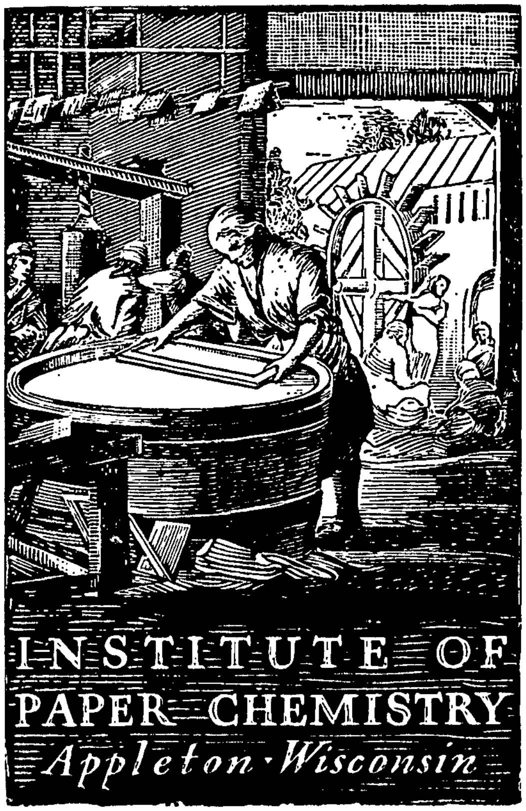

THE EFFECT OF CARBON DIOXIDE GENERATION ON SMELT-WATER EXPLOSIONS

Project 3473-2

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

July 15, 1982

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE EFFECT OF CARBON DIOXIDE GENERATION ON SMELT-WATER EXPLOSIONS

SUMMARY

Contained in this report are the results of an experimental program designed to determine if CO_2 release in a smelt would inhibit smelt water explosions. Previous laboratory research had suggested that CO_2 release agents decrease the probability of a smelt-water explosion occurring. This observation and a new theoretical understanding of the smelt-water explosion mechanism offered the possibility that CO_2 release agents could produce a nonexplosive smelt.

The experimental objectives of this project were to characterize the CO_2 release rates of acceptable inorganic smelt additives and correlate these CO_2 release rates with smelt explosivity. The CO_2 release rates were characterized in terms of rate expression, activation energy and frequency factor. This allowed calculation of CO_2 generation rates during explosion trials when direct measurement was impossible. Explosion trials were conducted by dropping a steel rod holding 40 milligrams of water into 30 grams of smelt containing a CO_2 release agent. By monitoring the melt temperature and using the previously developed rate expression, the calculated CO_2 release rate at the time of the explosion trial was correlated with explosivity.

With $NaBO_2$ and SiO_2 as CO_2 release agents, no correlation was found between CO_2 generation and smelt explosivity. Other CO_2 release agents including Fe_2O_3 and $CaCO_3$ were screened for smelt water explosion inhibition and were found to be ineffective in preventing smelt water explosions. Possibly due to the formation of Na_2O (a known sensitizer), several of the CO_2 release agents ($NaBO_2$ and SiO_2) increased the explosion sensitivity of the smelt.

During laboratory scale explosions trials, CO_2 release did not prevent smelt-water explosions. However, small laboratory scale explosions do not duplicate the events involved in a large explosion, and CO_2 release may be effective in decreasing the violence of large scale explosions.

INTRODUCTION

One of the hazards associated with the operation of a kraft recovery furnace is the possibility of a smelt-water explosion. Smelt-water explosions are vapor explosions which result from the extremely rapid vaporization of water in contact with molten smelt. In recent years, smelt-water explosions in North America, which resulted in damage to the recovery furnace, have averaged approximately three per year (1).

Recently, an improved theoretical understanding of the mechanism of vapor explosions has been developed. This mechanism suggests that the presence of a noncondensable gas could inhibit a vapor explosion. It was noted that earlier experiments had found that there appeared to be some relationship between the amount of CO_2 in the atmosphere above a smelt and its insensitivity to explosions. This naturally suggested that agents which generate CO_2 in smelt might serve as practical desensitizers for smelt-water explosions.

Accordingly, a systematic study of the effects of CO_2 generation on smelt explosivity was initiated. This study focused mainly on the effect of CO_2 generation in smelt using autocausticizing or decarbonizing agents. In order to obtain an unequivocal result, the study was carried out in two distinct parts:

1. Kinetic studies in which CO_2 release rates for various agents were measured as a function of temperature and concentration.
2. Explosivity tests in which the temperature history of the smelt was monitored and calculated CO_2 release rates could be correlated with the observed explosion behavior.

PREVIOUS RESEARCH

Only those areas of past research and the vapor explosion theory which focus directly on the area of research pursued during this project are discussed in this report. For a complete review of previous vapor explosion research and the development of the vapor explosion theory, the reader is referred to a recent report by P. E. Shick and T. M. Grace (2).

In 1963 the Smelt-Water Research Group, composed of 53 pulp manufacturers and the Fourdrinier Kraft Board Institute, Inc., was organized to sponsor research into smelt water explosions. This research was conducted by the two-boiler manufacturers and coordinated by The Institute of Paper Chemistry (3). Experimental results from this project showed that smelt-water explosions are highly dependent on smelt composition. In laboratory experiments pure Na_2CO_3 was found to be nonexplosive. However, many inorganic compounds when added to Na_2CO_3 produced a smelt which was highly explosive with water. Among the inorganic compounds that were found to be sensitizing agents were NaCl, NaOH and Na_2S.

A few agents, $CaCO_3$, Fe_2O_3, and $NaAlO_2$, were found to exhibit some inhibiting influence on the explosivity of a sensitized smelt. Although these agents decreased the probability of an explosion occurring, they did not make a sensitized smelt totally nonexplosive. A common characteristic of these compounds is that they decompose or react with Na_2CO_3 to produce CO_2. It was also found that a CO_2 environment over the smelt tended to reduce the explosivity.

The work sponsored by the Smelt-Water Explosion Group was later reviewed by Battelle and Arthur D. Little, Inc. Later, Battelle conducted additional research on smelt-water explosions (4). Included in the experimental work conducted by Battelle was a study of the effect of sensitizing and desensitizing agents on the rate of decomposition for Na_2CO_3 under near vacuum conditions. It was found that when the sensitizing agents NaCl and Na_2S were added to Na_2CO_3, the CO_2 release rate decreased slightly. Although some decrease in CO_2 release is expected because of a lower concentration of Na_2CO_3, the decrease found was more than could be accounted for by a concentration change. The desensitizing agents $CaCO_3$ and $NaAlO_2$ were found to increase CO_2 release during vacuum decomposition of Na_2CO_3.

