

SUMMARY REPORT

TO

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THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

✓ Project 2419

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

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SUMMARY REPORT OF THE BABCOCK & WILCOX COMPANY
ACTIVITIES ON
INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

In the Kraft recovery process, concentrated waste liquor from the pulping step, containing combustible material and inorganic chemicals, is burned such that the inorganic materials are converted to a molten salt mixture, termed smelt. The smelt, consisting primarily of sodium carbonate and sodium sulfide, is continuously tapped from the furnace so that it may be recovered and returned to the pulping process.

If liquid water enters the smelt bed by accident (or otherwise) a potentially dangerous situation arises which may result in a furnace explosion. These explosions, which are frequently severe, cause extensive damage to the recovery unit and may result in serious injury and loss of human life. A recent survey^{(1)*} cites numerous instances of pressure part failures where presumably water had entered the smelt bed, but explosions did not occur. Nevertheless, enough evidence has accumulated to show that severe explosions have occurred under these conditions and smelt-water explosions are indeed a serious problem for both the pulp and paper industry and the equipment manufacturers.

To date there has been a limited amount of experimental work aimed at determining the mechanism of the observed explosions. Rogers, Markant, and Dluhosh⁽²⁾, produced explosions on a pilot plant apparatus by injecting water into molten smelt, held at temperatures between 1600° F and 2000° F; explosions of variable intensity and sometimes a series of explosions were

*Numbers in parentheses refer to bibliography at the end of the text.

observed. These workers attributed the explosions to a chemical reaction producing hydrogen as the principal product. Nelson and Kennedy⁽³⁾ investigated explosions taking place in dissolving tanks. As explosions took place beneath the water surface there appeared to be little possibility of a combustion gas explosion. It was concluded that explosions taking place under these conditions could best be explained on the basis of a physical reaction generating steam. While it is, therefore, generally agreed that explosions take place as a result of interactions of smelt with water, the nature of these interactions, whether they be physical or chemical, was not understood.

There is another important aspect to the smelt-water explosion problem - determining the safest method of shutting down the recovery unit once a hazardous condition occurs. The present recommended procedure involves quenching the active bed with heavy black liquor and shutting the unit down under fuel-rich conditions. Pyrolysis of the fuel and air leakage into the furnace could conceivably result in an explosive mixture of gases in the furnace and be ignited by a spark in the char bed, hot ash deposits, etc. Hence, there is some concern as to whether this is always a safe shut-down procedure.

The Babcock & Wilcox Company and Combustion Engineering, Inc. . . under the sponsorship of pulping companies forming the Smelt-Water Research Group, have undertaken a research program, extending over the past two years, in an attempt to resolve the uncertainties concerning the nature of the smelt-water reaction. Having obtained a better understanding of the explosion mechanism, it was anticipated that preventive measures and improved shut-down procedures, based on this knowledge, could be proposed.

Objectives

By agreement with the sponsors, The Babcock & Wilcox Company studies were concerned primarily with the chemical aspects of the reactions involved in the explosion problem. The objectives initially outlined at the beginning of this work were:

1. To determine the chemical reactions taking place between smelt, char and water and their possible contribution to the explosion problem.
2. Based upon the chemistry of the smelt-water system, to suggest preventive measures to be taken (a) during operation to reduce the explosion hazard and (b) after it has been established that a hazardous condition exists.

Additional objectives, added by mutual agreement with the Technical Advisory Committee were:

3. To determine the characteristics of black liquor decomposition and their effect on shut-down procedures.
4. Although somewhat related to (1), specifically to determine which role, if any, elemental sodium might play in smelt-water explosions.

Approach

In order to understand as thoroughly as possible the chemical aspects of the problem, a combined theoretical and experimental approach was used which was divided into two parts: (a) smelt-water reactions, and (b) pyrolysis and combustion of black liquor.

Smelt-Water Reactions:

1. Thermodynamic calculations were first made on twenty-one possible chemical reactions to isolate those most likely to take place, to assess their possible contribution to the explosion mechanism, and to provide a sound basis for experimental design and interpretation of test results.
2. Experimental studies were made on smelt under highly reducing conditions to determine the probability of generating enough elemental sodium for it to be a significant contributor to smelt explosions.
3. The reaction between molten smelt and water vapor was studied experimentally under near-equilibrium conditions to test the validity of theory and extend it, if possible.
4. Experiments were conducted in which increments of water were injected into molten smelt in an effort to determine the conditions necessary for a violent explosion. A number of variables were explored:
 - (a) smelt composition (especially the effect of minor constituents - NaOH, NaCl)
 - (b) temperature
 - (c) method of injecting water
 - (d) atmosphere

The magnitude of the explosion, and reaction products (both gaseous and condensed) were determined in most instances in an attempt to understand the mechanism of the explosion and how it might be prevented.

Pyrolysis and Combustion of Black Liquor:

1. The equilibrium compositions of gaseous and condensed species from the combustion of a typical black liquor were computed for various fuel-air ratios and temperatures to determine the theoretically possible products under the widely varying conditions possibly existing in a recovery unit.
2. Whether the decomposition of black liquor was an exothermic or endothermic process was determined by differential thermal analysis; the manner in which the decomposition took place was determined by thermogravimetric analysis.
3. The amount and composition of gases evolved from the thermal decomposition of black liquor solids was determined experimentally as a function of temperature in a closed system.

In addition, although not funded by this contract, but pertinent to the over-all explosion problem, two field tests of a shut-down procedure were carried out.

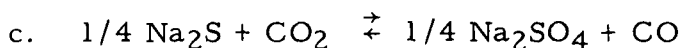
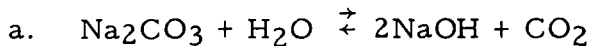
A series of seven progress reports was issued during the course of this investigation. This is the final report which summarizes The Babcock & Wilcox Company's activities on the project during the period between December 1, 1963 and March 31, 1966. Actual experimental work on this project began April 1, 1964 and ended February 15, 1966.

Method of Presenting Findings in this Report

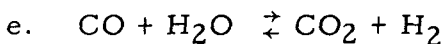
In this report a Summary of Results and Conclusions from this work follows this, introductory, part of the report, and Recommendations follow the Summary. The individual aspects of the over-all program are then described and discussed.

SUMMARY OF RESULTS AND CONCLUSIONS

1. As a result of theoretical and experimental studies of the chemical reactions of smelt and water, summarized in Figures 1-5, it is concluded that the following are important chemical reactions that take place in this system.

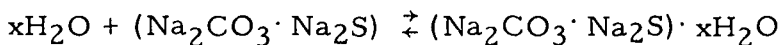


If char is present with the smelt, depending on the temperature, the following additional reactions take place:



These reactions are relatively well known and none are considered to be explosive by themselves.

2. In addition to the reactions outlined above experimental evidence, summarized in Table I, showed that molten smelt absorbs water vapor at 1600° F. Furthermore when the water vapor over-pressure was removed, the smelt released water vapor, hydrogen, CO and CO₂ (Figure 6) as a result of an interaction of the absorbed water with smelt constituents. It is concluded that an additional reaction between smelt and water, termed a hydration reaction, takes place and may be written as follows:

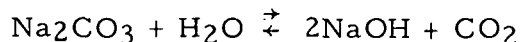


This reaction tends to be in equilibrium with the other reactions outlined in (1) above. The quantitative characteristics of this

reaction are not well-known, but its behavior in smelt suggests that chemical bonding of molecular water takes place.

3. Under certain conditions explosions were observed as a result of the action of water and laboratory-prepared molten smelt in a helium atmosphere (Table II). It is concluded that an explosive reaction not associated with combustion does take place between smelt and water.
4. Explosions were produced when water was added to smelt over a temperature range of 1500° F to 1800° F and over a concentration range of 21.8% to 37.9% Na₂S (in smelt) (Table II) and it is concluded that smelts in these temperature and concentration ranges are sensitive to smelt-water explosions. Since the effects of temperature and composition outside of these ranges were not investigated, the ranges of temperature and Na₂S concentration explored should not be considered to define the explosion limits and explosions may occur outside of these ranges.
5. In general, normal smelts exploded only after more than one 2-cc addition of water (Table II). It was found that sodium hydroxide was formed, not only from a reaction of water with pure sodium carbonate, but also from a reaction of water with molten smelt (Table III). Since the addition of 5% sodium hydroxide to smelt resulted in a smelt composition that exploded in four out of five cases at the first water addition (Table IV), it was concluded that sodium hydroxide not only increases the tendency for smelt-water explosions, but also that smelts of sufficient sulfidity are carried

into the explosive range by the presence of NaOH formed by the reaction



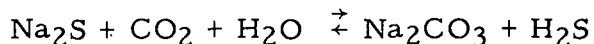
6. Sodium sulfate was also formed as a product of the smelt-water reaction (Table III). While the effect of added sodium sulfate, in one test (Table IV), increased the sensitivity of smelt to explosions, not enough data were obtained to draw firm conclusions concerning its effect or its possible interaction with hydroxide.
7. From the results of the experimental investigation of several possible exothermic reactions, it was concluded that exothermic, self-sustaining chemical reactions do not contribute in any substantial manner to smelt-water explosions.

This conclusion is based on the results of the following experiments:

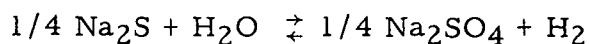
- (a) It was found that very little elemental sodium was retained in smelt under laboratory-simulated conditions of the highly reducing smelt-char bed (Table V). As a result, the reaction of elemental sodium with water was virtually eliminated as a possible contributor to explosions.
- (b) Sodium oxide, when added to smelt did not increase the sensitivity of smelt to explosions (Table VI). This finding eliminated the following exothermic reaction from consideration:



- (c) Smelt-water explosions were not observed in a CO₂ atmosphere (Table VI). These results eliminated the following exothermic reaction from consideration:



- (d) Cold smelt, to which water had been added, then heated to test temperature, exploded readily upon water additions (Table VI). If the heat from the smelt hydration reaction were causing explosions, no explosion should have been observed and this reaction therefore was eliminated as a possible contributor to the explosion insofar as its possible exothermic character is concerned.
8. Hydrogen was found as a reaction product whenever water or water vapor contacted molten smelt. The conversion of water to hydrogen was variable and dependent upon experimental conditions but ranged from 9.9 - 54.9% (Figures 4 and 7). It is therefore concluded that the hydrogen generated from the reaction



may contribute to a possible hazard from the point of view of providing fuel for a combustion explosion. This hazard is separate and apart from the risks of direct explosive reactions between smelt and water.

9. Hydrogen was found in significant quantities after water was added to smelt whether or not an explosion was observed (Table VII). Furthermore, carbon monoxide and carbon dioxide were always found in only very low concentrations when an explosion took place.

Since exothermic chemical reactions were virtually excluded from consideration as a possible cause of explosions, it is concluded by elimination of other possibilities that the observed explosions resulted from the exceedingly rapid (explosive) release of water vapor.

10. Sodium chloride added to smelt increased the tendency for smelt-water explosions (Table VIII, Runs 24 and 32).
11. No explosions could be effected between smelt and water when the smelt had been exposed to a CO₂ or 15% CO₂ - 85% He atmosphere for a sufficiently long time (Table VIII). Such an atmosphere tended, in the presence of water, to reduce the smelt sulfidity and it is concluded that a CO₂ atmosphere can prevent smelt-water explosions if sufficient time for reaction is allowed.
12. When carbon was added (as sugar charcoal) to smelt, in duplicate tests, no explosions were observed at 1800° F but in each case explosions were produced at one water injection when the temperature was lowered to 1600° F (Table IX). At 1800° F, the gas analysis indicated that a preferential carbon-water reaction took place. It is concluded that there are strong indications that the presence of carbon inhibits the smelt-water explosive reaction at 1800° F, but not at 1600° F.
13. Results of studies of black liquor decomposition showed that:
 - a. The decomposition of black liquor is an endothermic (heat absorbing) process taking place in essentially two steps:
 - (1) the evolution of steam, and (2) the evolution of gaseous

decomposition products (Figure 8).

- b. Black liquor solids decompose when heated, yielding variable volumes of gas, increasing with the temperature of decomposition and equal to approximately 12 ft³/lb of solids (STP) at 1800 °F (Figure 9).
- c. The gas composition from the thermal decomposition of black liquor solids is a function of temperature (Table X). At the higher temperatures (1600°F - 1800°F) the evolved gas is predominantly hydrogen and carbon monoxide.

It is concluded from these studies that the presently accepted emergency shut-down procedure results in a potentially hazardous condition from the point of view of a combustible gas explosion.

14. The results of the field testing indicated that Kraft recovery units can be shut down without hazard of combustible gas explosion by shutting off black liquor flow while maintaining an air-rich atmosphere in the unit above the smelt bed.

RECOMMENDATIONS

Operation

1. As preventive measures, while the unit is operating normally, it is recommended that all possible precautions be taken to prevent water from entering the smelt bed. This recommendation implies (a) the use of proper boiler water treatment and control to prevent internal corrosion and subsequent failure of pressure parts, and (b) periodic inspection of the external surfaces of boiler tubes for

evidence of external corrosion. It is not possible to tabulate all possible sources of water that could enter the furnace but each mill should make an exhaustive survey of its operation and correct any potential hazard of this nature which might exist.

2. The Kraft recovery unit should be operated such that the sodium hydroxide content of the smelt as determined by periodic analysis is zero. It is recognized that the variables of furnace operation are such that the conditions necessary for achieving this goal cannot now be specifically outlined. Therefore, it is recommended that further experimental data be obtained on operating units to determine the interrelationship of the significant factors affecting the sodium hydroxide content of smelt. As sodium sulfate may be a contributing factor to the smelt-water explosion, it is tentatively recommended (admittedly arbitrarily) that its concentration be at a minimum.
3. If at all feasible, the sodium chloride concentration in smelt should be kept below 1%.
4. Kraft units should be operated to minimize pools of smelt in the furnace.
5. It is recognized that recommendations of measures to be taken after it has been established that water has entered the smelt bed should be subjected to proof testing. Therefore, the following procedures are suggested as possible remedial measures to be taken after an emergency condition is known to exist:

- a. The emergency shut-down procedure should be one that eliminates the possibility that a combustion gas explosion can take place. It is therefore suggested that the shut-down procedure be based on the principle that an air-rich atmosphere be present during the shut-down.
- b. Consideration should be given to the possibility of maintaining a CO₂ atmosphere over the smelt bed, possibly by means of auxiliary gas or oil burners.

Future Work

There still remain a number of unresolved questions concerning the mechanism of smelt-water explosions as well as the limiting factors determining whether the explosion will take place. It is therefore recommended that the following experimental program be carried out.

1. The explosive species and mechanism producing explosions must be firmly and unquestionably established since practical, safe, consistent remedial measures can only result through such understanding.
2. The absorption and desorption of water by molten smelt should be thoroughly studied as a function of temperature and water vapor pressure. At the same time the relationships of water absorption, CO, CO₂ and H₂ production should be determined as a function of the sodium hydroxide content of the smelt. The desorption, or release, of water vapor should be studied in order to determine the conditions, if any, under which smelt will release steam explosively.

3. Research should continue by carrying out additional, carefully controlled, statistically designed series of experiments investigating the interaction of the variables - temperature, mass, and composition (in particular minor constituents such as sulfate, chloride and hydroxide). Furthermore the effect of carbon, in the form of black liquor char, should be more thoroughly investigated, for its reactivity could conceivably be greater than the sugar charcoal used in the experiments carried out in the work reported here.
4. Having carried out items 2 and 3 above, further tests on a pilot plant scale should be considered. Such tests should be aimed at the testing of proposed remedial measures and shut-down procedures.

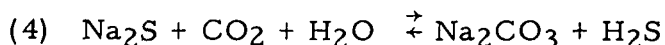
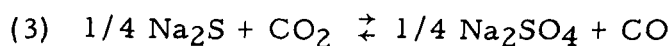
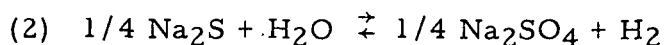
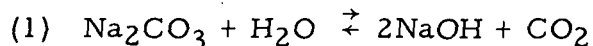
SMELT-WATER (VAPOR) REACTIONS - EQUILIBRIUM STUDIES

Although one of the ultimate goals of this work was to determine the chemical reactions of molten smelt with liquid water, theoretical predictions, based on thermodynamic considerations, can be made only on the basis of chemical equilibrium and other simplifying assumptions (for example, water must be present as water vapor). It was recognized that the actual smelt-liquid water reaction was definitely a non-equilibrium process; nevertheless calculations and experiments of the equilibrium reactions were considered to be a necessary preliminary if the smelt-liquid water reactions were to be understood.

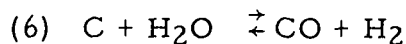
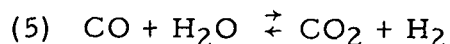
Prediction of Important Reactions

The available thermodynamic data for smelt-char constituents were obtained, critically evaluated, and the equilibrium constant as a function of temperature for individual reactions was calculated from what was considered to be the best available information. Based largely on the data from Rosén^(4, 5), but also from the JANAF Thermochemical Tables⁽⁶⁾, twenty-one chemical reactions that could possibly take place between smelt-char constituents and water were examined. The results of these calculations were given, as plots of log K vs temperature, in Progress Report Nos. 4 and 5^(7, 8).

