Na₂CO₃ smelt. If so, then the upper explosive concentration would be expected to be about 17% NaOH. There are some data from the Smelt-Water Project (3) in which no explosions were produced on injection of water into melts containing 15, 20, 50 and 100% NaOH. On the other hand, there are several reports (2,3) of violent surface interactions of water on pure NaOH melts.

Kraft Smelts

Kraft smelts normally consist of Na₂CO₃ and Na₂S with relatively small concentrations of other sensitizers such as NaCl and NaOH. Data from Nelson (2) on the effect of smelt composition in dissolving tank explosions are summarized in Table 4. Also included in Table 4 are the calculated NaCl equivalent concentrations using the following equivalencies.

$$1\% \text{ NaCl} = 1.43\% \text{ NaOH} (1/0.7) = 2.78\% \text{ Na}_2\text{S} (1/0.36)$$

(Table 4 here)

It can be seen that the lower limit for equivalent NaCl concentration is about 7%. This is in very good agreement with Sallack's (1) results for NaCl-Na₂CO₃ smelts. It is also in close agreement with the predicted lower limit of 7% NaCl at the interface from the salt bridge theory.

If each of the NaCl equivalencies are divided through by the molecular weights of the salts, the proportions become;

$$1 \text{ NaCl} = 2.09 \text{ NaOH} = 2.08 \text{ Na}_2\text{S}$$

Although these ratios may be coincidences, it is tempting to speculate that one mole of NaCl has the same effect as a sensitizer as two moles of NaOH or Na₂S.

EFFECT OF SALT CONTENT OF QUENCH WATER ON EXPLOSIONS

It has been shown (2,3,4) that green liquor (an aqueous solution of smelt) resulted in more severe explosions than pure water even though the salt concentration (excluding Na_2CO_3) is typically not more than 3% NaCl equivalent in green liquor. Other data (3) showed violent explosions for smelt with 24% Na_2S quenched by 5% NaCl solution and 20% Na_2S smelt quenched by 10% NaCl solution, but 15% NaCl solution poured into smelt with 27% Na_2S gave only mild pops on each of 18 tests.

The salt bridge model can be used to explain why the dilute salt solutions resulted in more violent explosions than the more concentrated ones. The NaCl equivalent concentration at the interface for 27% Na_2S quenched by 15% NaCl solution is calculated to be 12.4% which would be just above the upper boundary of 12% from the salt bridge theory. The two smelts quenched with 5 and 10% NaCl solution have interface concentrations of 6.8 and 8.6% respectively, one of which is close to the lower bound and the other is within the predicted explosive region. Considering the assumptions made in calculating the interface concentrations and the theoretical explosion boundaries, one should not attach much significance to exact numerical values. What is significant is that the salt bridge theory does predict that there should be a range of aqueous NaCl concentrations in which the explosivity of the system is enhanced, and this is borne out by the data. It is also significant that the concentration range is about at the magnitudes where it would be expected to be from the salt-bridge model.

EFFECT OF WATER TEMPERATURE ON EXPLOSIONS

Both Sallack (1) and Nelson (2) found that the temperature of the quench liquid, but not that of the smelt, had a major effect on explosion behavior. In

general, the hotter the quench liquid, the less frequent and violent were the explosions. Some smelts which gave immediate, very violent explosions in cold water produced only mild explosions in water at 210°F. Battelle also found that the explosion probability decreased with increasing water temperature. There were exceptions. Nelson (2) reported "Another composition which gave an immediate violent surface explosion in cold water produced a terrifically violent deep explosion in hot quenching water. This blast, the most violent of all, was heard more than a quarter of a mile away." Hohmann (27) also found a shift from surface interaction to violent explosion in NaCl-water experiments when the water temperature was increased from 20 to 50°C.

The above phenomena can not be explained by considering the interface temperature alone, since it would respond to changes in either smelt or water temperature. The salt bridge model can provide a qualitative explanation. In most of the dissolving tank experiments, the salt content of the smelt is near the lower concentration limit. The diffusion coefficient on the coolant side increases by a factor of 3.6 in going from 25 to 95°C. This could lead to a dramatic decrease in the interface concentration as the coolant temperature is increased which could easily drop the concentration below the explosive range.

