THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES

NUMBER 315

REACTIONS OF HYDROGEN WITH ALKALI CARBONATE/SULFATE SMELT

JOHN H. CAMERON

DECEMBER, 1988

Reactions of Hydrogen with Alkali Carbonate/Sulfate Smelt

John H. Cameron

This manuscript is based on results obtained in IPC research and was presented at the 1988 Annual AIChE Meeting

Copyright, 1988, by The Institute of Paper Chemistry

For Members Only

NOTICE & DISCLAIMER

The Institute of Paper Chemistry (IPC) has provided a high standard of professional service and has exerted its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for the internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPC does not recommend particular products, procedures, materials, or services. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPC or its employees and agents have any obligation or liability for damages, including, but not limited to, consequential damages, arising out of or in connection with any company's use of, or inability to use, the reported information. IPC provides no warranty or guaranty of results.

REACTIONS OF HYDROGEN WITH ALKALI CARBONATE/SULFATE SMELT

John H. Cameron
The Institute of Paper Chemistry
P.O. Box 1039
Appleton, WI 54912

ABSTRACT

This paper describes the reactions of hydrogen with alkali carbonate-sulfate-sulfide smelts. These reactions were studied by contacting sodium sulfate-sulfide-carbonate melts with a purge containing various mixtures of hydrogen, water vapor, and carbon dioxide in nitrogen. The results of this study help to determine the importance of the H_2 reactions within the kraft furnace.

The reactions of H_2 with a Na_2CO_3-Na_2SO_4 melt were found to generate both Na_2S and NaOH and to be dependent on the gas-melt interfacial area. These reactions occur in the interfacial melt film with H_2 never achieving equilibrium with the melt. Initially, both the reduction of Na_2CO_3 to form NaOH and the reduction of Na_2SO_4 to form Na_2S are very rapid with 80% of the H_2 supplied to the melt consumed. Once a few percent of NaOH is formed, the reduction of Na_2CO_3 becomes quite slow.

Hydrogen reduction of Na_2SO_4 was found to be an autocatalytic reaction with the autocatalytic behavior due to the formation of Na_2S. It was found to be nearly first order in H_2 partial pressure and to have an activation energy of 22,000 cal/mol.

INTRODUCTION

Hydrogen may occur in the kraft furnace from either black liquor pyrolysis or from the reaction of CO with H_2O. Borg, et al. (1) reported H_2 concentrations of 3% directly above the bed. Hydrogen may either react with the Na_2SO_4 to form Na_2S and H_2O, or it may react with Na_2CO_3 to form NaOH and CO. The objective of this project is to identify the H_2 reactions that will occur within the kraft furnace, and to determine the rate controlling process and significance of these reactions. Two products of these reactions, Na_2S and NaOH, are important to the operation of the kraft furnace. The first, Na_2S, is the desired form of sulfur, and the second, NaOH, has been implicated in corrosion problems within the furnace. Through increased knowledge of how these compounds are formed, it may be possible to control their formation within the furnace.

PREVIOUS RESEARCH

Little quantitative information is available on the reactions of H_2 with alkali carbonate-sulfate melts. Atomics International (2) conducted the most extensive research on these reactions. In this research, H_2 reduction of sulfate was studied by bubbling hydrogen through an alkali carbonate-sulfate melt contained in a graphite crucible. The reaction was followed by periodically sampling the melt and analyzing it for sulfide. The melts used for this study consisted of sodium-potassium-lithium carbonates, which form low-temperature melting systems and which enabled the reaction to be studied over a temperature range of 600 to 840°C. It was believed that at these temperatures the sole reaction that would occur was hydrogen reduction of sulfate. Although carbon dioxide was not normally collected during these experiments, it was sampled during a few experiments and was detected at levels indicating hydrogen reduction of carbonate was also occurring. At these temperatures the reaction was slow, with most reduction experiments requiring 14 to 40 hours. Water was collected during the experiments but was not used to follow the reaction rate.

Hydrogen reduction of sulfate was found to be an autocatalytic reaction with the rate increasing as the sulfide content of the melt increased. The reaction was also catalyzed by iron and tin salts. The reaction was zero order in sulfate and was dependent on the H_2 partial pressure to the 0.65 power at H_2 pressures from 0.25 to 10 atm. Using limited temperature data, the iron catalyzed reaction was determined to have an activation energy of 28.0 kcal/mol. The reaction rate was dependent on the melt-gas interfacial surface area.

