SUPERHEATED LIQUIDS
A LABORATORY CURiosITY
AND, POSSIBLY, AN INDUSTRIAL CURSE

Part 3: Discussion and Conclusions

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MOLTEN SALT-WATER EXPLOSIONS

ANDERSON AND ARMSTRONG (1973) injected water into molten sodium chloride under carefully controlled laboratory conditions (Figure 19). The vertical force resulting from the explosion was monitored with a transducer as shown. High speed motion pictures were also obtained. The key results are:

- explosions could begin in the bulk salt or at points on the crucible wall touched by the water jet,
- the water jet was coherent and separated from the salt by a vapor film until the explosion occurred,
- no freezing of the salt was noted,
- there were delay times of a few ms to a few hundred ms between injection and explosion,
- the explosion step developed very rapidly. Even with the highest framing speed (65 μs/frame), the explosion occurred between successive frames.

In a later study, to explore larger scale interactions, water columns were allowed to fall upon a molten-salt surface (Anderson et al., 1975). Surprisingly, no coherent explosions were noted. High speed photographs showed, however, that the coherent water column was always preceded by a few drops of water. As the authors noted: “The contact of these leading water droplets with the salt caused minor explosions of sufficient magnitude to either break the apparatus or reverse the motion of the water column and prevent major contact between the molten salt and water.”

Throughout, we have continued to suggest vapor explosions may occur when the volatile fluid superheats, nucleates, and fragments both the hot and cold liquids thus sustaining and enhancing the violence of the ultimate explosion. Yet Anderson and Armstrong’s careful experiments force us to re-examine this model. Refer to Figure 20 from their paper. This bar graph indicates the important temperature levels of the NaCl-water system. Water at 20°C contacts salt at 1000°C. At the water-vapor film boundary, the temperature is presumably close to 100°C while in the salt-vapor boundary it is between 800 and 1000°C. The calculated interface temperature using a two-slab, perfect-contact theory* is 691°C—a value exceeding the minimum film boiling temperature of 500°C (Henry, 1972). The critical temperature of water is 373°C, and the homogeneous nucleation temperature is ~300°C. These values indicate that liquid-liquid contact should not be possible as the resulting interface temperature would cause immediate film boiling of water and freezing of the salt.

Similar temperature bar-graphs could have been constructed for the titanium-water, smelt-water, and aluminum-water cases described in Part 2. Similar conclusions could also be drawn; how can superheating and homogeneous nucleation processes play a role in such cases?

A valuable observation is provided by Anderson and Armstrong (1973): “Reinspection of the . . . NaCl-H₃O movies show that every explosive case was initiated by an external force which tended to drive the two liquids across the insulating vapor film into near or actual contact with each other.” The external force may be due to instabilities in the film, external causes, etc. However, as noted “(if) the fluids actually come into

*Eq. (11), Part 2.
contact, the theory would predict immediate surface vapor production which, in turn, would inhibit further heat transfer between liquids.

Anderson and Armstrong proposed this "dynamic impact heating model" and indicated that, when the hot and cold liquids are in close proximity, the heat transfer rate may be high enough to vaporize water in a short period of time. This vapor production then causes (somehow) other near contacts and the explosion propagates.

Perhaps there is a critical impacting force. If too small, then, as the liquids approach, the increase in vapor generation opposes the force and the gap widens. On the other hand, for impacting forces greater than the critical value, very close contact may be achieved. Evaporation increases rapidly but may there be a limit to this rate? Kinetic theory suggests that the limit would occur when the flux \( \sim (1/4) \rho v \Delta H_r \). The energy flow into the water is given as

\[
q_{in} = \frac{k}{\delta} (\Delta T)
\]

with \( k \) the average thermal conductivity in the film of thickness \( \delta \). Using the NaCl-H_2O system as an example, when \( q_{in} = q_{asp}, \delta \sim 0.3 \mu m \). If the film thickness should become less than this value, energy is conducted into the bulk water to raise its temperature above \( 100^\circ C \). Should temperature of \( \sim 300^\circ C \) be attained, homogeneous nucleation would result and intense, local shock waves develop. These, in turn, could provide the force to propagate the microevent to a macroexplosion.

The critical impacting force should vary from system to system and should increase as the temperature of the hot fluid increases. Experiments involving impinging drops of a volatile liquid onto a hot surface (preferably liquid) could be of value in testing this hypothesis. Unfortunately, most such experiments have employed small drops with sufficient drag to limit the impact velocity. However, if the hot fluid is only slightly above the homogeneous nucleation temperature of the cold liquid, then a less drastic model may suffice. Waldram et al. (1976) obtained vapor explosions with drops of many organic liquids on hot silicone oil.