Smelt-Water Reactions. From a consideration of these reactions, it was initially concluded that the following major reactions were important to the smelt-water reaction and their equilibrium constant vs temperature relationships are shown in Figure 1.



Smelt-Char-Water Reactions. If it is considered that char consists largely of carbon particles, the additional reactions of carbon with water,



become important. The equilibrium constants for these reactions as a function of temperature are also shown in Figure 1.

It will be noted that the carbon-water reactions (Reaction (5) and (6) in Figure 1) are highly favorable in the temperature region of interest and from purely equilibrium considerations would be the predominant reactions in a smelt-char-water system.

In order to assess the relative contributions of each reaction in a purely smelt-water system, Reaction (4) was first considered to be of minor importance and simultaneous calculations carried out on the first three equations. Using as a basis for the calculations the conditions outlined in Progress Report No. 5⁽⁸⁾, and given in Figure 2, a calculated yield of each gas was obtained by considering the equilibrium relationships of the three reactions as a function of sodium hydroxide concentration. Reaction (4) was then considered and found (at 1600°F) to have a small, insignificant contribution. The equilibrium yields of gaseous products, as a function of mol ratio of NaOH/Na₂CO₃ and at 1600°F and 2000°F, are plotted in Figure 2, and illustrate the dependence of the gaseous products on the sodium hydroxide content of the smelt.

It should be emphasized that in spite of what appear to be unfavorable equilibrium constants for these reactions, theory predicts that they proceed to the right under certain conditions. The conditions required, satisfied by the molten smelt, are that the condensed products (NaOH and Na₂SO₄) are dissolved in the melt and exist only in low concentrations in the melt (hence their activities are much less than one). The absence, or presence in low concentrations, of these products produces the driving force required to make the reactions proceed.

Thus it was concluded that theoretical considerations showed that CO, CO₂ and hydrogen should be the major gaseous products of a smelt-water reaction and the relative amount of each was dependent largely on temperature and sodium hydroxide content. The dependence of the CO/CO₂ ratio and H₂ yield on sodium sulfate concentrations was also implied and could be shown by calculations based on higher (3%) Na₂SO₄ concentrations.

Confirming Studies

It was considered necessary to carry out experiments to confirm the theoretically predicted reactions as well as to determine whether some other, heretofore unknown, reactions would take place.

The procedure followed was outlined in detail in Progress Report No. 5⁽⁸⁾. Briefly, water-saturated argon (vapor pressure of H₂O \approx 35 mm Hg) was passed through molten smelt at a rate of 0.5 liter of argon/minute in the apparatus shown in Figure 10. The emerging, non-condensable gases were analyzed by gas chromatography and the water vapor content was determined by absorption in a drying agent. The flow was monitored with a wet test meter so that mass balances of the reactants could be carried out.

Although no attempt was made to insure complete equilibrium, in view of the very low amount of water contacting the smelt per unit time (\approx 2 gms H₂O/100 gms smelt/hr), it was assumed that equilibrium conditions were closely approximated. Three successful tests were completed, one using a graphite crucible, the other two using a stainless steel crucible at two levels of sodium sulfate concentrations. Because of the difficulty of preparing hydroxide-free smelt, the initial smelt charge in each test contained .5% NaOH (.056 mols/mol Na₂CO₃). All of the tests were carried out at 1600°F.

The results of these experiments are summarized in Figures 3, 4, and 5. In these figures the gas analyses of samples taken at 10 - 15 minute intervals during the test is shown on the basis of the percent of water, instantaneously converted as it passed through the smelt, as a function of the total amount of water added to the smelt.

These results confirmed that hydrogen, carbon monoxide and carbon dioxide were the major products of the smelt water vapor reaction. Hydrogen sulfide was detected by its characteristic odor, but its concentration was below the sensitivity of the chromatograph (< 0.1%). A mass spectrometric analysis of the emerging gases did not detect the presence of any other gaseous products. It will be noted that the yields of the gaseous products, particularly hydrogen, rose to a steady state value only after a period of time had elapsed. The significance of this behavior is discussed in the subsequent section.

Although not thoroughly investigated, the effect of carbon, indicated by the effect of graphite crucible containment vessel, was to increase the yield of hydrogen and carbon monoxide (Figure 3). As pointed out in Progress Report No. 5, there was evidence of carbon-water reaction in this experiment. The effect of higher sodium sulfate concentrations (Figure 5) was qualitatively as would be predicted; i. e., to decrease the hydrogen yield and increase the CO₂/CO ratio. It was concluded that these results confirmed, on a semi-quantitative basis, the predicted equilibrium reactions of a smelt-water system.

From a quantitative viewpoint these experiments indicated that the yields of hydrogen were greater than predicted - approximately two times the calculated amount. Furthermore, the presence of 2.79% Na₂SO₄ resulted in a higher CO/CO₂ ratio than could be predicted (at .01% Na₂SO₄ this ratio

water could be accounted for in the carbon crucible.) As pointed out in Progress Report No. 5, the major portion of the water absorption took place while the production of hydrogen was rising to its steady state value, thus indicating that the absorption was somewhat preferential to the hydrogen-producing reaction.

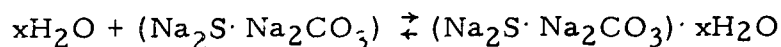
In Progress Report No. 5 several alternatives were proposed concerning how this might occur:

- a. $\text{Na}_2\text{O} + \text{H}_2\text{O} = 2\text{NaOH}$
- b. A physical solubility of water
- c. A hydrate formation.

Although alternates (a) and (b) remain as possibilities, at the present time alternate (c) appears more probable. This suggestion is based upon the well-known property of sodium sulfide to form hydrates at low temperature and the difficulty of obtaining anhydrous sodium sulfide. Furthermore, although this phenomenon is not common, molten lithium salts have been found to hydrate readily^(10, 11). In addition, in a preliminary study, mentioned in Progress Report No. 3⁽¹⁷⁾, the anhydrous sodium sulfide apparently absorbed water vapor, at 4.5 mm partial pressure, at 1400°F. As the absorption of water vapor by smelt at 1600°F was an observed experimental fact, it is postulated that the sodium sulfide component was the predominant factor in this absorption (sodium carbonate is readily dehydrated and would not be expected to contribute to this behavior).

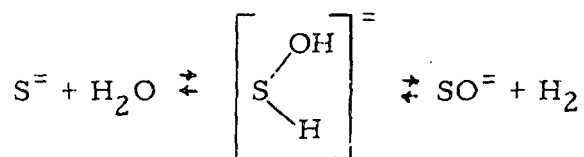
Since the water absorption took place under relatively low water vapor pressure (35 mm) at 1600°F, it appeared that relatively strong bonding between water and sulfide ion (in the melt) takes place. Hence it is proposed

that an additional reaction between smelt and water takes place and is written as follows:

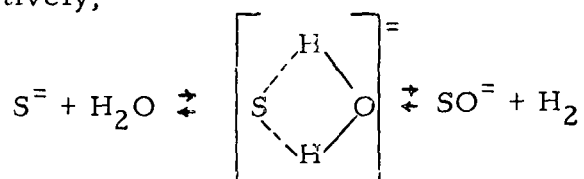


Written as an equilibrium reaction, the reaction is believed to play a role, along with the previously mentioned reactions, in the over-all smelt-water reaction equilibrium relationships.

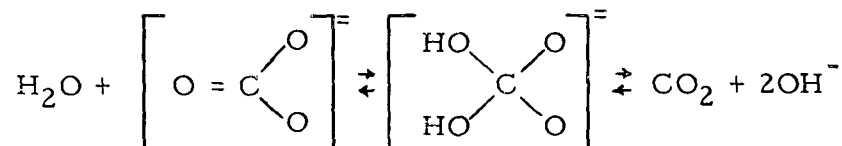
It is postulated that the formation of hydrogen and carbon monoxide takes place through intermediate molecular compounds of sulfide and carbonate ions. Thus, hydrogen apparently must form from the (highly simplified) reaction:



or, alternatively,



The oxidized sulfur must react with more water and go through a series of complex reactions until it ultimately becomes the stable SO_4^- ion. Similarly, the carbonate ion must associate with water and then decompose to CO_2 and hydroxyl ion.



The main point is that a molecular association of water to form an intermediate species seems to be necessary to produce the reaction products observed. The finding that the smelt absorbs water would tend to show that some of the intermediate species are reasonably stable.

Some experimental evidence was found indicating that the hydrated smelt existed in equilibrium with other species in the smelt. For example in the equilibrium studies of the water vapor-smelt reaction, described in Progress Report No. 5⁽⁸⁾, when the water vapor pressure was removed from the reaction, the smelt evolved, not only water vapor, but also hydrogen, carbon monoxide and carbon dioxide (Figure 6). The proportions of each were also found to be temperature dependent, indicating that the hydrated smelt tended, not only to satisfy its own equilibrium constant (with water), but was inter-related to the other pertinent equilibrium constants applicable to the smelt-water system. This behavior of the hydrated smelt also tended to support the viewpoint that the water was held as molecular water in the smelt rather than a physical solubility.

The importance of this reaction lies in the fact that it takes place simultaneously with the other reactions of smelt and water; the fraction of the water taking part in this reaction should be dependent on the composition and temperature of the smelt. As this reaction may affect smelt explosibility, it is recommended that further work be carried out to determine (a) if it is indeed a valid chemical reaction, obeying equilibrium relationships, and (b) the quantitative characteristics of this reaction.

SMELT-WATER EXPLOSION STUDIES

Having established the chemical reactions taking place between smelt-char and water vapor under near-equilibrium conditions, it was essential to investigate the liquid water-smelt reactions under conditions conducive to explosions.

As it was one of the primary purposes of these experiments to determine whether chemical reactions affected smelt explosions, increments of water were injected into the smelt, the gas composition determined at each incremental addition, and the smelt composition determined after the test had been completed.

Preliminary Experiments - Effect of Method of Water Addition

The first set of experiments, described and reported in Progress Report No. 6⁽¹⁸⁾, were carried out in a pressure vessel containing a small furnace and instrumented with a pressure transducer, pressure gauges and thermocouples. The pressure signal was recorded by a Visicorder. Water was introduced beneath the surface of the smelt, held in a helium atmosphere, by means of hypodermic tubing of .0465" I. D.; such a method of water addition did not produce the sharp pressure rises later found to be characteristic of explosions resulting from the use of a water-cooled injection system and a somewhat larger I. D. (.0625"). The results from these experiments, shown in Table XI, confirmed that H₂, CO and CO₂ were formed from the smelt-liquid water reaction and some indication of the conversion of water under these conditions was obtained. Hydrogen yields of up to 55% were found and indicated that hydrogen formation could be a significant factor in combustion gas type explosions from smelt-water interactions. Furthermore, some evidence was found that equilibrium considerations were qualitatively applicable, i. e., there was a tendency for CO and CO₂ yields to be inversely dependent on hydroxide content. In addition, some slight differences in reactivity were noted and were also inversely correlated with CO₂ and CO production.

That no violent explosions were produced was attributed to the method by which the water was added. The reason for this may have been that the water was heated during introduction through the smaller tubing or that the smaller stream exposed more surface area of water droplets to the molten smelt such that the explosive reaction did not take place. Whatever the reason, it was concluded that the explosive reaction was sensitive to the manner in which water is introduced as well as to water temperature.

Helium Atmosphere Explosions

There appeared to be sufficient evidence from the previously described experiments that sufficient hydrogen was formed from the smelt-water reaction to be a factor in a possible combustion gas type explosion. There remained, however, the problem of determining whether or not some other explosive reaction which was not associated with combustion took place between liquid water and molten smelt. If explosions between smelt and water could be produced in an inert atmosphere, e. g., helium, this would be considered valid proof that such a reaction indeed took place. In order to investigate such a possibility, the same pressure vessel apparatus used in the preliminary experiments was modified so that more reproducible injections of a larger stream of water could be made, ensuring that liquid water would penetrate the surface of the smelt. This preferred design of the apparatus is shown in Figure 11.

The detailed procedure (as well as the results) was given in Progress Report No. 7⁽¹²⁾. Briefly, laboratory-prepared smelt of known composition was charged to the reactor, heated to 800° F under vacuum, then to test temperature in helium. Fresh helium at one atmosphere pressure was

then introduced into the reactor and small amounts, initially one-cc and later two-cc of water were forcibly injected into the molten smelt. A gas analysis was then carried out, and if no explosions took place, the vessel was evacuated and pure helium again added so that one atmosphere pressure was again present. The procedure was repeated until an explosion, as indicated by the Visicorder, or oscilloscope, took place or the test was terminated. The smelt was analyzed after each test for all smelt constituents by the Mead titration procedure.

The results of the experiments, carried out using laboratory-prepared smelt, are summarized in Table II. It will be noted that unequivocal explosions were observed in five out of eight experiments. These explosions were characterized by fast pressure rises (1-5 millisecond rise times) and a weakly audible, sharp noise was heard when the explosion took place. After the experiment was completed, the smelt was found uniformly distributed over the inside top and sides of the vessel. Of the three tests that did not explode, one test (Run No. 3) was deliberately terminated prior to the explosion and another test (No. 18) apparently exhibited a mild reaction, enough to lift the smelt from the crucible. The third test did not explode, but the evolved gas analysis and post-test smelt analysis both were somewhat unusual and the significance of this will be discussed later.

The important conclusion drawn from these results was that an explosive reaction not associated with combustion could take place between molten smelt and water.

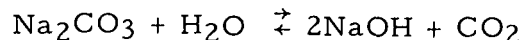
Effect of Temperature on Explosions

It will be noted from Table II that explosions were produced at smelt temperatures of 1500°F - 1800°F. Hence, it is concluded that smelt-water explosions can take place over this temperature range. As no experiments were carried out outside of this range, such a range of temperatures cannot be considered as limiting and explosions may take place at higher or lower temperatures. Further work is recommended to establish the temperature limits, if any, for the smelt-water explosion.

Effect of Composition on Smelt-Water Explosions

In addition to temperature, smelt composition is another variable of possible significance in smelt-water explosions. Furthermore, as carbon apparently influenced the equilibrium smelt-water reaction, it was pertinent to determine whether the presence of carbon, always possibly present in smelt, would affect smelt water explosions. Time did not permit a thorough investigation of all of these variables, but the results of these experiments furnished some indication of the effects of individual constituents.

Sodium Hydroxide. Sodium hydroxide may be present in smelt; Nelson and Kennedy⁽³⁾ found small amounts in plant smelts and further found that sodium hydroxide was a factor in dissolving tank explosions. Furthermore, as the formation of sodium hydroxide and CO₂ from the reaction



was predicted and verified experimentally (see further below) as an important reaction between smelt and water, the determination of the effect of sodium hydroxide on smelt explosions was important. Experiments were carried out

in which 5% sodium hydroxide was added to smelt and water injected in the usual fashion.

The results of these experiments are summarized in Table IV. It will be noted that explosions were observed in four out of five tests and it is particularly noteworthy that the explosions occurred at the first water addition. Thus it was concluded that sodium hydroxide, added at the 5% level (but found to be somewhat less after the test was completed - see Progress Report No. 7) ⁽²⁾ increased the sensitivity of smelt to explosions.

As noted above, and was discussed more thoroughly in Progress Report No. 7, ⁽¹²⁾ it seemed significant that normal smelt exploded only after multiple injections of water, but smelt with added hydroxide was sensitive to the first water addition. Furthermore, in every case that normal smelt exploded a larger amount of hydroxide was found after the explosion than was present in the initial smelt. In addition, at 1800° F the one normal smelt exhibiting no explosive behavior whatsoever (Table II. Run 19) was found, after the test, to contain lower amounts of hydroxide than initially present. It was postulated that the lower hydroxide content was the result of a reaction with the crucible.

This evidence led to the conclusion that the significance of the required multiple injections of water for an explosion to take place (particularly at 1500 - 1600° F) involved the production of sodium hydroxide. It furthermore appeared that approximately 1.5% of sodium hydroxide was required for the explosion to take place. It was therefore proposed that the formation of sodium hydroxide may be an intermediate step in the explosion reaction.

Effect of Sulfide Concentration. It will be noted from Table II that smelt compositions from 21.8 - 37.9% Na₂S produced explosive reactions with water in a helium atmosphere. Thus it is known that such concentrations may be explosive, but it is not known what, if any, the critical Na₂S level must be in order for explosions to take place. It could be speculated that such a concentration level would be dependent on other constituents (as well as other factors such as temperature) of the smelt.

Effect of Chloride. The effect of sodium chloride in smelt was briefly investigated. Explosions were produced at a NaCl concentration of 5.7% at the first water injection, in a helium atmosphere as well as in a CO₂ atmosphere, when the CO₂ had been present for a short period of time. (Table VIII) Thus it was concluded that sodium chloride, like sodium hydroxide was a sensitizing agent. In Progress Report No. 7⁽¹²⁾ it was suggested that sodium chloride may possibly hydrolyze to sodium hydroxide in the molten smelt-water mixture. Further experimental work would be required to establish this hypothesis.

