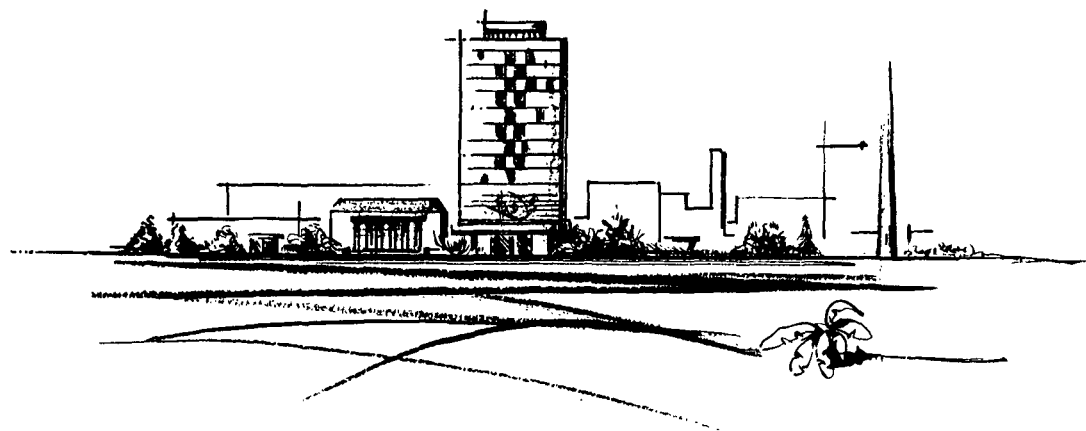TXU

RESEARCH REPORT

FEASIBILITY STUDY ON
SMELT-WATER EXPLOSIONS

to

FOURDRINIER KRAFT BOARD
INSTITUTE, INC.

May 3, 1968

Project 2419

BATTELLE MEMORIAL INSTITUTE

COLUMBUS LABORATORIES

SUMMARY REPORT

on

FEASIBILITY STUDY ON
SMELT-WATER EXPLOSIONS

to

FOURDRINIER KRAFT BOARD
INSTITUTE, INC.

May 3, 1968

by

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INTRODUCTION

With a view to complementing and extending the investigations on smelt-water explosions conducted for the Smelt-Water Research Group by the Babcock & Wilcox Company and by Combustion Engineering, Inc., with Coordination by the Institute of Paper Chemistry, the Columbus Laboratories of Battelle Memorial Institute have conducted for FKI a study to ascertain, by detailed analysis of available information, whether and what additional research is feasible, directed toward preventing or reducing the probability of explosion when water or water solutions contact molten smelt. Information pertinent to smelt-water explosions that was reviewed and analyzed in this study was obtained principally from published literature, from the reports to the Smelt-Water Research Group[1][*], and by consultations with personnel of Combustion Engineering, Babcock & Wilcox, and pulp manufacturers, and with Dr. H. S. Gardner, coordinator of the project conducted by Combustion Engineering and by Babcock & Wilcox for the Smelt-Water Research Group. Also, the director of this study, Dr. E. H. Lougher, accompanied Dr. Gardner during his investigation of a recovery-furnace explosion which occurred in the course of the study.

This is the Summary Report on the project and covers the period from July 1, 1967, to May 1, 1968.

SUMMARY

Identification of Smelt-Water Explosions

Primary emphasis during this project was on assessing the probability of success in further research directed toward reduction of the explosion hazard resulting from

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[*]References are given at end of the report.

contact between molten smelt and water.* However, since information derived from examination of recovery boilers after explosions is important to such research, a brief effort was devoted to the review of a criterion currently used for distinguishing between smelt-water and fuel explosions, i.e., localized damage of the furnace floor. It was concluded that whereas it is highly probable that such damage indicates a smelt-water explosion, the possibility that fuel explosions in fissures in the char bed could, under some conditions, cause a small amount of such damage cannot be completely discounted on the basis of available information.

Explosion Mechanisms

The mechanism of smelt-water explosions is not understood. Additional research should be conducted to develop greater understanding which would, in turn, provide guidance in developing means for alleviating the explosion problem. It is possible that the explosions are not the result of a single, easily defined process, but are the result of a set of processes, none of which alone is capable of producing the violence observed. Several postulated mechanisms were examined in detail in this study. It was concluded, on the basis of theoretical analysis, that the encapsulation process previously proposed is not likely to be a primary explosion mechanism or a triggering mechanism, since the shell of frozen smelt would not be strong enough to contain any significant pressure. A mechanism in which the expansion is momentarily constrained (causing the pressure to rise) by inertial reaction of the water and smelt was found theoretically to be incapable of causing explosion if heating of the water is only by infrared radiation and thermal conduction through the smelt and steam. However, if other, more rapid, heat-transport processes are important, e.g., turbulence and conduction by complex vapor molecules such as $(NaOH)_2$ and Na_2OHCl, the inertial-reaction mechanism may be a contributing factor in smelt-water explosions. Additional work should be done to clarify this point. Exothermic physical and chemical processes, particularly gas-forming reactions, are potential sources of explosion energy which should be given additional scrutiny. Exothermic dissolution of smelt components (particularly NaOH) in water, with consequent heating of the water and generation of steam, appears to be a potential contributor which should be investigated further.

Effects of Smelt Composition on Explosiveness

The results of several laboratory studies cast some light on the explosive composition ranges of smelts in contact with water. With no sensitizers present, the minimum explosive Na_2S concentration under the laboratory conditions employed appears to be in the vicinity of 20 percent by weight. However, small concentrations of NaOH or NaCl can sensitize low-sulfidity smelts to explosion and can increase the violence of explosion with smelts of higher Na_2S content. In view of the complex interactions among the components of smelt, and since NaOH is formed in smelt-water reactions and could thus provide a sensitizer in a smelt-water emergency even if none were present initially, it does not appear appropriate to conduct additional research in an attempt to determine "safe" concentrations of normal smelt components.

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*Recommendations for future research are summarized briefly in this section and are presented in detail in the final section of this report.

Modification of Smelt to Prevent Explosion

A large group of inorganic compounds have been studied as possible smelt additives to eliminate explosions. Of these, $NaAlO_2$ and Fe_2O_3 were found to have beneficial effects. The range of applicability of $NaAlO_2$ in desensitizing smelt should be investigated (iron in cooking liquor would cause pulp discoloration). It is not recommended that additional screening studies be made in an attempt to identify other beneficial additives, at least until more is known about the explosion mechanism, since no patterns are evident from past work to provide guidance in selection of materials.

Effect of Black Liquor Composition on Explosiveness

Limited laboratory studies on the reaction of black liquor with smelt suggest that the solids content must be at least 50 to 60 percent to prevent explosion under laboratory conditions. However, the composition of black liquor varies widely, and the character of the organic materials present is not known and is dependent on mill practice and the wood used. Thus, while it seems likely that there is a limiting solids content above which no explosions would result regardless of specific smelt and black liquor compositions, determination of this concentration would be an enormous undertaking and is not recommended. However, a limited study to determine the explosiveness, at various degrees of dilution, of black liquors from several mills could provide useful information on whether normal firing concentrations should be increased, and such a study should be conducted. Also, the effects on explosiveness of the concentration in black liquor of the known smelt sensitizers, NaOH and NaCl, should be studied.

Modification of Boiler Water to Prevent Explosion

A brief investigation of the effects of some surface-active agents in water injected into smelt suggested that they might tend to inhibit explosions. These materials could then be considered as possible boiler-water additives. While a systematic study of the effects of these materials might be productive, such a study would be of low priority, and is not recommended at present.

Explosion Inhibition by Carbon Dioxide

Carbon dioxide was found to inhibit explosion on water injection under laboratory conditions, but the sulfide level in the smelt was reduced. Some further study may be warranted on the range of applicability of this means of explosion prevention in the presence of NaCl and NaOH, and also to determine whether practical sulfidity levels can be maintained if a CO_2 atmosphere is maintained over the smelt during normal operation. However, the capital cost for such operation might be prohibitive. For emergency shutdown, CO_2 might reduce smelt explosiveness, but this process probably would be slow.

Explosion Inhibition by High-Frequency Vibration

Use of high-frequency vibration was ruled out as a possible inhibitory mechanism for smelt-water explosions, both from the viewpoint of lack of a convincing mechanism for such inhibitory behavior, and also from the viewpoint of the large capital expenditure

that would be required to provide for reasonably good sonic-irradiation coverage of the smelt in a furnace.

Quenching of Smelt in Emergency Shutdown

Review of past work related to liquid quenching of hot smelt during emergency shutdown revealed that aqueous solutions of some organic polymers and also of several inorganic materials, principally ammonium compounds, have promise for this application and should be studied further. Some other inorganic salts (sodium and calcium carbonates, sodium sulfate) in solution, slurry, or dry form also should be considered. While black liquor with a solids content of greater than about 50 to 60 percent may be a safe and convenient coolant, its variability in composition, along with the variability of smelt composition and furnace conditions, would make research to determine the minimum solids content that would be safe under any conceivable conditions an endless task and, hence, is not recommended.

Formation of Porous Smelts

The potentially beneficial effects of continuously bubbling gas through the smelt during normal operation were considered. These potential benefits include probable inhibition of smelt-water explosions by providing pressure-relief surfaces, better smelt flow characteristics, and more rapid cooling of the smelt in emergency shutdown. For shutdown, cold gas in combination with safe liquid coolants could replace the hot gas that is normally being injected, if such a system were in use. Although the concept seems attractive in principle, further investigation is not recommended because of probable prohibitive capital cost and operational complications.

Rate of Solidification of the Smelt

The rate of solidification of the smelt on shutdown by conduction to the water-cooled furnace floor and by radiation and convection from the upper surface of the smelt bed also was considered. A computer analysis could be made of this problem, if sufficient data were available on smelt properties. While the cost of obtaining the experimental data required for a detailed analysis would be prohibitive, a limited study of this type appears appropriate, particularly since some of the data needed would also be required in connection with the computer evaluation of explosion-mechanism models. The information derived from the smelt-solidification study would be particularly useful as a base line against which to evaluate the effectiveness of cooling the smelt by means of quenching agents.

DISCUSSION

Identification of Smelt-Water Explosions

One of the problems in the postmortem analysis of an explosion in a chemical recovery furnace is identification of the cause of the explosion. If there is obvious leakage

of water, then there is usually little doubt that the explosion was of the smelt-water type. On the other hand, if auxiliary firing was being used, or had been used only a short time prior to the explosion, the possibility must be considered that the explosion was the result of sudden ignition of a combustible mixture in the furnace, particularly if the burners were not monitored. It is clear that in the interest of applying corrective measures for future safety, the proper interpretation of the cause of any explosion is necessary.

It has been customary to ascribe to smelt-water explosions the characteristics of large local deflection or large-scale dimpling of the furnace floor, while combustion explosions are considered to be characterized by a more even distortion of the furnace structures. This differentiation is based on the reasoning that pressure from an explosion of a combustible mixture will be applied more gradually to the structure, and over the entire internal surface. This was shown, on the basis of reasonable assumptions, in an excellent theoretical study on flame propagation through a combustible mixture in a furnace by Williams and Sarofim.[1]

The purpose of this discussion is to examine further the possibility that large-scale local loads, and thus permanent deflection, might in some cases be a result of the explosion of a combustible mixture, rather than necessarily being indicative of a smelt-water reaction. Two possibilities are considered here, based on the alternatives of (1) penetration of liquid fuel into and under the char bed through fissures and (2) production of a combustible mixture above the smelt bed.

Liquid-Fuel-Induced Explosions in the Smelt

In a discussion of chemical recovery boilers, Deeley and Kirby[2] suggested that under some conditions, secondary fuel and air may penetrate the char bed and explode, even after the auxiliary burners have been withdrawn. Coykendall[3], of Babcock & Wilcox, concurred on this point. He said that if there were no burners being used and if there was a source of water (such as water collecting in the primary air duct and being blown out into the smelt), he would assume that the explosion was a smelt-water explosion. On the other hand, if a primary burner was in use or had just been in use, and no source of water could be found, he would be inclined to suspect a fuel explosion.

The type of destruction that would result from such a liquid-fuel-induced explosion is related to the speed at which the flame propagates through fissures filled (we assume) with a combustible mixture. The worst case would be the propagation of a detonation wave, which would result in high, and nearly instantaneous, local pressure rises. Unfortunately, there is little information in the literature that can be used to judge the possibility of a detonation in a system burning liquid hydrocarbon fuels with air. Data indicate that detonations can be produced by aerosols of liquid fuels, and that the maximum strength of the detonation is far on the fuel-rich side because of the remains of large fuel droplets after the detonation wave passes. It is questionable whether any droplets larger than 10 microns enter into the detonation itself. There is evidence that the wave breaks down large droplets to some extent, and can produce droplets from a liquid film or surface.

The minimum diameter of duct necessary to propagate a detonation in fuel-air mixture is not well documented. The minimum diameter appears to decrease as the molecular weight of the fuel increases, and to decrease significantly at lower molecular weights. Manson, et al.,[4] give a value of about 4 inches for a stable detonation in a stoichiometric mixture of C_3H_8 and air, but indicate that unstable detonation can occur

in ducts of only about 5/8-inch diameter. Thus, in channels and fissures, there appears to be a good chance of detonation, or at least of a combination of detonation and high-speed deflagration, propagating through a combustible mixture.

There is still the question of an ignition source, but a small hot region could be adequate. It is well known that once the flame starts propagating as a deflagration through a channel, roughness of the wall can cause acceleration of the flame and consequent inception of a detonation.[5]

Averaging out the expansion and rarefaction waves in the products of combustion behind a detonating combustible mixture, one can picture a region of pressure jump in the fissures, expanding along the fissures at the speed of sound in the burned gases. The total load imparted to the furnace floor would depend on the total area of fissure. Whether this load could be sufficient to cause local distortions of the structure is not obvious, but it seems improbable that severe damage could result from such a process.

At this point, it can be said only that, although highly localized damage to the furnace floor probably indicates the occurrence of a smelt-water explosion, the possibility that auxiliary fuel might have been involved, particularly if the damage is slight, should be considered. Although this small element of doubt remains, it does not seem worthwhile to conduct further research to clarify the situation, in view of the high costs anticipated for such research.

Gaseous Explosions in the Furnace

The question considered here is not whether there can be a gaseous explosion in the furnace volume itself, but whether the explosion can be localized in violence sufficiently that local structural deformations result therefrom. We will consider two points: the propagation rate of a deflagration and the possibility of detonation.

Williams and Sarofim[1] set up equations for predicting the pressure rise throughout the chamber for reasonably low velocity deflagrations. They assume a maximum value of turbulent flame speed of 4.7 fps, five times their assumed laminar velocity. However, much higher values of turbulent flame speed are possible. Putnam, Clough, and Kenworthy[6], for instance, obtained turbulent flame speeds over eight times the laminar burning velocity, using a grid of 60 percent blockage with 1/2-inch holes and a relative stream velocity of only 10 fps to generate the turbulence. This amounts to a relatively low level of turbulence compared with what one might expect in a furnace. Thus, the rate of pressure rise in the furnace may have been underestimated by Williams and Sarofim. However, it would require drastic changes in the flame-propagation rate to produce local deformation. A flame speed that would produce such effects would act in a duct as a precursor of a detonation. In a cylindrical expansion of a flame, the factors leading to increases in flame-speed rate and to detonation are lessened by the increase in area with time; in spherical expansion of a flame, the factors promoting rapid flame speed and subsequent detonation are weakened even further. Thus, we might examine the possibility of detonations occurring in a large volume of combustible mixture, such as might occur in a recovery furnace.

Harris[7, 8], in a study of pentane-air explosions in large vessels, concluded that the maximum pressure in a nondetonating mixture (no detonations were observed) is essentially that obtained in a spherical vessel at least 4 liters in capacity. For nonturbulent flames in a 60-cubic-foot vessel away from the stoichiometric region, the pressure

was consistently lower than that in the 4-liter vessel because of thermal losses. A second conclusion was that the rate of pressure rise (and thus the turbulent flame speed) increased with the degree of turbulence in the system. A third observation was that turbulence suppressed oscillatory combustion effects. Finally, when blow-out disks were used, turbulence tended to suppress the effects of the disks relative to the maximum pressure reached.

Kogarko et al., [9] in a study of spherical detonations of gas mixtures, used, among other things, stoichiometric mixtures of methane and air and of propane and air in spheres of 350 to 530-cubic-foot volume (up to a 5-foot radius). Centrally ignited mixtures did not detonate in this size sphere. However, 155 grams of TNT would cause detonation in the propane-air mixture, and 1000 grams would cause detonation in the methane-air mixture. The authors indicate that they believed that detonation would occur in larger vessels, because the flames became turbulent. By the same reasoning, if the initial mixtures had been turbulent rather than quiescent, one could expect detonation to occur, but in what size vessel and with what degree of initial turbulence are unknown. Unfortunately, the only work with large vessels, wherein the sizes approach more closely that of recovery furnaces, has been on methane-oxygen and propane-oxygen mixtures. In two such studies[10, 11], methane-oxygen mixtures were detonated in balloons from 3 to 110 feet in diameter, and propane-oxygen mixtures were detonated in hemispheres from 17 to 125 feet in diameter. Explosive charges were used to start the detonations. However, we also note that in some earlier work on a smaller scale with natural gas, ethane, propane, and some other hydrocarbons with oxygen (natural gas in balloons from 1 to 2 feet in diameter), an explosive charge, rather than a hot wire or spark, was required to produce a detonation in most cases. [12]

One can conclude from the literature that, in general, it is probable that a spherical detonation can develop from a starting deflagration in a combustible, near-stoichiometric mixture, provided sufficient volume of mixture is available. Furthermore, the presence of turbulence will reduce the necessary volume. However, the volume required is large enough that it is difficult to picture a local deformation (even several feet in diameter) resulting therefrom. Also, since the occurrence of turbulent flame speeds of high enough velocity to cause effects similar to those expected from a detonation can be considered as a precursor to detonation, the same argument is justified in relation to the occurrence of high-speed deflagrations. Hence, it does not seem probable that explosions in the furnace gases would lead to localized heavy damage as do smelt-water explosions.

Potential Explosion Mechanisms

Initial effort in any program directed toward alleviation of the smelt-water explosion problem should include consideration of possible mechanisms of explosion. Research to characterize the explosion mechanism conceivably could lead to complete solution of the problem; corrective measures may be obvious and readily applied, once the explosion process is understood. However, it must be recognized, in view of the complexity of the chemical system involved, that attainment of complete understanding of the explosion process may not be economically feasible. In such event, of course, substantial gains in reducing the frequency and violence of smelt-water explosions may be achievable by empirical means.

