

EXPLOSIVE-VAPOR FORMATION

A Thesis

Presented to
the Faculty of the Department of Mechanical Engineering
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Mechanical Engineering

by
James Edward Bouvier

January, 1970

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ABSTRACT

The vapor explosion, resulting from the very rapid heat transfer process that can take place when a hot, molten material comes into contact with a cooler liquid (which has a boiling point much less than that of the molten material), was analytically investigated. Fragmentation or particle atomization was shown to be a necessary prerequisite for vapor explosions. Also, the various mechanisms of fragmentation of molten materials which have been proposed were critically examined and compared to available data from controlled experiments and recorded explosion disasters.

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CHAPTER I

INTRODUCTION

The reaction that can take place when an extremely hot or molten material comes into contact with a cooler liquid (which has a boiling point much less than that of the molten material), is of a destructive nature capable of destroying life and property as easily and with as much violence as the detonation of a high explosive. Recorded incidents indicate that industrial situations subject to this kind of explosion are limited only by the presence of a molten material with a cooler liquid being in close proximity. Such explosions have unfortunately become common in the steel and paper industry and repeated occurrences have stirred interest in the need for a solution to the problem. One such accident was recorded by the Denver Post, February 14, 1966.^{1*}

Foundry Blast - On February 14, 1966, a metal-water reaction occurred at the Western Foundries Company plant southeast of Longmont, Colorado. "...the men had just poured 3,000 pounds of molten steel from an electric furnace into a tile lined ladle - a big bucket from which the steel is then poured into molds to make castings. A cable on an electric crane holding the ladle broke, dropping the hot steel into a water filled pit below." The result was a violent explosion injuring three men and tearing a 20' x 30' hole in the roof of a 60' x 200' building. The explosion was heard three miles from the foundry and shook much of southeast Longmont.

*Numbers in superscript refer to references.

A similar accident occurred at the Mallory-Sharon Titanium Corporation.²

Mallory-Sharon Incident - On June 11, 1954, a titanium melting furnace, water cooled, exploded at the plant of the Mallory-Sharon Titanium Corporation, Niles, Ohio (15 miles northwest of Youngstown, 50 miles southeast of Cleveland). Four men were killed, five others seriously injured, and property damage of about \$30,000 was incurred in this accident.

Nuclear reactors are susceptible to metal-coolant explosions during accidental power excursions. The overheated fuel core material furnishes the molten metal and the reactor coolant provides the second required ingredient, a cooler liquid (which has a low boiling point relative to that of the fuel material). Here, because of radioactive materials inherent to the operation of a reactor, the consequences of an explosion are amplified many times.²

Borax I Reactor - On July 22, 1954, the Borax I reactor at the National Reactor Testing Station at Arco, Idaho was deliberately destroyed in a reactor safety test, primarily designed to examine the effect of nuclear transients. A power excursion lasting about 30 milliseconds was observed, reading a peak power of 19,000 megawatts, with a total energy release of 135 megawatts-seconds. "The power excursion melted most of the fuel plates. The pressure resulting from the molten metal in contact with the reactor water burst the reactor tank ($\frac{1}{2}$ inch steel) ... was probably higher than 10,000 psi... . The sound of the explosion at the control station half a mile away, was comparable to that resulting from the explosion of 1 to 2 pounds of 40 per cent dynamite."

In each instance, under varying circumstances, a molten material fell, dropped, or spewed into a mass of cooler liquid to produce an explosion. Unlike the causes of most types of explosions, the complex mechanisms triggering this kind of reaction are not completely understood, and thus the prevention of such incidents is difficult.

During recent years there has been relatively little work done, experimentally or analytically, on the mechanics of non-chemical, metal-water explosions. The majority of the experimenters who have pursued an active interest in the problem have not corroborated their data with others and have been satisfied to simply offer their own theories, irrespective of parallel or contradictory work already established. There is then, a strong possibility that there are some common denominators in the works and results of the various experimenters that, when correlated, would lead to a clearer definition of the metal-water explosion and its cause. This would ultimately allow insight into the control and prevention of such explosions.

Therefore, it is the purpose of this study to investigate: (1) the various physical conditions leading to such industrial accidents as those described previously, and (2) the results of those who have researched the metal-water reaction phenomenon, in the hope of at least identifying the controlling mechanisms. The investigation was entirely analytical. The sub-mechanisms that lead to the phenomenon of the vapor explosion that have been postulated were examined

critically with respect to the available information from both records of accidents and controlled experiments.

CHAPTER II

PRELIMINARY INVESTIGATION

When considering an explosive incident in which molten and a coolant are involved, there are two cases which we should consider. They are:

1. Chemical Reaction - An extremely rapid chemical reaction between the molten globule and the coolant causes an explosion.
2. Vapor Explosion - A rapid generation of vapor as a result of the heat transfer from the globule to the coolant results in an explosion.

Some investigators theorize that molten metal reacts chemically with water to form hydrogen and that it is the ignition and combustion of the hydrogen gas which ultimately produces the explosion. However, molten sodium carbonate and water do not react to form hydrogen, yet Sallack³ produced explosions by discharging this molten material (sodium carbonate) into water.

Still others postulate that a chemical reaction takes place between the molten material and water forming a metal oxide. Thus it is the heat generated by this reaction which produces the explosion. Metals such as zirconium and zirconium base alloys will react in water to form a metal oxide if the initial temperature of the metal is high enough (1800 - 2000 °C). Experiments conducted by Higgins⁴ indicated that violent explosions and extensive chemical

reactions can be obtained from the quenching of molten zirconium in water. However, there have been experiments conducted to show that a tremendous explosion can occur when quenching a molten metal in water with little or no chemical reaction present. Elgert and Brown⁵ discharged molten aluminum at 1400 °F into water in a closed container and analyzed the gases following the violent explosion. In tests in which a peak pressure of 23,000 psi was registered, they found that only 0.2 per cent of the aluminum had reacted chemically with water to produce aluminum oxide. They also determined reaction times of 1 to 3 milliseconds for development of peak pressures. This reaction time for the explosion corresponds to the times measured by Higgins for similar explosions. It seems then, that even though a chemical reaction can take place during the explosive vapor formation, a purely mechanical mechanism is capable of producing the explosion alone. The chemical reaction appears to augment the explosion while the mechanical mechanism (rapid generation of vapor) dominates the energy contribution.