**SODIUM-URANIUM DIOXIDE EXPLOSIONS**

To illustrate that vapor explosions are not confined to systems involving water, one need only cite the results obtained at the Argonne National Laboratory where the system molten sodium-molten uranium oxide has been studied. Obviously, these experiments were motivated by concern should a nuclear reactor ac-

![Figure 19: Injection of water into molten NaCl](image-url)

1000 — Initial NaCl temperature
900
800 — NaCl freezes
700 — Instantaneous interface temperature between 1000° NaCl and 100° H_2O
600
500 — Film boiling temperature
400 — Critical temperature of water
300 — Homogeneous nucleation temperature for water
200
100 — Water boils

![Figure 20: Temperatures associated with H_2O-NaCl injection experiments](image-url)
cident in the LMFBR lead to this type of liquid-liquid contact.

The facts indicate that if liquid sodium is injected into molten UO$_2$, vapor explosions are consistently produced (Armstrong et al., 1975; Henry et al., 1974). Sodium temperatures have ranged from the melting point to above 600°C with UO$_2$ temperatures up to 3200°C. Injection velocities varied from 0.35 to 35 m/s.

The important temperatures for this system are shown in Figure 21 (Fauske, 1977) assuming the sodium is initially at 400°C and the UO$_2$ at 3200°C. There are some significant differences between this case and the NaCl-H$_2$O case discussed earlier.

First, the very high temperature required for film boiling indicates that contact between liquid sodium and liquid UO$_2$ would result in nucleate boiling—assuming that sufficient nucleation sites are available. Thus, the problem of heat transfer through a thin vapor sodium film is not present. However, if these two liquids do come into contact, and if boiling is suppressed, the theoretical two-slab interface temperature is only 1082°C; this is below the temperature required for the homogeneous nucleation of sodium, so it would appear unlikely that a vapor explosion could result in a simple contact experiment.

Yet vapor explosions do seem to occur when liquid sodium is injected into molten UO$_2$!

The model proposed by Fauske (1973, 1974) assumes that the injected sodium breaks up (at least partially) to form some small liquid sodium drops. A Weber number criterion of about 10*

\[ W_e = \frac{\rho \cdot V^2 \cdot z}{\sigma} \]

indicates that stable drop radii can be as small as 20 µm. With a drop of this size, the theoretical two-slab interfacial temperature in Figure 21 is not relevant and the drop tries to heat up to the bulk UO$_2$ temperature. When the homogeneous nucleation temperature is reached, it explodes and the local shock waves propagate the reaction by causing further fragmentation. In this model a delay is predicted between injection and explosion and this prediction is confirmed by experiment.

**DISCUSSION AND CONCLUSIONS**

We know superheated liquids exist. In the laboratory they behave as expected from theoretical considerations and disintegrate violently when heated to their superheat limit temperature.

We also know of numerous instances where discrete masses of hot and cold liquids have been contacted (on purpose or as the result of an accident) and where this contact has resulted in an explosion. Of course, we must also admit that in a number of other similar cases contact led to no explosion.

In this paper we have taken a biased position in an attempt to link superheated liquids to vapor explosions. This is a minority position and the field is active and in ferment as new theories and experiments appear and demand to be given their due before any general explanation is accepted. There may, in fact, be no single, universal cause for vapor explosions and each particular situation should then be examined separately. We have rejected this hypothesis since there are too many commonalities in the various events reported. It is true, however, that in various vapor explosions there may be different parameters which assume primary importance in determining if a coherent vapor explosion will occur.

In the past decade, numerous theories have been proposed which do not involve superheated...
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liquids. Most have been rejected as new data accumulate. We discuss the major ideas below and show that few are still viable.

Entrapment/Entrainment Theory. When hot and cold liquids are contacted, fragments of the cold (volatile) liquid are assumed to be entrapped or entrained in the hot liquid (Groenveld, 1972; Brauer et al., 1968). Rapid vaporization results and the hot liquid is dispersed. The resultant large area for heat transfer then leads to an explosion. Variations in this hypothesis consider a crust forming on the hot liquid so that any entrained cold liquid, while vaporizing, develops a high pressure. Rupture, when it occurs, leads to the fragmentation of the hot liquid. Another, similar theory, assumes that the cold liquid is trapped on a wall or bottom by the hot fluid and, as noted above, boils so violently that immediate dispersal of the hot fluid results.