In devising a working hypothesis of the explosion mechanism, one must give proper consideration to the role of high-temperature and high-pressure chemical reactions and energy- and mass-transport processes, which may be quite different from those encountered under more usual conditions. Thus, in order to evaluate properly the potential explosion models and to predict the effects of variables, such as composition, mass, temperature, and geometry on explosive tendency, it is necessary to take account of basic physical, chemical, and thermodynamic information applicable in the temperature and pressure regions involved. Although the results of past work provide strong evidence that the smelt-water explosion is of physical – rather than chemical – nature, involving rapid generation of steam, it is also clear that chemical factors are of importance in setting the stage for explosion.

The mechanism of smelt-water explosions is not necessarily a simple, readily definable process. It could, conceivably, consist of a large set of processes, each alone incapable of producing destructive impulse but collectively resulting in great violence. The relative importance of these various processes may vary from one explosion to another, as a result of varying conditions of temperature, reactant compositions, geometry, etc. For example, the explosion might result partially from a combination of several exothermic – and, thus, self-sustaining – processes (dissolution of smelt components in water, various chemical reactions) with consequent simultaneous generation of steam and other gases. Additional energy for the explosion, beyond that available from the exothermic processes, could be provided by the surrounding hot smelt, with heat being transported to the reacting system by thermal conduction, infrared radiation, and convection.

In this section, some processes which are potential contributors to solely physical mechanisms of smelt-water explosions are analyzed in detail. The possibility that exothermic chemical reactions may supply at least some of the energy for a physical explosion is discussed in a later section.

The Encapsulation Mechanism

One model that has been postulated to explain smelt-water explosions is the encapsulation mechanism. This model has been examined theoretically to ascertain whether or not it can provide a realistic basis for understanding the explosion process.

The encapsulation mechanism for smelt-water explosions involves the formation of a shell of solid smelt surrounding a water (or liquor) droplet immersed in the smelt, as a result of cooling of the smelt in the vicinity of the droplet below the freezing point by transfer of heat to the water. Pressure builds up within this shell as the water within it increases in temperature and as steam is generated after the water begins to boil. The frozen smelt capsule presumably disrupts suddenly when the tensile stress exceeds the tensile strength at some point in the capsule. The sudden release of pressure and subsequent rapid generation of more steam from the superheated water generates a shock wave in the smelt. This outwardly propagating shock wave may constitute the violent explosion. The bursting of the smelt shell well before the contained water has reached its boiling, as is presumably shown to occur in Appendix III-C (Progress Report of Combustion Engineering, Inc.) of Report Three on Research on Smelt-Water Reactions, could result in ejection of atomized particles of water at high velocity into the smelt. An explosion involving one or more of these, by some mechanism such as encapsulation, could then trigger explosion of the others.

Mathematical Analysis. Let r be the mean radius and t be the wall thickness of a hypothetical spherical capsule of solid smelt that encloses n grams of water. If p is the internal pressure at which the capsule ruptures, the tensile strength of the shell, σ_t, is equal to the tensile stress at rupture, i.e.,

$$\sigma_t = (p - p_{at})\, r/2t \text{ for } t << r \quad . \tag{1}$$

where p_{at} is the ambient pressure (mostly atmospheric).

If T_o is the original temperature of the n grams of water and α is the fraction of the mass of water that is in the form of steam just prior to rupture, the amount of heat that has been transferred to the water at rupture is given by

$$H_w = n[\, C_w(T_b - T_o) + \alpha L_w] \quad , \tag{2}$$

where T_b is the boiling point and L_w is the latent heat of vaporization of water, both of which depend upon the value of p. C_w is the specific heat of water, which is reasonably constant. In terms of ρ_w, the density of water (reasonably constant), and ρ_{st}, the density of steam (function of p and T_b), we may also write

$$(1 - \alpha)n/\rho_w + \alpha n/\rho_{st} = (4\pi/3)(r - t/2)^3 \approx (4\pi/3)r^3 \text{ for } t << r \quad . \tag{3}$$

It is assumed in writing Equations (2) and (3) that the liquid water in the capsule is in thermal equilibrium with the steam at temperature T_b.

If T_a represents the ambient temperature of the molten smelt, T_f the freezing temperature of the smelt, and T_r the average temperature of the solid-smelt capsule at rupture, the heat that has gone out of the smelt in the capsule is given by

$$H_{sm} = 4\pi r^2 t \rho_{sm}[\, C_{lsm}(T_a - T_f) + C_{ssm}(T_f - T_r) + L_{sm}] \quad , \tag{4}$$

where ρ_{sm} is the density of the liquid smelt, C_{lsm} and C_{ssm} are the respective specific heats of liquid and solid smelt, and L_{sm} is the heat of fusion of smelt.

It is now assumed that $H_w = H_{sm}$, i.e., that all of the increase in heat content of the water comes from the decrease in heat content of the smelt capsule material. In reality, temperature gradients exist in the liquid smelt outside the capsule, so that some of the heat content of the water originates from smelt which remains liquid. The actual thickness of the solid-smelt shell would thus be less than that computed by assuming that $H_w = H_{sm}$. Making this assumption is thus tantamount to giving the postulated encapsulation mechanism the benefit of the doubt.

Combining Equations (1) through (4) so as to eliminate n and r/t and setting $H_w = H_{sm}$ results in

$$\frac{\sigma_t}{p - p_{at}} = \frac{3}{2} \frac{C_{lsm}(T_a - T_f) + C_{ssm}(T_f - T_r) + L_{sm}}{C_w(T_b - T_o) + \alpha L_w} \left[(1 - \alpha)\frac{\rho_{sm}}{\rho_w} + \alpha \frac{\rho_{sm}}{\rho_{st}}\right] \quad . \tag{5}$$

We will consider two cases:

Case I – A considerable fraction of the water within the capsule has already been converted to steam when the capsule ruptures ($\alpha \approx 1$)

Case II — Very little or no steam has been generated within the capsule prior to rupture. What actually takes place could be determined by solving the combined heat transfer-hydrodynamic problem to be discussed later. However, for the purposes of evaluating the validity of the encapsulation model, it is sufficient to consider these two limiting cases.

For Case I the final average temperature of the frozen smelt could not be too greatly different from its initial temperature T_a, because of the much lower thermal conductivity of steam than of smelt or water. Indeed, if we assume that the initial temperature of the liquid smelt bed is at or only slightly above its melting point, the greatest shell thickness of smelt would result, thus favoring the encapsulation-mechanism hypothesis. This is reflected in Equation (5) by seeking for the conditions leading to as small a value of $\sigma_t/(p - p_{at})$ as possible. Hence for $\alpha \approx 1$, we can approximate Equation (5) by

$$\frac{\sigma_t}{p - p_{at}} = \frac{3}{2} \frac{L_{sm}}{C_w(T_b - T_o) + L_w} \frac{\rho_{sm}}{\rho_{st}} \quad . \tag{6}$$

Using the heat of fusion of pure Na_2CO_3 = 7000 cal/mole, L_{sm} = 66 cal/g. Also, ρ_{sm} = 2.0 g/cm^3. The values of T_b, L_w, and ρ_{st} depend upon p in accordance with Table 1, in which the corresponding calculated values of σ_t are also listed. C_w = 1.0 cal/g, essentially independent of temperature within the range of interest, and we will take T_o = 300°K (= 27°C).

Table 1 presents computed values of the tensile stresses at several pressures. It is to be emphasized that the calculated values of σ_t are minimum values for Case I. In practice, the values of σ_t would be greater because the initial smelt temperature is usually 50 to 100°C above its melting temperature and the average value of the capsule temperature would be about 50 to 100°C below the melting temperature. We have also assumed that all of the heat added to the water came from the solidified portion of the smelt, as previously discussed.

TABLE 1. TENSILE STRESSES IN SOLID-SMELT CAPSULE FOR VARIOUS INTERNAL PRESSURES FOR CASE I: WATER MOSTLY CONVERTED TO STEAM BEFORE RUPTURE

p, atm	T_b, °C	L_w, cal/g	ρ_{st}, g/cm^3	σ_t, psi
1.0	100	539	0.60×10^{-3}	0
1.5	112	531	0.88×10^{-3}	2700
2.0	120	525	1.12×10^{-3}	4200
4.0	144	509	2.19×10^{-3}	6400
10.0	180	480	5.20×10^{-3}	8000
20.0	213	452	10.16×10^{-3}	8600
218.3	374.2	0	326.0×10^{-3}	5600

For Case II, $\alpha \approx 0$, Equation (5) becomes

$$\frac{\sigma_t}{p - p_{at}} = \frac{3}{2} \frac{C_{lsm}(T_a - T_f) + C_{ssm}(T_f - T_r) + L_{sm}}{C_w(T_b - T_o)} \frac{\rho_{sm}}{\rho_w}$$

$$\approx \frac{3}{2} \frac{T_a - T_r + L_{sm}/C_w}{T_b - T_o} \quad , \tag{7}$$

assuming $C_{lsm}/C_w \approx 0.5$ and $\rho_{sm}/\rho_w = 2.0$. In this case, the final average temperature of the solid smelt capsule would be about halfway between the original ambient temperature of the molten smelt and the boiling temperature of the water, assuming that the thermal conductivities of water, molten smelt, and solid smelt are about the same and that all of the heat added to the water originates from the smelt that solidifies into the capsule. In practice, the existence of temperature gradients in the molten smelt outside the capsule (assuming $T_a > T_f$) would result in T_r closer to T_b and a greater value for $\sigma_t/(p - p_{at})$. Assuming $T_a = 1200°K$, $T_r = (T_a + T_b)/2$, and $L_{sm}/C_w = 66°C$, the results of computations of σ_t for Case II are listed in Table 2.

TABLE 2. TENSILE STRESSES IN SOLID-SMELT
CAPSULE FOR VARIOUS INTERNAL
PRESSURES FOR CASE II: LITTLE
STEAM GENERATED BEFORE
RUPTURE

p, atm	T_b, °C	σ_t, psi
1.0	100	0
1.5	112	60
2.0	120	110
4.0	144	260
10.0	180	570
20.0	213	950
218.3	374.2	8500

The actual situation, assuming the encapsulation mechanism to be a plausible model, would be between Cases I and II, but much closer to Case I than to Case II; i.e., a considerable amount of expansion of the volume of the droplet would have taken place by the steam's emanating from its surface before the capsule of solid smelt is formed. This is concluded from consideration of the actual thermohydrodynamic problem, to be discussed later, which showed that heat transfer into the water droplet by the ordinary thermal-conduction process is so slow that when steam begins to form at its surface, only the outermost layers of the droplet have increased in temperature to any appreciable extent above the initial temperature of the water.

The latent heat of fusion of about 9 grams of smelt is required to form each gram of steam from water initially at 27°C, almost independently of the pressure. At 1 atmosphere pressure, there is a 1670-fold expansion in volume of the water droplet so that

$(4\pi/3)r^3/4\pi r^2 t = (1/9)\rho_{sm}/\rho_{st} = (1/9)(3340),$ or $r/t = 1100$. The latent heat of fusion from a layer of smelt less than 0.001 of the radius of the steam bubble in thickness is all that is needed to form the steam. The situations of interest from the viewpoint of smelt-water explosions, however, are those entries beyond the first row of Table 1, for which the internal pressure exceeds the external pressure. These correspond to smaller ratios of r/t for the same 9 grams of smelt for each gram of steam, as can be seen from the larger values in the ρ_{st} column, but the required tensile stresses in the capsule wall rapidly rise into the thousands of psi as soon as p is only a fraction above an atmosphere.

Approach to the Case II condition would require the existence of some physical or chemical mechanism for the much more rapid transfer of heat into the interior of the water droplet from the smelt surrounding it than the ordinary thermal-diffusion process. It is presumed for this case that all of the water would be raised to the boiling point corresponding to the pressure in question before any appreciable amount of steam is generated. The r/t ratios would be much smaller in this case, since expansion of the water droplet would be negligibly small compared with that in Case I. This results in much lower tensile stresses in the capsule wall, as can be seen in Table 2.

The last entry in Table 2 corresponds to the critical point for water, above which temperature it can exist only as steam, regardless of the pressure. Rupture of the capsule would release all of the water as steam, but encapsulation in this case is out of the question because of the high tensile strength required for the capsule material. Cases I and II coincide at the critical point. The higher value for σ_t tabulated for Case II in Table 2 as compared with that for Case I in Table 1 is the result of a smaller value for r/t for Case II. This is because we have assumed that the solid smelt in the capsule wall is cooled down to a temperature halfway between T_0 and the boiling point of the water in Case II, whereas it remains at T_f in Case I.

The compressive strengths of the strongest smelts are in the low thousands of pounds per square inch at room temperature, and the room-temperature tensile strengths of brittle materials are expected to be an order of magnitude less than their compressive strengths. At temperatures near their melting points, such materials would yield at even lower stress levels, say in the low tens of pounds per square inch. It is clear that the capsule could not contain more than a few tenths of an atmosphere of pressure above ambient before rupturing even for the Case II situation, and less than 0.01 atmosphere for Case I.

The encapsulation mechanism cannot, therefore, be seriously considered either as a primary means or as a trigger for producing smelt-water explosions. The contained pressure at rupture would be too small either for generating shock waves or for atomizing and propelling water droplets into the smelt. In any event, it would still be necessary to postulate some other primary mechanism for the explosion of one or more of these water droplets, since the above conclusions on the pressure-containing capability of encapsulations are independent of droplet size. It is conceivable, however, that any capsule of solid smelt that may form under certain circumstances could augment slightly the pressure-retaining capabilities of whatever is the primary means of retaining pressure.

The Inertial Reaction Mechanism

It is not necessary to have a solid material, such as a relatively rigid container of sufficient tensile strength, as a means for retaining pressure for explosive conditions to be developed. Dynamic forces in liquids or gases, developed by reactions to velocity (viscous resistance) or to acceleration (mass inertia), may serve equally well or better to contain explosive pressure, depending upon the time scale involved in the buildup of this pressure. For example, if heat were developed slowly enough in a mass of combustible or fissionable material suspended in a vacuum, such as an uncased bomb in outer space, no explosion would result if plenty of time were allowed for expansion as the temperature increased. However, for rapid enough increases in internal temperature of the mass of material, internal pressures develop that are counterbalanced by the inertial reaction to acceleration of the outer layers of bomb material. The faster the rate of generation of heat, the greater the inertial reaction to expansion, and the more potent the explosion. In the case of the water droplet in smelt, not only is there an inertial reaction to the outward acceleration of the outer layers of the droplet, but there is also an inertial reaction to the outward acceleration of the surrounding liquid (plus possibly also some solid) smelt. Such reactions could contribute to the explosive violence even if they are not responsible for the primary mechanism. Whether or not these inertial reactions can form the primary mechanisms for smelt-water explosions will now be examined.

Mathematical Analysis. The mathematical analysis for the inertial reaction mechanism is essentially an extension of that described in Appendix III-c of Report Three on Research on Smelt-Water Reactions. This latter analysis is strictly a solution of a heat-transfer problem with a phase change, from which capsule thickness as a function of time is obtained under the assumption that the water temperature is always uniform throughout the droplet. Capsule-wall tensile stresses also were computed under the very unrealistic assumption of an effectively rigid capsule [elastic modulus of capsule material >> (3r/2t) times the bulk modulus of water] .

Investigation of the inertial reaction mechanism of smelt-water explosions entails solving not only the heat-transfer equation described in Appendix III-c but simultaneously three other equations as well; the continuity equation, the equation of state, and the balance between net force and rate of change of momentum. The last equation is the quantitative expression of the inertial reaction mechanism.

For computation purposes, the water droplet, the smelt surrounding it, and the layer of steam between them are subdivided into concentric shells. Figure 1 shows a portion of one of these shells. The notations used in the mathematical analysis below are defined in Figure 1, with quantities pertinent to the inner boundary of the shell carrying the subscript n-1 and those pertinent to the outer boundary carrying the subscript n. Quantities averaged over the material in the shell are denoted by superimposed bars, or superimposed dots for their time derivatives, and also carry the outer boundary subscript.

Heat-Transfer Equation. In differential form, the heat-transfer equation is

$$V \cdot (KVT) = DC \, \dot{T} + V \cdot (PV) \quad , \tag{8}$$

Legend

R = radius
T = temperature
G = temperature gradient
P = pressure
V = velocity
D = density
K = thermal conductivity
C = specific heat
W = weight
B = bulk modulus
A = thermal-expansion coefficient

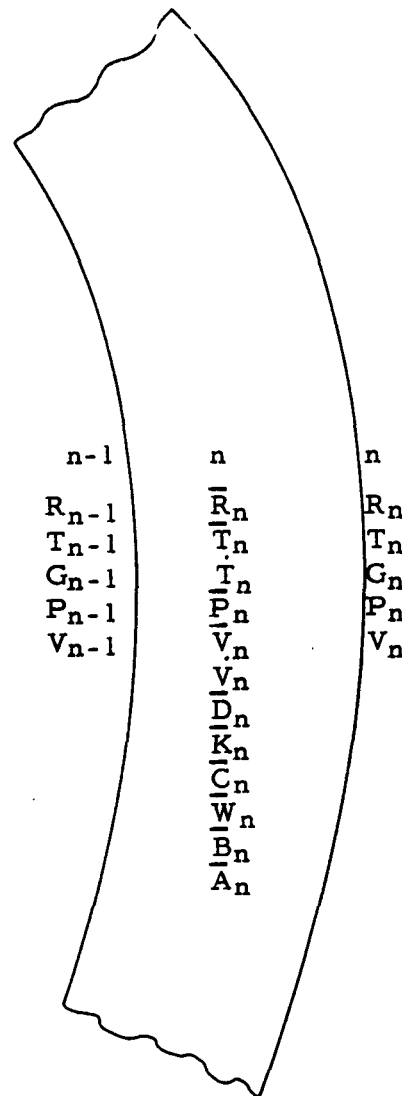| $n-1$	n	n
R_{n-1}	$\overline{R}_n$	R_n
T_{n-1}	$\overline{T}_n$	T_n
G_{n-1}	$\overline{T}_n$	G_n
P_{n-1}	$\overline{P}_n$	P_n
V_{n-1}	$\overline{V}_n$	V_n
	V_n	
	$\overline{D}_n$	
	$\overline{K}_n$	
	$\overline{C}_n$	
	$\overline{W}_n$	
	$\overline{B}_n$	
	A_n	

FIGURE 1. A PORTION OF THE nth SPHERICAL SHELL WITH NOTATIONS
USED IN THE MATHEMATICAL DEVELOPMENT OF THE
INERTIAL REACTION MECHANISM ANALYSIS

where

$$V \cdot (KVT) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 K \frac{\partial T}{\partial r} \right)$$

$$\dot{T} = \frac{\partial T}{\partial t}$$

$$V \cdot (PV) = P \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 V) \quad .$$

Only the case of spherical symmetry is considered; hence all variables are functions of the single spatial variable r, the radius, and t, the time. In the finite-difference form suitable for the digital-computer solution of the problem, Equation (8) for the nth shell becomes

$$\dot{T}_n = \frac{R_n^2(\overline{K}_{n+1}G_n - P_nV_n) - R_{n-1}^2(\overline{K}_nG_{n-1} - P_{n-1}V_{n-1})}{(R_n - R_{n-1})\overline{R}_n^2\overline{D}_n\overline{C}_n} \quad . \tag{9}$$

The thermal gradient G_n refers to that on the right-hand side of the boundary n, so that it must be multiplied by the value of the average thermal conductivity for shell n+1, K_{n+1} to obtain the heat flow across boundary n into shell n. The values of K·G must be continuous across each boundary, except at the boundary at which steam is being formed.