Many physical properties of molten smelt and the effect of additives on these properties were determined by Battelle. Among the physical properties studied were surface tension, viscosity, density, and velocity of sound through the smelt. Although the inorganic additives changed these properties, none of the changes were judged to be large enough to account for the changes in explosivity of the smelt.

VAPOR EXPLOSION THEORY

In addition to smelt-water systems, vapor explosions occur in many systems involving the mixing of a hot and cold liquid. Systems capable of vapor explosions include titanium-water, cryogenic liquids-water and molten sodium-uranium oxide. Water is not necessarily the material vaporized as shown by the cryogenic-water and molten sodium-uranium oxide systems. Since the nuclear power industry must estimate the probability of a vapor explosion occurring during a reactor melt-down, a considerable amount of research has been conducted on explosive systems that may exist during a reactor melt-down. Through these research efforts, a theory on the nature of vapor explosions has evolved.

One of the basic requirements of any vapor explosion theory is that it must account for the extremely rapid vaporization of the liquid. There are two means by which this rapid vaporization could occur. First, energy or heat could be relatively slowly transferred to the explosive liquid from the hot liquid and stored in a metastable state. Such a metastable state would constitute a superheated liquid, that is, a liquid heated above its normal boiling point. Once the liquid is superheated, a disruption or triggering event could occur, resulting in a rapid vaporization and explosion. One of the difficulties of this theory is that extensive vaporization must be prevented until a large quantity of the explosive liquid is heated above the superheat limit temperature, i.e., the temperature of self nucleation.

The second method through which rapid vaporization could occur is with heat transfer occurring simultaneously with the explosion. The necessary condition here is that a large amount of surface area be available to allow for this rapid rate of heat transfer.

Rapid motion picture studies of vapor explosions occurring when water was injected into molten NaCl showed that the water existed as a coherent particle and was separated from the salt by a vapor film until the explosion occurred. A calculation of energy transfer into the particle revealed that only a small fraction of the total energy of the explosion could have been conducted into the particle if it were in direct contact with the salt in the time interval between the water injection and the explosion (5). This indicates that the explosive event did not involve a superheated liquid but that the explosion occurred simultaneously with rapid heat transfer.

After reviewing the available literature on vapor explosions, Board and Hall (6) concluded that three distinct stages occur during an efficient large scale explosion. These stages are referred to as the initial configuration, triggering, and propagation.

In the initial configuration, the hot and cold liquids are mixed on a macroscopic scale. This metastable state is believed to be stabilized by film boiling. The size of the intermixed particles must be of the same order as the width of the explosion pressure wave for an efficient explosion to occur. The nature of this initial configuration is believed to determine the magnitude of the energy released during the explosion.

The next stage in the vapor explosion model is the triggering event. This event initiates a shock wave in the system which escalates into an explosion. Triggering events which have been identified include: spontaneous nucleation in one of the coarse mixed particles, collapse of the film boiling around one particle, thermal stress fragmentation, and an external mechanical disturbance (2).

Propagation is the final stage of the vapor explosion model. As the shock wave passes through the system, it collapses the film surrounding the coarse mixed particles. This results in fragmentation of these particles, rapid heat transfer, and an explosion adding energy to the expanding shock wave.

CARBON DIOXIDE EFFECT

Many of the explosivity effects of various inorganic smelt additives appear to be correlated to the carbon dioxide generation properties of these agents. Carbon dioxide is a noncondensable gas, and if released in the smelt, may collect at the smelt-water interface. The presence of carbon dioxide at this interface could affect the explosivity of the smelt in a number of ways:

1. It would increase the stability of the film boiling and prolong the metastable coarse intermixing stage, possibly allowing most of the water to vaporize.

2. It could eliminate self-triggering due to the spontaneous collapse of the vapor film.
3. It could provide a barrier to energy transfer during the propagation phase, since the carbon dioxide would tend to remain as a gas film when the shock wave pressure pulse passed through the metastable mixture.

One category of materials which produce carbon dioxide in molten smelt is amphoteric metal oxides or their salts. These materials react with Na_2CO_3 to release CO_2 and form a Na_2O-metal oxide salt. When added to water, these salts form caustic and the metal oxide. Currently, research is being conducted in Finland and Australia on the use of these materials to eliminate the current causticizing and calcining stages of the kraft process (7-9). The basic decarbonizing reactions of Na_2CO_3 with amphoteric metal oxides are illustrated by Eq. (1) and (2).

$$Na_2CO_3 + n\, M_xO_y \longrightarrow Na_2O \cdot (M_xO_y)_n + CO_2 \qquad (1)$$

$$Na_2CO_3 + Na_2M_xO_{y+1} \longrightarrow Na_2O \cdot Na_2M_xO_{y+1} + CO_2 \qquad (2)$$

Here, M_xO_y represents an amphoteric metal oxide such as B_2O_3, P_2O_5, SiO_2, Al_2O_3, TiO_2, and Fe_2O_3 (10).

Decarbonizing agents can be divided into two basic classes: those which are water soluble and those which are not. In the water soluble case, caustic and the metal oxide are formed in the dissolving tank. Being water soluble, the metal oxide remains in the system as part of the dead load and will eventually reach steady state. Examples of water soluble amphoteric oxides include BO_2, P_2O_5, and SiO_2.

Like water soluble metal oxides, water insoluble metal oxides form caustic and metal oxide in the dissolving tank. Being water insoluble, the metal oxide will precipitate from the solution and can be filtered and readded to the recovery furnace. Examples of water insoluble amphoteric oxides are TiO_2 and Fe_2O_3.

PROJECT OBJECTIVES

The basic objectives of this project were to:

1. Characterize the carbon dioxide release rates of acceptable inorganic smelt additives.
2. Correlate the carbon dioxide release rates of these additives with smelt explosivity.

An acceptable inorganic smelt additive is one having the following characteristics:

1. The total cost for using the agent should not exceed a few dollars per ADT pulp and preferably should be less than $1/ADT.
2. It should be effective over a range of temperature from about 1450°F to 1800°F.
3. It should be effective on a time scale comparable to the smelt residence time in the furnace, i.e., about 30 minutes.
4. The viscosity of the smelt should not be increased to a major extent, since the smelt must still flow easily out of the furnace.
5. The agent must operate in (or at least not be chemically changed by) a reducing atmosphere suitable for converting sulfate to sulfide.