Effect of Carbon. The limited number of experiments on the influence of carbon (in the form of sugar charcoal to simulate char) on the smelt-water reaction indicated several possibly significant effects. It will be noted in Table IX that at 1800°F no explosions were produced with carbon additions to normal smelt, in duplicate tests, after four water additions. In each case, upon lowering the temperature to 1600°F an explosion was produced at the first water injection. At 1800°F, the larger proportion of hydrogen and carbon oxides found was interpreted to indicate that

the kinetics of the carbon-water reaction at this temperature were sufficiently faster to compete successfully with the smelt-water reactions. On the other hand, at 1600° F the reaction rate of the carbon-water reaction apparently is slower and the smelt-water reactions predominate.

It is therefore indicated, subject to additional experimental work, that at the high temperatures (>1800° F) with carbon, the water-gas reaction predominates and inhibits the smelt water reaction; at the same time it produces hydrogen and carbon monoxide, potential hazards from the point of view of a combustible gas explosion. As the smelt cools, there is a greater tendency for the smelt-water physical type explosion to take place but, on the other hand, less combustible gas tends to form from the carbon-water reaction.

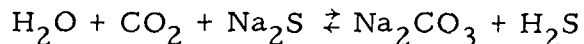
Effect of Sulfate and Other Minor Constituents. The effect of added sodium sulfate by itself, was investigated in one test (Run No. 6, Table IV). As this smelt exploded at the second addition of water, there is some evidence that sulfate also sensitizes smelt. If the sulfate contents before and after the tests are compared, as shown in Table III, it will be noted that the sulfate content usually increases and this would be expected from the results of the hydrogen analyses (Table VII). The experimental data suggests that a certain quantity of sulfate may be necessary for the explosive reaction to take place. However, not enough data is available on this effect to warrant a firm conclusion.

Although analyses were carried out for other minor constituents, including sulfite and thiosulfate (Progress Report No. 7)⁽¹²⁾ no correlation could be made between explosibility and other sulfur species.

Effect of CO₂ Atmosphere on Smelt Explosions

Experiments were carried out in a CO₂ atmosphere in order to test the hypothesis that the formation of sodium hydroxide was a critical factor in smelt-water explosions. As CO₂ would be expected to react with sodium hydroxide, it seemed possible that smelt-explosions could be prevented in such an atmosphere. Tests were carried out with normal smelt in 100% CO₂ as well as 15% CO₂ - 85% He. In addition tests were carried out with 5.7% added sodium chloride in 100% CO₂.

The results of these experiments are summarized in Table VIII. It will be noted that no explosions were observed in a CO₂ atmosphere except in Run No. 32, containing sodium chloride. (In this run the CO₂ atmosphere apparently was not present for a long enough time prior to water injection to have any inhibiting effect.) Upon water injection a rapid reaction must have taken place, the net effect of which was to reduce the sulfide content of the smelt, possibly through the reaction,

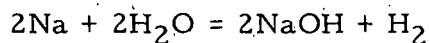


In the case of normal smelts, the sulfide content may have been lowered below the explosive range. However, in duplicate experiments, with sodium chloride added to the smelts no explosions were observed and yet the sulfide content after the experiment ended was sufficiently high, particularly in the presence of NaCl, to have exploded in a helium atmosphere.

Elemental Sodium

May⁽¹³⁾ initially suggested, on the basis of equilibrium considerations, that elemental sodium could form in the reducing atmosphere of the smelt bed and could be a possible contributing factor to smelt-water explosions. Rosén⁽¹⁴⁾ also indicated that elemental sodium would form and the calculated equilibrium concentrations of all major species reported in this work confirmed that small, though significant, quantities of sodium vapor may exist in the smelt bed (Progress Report No. 4)⁽⁷⁾. It should be emphasized that these thermodynamic calculations are based on the properties of sodium vapor at temperatures above its boiling point (1616°F). As the sodium vapor is continuously being swept from the lower furnace it does not seem probable that the reaction of the vapor with water need be seriously considered as a contributor to smelt-water explosions.

There existed, however, the possibility that the smelt, under a reducing atmosphere and a sodium vapor atmosphere could dissolve the elemental sodium. The sodium might then undergo its well-known reaction (exothermic) with water.



For this reaction to be of importance elemental sodium would have to exist in significant amounts in the smelt bed. Therefore experiments were carried out in order to determine whether a significant amount of sodium could be formed and held in smelt at furnace bed temperature.

The detailed procedure was outlined in Progress Report No. 7⁽¹²⁾. Briefly, mixtures of synthetic smelt and sugar charcoal, contained in a

graphite liner within a stainless steel capsule, were brought to test temperature (1700 - 2000°F), quenched under an inert atmosphere and removed for analysis in a dry box containing argon. The elemental sodium was determined from the production of hydrogen upon water addition to the cold smelt.

The results of these experiments are summarized in Table V and it appears reasonable to conclude that very small amounts are retained in molten smelt under these conditions of temperature and reducing atmosphere.

If it is also taken into account (a) that the sodium oxide-water reaction, also exothermic, did not enhance the smelt-water explosion (discussed below) and (b) that explosions took place by some other mechanism under conditions where elemental sodium would not form or exist, it is concluded that the reaction of elemental sodium with water does not contribute significantly to smelt-water explosions.

Na₂O-Water Reaction

When Na₂O was added to smelt, no increased reactivity was noted (Table VI). Therefore it is concluded that this reaction could be eliminated as a cause of explosions.

H₂O + CO₂ + Na₂S Reaction

This reaction took place during the experiments conducted in the CO₂ atmosphere, described previously and summarized in Table VIII. Smelt sulfidity was reduced by the reaction, but no explosions were observed. Therefore this exothermic reaction could be eliminated as a principal cause of explosions.

Smelt Hydration

As pointed out in Progress Report No. 5⁽⁸⁾ there was a possibility that the hydration reaction was exothermic and thus might have an effect on explosions. In order to investigate this possibility an attempt was made to inhibit explosions by fully hydrating the smelt (i. e., adding water to cold smelt, then heating to test temperature). These experiments, shown in Table VI, showed that this procedure did not prevent explosions and it appeared that any exothermic energy release from this reaction was not a factor in smelt water explosions.

EXPLOSION MECHANISM

It was pointed out in Progress Report No. 7⁽¹²⁾ that, by elimination of other gaseous species, the explosion mechanism apparently involves the exceedingly rapid release of water vapor. As the water is released over a very short time interval, the basic question to be answered is: by what mechanism can such an exceedingly fast rate of energy transfer and release be obtained? At the present time an unequivocal answer to this question cannot be offered and more experimental work is required to establish this point.

Two closely related characteristics of smelt appear to be important: (a) the ability of smelt to hydrate and the interaction of this reaction with other chemical reactions and, (b) the extreme solubility of smelt in water. Hydrogen was found in the reaction vessel after explosions occurred, and this finding was considered to be an indication that some chemical

combination and reaction had taken place. The finding of sulfate formation when smelts exploded at the first water injection was confirming evidence for this point of view. In view of this experimental evidence it seems reasonable to assume that diffusion across the water- (steam) smelt interface does not seriously restrict the mass transfer of water to the smelt. Furthermore in order for hydrogen and sulfate to form, it is necessary to assume a prior, intermediate, molecular association of water with sulfide ion. Based on these characteristics, at least three alternative hypotheses of the mechanism of smelt-water explosions should be considered.

1. The build up of unstable hydrated ions whose decomposition is triggered by some as yet unknown agent.
2. The local hydration of smelt under the influence of local cooling by water with the subsequent release of water vapor when the local cooling is no longer effective.
3. An extension of (2), whereby the smelt actually dissolves in the water, is heated above its saturation temperature and releases superheated steam explosively. This process might be similar to that observed when a highly concentrated solution of soluble salts is heated on a hot plate. Under these conditions the solution has a tendency to superheat if no nucleating agent is present and may suddenly erupt violently.

Figure 12, illustrates a possible sequence of events, highly simplified, that could take place during alternate (2) above. Thus, initially water droplets would be expected to form steam and locally cool the smelt. The water vapor would not react significantly with the cool smelt, but rather the smelt would tend to hydrate at the lower temperature; as water vapor is transported to the higher temperature smelt more reactions would take place, yielding NaOH, CO₂ and hydrogen. When the water no longer effectively cools the smelt the heat flux from the bulk smelt would raise the temperature of the hydrated smelt and effect a release of water vapor. Thus the heat content of the bulk smelt furnishes the energy for the explosive reaction. As previously stated, there is insufficient basic knowledge concerning the absorption of water (or hydration) or the conditions effecting a rapid release of water and these factors must be investigated before a sound and positive understanding of smelt-water explosions can be developed. Until this has been firmly established, it is difficult to confidently propose remedial measures such as smelt additives intended to render smelts non-explosive.

PYROLYSIS AND COMBUSTION OF BLACK LIQUOR

Theoretical Combustion Studies

As an aid to an understanding of the complex chemical equilibria involved in the burning of black liquor under highly variable amounts of combustion air and temperature, the equilibrium concentration of all of the products of combustion, both gaseous and condensed were calculated. The

Free Energy Minimization technique⁽¹⁵⁾ was applied, using a computer program included as a part of Progress Report No. 7⁽¹²⁾. As pointed out previously the results of this work were used largely to establish the possible presence of elemental sodium in the primary furnace of the Kraft unit.

Pyrolysis Studies

The decomposition characteristics of black liquor are of particular importance as applied to the currently recommended shut-down procedure involving the quenching of the active bed with black liquor. As it was important to determine whether or not this decomposition was an exothermic process, Differential Thermal Analysis (DTA) was used to study the possible heat evolved in the decomposition. It was furthermore of interest to determine the characteristics of the thermal decomposition as a function of time and Thermogravimetric Analysis (TGA) techniques were applied to this study. In addition the quantities of gas evolved from black liquor solids as a function of temperature were determined by introducing a known weight of solids into the heated zone of a tubular furnace and measuring the pressures generated. The gas samples were analyzed by gas chromatography.

The results of these studies, discussed in Progress Reports 2⁽¹⁶⁾ and 3⁽¹⁷⁾ showed that the decomposition of black liquor was an endothermic process. The decomposition of black liquor takes place in two fairly distinct steps - first, the release of steam and finally, the release of gaseous products of decomposition (Figure 8).

The total amount of gas evolved as a function of temperature is shown in Figure 9 and the dependence of gas composition on temperature is shown in Table X.

Referring to Figure 9 and assuming, for example, a 390 ton unit burning 75,500 lbs of liquor per hour of 60% solids content, it can be shown that about 15 - 30,000 cubic feet (depending on temperature) of gas can be generated per minute. While there are a variety of factors (amount of air leakage, capacity of I.D. fan, rate of flow out of the furnace, etc.) that render an exact calculation impossible, qualitatively it can be appreciated that in a typical unit of this capacity having a cross-sectional area of 520 ft², there will be a tendency for the furnace to accumulate a large quantity of combustible gas. As there is always the possibility of air in-leakage or back diffusion from the atmosphere as well as the possibility of an ignition source the danger of a combustion gas explosion is apparent. The severe damage experienced in utility boilers from explosions of this type is well known.

It is therefore proposed, subject to further testing, that emergency shut down procedures based on keeping the unit on the air-rich side be considered to reduce the potential hazard of a combustible gas explosion, inherent in the presently accepted procedure.

SHUT-DOWN TESTS

As pointed out above the emergency shut-down procedure, now in effect, involves quenching the active char with black liquor. This

procedure may result in the possibility of a combustible gas-air explosion. An alternate approach to an emergency shut-down could involve the concept of no black liquor quenching, shutting off the primary air and increasing the secondary air so that an air rich atmosphere exists immediately above the smelt-char at all times during the shut-down.

Two field tests were carried out using this concept of a shut-down procedure. Gas and bed temperatures were monitored and the gas composition at several points in the unit was determined by analysis.

The results of these tests were reported in detail in Progress Reports Nos. 6 and 7^(18, 12). In general both tests showed that the units could be shut down smoothly and quickly and at no time was there any danger of a combustible gas explosion.

LIMITATIONS

Extrapolation to Operating Kraft Units

It should be pointed out that some results of this work are difficult to translate directly to smelt-water explosions as they are experienced in operating units. Although the chemical reactions taking place between smelt and water in an actual unit should be the same as those taking place in the laboratory the rates of formation of the various products may not be the same. Under the distinctly non-equilibrium conditions existing when liquid water and molten smelt co-exist, it would be expected that the amount of each product might depend upon the relative mass of water and smelt involved. As the mass of smelt and water investigated in this study

are orders of magnitude less than actually may exist and cause explosions in recovery units some caution in extrapolating our laboratory results is necessary.

Experimental Limitations

The experimental work summarized in this report was carried out under some conditions which did not lend themselves to strict experimental control. Consequently, the interpretation of the results, in some cases, was not as straightforward as might have been desired. These limitations were concerned primarily with the following items:

1. Smelt preparation
2. Crucible materials
3. Analysis of smelts
4. The number of experimental variables.

Smelt Preparation. Ideally, a smelt of known composition might best be prepared from pure anhydrous sodium sulfide and sodium carbonate. Practically, however, such a goal is difficult to achieve mainly because sodium sulfide is particularly laborious to prepare in a pure, anhydrous form. Furthermore, it is not available from commercial sources in this state of purity. In this work the procedure outlined by Rosén⁽⁵⁾ was initially used, involving vacuum dehydration of the hydrated material and heating in a hydrogen atmosphere. The resulting product was about 98.5% Na₂S, but apparently complete dehydration was not achieved. This material was used (mixed with sodium carbonate when a synthetic smelt was required) in initial experiments, but the time involved in its

preparation led to an alternate method of smelt preparation. This latter method involves the fusion of $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$, technical grade, with Na_2CO_3 C. P., in a graphite container at 2000°F . Chemical analyses were carried out on the fused product. Unfortunately, the chemical analysis for hydroxide, a constituent considered to be important in the explosion mechanism, is not as accurate as might be desired (see discussion below), and further, all smelts prepared in this manner contained initially small amounts of hydroxide.

In order to eliminate uncertainties of smelt starting material in any future work it is recommended that special care be taken in the preparation of the smelt charge. In particular the hydroxide content should be eliminated as a variable - possibly through a second treatment of the fused smelt with ammonium or sodium bicarbonate.

Crucible Materials. It is well known that molten smelt is a particularly corrosive material; it was noted that small amounts of sodium sulfate and sodium chloride impart an even more corrosive action on the metal crucibles used in this work. Although graphite crucibles were seriously considered for this work, it was found in the equilibrium-type experiments (Progress Report No. 5⁽⁸⁾) that the crucible interacted with the water additions to smelt such that the interpretation of the results was difficult. It was confirmed in the pressure vessel experiments (Runs No. 26 and 27, Table IX) that at 1800°F , water additions to smelt to which carbon had been added resulted in higher yields of CO and hydrogen than when water was added to smelt alone. As stainless steel (Type 304) was also attacked

by smelt, a hard chrome plate was given to the stainless steel and resulted in a crucible with somewhat improved resistance. Nevertheless, it is not considered that this was a completely satisfactory material, particularly for investigations above 1700°F. Therefore, in order to eliminate this variable as a possible interference, in future work it is recommended that a serious effort be made to obtain a more satisfactory smelt containment material.

Chemical Analysis of Smelt. The uncertainties of the chemical analysis procedures for the minor constituents of smelt (except sulfate) have been previously pointed out in Progress Report No. 7⁽¹²⁾. It is sufficient to state that these procedures are inherently not capable of high accuracy and conclusions based on the analysis of the minor constituents must be made with this qualification.

Experimental Variables. There were a large number of variables involved in the laboratory studies, in particular the pressure vessel studies. While the individual effects of several variables were determined it was difficult to determine their interaction. Such tests lend themselves to a set of statistically designed experiments and it is recommended that any future experiments be based on this kind of approach.

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TABLE I. WATER MASS BALANCE.
 SMELT-WATER (VAPOR) REACTION.
 BASIS: 100 GMS SMELT.

	Run 2 (.01% Na ₂ SO ₄)	Run 5 (2.79% Na ₂ SO ₄)
<u>Water In</u> (gms)	2.11	1.38
<u>Water Out</u> (gms)		
As H ₂ O	.36	.39
Converted to Gaseous Products	<u>1.23</u>	<u>.40</u>
Total Water Accounted For	<u>1.59</u>	<u>.79</u>
<u>Water Retained In Smelt</u> (gms)	.52	.59

TABLE II. SMELT-WATER EXPLOSION EXPERIMENTS.
(NORMAL SMELT, HELIUM ATMOSPHERE.)

Temp. OF	Run No.	% Na ₂ S (After Explosion)	No. Water Additions*	Explosion	Maximum Pressure (psig)	Remarks
1500	15	37.6	5	Yes	44	
1600	2	36.0	6	Yes	55	
1600	3	38.5	5	No	7	Stopped Water Injections to Check Composition Prior to Explosion
1600	20	21.8	4	Yes	55	
1800	16	37.9	2	Yes	96	
1800	18	37.7	2	No	25	Apparently a Surge At First Injection.
1800	19	28.1	6	No	18	Generated Unusual Amounts of CO and CO ₂ . Low Hydroxide Found at End of Run. Possible Reaction of NaOH with crucible.
1800	21	21.8	1	Yes	57	

*In general 2-cc quantities. In some cases initial additions were 1-cc.

TABLE III. SODIUM HYDROXIDE AND SULFATE FORMATION FROM SMELT-WATER REACTIONS.