It should also be pointed out that Sallack³ conducted a series of tests in the dark. He dropped molten sodium carbonate into green liquor. Similarly, Long⁶ dropped molten aluminum into water at night. Neither investigator noted any evidence of a flash when the explosions took place. The presence of a flash would have indicated the ignition of hydrogen gas evolved from a chemical reaction.

During an investigation of metal-water reactions (drop tests), Long found that explosions did not always occur, depending on the volume of coolant into which the metal was dropped.⁶ It seems reasonable to assume that there may be some value of the molten metal to coolant ratio beyond or under which an explosion will not take place. Long, during his investigation, dropped molten aluminum at various temperatures into a tank of water. The technique that Long used in his drop tests will be discussed in more detail in Chapter III. The depth and lateral dimensions of the water tank were varied to determine which parameters were critical. Several cases from these tests were selected in order to calculate the volume of metal to volume of coolant ratio. These results are presented in Table 1.

As denoted in the table (by a shaded triangle) there are two cases which have the same metal to coolant ratio and have the same initial metal temperature. However, in one of these cases there was a definite explosion recorded and in the other case there was no explosion. Therefore, there must be some other controlling parameter which affected the metal-water explosion. The only other parameter involved which is not the same for both cases is the depth of the coolant tank (as measured from the water surface to the container bottom).

For a given initial metal temperature and depth of coolant (i.e., 670°C and 3 inches) the volume of metal/volume

Table 1 METAL/COOLANT RATIO

MASS OF METAL (LB)	TEMP OF METAL (°C)	DEPTH OF H ₂ O (IN)	V _w (FT ³)	TANK DIMENS (IN SQ)	V _m (FT ³)	V _m /V _w	EXPLOSION
50 lbm **	670	3	0.067 ↓ 1.000	6.5 ↓ 24.0	0.298	4.400 ↓ 0.298	yes
	670	6	0.140 ↓ 2.000	6.5 ↓ 24.0	0.298	2.120 ↓ 0.150	yes
	670	6	7.900	48.0	0.298	0.037	no
	▲ 750	10	0.240 ↓ 3.30	6.5 ↓ 24.0	0.298	1.240 ↓ 0.090 ▲	yes
	750	6	0.50	12.0	0.298	0.596	yes
	▲ 750	20	0.49 ↓ 6.60	6.5 ↓ 24.0	0.298	0.608 ↓ 0.040 ▲	no
100 ***	2840	18	10.4		0.208	0.020	yes

V_w - Volume of water

V_m - Volume of metal

** See Reference 6

*** See Reference 7

of coolant ratio can be varied over a wide range and still produce an explosion. However, if the depth of coolant is increased past a critical point (the critical point will be discussed in more detail in Chapter III) for a given initial metal temperature then there will be no explosion regardless of the lateral dimensions of the coolant tank. It appears that the depth of coolant in the tank is a strong influencing parameter in explosive vapor formation.

Metal-water reactions result in an explosion due to the extremely high heat transfer rates from the molten metal to the coolant. These rates can be estimated by examining known data from an actual explosion. For instance, after an investigation of the Quebec incident⁷ (during which approximately 100 pounds of molten steel was accidentally spilled from a ladle into a tank of water), it was found that 100 pounds of molten steel heated to a temperature of 2840 °F could have converted no more than 35 pounds of water to steam. Assuming an elapsed time for the explosion of 3 milliseconds, the total heat transfer rates can be calculated.

$$35 \text{ pounds of water; } h_{fg} = 970 \frac{\text{BTU}}{\text{lbm}}$$

$$Q = 970 \times 35 = 33,950 \text{ BTU}$$

$$\text{Elapsed time } 0.003 \text{ seconds}$$

$$\frac{Q}{t} = \frac{33,950}{3 \times 10^{-3}} = 11.316 \times 10^6 \frac{\text{BTU}}{\text{sec}}$$

$$\frac{Q}{\text{hr}} = (11.316 \times 10^6 \text{ BTU/sec}) \times (3600 \text{ sec/hr})$$

$$\frac{Q}{\text{hr}} = 4.074 \times 10^{10} \frac{\text{BTU}}{\text{hr}}$$

Surface area of a 100 pound mass steel sphere
assuming a single sphere - 1.18 ft^2