CARBON DIOXIDE GENERATION

During the first phase of the experimental program, the carbon dioxide release characteristics of four inorganic smelt decarbonizing agents, $NaBO_2$, SiO_2, Fe_2O_3, and $CaCO_3$ were determined. Because of its relative low cost and compatability with the kraft process, $NaBO_2$ was considered the most promising of the proposed decarbonizing agents. A previous study of nonconventional causticizing technologies for kraft chemical recovery (11) evaluated systems based on different decarbonizing agents and concluded that of the nonconventional causticizing technologies only those evolving $NaBO_2$ and TiO_2 were technically feasible. Although a decarbonizing system based on TiO_2 is technically feasible, the high cost of TiO_2 makes the use of TiO_2 unattractive for either a carbon dioxide release agent or as the basis of a nonconventional causticizing system.

Although SiO_2 is a possible decarbonizing agent, smelts containing silicates tend to be glassy and dissolve slowly. Also, experience with systems containing large amounts of silicates has shown that these systems tend to form glassy evaporator scales.

Since previous researchers (3) have identified Fe_2O_3 and $CaCO_3$ as possible smelt desensitizers, these agents were also chosen for study. However, because of the formation of insoluble FeS, Fe_2O_3 is incompatible with the kraft process.

The objectives during this phase of the experimental program were to identify the reactions occurring between Na_2CO_3 and the decarbonizing agents and to determine the rate constants and activation energy for these reactions. Once the carbon dioxide release characteristics for these reactions were defined, the explosion desensitizing properties of the more promising agents could be determined.

Since the decarbonizing agents convert Na_2CO_3 to Na_2O, any correlation between decarbonizing agent and smelt explosivity must include the exact smelt composition at the time of the explosion trial. Therefore, defining the decarbonizing reaction is not only necessary to determine the quantity of carbon dioxide being evolved but also to predict smelt composition.

EXPERIMENTAL SYSTEM

The smelt in the lower bed of a kraft recovery furnace consists principally of Na_2CO_3 and Na_2S. To simulate a kraft smelt, the decarbonizing reactions were studied in a melt containing 75<u>M</u>% $NaCO_3$ and 25<u>M</u>% Na_2S plus enough decarbonizing agent to react with either 5 or 10<u>M</u>% of the Na_2CO_3.

Figure 1 illustrates the experimental reactor used to study the decarbonizing reactions. The reactor consists of a ceramic crucible contained in a steel crucible. The steel crucible is heated using an induction heating coil energized by a 20-kw Lepel high-frequency power supply. The ceramic crucible is then heated by radiation from the steel crucible. The decarbonizing agents, Na_2CO_3 and Na_2S, were premixed and added to the ceramic crucible. In a typical decarbonizing experiment, the ceramic crucible contained approximately 85 g of smelt. The radio frequency furnace allowed rapid heating of the sample. Normally, ten minutes of heating were required to melt the mixture. A faster melt time could be achieved by using a higher power output from the radio frequency furnace. However, this increased the risk of damaging the ceramic crucible during the rapid heating period.

Once a molten state was obtained, the nitrogen purge to the reactor was started. This purge stream continuously stripped the melt of any carbon dioxide generated. A chromel-alumel thermocouple was used to monitor smelt temperature.

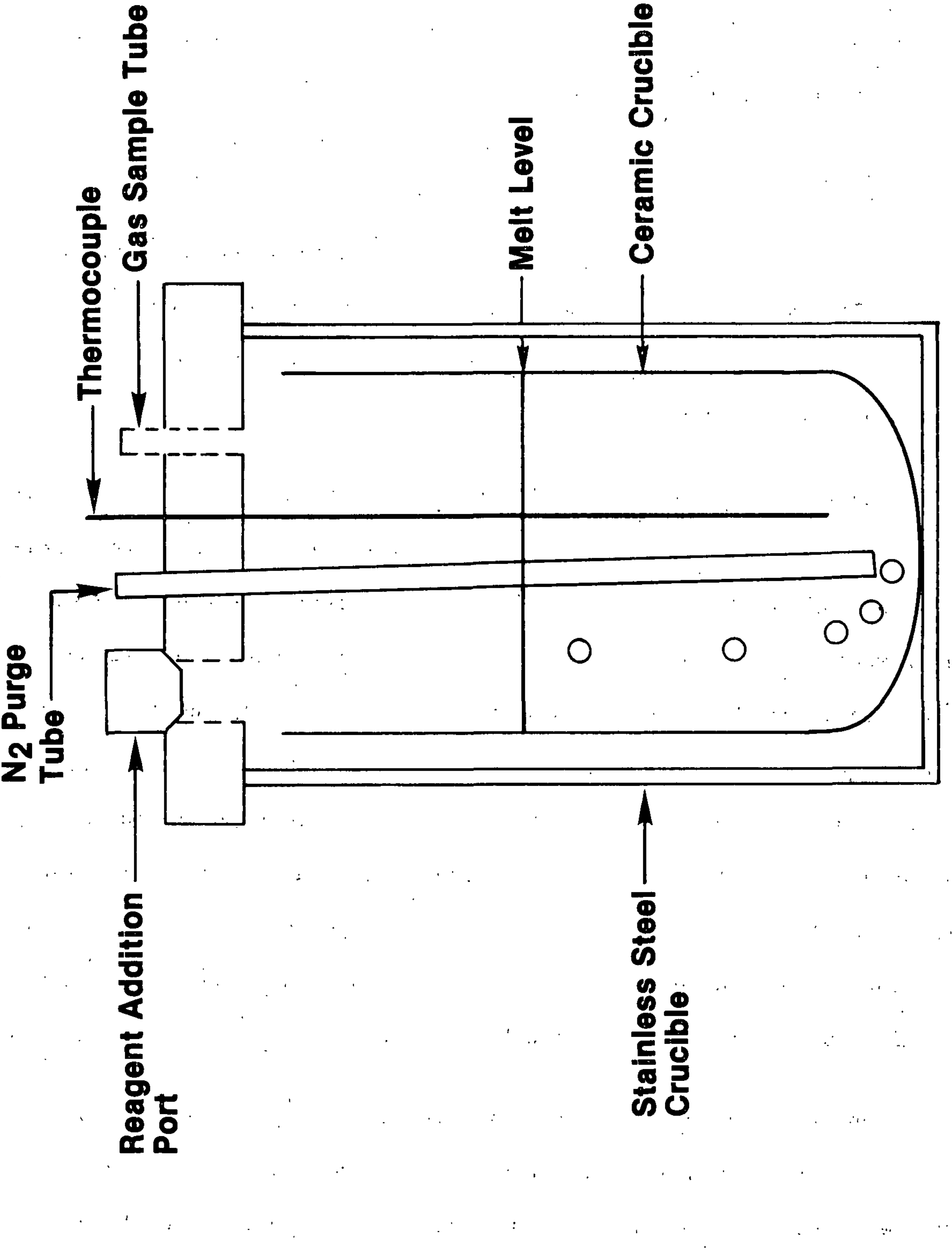

Figure 1. Experimental reactor.