Except for the P_nV_n and $P_{n-1}V_{n-1}$ terms, Equation (9) is equivalent to the heat-transfer equation given in Report Three [Equation (5) of Appendix III-c], since the appropriate value for the average radius of the shell, $\overline{R}_n$, is given by

$$\overline{R}_n = \sqrt{(R_{n-1}^2 + R_{n-1}R_n + R_n^2)/3} \quad . \tag{10}$$

The inclusion of the PV terms in Equation (9) accounts for the portion of the net heat-energy input to the nth shell that is converted into mechanical work instead of raising the temperature of the shell material. These PV terms must be multiplied by a factor to take into account the mechanical equivalent of heat. If P is in atm and V is in cm/sec, PV must be multiplied by $10^6/4.187 \times 10^7 = 1/41.87$ to obtain heat flow in cal/(cm^2)(sec).

The Continuity Equation. This equation states that the mass of material in the nth shell remains invariant as that shell expands or contracts in thickness and as its mean radius increases. In finite-difference form, this is simply

$$(4\pi/3)\overline{D}_n(R_n^3 - R_{n-1}^3) = 4\pi\overline{D}_n\overline{R}_n^2(R_n - R_{n-1}) = \overline{W}_n \quad , \tag{11}$$

where $\overline{W}_n$ is the weight of the material originally placed into the nth shell.

The Equation of State. The equation of state, or constituative relationship, is the relationship between temperature, pressure, and density that must be satisfied at all times for the material in each shell. For the water, and also for the smelt, this equation is

$$\frac{\overline{D}_n}{D_o} = 1 - \overline{A}_n(\overline{T}_n - T_o) + (\overline{P}_m - P_o)/\overline{B}_m \quad , \tag{12}$$

where D_O, T_O, and P_O are the original density, temperature, and pressure, respectively, at the beginning of the problem. For the shells containing steam the ideal gas law is used, namely:

$$\frac{\overline{P}_n}{\overline{D}_n \overline{T}_n} = \text{constant} \quad , \tag{13}$$

with the value of this constant set at 4.6 for P in atmospheres, D in g/cm^3, and T in °K. Both Equations (12) and (13) are approximate relationships, but their accuracies are sufficient for the subject computations.

Momentum Balance Equation. This equation is a representation of Newton's second law of motion applicable to a continuous fluid medium. In differential form it is

$$-VP = \frac{\partial}{\partial t}(DV) \quad , \tag{14}$$

from which we get

$$\dot{V}_n = \frac{P_n - P_{n-1}}{\overline{D}_n(R_n - R_{n-1})} \tag{15}$$

The right-hand side of Equation (15) must be multiplied by 10^6 for P in atmospheres, D in g/cm^3, and $\dot{V}$ in cm/sec^2.

In the actual computer program both Equations (9) and (15) contained additional terms to take the effects of viscosity into account, in accordance with the Navier-Stokes law. These are omitted here for simplicity, since they made little difference in the final results.

Computational Procedure. The usual computational procedure was to begin the computer solution with a water droplet of given initial size, say one of 1-millimeter radius, and of a given uniform temperature, say 300°K, immersed in smelt of a given uniform temperature, say 1200°K. The water droplet is usually divided into 10 concentric spherical shells and the surrounding smelt into 100 such shells.

Starting with the initial conditions, $\dot{T}$ and $\dot{V}$ are computed for each shell. These are integrated by a special technique, available as a "library subroutine" in the computer software called the Runge-Kutta-Gill method, to obtain $\overline{T}$ and $\overline{V}$. This special technique gives more accurate results than simply multiplying each derivative by the chosen small time interval, Δt, and adding to the previous values of $\overline{T}$ and $\overline{V}$; it involves utilization also of derivatives at the midpoint of the time interval. Rules are then programmed into the computer for determining the new values of T, G, and V at the boundaries and also the new values of P, D, R, etc., so as to satisfy the constituative and continuity equations. Rules are also established regarding the conditions for water to be converted to steam, involving the relationship between boiling point and pressure and also the relationship between heat of vaporization and boiling point.

In order to obtain meaningfully accurate results, and also to avoid the development of "mathematical instabilities" in the computations resulting from accumulation of small errors, it is necessary to use extremely small time intervals for the repeated integration technique. The values of Δt should be no greater than, and preferably less than,

the time required for an acoustic wave to traverse the distance across a shell thickness. For a 0. 1-centimeter droplet radius, shell thickness is 0. 01 centimeter, which corresponds to about 0. 07 microsecond of travel time for a sound wave in water. Because all four equations and several auxiliary conditions had to be solved for each shell five times in each time interval a great deal of computer time is involved in these computations, even for a fast computer. For example, it takes about 15 minutes of computing time on the CDC 6400 computer before only about 1 percent of the first shell is converted into steam. Efforts were made to develop shortcuts and approximations to reduce the computational effort. So far, these have been unsuccessful. However, although no computation has been carried out to the point where all of the water has been converted to steam, computations have been carried out far enough to draw meaningful conclusions on the validity of the inertial reaction mechanism.

Results of Computations. Initially, there is a very high temperature gradient across the interface of the water droplet and the smelt. The resultant rapid heating of a thin layer of the former and the rapid cooling of a thin layer of the latter set up positive and negative pressure disturbances, respectively, because inertia prevents the thermal-expansion and -contraction processes from occurring instantaneously. Acoustic waves, amounting to about 0. 003 to 0. 004 atmosphere in magnitude over and above atmospheric pressure, propagate away from the interface, both radially outward into the smelt and radially inward into the water droplet. The latter waves "pile up" momentarily at the center of the droplet and reradiate outward.

As soon as steam begins to form on the outer surface of the water droplet, the above minor disturbances are overridden by a major pressure pulse, of amplitude up to about 100 atmospheres, since the expansion of the steam is temporarily inhibited by the inertial reaction of the overlying smelt to the rapid rate of change in its outward velocity. This is the effect we were looking for. However, the peak pressure of this pulse is reached in only about 1. 75 microseconds after the outer layer of water begins to boil, for a water droplet of 0. 1-centimeter radius. As the outward velocity of the smelt increases, the pressure decreases rapidly. When the smelt is moving outward at a rate sufficient to increase the volume available for steam as fast as it is being generated, the pressure drops down again to atmospheric. Superimposed on this general pattern are pressure fluctuations resulting from the combination of inwardly and outwardly propagating acoustic waves. However, these fluctuations eventually dissipate because of the net outward radiation of acoustic energy. In about 200 microseconds the pressure has returned to the normal 1 atmosphere plus relatively minor fluctuations. At this stage only about 0. 5 percent of the mass of the outer shell of water has been converted to steam, which represents 0. 15 percent of the entire mass of the water droplet (for 10 shells of equal thickness). Clearly, the explosion produced by this mechanism is a very minor one. It involves only a small fraction of the heat energy that eventually enters the water droplet.

Similar phenomena result from computations with a droplet of 0. 01-centimeter initial radius. The time scale of all events is reduced by a factor of 1/100 compared with that for the 0. 1-centimeter droplet. This is to be expected, since the physical dimensions of the thermal-diffusion constant K/DC are cm^2/sec. Higher peak pressures are obtained with the smaller droplet, however. This is also to be expected, since the pressures due to inertial effects would be independent of scale factor only if the time scaled directly as droplet-diameter factor and not as its square, in accordance with the laws of similitude. A peak value of about 600 atmospheres was recorded, but a larger value might have been missed at some intermediate time interval. Here again, these pressure

pulses are very localized and highly transient. They do not represent any appreciable explosion. For water droplets of about 1 cm and up in radius, they would be negligibly small.

In practice, of course, we do not have a perfectly spherical water droplet that is instantaneously immersed into a bed of smelt well below the smelt-bed surface. (The effects of the smelt-bed surface or of the bottom of the smelt bed are ignored in these computations by assuming the water droplet to be at a distance from these boundaries a few times greater than its radius.) The particular values for the pressures, times, and other quantities mentioned above relative to the minor initial shock wave must, therefore, not be taken too literally. In practice the peak pressures would be lower because of the finite time required for a droplet to become immersed in the smelt. However, the general conclusion below would still be valid even if the above quantities were incorrect by an order of magnitude. This conclusion is that the inertial reaction mechanism alone cannot explain smelt-water explosions when the rate of transfer of heat from the smelt to the water is limited by the ordinary process of thermal conduction. As previously discussed for the encapsulation mechanism, explosive tendency by whatever is the primary mechanism may be enhanced by any water-droplet atomization and dispersion into the smelt that may be produced by the transient pressure pulse.

Effect of Energy Exchange or Generation Rate. What has been shown in the foregoing considerations is that the inertial reaction mechanism cannot explain the tendency for an explosion to occur when a water droplet is immersed in liquid smelt, if the rate at which energy diffuses into or is generated within the water droplet is as slow as that determined by the ordinary thermal-diffusion process alone. What also has been shown is that the inertial reaction mechanism does permit the occurrence of momentary high pressure confinement. It could, therefore, account for the explosive tendency if the rate of energy transfer into, or generation in, the water droplet were considerably more rapid than that resulting from thermal diffusion. The encapsulation mechanism for either slow or fast energy exchange has already been ruled out, since the analysis for this case involved quantities of heat transfer but not rates.

The most likely explanation for the onset of smelt-water explosions is, therefore, the existence of some rapid means for buildup of thermal energy in the water, combined with the inertial mechanism for temporary pressure confinement. This rapid means of thermal-energy buildup, whether it be physical or chemical, must be rapid enough to superheat essentially all of the water in less than roughly D_0 millisecond, where D_0 is the diameter of the droplet in centimeters. Some processes by which this may occur are considered below.

Infrared Radiation. Infrared radiation affords an additional means for transporting heat from a warmer to a colder portion of a medium that is semitransparent to infrared, particularly at temperatures above room temperature for which the energy density of infrared photons is significantly high. In fact, the transport of heat by infrared waves complicates the task of measuring the thermal conductivities of certain materials at elevated temperatures.

The propagation of electromagnetic radiation in a medium is characterized by an absorption coefficient, α, per unit distance of travel. The reciprocal of α is the mean free path of an infrared photon, the average distance it travels before it is absorbed or scattered. The absorption coefficient is, in general, a function of wavelength; but for

simplicity in this discussion it will be considered to have some average value that is a function of the temperature.

Consider first the water or liquor droplet. If its absorption coefficient were so great that the mean free path were only a small fraction of the droplet diameter, all infrared radiation coming from the hot smelt would be absorbed in a relatively thin layer near the surface of the droplet. Infrared radiation could then contribute little to the transfer of heat into the droplet. Conversely, if the mean free path exceeded several times the droplet diameter, little radiation would be absorbed within the effectively transparent drop. Most of it would pass through the drop to propagate through or be absorbed by the smelt. The worst case from the viewpoint of explosive tendency would seem to be one in which the mean free path is comparable to the droplet diameter. This may be a contributing factor to the greater explosive tendency with green liquor than with either clear water or black liquor.

Consider second the smelt itself. The more transparent it is to infrared radiation, i.e., the lower the absorption coefficient in the smelt, the more readily could heat propagate from the more distant portions of the smelt to the droplet. The cooling down of the smelt in the vicinity of the droplet would then have less effect in slowing down the rate of heat transfer, since the droplet could always "see" the more distant, hotter portions of the smelt, just as the sun's rays heat up an absorbing ground more rapidly through a cold but transparent atmosphere than if they had to heat up the intervening atmosphere first.

Plans have been made to modify the computer program to include the effects of radiation in the heat transfer-hydrodynamic problem, but this program has not yet been implemented. It would involve considerably more computation for each interval and hence a longer time to run the program. However, a "most-favorable limiting case" type of computation can readily be made to ascertain whether or not the infrared radiation mechanism of heat transport can account for the explosive tendency of the smelt-water system.

Mathematical Analysis of Limiting Case. For the limiting-case computation it will be assumed that the smelt is essentially transparent, so that the water droplet always "sees" the radiation from the smelt at its ambient temperature T_{sm}. It will be assumed furthermore that all of the radiation that enters the water droplet is absorbed and converted to heat.

The intensity of radiation from the smelt to the water droplet is given by

$$I = \epsilon \sigma T_{sm}^4 \quad , \tag{16}$$

where ϵ is the emissivity and $\sigma = 5.679 \times 10^{-12}$ watt/(cm^2)($^\circ$C)^4 is Stefan-Boltzmann's constant. For $\epsilon = 0.5$ and $T_{sm} = 1200\,^\circ$K, $I = 1.40$ cal/(cm^2)(sec). The reradiation from the water at its boiling point of 373$\,^\circ$K at atmospheric pressure can be neglected by comparison because of the fourth-power temperature dependence. The rate at which steam is produced, assuming that essentially all of the water in the droplet has reached its boiling point because of an assumed fairly uniform absorption of radiation throughout the droplet, is given by

$$\alpha = I/L_w \tag{17}$$

per unit area of droplet surface, where L_w is the heat of vaporization of water. For $L_w = 539$ cal/g, $\alpha = 2.60 \times 10^{-3}$ g/(cm^2)(sec).

A preliminary consideration of the dynamics of the problem, involving numerical integration of a pair of differential equations, shows that, for the above value of α, the pressure in the droplet never departs appreciably from atmospheric, except for a relatively short-duration transient at the beginning of the process. The magnitude of this pressure transient is much less than that obtained for the thermal-conductivity computations discussed previously. The heat flux due to thermal conductivity is initially much higher than that due to infrared radiation, because of the initially very large temperature gradient at the interface between the smelt and the droplet. However, the thermal-conductivity heat flux rapidly decreases to a value much below the radiant flux value as this temperature gradient decreases.

If the steam pressure is close to atmospheric throughout the process of steam formation, the rate of increase in volume of the droplet due to expansion of the steam is $4\pi r^2\alpha/\rho_{st}$, where r is the instantaneous radius of the droplet and ρ_{st} is the density of steam. This quantity must equal $4\pi r^2 v$, where v is the velocity of outward motion of the interface between droplet and smelt. We have then, simply

$$v = \alpha/\rho_{st} = 4.46 \text{ cm/sec} \tag{18}$$

independent of r.

At this low a velocity, inertia and compressibility effects in the smelt may be neglected. The outward velocities of the concentric shells of smelt surrounding the droplet are thus inversely proportional to the squares of their radii. When all of the water in the droplet has been converted to steam, simple integration shows the total kinetic energy of motion imparted to the smelt to be given by

$$K.E. = 1/2(4\pi\rho_{sm}R_o^3)v^2 \quad , \tag{19}$$

where R_o is the radius of the sphere of steam and ρ_{sm} is the density of smelt. In other words, the effective inertial mass of the smelt surrounding the steam bubble is equal to three times the mass of the smelt displaced from the bubble volume. Since the total heat input to form the steam is

$$H = 4/3\pi R_o^3 \rho_{st}L_w \quad , \tag{20}$$

the fraction of this heat input that is converted to energy of motion of the smelt is

$$F = K.E./H = 1.5 I^2 \rho_{sm}/(L_w \rho_{st})^3 J \tag{21}$$

as obtained by using also Equations (17) and (18). J is the mechanical equivalent of heat = 4.187×10^7 ergs/cal.

Results. Numerical substitution of the pertinent quantities results in F = 4.53 x 10^{-6}. In practice, F would be even smaller, because of the most-favorable-case assumptions made as the basis for this simplified analysis. Clearly, heat transfer by infrared radiation is also too slow to account for the explosive tendency.

Reference to Equation (21) shows that the efficiency of conversion of heat to explosive energy varies at I^2. Thus we must look for a mechanism of energy transfer into the droplet that is about 100 times or more as rapid as infrared radiation. If I is increased by a factor of 100 to 140 cal/(cm^2)(sec), the value of F would increase to 4.53 percent in accordance with Equation (21), if the pressure were still not too high above atmospheric. (Actually, ρ_{st} would be increased because of the higher pressure, but there would then also be some potential energy for further expansion after complete conversion to steam.)

Other Means of Thermal-Energy Buildup. The generation of turbulence, because of the instability of purely radial flow, may provide the mechanism for the required 100-fold or more increase in heat transfer. The transfer rate could be raised considerably by continuous removal of the steam layer separating liquid water from molten smelt, as a result of mechanical shear. Investigation of turbulence effects would be complicated by the fact that the problem could then no longer be modelled as a spherically symmetric system except, perhaps, in a statistical way. It may be necessary to develop a statistical theory of turbulent mixing for the case of a water droplet immersed in a hot liquid medium, if no such theory exists.

Considerably higher heat-transfer rates are also known to occur for some fluids near their critical points. Since the temperature of the molten smelt is above the critical temperature of water, the outer layers of steam surrounding a given droplet could readily reach this temperature, particularly in view of the poor thermal conductivity of steam at atmospheric pressure. A pressure pulse originating from a neighboring droplet could well result in the development of critical conditions for some portion of this high-temperature steam. We have seen that high pressure pulses can develop momentarily, just when the boiling point is exceeded at the outer layer of a droplet. If heat is then transferred rapidly enough into the original droplet through the layer of water under critical conditions, the reaction might become self-sustaining. This explosion mechanism possibility may warrant further consideration.

Additional heat transport also may be provided by the existence of complex high-temperature gaseous molecules such as NaOH, NaCl, their dimers, and Na_2OHCl in the steam layer surrounding the water.