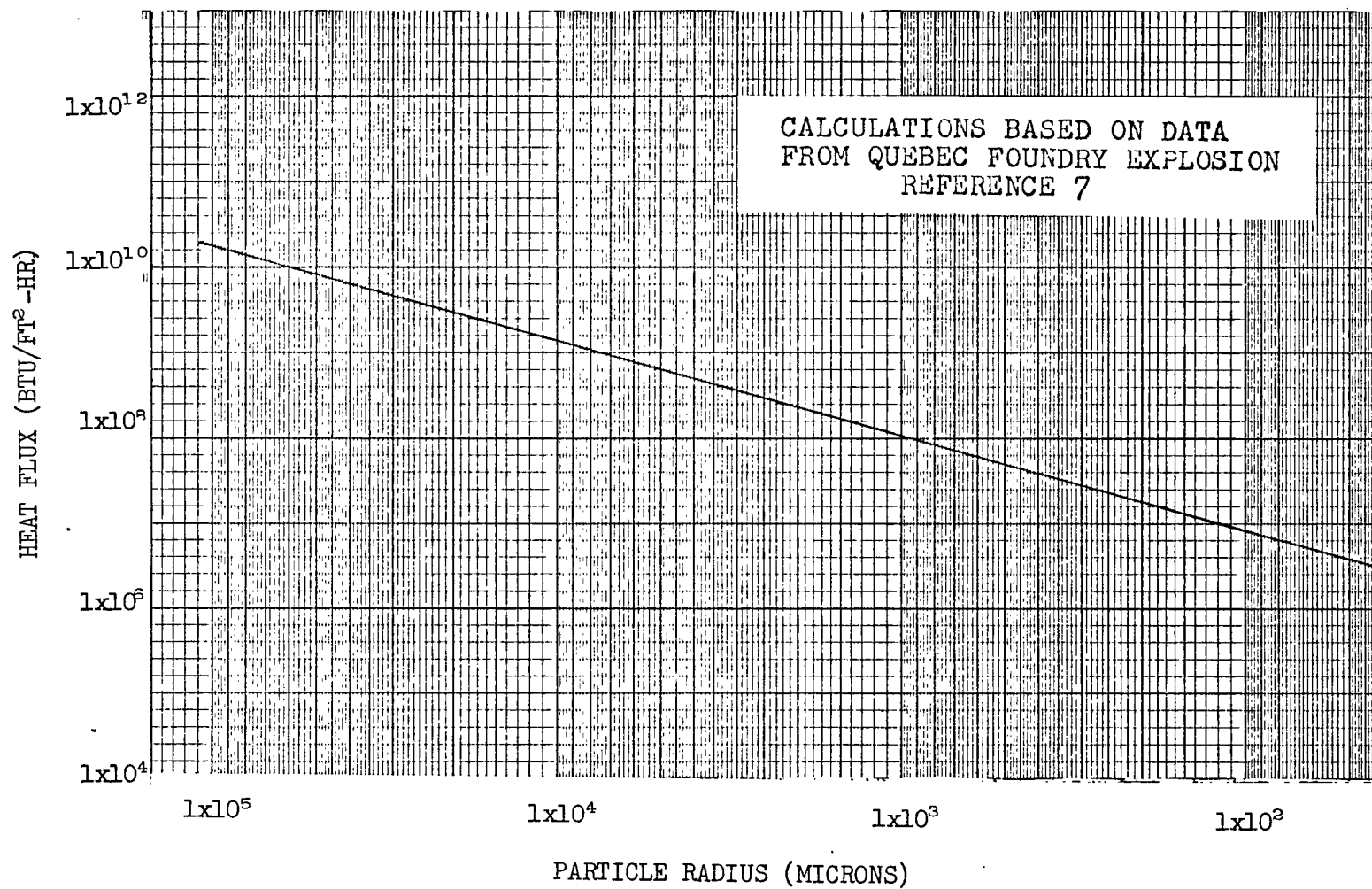
$$\therefore (4.074 \times 10^{10} \text{ BTU/hr}) / 1.18 \text{ ft}^2 = 3.44 \times 10^{10} \frac{\text{BTU}}{\text{hr-ft}^2}$$

Total heat transfer rate $3.44 \times 10^{10} \text{ BTU/hr-ft}^2$

This is not a reasonable heat transfer rate for a boiling process (10^6 BTU/hr-ft^2). One way to reduce the calculated total heat transfer rate is to increase the exposed surface area of the molten metal.

By assuming a spherical shape for simplicity, heat transfer calculations were made based on an increasing number of spheres making up the total mass of 100 pounds of steel (increasing the number of particles increases the total exposed surface area but decreases the total heat transfer rate). These calculations are plotted in Figure 1. The results indicate that as the number of particles is increased the heat rate decreases until finally for a particle radius of approximately 100 microns, the total heat transfer rate begins to approach a reasonable range (10^6 BTU/hr-ft^2). This tends to indicate that in order to

Figure 1 HEAT FLUX vs. PARTICLE RADIUS



produce the high heat rates which are known to accompany metal-water explosions, the metal mass must experience some manner of fragmentation. This fragmentation or particle dispersion appears to be a requirement for explosive metal-water reactions.

Experiments which have been conducted at Aerojet General also indicate that the metal-water explosion is a strong function of particle size. Higgins⁸, who conducted the experiments, was seeking a relationship between the percentage of chemical reaction of the metals tested (molten uranium and zirconium alloys) and water versus particle size. The percentage of oxidation of the residue following each test was obtained from measurements of oxide film thickness and average particle size.

Even though it has already been established that a chemical reaction is probably not the dominating mechanism in the explosive vapor formation phenomena, it is common knowledge that oxidation of the hot metal would take place as heat is transferred from the metal to the water producing steam. Also, since the relative violence of each of the reactions produced was recorded along with the average metal particle size, the data from the experiments is useful in this investigation.

Higgins first attempted to produce explosions by discharging molten metal in a one-inch diameter stream into a tank of cold water. The metal was dropped from a heated

graphite crucible located 19 inches above the surface of the water. This technique produced no explosions using various metals at several temperatures. Next, a blasting cap (No. 6 containing 0.66 grams of high explosive) was located 5 inches below the surface of the water in the tank and aligned directly beneath the discharge hole of the graphite crucible. A sensing device triggered the blasting cap when the molten metal was in close proximity to the explosive. This resulted in an intentional fragmentation of the molten metal. Approximately 800 calories of energy were added to the metal due to the blasting cap. In almost every instance it was found that the fragmentation caused by the blasting cap greatly enhanced the reaction (vapor explosion). The relative violence of each reaction was described as; no explosion, slight explosion, moderate explosion, heavy explosion, or very heavy explosion. Out of 12 experiments where very heavy explosions were recorded, 9 had an average metal particle radius less than 100 microns. In addition, there was very little reaction recorded for those experiments involving an average particle radius greater than 700 microns. This is reasonable evidence that fragmentation is required to produce vapor at the explosive rates demonstrated in the metal-water reactions. The question now seems to be by what mechanism is the molten metal mass broken up or dispersed into fine particles when it is not initially in that form.