Figure 2 illustrates the configuration of the experimental system. To accurately measure the flow rate of the nitrogen purge stream, the nitrogen was metered from a pressurized gas cylinder through a thermal mass flow meter. This flow meter provided an instantaneous reading of gas flow rate and a 0 to 5 V output signal. A mercury manometer monitored purge pressure and served as a pressure release valve. If the purge line from the reactor became plugged, the mercury in this manometer would be blown into a vial, releasing the purge pressure and preventing over-pressurization of the reactor.

The nitrogen purge stream plus any carbon dioxide or carbon monoxide generated by the decarbonizing reaction was conveyed from the reactor in a 1/4-inch steel tube. This gas stream then passed through a filter to remove any particles and to a carbon monoxide - carbon dioxide gas analyzer Model IR 702-703, Infrared Industries, Inc., Santa Barbara, California. This infrared analyzer was capable of simultaneously measuring both the carbon monoxide and carbon dioxide concentrations over a 0 to 30% range and provided a 0 to 100 mV output signal.

Although the sample gas from the reactor contained essentially carbon dioxide and nitrogen, a small amount of carbon monoxide was present from the oxidation of sodium sulfide with carbon dioxide, Eq. (3).

$$Na_2S + 4CO_2 \rightleftarrows 4\ CO + Na_2SO_4 \tag{3}$$

To maintain a constant smelt temperature, the temperature of the steel crucible was monitored with an optical pyrometer and controlled by adjusting the power to the furnace with a PID controller. The controller also provided a visual display of the steel crucible temperature and a 0 to 5 V output temperature signal.

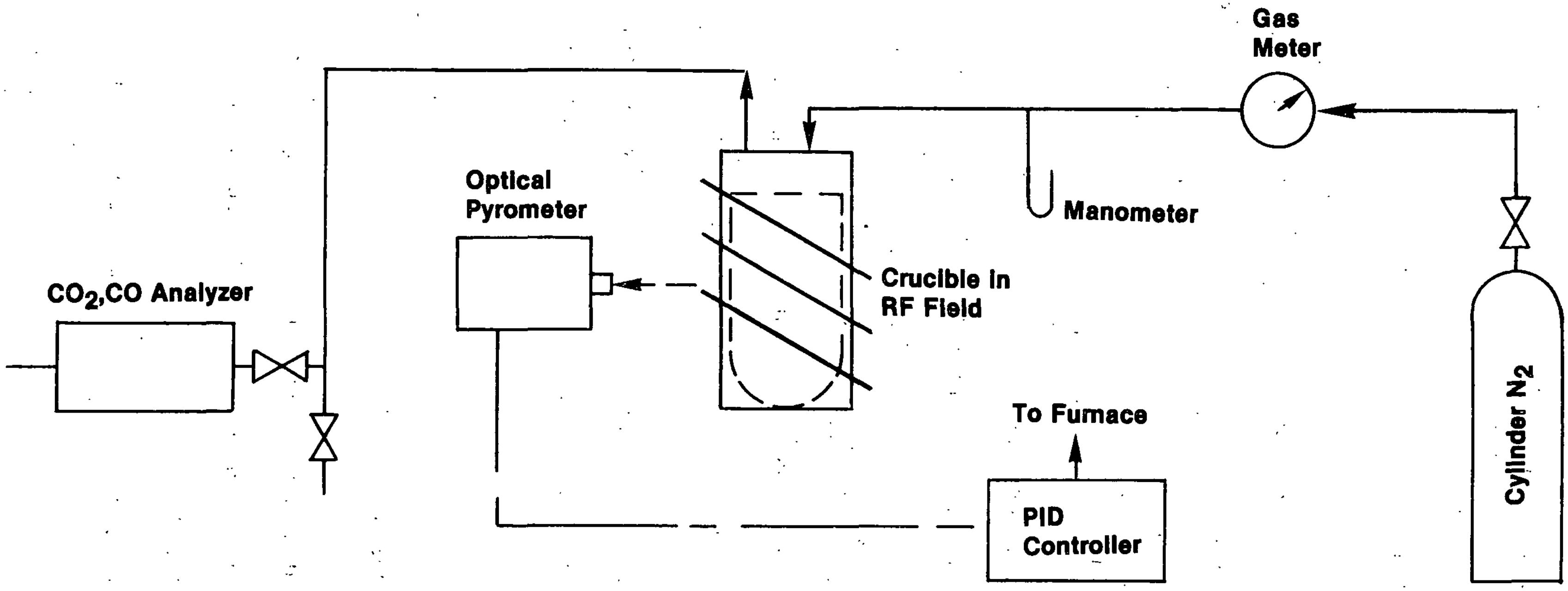

Figure 2. Experimental system.

The data acquisition system is illustrated in Fig. 3. In this system, the analog inputs from the infrared gas analyzer, melt thermocouple, optical pyrometer, and mass flow meter are first converted to digital inputs. These inputs are then sampled several times a second, and an average value over a set time interval is recorded. During an experimental trial, the data acquisition program integrates the reaction rates, determines the smelt composition, and provides a printer copy of the input data, reaction rates, and smelt composition.

EXPERIMENTAL RESULTS

One of the objectives of this project was to define the decarbonizing reactions in terms of reaction products, stoichiometry, rate, and temperature dependence. This information is essential for determining the CO_2 generation rate and melt composition during the explosion trials. Contained in this section are the experimental results which define the decarbonizing reactions.

Sodium Metaborate

As part of a study of alternate causticizing technology, Janson (7) recently investigated the decarbonizing reaction between $NaBO_2$ and Na_2CO_3. To identify the borate compound formed, various levels of NaOH were added to Na_2CO_3 and H_3BO_3. As this mixture is heated, water is lost from H_3BO_3 to form B_2O_3, Eq. (4).

$$2\ H_3BO_3 \longrightarrow B_2O_3 + 3\ H_2O\uparrow \tag{4}$$

The boric oxide, B_2O_3, will then react with NaOH to form either $Na_4B_2O_5$ or Na_3BO_3 and any remaining B_2O_3 will decarbonize Na_2CO_3. Depending on the amount of Na_2CO_3 decarbonized, the borate product can be identified. From the results of this work, Janson concluded that the decarbonizing reaction proceeds as shown by Eq. (5).