There are two reasons why a temperature change on the smelt side does not have a major influence on explosions. First, the smelt side diffusion coefficient temperature dependence is only about 1/3 that of the coolant side diffusivity. Secondly, an increase in smelt temperature will increase both the interface temperature and the smelt-side diffusivity. But an increase in smelt side diffusivity will tend to increase the interface concentration which will tend to cancel out the effect of the higher interface temperature. On the coolant side, these two effects will be additive.

DISCUSSION OF RESULTS

In general, the salt-bridge model provides a very good, semiquantitative interpretation of the effects of smelt composition on explosion behavior. The lower concentration limit appears to be more sharply defined experimentally and more universally obeyed. There is also, generally, an indication of an upper concentration limit as well, but the exact boundary appears to be much more sensitive to the details of the contacting process and to external events.

It is possible to interpret the explosion criterion used in the salt-bridge model in terms of the 4-stage detonation model of explosions and this provides further insight into the phenomena. Basically, the "explosive range" is bounded by two temperatures. The lower temperature limit (which corresponds to the high concentration limit) is the spontaneous nucleation temperature, a condition for immediate boiling on contact. This establishes film boiling independently from hydrodynamic considerations and allows the two fluids to mix without being immediately blown apart. The upper temperature limit (which corresponds to the low concentration limit) is the critical temperature of the coolant. Above this temperature, the two fluids are unable to wet each other and film boiling becomes very stable. Large impulses are needed to bring the two liquids into direct contact.

At interface concentrations below the lower concentration limit, the interface temperature is greater than the critical temperature and film boiling will be very stable. This is favorable for extensive intermixing. This effect would tend to make a system prone to a large violent explosion. However, the very stability of the film boiling would in turn require highly energetic triggers to start an interaction and the inability of the two fluids to wet each

other would interfere with the fragmentation and rapid heat transfer that are essential to the escalation step. Thus one would expect explosions to be infrequent and relatively nonviolent. This seems to be what is generally observed in the smelt-water system. The lower concentration boundary seemed to be more sharply defined and there were fewer exceptions.

At interface concentrations above the upper concentration limit, the interface temperature would be below the spontaneous nucleation temperature and a vapor layer would not immediately form on contact of the two fluids. The fluids would be able to interpenetrate each other without being stabilized. Thus the coarse intermixing stage which is necessary for a large coherent explosion would not be able to take place to any great extent. The system would have a tendency to experience surface interactions which would tend to blow the fluids apart before a major interaction could take place. In effect the system would be too unstable to allow a large violent explosion. Instead vaporization would proceed incoherently as spatters, sizzles, etc. This also is in accord with the experience in the smelt-water system. The upper concentration boundary was less rigidly defined and there were more exceptions. The behavior was also more sensitive to external disturbances.

It might be conjectured that the region between the spontaneous nucleation temperature and the critical temperature is the region where self-triggering due to spontaneous film boiling collapse is most likely. If this is the case, then the composition effects would be expected to be most marked in simple contacting experiments without external triggers. This also seems to be the case. The Swedish studies (26) in which detonators were used showed much less dependence on composition. Interestingly enough, composition effects observed in dissolving tanks at pulp mills corresponded quite closely to those found in laboratory

experiments in which smelt was poured into the quench liquid. This suggests dissolving tank explosions may also be easily self-triggered.

The experience of smelt-water explosions within the recovery furnace itself is quite different. No evidence has accumulated to suggest that the frequency or violence of explosions is greater for mills having high concentrations of NaCl in the smelt or those operating at higher sulfidity (a higher concentration of Na_2S). Recovery boiler explosions are also generally characterized by delay times ranging from a few minutes to several hours between the first opportunity for water to contact smelt and the explosion. Recovery boiler explosions are also rather infrequent. Most instances where water has an opportunity to come in contact with smelt in a recovery furnace do not result in an explosion. A part of this behavior is undoubtedly simply contact geometry. The molten smelt is present on the hearth of the furnace along with a substantial amount of frozen smelt and unburned carbonaceous char, and water entering the furnace may not have direct access to the smelt. However, something besides access may be involved. Perhaps large-scale furnace explosions require a fairly stable pre-mixing period, and thus an energetic, external trigger. Perhaps the water entering the furnace must first dissolve some of the smelt to form a green liquor pool within the furnace before the explosive range is reached. In this latter case, the salt-bridge model might provide some guidance.