In general, in a nuclear reactor, clad fuel elements are used. The fuel element is surrounded by a shell of cladding metal. During an accidental power excursion of the reactor, the fuel element could overheat and eventually melt causing a pressure to build up on the inside of the cladding shell due to thermal expansion. If the cladding material were to rupture, the fuel material would spray out into the coolant surrounding the fuel core. Thus, the required prerequisite for a vapor explosion, fragmented or atomized molten metal, is present. It is not hard to conceive of an accident like this occurring. Higgins⁹ suggests that "...the possibility of this occurring would be lessened if the cladding metal had a lower melting temperature than the fuel core or if the coefficient of thermal expansion of the fuel was small."

Fragmentation of molten metal in a nuclear reactor was found to be conceivable, but how could a 100-pound mass of molten steel (foundry accident⁷) falling into a trough of water be broken into fine particles, much less particles the size required for the vapor explosion (less than 200 microns in diameter)?

Recently, there have been several theories offered to explain this fragmentation process and some experimental work done to substantiate those theories. However, there has been very little correlation between the work of the experimenters. Given below is a compilation and a brief

description of those theories which have been offered.

Encapsulation - Water is trapped between the globule and the bottom of the container into which it fell. The water vaporizes and rapidly expands, blowing the globule apart.

Violent Boiling - The tremendous forces generated by the transition from film to nucleate boiling of the coolant overcomes the surface tension of the globule and tears it apart.

Shell Theory - Water or coolant trapped inside the falling globule is suddenly vaporized due to the heat transferred from the globule. The expanding vapor then blows the globule apart.

Weber Number - By definition, the globule either exceeds the critical size or the critical velocity while in motion through the coolant. In either case, the inertial forces exerted on the globule by the coolant overcomes the surface tension of the globule and tears it apart. The value of the critical Weber Number has to be determined experimentally.

CHAPTER III

FRAGMENTATION MECHANISMS

ENCAPSULATION

One of the earlier theories for the fragmentation of a molten metal mass being discharged into a coolant was proposed by Long⁶ at the Alcoa Research Laboratories. Long's work was experimental and based on a series of aluminum drop tests. "The procedure consisted of suspending a crucible containing a weighed amount - usually 50 pounds - of molten, commercially pure aluminum above a container partially filled with water. The metal was poured into a preheated crucible, the crucible taken to the test cell and the test set up. When the metal had cooled to the desired temperature, a remotely operated tripping mechanism lifted the plunger and stopper and the metal flowed through the tap hole in the bottom of the crucible into the water." Long noted that under certain conditions the molten aluminum blob falling into the water tank produced a violent explosion. However, when a steel grid was placed over the top of the water tank, to prevent the aluminum from entering as a blob intact, there was no explosion. From his work Long concluded that the molten aluminum must enter the water tank and reach the bottom of the container intact and with enough surface area to trap water between the metal and the container surface. Long also noted that the

application of certain coatings to the inside bottom of the water container prevented explosions from occurring. This supports Long's idea that the explosion takes place on the bottom of the container rather than during the flight of the metal mass through the water.

Higgins, while doing research at Aerojet-General on the reaction of metals and water reviewed the work which Long had done and concluded⁹ "...in the Alcoa tests on molten aluminum, dispersion sufficient to cause a self-sustaining violent reaction probably was produced as follows:

- 1.. The large molten blob fell through the water and came to rest on the bottom of the tank, trapping some water between the blob and the tank.
- 2.. The entrapped water was flashed into steam by the molten metal. The steam, being restrained by the inertia of the blob, was superheated and expanded further.
- 3.. The blob finally gave way under the pressure of the steam pocket and was broken into small particles, thus exposing fresh, unprotected metallic surfaces to the steam. These clean, oxide free surfaces were readily attacked by the steam, generating heat and liberating hydrogen.

4. If the exposed surface was great, sufficient heat and gas would be generated to further break up the metal, exposing new surfaces. This would then be a self sustaining reaction.

The conditions which must be met in order to produce this sequence of events are: (1) the molten blob must be large enough to trap a pocket of water and afford some confinement, and (2) the molten metal must reach the bottom with a sufficient reserve of heat to generate a quantity of steam and still remain in the molten state." Although Higgins seemed to have given an accurate description of the fragmentation mechanism, he described the ultimate explosion as being caused by a chemical reaction rather than a steam explosion. However, it has been shown generally that a chemical reaction does not contribute the major portion of energy to explosive vapor formation.

Long⁶ noted in his experiments that for a given initial molten-metal temperature, drop height and depth of water in the water tank, violent explosions were apparent. However, when the depth of the water was increased past a critical point (holding all other variables constant) there was no explosion. To again produce an explosion Long had only to increase the initial temperature of the molten metal prior to the drop. This information indicates that

if the water is too deep or the temperature of the metal prior to the drop is too low or both, then the metal does not fragment and there is no explosion. For as soon as the metal temperature drops below its melting point (prior to contact with the bottom of the container) the mass would no longer possess the pliable characteristics necessary to deform properly and trap the water on the container bottom. Long experimentally determined several water depths and corresponding initial metal temperatures for which explosions did and did not occur. This data is summarized in Table 2. If an explosion occurred for a pair of conditions given in the table, it must be assumed that the aluminum in the water tank was above its melting point at that water depth. It seems reasonable to assume then that if the transient cooling rate of the molten metal blob could be calculated, the initial metal temperatures and coolant depth could be estimated at which an explosion would or would not occur.