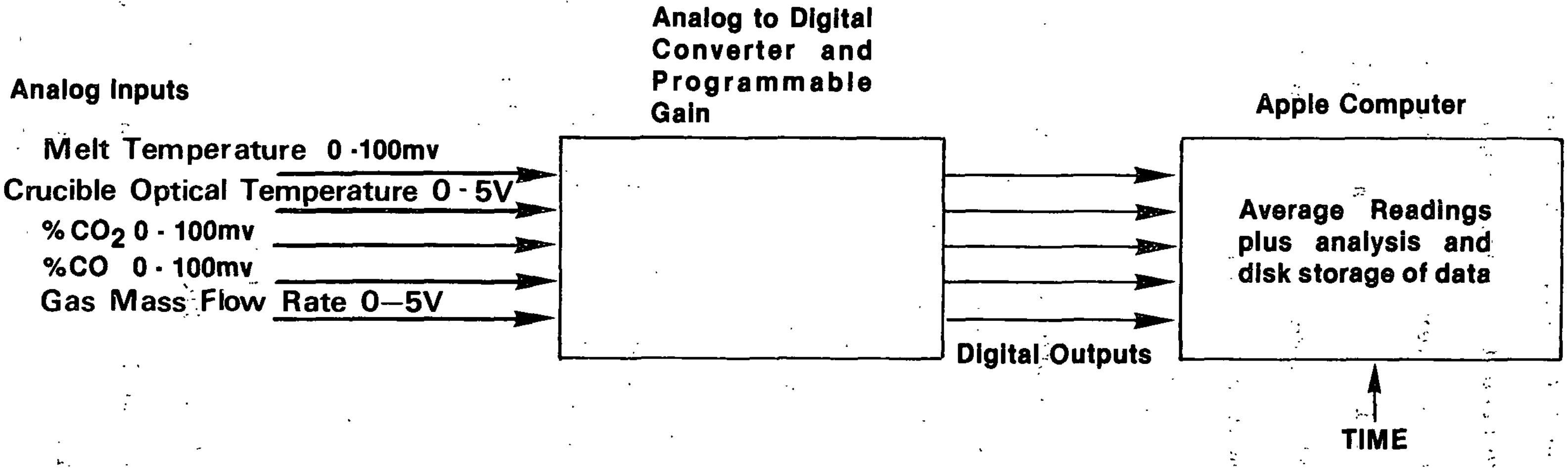

Figure 3. Data acquisition system.

$$Na_2CO_3 + 2\ NaBO_2 \longrightarrow Na_4B_2O_5 + CO_2\uparrow \qquad (5)$$

Here, $Na_4B_2O_5$ is a stable product and will not react further with Na_2CO_3.

To determine the rate and activation energy of the decarbonizing reaction between Na_2CO_3 and $NaBO_2$, Janson heated mixtures of Na_2CO_3 and $NaBO_2$ in a muffle furnace at different temperatures. After a set time period, the samples were cooled and analyzed for carbonate. Using this technique, the activation energy was determined to be 35.4 kcal/mole.

In 1949 Carrière <u>et al</u>. (<u>12</u>) studied the decarbonizing reaction between $NaBO_2$ and Na_2CO_3 and found, in contrast to Janson's results, that Na_3BO_3 was the reaction product, Eq. (6).

$$NaBO_2 + Na_2CO_3 \rightleftarrows Na_3BO_3 + CO_2\uparrow \qquad (6)$$

The identification of the reaction product is the essential difference between Carrière's and Janson's work.

In support of Carrière's results, Adam (<u>13</u>) states that when B_2O_3 is added to molten NaOH, three molecules of water are lost per mole of B_2O_3, indicating that $3Na_2O \cdot B_2O_3$ or Na_3BO_3 is formed, Eq. (7).

$$6\ NaOH + B_2O_3 \longrightarrow 3Na_2O \cdot B_2O_3 + 3\ H_2O \qquad (7)$$

To evaluate $NaBO_2$ as an explosion desensitizing agent it was necessary to determine the decarbonizing reaction rate and product. Using the experimental apparatus illustrated in Fig. 2, the decarbonizing reaction between $NaBO_2$ and Na_2CO_3 was followed through the evolution of CO_2. A Na_2CO_3 - Na_2S mixture similar to that found in the bed of a kraft recovery furnace was prepared and enough $NaBO_2$ added, depending on the reaction products, to decarbonize 5 to 20% of the Na_2CO_3 present.

The results of a typical decarbonizing experiment are shown in Fig. 4. Here, each mole of $NaBO_2$ generates approximately one mole of CO_2. These results are representative of the decarbonizing experiments with 1 to 1.3 moles of CO_2 generated per mole of $NaBO_2$ which is in agreement with Carriere's results. The slight excess CO_2 may be due to the natural decomposition of Na_2CO_3. Based on these results, it is evident that Na_3BO_3 is the decarbonizing reaction product, Eq. (8)

$$NaBO_2 + Na_2CO_3 \xrightarrow{K_1} Na_3BO_3 + CO_2\uparrow \tag{8}$$

Decarbonizing with $NaBO_2$ was found to be first order in both $NaBO_2$ and Na_2CO_3 and to follow an Arrhenius type temperature dependency. Equation (9) represents the CO_2 generation rate.

$$\frac{d[CO_2]}{dt} = K_1 \, [NaBO_2] \, [Na_2CO_3] \, e^{-\Delta E_1/RT} \tag{9}$$

Using a nonlinear regression analysis program the frequency factor and activation energy, Table I, were determined.

TABLE I

FREQUENCY FACTOR AND ACTIVATION ENERGY FOR THE REACTION OF SODIUM METABORATE WITH SODIUM CARBONATE

		SI Units
Frequency factor	$K_1 = 2,581 \pm 400$ (liters/mole-sec),	2,581 (cm^3/mole-sec)
Activation energy	$\Delta E = 35,000 \pm 2,500$ (cal/mole),	146,000 (J/mole)

Sodium Silicate

Vail (14) states that SiO_2 reacts with Na_2CO_3 to form metasilicate which in turn reacts to form orthosilicate, Eq. (10-11). Here, one mole of SiO_2 generates two moles of CO_2 in the smelt.