As evidence against the entrapment theory, Anderson and Armstrong (1972b) injected water into molten NaCl and reported that, from high-speed movies, there existed a gas layer “between the two liquids during the injection and remained there until the explosion.” The explosion duration was less than 65 μm and no salt crust formed. There is no evidence of any stray water droplets encapsulated in the molten salt. Also, in all the hydrocarbon-water tests where the cryogen was spilled on water, there was no indication that entrapment or entrainment occurred.

One method suggested for entrainment of cold liquid is that it would be drawn through voids in the surface crust as the interior hot liquid cools and contracts. This explanation does not seem viable since explosion-fragmentations have also been observed with hot mercury (which did not solidify) and with molten bismuth (which expands rather than contracts upon freezing). Finally, in some experiments (Witte et al., 1973), where there were several molten metal fragments near each other, a vapor explosion or fragmentation in one would trigger like events in those nearby. This behavior is not indicative of an entrapment.

Weber Instability Theory. Another theory often mentioned as a partial explanation for vapor explosions is the hydrodynamic instability associated with the jetting of one liquid into another under conditions where inertial forces exceed surface tension forces. In such cases there will be a spontaneous fragmentation of the jetted stream into smaller fragments. The increase in area has been cited as a possible trigger to initiate rapid vapor production, further fragmentation, and finally an explosion.

While this instability is well known and may occur in some experiments, vapor explosions have been observed in many cases where this phenomenon could not play a part. No Weber instability was evident in the high speed movies of Anderson and Armstrong (1972b) when they jetted water into molten NaCl. Also, the spill tests in the cryogen-water studies could have had no initial fragmentation. Witte et al. (1970, 1973) conclude that, even if the critical Weber number were exceeded, and some break-up has occurred, this process has little or no effect on the probability of a vapor explosion occurring at the same or at a later time. McCracken (1973) discounts any Weber number effect as his experiments with injection of molten metals into water indicated a sharp transition between explosions and no-explosions as the coolant temperature was varied over only a few degrees. Such a variation would have little effect on Weber instabilities.

Henry and Armstrong (1976) studied the reaction of single drops of organic liquids in water when exposed to shock waves generated by an exploding wire. Even though the conditions were such as to greatly exceed the drop’s critical Weber number for a few μs, no drop fragmentation was noted. Thus, extreme local interactions would not seem to be important in fragmenting drops via a Weber instability.

It is, therefore, now generally accepted that this hydrodynamic effect, though it may occur in certain experiments, plays no major important role in vapor explosions.

In this paper we have taken a biased position in an attempt to link superheated liquids to vapor explosions. This is a minority position and the field is active and in ferment as new theories and experiments appear and demand to be given their due before any general explanation is accepted. There may, in fact, be no single, universal cause for vapor explosions and each particular situation should then be examined separately.

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Transition Boiling. In this hypothesis, the cold liquid begins to vaporize in the film boiling regime, but as the temperature difference between the two liquids decreases, the Leidenfrost point is reached and transition boiling begins. In this regime, there is some liquid-liquid contact as the vapor bubbles form and leave; if the cold liquid is sub-cooled, the bubbles may even collapse as the turbulence in the interface region increases. It is further postulated that the violence of boiling in this regime is sufficient to fragment the liquids so as to expose extensive area for heat transfer; if this fragmentation is sufficient, an explosion results.

This explanation was first proposed by Swift (1965) and is discussed in detail by Stevens and Witte (1972) and Witte et al. (1970). But, in later papers (Witte and Cox, 1971; Witte et al., 1973), the transitional boiling hypothesis is rejected since the oscillations associated with this regime are in the ms time scale range, much too long unless the very initial contact between liquids is all that is necessary for rapid fragmentation. Brauer et al. (1968) saw no evidence of violent boiling prior to explosions when high speed photographs were studied, but McCracken (1973) feels that the sensitivity of metal-water explosions to water temperature is in agreement with the transition boiling hypothesis.

A number of analyses have been made to predict the temperature difference between fluids when the minimum flux is attained and transition boiling could begin (Henry, 1972; Berenson, 1961; Spiegler et al. 1963; Baumeister and Simon, 1973; Sciance and Colver, 1970; Bell, 1967). Some are based on hydrodynamic and heat transfer models while others are related to thermodynamic stability. No correlation fits all the data with much accuracy; of course, there is a wide spread in some experimental measurements and this indicates that probably there exists a temperature range over which there is a transition from film to transitional boiling. It is also interesting to note (Baumeister and Simon, 1973) that for organic liquids or low-boiling inorganic cryogens, a good estimate of the Leidenfrost point is often given by the hot surface temperature, \( T_h \), where \( T_h \) is the expected value where for the cold liquid, \( (dP/dV) \tau = 0 \). This is the same criterion introduced in Part 1 to obtain the superheat-limit temperature for pure components.