The following model was used in the velocity and heat transfer calculations. For simplicity, the shape of the metal mass was assumed to be spherical. The velocity of the sphere at the surface of the coolant was based on the height above the surface from which it was dropped (4 feet) and calculated by the techniques of physics neglecting air resistance. At the surface of the coolant a discontinuity was assumed, the effects due to impact were neglected. Therefore, the velocity equation was based on the

WATER DEPTH*	INITIAL METAL TEMPERATURE		
	670 °C	750 °C	900 °C
3 inches	YES	YES	YES
6 inches	YES	YES	YES
10 inches	NO	YES	YES
20 inches	NO	NO	YES
30 inches	NO	NO	NO

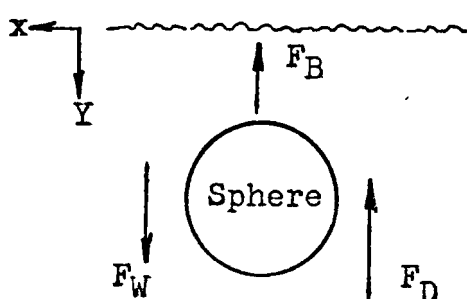
YES - INDICATES THAT THERE WAS AN EXPLOSION

NO - INDICATES THAT THERE WAS NO EXPLOSION

* - DISTANCE MEASURED FROM WATER SURFACE TO
CONTAINER BOTTOM

Table 2 INITIAL METAL TEMPERATURE
VERSUS WATER DEPTH

sphere starting at the surface of the coolant with the displacement equal to zero and the initial velocity equal to that velocity achieved from the four-foot drop.



F_B - Buoyant Force

F_D - Drag Force

F_W - Weight of Sphere

Y_0 - Initial Displacement

$\dot{Y}_0$ - Initial Velocity

$$Y_0 = 0$$

$$\dot{Y}_0 = 16 \text{ ft/sec}$$

The following equation was written and solved for velocity and displacement as a function of time, but for the displacements (depth of coolant) being considered here the velocity was very nearly constant..

$$\ddot{Y} + \left[\frac{C_D A_E \dot{Y}^2}{2(4.189) r^3 \sigma} \right] + \left[\frac{-\sigma + \rho}{\sigma} \right] g = 0$$

Where:

A_E - effective area of sphere

r - radius of sphere

σ - density of metal

C_D - drag coefficient

ρ - density of coolant

g - acceleration of gravity

The transient cooling rate of the sphere was calculated by using Newton's homogeneous cooling (uniform temperature throughout the sphere) equation.¹⁰

$$-c\rho VdT = hA_s(T-T_\infty)d\theta \quad (1)$$

Where:

c - The specific heat of the sphere

ρ - Density of the sphere

V - Volume of the sphere

T - Temperature of the sphere (assuming uniform temperature)

A_s - Surface area of the sphere

dT - Temperature change in time $d\theta$

h - Heat transfer coefficient

T - Temperature of water (assumed constant)

After separation of variables, equation (1) becomes

$$\frac{d(T-T_\infty)}{(T-T_\infty)} = \frac{-hA_s d\theta}{c\rho V} \quad (2)$$

After integration of equation (2)

$$\int_{T_o}^T \frac{d(T-T_\infty)}{(T-T_\infty)} = \int_0^\theta \frac{-hA_s d\theta}{c\rho V} \quad (3)$$

$$\ln \left\{ \frac{T-T_\infty}{T_o-T_\infty} \right\} = \frac{-hA_s \theta}{c\rho V} \quad (4)$$

$$\frac{T-T_\infty}{T_o-T_\infty} = e^{-\left[\frac{hA_s}{c\rho V} \right] \theta} \quad (5)$$

Thus,

$$T_{\text{sphere}} = (T_o-T_\infty) \exp \{ -(hA_s/c\rho V)\theta \} + T_\infty \quad (6)$$

Heat transfer coefficients (h) of 3000 and 7500 BTU/ft²-hr-°F were used to evaluate equation (6). The results of the solutions to the equations using each of the heat transfer coefficients are plotted versus water depth (obtained from velocity equation) in Figure 2. The dotted line represents the melting point of aluminum. These results show that using the lower value of heat transfer coefficient (h) none of the data correlated with Long's experiments, and using the higher value of heat transfer coefficient (h) only the case at 670 °C (refer to Table 2) correlates with Long's experiments. This data is so far from a complete correlation with Long's data that a more accurate solution (i.e., non-homogeneous cooling) is not warranted without more accurate information on the heat transfer coefficient and the complex boiling phenomena which is taking place at the surface of the metal sphere. This discrepancy in correlation between the calculated values and Long's data could possibly be in the selection of the simplified model (sphere), using a constant heat transfer coefficient for each metal temperature, or in the assumption of the fragmentation mechanism itself.