EXPERIMENTAL SYSTEM

The reaction of hydrogen with the alkali carbonate-sulfate melts was studied by either bubbling H_2 through the melts or introducing H_2 above stirred melts and monitoring the H_2, CO, and CO_2 content of the off-gas. These experimental systems are illustrated in Fig. 1 and 2. The H_2 and N_2 were metered through the mass flow meters and entered the melt through a ceramic tube. The off-gas from the reactor passed through an adsorbate water trap to a CO_2-CO analyzer. From this analyzer the gases passed through a CO_2 trap before entering an H_2 analyzer.

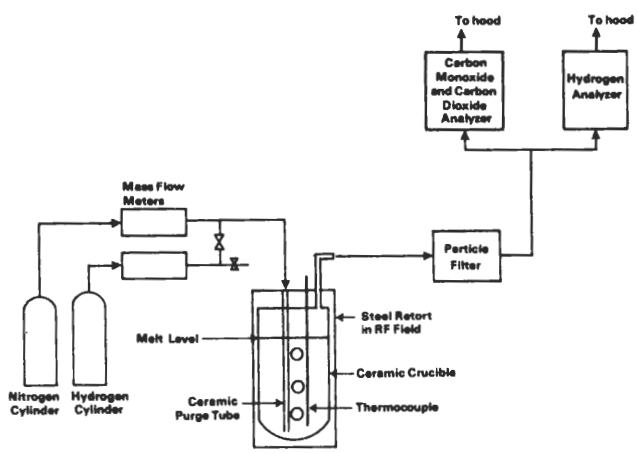

Figure 1. Experimental system with gases introduced below melt's surface.

These experimental systems allowed the effects of the temperature, melt composition, gas composition, and gas flow rate on the reactions to be studied. One deficiency of the system with the purge introduced below the melt's surface is that it does not

allow the gas-melt interfacial area to be varied independently from the degree of melt mixing. For example, any change in the purge rate will affect both the interfacial surface area and the degree of mixing in the melt. Therefore, the effect of gas-melt interfacial surface area was studied with the H_2 introduced above the melt's surface.

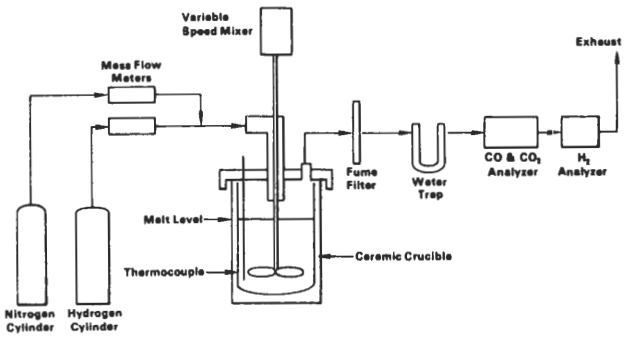

Figure 2. Experimental system with stirred melt and gases introduced above the melt.

EXPERIMENTAL RESULTS

Reactions Identified

The reaction of H_2 with an alkali carbonate-sulfide-sulfate melt produces H_2O, CO, and CO_2. Figure 3 shows the rate of H_2 consumption and CO-CO_2 generation when H_2 is bubbled through a Na_2CO_3-Na_2SO_4-Na_2S melt. After 30 minutes of reaction, the melt in Fig. 3 was cooled under a N_2 purge and analyzed. This analysis and that of a melt from a similar experiment are given in Table 1.

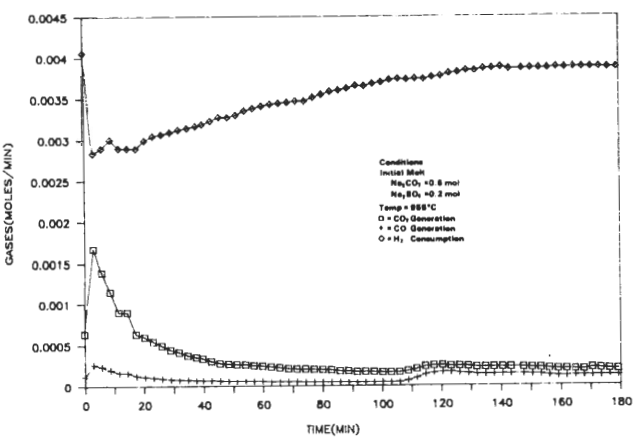

Figure 3. Hydrogen reduction of a sodium sulfate-carbonate melt.