Most investigators now reject the transition-boiling hypothesis as the major cause of vapor explosions. It is granted that in this boiling regime, the interactions at the surface are rather violent and chaotic; however, this wetting/vaporization/wetting cycle is believed to operate on too long a time scale to cause the very rapid phenomenon of vapor explosions. Also, no one has noted the onset of transitional boiling before a vapor explosion occurred. Rather, there is sometimes a stable film boiling process which, for some reason, ceases, the film collapses very fast and an explosion follows almost simultaneously.

Chemical Reaction Theory. Basically, this concept envisages a rapid (usually exothermic) chemical reaction occurring at the interface. No evidence is available to suggest this is a viable concept.

Inertial Theory. This model is the most difficult to describe in simple terms. A hot and cold liquid are assumed to contact over a limited surface area. Some vapor is formed in the cold but volatile liquid. This vapor film begins to grow but is restrained by the inertia of the bulk liquid phase. The pressure rises. The expansion, while slow initially, accelerates and the bounding liquid is forced away from the interface. The inertial movement of this liquid continues even as the pressure of the vapor drops—and, in fact, can proceed so far as to produce a very low pressure in the vapor film. The bounding liquid then springs back and at this point there are several different theories, all of which predict further oscillations leading eventually to violent gross mixing, fragmentation, and explosive boiling.

It is difficult to find compelling reasons either to reject or accept the inertial theory. It may, in fact, be integrated into the superheat-limit theory by providing the mechanism to bring the hot and cold liquids into contact (or near contact).

Board et al. (1974) suggest a somewhat similar concept but they propose that upon film collapse a
jet of liquid is driven across the thin vapor film; fragmentation that results leads to a repeating chain mechanism that is noted in its entirety as an explosion.

CONCLUDING REMARKS

BOARD AND CALDAROLA (1977) have reviewed the extensive data of importance to fuel-coolant interactions in fast reactors and, in addition, discussed much of the available information concerning molten metal-water explosions. From this detailed study, they conclude that energetic vapor explosions always involve three sequential stages:

- a relatively quiescent mixing phase where there is formed a coarse mixture of the hot and cold liquids. The “dwell” time corresponds to this period. The hot and cold liquid fragments are believed to be separated by a vapor film.
- a trigger of short duration (which may be highly localized) that leads to the collapse of the vapor film.
- a propagation step where the interaction rapidly spreads throughout the mixture.

One may infer that vapor explosions could be prevented by eliminating either or both of the first two steps. As stated by Board and Caldarola, “. . . it is difficult to determine the true explosive potential of a material pair from experiments in which the initial mixing or triggering conditions are left to chance”.

Few careful experiments have been carried out to study each of these steps. The R-22 studies by Anderson and Armstrong (1977) do, however, provide some support.

In our work with light hydrocarbons on water, we have possibly neglected the importance of having an initial coarse mixing step and emphasized only the trigger—which we have associated with the cold cryogen film adjacent to the water attaining the superheat-limit temperature. In our direct pours of light hydrocarbons into water, there may indeed have been significant mixing and fragmentation prior to any trigger. But, we also have contacted LNG by tangentially skimming the cryogen over the surface and, even here, we have noted vapor explosions in the same compositional ranges as those found in direct pour experiments.

Also, we have possibly been in error in neglecting the mixing step as being of prime importance because we have been able to obtain or prevent vapor explosions by relatively small changes in either the composition of the LNG or the initial water temperature. We assumed that such minor changes would have an insignificant effect on the mixing step and only affect the trigger. An active or inactive trigger could be explained well by superheated liquid theory for either variations in LNG composition or water temperature. As pointed out by Anderson (1977), however, the LNG composition and water temperature effects may also affect the film boiling characteristics of the system and this effect could be more important than that involving homogeneous nucleation of a superheated liquid. This critique is important because if superheating plays no real role in the triggering step, then one must (as Anderson states) “recognize the possibility of an explosion in a system where a gas or vapor film is present even when the interface or hot liquid is below the homogeneous nucleation temperature”.

More definitive research is needed to clarify the mechanism(s) for vapor explosions. It is, nevertheless, important that any acceptable theory should consider all the facts and experimental data. We still believe that homogeneous nucleation of superheated liquids plays an important role and may even explain the old Blacksmith’s adage as told by Dr. Beall:

“When you spit on a piece of red hot iron, it dances around in a little ball. If you hit the ball with your hammer, the explosion will throw the hammer over the barn and blow a hole in the iron!”

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REFERENCES


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