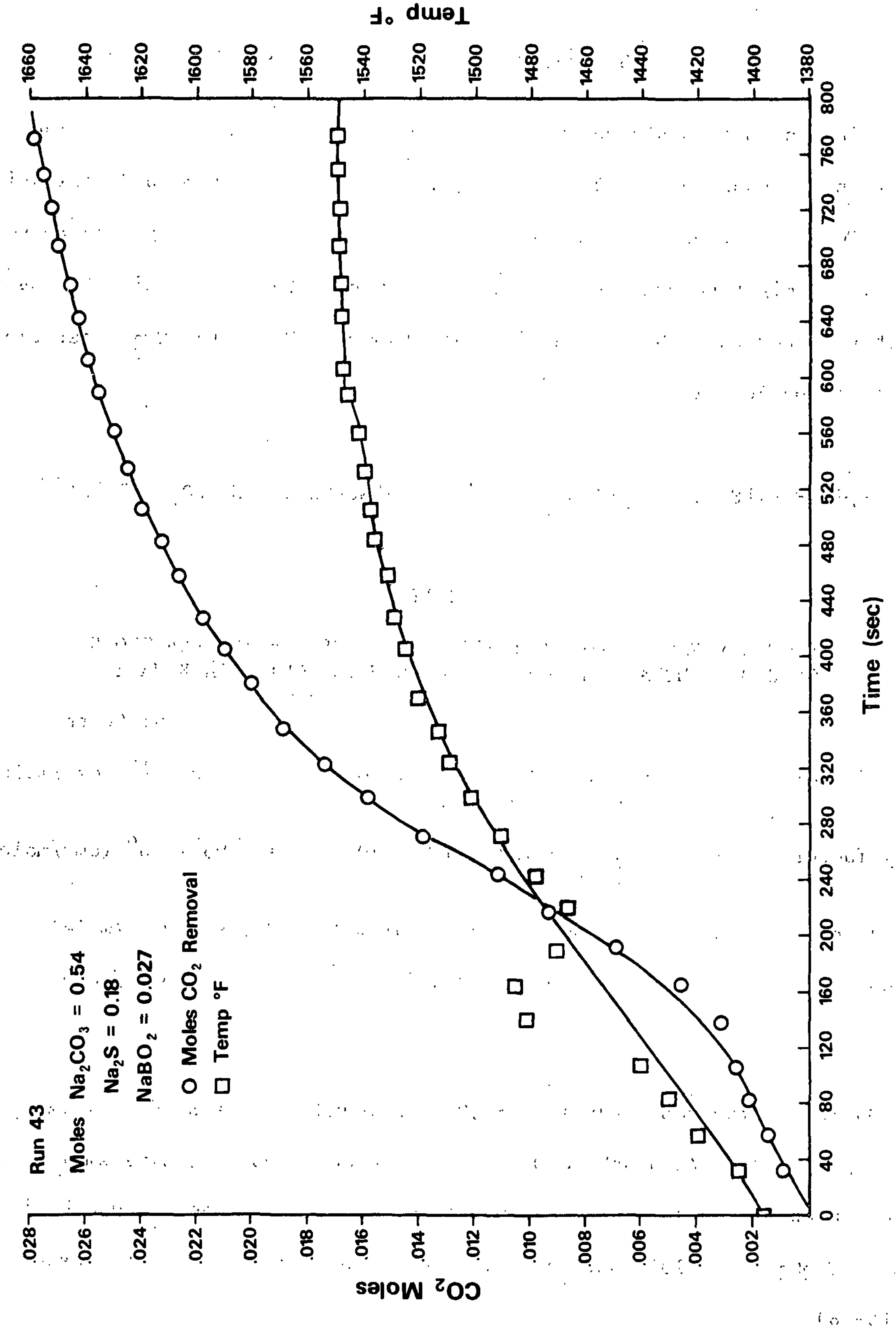

Figure 4. Temperature and CO_2 generation versus time for decarbonizing Na_2CO_3 with $NaBO_2$.

$$SiO_2 + Na_2CO_3 \xrightarrow{K_1} Na_2SiO_3 + CO_2\uparrow \tag{10}$$

$$Na_2SiO_3 + Na_2CO_3 \xrightarrow{K_2} Na_4SiO_4 + CO_2\uparrow \tag{11}$$

Using the previously described experimental technique, the reaction rates were determined. Contained in Table II are the frequency factors and activation energies. The activation energies of these reactions are quite high and approximately equal. As might be expected, the decarbonizing rate of SiO_2 with Na_2CO_3 is considerably faster than that of Na_2SiO_3 with Na_2CO_3. Here, the CO_2 generation rate is represented by Eq. (12)

$$\frac{d[CO_2]}{dt} = K_1[SiO_2]\,[Na_2CO_3]\,e^{-\Delta E_1/RT} + K_2[Na_2SiO_3]\,[Na_2CO_3]\,e^{-\Delta E_2/RT} \tag{12}$$

TABLE II

FREQUENCY FACTOR AND ACTIVATION ENERGIES FOR THE REACTIONS OF SODIUM META- AND ORTHOSILICATE WITH SODIUM CARBONATE

			SI Units
Frequency factor	K_1	$= 4.4 \times 10^{10} \pm 0.4 \times 10^{10}$ (liters/mole-sec)	$= 4.4 \times 10^{10}$ (cm^3/mole-sec)
Frequency factor	K_2	$= 1.95 \times 10^{9} \pm 0.5 \times 10^{9}$ (liters/mole-sec)	$= 1.95 \times 10^{9}$ (cm^3/mole-sec)
Activation energy	ΔE_1	= 69,000 ± 6,000 (cal/mole)	= 289,000 (J/mole)
Activation energy	ΔE_2	= 68,000 ± 16,000 (cal/mole)	= 285,000 (J/mole)

Ferric Oxide

During a previous study (3), Fe_2O_3 was found to have a desensitizing effect on smelt explosivity. Although Fe_2O_3 did not produce a nonexplosive smelt, the probability of an explosion occurring decreased when Fe_2O_3 was added. Decarbonizing of Na_2CO_3 with Fe_2O_3, Eq. (13), has been reported to be first order with respect to Na_2CO_3 (15-16).

$$Fe_2O_3 + Na_2CO_3 \xrightarrow{K_1} Na_2Fe_2O_4 + CO_2\uparrow \quad (13)$$

In this study, decarbonizing with Fe_2O_3 was found to be first order with respect to both Fe_2O_3 and Na_2CO_3 and can be represented by Eq. (14). The frequency factor and activation energy are shown in Table III.

$$\frac{d[CO_2]}{dt} = K_1 \; [Fe_2O_3] \; [Na_2CO_3] \; e^{-\Delta E_1/RT} \quad (14)$$

TABLE III

FREQUENCY FACTOR AND ACTIVATION ENERGY FOR THE REACTION OF FERRIC OXIDE WITH SODIUM CARBONATE

			SI Units
Frequency factor	K_1	= 26,600 ± 600 (liters/ mole-sec)	= 26,600 (cm^3/mole-sec)
Activation energy	ΔE_1	= 47,000 ± 2,000 (cal/mole)	= 197,000 (J/mole)

Calcium Carbonate

Another compound reported to have a desensitizing influence on smelt explosivity is $CaCO_3$ (3). As with Fe_2O_3, $CaCO_3$ was reported to decrease the probability of a laboratory smelt exploding during an explosion trial but did not produce a nonexplosive smelt. At high temperatures, $CaCO_3$ decomposes to form CaO and generate CO_2, Eq. (15).

$$CaCO_3 \xrightarrow{K_1} CaO + CO_2\uparrow \quad (15)$$

The rate of $CaCO_3$ decomposition was followed through CO_2 generation. This reaction was found to be first order in $CaCO_3$ and can be described by Eq. (16).

$$\frac{d[CO_2]}{dt} = K_1 \; [CaCO_3] \; e^{-\Delta E/RT} \quad (16)$$

The frequency factor and activation energy for $CaCO_3$ decomposition are contained in Table IV.