Charge	Run No.	Temperature OF	Total H ₂ O Added-cc	Hydroxide Concentration		Sulfate Concentration	
				<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
Na ₂ CO ₃	B-1	1650 - 1700	2*	0.0%	1.6%	--%	--%
Na ₂ CO ₃	B-9	1600	6*	0.0	4.4	--	--
25% Na ₂ S	20	1600	8	0.6	2.1	.17	.88
25% Na ₂ S	21	1810	2	0.6	1.1	.17	.07
35% Na ₂ S	15	1500	9	0.7	1.3	.17	3.80
35% Na ₂ S	2	1590 - 1750	10	0.7	1.5	.17	2.75
35% Na ₂ S	3	1600	7	0.7	1.5	.17	1.28
35% Na ₂ S	16	1800	3	0.7	1.1	.17	.30
35% Na ₂ S	18	1800	4	0.7	4.4	.17	3.76

*Water injected beneath melt through .0465" I.D. tubing.

TABLE IV. EFFECT OF ADDED SODIUM HYDROXIDE ON SMELT-WATER EXPLOSIONS. 35% Na₂S. HELIUM ATMOSPHERE (EXCEPT AS NOTED).

Amount Added	Run No.	Temperature OF	No. H ₂ O Additions	Explosion	Maximum Pressure (psig)	Remarks
5% NaOH	4	1600	1	Yes	60	
5% NaOH	5	1600	2	No	10	
5% NaOH	9	1600	1	Yes	21	Air Atmosphere Explosion, Indistinguishable from He Atmosphere
5% NaOH	12	1600	1	Yes	60	
5% NaOH	13	1560	0	Yes	?	He + H ₂ O Atmosphere
5% NaOH	14	1600	1	Yes	27	He + H ₂ O Atmosphere. Pressure Excursion to 25# while Heating to Test Temperature
5% Na ₂ SO ₄	6	1620	2	Yes	60	

TABLE VI. RESULTS OF EXOTHERMIC REACTION EXPERIMENTS.

Charge	Atmosphere	Run No.	Temperature °F	No. H ₂ O Additions (2-cc)	Explosion	Remarks
3% Na ₂ O + 3% NaOH (35% Na ₂ S)	He	10	1475	1	No	
3% Na ₂ O + 3% NaOH (35% Na ₂ S)	He	11	1600	4	No	
30% Na ₂ S	CO ₂	22	1600	7	No	Na ₂ S reduced to 5.7%
30% Na ₂ S	CO ₂ then He	23	1700	8	No	
			1600	9	No	Na ₂ S reduced to 8.0%
30% Na ₂ S	15% CO ₂ 85% He ²	29	1600	5	No	Na ₂ S reduced to 16.5%
30% Na ₂ S	15% CO ₂ 85% He	30	1800	3	No	Na ₂ S reduced to 19.1%
5% NaOH + 3 cc H ₂ O (35% Na ₂ S)	He	13	1560	0	Yes	Manometer blew out while heating
5% NaOH + 3 cc H ₂ O (35% Na ₂ S)	He	14	1600	1	Yes	Pressure excursion to 25# while heating

TABLE VII. COMPARISON OF HYDROGEN CONCENTRATIONS, EXPLOSIVE VS NON EXPLOSIVE WATER ADDITIONS.

Run No.	Temperature Of	H ₂ Found (Dry Basis) in Helium After Water Addition (2 cc)	
		<u>No Explosion</u>	<u>Explosion</u>
2	1620 - 1750	7.5 - 11%	8.8%
3	1600	5.5 - 6.4	-
4	1600	-	11.3
5	1600	11.9 - 17.0	-
6	1620 - 1640	4.8	7.5
7	1595	-	9.9
8	1600	-	5.3
9	1600	-	7.0
11	1600	12.2 - 14.0	-
12	1600	-	15.0
14	1600	-	15.8
15	1500	9.1 - 12.1	7.7
16	1800	-	17.0
17	1600	19.8	17.2
19	1800	23.6 - 27.0	-
20	1600	16.0 - 18.0	10.8
21	1810	-	20.9

TABLE VIII. EFFECT OF CO₂ ATMOSPHERE ON NORMAL SMELT AND SODIUM CHLORIDE ADDITION.

Charge	Run No.	Atmosphere	Temperature OF	No. H ₂ O Additions (2 cc)	Explosion	Final Na ₂ S Concentration
30% Na ₂ S	22	CO ₂	1600	7	No	5.7%
30% Na ₂ S	23	CO ₂	1700 1600	8 9	No No	8.07
30% Na ₂ S	29	15% CO ₂ 85% He	1600	5	No	16.5
30% Na ₂ S	30	15% CO ₂ 85% He	1800	3	No	19.1
30% Na ₂ S + 5.7% NaCl	24	He	1600	1	Yes	32.7
30% Na ₂ S + 5.7% NaCl	32	He, then CO ₂ for 7 min.	1610	1	Yes	26.1
30% Na ₂ S + 5.7% NaCl	25	CO ₂	1600	2	No	24.8
30% Na ₂ S + 5.7% NaCl	31	CO ₂	1600	2	No	22.4

TABLE IX. EFFECT OF CARBON (SUGAR CHARCOAL) ON SMELT-WATER REACTION.

Charge	Run No.	Temperature °F	No. H ₂ O Additions (2 cc)	Explosion	Gas Analysis (Dry Basis)	
					H ₂	(CO + CO ₂)
30% Na ₂ S + 5% Carbon (Sugar Charcoal)	27	1800	4	No	19.5-30.1	6.3-19.0
		1600	1	Yes	21.7	<0.1
30% Na ₂ S + 5% Carbon (Sugar Charcoal)	28	1800	4	No	22.0-28.4	4.7-12.2
		1600	1	Yes	23.1	<0.1
Sugar Charcoal	26	1650	1*	No	22.8	21.8
		1790	1*	No	23.8	27.9
		1840	1*	No	25.1	31.9

*1 cc additions

TABLE X. ANALYSIS OF GAS FROM THERMAL DECOMPOSITION OF BLACK LIQUOR SOLIDS.

TEMPERATURE-F	600 ^o	800 ^o	1000 ^o	1200 ^o	1400 ^o	1600 ^o	1800 ^o
COMPOSITION							
H ₂	Trace	0.9%	8.8%	32.0%	40.0%	36.%	30.4%
CO	32.5%	27.0	21.8	16.5	23.0	41.	54.1
CH ₄	1.7	5.2	10.5	13.0	9.2	5.8	4.7
H ₂ S	11.1	8.3	8.3	4.5	1.8	1.2	0.5
COS	Trace	0.8	1.3	1.6	0.5	0.2	0.2
SO ₂	14.9	17.4	14.4	7.6	3.0	0.5	0.5
CO ₂	40.0	41.0	35.0	25.0	22.3	15.0	9.5
VOLUME (STP)							
cc/gm solids	46.2	63.3	107	151	303	459	720
ft ³ /lb solids	.74	1.01	1.71	2.42	4.85	7.35	11.5

TABLE XI. SUMMARY OF RESULTS OF PRESSURE VESSEL EXPERIMENTS
 (.0465" I.D. Hypodermic Tubing as Water Injector).

Run #	Charge	Temp. °F	H ₂ O cc	Visicorder P _{max} (psig)	Gas Yield % of H ₂ O Added			Analysis After Run	
					H ₂	CO	CO ₂	Na ₂ S	NaOH
B-1	Na ₂ CO ₃	1650	1	6	3.1	15.1	22.5	-	1.64%
		1700	1	6	6.5	17.3	23.8		
B-2	Smelt A	1600	1	-	20.5	-	-	20.7	14.3
		1570	1	4	28.6	4.4	-		
B-3	Smelt A	1800	1	0	36.7	2.2	.9	26.7	4.9
		1690	1/2	7	37.5	.6	.4		
B-4	Smelt A	1910	1	6	54.9	7.85	.3	-	-
B-5	Smelt B	1605	1	3	23.2	1.5	3.1	19.9	3.4
		1600	1	3	19.4	.9	3.2		
		1595	1	3	9.9	.9	2.3		
		1608	1*	5	18.5	.5	1.0		
B-6	Smelt A	1590	1	0	25.1	.5	.75	32.2	2.4
			1	5	24.9	.4	.1		
B-7	Smelt A	1600	1	1.0	15.9	.7	6.7	35.3	.43
		1600	1	6.9	13.7	.6	3.9		
B-8	Smelt B	1600	1	4.2	11.4	.7	8.0	25.2	.66
		1600	1	4.6	11.6	.2	11.9		
B-9	Na ₂ CO ₃	1600	1	6.0	1.9	1.1	15.2	-	4.4
		1600	1	6.0	1.2	.9	17.6		
		1600	1	4.2	1.2	.4	9.8		
		1600	1	7.2	1.1	.5	5.2		
		1600	1	7.0	1.6	.5	4.2		
		1600	1	4.3	1.5	.2	3.9		
B-10	Smelt B	1600	1**	3.1	21.4	1.0	6.0	27.5	1.5
		1600	1**	3.0	20.2	.6	4.2		
		1600	1**	3.0	17.1	.2	2.5		
		1600	3**	8.1	12.5	.2	1.5		

*100% water liquid

**water injected on top of smelt.

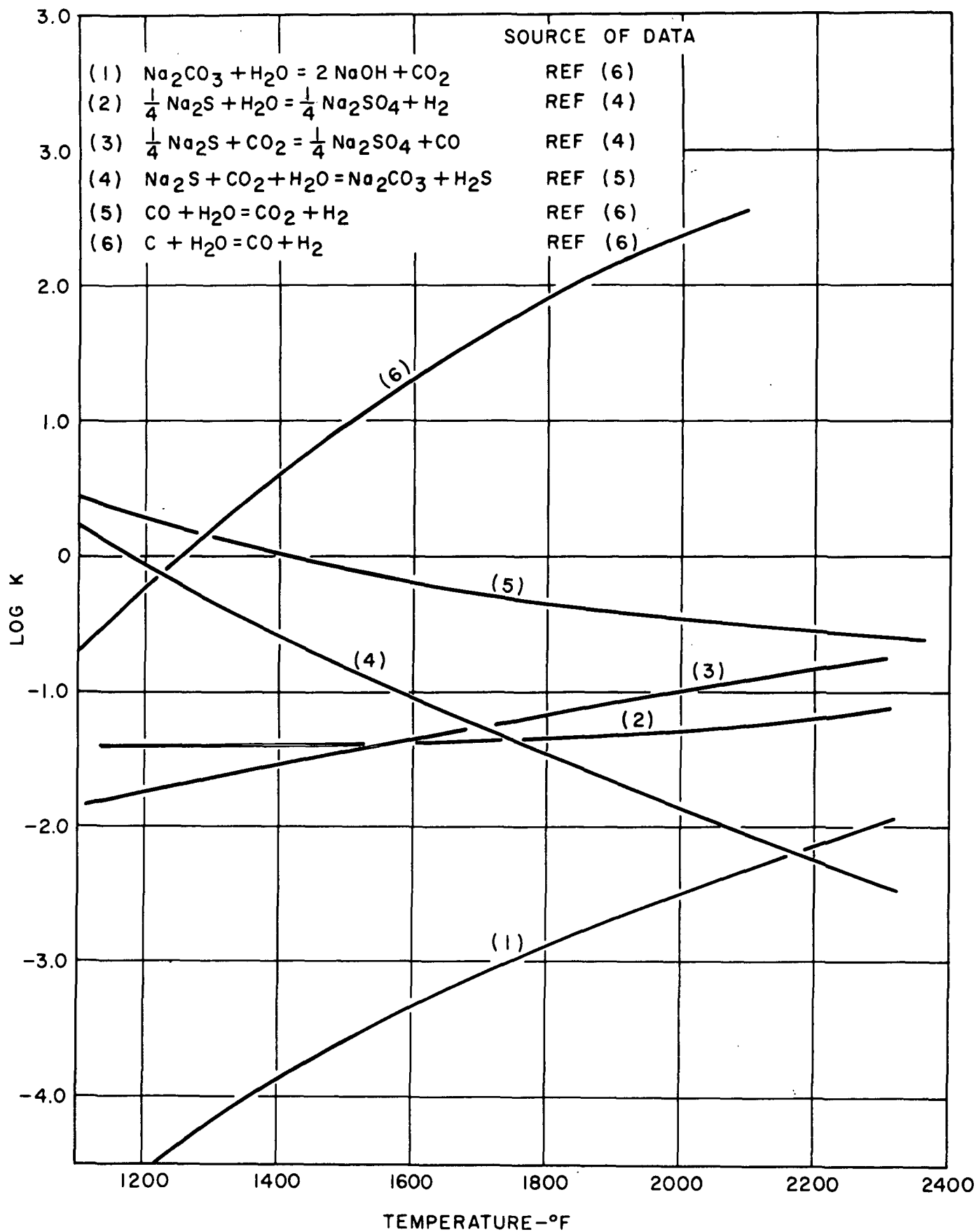
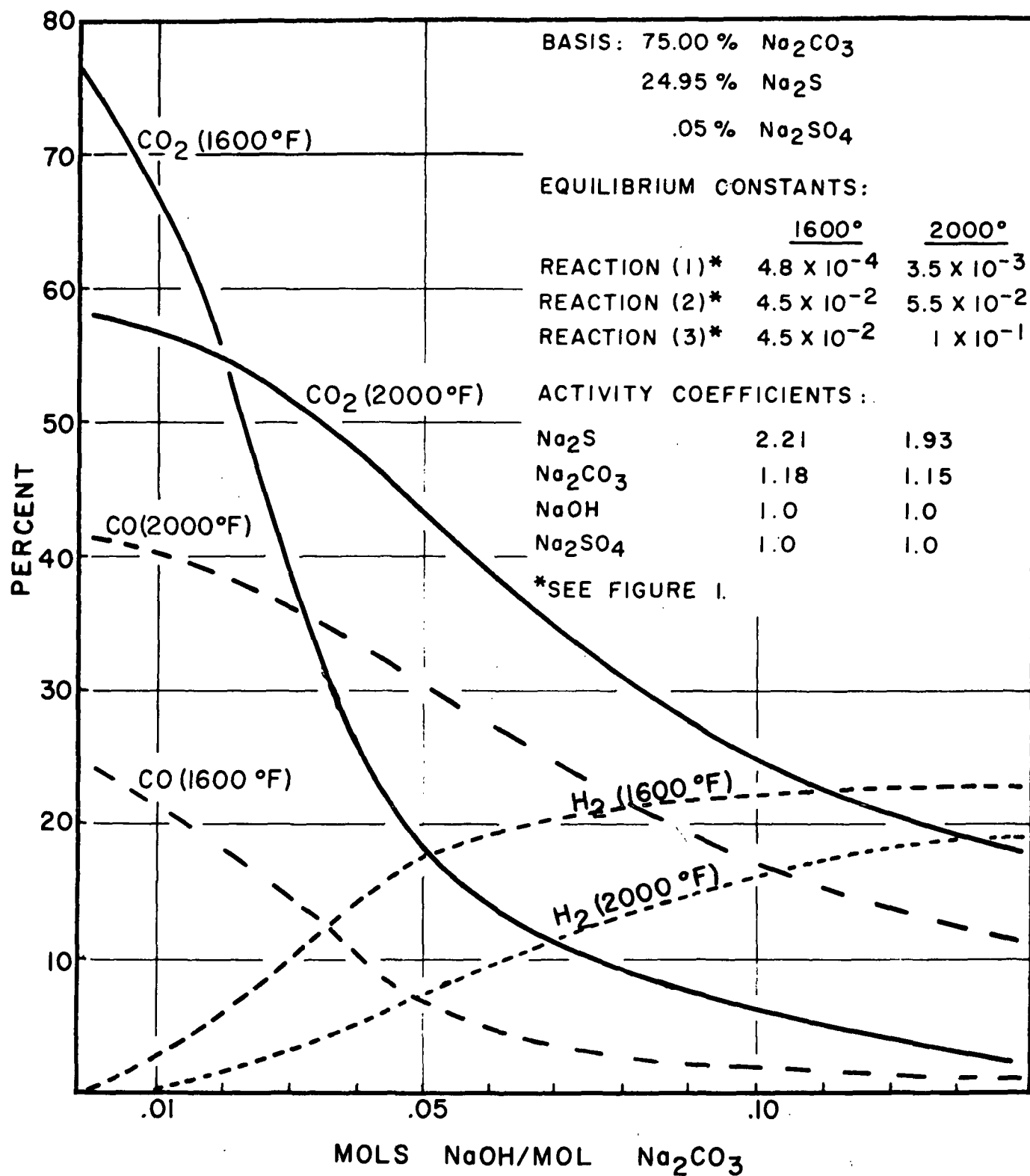
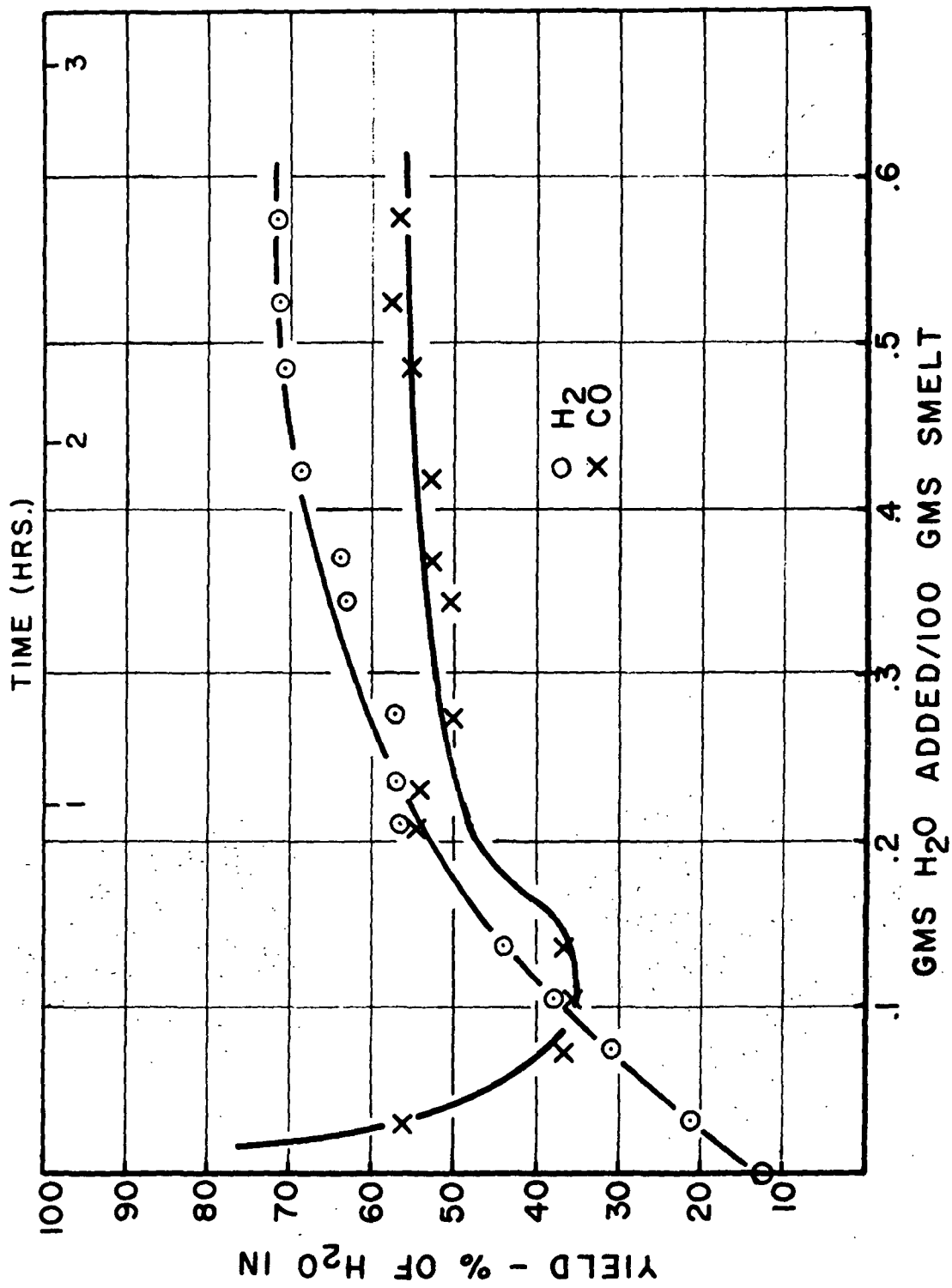