The standard deviations shown in Table 1 were obtained by dividing the samples into three sections and analyzing each section. Sulfur, hydrogen, and oxygen balances were made by comparing the initial melt composition to the final melt composition and the off-gas generated during the experiments. Generally good agreement was obtained with these balances.

Table 1. Analysis of melt from hydrogen reduction.

Run 71

Initial Melt Composition:

Compound	Moles
Na_2S	0.024
Na_2SO_4	0.036
Na_2CO_3	0.77

Experimental Conditions:

Temperature: 955°C

Purge Rates N_2 = 1.0 L/min, H_2 = 0.1 L/min (STP)

Results after 30 min reaction

H_2 consumed = 0.097 mol
CO_2 generated = 0.0346 mol
CO generated = 0.0064 mol
H_2O generated = 0.07125 mol

Analyzed Melt Composition

Compound	Moles	SD
NaOH	0.0646	0.018
Na_2S	0.0395	0.006
Na_2SO_3	0.008	0.006
Na_2SO_4	0.013	
Na_2Sx	0.0	
Elemental S	0.0	

Balances

S: S in final melt/S in initial melt = 0.0605/0.06 = 1.0

H_2: $(NaOH/2 + H_2O)/H_2$ consumed = 0.104/0.097 =1.07

O_2: O_2 in exhaust gases/O_2 lost from melt: = $(H_2O/2 + CO_2 + CO/2)/(NaOH/4 + O_2$ lost from sulfur species) = 0.0734/0.07 = 1.05

C: C in off-gas/C lost from melt = $(CO+CO_2)/(NaOH/2)$ = 0.041/0.0323 = 1.27

Autocatalytic Nature of Reaction

The rate of sulfate reduction with H_2 in a carbonate melt increases as the reaction proceeds. This is shown in Fig. 3, where the hydrogen consumption rate is shown vs. time. In addition to the increase in the rate of H_2 consumption with time, more H_2 is consumed in reducing Na_2SO_4 and less in reducing Na_2CO_3 as the reaction proceeds. Initially, 60% of the H_2 reacts with Na_2CO_3 to form NaOH, as evidenced by the quantities of CO_2 and CO being evolved from the melt. After approximately 40 min, the combined CO and CO_2 evolution rates are only 10% of the H_2 consumption, indicating that 90% of the H_2 is consumed in reducing Na_2SO_4 to Na_2S.

The autocatalytic behavior observed for this reaction results from the increase in sulfide. This is shown in Fig. 4, where the hydrogen consumption rate is shown vs. time under conditions similar to those in Fig. 3, but with the melt initially con-

taining equal moles of Na_2SO_4 and Na_2S. In this experiment the initial H_2 consumption rate is the same as the H_2 consumption rate in Fig. 3 after 2 hr of reaction, and no increase is observed in the consumption rate with time. The H_2 consumption rate in this figure remains constant until all the Na_2SO_4 is reduced, at which time the H_2 consumption rate rapidly decreases.

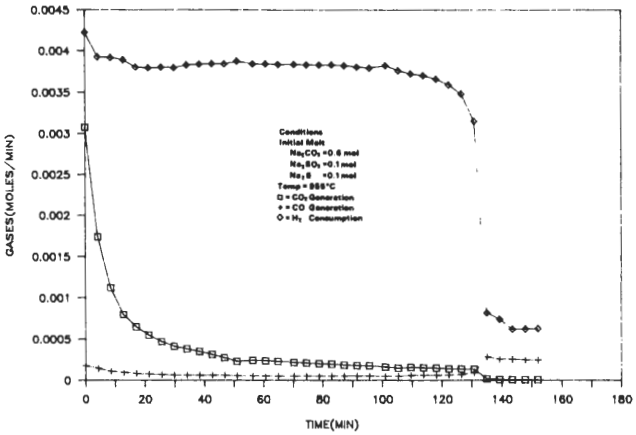

Figure 4. Effect of sulfide on hydrogen reduction of sodium sulfate.