The thermal conductivity of a gas is proportional to the product of viscosity and heat capacity. The heat capacity is sensitive to the number of ways (modes) in which the molecule can vibrate, which depends on the number of atoms in the molecule and on the "stiffness" of the vibrations. The latter, in turn, depends upon the bond strengths and mass of the vibrating atoms. Thus, a molecule consisting of many heavy atoms would be an excellent candidate to provide a high rate of heat transfer because of its high heat capacity. For example, a molecule such as $(NaOH)_2$ [C_p ~26 kcal/(mole)(°C)] can easily have more than three times the heat capacity of a molecule like water [C_p ~9 kcal/(mole)(°C)] , so that thermal conductivity of the former is much higher also.

The absorption of infrared radiation would also be enhanced by any appreciable concentration of these complex molecules, both because of the fact that more ionic bonds cause greater absorption and also because the low-frequency vibrations of these kinds of molecules lie in the wavelength range where there is the greatest amount of infrared flux at molten-smelt temperatures.

It is known that quenching of metals occurs much more rapidly in NaOH solution than in pure water. This may be a result of the improved heat transfer resulting from the existence of NaOH and $(NaOH)_2$ vapor in the steam layer separating the metal from the water, as discussed above, although the increased boiling point of the solution over that of pure water also would be expected to provide some improvement. A similar effect may take place in transfer of heat into water immersed in molten smelt.

The Hydration Mechanism

In the previous studies of the smelt-water reaction that were supported by the Smelt-Water Research Group[1], it was concluded that smelt-water explosions are non-combustible, and it was suggested that a reaction between smelt and water, termed a hydration reaction, is involved. However, no direct investigation or technical evaluation of the various possible hydration and noncombustive smelt-water reactions was made in that previous work.

Data readily available on known hydrates of the major constituents of smelt, given in Table 3, indicate that such hydrates are stable only at relatively low temperatures. As can be seen, most of the known hydrates decompose at temperatures below 100°C, the normal boiling point of water. The 700°C limit given for the decomposition of sodium sulfide monohydrate is the temperature required to obtain an anhydrous salt; most of the

TABLE 3. HYDRATES OF THE MAJOR CONSTITUENTS OF SMELT

Hydrate and Decomposition Mode	Decomposition Temperature, °C
$Na_2CO_3 \cdot 10H_2O \rightarrow Na_2CO_3 \cdot H_2O$	32.96
$Na_2CO_3 \cdot 7H_2O \rightarrow Na_2CO_3 \cdot H_2O$	35.37
$Na_2CO_3 \cdot H_2O \rightarrow Na_2CO_3$	149.
$Na_2S \cdot 10H_2O \rightarrow Na_2S \cdot 9H_2O$	4.7
$Na_2S \cdot 9H_2O \rightarrow Na_2S \cdot 5.5H_2O$	48.9
$Na_2S \cdot 5.5H_2O \rightarrow Na_2S \cdot H_2O$	94.
$Na_2S \cdot H_2O \rightarrow Na_2S$	<700.
$Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4$	32.4
$NaOH \cdot H_2O \rightarrow NaOH$	66.
$NaOH \cdot H_2O \rightarrow NaOH \cdot 0.5H_2O$	60.
$NaOH \cdot 0.5H_2O \rightarrow NaOH$	93.
$NaCl \cdot 2H_2O \rightarrow NaCl$	0.2

water of hydration is evolved at lower temperatures. Although these hydrates contain appreciable concentrations of water, ranging from 38 weight percent in $NaCl \cdot 2H_2O$ to 69.5 weight percent in $Na_2S \cdot 10H_2O$, virtually all the water is evolved and is present as free water below the normal boiling point. Vapor pressure-temperature characteristics obtained on heating the hydrates above the decomposition temperatures would be essentially those of free water. These hydrates, therefore, are not seen to be sources of the significant quantities of superheated water that are believed to be generated in the smelt-water reaction.

The Solution Mechanism

Physical solutions of water in inorganic salts are formed and may contain appreciable concentrations of water at elevated temperatures. For example, as can be seen in Table 4, a saturated sodium bromide-water solution contains about 22 mole percent water at 678°C (1250°F), while a saturated sodium iodide-water solution contains about 26 mole percent water at 521°C (970°F). As can be seen in Table 5, a saturated solution of sodium chloride contains about 49 mole percent water at 646°C (1195°F).

TABLE 4. VAPOR-PRESSURE DATA FOR SATURATED AQUEOUS SOLUTIONS OF SODIUM BROMIDE AND SODIUM IODIDE[13]

Temperature, °C	Vapor Pressure, atm	Solubility, mole fraction of salt
Sodium Iodide		
293	35.4	0.249
396.0	92.56	0.328
460.0	131.6	0.390
493.8	153.3	0.436
567.0	174.9	0.555
678	109.7	0.783
Sodium Bromide		
185.0	2.40	0.336
240.8	8.51	0.390
300.2	17.58	0.454
342	26.36	0.502
372	34.63	0.538
389.5	38.79	0.559
444.0	61.2	0.624
493.0	88.5	0.690
521.4	100.04	0.735
600.0	189.1[a]	0.888

(a) Unsaturated.

TABLE 5. VAPOR-PRESSURE DATA FOR
SODIUM CHLORIDE-WATER[13]

Temperature, °C	Vapor Pressure, atm	Solubility, mole fraction of NaCl
183. 0	7. 27	0. 120
205. 1	11. 76	0. 124
230. 2	19. 29	0. 130
246. 7	25. 08	0. 135
254. 6	27. 51	0. 138
299. 3	56. 03	0. 155
327. 3	78. 50	0. 169
344. 4	96. 29	0. 178
354. 3	106. 4	0. 183
385. 7	145. 0	0. 205
410. 0	178. 9	0. 217
442. 5	230. 1	0. 238
467. 5	269. 0	0. 251
485. 5	294. 4	0. 270
514. 2	335. 1	0. 285
550. 5	370. 1	0. 335
600. 0	388. 7	0. 411
646. 2	368. 5	0. 505

Plots of the data for the salt-water solutions (Figure 2) show that, as the temperature is increased, the vapor pressure of the solution (essentially water-vapor pressure) initially increases. Since the fraction of water in the saturated solution of the highly soluble salts decreases with increasing temperature, the vapor pressure passes through a maximum and decreases to zero. The high-temperature intercept with the abscissa corresponds to the melting point of the salt; above this temperature the liquid is molten salt containing essentially no water. Of significance is the fact that vapor pressures of solutions of the highly soluble salts (NaCl, NaBr, NaI) are much lower than corresponding vapor pressures of water (curve at extreme left in Figure 2), and that the intermolecular forces in the solutions appear to be strong enough to prevent critical conditions (i. e., vaporization) at temperatures as high as 800°C (1480°F).

Similar vapor pressure-temperature relationships have been observed for other salts, including potassium chloride, potassium iodide, calcium nitrate, boric oxide, and potassium silicate. Thus, nonnegligible concentrations of water can be taken into solution in inorganic salts at elevated temperatures up to the melting point of the pure inorganic salts.

Solutions of the sparingly soluble salts, sodium carbonate and sodium sulfate, however, show different characteristics. As can be seen also in Figure 2, the pressure-temperature curves for saturated solutions of sodium carbonate and sodium sulfate fall near to that for pure water, with solubilities being negligible from the critical temperature of water upward, thus terminating the curve at that temperature.
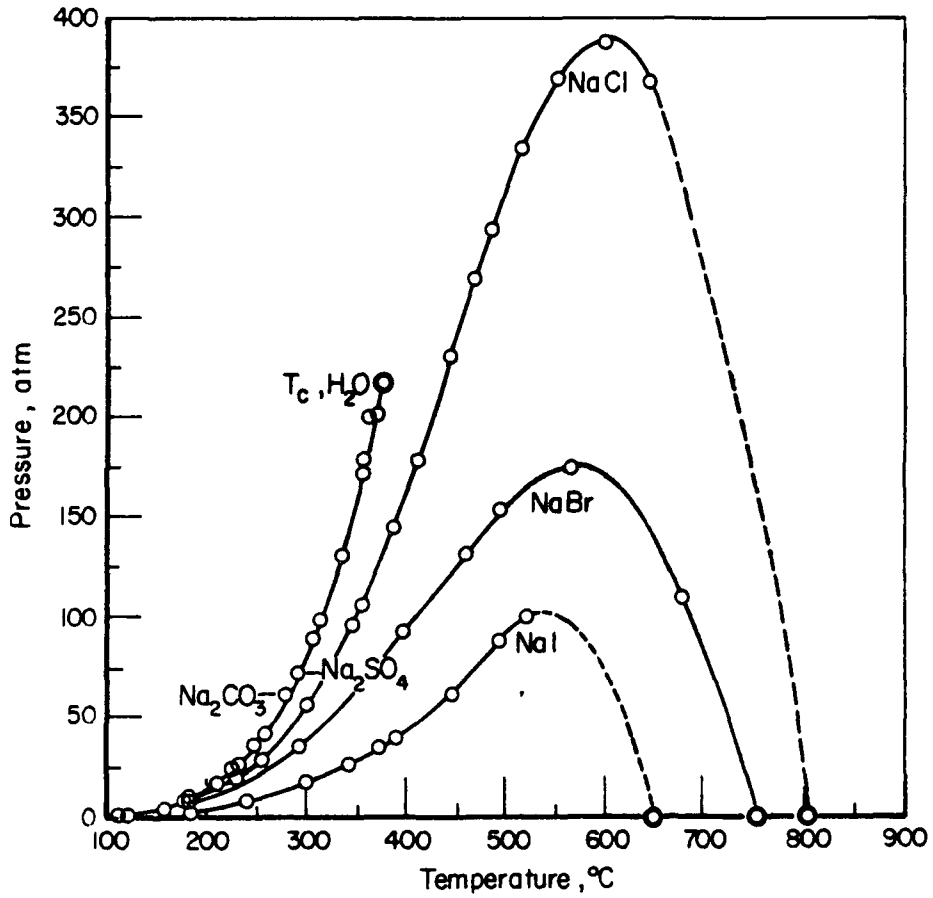
FIGURE 2. VAPOR-PRESSURE CURVES OF AQUEOUS SOLUTIONS
OF SEVERAL SODIUM SALTS[13]

Figure 3 has been constructed to give an idealized picture of vapor-pressure versus temperature for solutions containing various concentrations of water. The solid curve in the figure is the vapor-pressure curve for saturated solutions. For the solid solutions containing less than the saturation concentrations of water, the vapor pressures would be less, and the curves would lie under the saturation curve, as indicated by Curves a, b, and c, for progressively decreasing concentrations of water. For the salt alone, the vapor pressure would be virtually zero, and the curve would coincide with the abscissa. For solutions containing greater than saturation concentrations of water, the vapor pressures would be higher, and the curves would be above the saturation curve, as indicated by Curves d and e for progressively increasing concentrations of water.

When water is brought into contact with molten salt (such as smelt), salt-water solutions tending to form initially at the interface might be of two types: (1) those formed at or near temperatures of the aqueous phase, essentially solutions of salt in water, corresponding to solutions toward the left end of the curves in Figure 3, and (2) those formed at or near temperatures of the molten-salt phase, essentially solutions of water in molten salt, corresponding to solutions near the right terminus of the curves in Figure 2. Whether or not the solution formation (or decomposition) could figure prominently in smelt-water explosions depends upon the rate (kinetics) of the solution processes, the energy changes associated with the processes, and the heat-transfer mechanisms. A solution process can be an important causative factor in smelt-water explosions only if (1) the process can occur at a very high rate and (2) the reaction is exothermic and thus produces a self-propagating, avalanching vaporization of water.

Consideration of the dissolving of molten salts in the aqueous phase gives evidence that this process could provide the energy for the vaporization of large quantities of water. Examination of some pertinent properties of the major components of smelt, which are presented in Table 6, reveals that NaOH, which is indicated to be a primary explosion sensitizer by a preponderance of evidence, is unique with respect to its extremely high solubility in water. As is indicated in the table, if molten NaOH goes into solution in water, giving up its heat to the solution as it forms, the net heat effect can be significant. In the limiting, somewhat idealized, case used in making the rough estimates presented in Table 6, if about 8.7 moles of molten NaOH is dissolved in 0.5 liter of water, enough net heat is contributed to the solution to vaporize about 400 milliliters of the water, leaving a saturated solution of NaOH in the remaining 100 milliliters of H_2O. In a sample computation, it has been estimated that the explosive vaporization of only about 8 pounds of water can account for sufficient pressure rise to inflict serious damage on a 250-ton recovery furnace. This corresponds to the dissolving of only 7.1 pounds of NaOH in 10 pounds of water. (An essentially negligible amount of additional energy would be required to superheat the steam sufficiently to give explosive violence.) It is unlikely, of course, that precisely such solution formation as has been discussed would take place in a furnace. However, solution formation of the type discussed could occur, involving perhaps different concentrations, salt mixtures, etc., and giving a smaller specific effect, but involving larger quantities of materials, and thus producing rapid vaporization of large quantities of water.* It is not obvious whether the rates of mixing and solution could be high enough to generate steam explosively.

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*One of the authors recalls vividly the time he, as an undergraduate, abruptly dumped several grams of NaOH pellets into a flask of boiling water.
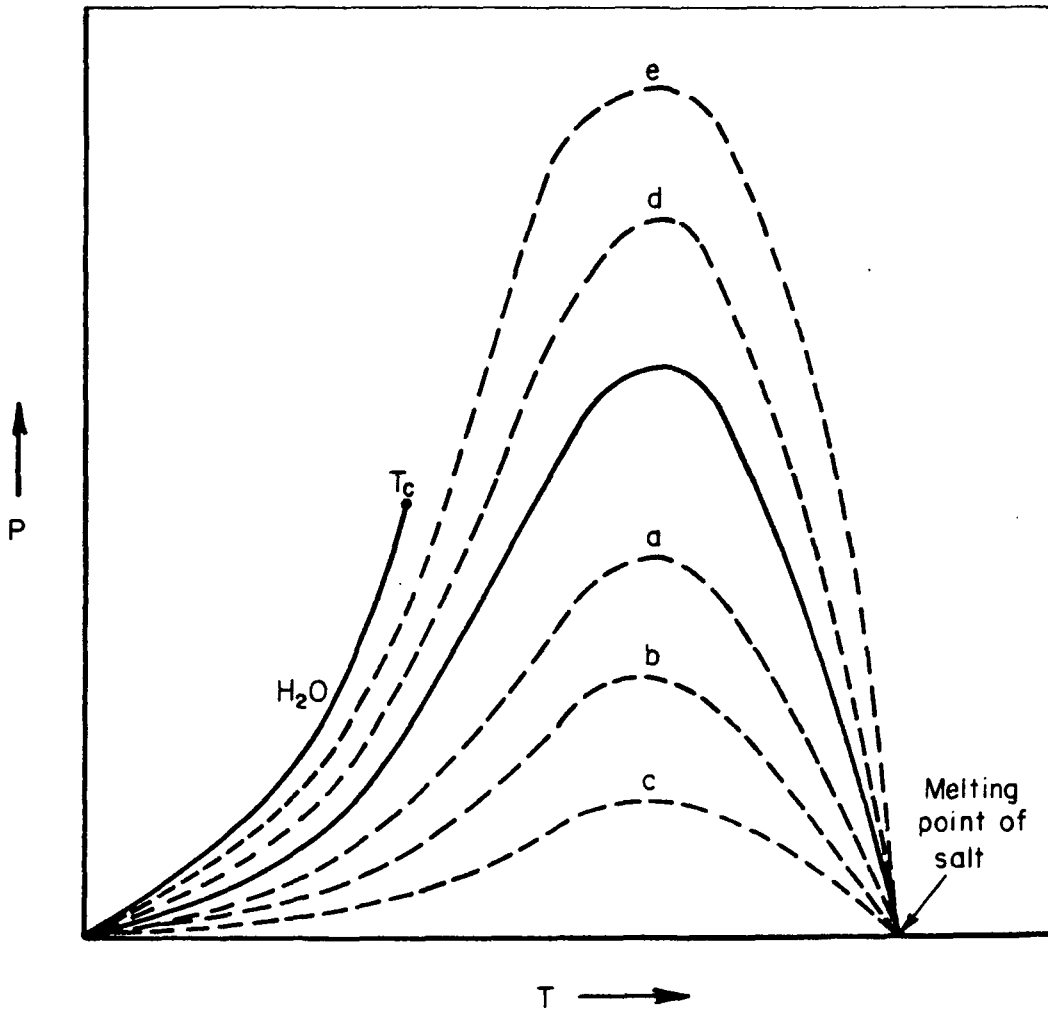
FIGURE 3. IDEALIZED PRESSURE-TEMPERATURE CURVES
FOR SALT-WATER SOLUTIONS

TABLE 6. DATA PERTINENT TO SOLUTION PROCESS

	Material				
	NaOH	NaCl	Na_2CO_3	Na_2SO_4	Na_2S
Solubility. g/100 ml water at 100°C	347	39. 1	45. 5	42. 5	57. 2
Solubility, moles/100 ml water at 100°C	8. 7	0. 67	0. 43	0. 40	0. 73
Heat of Fusion, kcal/mole at mp	1. 5	6. 7	6. 7	5. 7	--
Specific Heat (C_p), cal/(mole)(°C)	19. 9	16	24	--	--
Heat of Solution[a], kcal/mole at 25°C, 1 atm	-10. 3	+1. 3	-5. 6	-0. 6	-15
Heat to Solution per Mole of Salt Dissolved[b], kcal	27. 7	18. 2	31. 5	20. 7[c]	35. 4[c]
Net Heat to System From Dissolution of Quantity of Salt to Saturate 100 ml Water[d], kcal	240. 3	11. 5	16. 9	7. 6	25. 2
Amount of Water Net Heat Can Vaporize[e], g (ml)		19	28	13	41

(a) Positive values denote that heat is absorbed as salt is dissolved.

(b) Assuming the salt initially is at 900°C (1650°F) and is dissolved in water at 100°C.

(c) Calculated using estimated values for heat of fusion and/or specific heat.

(d) Assuming the water [C_p = 1 cal/(g)(°C)] to dissolve salt initially is at 30°C and must be heated to 100°C.

(e) Assuming the water initially is at 30°C, is heated to 100°C, and is vaporized (heat of vaporization 540 cal/g) at 1 atm.