FIGURE 1



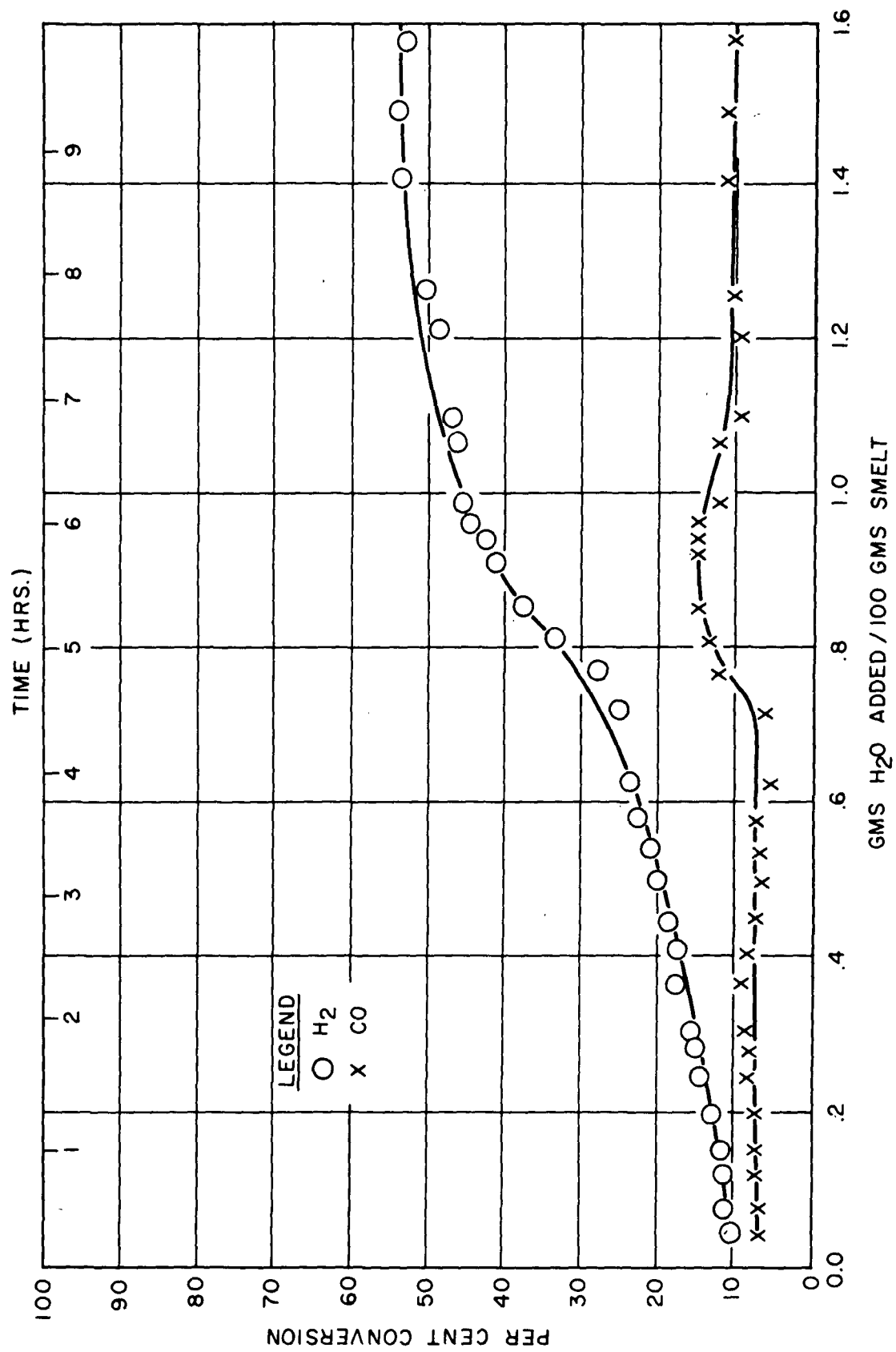
THEORETICAL GAS YIELDS
 FROM SMELT-WATER REACTION
 AS FUNCTION OF $\text{NaOH}/\text{Na}_2\text{CO}_3$ RATIO

FIGURE 2



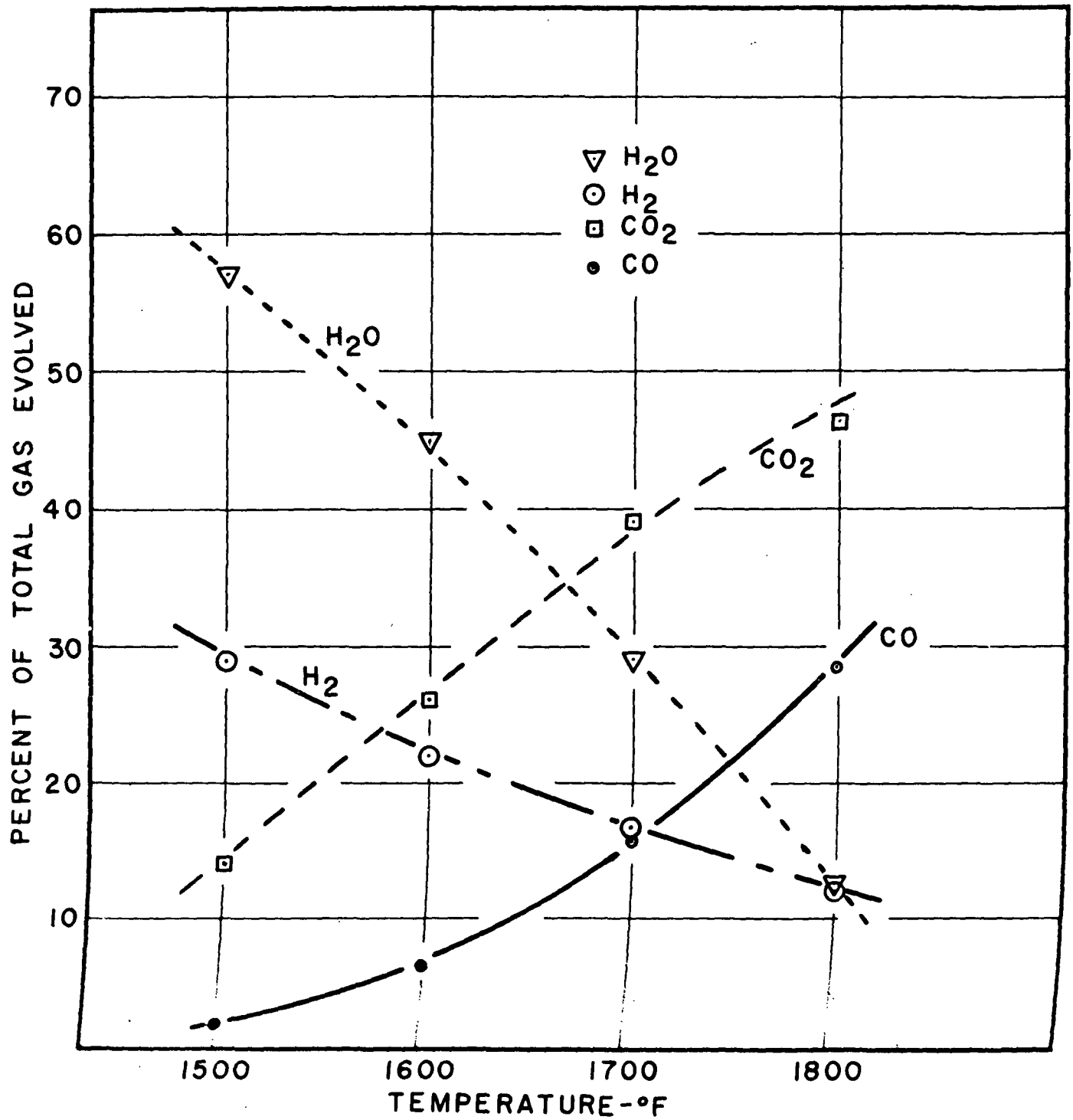
EFFECT OF AMOUNT OF WATER
 ADDED ON INSTANTANEOUS CONVERSION
 OF WATER VAPOR TO H₂ AND CO
 (25% Na₂S, .5% NaOH, CARBON CRUCIBLE)

FIGURE 3



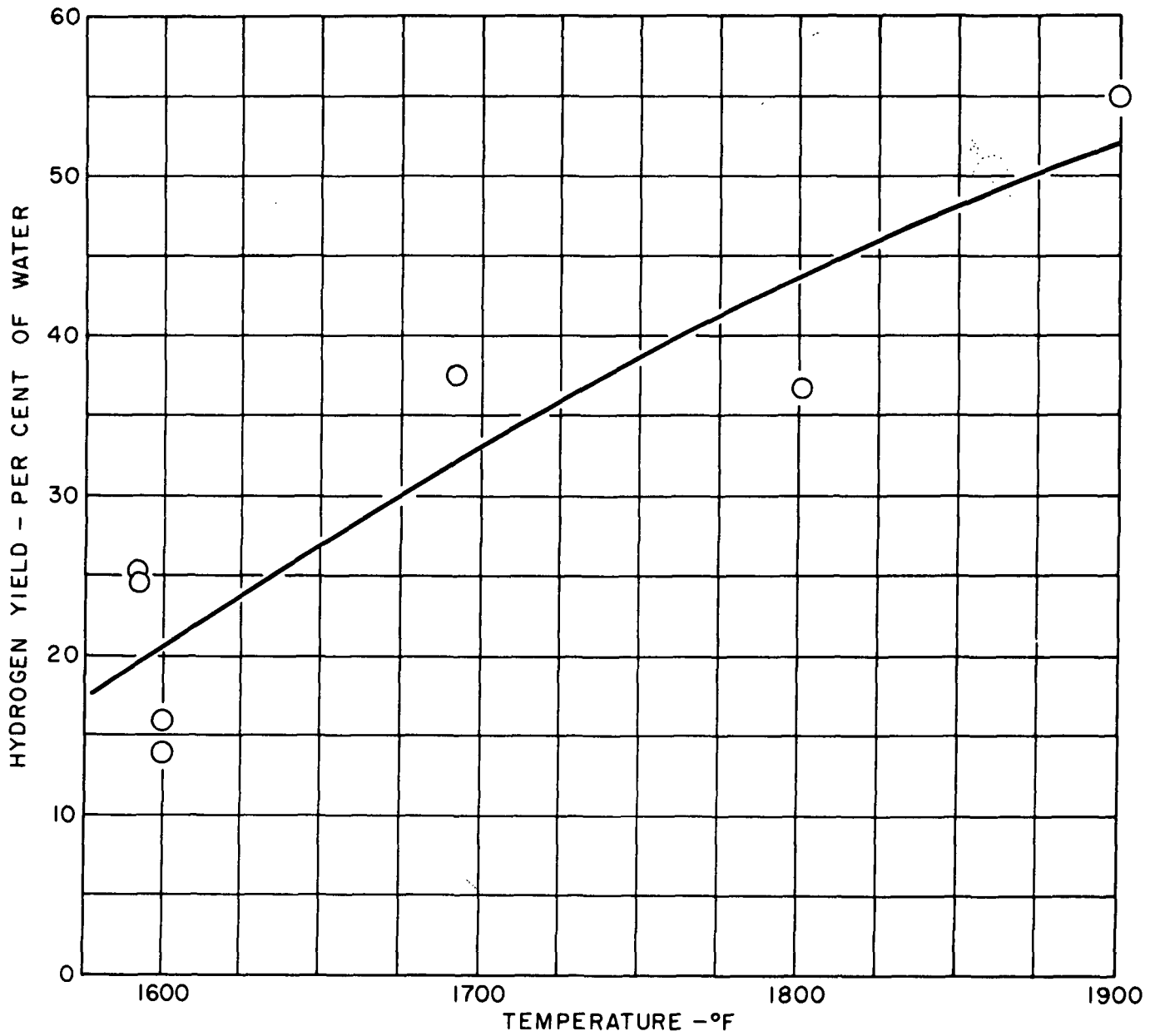
EFFECT OF AMOUNT OF WATER ADDED
 ON INSTANTANEOUS CONVERSION OF WATER VAPOR TO H₂ AND CO
 (24.49% Na₂S, 0.5% NaOH, .01% Na₂SO₄, SS CRUCIBLE)