TABLE IV

FREQUENCY FACTOR AND ACTIVATION ENERGY FOR CALCIUM CARBONATE DECOMPOSITION

Frequency factor	= 346,000 ± 2,600 (1/sec)	= 346,000 (1/sec)
Activation energy	= 48,000 ± 1,000 (cal/mole)	= 201,000 (J/mole)

Carbon Dioxide Generation Rates

Contained in Table V are CO_2 generation rates for the four decarbonizing agents; SiO_2, $NaBO_2$, Fe_2O_3, and $CaCO_3$ in a Na_2CO_3-Na_2S melt. The rates are based on a Na_2CO_3 concentration of 13.5 mole/L and a Na_2S concentration of 5.6 mole/L. Using the same level of decarbonizing agent, the CO_2 generation rates are calculated at 1000°K and 1200°K. Relative to $NaBO_2$ and SiO_2, the CO_2 generation rates using $CaCO_3$ and Fe_2O_3 are quite low. Therefore, only a limited study of the effects of $CaCO_3$ and Fe_2O_3 on smelt explosivity was conducted, and the major portion of the explosivity study focused on CO_2 generation effects using $NaBO_2$ and SiO_2.

TABLE V

EFFECT OF DECARBONIZING AGENT ON CO_2 GENERATION

Decarbonizing Agent	Concentration (mole/L)	Rate (mole/L-sec) 1000°K	Rate (mole/L-sec) 1200°K
$NaBO_2$	0.7	0.000546	0.0103
SiO_2	0.7	0.000346	0.113
Fe_2O_3	0.7	0.0000134	0.000693
$CaCO_3$	0.7	0.0000078	0.000438

EFFECT OF CARBON DIOXIDE GENERATION ON SMELT EXPLOSIVITY

The second phase of this study was to determine the effect of CO_2 generation on smelt-water explosivity. Using the CO_2 rate equations developed in the previous section, it was possible to determine if any correlation exists between explosivity and CO_2 generation. This was accomplished by conducting explosion trials at various CO_2 generation rates. The results of these trials are contained in this section.

EXPERIMENTAL EXPLOSION SYSTEM

The experimental system used to study the effect of CO_2 generation on smelt explosivity is illustrated in Fig. 5. This system consists of a hastelloy crucible within a radio frequency field, a 1/4-inch diameter stainless steel rod, a data acquisition system, and an Apple Computer.

The rate of CO_2 generation in the hastelloy crucible was essentially the same as that obtained using the alumina crucible. Graphite and steel crucibles were also examined but proved unacceptable because of reactions between the crucible and smelt.

The temperature of the melt was monitored using a chromel-alumel thermocouple. The temperature monitoring system produced a visual digital output and provided the computer with an analog voltage signal corresponding to melt temperature. Using this signal and the previously determined reaction rates, the computer program calculated the CO_2 generation rate and melt composition. This system provided a continuous printed output of melt temperature, furnace temperature set point, CO_2 generation rate, and melt composition.

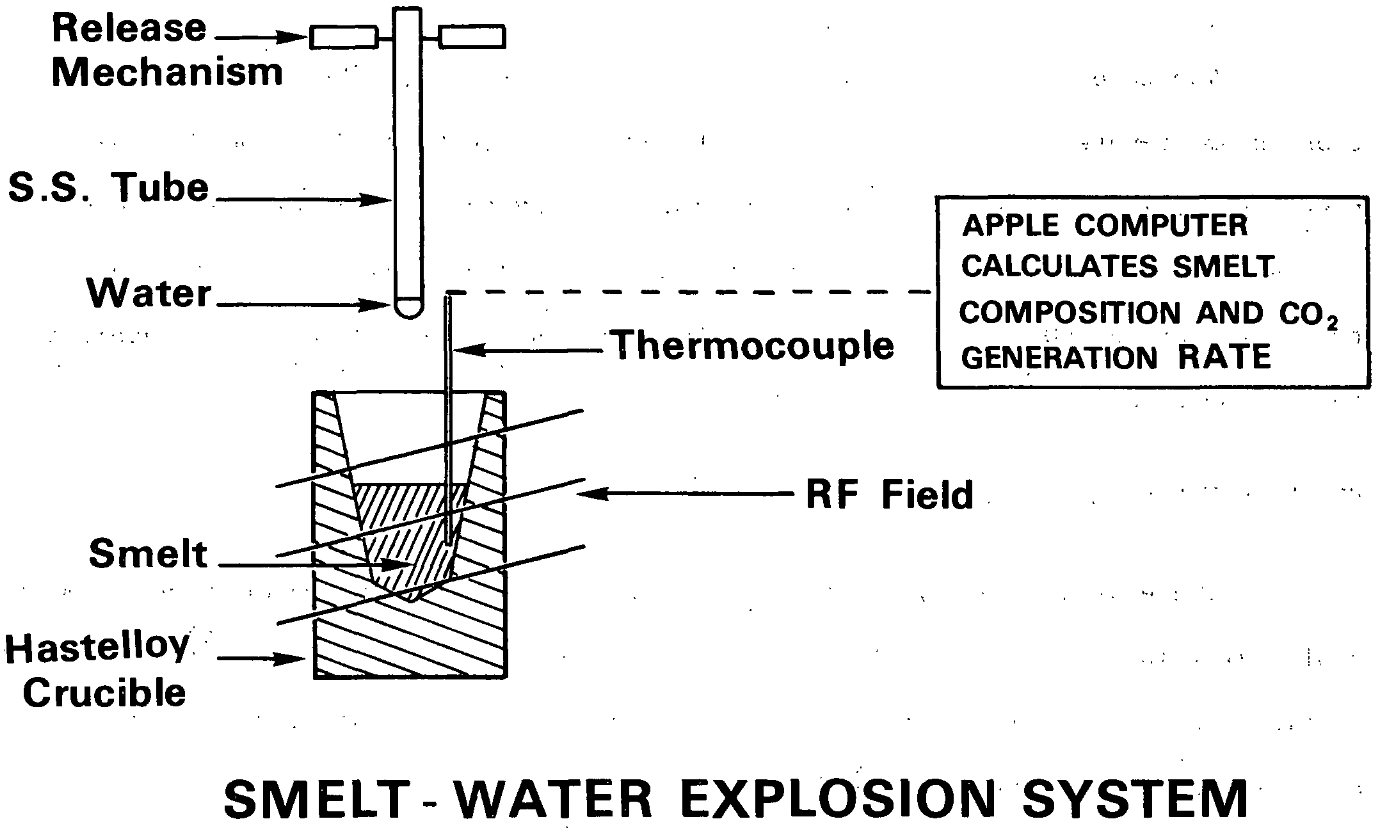

Figure 5. Experimental explosion system.