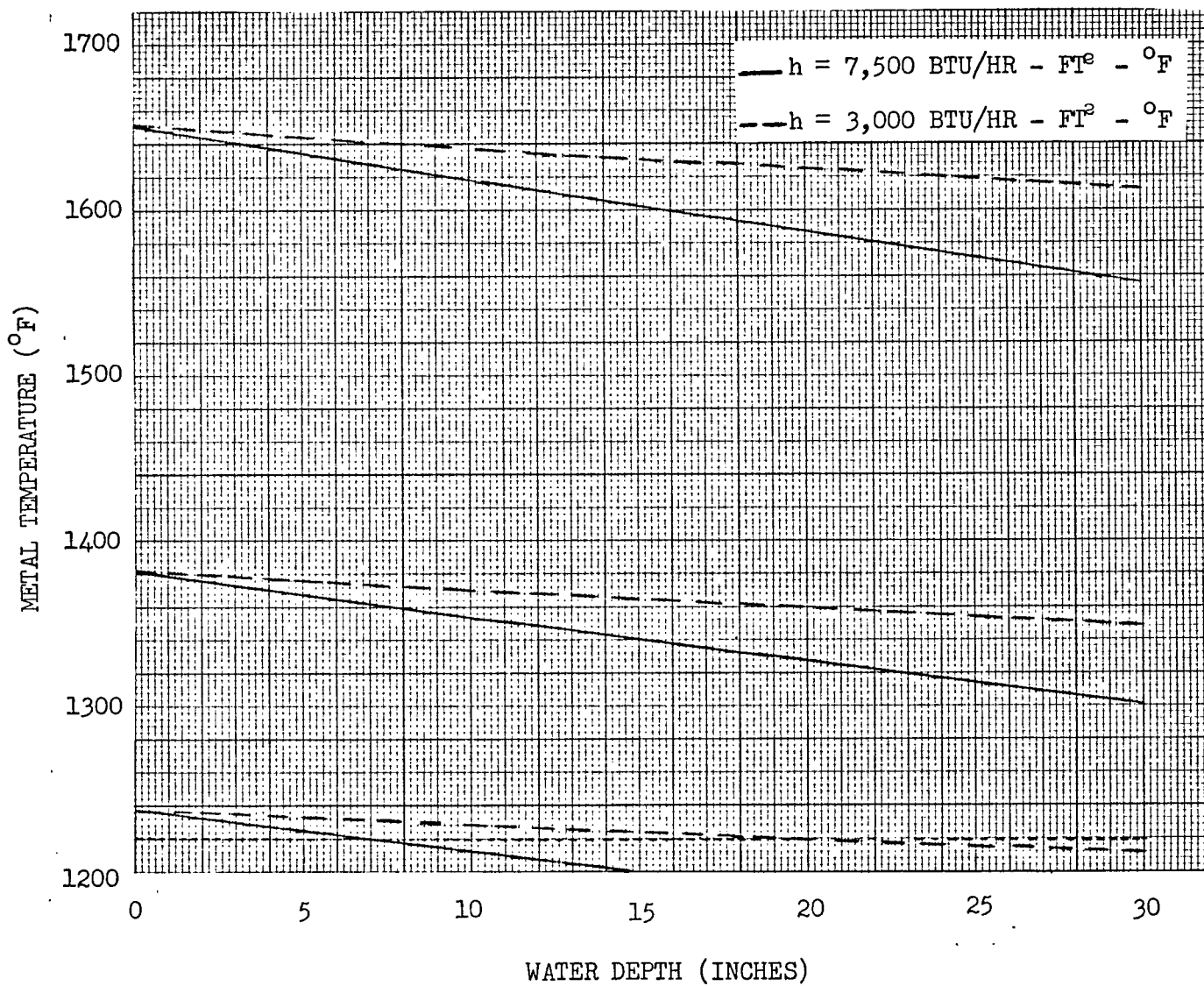


Figure 2
NEWTONIAN COOLING CURVE
FOR A MOLTEN METAL SPHERE

VIOLENT BOILING

Another proposed mechanism for fragmentation of a molten metal mass in a coolant is that of violent boiling, which has received support from workers at the Argonne National Laboratory.¹¹ The natural quenching of a molten-metal mass in a coolant proceeds generally from film boiling (where the metal surface is completely enveloped in a vapor blanket) which is hydrodynamically "quiet", through a transition region (an extremely violent region of vapor film collapse and growth) to fully developed nucleate boiling (which is hydrodynamically turbulent due to the growth and collapse of bubbles emitted from the metal surface), and finally to free convection (no bubble formation at all). According to the violent boiling hypothesis, if a metal has a melting point in the nucleate boiling region then the turbulence caused by the hydrodynamic agitation of the liquid layer close to the surface is sufficient to overcome the surface tension forces of the metal and cause the mass to fragment. This phenomena would be even more severe if the liquid coolant were subcooled (the liquid temperature less than the saturation temperature). In this case, the bubbles would collapse more violently and closer to the metal surface, thus generating even more intense turbulent forces on the metal surface. Based on this theory fragmentation would not be a function of metal velocity through the coolant. According to Grober, Erk,

and Grigull¹⁰, once the heat transfer is established in the fully developed nucleate boiling range the forced convection case is the same as free convection. However, if the molten metal mass were to cool sufficiently during the film boiling phase of heat transfer, then the transition to nucleate boiling would generate insufficient forces to break up the hardened shell around the metal mass.

Brauer¹² postulated that "...if it is assumed that nucleate boiling cannot occur on a surface with a temperature higher than the critical temperature of the liquid, the transition region for water would be at the critical temperature of 373 °C. On the basis of Argonne's hypothesis aluminum with a melting point of 660 °C should not fragment on quenching in water because the aluminum would be fully solidified before reaching the temperature of violent boiling in water. Aluminum, however, fragmented violently in the shock tube experiment." In this experiment, conducted at Space Technology Laboratories,¹³ water was dropped on a pool of molten aluminum. In support of these results, experiments conducted by Witte at the University of Houston¹⁴ indicate that the onset of transition can occur well above the critical temperature of water. During the experimentation conducted by Brauer, molten samples of aluminum and lead were quenched in 4 °C water and photographed using a high-speed camera at 4000 frames/second. Brauer indicated that a large bubble was formed and ruptured on the aluminum sample but that the molten picture did not show "...any

evidence of violent boiling during the formation of this bubble." The lead samples similarly did not indicate any boiling. Therefore, Brauer concluded that "...these experimental observations are not in accordance with a violent boiling hypothesis."