Composition effects similar to those exhibited by smelt-water would be expected for any system in which one or more components from one fluid are soluble in the other. Where this is the case, it will be extremely difficult to extrapolate results from laboratory scale tests to predict behavior in industrial scale systems, because the laboratory scale tests are easily dominated by triggering phenomena and details of the contact geometry. The lack of

correlation between laboratory explosion tests and the experience with recovery boiler explosions is a good example of this problem.

CONCLUSIONS

A salt bridge model, which takes into account mass transfer of components between the two fluids, was developed and proved successful in interpreting the effects of composition on explosiveness in the smelt-water system. The model is based on the fact that the main smelt constituent, sodium carbonate, is not soluble in water at temperatures approaching the critical point, while certain other constituents are soluble. The soluble substances allow a substantial increase in the critical temperature of the solution. This in turn shifts the range of contact interface temperatures (between the spontaneous nucleation temperature and the critical temperature of the coolant) at which spontaneous explosions can occur to higher values. The model was able to provide a semi-quantitative interpretation of the available data on smelt-water.

At least in the smelt-water system, laboratory scale explosion experiments have limited predictive capability for the behavior in industrial scale systems. Experiments without external triggers show great sensitivity to minor composition effects and to system disturbances. Experiments with external triggers merely shift the industrial scale problem to one of trying to predict the magnitude of the triggering impulses. The large scale experience with smelt-water explosions in recovery furnaces is not easily interpretable and is not in accordance with the experiences in laboratory explosion experiments.

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Table 1. The Effect of Varying the Concentration of Salt in the Smelt on Laboratory Test Explosions.

Percent Salt in Smelt	Percent Sodium Carbonate in Smelt	Number of Tests Made	Number of Tests Causing Explosions	Percent of Tests Causing Explosions
0.0	100.0	5	0	0.0
1.0	99.0	1	0	0.0
2.0	98.0	1	0	0.0
3.0	97.0	2	0	0.0
4.0	96.0	1	0	0.0
5.0	95.0	7	0	0.0
6.0	94.0	6	2	33.3
7.0	93.0	7	5	71.4
8.0	92.0	1	1	100.0
9.0	91.0	1	1	100.0
10.0	90.0	18	18	100.0
15.0	85.0	1	1	100.0
20.0	80.0	1	1	100.0
30.0	70.0	1	1	100.0
50.0	50.0	1	1	100.0
80.0	20.0	1	1	100.0
100.0	0.0	1	1	100.0

Table 2. Effect of Sodium Sulfide Concentration on Laboratory Test Explosions

Na ₂ S (wt.%) in Smelt	Explosion Result	References
8.9	None	2
15.9	None	2
19.1	None	2
22.9	None	3
25.0	Moderate	3,4
27.5	Violent	3
30.0	Violent	3,4

Table 3. Effect of Sodium Hydroxide Concentration on Laboratory Test Explosions (1,2)

NaOH (wt.%) in Smelt	% Test Causing Explosions	Explosion Result
0.0	0	--
3.0	0	--
5.0	0	--
8.0	0	--
10.0	25	Violent Deep
12.0	100	--
15.0	100	Very Violent Deep
100.0	100	Violent Surface

Table 4. Effect of Smelt Composition on Dissolving Tank Explosions

Smelt Composition (wt.%)			Explosion Result	NaCl Equivalence
Na ₂ S	NaCl	NaOH		
8.9	0	2	None	4.60
8.9	2	0	None	5.20
15.2	0	1	Mild	6.16
15.5	0	2	Violent Deep	6.98
15.5	2	0	Violent Deep	7.58
19.1	0	1	Violent Deep	7.58
19.1	0	2	Violent Deep	8.28
19.1	2	0	Violent Deep	8.88