FIGURE 4



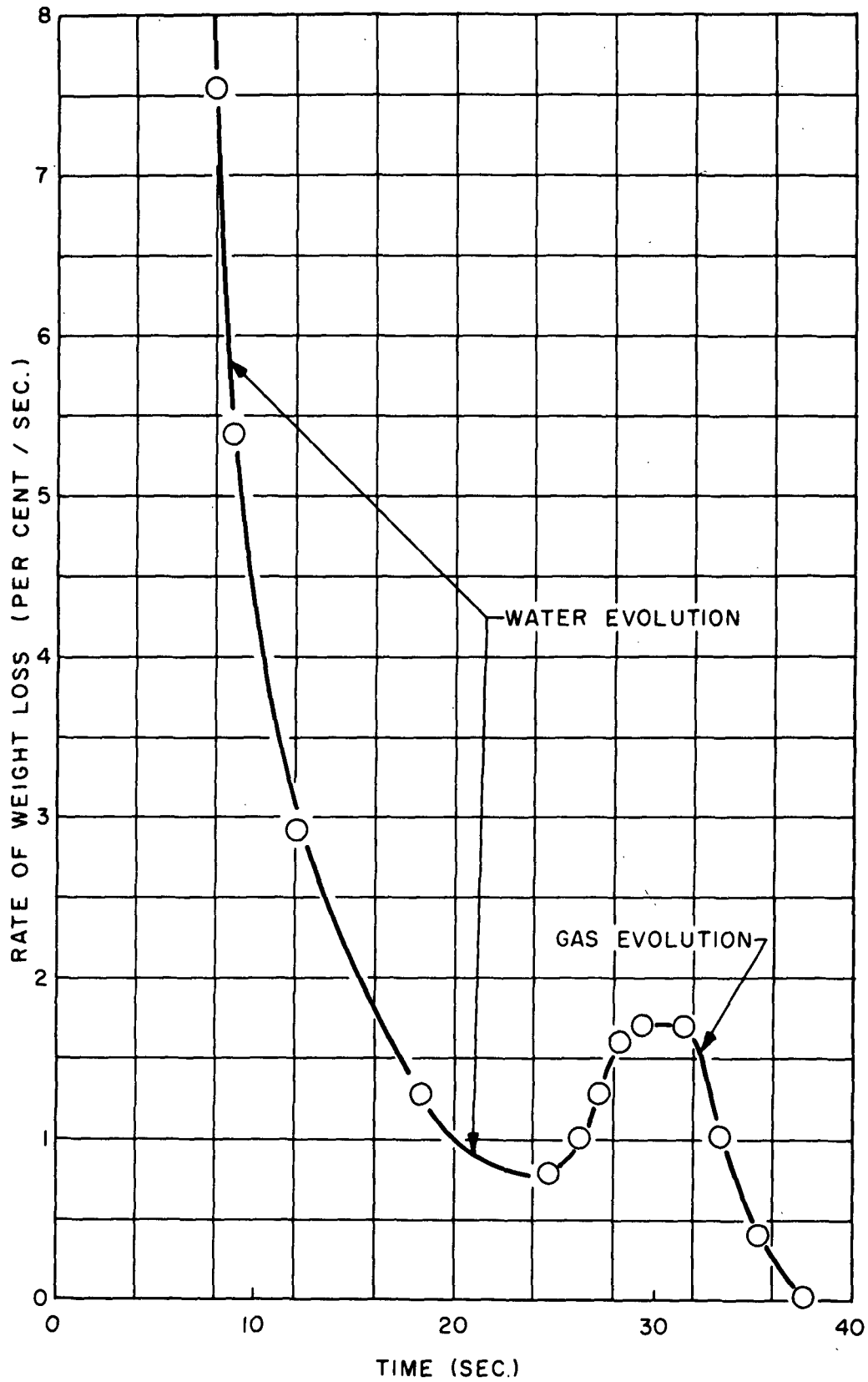
COMPOSITION OF GAS EVOLVED AS FUNCTION OF TEMPERATURE (2.79% Na₂SO₄, 24.5% Na₂S)

FIGURE 6



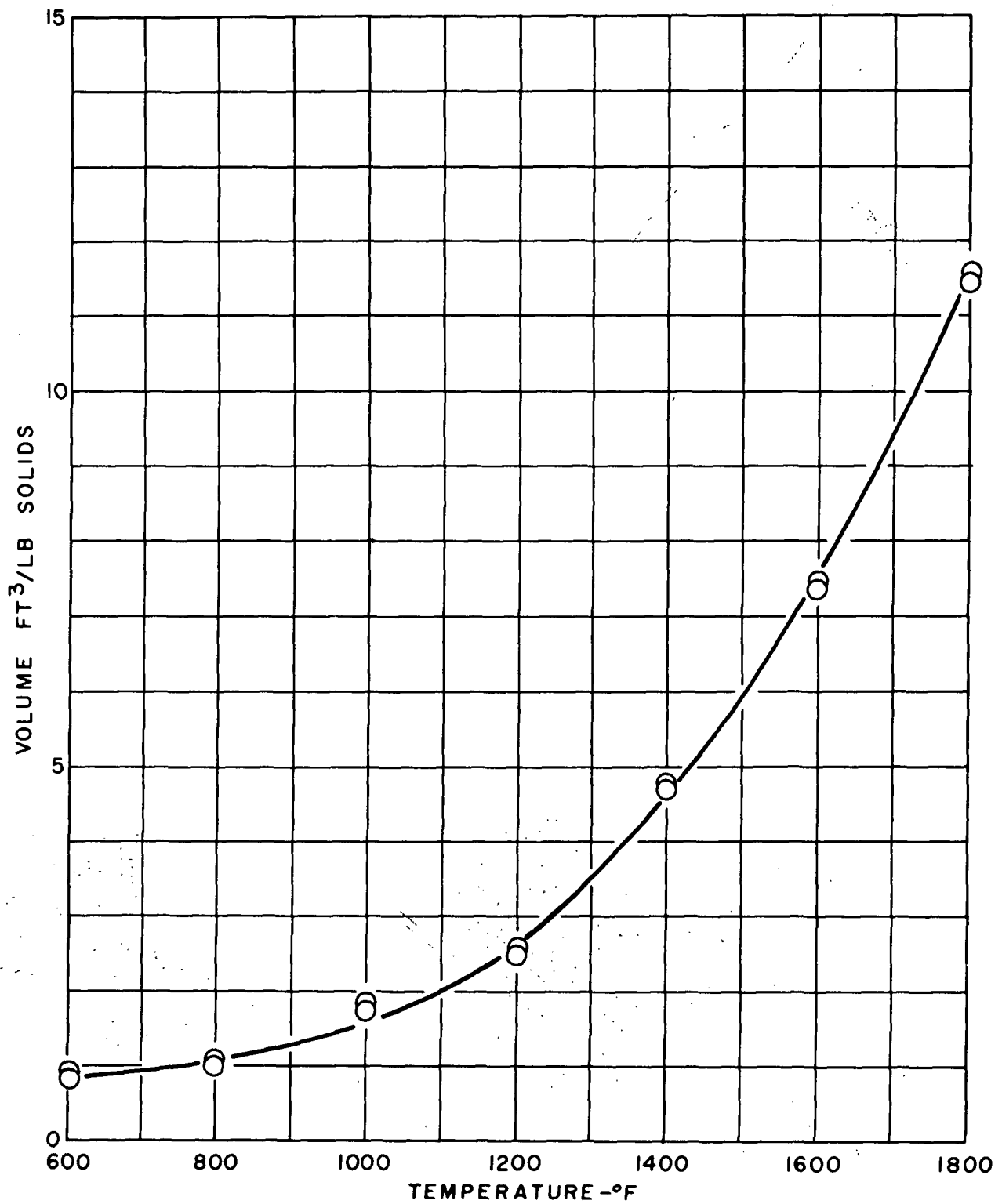
HYDROGEN YIELD VS TEMPERATURE

FIGURE 7



DIFFERENTIAL TGA PLOT OF BLACK LIQUOR
 DECOMPOSITION 1400 °F FURNACE

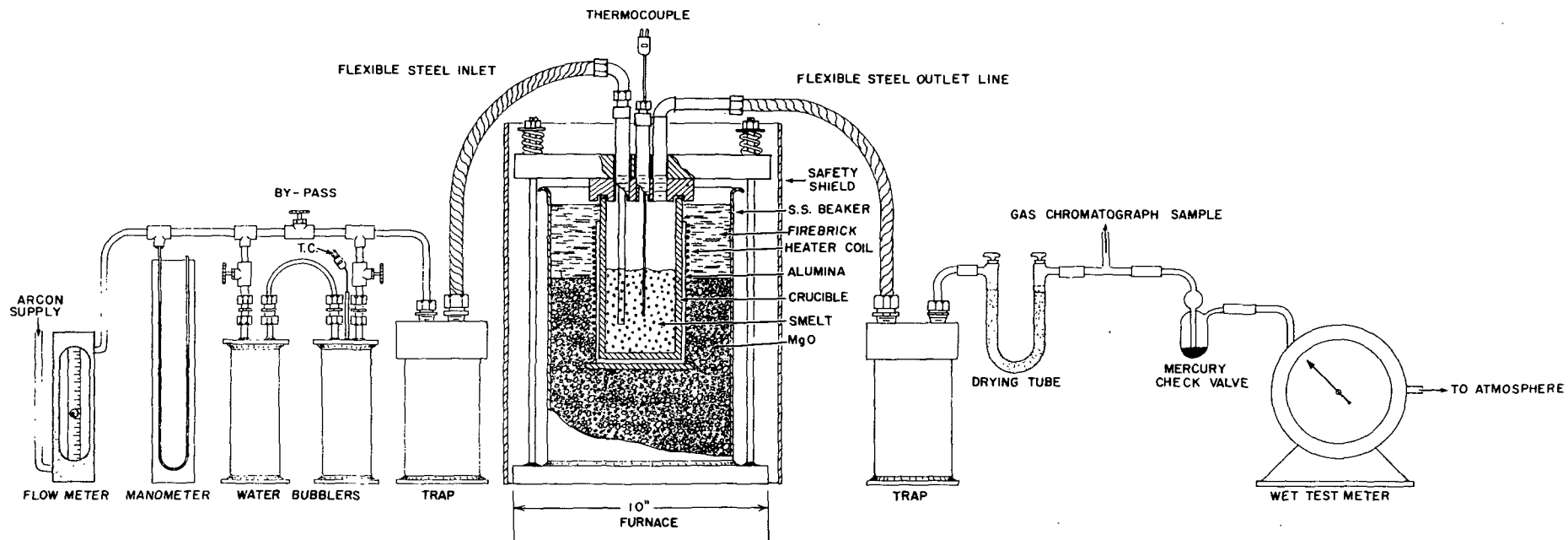
FIGURE 8



VOLUME (STP) OF GAS EVOLVED FROM BLACK LIQUOR SOLIDS
AS FUNCTION OF TEMPERATURE

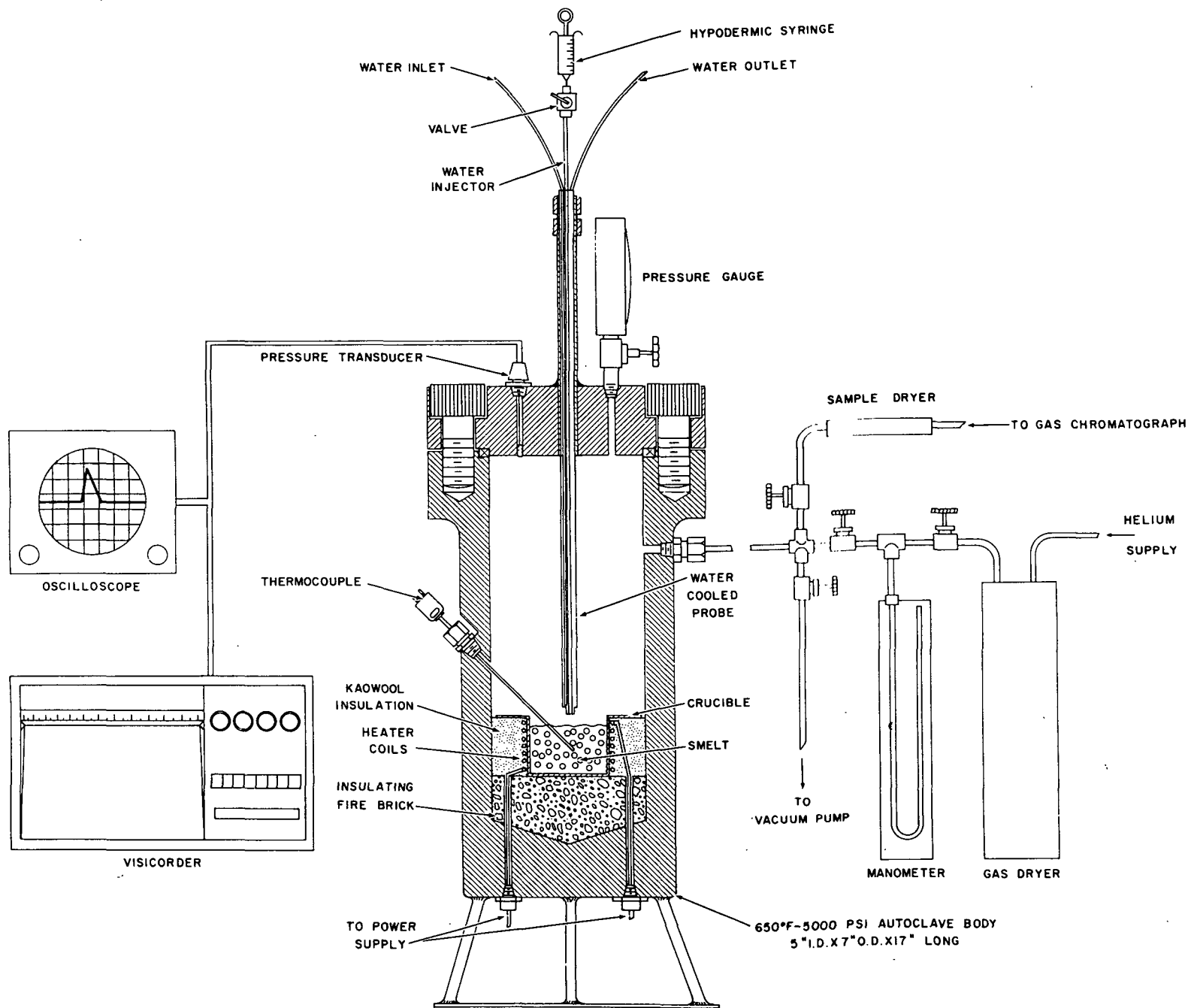
FIGURE 9

FIGURE 10

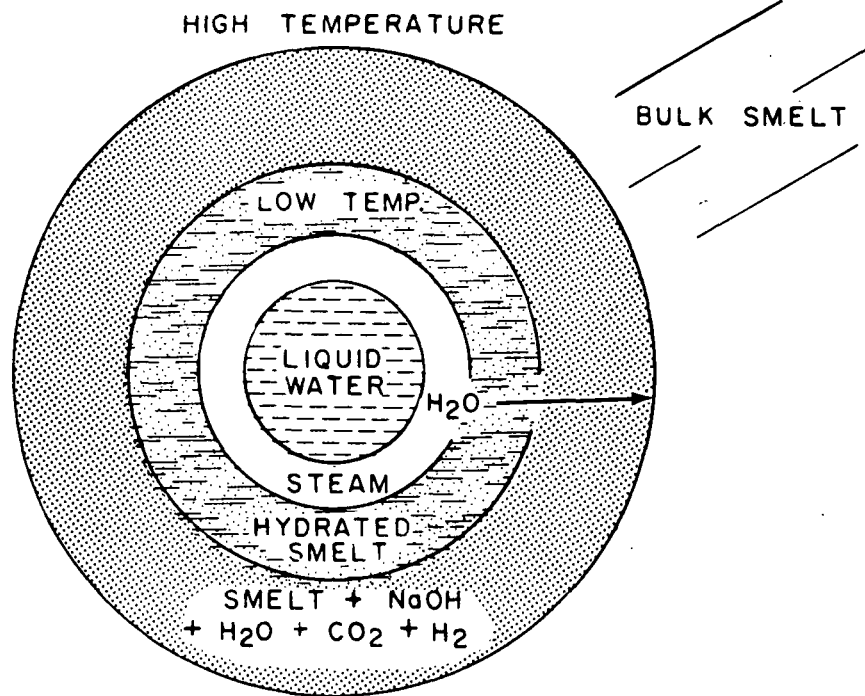


APPARATUS FOR STUDYING SMELT-WATER VAPOR REACTIONS

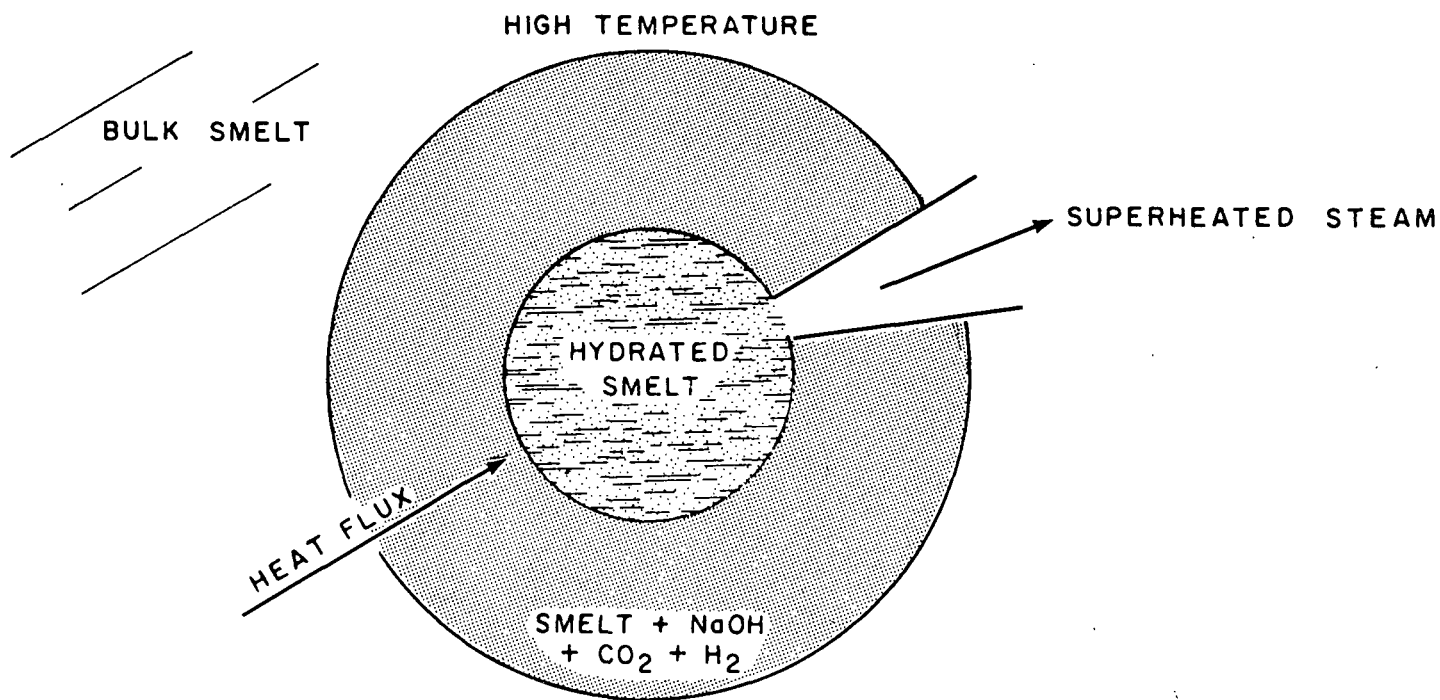
FIGURE 11



SCHMATIC DRAWING OF EXPLOSION APPARATUS



SMELT AFTER WATER INJECTION



SMELT AT MOMENT OF EXPLOSION

STEPS IN SMELT-WATER EXPLOSION HYPOTHESIS

FIGURE 12

Summary Report

on

The Combustion Engineering Program for Determining
The Nature of and Remedies for Explosive Reaction (s)
Between Smelt and Water in Kraft Chemical Recovery Furnaces

to

Dr. H. S. Gardner, Project Coordinator
The Institute of Paper Chemistry

July 25, 1966

Submitted by

Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

This study was conducted by Combustion Engineering, Inc. for the Board of Directors, Smelt-Water Research Group. No reproduction or other use of the information contained herein is permitted without the written approval of the Advisory Technical Committee, Combustion Engineering, Inc., The Babcock & Wilcox Company, and the Institute of Paper Chemistry.