At the temperature of the experiments shown in Fig. 3 and 4 (955°C), the rate of H_2 consumption is quite rapid. With no sulfide present, the initial rate of H_2 consumption is 0.003 mol/min and the reaction is consuming 66% of the H_2 supplied. After two hours of reaction with H_2, the rate is 0.004 mol/min and the reaction is consuming 90% of H_2 supplied. Since the initial H_2 consumption rate is high, the potential rate increase with increasing sulfide level is limited. To expand the potential for an increase in rate with an increase in sulfide content, this reaction was studied at 816°C. The rate of H_2 consumption vs. time at this temperature is shown in Fig. 5. Here, the initial rate is 0.0013 mol/min and the reaction is consuming 28% of the H_2 supplied. After 2 hr the rate is 0.0025 mol/min and the reaction is consuming 54% of the H_2 supplied. This demonstrates that the presence of sulfide in the melt can substantially increase the rate of sulfate reduction.

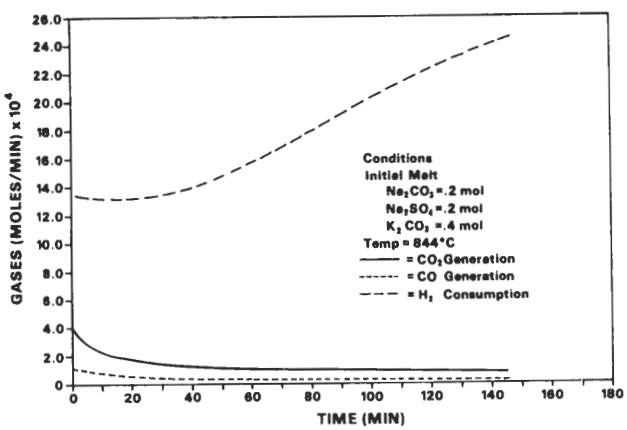

Figure 5. Autocatalytic nature of sulfate reduction with hydrogen.

Effect of Experimental Variables

Experimental results using both experimental systems (that with the H_2 introduced below the melt's surface and that with the H_2 introduced above a mixed melt) are described in this section. These variables include the hydrogen partial pressure, the melt composition, melt quantity, temperature, and melt-gas interfacial area. Most of the experimental data were obtained with the H_2 introduced below the melt's surface, and the effect of the experimental variables in this mode of gas-melt contact is described first.

Purge Introduced Below Melt's Surface

1) Sulfate Effect:

To determine the effect of sulfate concentration on the rate of H_2 consumption, the reaction was studied in melts containing Na_2CO_3, Na_2S and different levels of Na_2SO_4. The effect of Na_2SO_4 is shown in Table 2, where the reaction rate was measured with 0.4 mole of H_2 consumed.

Table 2. Effect of sulfate on the rate of hydrogen consumption.

Conditions

Temperature = 955°C

Initial Melt Composition	Purge Rates
Na_2CO_3 = 0.77 mol	N_2 = 1.0 L/min
Na_2S = 0.03 mol	H_2 = 0.1 L/min
Na_2SO_4 = variable	

Initial Na_2SO_4, mol	H_2 Consumption Rate, mol/min
0.01	0.00285
0.03	0.00312
0.06	0.00319
0.09	0.0035
0.15	0.00346

As shown in this table, the level of sulfate has only a slight effect on the rate of H_2 consumption. Although there is a slight increase in consumption rate with increasing sulfate, this increase is likely a result of increasing melt volume and melt-gas interfacial area. Since the purge tube location was fixed the addition of more sulfate increased the melt height and resulted in the gas bubbles traversing a greater distance in the melt. As is shown later, an increase in melt-gas interfacial area increases the reaction rate.

2) Hydrogen Partial Pressure:

The effect of hydrogen's partial pressure on the hydrogen consumption rate was studied at 816°C. In this experiment, different H_2/N_2 mixtures were bubbled through the melt and the rate of H_2 consumption was measured at 0.01 mole of H_2 consumed. The effect of H_2 on the reaction rate was determined by assuming that the rate of H_2 consumption can be expressed by Eq. (1).

$$\text{Rate of } H_2 \text{ Consumption} = P_{H_2}^{n} \times f(\text{temperature and other composition effects}) \quad (1)$$

To determine the order of reaction with respect to the partial pressure of H_2, the ln of the rate of H_2 consumption was plotted vs. the ln of the average H_2 partial pressure as shown in Fig. 6.