As can be seen from examination of data for the compounds other than NaOH, some vaporization of water can result from the solution of the salts also; however, the effect is much smaller than with NaOH, and the expected contribution to the hypothesized solution mechanism for smelt-water explosions would be much smaller. The indication of near-negligible effects with Na_2CO_3 and Na_2SO_4 is in line with observations as to the virtually inert behavior of these salts in smelt-water contact tests. Although the data in Table 6 indicate that the effect would be somewhat greater with Na_2S than with the carbonate and sulfate, the predicted effect here also is relatively small. However, experimental evidence indicates that the reaction

$$Na_2S + 4H_2O \rightleftharpoons 2NaOH + H_2S$$

produces NaOH from Na_2S at high rate when the concentration of NaOH is low. In addition, in the molten-salt melange, the following reaction also may occur:

$$Na_2S + H_2O \rightleftharpoons NaOH + NaSH \quad .$$
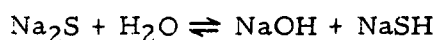
Both of the products of the reaction may be high-solubility species. NaCl, which also is indicated to produce only a minor solution effect, has been established as a smelt-water explosion sensitizer. Although NaCl itself may not be "active" in the low-temperature solution mechanism, it may be a precursor for NaOH. The reaction

$$NaCl + H_2O \rightleftharpoons NaOH + HCl$$

has been reported[1] to proceed to the right under high-temperature, nonequilibrium conditions. A second possibility is that the NaCl activity develops through formation of an active high-temperature compound such as Na_2OHCl.

Thus, prior art indicates that the major components of smelt that appear to have been sensitizers in smelt-water explosions could be directly or indirectly active through the low-temperature solution mechanism.

In addition to the low-temperature solutions, it is possible that the high-temperature (i.e., near the right terminus of the curves in Figure 3) salt-water solution process could contribute to smelt-water explosions. It is postulated that when the molten salt and water come into contact, layers of the molten salt are cooled to temperatures below the liquidus of the anhydrous salt and water goes into solution in the salt. As the material is reheated by the adjacent or surrounding molten salt, the water will be expelled from solution. This could be a process contributing significantly to smelt-water explosions if the water-evolving process is exothermic. Information is not available for evaluation of this high-temperature-solution mechanism.

Chemistry of Smelt-Water Reactions

General Considerations

In the previous investigations of smelt-water explosions, it generally has been concluded that such explosions are noncombustive in nature. The explosions have been produced in inert atmospheres and under water – with no evidence of a combustive flame or flash.

Nevertheless, evidences of chemical reaction and the influences of chemical species were observed. As a result of the laboratory-produced smelt-water reactions, H_2, CO, and CO_2 were found to be formed with synthetic Kraft smelts, and concentrations of hydroxide and sulfate in the molten-salt phase were observed to increase. With hot water, no explosions occurred, but the reactivity was observed to be directly related to hydroxide concentration, while the formation of CO and CO_2 is inversely related to it. With cold water and synthetic smelts, explosions are produced which appear to involve Na_2S; the presence of NaOH and/or NaCl has generally been found to increase the probability of explosion on first introduction of water.

The following have been identified as major reactions for the smelt-water system:

(1) $Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2$

(2) $Na_2S + 4H_2O \rightleftharpoons Na_2SO_4 + 4H_2$

(3) $Na_2S + 4CO_2 \rightleftharpoons Na_2SO_4 + 4CO$

(4) $Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S$,

and two smelt-char-water reactions have been identified:

(a) $CO + H_2O \rightleftharpoons CO_2 + H_2$

(b) $C + H_2O \rightleftharpoons CO + H_2$.
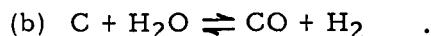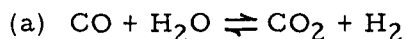
Although appreciable concentrations of combustible materials were produced by these reactions, no explosive combustion reaction has been observed in the laboratory experiments, and no highly energetic, exothermic chemical reaction has been identified. Physical mechanisms, for which evidence appears to exist in the type of damage inflicted on recovery furnaces, have been proposed as primary mechanisms.

That Na_2S is involved at some stage in the explosion-producing smelt-water reaction seems to be well established. Also, the sensitizing effect of minor concentrations of NaOH and NaCl appears to be adequately documented. The effects may be chemical, physical, or both. However, overall explanation of the phenomena and their interrelations probably will not be found entirely in "ordinary" low-temperature and solution chemistry. To develop a sufficiently comprehensive and useful understanding, attention must be turned partially to the high-temperature chemistry of the system and to the "unusual" reactions and species of that regime. Some possible roles of "unusual" species such as $(NaOH)_2$, $(NaCl)_2$, and Na_2OHCl have been discussed in preceding sections of this report. Consideration of the high-temperature reactions and their potential roles in explosion reactions, smelt modification, and emergency procedures also is called for.

In the course of the previous investigations of smelt-water reactions, no combustive, exothermic chemical reaction was identified which could account for the characteristics of the primary explosion process; however, chemical reactions were considered primarily as means of generating combustible materials which could then explode. While it seems probable that smelt-water explosions result from rapid generation of steam, it is believed that consideration of the possibility that gas-producing chemical reactions, particularly exothermic ones, contribute to the explosions is warranted. For example, the oxidation of Na_2S by water produces hydrogen. Sufficiently rapid evolution of hydrogen would, in itself, constitute an explosion, exclusive of detonation or deflagration of a hydrogen-air mixture.

It is believed that the present state of knowledge of the char bed and its interplay with both smelt recovery and smelt-water reactions must be substantially advanced before smelt-liquor-char-water interactions can be well understood. The chemical system is a complex one. Consider briefly the conversion processes which occur in the recovery boiler as black liquor transforms to smelt. Large quantities of liquor, whose chemical content can be highly variable, pour through the chamber. The massive solid bed resides in the boiler for long periods, but its composition varies with time. The bed is bounded by the water-cooled floor, 1500°F flowing smelt, and frozen smelt; and its hot (2200°F), porous-char upper face is bathed in the products of the black liquor spray. Large thermal gradients exist within the bed. In addition, there are great chemical inhomogeneities, associated with both the normal effects of the thermal gradient on chemical reactions and the changes in black liquor feed, furnace heating conditions, etc., during the boiler's operation. Indeed, it might be anticipated that the bed can scavenge impurities from the smelt and build them up to considerable proportions.

Thus, the smelt-producing recovery boiler is not an isothermal, steady-state reactor. The char bed on the floor of the boiler represents perhaps the region of greatest thermal and chemical gradients, both in space and time. The porous-char surface of

the bed has significantly greater surface area than the smooth-walled laboratory vessels utilized in previous studies. In addition to the heat transfer and solid-liquid reaction-rate implications of vessel topology, char porosity may be of paramount importance if the smelt-water reaction occurs on a solid interface.

As for the most appropriate means to study the contribution of the char bed to the present problem, the present state of knowledge does not permit design of an appropriate laboratory model. Perhaps the most practical suggestion in this regard would be that installation of high-speed cameras, infrared sensors, and chemical sampling devices on one or more mill recovery boilers be considered, to study the appearance, movement, temperatures, and chemical analysis of functioning char beds.

Another approach to the study of the complex chemical system is by use of computer analysis. Ideally, the computer calculations should be done in such a way as to predict concentrations of all possible products. A computer program available at Battelle can generate all the data in the JANAF thermochemical tables, as well as data for any additional molecules which one may wish to postulate and characterize thermodynamically by statistical mechanical means. This program will accept a number of input reactants containing up to six different atoms and, using the stored JANAF data, calculate the concentrations of molecules containing these atoms for up to a maximum of 70 products. The program has already been successfully applied to rocket-propellant evaluations and has proved to be both versatile and relatively inexpensive.

Several test runs have been made and applied to further examination of smelt-water reactions with and without additives (such as NaOH, NaCl, CO_2, etc.). Although simplifying assumptions regarding activities, etc., are made, the computations elucidate an equilibrium state that can be approached if the kinetics of the reactions are favorable. Although the analysis is of equilibrium processes (in contrast to the nonequilibrium processes of the recovery furnace and the explosion phenomenon) the computer calculations can be useful for the rapid and inexpensive identification of "allowed" reactions. In addition to predicting the products that form, the overall ΔH for the reactions that occur is calculated. Results of the test runs made indicate that exothermic chemical reaction(s) do occur.

In a full investigation, computer calculations would be made utilizing various smelt compositions, various concentrations of components, various combinations of ancillary reactants such as water, carbon, CO_2, and other atmospheres, etc. The product species and their concentrations would be calculated, along with overall enthalpy. Examination of the latter would identify general conditions under which exothermic reactions occur. In these areas, individual reactions would be studied more closely to identify those which give large heat effects conducive to explosive release of energy. As has been inferred, the computer program also can be turned to analysis of the effectiveness of explosion-inhibiting measures and emergency procedures. The data obtained would be utilized for design of critical experiments to evaluate concepts and approaches in the real, nonequilibrium world.

Effects of Smelt Composition on Explosiveness

There is little information available on the composition of plant smelts. The best compilation of analytical data on smelt composition at a number of mills was published by Nelson and Kennedy.[14] Thirty-eight samples of Kraft smelt from 15 different mills

were analyzed, and the violence of their reaction with the green liquor in the dissolving tank was recorded. Their data are shown in Table 7. For mills which do not have salt water in their logs, a fairly wide range of composition was found for the important constituents of the smelt:

	Percent
Na_2CO_3	69.6 to 85.5
Na_2S	8.5 to 23.9
Na_2SO_4	0.2 to 3.6
NaCl	0.4 to 2.1
NaOH	Up to 3.2

These wide composition ranges point up the difficulty in comparing mill operations and also in choosing a "typical smelt composition" for laboratory experiments.

Smelt-water reactions can be explosive both (1) when a relatively small amount of smelt reacts with a large amount of water, as in the normal dissolving-tank operation, and (2) when a relatively small amount of water reacts with a large amount of smelt, as in the abnormal condition of a water leak in a recovery furnace. Although this study is concerned only with the recovery-furnace explosion problem, and although the mechanisms are not necessarily identical in the two cases, there appears to be enough in common between the two types of smelt-water interaction to warrant giving consideration to data obtained under both conditions.

Na_2CO_3. The major component of smelt, Na_2CO_3, has been demonstrated to be nonexplosive under a wide variety of temperature and water-injection conditions. It is a generally accepted fact that pure molten Na_2CO_3 will not react explosively with water under any conditions.

Na_2S. Na_2S plays an important role in smelt-water reactions. Data obtained by Combustion Engineering on the explosiveness of Na_2S-Na_2CO_3 mixtures on the first water injection are shown in Figure 4. Of the 19 runs in which Na_2S was present, 6 produced significant explosions, 8 were only mildly explosive, and 5 were nonexplosive. The scatter of mild reactions among violent ones indicates a need for further research to discover why water can sometimes contact smelt of high Na_2S content without violent explosion. It also appears that a line might be drawn which would separate explosive compositions from nonexplosive ones. More data points, particularly in the lower section of the graph, would be needed to permit this, however.

The effect of repeated additions of water to the nonexplosive or mildly explosive smelts depicted in Figure 4 is shown by a similar plot in Figure 5, in which the total amount of water used is expressed as weight percent of the smelt. Two of the smelt compositions that were nonexplosive on the first injection, and one that was mildly explosive, became violently explosive after enough water was added. This result suggests that a sensitizing chemical reaction, such as the hydrolysis of Na_2S to form NaOH, may occur upon addition of water.

Smelt compositions containing Na_2S in the range 21.8 to 38.5 percent were studied by Babcock & Wilcox. Five of eight water-injection experiments resulted in explosions, and it is significant that two of the nonexplosive runs were at the highest Na_2S

TABLE 7. ANALYSIS OF PLANT SMELTS

Mill	State[a]	Type	Water Insol.	Na_2CO_3	Na_2S	NaOH	Na_2SO_4	$Na_2S_2O_3$	NaCl	Na_2SiO_3	Na_3PO_4	CaO	MgO	$Fe_2O_3+Al_2O_3$	K as K_2O	NH_3	Total	Reduction	Sulfidity	Total Sulfur	
A	Me.	Soda–normal	1.2	93.7	1.0	1.6	0.8	0.2	1.3	0.3	0.2	None	None	0.1	1.5	0.055	100.9	69.1	1.3	0.6	Soda Smelts
A	Me.	Soda–normal		92.1	0.9	2.1			1.4						1.5	.	98.0				
A	Me.	Soda–normal		91.5	1.1	1.1			1.6						1.7		97.0				
B	Pa.	Soda–normal–white	0.14	93.2	0.4	0.2	0.1	0.2	2.0	0.4	0.2	None	None	0.4	2.7	0.079	100.0	91.7	0.6	0.4	
B	Pa.	Soda–flush–black	1.25	92.8	0.4	0.2	0.1	0.1	1.9	0.1	0.2	None	None	0.2	2.7	0.076	100.1	87.9	0.5	0.3	
C	Me.	Kraft–normal	0.55	71.9	17.3	-1.4	3.5	1.6	2.0	0.2	0.2	None	None	0.1	5.3	0.003	102.7	90.1	4.7	8.8	Kraft smelts
D	Va.	Kraft–normal	0.54	75.9	16.3	-1.3	2.4	0.3	0.7	0.1	0.1	0.2	None	0.1	1.9	0.020	98.3	92.6	2.6	8.0	
E	Tenn.	Kraft–normal	0.41	77.7	16.2	-0.2	1.2	0.1	1.6		0.4				2.2		99.8	96.1	2.1	7.5	
F	Ga.	Kraft–explosive	0.35	73.1	18.8	0.5	0.8	0.1	1.1		0.3				3.6		98.7	97.7	5.7	8.8	
G	Ga.	Kraft–normal	0.30	79.3	13.0	None	2.1	0.2	1.9		0.4				2.2		99.4	92.0	8.2	6.4	
H	Ga.	Kraft–normal	0.76	85.3	8.5	None	0.2	0.1	1.8		0.3				1.8		98.7	99.0	11.9	4.0	
I	Ga.	Kraft–normal	0.20	75.6	16.8	0.2	1.4	0.1	1.6		0.3				1.5		97.7	95.7	23.1	7.8	
I	Ga.	Kraft–explosive	0.43	79.1	15.9	0.3	0.3	0.2	2.1		0.6				1.8		100.7	99.0	1.4	7.1	
J	Ga.	Kraft–normal	0.57	73.8	16.9	-0.1	3.6	0.1	1.5		0.5				2.3		99.3	89.6	23.7	8.7	
J	Ga.	Kraft–high bed	0.41	75.3	17.7	-0.4	2.0	0.1	1.5		0.6				3.1		100.7	94.2	24.2	7.9	
J	Ga.	Kraft–flush	0.47	78.2	17.1	-1.6	0.8	0.1	1.2		0.6				3.3		101.8	97.4	22.9	6.9	
K	Ga.	Kraft–normal	0.38	69.8	21.7	0.3	2.4	0.1	1.5		0.4				1.7		98.3	94.4	29.6	10.0	
K	Ga.	Kraft–normal		75.6	18.2	-1.4	3.0		1.4						2.2		100.4	91.7	24.6		
L	Ga.	Kraft–normal	0.35	70.8	-20.0	0.2	3.5	0.2	1.2		0.5				1.3		98.1	91.2	27.7	9.4	
L	Ga.	–N. bed. High S[b]	0.36	70.0	23.9	-1.4	1.7	0.3	1.1		0.4				2.1		99.9	96.4	31.7	10.4	
L	Ga.	–N. bed. high S[b]	0.41	70.3	23.1	-0.6	1.7	0.2	1.3		0.4				1.9		99.3	96.1	30.9	10.4	
L	Ga.	–High bed	0.30	71.0	21.1	-0.4	2.3	0.3	1.3		0.5				2.3		99.1	94.4	28.7	9.9	
L	Ga.	–High bed	0.37	71.8	21.0	-0.7	2.4	0.2	1.2		0.6				1.3		98.9	94.2	28.4	10.0	
L	Ga.	–High bed	0.28	74.2	19.9	0.2	1.6	0.2	1.2		0.5				1.7		98.8	95.7	26.6	9.1	
L	Ga.	–High bed, high S	0.27	74.5	19.7	0.4	1.7	0.2	1.2		0.6				1.6		100.2	95.6	26.3	9.1	
M	Pa.	–Normal	0.26	84.3	9.5	0.7	0.2	0.2	1.9		0.5				3.1		100.7	99.1	13.1	4.6	
N	Wash.	–Normal		79.7	14.8	-0.2	2.6		1.7						0.8		99.6	91.2	20.1		
N	Wash.	–N. bed, high S		77.8	17.4	-0.9	2.5		1.6						1.1		100.4	92.7	21.2		
N	Wash.	–Normal		79.7	16.6	0.5	0.7		1.6						1.3		100.4	97.7	21.9		
N	Wash.	–N. bed, high S		78.3	17.6	-0.5	1.0		1.6						1.1		99.6	96.9	23.4		
N	Wash.	–N. bed, 15 psi[c]		74.7	23.2	-1.7	0.5		1.7						1.3		101.4	98.8	29.7		
N	Wash.	–N. bed, 20 psi		79.0	16.0	0.3	0.5		1.8						1.1		98.7	98.3	21.5		
N	Wash.	–Jelly		79.4	14.0	3.2	0.2		1.7						1.0		99.5	92.7	19.3		
N	Wash.	–Large flush		78.7	17.2	0.5	0.3		1.7						1.9		100.3	99.0	22.7		
N	Wash.	–Very violent		80.2	15.6	0.6	0.3		1.6						1.5		99.8	99.0	20.1		
N	Wash.	–Very violent		81.4	15.6	-1.0	0.3		1.7						1.5		100.5	99.0	20.7		
O	Wash.	–Unshattered–v. quiet		76.4	15.8	0.1	2.3		4.4						1.2		100.2	92.6	21.9		
P	B.C.	–Normal, Unit B		70.6	14.6	0.5	0.2		12.2						1.8		99.9	99.2	21.8		
P	B.C.	–Normal, Unit B		68.7	15.4	0.5	0.1		12.5						1.7		98.9	99.7	20.9		
P	B.C.	–Normal, Unit A		68.2	15.8	None	0.5		11.8						1.7		98.0	98.4	23.9		
P	B.C.	–Normal, Unit B		75.4	12.4	1.2	0.2		9.1						1.9		100.2	99.1	18.8		
P	B.C.	–Normal, Unit B		71.8	13.2	1.3	0.2		8.9						1.9		97.3	99.1	19.6		
Q	N.Car.	–Normal		78.5	18.6	-0.4	1.3		0.4						1.6		100.4	96.3	24.3		