I Introduction

Previous reports have stressed the theoretical aspects of smelt-water explosions. Knowing how explosions occur is of more than academic interest. Proper identification of the explosion mechanism will, in the long run, expedite a practical remedy in operating chemical recovery furnaces.

The C.E. research work has proved conclusively that non-combustible (physical) smelt-water explosions can occur under laboratory conditions. (This was later confirmed by research work of the present Babcock and Wilcox study.) Investigation of six actual recovery furnace explosions at plant sites during the period of our research has produced strong evidence that such non-combustible smelt-water explosions were either the sole cause of serious damage or were major contributing factors in the damage encountered at all of these plants. Destructive furnace explosions occurred in several furnaces while active burning and full steam load were maintained, and thus could not have been combustible explosions.

The production of flammable gases from thermal decomposition of black liquor applied to the char bed of a chemical recovery furnace might be assumed to constitute a major explosion hazard. Combustion Engineering, however, is aware of no information or supporting data which would indicate that a combustible gas explosion has ever resulted from adding only black liquor to a chemical recovery furnace.

As a result of these laboratory and field observations, Combustion Engineering feels that prevention of non-combustible explosions resulting from contact of molten smelt either with water or with most water solutions, including black liquor below normal firing concentration, is by far the most important consideration in any complete solution to the recovery boiler explosion problem. This report emphasizes the practical aspects of C.E.'s two year research study of smelt-water explosions.

II Review of Research Work

Violent non-combustible explosions are caused when liquid water or water solutions of most chemicals, including black liquor below normal firing concentration or green liquor, become submerged beneath the surface of molten smelt under the proper conditions. Known methods of submerging are outlined as follows:

1. Water or water solutions can become submerged in smelt by forcible injection, as from a tube leak.
2. Water or water solutions can become submerged in smelt by violent spontaneous thermal agitation which occurs at the interfacial contact area between molten smelt and a body of water or water solution resting on the smelt surface. No injection velocity is required to produce an explosion under these conditions.
3. Molten smelt can flow into a pool of water or water solution.

Investigations by this laboratory have shown that similar explosions result when water is introduced into molten smelt or smelt into water (1). In general, the larger the injected volume of water, the more violent the explosion. Volumes from 0.5 to 88 ml per injection were tried.

Smelt caused explosions within only about a 300°F range, roughly 1425-1725°F under the wide variety of laboratory quenching conditions explored. This is only a portion of its molten range. The lower limit was the melting point of the smelt composition present. Most quenching experiments were started at about 1900°F smelt temperature. No explosion ever occurred in hundreds of tests with kraft smelt until successive water injections had cooled it below about 1725°F. An explosion often resulted on the very first injection of water, however, if the smelt had been previously air cooled to a temperature within this range. Melting point versus composition and percent sulfidity are shown by Figure 1, reproduced from an earlier paper. (1) Composition of the smelt affected the explosive range. Increase of sodium sulfide content, especially above about 22%, (corresponding to 28% sulfidity) increased explosiveness. The presence of materials like sodium chloride, other halide salts, or sodium hydroxide in the smelt also broadened the critical temperature range and made explosions more violent. The same applied to many extraneous materials like aluminum borate, zirconium oxide, etc. (2,3).

Black liquor itself caused severe non-combustible explosions at 51% solids or less if it became submerged beneath molten smelt. (4,5) The high sulfide, chloride smelt used, however, was much more explosive than any from furnaces in commercial operation. Probably liquor of lower solids content could be applied safely to smelt of normal plant composition. Liquor of 50% concentration is viscous even when hot, and if injected considerable injection force is required to cause an explosion. Probably liquor of lower solids concentration, behaving somewhat like water, is fluid enough to cause explosions without forcible injection if present in large volume on the surface of molten smelt. Increased dilution of black liquor below about 50% solids content caused increasingly violent explosions.

Liquor containing 60% solids, by contrast, did not produce an explosion with molten smelt in any of eight laboratory experiments using a variety of mixing methods.

The 60% solids liquor has the desirable property of quickly pyrolyzing in a thin layer at the contact area with molten smelt to provide a water insoluble barrier of char. If enough 60% black liquor, approximately a 3" depth, was applied to molten smelt in laboratory tests, the char layer rapidly became thick enough to resist subsequent forcible injections of a stream of water and prevent explosions. A diagram of the behavior of heavy liquor on smelt based on observation of laboratory experiments in a graphite crucible appears as Figure 2.

Pyrolysis of black liquor did not provide the proportion of flammable gases necessary for a flame-up under these conditions. A large volume of steam was formed from water in the liquor. Substantial pyrolysis did not occur unless most of the 40% water content of the black liquor was allowed to distill off, due to a restricted addition of liquor. The smelt itself was cooled quickly and non-explosively by the heat-absorbing vaporization of water and pyrolysis of organics which followed the application of a deep layer of 60% solids liquor to molten smelt in each of these tests.

The present study identified two other water solutions which cooled smelt rapidly below its explosive temperature range. These were 40% ammonium sulfate solution, whose gaseous quenching products with smelt are essentially non-flammable, and 10 to 50% polyethylene glycol 400 solution (6) which did not give off ignitable proportions of combustible pyrolysis gases until most of the 50-90% of water was evaporated. Here a remedy to the production of flammable gases from the organic residue, as with black liquor, may be to apply enough bulk solution to maintain its water content above the concentration which permits pyrolysis to substantially exceed the rate of production of water vapor.

The ideal means of preventing smelt-water explosions would be to modify the composition of kraft smelt to render it non-explosive, like soda smelt, on contact with water. This goal was not reached in current research efforts, although some results were encouraging. For instance, it was found that small proportions of two additives, calcium carbonate or sodium aluminate, in some smelt compositions prevented explosions on water injection (7,8). They also decreased the mechanical strength of the solid smelt. This correlation between explosions and solid smelt strength appears to relate directly to the encapsulation mechanism proposed for physical explosions. (9,10,11,12)

Smelt-water explosions proved to be radically different in nature and damage pattern from combustible gas explosions. The smelt-water laboratory explosions (all non-combustible) were characterized by a highly localized release of energy in the form of shock waves. These waves travel faster than the speed of sound. Several such explosions were estimated from high speed movies to travel at about 2400 ft/sec initial velocity which is more than 1600 miles/hour or twice the speed of sound. The pressure rise in a smelt-water laboratory explosion occurs in about one millisecond. In a combustible gas explosion (deflagration), the pressure rise is very much slower, and the time to peak pressure depends on the volume of the air-gas mixture and the burning velocity of its flame front. The burning velocity of a methane-air mixture is about 2 to 5 feet per second, depending on turbulence, with respect to the unburned gas. The expansive forces from a combustible gas explosion are transmitted through the gas volume at the speed of sound, approximately 1,100 feet per second, and the slowly rising pressure is uniformly exerted over the containing surfaces. The slow uniform pressure rise of a gas explosion is in strong contrast to the sudden locally concentrated energy release of a smelt-water explosion. In addition, the 1700-fold volumetric expansion possible from converting water into steam, contrasts with an approximately 6-fold expansion of combustion products from a methane-air explosion, which involves no change of phase.

III Relation of Laboratory Explosions to Plant Site Explosions

A concentrated release of energy in several of the recovery boiler furnace explosions which we investigated produced highly localized damage patterns in the furnace floor. We interpret this localized damage as defining the site where destructive non-combustible explosions occurred in the smelt bed of these units because of contact between molten smelt and water. Damage in several cases was evidenced by 3"-4" deep depressions 3' to 6' across the strongly supported furnace floor tubes and by corresponding localized deformations in heavy wide-flange beams beneath the explosion site. Although some of these plant explosions were highly destructive, all were described by personnel nearby as "muffled" in sound. This is probably due to the sound-deadening nature of the furnace cavity.

Smelt-water explosions may also cause severe damage far above the bottom of the furnace where the explosion originates. Vertical corners above the operating floor have been split vertically over distances of 50' and the economizer roof is usually ripped open. We believe the spherically expanding shock waves from the bottom of the furnace, which decay rapidly in pressure with distance from the floor, nevertheless have sufficient residual force even above the operating floor to tear open corners which are natural stress relief locations in the boiler and bulge the sides of the furnace. Combustible gas explosions also can damage upper furnace walls and split out corners. Hence, damage above the operating floor cannot at present be accurately attributed to one or the other cause, except in cases where known operating conditions rule out one type of explosion.

We can generalize that the pattern of explosion damage in a furnace appears to be a function of the location of the explosion, the nature and force of the explosion, and the distribution of furnace containment strengths as discussed in more detail in the Appendix of C. E. Report 6.

IV Potential Hazards of Operating With Black Liquor Too Low in Solids

Possible sources of accidental water introduction into recovery furnaces have been covered thoroughly by others and need no reiteration here. Faulty operation and liquor cycle design, however, can also add water. They are singled out for special emphasis in Sections IV and V since their correction can also prevent explosions.

Operating conditions of a recovery furnace can usually be adjusted by an experienced crew so that black liquor with solids content well below 60% can be burned with apparent safety. A damaging non-combustible explosion, however, can result when black liquor at less than normal firing concentration contacts molten smelt. Burning of low solids liquor was the apparent cause of three recovery furnace explosions in 1965 and one explosion in the first five months of 1966. Each of these incidents was related to a start up or abnormal furnace operation. Proper concentration of liquor in the direct contact evaporators when starting a furnace with auxiliary

fuel-firing must often be achieved by recirculating liquor through the evaporators.

Experimental results have indicated a safe range of liquor solids content under our laboratory conditions. Liquor of 51% or lower solids content exploded (non-combustibly) if injected with force into high sulfide (very explosive) smelt or if this molten smelt were poured into it, while 60% solids liquor did not explode in any of eight tests under a variety of mixing conditions.

These percent solids limits from laboratory experiments may not be directly applicable to boiler operation for defining a safe limit of solids content over the wide range of operating conditions and smelt compositions present in the field. However, any combination of solids content and operating conditions which places wet black liquor of about 50% solids or less in contact with smelt in a furnace should be considered hazardous. Drying of low solids liquor should not be completed on the bed by using auxiliary-fuel-fired hearth burners.

The periods of furnace operation approaching or recovering from a furnace blackout due to low solids black liquor are more prone to non-combustible explosions. The combination of cooler-than-normal liquor temperature together with high water content may be a reason. Low liquor temperature would prevent the rapid flashing of water and consequent dispersal of liquor entering the furnace from the gun nozzles. These conditions would therefore tend to inject slugs of unatomized high-water-content liquor into molten smelt in the bottom of the furnace where auxiliary fuel fired hearth guns may be in operation. Removing the sprayer plates from liquor gun nozzles to increase the flow rate or prevent plugging may also tend to cause injection of undispersed streams of wet liquor into the bed when the liquor is both cool and dilute.

V Potential Hazards of Adding Miscellaneous Chemical Streams to Black Liquor

One serious explosion investigated by the writers was the result of spraying a water solution of spent acid and salt cake, from tall oil acid manufacture, directly into the chemical recovery furnace. Several years ago, another pulp mill injected a separate stream of tall oil soap directly into the furnace. An explosion resulted when the feed pump drew in low solids black liquor which had collected beneath the soap layer in the feed tank. Still another mill added salt cake make-up as a slurry in black liquor of variable concentration. A non-combustible explosion occurred here also.

The authors believe adding water or water solutions of chemicals other than heavy black liquor directly into a chemical recovery furnace under any circumstance is dangerous. The same applies to adding such materials to the black liquor stream after it leaves the cascade evaporators because such a practice prevents the control of solids content necessary to operate safely.

VI Discussion of Possible Measures to Reduce the Likelihood of Explosions in Recovery Boilers in Case of a Tube Leak

The ideas which follow should not be interpreted as recommendations for plant practice. They are subjects for further thought, and if of sufficient interest to the sponsors, test work in other experimental equipment as the next step in developing practical remedies which are safe for commercial furnace use.

a) A Possible Preventive Measure for Smelt-Water Explosions

The most promising current means of reducing the chance of a smelt-water explosion, once a pressure part or other water leak of any size is discovered, appears to the writers to be cooling all smelt in the furnace as rapidly as possible below about 1425°F, its freezing point, before water from the leak can cause an explosion. Auxiliary fuel and the F. D. fan would be shut off as soon as possible. This would be followed by spraying a deep layer (3"-6") of 60%, or preferably stronger, black liquor on the bed to afford mechanical shielding protection from water due to the layer of water-insoluble char which pyrolysis creates, and to hasten cooling of smelt to the freezing point.

A number of variables might complicate this simplified version of explosion prevention with deep black liquor quenching. If the tube leak were a wide-open one, the large stream of water could wash away black liquor or dilute the liquor to an explosive level of solids content before it had the chance to form a protective layer of char. A small spray-creating tube leak might not pose this problem. Coating rapidly the entire ash and smelt bed in a large furnace with black liquor may present other practical difficulties. "Geysers" may eject vertical streams of molten smelt from fissures which form in the solidified crust on smelt when it is cooled rapidly.

Use of a deep enough layer of 60% black liquor, however, would be expected to help reseal fissures and maintain enough water in the liquor layer to substantially retard pyrolysis. The 60% solids black liquor does not form flammable proportions of combustible gas due to pyrolysis until most of its approximately 40% water content has been eliminated. Considerable volumes of inerting steam would thereby be produced in the lower furnace area. This would reduce the chance of a combustible explosion. In normal furnace operation, of course, the sprayed liquor absorbs heat and is flash-dried essentially free of residual water in the hot furnace atmosphere. Only then does it become a fuel. Coating the bed with a deep layer of 60% or stronger liquid black liquor would rapidly stop combustion in the ash bed. This would allow smelt to cool faster and eliminate an important ignition source. Stopping the F. D. fan would also reduce burning in the ash bed and hence allow the smelt to cool faster. Thus the application of 60% black liquor in this manner would be expected to combat both non-combustible and combustible explosions.

Steam should be supplied to the black liquor heaters at a normal rate so that the liquor used for blacking out will be sprayed onto the bed rather than striking it in a massive undispersed stream as will occur if the liquor is reduced in temperature. Proper timing of liquor application to the bed would be essential.

Liquor should be sprayed on the bed as soon as possible in order to cool and seal it from the tube leak. Black liquor flow into the cascades from the multiple effect evaporators should be cut off in order to maintain a high solids content of the liquor used for quenching the bed.

An interesting application of the foregoing is the recent installation on a kraft furnace in Finland which has been equipped with a water leak emergency system that: (a) trips out the forced draft fan and (b) allows heavy black liquor to spray on the ash bed (i.e., black out) for 30 minutes, and (c) sounds an alarm. This places about 20 cubic yards of liquid black liquor on the bed which is enough to fill up the furnace almost to the primary air ports.