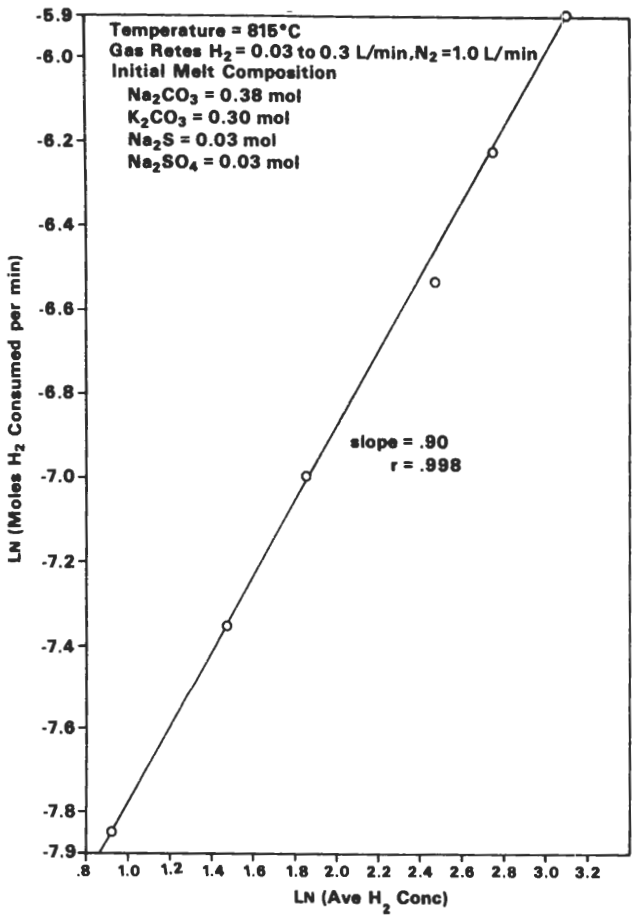

Figure 6. The effect of hydrogen on the rate of hydrogen consumption.

The melts in these experiments initially contained 0.03 mole of both Na_2S and Na_2SO_4. Therefore, there was only a small increase in the Na_2S level and the rate of H_2 consumption remained nearly constant over the course of this experiment. The H_2 partial pressure in Fig. 6 is the average of the inlet and exhaust partial pressures. During these experiments approximately 20% of the H_2 supplied to the melt was consumed. Therefore, there was not a large difference between the inlet and exhaust partial pressures of H_2. From the slope of the curve in Fig. 6, the reaction order with respect to H_2 is 0.9. The rate of H_2 consumption is then approximately 1st order in H_2 partial pressure.

3) Temperature Effect:

The effect of temperature on the rate of hydrogen consumption was studied by measuring the rate of H_2 consumption at different temperatures. It was assumed that the temperature effect could be described by the Arrhenius equation as shown in Eq. (2).

$$\text{rate} = f(\text{composition})e^{-\Delta E/RT} \qquad (2)$$

Here, f(composition) is the effect of composition, ΔE is the activation energy, R is the gas constant, and T is the absolute temperature.

The activation energy was determined by plotting the ln of the rate, (corrected for difference in H_2 partial pressure) vs. 1/T, °K. as shown in Fig. 7. The reaction rates were measured at temperatures ranging from 770 to 1009°C in alkali carbonate-sulfate-sulfide melts with the melts containing identical levels of sulfide and sulfate. The cation in these melts was either Na or a Na-K mixture. As shown in Fig. 7, the replacement of Na with K had no effect on the reaction rate. Over the temperature range of this study, the consumption of H_2 has an Arrhenius type temperature dependence with an activation energy of approximately 23,000 cal/mol. This activation energy is in the range of kinetically controlled processes.