(a) Each letter represents a different mill.
(b) High sulfur sampled after sulfur bag(s) addition to the ash bed.
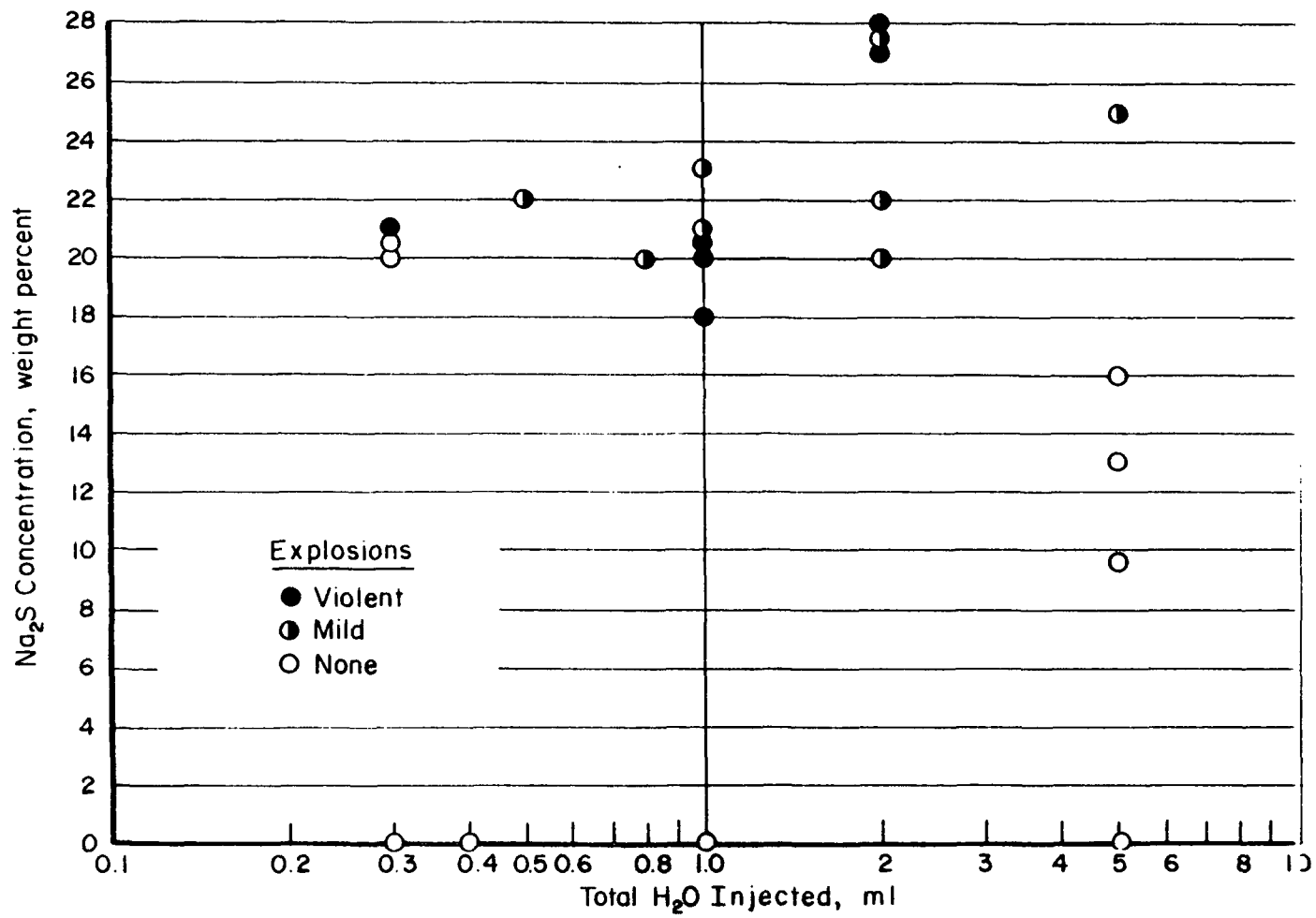(c) Violence rated in psi shatter steam.

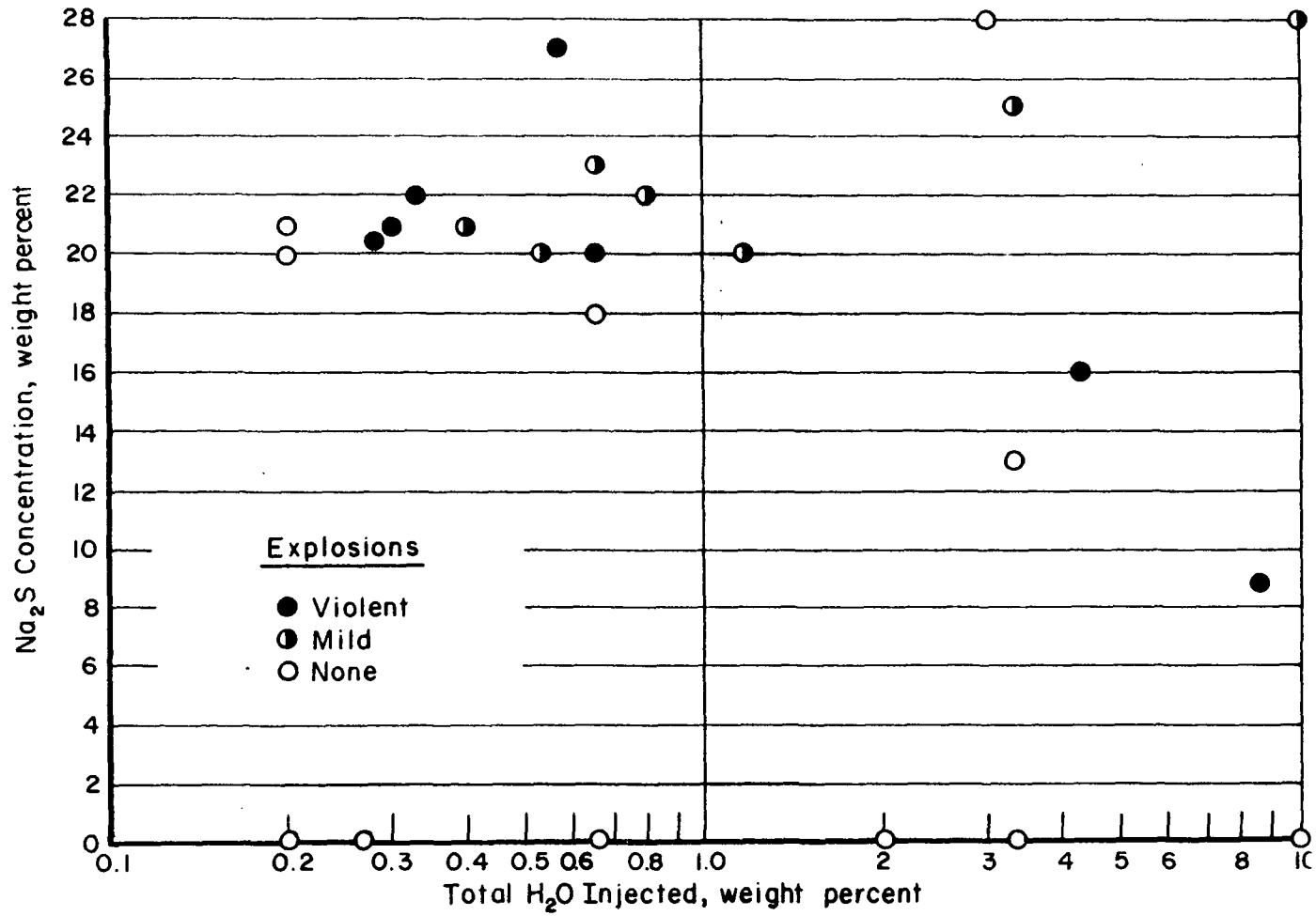FIGURE 4. EXPLOSIVENESS OF Na_2S-Na_2CO_3 MIXTURES ON FIRST WATER INJECTION

FIGURE 5. EXPLOSIVENESS OF Na_2S-Na_2CO_3 MIXTURES WITH WATER ADDED

concentrations. (Data from these experiments are not plotted on Figures 4 and 5 because the conditions were considerably different.)

Comparing these data with those obtained by Nelson and Kennedy in their study of dissolving-tank explosions reveals similarities. With smelt containing only Na_2S and Na_2CO_3, mild explosiveness began at 19.1 percent Na_2S in the dissolving-tank studies. With sensitizers present, explosions occurred with as little as 15.5 percent Na_2S. The data of Figures 4 and 5 suggest that for small amounts of water without sensitizers present, about 20 percent Na_2S is the maximum safe concentration under the conditions of the Combustion Engineering furnace experiments.

The research reported to date shows that Na_2S plays a part in the smelt-water explosion, but the maximum safe concentration of Na_2S is influenced greatly by the known sensitizers NaOH and NaCl.

Na_2SO_4. As noted earlier, Na_2SO_4 is a minor component of all plant smelts. Operating conditions of the recovery furnace determine the percent reduction of the Na_2SO_4 and its concentration in the smelt. In the Babcock & Wilcox work, smelt-water reaction was found to increase the Na_2SO_4 concentration in the smelt significantly. The addition of 5 percent Na_2SO_4 to smelt containing 35 percent Na_2S resulted in explosion when water was injected, although in similar experiments at 37 to 38 percent Na_2S without added Na_2SO_4 there was no explosion.

A series of experiments at Combustion Engineering demonstrated that at low Na_2S concentrations (17 to 18 percent), as much as 10 percent Na_2SO_4 could be added without explosion, whereas, when the Na_2S concentration was raised to the 25 to 28 percent level, explosions occurred with less than 10 percent Na_2SO_4 present. However, the Na_2S concentrations at which explosions occurred in the presence of added Na_2SO_4 were high enough to have resulted in explosions from the Na_2S alone, as indicated in Figures 4 and 5. Figure 6 shows the results of these experiments with various concentrations of Na_2S and Na_2SO_4; in all cases, the temperature was 1800°F and 3 milliliters of water was injected.

Earlier work by Rogers et al.[15] also showed that smelt containing 20 percent Na_2S and 5 percent Na_2SO_4 was explosive, but not at all temperatures. (Here again the sulfide concentration was high enough to permit explosion without addition of sulfate.) At 1600 and 1800°F "loud pops" were noted, whereas at 2000°F a loud explosion occurred. It appears to be significant that delayed pops and explosions were noted in these experiments, as though a chemical reaction were occurring and possibly generating a sensitizing component such as NaOH.

The effect of Na_2SO_4 in smelt is one point on which the results of laboratory experiments under recovery-furnace conditions were not in complete agreement with those simulating dissolving-tank operation. In their dissolving-tank experiments, Nelson and Kennedy[14] found that with 7 percent Na_2SO_4, a very mild explosion occurred in smelt with 15 percent Na_2S present. However, under these conditions it appeared that the smelt was not sensitized by 1 percent NaOH, as it had been without Na_2SO_4, so it was concluded that Na_2SO_4 can be an inhibitor for dissolving-tank explosions but not for recovery-furnace explosions.

On the basis of the available experimental data, Na_2SO_4 does not appear to be a sensitizer for recovery-furnace explosions. However, additional experiments are
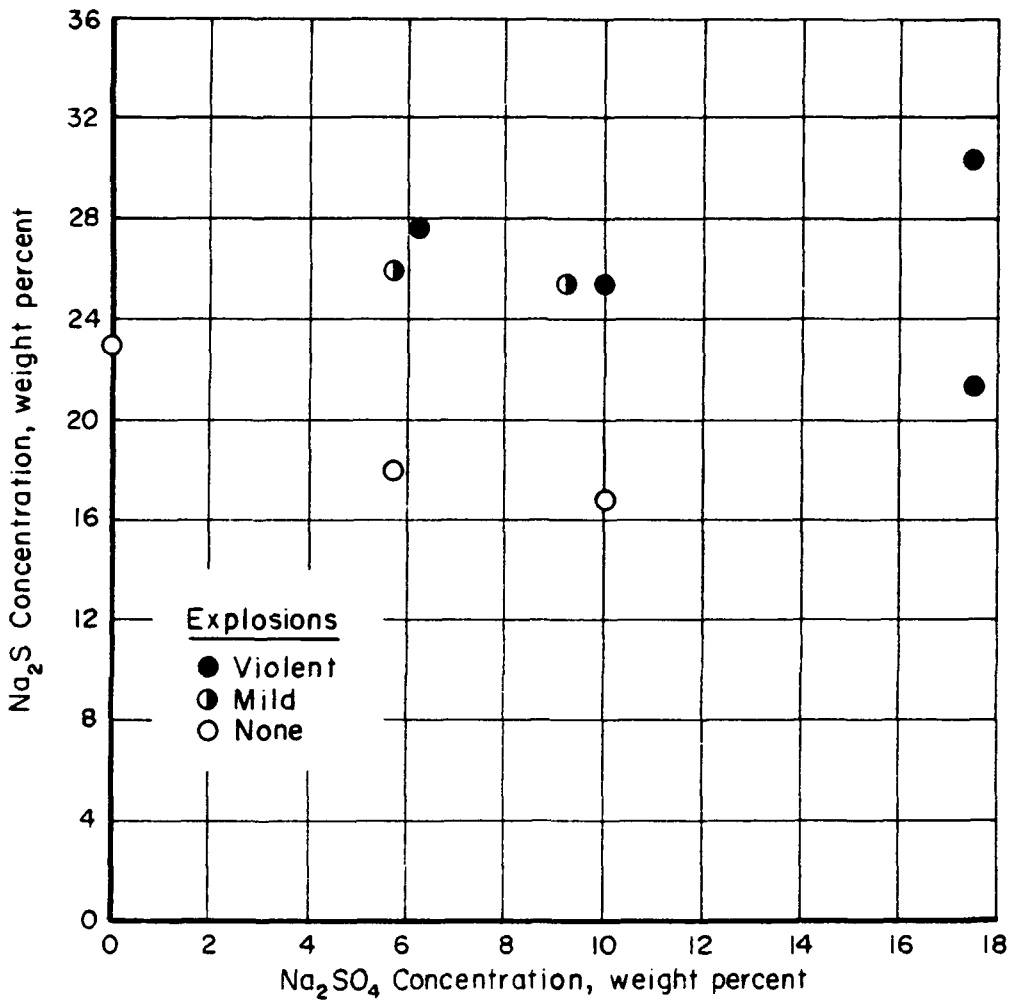
FIGURE 6. EXPLOSIVENESS OF Na_2S-Na_2CO_3 MIXTURES
WITH Na_2SO_4 PRESENT

needed with Na_2SO_4 additions to smelts having low Na_2S concentrations before a firm conclusion can be reached on this point.

NaOH. Another minor constituent of smelt is NaOH (or Na_2O), which exerts great influence on explosive tendency, even in low concentrations. It is generally agreed that NaOH is a sensitizer for smelt-water explosions. When 5 percent NaOH was added to synthetic smelt containing 35 percent Na_2S in the Babcock & Wilcox work, explosion occurred with the first water addition in most cases, whereas smelt without NaOH (or other sensitizer) required several water additions for explosion.[*] It was also shown that the amount of NaOH in smelt could be increased by the initial reaction of the water with the Na_2CO_3:

$$Na_2CO_3 + H_2O \rightleftharpoons 2NaOH + CO_2 \quad .$$
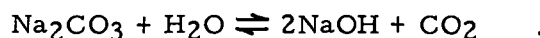
When normal smelt exploded, more NaOH was found after the explosion than had been present initially. Further experimentation demonstrated that smelt containing as little as 1.5 percent of NaOH was explosive.

The Combustion Engineering studies showed that $NaOH$-Na_2CO_3 mixtures were not explosive under simulated furnace conditions, although Sallack found that such mixtures were explosive in dissolving-tank-type experiments.[16] However, in the Combustion Engineering studies, smelt with 20 percent Na_2S exploded when 5 percent NaOH (or Na_2O) was present, but not when only 2 percent was added. In their earlier dissolving-tank studies, Nelson and Kennedy found that smelt containing 15 percent Na_2S and 2 percent NaOH was explosive. They also found that 1 percent NaOH sensitized smelt to explosion when 1.7 percent Na_2SO_4 was present.

Although most plant smelts normally contain less than 1 percent NaOH, both the inconsistency in the data and the possibility that reaction with water can increase the NaOH level in smelt point up the inadequacy of available information for assessing the sensitizing effects of NaOH under plant conditions.

NaCl. The concentration of NaCl in most plant smelts falls between 1 and 2 percent, as shown in Table 1. Experiments at Combustion Engineering showed that 2 percent NaCl in smelt containing 20 percent Na_2S did not produce explosion, but 5 percent NaCl did. At 25 percent Na_2S, as little as 1 percent NaCl gave an explosive smelt. The Babcock & Wilcox work confirmed the sensitivity of smelt to explosion with 5.7 percent NaCl present, but apparently no runs were made to establish a lower limit. In their dissolving-tank studies, Nelson and Kennedy found that 2 percent NaCl sensitized smelt when the Na_2S concentration reached 15.5 percent. However, at 19.1 percent Na_2S, only 0.5 percent NaCl rendered the mixture violently explosive.

It appears that NaCl sensitizes smelt to explosion in about the same degree as does NaOH. Possibly NaOH is formed by hydrolysis of NaCl, a reaction which is known to occur under some conditions at high temperatures. The lower limit for NaCl sensitization has not been established, and undoubtedly varies with concentrations of other smelt components.

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[*]Under the conditions of the Combustion Engineering work (Figures 4 and 6), 35 percent Na_2S is well into the explosive range, even without NaOH present. The fact that Babcock & Wilcox found such smelt nonexplosive probably is a result of the considerable differences in experimental conditions employed. It is worth noting here that there are undoubtedly even greater differences between laboratory and plant conditions.

Other Impurities. No information is available on the effects on explosiveness of minor impurities – thiosulfate, phosphate, etc. – normally found in plant smelts.

General Considerations. In view of the complex interactions among smelt components, and particularly since NaOH is formed by reaction of water with smelt, little would be gained by attempting to determine lower explosive limits of NaCl, NaOH, or other minor components. Also, while it is conceivable that there is a range of Na_2S concentration in which the incidence and/or violence of explosions is reduced, regardless of sensitizer content, this sulfide-concentration range apparently is too low to be compatible with mill practice. Hence, no further research to determine safe concentration ranges of smelt components is recommended.