The system has been tested for workability several times on an actively burning bed in the furnace. Safe, rapid shutdowns occurred. The company was pleased with these results and is installing a duplicate black liquor flooding system in the furnaces of two other mills.

b) Use of Other Quench Solutions

The use of 40% solutions of ammonium sulfate or 10-50% polyethylene glycol 400 in water should be explored for safe quenching of ash bed and smelt in other experimental equipment. The ammonium sulfate solution appears to offer more promise because of less likelihood for producing flammable decomposition products.

c) Influence of Smelt Composition and Physical Variables on Explosions

It might be feasible to operate a furnace and pulping cycle with sodium sulfide content of the smelt below about 20% (approximately 25% sulfidity) in order to reduce the non-combustible explosion hazard in case the smelt were contacted by water in the furnace. The proportion of sodium chloride and sodium hydroxide should also be limited since both, particularly the sodium hydroxide, increase explosion violence. It is not possible currently to define the safe composition limits of a mixture of these compounds in smelt, since all three collectively affect explosions. Time did not permit such an investigation. Smelt composition might be suspected to be of increased danger potential, however, if unusual violence of smelt quenching in the dissolving tank occurred at normal smelting rate, since water injection explosions and dissolving tank explosions are related. Samples taken during such periods could be analyzed to establish the concentration of known explosion sensitizers. (1)

The fact that a critical range of smelt temperature existed in laboratory tests may help to explain the often considerable time delay between the start of a tube leak and a resulting explosion in field furnaces. Time would be required for water sprayed from a tube leak to cool smelt down to the approximately 1425-1725°F explosive range while it concurrently absorbed heat from the burning ash bed.

This delay could be due to other physical factors as well. For instance, water containing dissolved salts produced more violent explosions than pure water. Water hotter than about

187°F did not cause explosions when injected into molten smelt (11) but even 215°F boiling green liquor (10%) did cause explosions. Thus water on smelt would dissolve some of it and become progressively more explosive with continued furnace residence time. Additional delay might be provided while the initial diffused spray of steam-water mixture with much flashing from a small tube leak is changed by decaying boiler pressure into a high velocity stream of predominantly steam-free water which could penetrate into molten smelt. Another type of delay may be due to the formation of a solid crust of frozen smelt on the surface of molten smelt during rapid quenching. The still-molten core beneath is placed under considerable pressure because of thermal contraction of the external boundary layers during solidification. In laboratory experiments with very rapid surface cooling due to application of quench solutions, the molten core was sometimes ejected upward with considerable velocity when fissures developed in the frozen crust. However, this might not be the case in a furnace which has substantial bottom cooling.

d) Other Possible Preventive Measures

Serious consideration should also be given to study of opening the boiler blow-down and the boiler safety valves to hasten the decay of boiler pressure and rate of leakage from a tube into the furnace cavity. It is generally agreed that the boiler feed water should be shut off in order to decrease the volume of water supplied to a leak.

Industry still needs to develop a reliable instrument for detecting a water leak so that safety measures can be initiated rapidly and the area cleared of non-essential personnel. An accurate means for continuously monitoring solids content of the black liquor stream supplied to the nozzles would help to reduce the chance of placing black liquor at unsafe firing concentration on molten smelt in the furnace. It would also increase the smoothness of operation. Personnel should be strictly forbidden to fire low solids liquor. Present equipment provides many warnings of decreasing solids, like decreasing cascade ampere readings, increasing fineness of liquor spray into the furnace, etc.

VII Evidence for a Non-Combustible (Physical) Explosion Mechanism

By initial agreement, the research on possible causes of smelt-water explosions has approached the explosion problem from two different standpoints, one, chemical and the other, physical. We believe that physical (steam-forming) explosions due to smelt-water contact are more important and are governing for the following reasons:

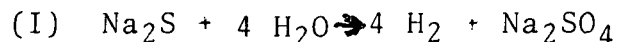
1. At least five furnace explosions inspected during this two-year study have taken place when water, water solution, or dilute black liquor was introduced into a furnace with actively burning bed and a substantially normal steam load. Such conditions would seem to preclude forming a pocket of combustible gas, mixing with air, and a subsequent combustible explosion.

2. It was demonstrated that laboratory smelt-water explosions can take place in a nitrogen-rich atmosphere far too lean in oxygen to support combustion of hydrogen or other gases. (12) Explosions also occurred deep beneath the surface of water after the smelt rested 5-10 seconds on the bottom of the water container, which would exclude the gaseous oxygen necessary for a combustible explosion. (1)
3. High speed movies of laboratory explosions (13) showed no flame or other indication of a combustible reaction. The explosions were non-luminous in every case and produced a white cloud of what appeared to be partially condensed steam. Observation by the writers of more than 670 laboratory explosion experiments showed none which produced the visible flash which accompanies a combustible explosion. Visitors also observed explosions in a darkened chamber and agreed that no light was produced.
4. The same type of explosion was caused in the laboratory on water injection when 20% of chemically inert sodium chloride was substituted for the 20% sodium sulfide in the sodium carbonate of kraft smelt. (14) (Molten sodium carbonate at any temperature does not explode with water). We do not know of any explosive chemical reaction between sodium chloride and water or any between sodium chloride and sodium carbonate which would create an explosive material. Addition of sodium chloride or sodium sulfide to sodium carbonate, however, substantially increased the mechanical strength of the cooled smelt, which is consistent with the encapsulation mechanism.
5. With standardized water injection tests, kraft smelt was found to have a critical explosive range, roughly 1425-1725°F. (15) in the laboratory. (This range could be altered by changing the composition of the smelt or aqueous solution). Smelt above this range did not explode. This behavior contrasts with that of chemical reactions which are accelerated by increasing temperature
6. Small injections of water into smelt did not explode if the water were above about 187°F, or if the water contained enough dissolved material (like methyl or ethyl alcohol, acetone, ammonia, etc.) to substantially increase its vapor pressure. (16)(17)(18) Explosions did not result even though the vapors from some of these solutions were flammable. With water solutions containing less than the minimum effective concentration of flammable materials

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like methyl alcohol (5%), an injection explosion occurred beneath the smelt even while flames of alcohol from a previous injection burned on the surface.

7. Explosive violence was increased when stable salts, like sodium chloride, sodium carbonate, smelt, etc. which are not chemically reactive with smelt, were dissolved in the water used for injection. This behavior also is not consistent with an explosion mechanism based on chemical reactions. These findings (19) are consistent with the physical explosion mechanism proposed.
8. Chemical reaction (I) between steam and sodium sulfide absorbs heat over the explosive range of smelt temperatures.



A chemical reaction must produce large quantities of heat to be explosive. In addition, the sodium sulfide in smelt is diluted 4 to 1 with non-explosive sodium carbonate. The equation shows that one volume of reactant steam yields one volume of product hydrogen, hence there is no increase in volume of products over reactants. Hydrogen could, therefore, not be generated explosively by this reaction

The contrasts between the interaction of molten smelt with the steam film beneath small water globules on its surface (or with steam bubbled into the smelt) and that with submerged liquid water indicate strongly that there are two types of concomitant smelt-water reactions:

1. A relatively slow, non-explosive, heat-absorbing chemical reaction occurs between steam and the sodium sulfide in molten smelt which yields hydrogen and sodium sulfate. See the preceding equation (I).
2. An explosive physical reaction occurs between submerged liquid water and molten smelt which generates large volumes of steam almost instantaneously due to extremely rapid heat transfer. The shock waves produced apply a highly localized shattering force to the smelt container and lesser damaging force to containment structures further removed from the explosion site.

The chemical reaction (I) must occur simultaneously, to a limited extent, with the physical but there is no doubt that the explosive reaction responsible for damage in the present laboratory test work is the physical reaction between smelt and liquid water. From the examination of explosion damaged furnaces in the field we

are likewise certain that highly localized distortion in strong furnace bottoms and supporting beams could not be due to a combustible gaseous explosion from the hydrogen produced by reaction (I) or from combustible gases due to pyrolysis of black liquor organics or from any other source. Combustible explosions of limited amounts of gas in a furnace can not produce the shock waves required for this kind of damage.

VIII Concluding Remarks

We believe that this study has provided new insight into a costly and difficult problem of the kraft pulp industry. (A similar explosion problem exists in the metal industry due to the contact of most molten metals with water). (20) The occurrence of physical (non-combustible) explosions between molten smelt and water or most kinds of water solutions was established. Some of the conditions which influence these explosions were clarified.

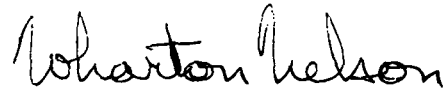
A better knowledge of explosion mechanism was gained. This aided in finding several preventive measures in the laboratory which appear worthy of further test work. Recognition of a non-combustible explosion mechanism eliminates as a complete preventive measure, any procedure based solely on obviating combustible explosions. Of particular importance also in this study were the findings that:

1. Black liquor of up to about 51% solids, like water, can cause explosions if placed in contact with molten high sulfide smelt. Since these are non-combustible explosions, the presence of a lighted auxiliary fuel burner in the furnace offers no protection against them.
2. Black liquor of greater than about 60% solids content is considered to be non-explosive with smelt. It probably can be used safely to black out a furnace quickly and reduce the chance of an explosion in case of a water leak emergency if a deep enough layer is applied to the bed in time.
3. A forty per cent ammonium sulfate solution in water or 10-50% polyethylene glycol 400 solutions in water also cooled smelt safely in laboratory tests.
4. Smelt-water explosions generate shock waves which create highly localized damage in the furnace floor and supporting beams as well as split out furnace corners above the operating floor and open the economizer roof.
5. The composition and temperature of both smelt and water solution and their amounts influence explosive violence. Additions to smelt which increase its mechanical strength when solidified also increase its explosiveness.


6. Mixing geometry affects explosive violence of the smelt-water system.

IX Acknowledgements

Grateful appreciation is expressed to personnel of the U. S. Bureau of Mines, Explosives Research Center at Bruceton, Penna., under the direction of Dr. R. W. Van Dolah, who extended help during many stages of project work. Dr. Glenn C. Williams of the Massachusetts Institute of Technology made important contributions in the application of explosion technology.



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July 25, 1966

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6. C. E. Report 7, pp. C4 -C8
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8. C. E. Report 7, pp. C6 -C7
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12. C. E. Report 5, pp. C4 -C7
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MELTING POINT - COMPOSITION DIAGRAM (1)

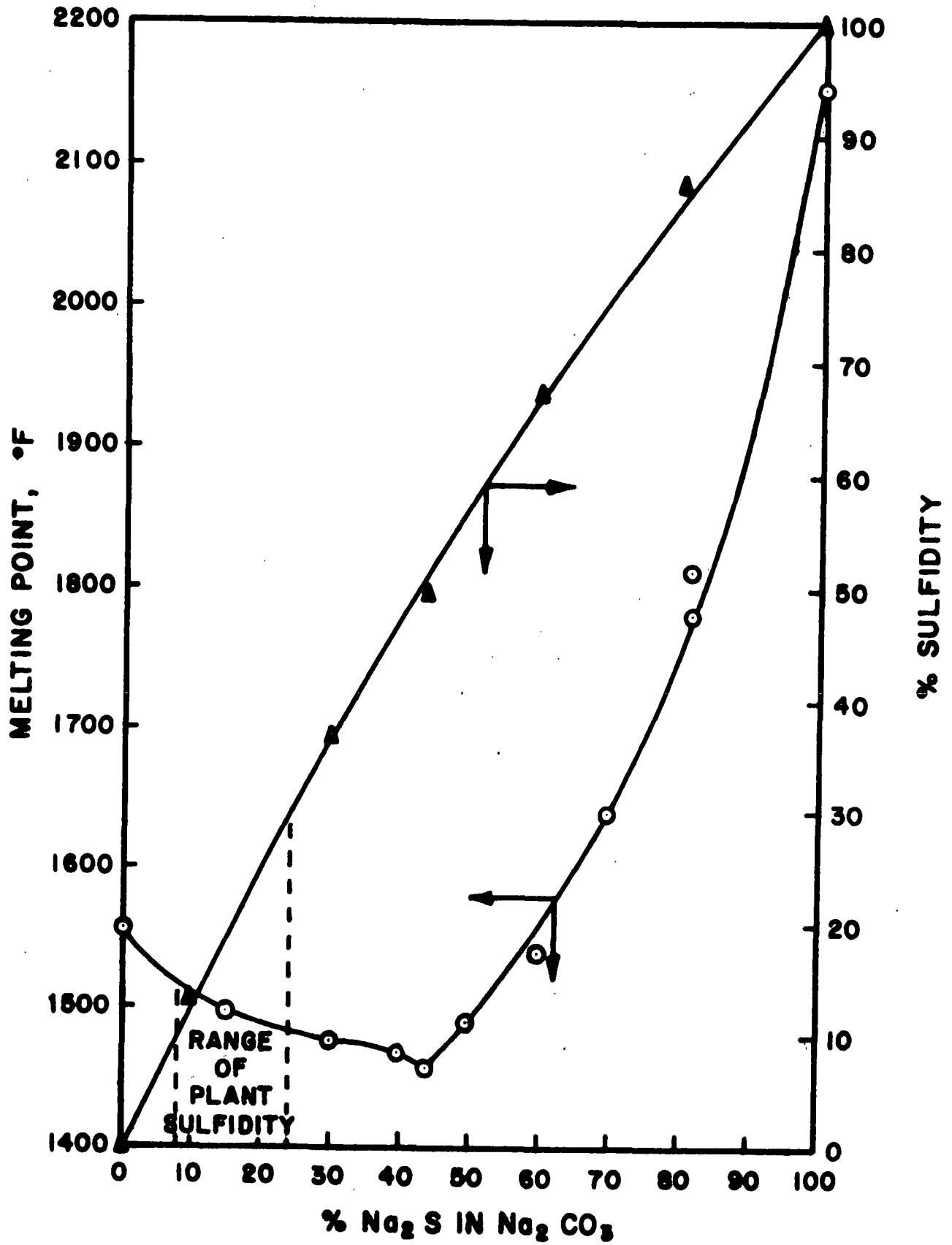


FIGURE 1

BLACK LIQUOR QUENCH OF MOLTEN SMELT

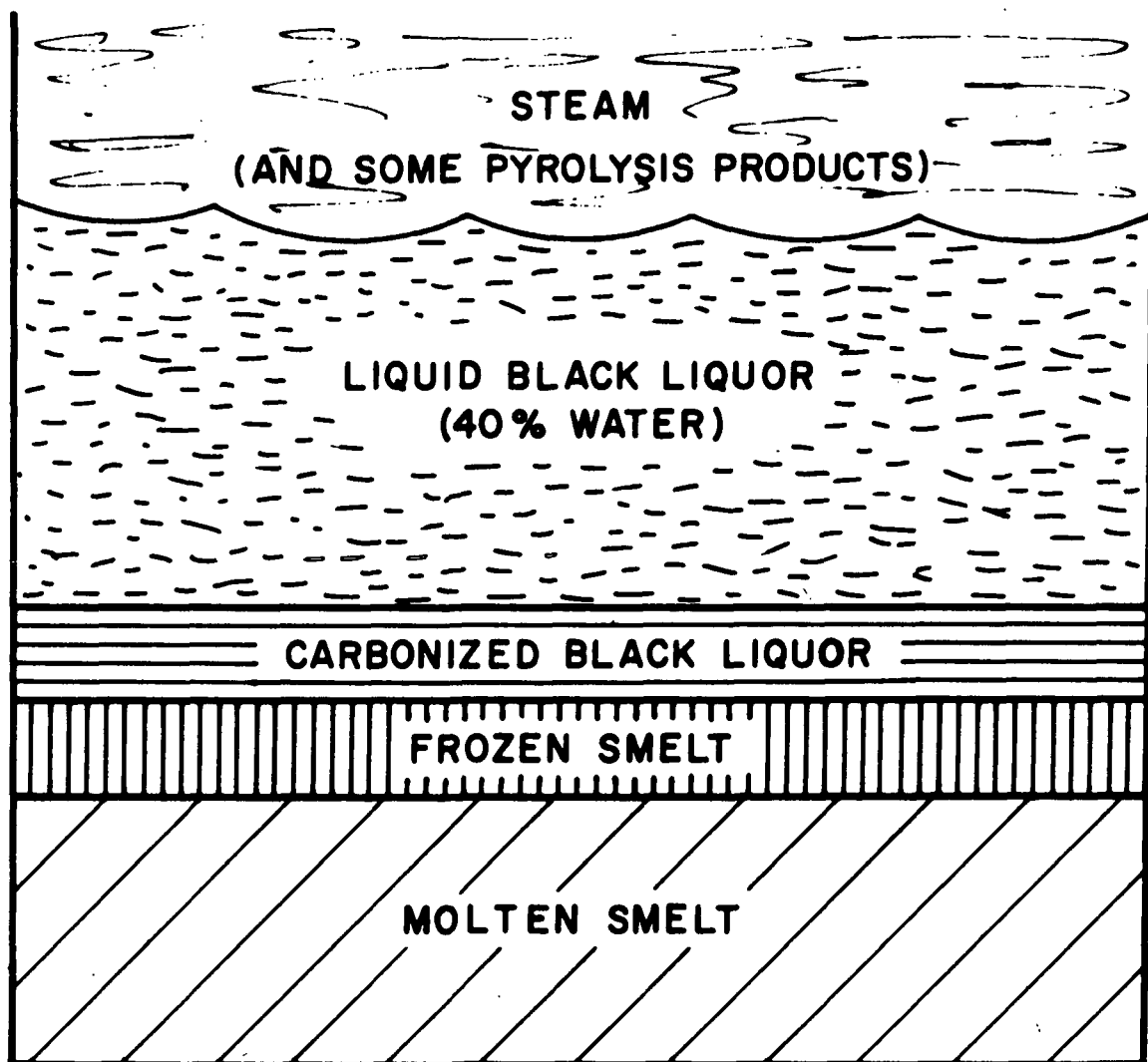


FIGURE 2