SHELL THEORY

Brauer, while discounting the violent boiling hypothesis,¹² proposed the following mechanism for fragmentation of a molten metal in a coolant. "The molten metal drop, upon contact with the quench liquid or shortly thereafter, forms a solid shell due to rapid heat transfer from the metal surface. Somehow, some of the quench liquid is trapped inside this shell. The trapped liquid is rapidly vaporized and produces a large internal pressure during expansion. The interior molten metal, due to this internal pressure, breaks through the weakest part of the metal shell and is dispersed." Even though high-speed motion pictures show evidence of the existence of an internally generated pressure in aluminum and lead drop tests, Brauer admits that the method of quench liquid entrainment is not clearly understood. He adds that "...a possible explanation is that the quench liquid is forced through a porous solid metal shell due to voids formed by an increase in the interior metal density." This mechanism is very similar to that proposed by Long. They both hypothesize the trapping or encapsulation of the quench liquid in the molten metal mass; it is only in the entrainment technique that they differ.

This theory has also received support from experimenters in the paper industry which has encountered explosive episodes in the past. Due to the frequent recurrence of explosions in the soda smelt (molten sodium carbonate)

dissolving operations, various laboratory experiments were undertaken to determine the cause and prevention of the accidents.. In this industrial operation, molten smelt (molten sodium carbonate) is sprayed into large tanks of green liquor. After extensive experimentation, Sallack³ proposed the following theory for the explosions. This theory incidentally, agreed precisely with the observations made by Nelson and Kennedy¹⁵ who had been doing similar experiments at Combustion Engineering, Inc.. "When an unshattered ball of smelt of proper size with the necessary physical properties falls intact below the surface of the green liquor, it immediately forms a hard outside shell surrounding the molten core.. With rapid cooling, fissures develop on the surface allowing liquid to penetrate to the molten portion. Vapor forms with explosive violence in these cracks causing segments of the shell to spall off much like shrapnel." Nelson and Kennedy also found "...the decisive bearing on the tendency of smelt to explode and on the violence produced.. Quenching violence increased with increasing particle size." This is very similar to the results that Long found. When the metal stream approaching the coolant was broken up by a steel grid placed over the coolant tank, there were no explosions.. However, under the same conditions when the metal mass hit the coolant intact there was a violent explosion.. Also, in all three groups of experiments described above (Long, Brauer, and soda smelt experiments), observations of the explosions were made

in the dark to determine whether or not combustion was taking place. The results were negative in all cases..

Still another experimenter that seemed to agree on an encapsulation theory for fragmentation was Bradfield.^{16,17} Bradfield was doing a study on liquid-solid contact in stable film boiling when he began an investigation on film boiling in the presence of a reacting surface out of curiosity.. He used a 6-inch long graphite cylinder (1500°F) in water at 165°F. On two occasions Bradfield noted that the severity of the reaction destroyed the containers in which the experiments were conducted. High speed photographs which were taken (2300 frames/second), indicated that the transition from stable film boiling to liquid-solid contact occurred in less than 0.001 second..

The graphite surface is rough, porous and wetting. With these characteristics in mind, Bradfield reasoned "...that the process begins by the occurrence of more or less uniform contact of the interface with the surface... . Because of the surface cooling which results and since the surface is both wetting and porous, the liquid is drawn by surface tension and driven by inertial forces deep into the surface, where intimate thermal contact with the primary heat source is established. As this occurs, an explosive evaporation takes place.... ."

Bradfield suggests that the liquid-solid contact came about by a contraction of the liquid-vapor interface. Motion pictures taken by Bradfield of a smooth chrome-plated

copper sphere being quenched in water, show that "...as the subcooling is increased, the normally wavy interface (which characterizes laminar quenching) gradually changes in appearance and becomes glassy smooth.. Frequently associated with this glassy appearance is an oscillation of the entire interface normal to the heated surface.. On a completely submerged spherical object this takes the form of a rhythmic expansion and contraction of the interface as a spherical shell.. Further increasing the subcooling results in intermittent and momentary contact between the liquid and solid surface as a result of the oscillation.. This is apparently of very substantial area, because for a very smooth heating surface the resulting hydrodynamic disturbance can be detected by loud "bumping" sounds associated with the phenomenon.. These hydrodynamic disturbances are presumed to result from flash evaporation of the liquid as it comes into contact with a large area of the surface." Therefore, there is probably a substantial amount of inertia driving the liquid into the porous graphite as the liquid-vapor interfacial shell contracts and collapses on the graphite surface.. Once in contact with the graphite surface, surface tension would probably be sufficient to hold and draw the liquid into the cylinder core as the liquid-vapor interfacial shell again expands outward.. Since the destructive vaporization of the liquid would begin immediately upon contact with the hot insides of the cylinder, a single oscillation of the interfacial shell could be

sufficient for an explosion..

This phenomenon of liquid-vapor interfacial oscillations has also been observed by high speed photography by Witte at the University of Houston.¹⁴ In this case, a smooth silver sphere at 900°F was quenched in water at 126°F. The liquid-metal contact between oscillations was apparent from the photographs and the large exposed surface area of the sphere was easily seen. The phenomenon was exactly as described by Bradfield and the hydrodynamic violence associated with the rhythmic oscillations of the liquid-vapor interfacial shell was apparent. Thus, it is not hard to accept the fact that there is a sufficient hydrodynamic driving potential to force liquid water through a porous material and into the core of the metal when the above discussed phenomenon is taking place..

CRITICAL WEBER NUMBER

Many experimenters feel that a possible mechanism responsible for the fragmentation process of a molten metal mass falling through a coolant is a high inertial force ($\rho V^2 R$) to surface tension force (σ) ratio. This ratio is termed the Weber Number ($\rho V^2 R / \sigma$). In the expression for Weber Number ρ is the density of the metal, V is the velocity of the metal mass, R is the effective radius of the metal mass and σ is the surface tension of the metal. If the Weber Number exceeds a critical value, the inertial forces produced by the size and velocity of the metal mass passing through the coolant would exceed the surface tension forces holding the mass together and the mass would fragment.^{18,19} Thus the necessary prerequisite for an explosion, small particle formation with large exposed surface area, would be complete.