Modification of Smelt to Prevent Explosion

It has been demonstrated that in smelts of sufficiently high Na_2S content, the addition of 5 percent NaOH or NaCl sensitizes the mixture to explosion on water injection. On the premise that other salts may desensitize the smelt, a large number of inorganic compounds were tried as smelt additives. Selection of compounds to use was based on the criteria that the material be thermally stable at smelt temperature, nontoxic, and reasonably available and inexpensive.

In general, the procedure was to melt 5 percent by weight of the additive into smelt containing 30 percent Na_2S, and make successive 3-milliliter injections of room-temperature water into smelt at 1800°F until explosion occurred or the smelt solidified. This smelt, when no additives were used, became violently explosive when successive water injections reduced the smelt temperature to about 1600°F. The amount of NaOH formed in the smelt by reaction with the water up to the time of the explosion was not determined. The presence of the additive did not reduce the inherent violence of the explosion in the majority of cases, although the explosion temperature was lowered by some additives. The explosiveness of the smelt was reduced to moderate violence by a fairly large number of compounds. Only three additives, $NaAlO_2$, $CaCO_3$, and Fe_2O_3, rendered the smelt nonexplosive. The results of the experiments are presented in Table 8.

For most compounds, only a single run was made. However, the three compounds which showed promise were investigated more extensively. It was found that $NaAlO_2$ was effective in preventing explosion down to 0.5 percent, although in one run at that concentration, a rapid succession of water injections gave a violent explosion. The behavior with $CaCO_3$ was erratic in that runs at 10 and 15 percent $CaCO_3$ did not explode, while those at 5, 7.5, and 20 percent were mildly explosive. With Fe_2O_3, 5 percent was mildly explosive and 10 percent was nonexplosive. Further experiments with $NaAlO_2$ and $CaCO_3$ showed that, in the concentrations used, they did not prevent explosion when 5 percent NaCl was present in the smelt.

In general, the effect of smelt additives presents a confusing picture. The method by which the experiments were performed leaves doubt as to the actual composition of the smelt at the time of explosion. The repeated 3-milliliter injections until explosion occurred gave time for chemical reactions to take place, as well as lowering the temperature. Hydrolysis of the Na_2CO_3 and Na_2S to form NaOH certainly could occur, and reaction with the additive might take place as well. There does not seem to be anything in common among the violently explosive additives. Many of them react with water to

TABLE 8. EFFECT OF ADDITIVES ON
EXPLOSIVENESS OF SMELT

Violent	Mild	Nonexplosive
$NaCl$	$Na_4P_2O_7$	$0.5-5\%\ NaAlO_2$
$NaBr$	$Na_2B_4O_7$	
$NaOH$		
Na_2O	Na_2CrO_4	
Na_2SO_3		
Na_2MoO_4		
$10\%\ Na_2SnO_3$	$5\%\ Na_2SnO_3$	
$Na_2S_2O_3$		
Na_2ZnO_2		
Na_2PbO_2		
Na_2SiO_3		
Na_2WO_4		
Na_3PO_4		
Na_3VO_4		
$KAlO_2$		
K_2CO_3		
K_2SO_4		
$LiAlO_2$	Li_2SO_4	
$LiOH$		
Li_2CO_3		
$Li_2B_4O_7$		
CaO	$5,\ 7.5,\ and\ 20\%\ CaCO_3$	$10\ and\ 15\%\ CaCO_3$
$CaSiO_3$	$CaSO_4$	
$CaCN_2$	CaS	
$Ca(AlO_2)_2$	$Ca_3(PO_4)_2$	
CaC_2		
CaF_2		
$Ba(OH)_2$	$10\%\ BaCO_3$	
BaI_2		
	$10\%\ SrCO_3$	
	SrO	
MgO	$MgSO_4$	
$MgCO_3$	$MgSiO_3$	
CdS		
ZnO	$Zn_3(PO_4)_2$	
ZnS		
Pb_3O_4	PbS	

TABLE 8. (Continued)

Violent	Mild	Nonexplosive
	CuO	
H_3BO_3		
$AlPO_4$	$Al(OH)_3$	
$AlBO_3$	$Al_2(CRO_4)_3$	
Al_2S_3	$Al_2(SO_4)_3$	
$Al_2(SiO_3)_3$		
	FeS	
	5% Fe_2O_3	10% Fe_2O_3
	Fe_3O_4	
	$Fe_4(P_2O_7)_3$	
Cr_2O_3	$Cr_2(SO_4)_3$	
10% NiS	5% NiS	
10% $NiTiO_3$	5% $NiTiO_3$	
$Ni(OOCCH_3)_2$	NiO	
	$NiSO_4$	
$CoSO_4$	CoS	
	Co_2O_3	
MnS	MnO	
$MnSO_4$	$Mn(OOCCH_3)_2$	
$MnCl_2$		
	C	
SiC	SiO_2	
SnS	CeO_2	
TiO_2	Sb_2S_3	
ZrO_2	B_4C	

form alkaline solutions, but so does NaAlO$_2$, which inhibited explosion. Many of the compounds which reduced the explosiveness to moderate violence are high-molecular-weight materials having several atoms per "molecule". However, the three most effective compounds have relatively simple formulas. The fact that no iron compounds gave violent explosions may be of some significance.

In general, no pattern seems to have been developed in these experiments that would indicate why one compound should be more effective than another or that would aid in prediction of the behavior of additives. Hence, it does not seem advisable to search for new smelt additives, at least until more is known about the mechanisms of inhibition and of smelt-water reactions involving the components normally found in smelt. At that point, firmer guidelines could be established for selection of promising compounds for evaluation. On the other hand, the range of conditions (temperature, smelt composition) over which NaAlO$_2$ inhibits explosion, as well as the concentration of this material required, should be studied. (Study of Fe$_2$O$_3$ is not recommended, since iron in cooking liquor causes pulp discoloration.) Analysis of reaction products could shed light on the inhibiting mechanisms and, hence, on the explosion mechanism. If the results of these studies are sufficiently promising, additional studies should be made with plant smelts.

Effect of Black Liquor Composition on Explosiveness

The effect of the total solids content of black liquor on smelt-water explosions was studied in the Combustion Engineering program. In one series of experiments, a smelt containing 27 percent Na$_2$S, which was explosive on injection of pure water, was used. This material also exploded on injection, from a hypodermic syringe, of Kraft black liquor containing 10, 25, and 35 percent solids, but did not explode with the liquor at 50 percent solids. The same results were obtained in duplicate runs.

Because of the difficulty encountered in syringe injection of 50-percent-solids black liquor, which is quite viscous, experiments at higher solids content were carried out by injection from a 1/8-inch nozzle and by pouring smelt into the liquor. The black liquor was heated to 170°F for these experiments, so that it would flow more readily. Explosions occurred on injection of liquor containing 43 and 51 percent solids. A more sensitive smelt containing 5 percent NaCl was employed for two of the experiments, and explosion occurred at 44 percent solids but not at 59 percent.

The remaining experiments were of the dissolving-tank type, with the smelt poured into the hot black liquor. Smelt containing 25 percent Na$_2$S and 5 percent NaCl exploded violently when the liquor contained 45 and 50 percent solids, but did not explode at 60 percent solids. It was also noted that the 60-percent-solids black liquor quickly pyrolyzed at the smelt-liquor interface to form a water-insoluble layer of char. This effect undoubtedly is related to the nonexplosive behavior of the high-solids black liquor.

No studies have been made of the effects on explosiveness of the specific chemical composition of black liquor. A point which comes to mind is the role of NaOH and NaCl. As components of smelt, these compounds are known explosion sensitizers and, thus, may also be sensitizers when present in black liquor.

The research results summarized above appear to indicate the possibility of a dividing line somewhere above about 50 percent solids between explosive and nonexplosive black liquors. However, solids content required to prevent explosion may vary widely, depending on the specific chemical composition (including organic species) of the black

liquor, the smelt composition, and local furnace atmosphere and temperature conditions. In fact, in recent years there have been recovery-unit explosions, identified as smelt-water reactions, in which there was no evidence of the presence of any aqueous liquid other than black liquor at normal firing concentration. While it seems likely that there is a black-liquor concentration above which no explosions would result regardless of specific composition or other factors, to determine such a concentration by empirical studies might be an endless task because of the enormous number and range of variables involved. Further, the critical concentration sought conceivably could be so high that the black liquor would be prohibitively viscous under practical firing conditions.

In view of the above considerations, it does not appear feasible to determine an "absolutely safe" black-liquor solids content, at least until better understanding of the explosion mechanism has been achieved. On the other hand, an investigation of the effects of varying the concentrations of the explosion sensitizers NaOH and NaCl in typical black liquor in contact with explosive laboratory smelt may provide information of immediate utility in plant operation. Also, a limited study of the explosiveness of black liquors from several mills at various degrees of dilution, when in contact with sensitive laboratory smelt, should be conducted to determine whether recommended minimum firing concentrations should be raised.*

As part of this investigation, it will be useful to study the interface between black liquor and smelt after various time intervals and as functions principally of black-liquor composition and smelt temperature. This can be done by pouring the black liquor onto the surface of the smelt, solidifying the liquor-smelt composite by cooling, sectioning the material normal to the interface, and examining the cross section thus exposed. The nature of the interface and the adjacent material would shed light on the initiation and type of reaction between smelt and liquor for the various compositions of black liquor, and perhaps would also shed some light on the initial or incipient stages of smelt-water reactions. For example, with some liquors the interface may remain well defined, with a porous char layer in the liquor adjacent to the interface. In others, intermixing may be seen, which may vary with additions, solids concentration, temperature, etc. The nature of the material in the layers adjacent to the smelt-liquor interface would give some indication as to the effectiveness of the black liquor as a quenching or cooling agent, and as to the compositions that could be so employed.

Modification of Boiler Water to Prevent Explosion

One way in which water can get into the smelt to cause an explosion is through a leak in a boiler tube. The possibility of modifying the boiler water so that it will not cause smelt-water explosions deserves consideration.

In his study of molten-aluminum explosions with water, Long[17] demonstrated that selected soluble oils and wetting agents prevented explosions when used at 0.5 percent concentration. At 0.01 percent, explosions with hot water were prevented, but not with ice water. However, he also noted that molten-salt explosions (50 percent NaCl-50 percent KCl) were not prevented by a soluble oil in the water. Long's experiments were carried out by pouring the molten metal or salt into water, as in dissolving-tank operation.

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*The Advisory Technical Committee of the Smelt-Water Research Group has suggested a minimum solids content of 55 percent (Letter and Statement of the Advisory Technical Committee, September 14, 1966).
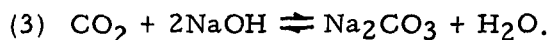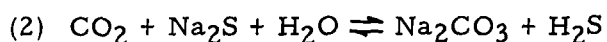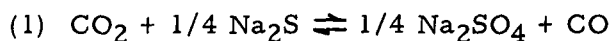
In a Combustion Engineering study simulating recovery-furnace conditions, injection of water containing the surface-active agent Aerosol OT (0.01 percent) at room temperature into smelt at 1640°F was not effective in preventing explosion. However, when injected at 160°F, this agent delayed the explosion and greatly reduced its force. A surface-active agent with a fluorocarbon tail did not prevent explosion when injected into a smelt at 1890°F, but at a lower smelt temperature (unspecified) it did prove effective. Another material designated FC-170 appeared to lower smelt explosiveness when used in conjunction with ammonium sulfate.

These fragmentary data indicate that there may be some promise in this approach, but a great deal more experimental work would be necessary. Boiler water must be highly purified to prevent corrosion and scaling, and any additives to it probably would have to be used at low concentrations. Small amounts of organic amines are sometimes used for corrosion inhibition in boiler water, and this type of additive may be of some value in inhibiting smelt-water explosions also. In some of the Combustion Engineering work, enthanolamines were effective in quenching smelt without explosion. They were used in fairly high concentration in these experiments, but perhaps could be effective at lower concentrations also. There seems to be enough possibility along these lines to indicate that investigation of various classes of surface-active agents might be productive. However, this type of study would be of low priority, and is not recommended at present.

Explosion Inhibition by Carbon Dioxide

Experiments carried out by Babcock & Wilcox showed that explosive smelt containing 30 percent Na_2S, 5.7 percent $NaCl$, and 1.6 percent $NaOH$ could be rendered nonexplosive by carbon dioxide. During the nonexplosive smelt-water reactions, the Na_2S concentration was reduced to 22 to 25 percent and 2 to 3 percent of Na_2SO_4 was formed. The $NaOH$ concentration was reduced only from 1.6 percent to less than 1 percent, so Na_2S must have been converted to Na_2CO_3 as well as to Na_2SO_4. When no $NaCl$ was present, the CO_2 reacted more extensively with the Na_2S, and the latter's concentration was reduced into the 6 to 8 percent range. Under an atmosphere of 15 percent CO_2-85 percent helium, the Na_2S concentration was reduced to 16 to 19 percent. In those runs under this atmosphere in which no $NaCl$ was present, the final $NaOH$ concentration was found to be in the 3 to 4 percent range.

The CO_2 could be involved in three different chemical reactions:

(1) $CO_2 + 1/4 \ Na_2S \rightleftharpoons 1/4 \ Na_2SO_4 + CO$

(2) $CO_2 + Na_2S + H_2O \rightleftharpoons Na_2CO_3 + H_2S$

(3) $CO_2 + 2NaOH \rightleftharpoons Na_2CO_3 + H_2O.$

In the thermodynamic analysis made by Babcock & Wilcox, both Reactions (1) and (2) were found to be more favorable than Reaction (3). The formation of Na_2SO_4 indicates that some of the Na_2S was being oxidized by the CO_2 as shown in Reaction (1). Conversion of Na_2S to Na_2CO_3 was undoubtedly occurring also, as in Reaction (2), since analysis made on one run showed a 13 percent increase in carbonate concentration. The CO_2 apparently does not react appreciably with the $NaOH$ (Reaction 3), since the concentration of $NaOH$ in the smelt increased.

From this series of experiments it appears that even the partial CO_2 atmosphere reduced the Na_2S concentration into a nonexplosive range, and the $NaCl$ did not sensitize

the smelt under these conditions. The greater reduction in Na_2S concentration when no NaCl was present indicates that the NaCl exerts influence on the reaction. The chloride concentration was reduced only from 5.7 to 4.1 percent in these experiments, so the part played by NaCl may be that of catalytic action. The possible use of a CO_2 atmosphere for explosion prevention appears to merit some further investigation, particularly at practical Na_2S concentrations and in the presence of commonly encountered amounts of NaOH and NaCl. It would have to be determined whether it is feasible to inhibit explosions by means of a CO_2-containing atmosphere above the smelt and still maintain a practical sulfidity level. (It must be recognized, of course, that CO_2 may inhibit explosion merely because it reduces sulfidity.) As pointed out earlier, a 15 percent CO_2 atmosphere, which is about the concentration in flue gases, reduced the Na_2S concentration to what may be a safe level. Hence, it may, in principle, be possible to inhibit explosions by proper utilization of gaseous combustion products during normal operation, although the cost of the required equipment modifications might be prohibitive. It is conceivable that CO_2 might also be useful in emergency shutdown, if the rate at which the gas could be absorbed by, and react with, the smelt is high enough to render the smelt nonexplosive within a practical length of time. It seems likely, however, that quenching the smelt with liquids or solids holds more promise as an emergency procedure.

Physical Methods of Explosion Inhibition

High-Frequency Vibration

A considerable amount of research and development has been conducted in the past 25 years on the physical, chemical, and biological effects of high-frequency and ultrasonic vibrations in solids, liquids, and gases and on the practical applications of these effects. A search through abstracts of the literature for this period reveals no reports on investigations on the effects of such vibrations on the explosive tendency of water immersed in molten metals or salts.

Effects of high-intensity, high-frequency vibrations on liquids include atomization, emulsification, formation of suspensions, enhanced diffusion, degassing, degradation of high polymers in solution or suspension, increase in convective heat transfer, cleaning of immersed solids, enhanced electrodeposition, and decreased grain size in crystallization of alloys. Many of these effects result from or are enhanced by the phenomenon of cavitation, wherein the tensile phase of the alternating acoustic pressure is great enough in amplitude to overcome the ambient pressure and the cohesive forces in the liquid. The liquid temporarily ruptures or "cavitates". Collapse of the cavities as the compressive phase is approached results in local very high stresses as inflowing jets of liquid impinge upon the cavity walls. Various chemical, physical, thermal, electrostatic, and other phenomena that are not too well understood result from these high stresses.

It is difficult to visualize how the cavitation phenomenon might be beneficial in inhibiting the explosive tendency. If anything, the stresses produced by collapse of the cavities might tend to trigger explosions. If this latter factor were not significant, however, some benefit might be obtained by the presence of the bubbles produced by the cavitation phenomenon as a result of release of dissolved gases and vapors into the cavitation voids. These bubbles would provide pressure-release surfaces that would tend to diminish the intensity of an explosion or to prevent its occurrence entirely, as will be discussed later. However, the same pressure-release effect could be obtained much more economically and with more uniform coverage over the entire smelt bed by bubbling

hot gas (possibly flue gas) through the smelt bed. The distribution in intensity of high-frequency sound throughout a liquid in a container is usually very nonuniform because of interference effects from multiple reflections between the sides and bottom of the container, the upper free surface, and immersed bodies.

At any rate, to expose a large smelt bed in a furnace to ultrasound with any reasonable degree of completeness of coverage would require a large number of transducers and associated electronic driving equipment. Special means would have to be provided to feed the high-frequency vibrations into the smelt bed, since the transducers would have to be outside the furnace. Neither piezoelectric nor magnetostrictive transducers can be exposed to temperatures anywhere near that of molten smelt. A very large capital investment in electronic equipment and controls, power supplies, and furnace modification would thus be required to apply high-frequency vibrations to a smelt bed. In view of these factors, it does not appear worthwhile to give further attention to this proposed method of preventing explosion.