To prepare for an explosion trial, the melt chemicals were premixed and added to the hastelloy crucible. Using the radio frequency furnace, this mixture was heated to its melt point in approximately 5 to 10 minutes.

Once the mixture began to melt, the computer program was initiated and the melt composition and CO_2 generation rate were calculated. As the desired temperature and CO_2 generation rate were approached, the radio frequency furnace was turned off. This prevented the exploding smelt from shorting the radio frequency heating coils. At this time, the water was added to the stainless steel drop tube. If the water had been added earlier, its temperature would have increased during the melting period, which would have influenced the explosivity trials. At the desired CO_2 generation rate and temperature, the smelt-water explosion trial was initiated by dropping the steel rod containing approximately 40 milligrams of water into the crucible containing approximately 30 g smelt. If an explosion occurred, the smelt was thrown from the crucible. The sound of the explosion varied from a sharp crack to a dull thump. The sound level appeared to be related to the explosion triggering event, and was not correlated to melt temperature or composition.

Explosion Results

Table VI contains the explosion trial results using SiO_2 and $NaBO_2$. As illustrated in this table, explosions occurred in approximately 80% of the explosion trials, and there was no correlation between CO_2 generation and smelt explosivity. The CO_2 generation rate varied from a very low rate of 1.4×10^{-6} mole/L-sec to a relatively high rate of 0.0147 mole/L-sec. The low CO_2 generation rate was achieved by allowing the reaction to proceed until the majority of the $NaBO_3$ had reacted, and the high CO_2 generation rate was obtained using equal molar ratios of $NaBO_2$ and Na_2CO_3.

Although the effect of CO_2 generation on smelt water explosivity using $CaCO_3$ and Fe_2O_3 as decarbonizing agents was not studied in depth, some explosivity trials were run with these agents. While $CaCO_3$ and Fe_2O_3 did not appear to increase the smelt's sensitivity toward explosion, they did not prevent explosions. The other agents $NaBO_2$ and SiO_2 did increase the sensitivity of a smelt toward explosions. This increase in smelt sensitivity may be due to the formation of Na_2O, a known sensitizing agent (3).

SIZE OF EXPLOSION SYSTEM

As described earlier, the smelt-water explosion mechanism is believed to involve three distinct stages: initial configuration, triggering, and propagation.

The majority of smelt-water explosion research has been limited to systems employing less than 1 g of water or 100 g of smelt. With these levels of water and smelt, the critical event in the explosion mechanism is the triggering event. Not enough water or smelt is present for the propagation stage to influence the explosion. Systems which are easily triggered explode in these small scale experiments, while systems that are difficult to trigger do not explode. For example, Na_2CO_3 is nonexplosive in small scale experiments. However, G. A. Bergman and H. Laufke (17) have found that Na_2CO_3 will explode in systems evolving relatively large amounts of salt and water. In these experiments, 10 to 100 g of water were either injected into 10 to 30 kg of water or placed in "ceramic bombs" which were shuttered by denominators. Although pure Na_2CO_3 systems are more difficult to trigger, an event evolving sufficient energy will trigger such systems and an explosion will result.

TABLE VI

EFFECT OF CARBON DIOXIDE GENERATION ON SMELT WATER EXPLOSIONS

Decarbonizing Agent	Level, mole/ mole Na_2CO_3	CO_2 Generation, mole/L-sec	Temp., °F	Explosion
$NaBO_2$	0.05	1.4×10^{-6}	1545	Yes
$NaBO_2$	0.05	1.0×10^{-3}	1486	Yes
$NaBO_2$	0.05	1.5×10^{-3}	1602	Yes
$NaBO_2$	0.10	2.4×10^{-3}	1478	No
$NaBO_2$	0.20	3.2×10^{-3}	1475	Yes
$NaBO_2$	0.10	3.4×10^{-3}	1646	No
$NaBO_2$	0.20	4.9×10^{-3}	1597	Yes
$NaBO_2$	0.20	8.7×10^{-3}	1651	Yes
$NaBO_2$	1.0	1.47×10^{-2}	1532	Yes
SiO_2	0.05	9.7×10^{-4}	1604	Yes
SiO_2	0.10	1.2×10^{-3}	1604	Yes
SiO_2	0.05	1.5×10^{-3}	1658	Yes
SiO_2	0.15	1.6×10^{-3}	1603	Yes
SiO_2	0.15	3.8×10^{-3}	1620	Yes
SiO_2	0.15	4.7×10^{-3}	1703	No
SiO_2	0.20	6.7×10^{-3}	1662	Yes

CONCLUSIONS

The major conclusion resulting from this study is that CO_2 generation within a smelt will not prevent smelt-water explosions. No correlation was found between CO_2 generation and smelt explosivity.

Many of the decarbonizing agents increased the explosive sensitivity of the smelt. This was apparently due to the formation of Na_2O, a known sensitizing agent, resulting from the decarbonizing of Na_2CO_3.

The experimental system used for this study examined only the triggering event in the vapor explosion theory. Although CO_2 generation did not prevent the explosion from being triggered, it may have some influence on the propagation stage and hence, on the violence of a large scale explosion.

It was determined that the decarbonizing reaction between $NaBO_2$ and Na_2CO_3 is described by Eq. (17).

$$NaBO_2 + Na_2CO_3 \rightleftarrows Na_3BO_3 + CO_2\uparrow \tag{17}$$

Here, one mole of CO_2 is removed for each mole of $NaBO_2$.

FUTURE WORK

No future experimental work is presently planned on smelt-water explosions. The experimental system is currently devoted to a study of reactions occurring in the char beds of kraft recovery furnaces. If any additional methods are proposed for preventing smelt-water explosions, these will be examined.

NOMENCLATURE

ΔE_i	Activation energy for reaction i
K_i	Frequency factor for reaction i
$[X]$	Molar concentration of X
$\frac{d[CO_2]}{dt}$	CO_2 generation rate

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