If the molten metal is dropped into the coolant from some height, as in Long's investigation, there are additional problems encountered. Not only must the Weber Number be considered for the metal-air interface and metal-water interface, but also there must be some consideration given to the impact of the molten metal with the surface of the coolant. The impact could possibly alter the effective radius of the metal mass and thus further complicate the calculation of the Weber Number. However, in order to investigate the fragmentation phenomena the problem will be

simplified by assuming that the molten mass begins its descent through the coolant from just under the surface of the coolant. This neglects the impact effects but allows the mass to begin its descent with the velocity gained from a free-fall drop.

Extensive molten-metal drop-tests were conducted at Argonne National Laboratories²⁰ to experimentally determine the critical Weber Number range for falling drops. In one experiment, mercury was dropped at room temperature into room temperature water to determine the fragmentation due purely to dynamic effects. Also additional tests were conducted with lead, bismuth, and tin at 600 °C dropped into water at 30 °C. The critical Weber Number range was found to be between 5 and 10. In general, fragmentation of the metal increased with increasing Weber Number. As an example, Long used aluminum in all of his drop tests. Argonne estimated a value for the surface tension of molten aluminum in water as $\sigma\{\text{AL} - \text{H}_2\text{O}\} = \sigma\{\text{AL} - \text{AIR}\} - \sigma\{\text{AIR} - \text{H}_2\text{O}\}$

This form was used because of the unfortunate lack of data on molten metal-liquid interfacial surface tension. Completing this expression with the values found in the AI of P. Handbook²¹, the surface tension is found to be $\sigma\{\text{AL}-\text{H}_2\text{O}\} = 765 \frac{\text{DYNE}}{\text{CM}}$. Then for a four foot drop height (typical height for those cases in which Long noted explosions), the molten mass would have achieved a velocity of 16 feet/second or 480 cm/second at the surface of the coolant. By assuming a critical Weber Number of 10 and substituting the above

values, the maximum stable radius of a molten aluminum sphere in water is $R_{\max} = (10)(765)/(1)(480)^2 = 0.032 \text{ cm} = 30 \text{ microns}$. This radius is extremely small compared to the initial radius of a sphere corresponding to the mass of molten aluminum that Long was dropping (10 pounds corresponds to a sphere of radius approximately 3 inches).

Although this data appears to be conclusive, Ivins²² determined from a group of tests concerning Weber Number that two mechanisms are evident. "One mechanism, a dynamic breakup at the lower temperatures, causes fragmentation proportional to the Weber Number of the falling drop when the Weber Number is greater than its critical value for fragmentation. The other mechanism occurs between 300 and 400°C, where a striking change in the extent of fragmentation is evident. The drop tests made at 400°C exhibit by far the greatest fragmentation, especially at low Weber Numbers, presumably because the drop passes through a violent (transition) boiling regime that exists over a temperature range between 300 and 400°C, particularly when the Weber Number is low, because the drop is in film boiling regime during most of its fall through the water." The data from these tests is summarized in Table 3. Therefore, the critical Weber Number is certainly a contributing explanation for fragmentation of molten metal falling through air. But, when the metal is falling through a coolant the dynamic forces described by the Weber Number may be suppressed by the boiling characteristics of the

coolant around the metal. This indicates that one of the other mechanisms may also contribute to the vapor explosions.

DROP HEIGHT (in.)	WEBER NUMBER	NUMBER OF FRAGMENTS AT INDICATED INITIAL GALLIUM TEMPERATURE*				
		50 °C	100 °C	300 °C	400 °C	600 °C
2	5.3	-	-	-	20.4	10.2
4	11.5	-	-	-	1.8	9.2
8	23	1.0	1.1	1.0	9.3	1.6
16	46	3.4	3.5	2.3	6.7	2.5
32	92	10.5	6.5	6.6	7.4	-

* Each data point represents the average of five drops of 0.37 centimeters in diameter

Table 3 FRAGMENTATION OF LIQUID GALLIUM
DROPPED INTO 30 °C WATER

CHAPTER IV

CONCLUSIONS

The explosive vapor formation phenomenon that can take place when a molten metal contacts a cooler liquid has been investigated. The conclusions drawn from this investigation may be summarized as follows:

1. Explosions may occur when a molten material contacts a cooler liquid (which has a boiling point much less than that of the molten material) as a result of the rapid expansion of vapor formed during a heat transfer process. An accompanying chemical reaction may augment the explosion but in many cases is not responsible for the tremendous energy release. For example, Long and Sallack noted no characteristic flash during explosions caused by dropping molten aluminum into water and molten sodium carbonate into green liquor.
2. A prerequisite for explosive vapor formation appears to be fragmentation of the molten material into very fine particles. Both the extent and the rate of fragmentation must be large.
3. The mechanism of fragmentation most consistent with experimental observations is the entrapment of liquid

adjacent to a region of molten material (encapsulation and shell theory)..

4. It is likely that the entrapment of liquid and violent transition boiling are intimately related.

It is recommended that the metal water reaction study be extended to cover the following future works:

1. Tests should be performed in which molten metals can be sprayed into a chamber of water under controlled conditions of particle size, confinement and temperature. If it is assumed that the jet would produce droplets of molten metal within a narrow, reproducible range of particle size, the effect of particle size and temperature could be investigated independently.
2. A test system should be devised so that high speed motion pictures can be used to monitor the entry of molten metals into the water. In this way it may be determined exactly how the water entrapment mechanism is taking place..
3. Experiments should be conducted to accurately determine the heat transfer coefficients for a molten metal cooling in water and the resulting cooling curve

of the metal.

4. Experiments should be conducted to accurately determine the value of surface tension (σ) for the metal-liquid interfaces involved in the various metal-vapor explosions (aluminum-water, aluminum-water vapor, steel-water, etc.)

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