Quenching of Smelt in Emergency Shutdown

The possibility of quenching smelt to its freezing point to reduce the probability of explosion in a smelt-water emergency was investigated in the Combustion Engineering study. The information obtained could be of great value in developing a safe procedure for emergency shutdown of a recovery furnace. On the principle that a nonreactive gas generated at the smelt-water interface might prevent explosion, solutions of NH_4HCO_3, which decomposes into CO_2, NH_3, and H_2O at about 150°F, were injected into explosive smelt containing 27 percent Na_2S. It was found that 1 percent NH_4HCO_3 was not effective in preventing explosion of the smelt, but a solution containing 5 percent NH_4HCO_3 could be injected without explosion. NH_4OH also was found to be effective. A search for a material with greater stability during storage than either of these ammonium compounds led to investigation of $(NH_4)_2SO_4$. A variety of experiments were carried out using this compound with smelts of different Na_2S and $NaCl$ concentrations. The results of these experiments are summarized in Table 9, along with those for NH_4HCO_3 and NH_4OH. As shown in the table, concentrated $(NH_4)_2SO_4$ solutions could be injected without explosion into very sensitive smelts containing as much as 15 percent $NaCl$. However, in experiments in which 40 percent $(NH_4)_2SO_4$ was poured onto the smelt, the maximum safe $NaCl$ concentration was 5 percent. A solution of 15 percent NH_4HCO_3 also was effective in preventing explosion under these same conditions.

Solutions of a variety of organic compounds also were investigated as quenching agents, on the basis that they might change the heat-transfer characteristics of the system. For most of these experiments, a sensitive smelt containing 25 percent Na_2S and 5 percent $NaCl$ was used. The results are shown in Table 10. Most of the solutions contained high-molecular-weight straight-chain compounds. Some of the compounds were effective in limiting the explosiveness of the smelt at the lower concentrations used, and made it nonexplosive at higher concentrations. Polyethylene glycol, polypropylene glycol, polyvinyl alcohol, and polyvinyl pyrrolidone appeared particularly effective, even in fairly low concentrations. Some other materials (Poly Em II and Keystone Keycut) also showed promise, but they are emulsions, which are considered undesirable from the standpoint of stability during storage.

Quenching with strong black liquor also was studied by Combustion Engineering. It was reported that char formed at the smelt-liquor interface, preventing further contact. (Possibly this occurs also with the polymers discussed above.) Black-liquor quenching

TABLE 9.   EFFECT OF INJECTING SOLUTIONS OF
AMMONIUM COMPOUNDS INTO SMELT

Smelt Composition, weight percent			Explosiveness		
Na_2CO_3	Na_2S	NaCl	Violent	Mild	Nonexplosive
73	27	--	1% NH_4HCO_3		5 and 20% NH_4HCO_3
73	27	--	2% NH_4OH		5 and 10% NH_4OH
70	30	--			10% $(NH_4)_2SO_4$
75	20	5	1% $(NH_4)_2SO_4$		2 and 10% $(NH_4)_2SO_4$
73	26	1	10% $(NH_4)_2SO_4$		
69	26	5	Ditto		
70	25	5	10% $(NH_4)_2SO_4$ + 3% NH_4OH		10% $(NH_4)_2SO_4$ + 9% NH_4OH
70	25	5			15% $(NH_4)_2SO_4$
68	27	5			20 and 40% $(NH_4)_2SO_4$
63	27	10			40% $(NH_4)_2SO_4$
59	26	15			40% $(NH_4)_2SO_4$

TABLE 10. EFFECT OF SOLUTIONS OF ORGANIC MATERIALS[a]
ON SMELT-WATER EXPLOSIONS

Violent	Mild	Nonexplosive
—	20% EG	
	10% DEG	20% DEG
	10% TEG	
	5% PEG 200	10% PEG 200
	5% PEG 400	10% PEG 400
		20% PEG 400
	10% PEG 600	
10% PEG 1000		10% PEG 1000[b]
	10% PEG 1540	10% PEG 1540[b]
		20% PEG 1540[c]
	10% PEG 6000	
	5% PVA (G1-30)	1.5% PVA (G 190-G)
	5% PPG 425	10% PPG 425
		20% PPG 425
	5% PVP K-15	10% PVP K-15
5% PVP K-30		10% PVP K-30
	5% PVP K-60	
	2.5% PVP K-90	
		5% Poly Em II Emulsion
		10% Poly Em II Emulsion
20% glycerin		
0.1% starch		0.1% starch[b]
20% sucrose		
10% ethanolamine		50% ethanolamine
	10% triethanolamine	
1% hydroxyethyl cellulose		
2% Keystone Keycut emulsion	5% Keystone Keycut emulsion	10% Keystone Keycut emulsion

(a) Notation: EG - ethylene glycol; DEG - diethylene glycol; TEG - triethylene glycol; PEG - polyethylene glycol; PVA - polyvinyl alcohol; PPG - polypropylene glycol; PVP - polyvinyl pyrrolidone.
(b) No NaCl in smelt.
(c) 10 percent NaCl in smelt.

is particularly appealing, in view of its convenience. However, the solids content of the liquor required to prevent explosion under all conceivable conditions is not known and may be extremely difficult to determine, as discussed in a previous section. In addition, during shutdown the direct-contact evaporators cease functioning, so that the solids content decreases. Hence, further exploration of this concept should await attainment of better understanding of the explosion process.

On the other hand, additional study to determine the applicability of quenching with solutions of ammonium compounds appears warranted. The concentration ranges required to prevent explosion with a wide range of plant smelts needs to be determined. In addition, the possibility of using solutions of the normal smelt components Na_2SO_4 and Na_2CO_3 should be studied. Also, dry solids (or slurries) which would decompose or dissolve in the smelt endothermically should be considered. Again, Na_2SO_4 and Na_2CO_3 are candidates, as is $CaCO_3$, which was shown in the Combustion Engineering work to be an explosion inhibitor when used as an additive to the smelt. Some compounds of particular interest are $FeSO_4 \cdot 7H_2O$ (copperas) and $NH_4Fe(SO_4)_2 \cdot 12H_2O$. Copperas is an inexpensive material which, if employed in an aqueous slurry, could act as a very effective quenching agent. Heat would be removed from the smelt by vaporization of the water, by decomposition of the hydrate (at 300°C) and vaporization of the water of hydration, and by thermal decomposition of the sulfate (with evolution of SO_2). In addition, the material remaining would be Fe_2O_3, a compound found in the Combustion Engineering studies to act as an explosion inhibitor when used as a smelt additive. $NH_4Fe(SO_4)_2 \cdot 12H_2O$ would function similarly, with the hydrate decomposing at 230°C, and with ultimate evolution of NH_3 and SO_2.

The four organic materials named above, i.e., polyethylene glycol, polypropylene glycol, polyvinyl alcohol, and polyvinyl pyrrolidone, also should be investigated further to assess their value as quenching agents. (Polyvinyl alcohol is subject to bacterial attack and oxidation on storage, but these factors probably can be controlled.) These materials inhibited explosion even at concentrations of 10 percent or less. It is not recommended that additional organic materials be screened as possible quenching agents, at least until better understanding of the explosion process has been gained, since there is no firm basis on which to make selection of materials for study.

Formation of Porous Smelts

Bubbling hot gas (possibly flue gas) continuously through the molten smelt during normal operation might not only permit easier penetration of safe coolants during emergency shutdown but could provide other benefits as well. For one thing, the flow properties of the smelt should be improved. It is also anticipated that a major benefit of the presence of finely divided bubbles of gas throughout the smelt would be to inhibit greatly the tendency for explosions to take place by providing for "pressure release" surfaces throughout the smelt.

In the inertial-reaction mechanism, the steam pressure has to accelerate not only the shell of smelt immediately surrounding it but also the successive layers of smelt to outward radial velocities that vary inversely as the squares of the shell radii. The inertial reaction would thus be greatly reduced by the presence of a gas bubble near the water droplet. On the side of the droplet where the gas bubble is located, no outer shells of smelt need be accelerated, and the steam could also expand into the bubble, thus reducing the pressure buildup. Many smaller bubbles in the vicinity of a relatively large water droplet might effectively nullify any explosive tendency.

The possible use of gas bubbling to induce smelt porosity appears attractive in principle. However, the probable capital cost and operational complications which would be incurred are formidable. For this reason, further pursuit of this concept is not recommended.

Rate of Solidification of the Smelt

The rate of solidification of the smelt on shutdown by conduction to the water-cooled furnace floor and by radiation and convection from the upper surface of the smelt bed could, in principle, be analyzed as a heat-transfer problem by well-known methods that have been established for solutions of such problems on the digital computer. To accomplish such a solution would require more knowledge regarding the pertinent physical constants of smelt than are available at present. Among these are the effective radiation emissivity as a function of temperature and composition, the effective absorption coefficient for internal propagation of infrared radiation as a function of temperature and composition, the temperature and composition dependencies of the thermal conductivity, density, specific heat, and viscosity, and the heat-transfer coefficient pertinent to the exchange of heat to the furnace floor, walls, etc. The geometry of the smelt bed would also enter into the analysis.

Since a study of this type would provide baseline information against which to evaluate the relative effectiveness of quenching of the smelt, some effort along these lines appears warranted, particularly since some of the experimental data required would also be needed in connection with the computer evaluation of explosion-mechanism models. However, in view of the complexity and inhomogeneity of bed geometry and composition, a detailed analysis would require many additional data which would be expensive to obtain, and thus does not seem warranted, since the results would still have to be considered as tentative and could be checked adequately only by shutdown tests on production boilers.

RECOMMENDED RESEARCH PROGRAM

It is recommended that a research program combining concurrent fundamental and empirical aspects be conducted, the former to elucidate the explosion mechanism for guidance in the research, the latter to determine the range of applicability and means of applying promising explosion-preventive measures. The empirical investigation would be reasonably straightforward, involving standard laboratory techniques in conjunction with an explosion chamber designed for the purpose. Much of the information needed for the fundamental study would be provided by the empirical work, but additional studies requiring use of specialized experimental techniques, discussed below, also would be required. In addition, the fundamental aspects of the investigation would involve theoretical interpretation and computer analysis of available information and of data obtained experimentally on the program.

One of the principal problems in research aimed at establishing the explosion mechanism is that of retaining the water in the high-temperature system so that the chemical reactions occurring can be studied. The injected water may either boil out of the smelt or cause an explosion before the reaction system can be quenched for analysis. The experimental data accumulated to date indicate that chemical reaction of water with components of the smelt, particularly Na_2S, $NaCl$, and $NaOH$, is related to the explosiveness of the smelt-water reaction. The sensitizing of the smelt to explosion by $NaOH$, $NaCl$, or large amounts of Na_2S, as well as the delay of the explosion, in many cases, until multiple injections of water have been made, points to the existence of chemical reactions that produce an explosive composition. The nature of these chemical reactions needs to be determined, regardless of what the ultimate explosion mechanism may be.

It is recommended that ultrapressure techniques be employed in the study of the reactions of water with molten smelt. These techniques, which were developed originally for synthesizing diamonds, make it possible to carry out reactions at pressures and temperatures of the order of 10^6 psi and 3000°F. The sample is contained in a small, electrically heated capsule, which is compressed in a die between two pistons. By using a lavite gasket around the sample, it is possible to retain volatile materials in the system under extreme conditions. Battelle scientists have had experience with these devices for several years, and have demonstrated that water can be retained in a reaction capsule to at least 1800°F.

The reactions of smelt components with water should be studied as functions of temperature by ultrapressure and other (bomb, autoclave) techniques with and without minor components ($NaCl$, $NaOH$, Na_2SO_4) present. Chemical analysis of the products, combined with computer analysis of the data, would provide quantitative information on the reactions taking place.

A second major problem in attempting to delineate the explosion mechanism is that nothing is known about the geometry of a water mass, immersed in the smelt, before explosion takes place. Knowledge of this geometry as a function of time is important to the understanding of both physical and chemical processes involved. A technique which will be useful for gaining such knowledge is flash radiography. This is a technique, analogous to ordinary flash photography, in which the sample is irradiated with short X-ray pulses and the radiation passing through the system under study is recorded on film. The flash radiographic system at Battelle-Columbus produces X-ray pulses at voltages as high as 300 kev with a 2×10^{-9}-second rise time and a duration of 20×10^{-9} second. The pulse can be triggered electronically by an external signal, and X-ray

cinematography may be achieved by repetitive pulsing of the unit at rates up to 200 times per second.

Flash radiography will permit direct observation of the geometry, as a function of time, of water masses injected into smelt. Observations should be made by this method on water injections into standard smelts under both explosive and nonexplosive conditions.

The major tasks of the recommended research program, outlined below, may be categorized as (a) fundamental studies for the purpose of developing understanding of the explosion process, (b) research directed toward development of methods for rapid cooling of the smelt on emergency shutdown, and (c) research aimed at identifying changes in the makeup of the recovery-boiler chemical system which could reduce explosiveness and which could be employed in normal boiler operation.

Fundamental Studies

1. Investigate chemical and dissolution interactions which take place in the smelt-water system, to identify processes of importance in the explosion mechanism, paying particular attention to exothermic processes

    (a) Employ computer program to predict reactions in the system and to compute heats of reaction

    (b) React components under pressure and analyze products to obtain quantitative information on reactions involved

        (1) Versus temperature

        (2) Versus concentrations of Na_2S, $NaCl$, $NaOH$, Na_2SO_4, and carbon.

2. Investigate physical processes of potential importance in the explosion mechanism

    (a) By computer analysis, evaluate the effects of including additional means of heat transport (turbulence, conduction by complex molecules), beyond those studied previously, on the inertial-reaction mechanism

    (b) As an aid in examination of physical processes, study the geometry, as a function of time, of water masses injected into smelt, using flash radiographic techniques, for both explosive and nonexplosive reactions.

Emergency-Shutdown Cooling

3. Investigate quenching of smelt with various inorganic compounds (particularly those which may decompose or react with smelt endothermically) and organic polymers, with the objective of identifying potentially useful procedures for use in emergency shutdown

    (a) Evaluate the effectiveness and safety of quenching molten smelt with inorganic materials, including ammonium compounds [e.g., $(NH_4)_2SO_4$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$], Na_2SO_4, Na_2CO_3, $CaCO_3$, $FeSO_4 \cdot 7H_2O$, by injecting the materials into and/or pouring them

onto molten smelts, and observing the resulting interaction and cooling rate

    (1) Versus concentration of inorganic material and with the materials applied in solution, slurry, and solid form

    (2) Versus smelt temperature

    (3) Versus concentration of sulfide in standard sensitive smelt

    (4) With plant smelts

  (b) Evaluate organic polymers (polyethylene glycol, polypropylene glycol, polyvinyl alcohol, and polyvinylpyrrolidone) as in (a) above. For these, also study solution-smelt interface by microscopy and possibly X-ray and other methods

    (1) Versus smelt temperature

    (2) Versus time at temperature.

4. Investigate the rate of cooling and solidification of smelt on furnace shutdown by computer analysis

  (a) Make laboratory measurements as required to provide reasonable estimates of physical parameters (infrared emissivity, etc.)

  (b) Make limited computer analysis, taking account of

    (1) Conduction to furnace floor

    (2) Radiation from smelt surface

    (3) Convection from smelt surface.

Operational Changes

5. Investigate the effects of black-liquor composition for the purpose of more closely defining the composition range required to reduce explosion probability

  (a) Evaluate the explosive tendency of standard smelt when black liquors are injected, by quantitative observation of intensity of reaction

    (1) Versus concentration of NaOH and/or NaCl in the black liquor

    (2) Versus dilution (i. e. , concentration of water in) of the black liquor

    (3) Versus smelt temperature

  (b) Study the black liquor-smelt interface by microscopy and possibly X-ray and other methods

    (1) Versus black-liquor composition

    (2) Versus smelt temperature

    (3) Versus time at temperature.

6. **Investigate possible modification of smelt to prevent explosion**

   (a) Evaluate the explosive tendency of smelts modified with $NaAlO_2$, by injecting water into the molten smelts and making quantitative observation of reaction intensity

      (1) Versus $NaAlO_2$ concentration

      (2) Versus smelt temperature

      (3) Versus sulfide concentration

      (4) With plant smelts

   (b) Investigate smelt physical properties, such as viscosity, surface tension, etc. for the purpose of identifying the mechanism of explosion inhibition

      (1) Versus $NaAlO_2$ concentration

      (2) Versus temperature.

7. **Investigate smelt-water explosion inhibition by use of a CO_2 atmosphere**

   (a) Evaluate the explosive tendency of smelt when water is injected into the smelt, by quantitative observation of reaction intensity

      (1) Versus amount of CO_2

      (2) Versus smelt temperature

      (3) Versus sulfide concentration in the (sensitized) smelt

      (4) Versus time

   (b) Analyze for concentrations of important chemical species in explosive and nonexplosive reaction products, to gain understanding of the processes involved.

It is the opinion of the Battelle staff associated with this feasibility study that the probability is high of substantially reducing the incidence and violence of smelt-water explosions through prosecution of a research program along these lines. In view of the facts that financial losses (direct plus use and operation) to the pulping industry as a result of these explosions average hundreds of thousands of dollars per year and that occasional personnel injuries and fatalities result, a research program of the magnitude suggested here seems warranted.

Of the research program outlined above, it is recommended that Items 1 through 4 (fundamental studies and emergency-shutdown cooling) be given highest priority. It appears highly probable that the fundamental studies (Items 1 and 2) would point the way toward measures to provide essentially complete solution of the explosion problem. It is not anticipated, of course, that such measures would be completely developed in the course of the program described; additional work would be required for this purpose, once adequate understanding of the explosion mechanism has been achieved. On the other hand, the study of emergency-shutdown cooling (Items 3 and 4) also is recommended for highest-priority consideration because it appears to offer high probability of short-range marked alleviation of the problem, although obviously not complete solution. Items 5 and 6 (black-liquor and smelt composition), although considered well worthwhile, seem to offer somewhat lower probability of success and, thus, should be given slightly lower priority than Items 1 through 4. Item 7 (inhibition of explosion by CO_2), even if

technically feasible, may not be feasible in practice because of operational complications and the need for large capital outlay, and thus should be considered of lowest priority.

ESTIMATED TIME AND COSTS

It is estimated that the costs of conducting the phases of the research described above would be as follows:

Fundamental Studies

1.	Chemical processes	$ 80,000
2.	Physical processes	65,000

Emergency-Shutdown Cooling

3.	Quenching	$175,000
4.	Cooling and solidification	20,000

Operational Changes

5.	Black-liquor composition	$ 85,000
6.	Smelt modification	60,000
7.	Explosion inhibition by CO_2	40,000

In addition, construction of an explosion chamber and associated equipment, to be used with Items 3 through 7, is expected to cost about $10,000.

The above estimated costs of the various phases reflect the degrees of emphasis recommended by the Battelle staff associated with the project, as described in the outline of the suggested program and in the discussion sections of this report. If desired, any of the phases of the work could be undertaken with greater or lesser emphasis and with proportionately changed cost and probability of benefit to the industry.

The entire program as outlined above could be conducted efficiently in a period of approximately 3 years. Items 1 through 4, the highest-priority group, could be carried out in about 2 years.

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