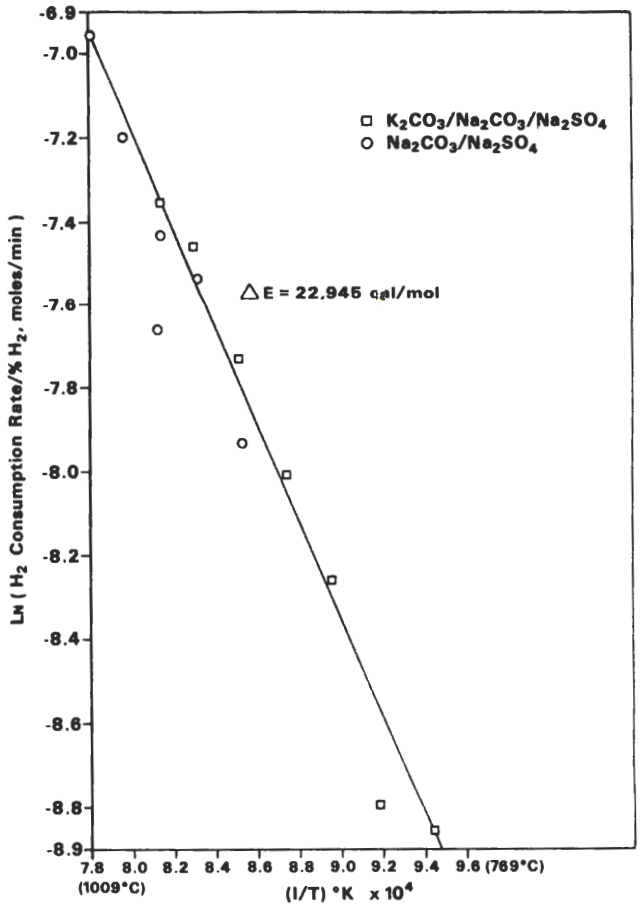

Figure 7. Effect of temperature on hydrogen consumption.

4) Melt Volume:

To determine if these reactions are kinetically controlled, the effect of melt volume was investigated. If the reaction occurs through H_2 achieving equilibrium with the melt and then reacting with Na_2SO_4, the reaction rate should be directly proportional to the melt's volume. The effect of melt volume on the rate of H_2 consumption is shown in Table 3.

As shown in this table, the rate of H_2 consumption is nearly independent of the melt's volume. Although there is a slight increase in reaction rate from 23.0 to 57.5 mL, this is similar to the effect of increased sulfate and also likely a result of the increase in gas-melt interfacial area. This indicates that the reaction is not occurring within the total melt.

Table 3. Effect of melt volume.

Conditions:

Temperature 955°C

Initial Melt Composition, wt.%

Na_2CO_3 = 92.5
Na_2SO_4 = 4.8
Na_2S = 2.7

Gas Flow Rates, L/min

N_2 = 1.0
H_2 = 0.1

Melt Wt., g	Melt Volume, mL	H_2 Consumption Rate, moles/min
44.1	23.0	0.00233
66.1	34.5	0.00298
88.2	46.0	0.00314
110.3	57.5	0.00307

Stirred Reactor

The stirred reactor shown in Fig. 2 was used to determine the effects of area and melt mixing on the rate of the reactions. In this reactor the gases were introduced above the melt's surface and the melt was stirred using a variable speed stirrer. The design of this reactor allowed the degree of melt mixing and surface area to be varied independently.

Reactions with Stirred Reactor

Figure 8 shows the rate of CO_2 and CO generation and H_2 consumption vs. time with the H_2 and N_2 introduced above a stirred melt.

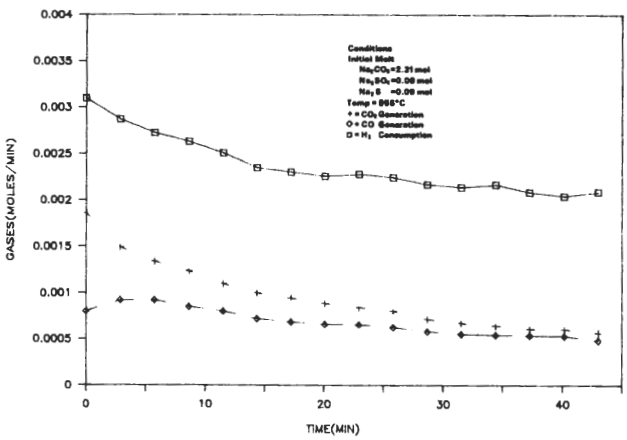

Figure 8. Hydrogen reaction with stirred melt.

Effect of Degree of Mixing on Reaction Rates

The effect of the degree of mixing on the reactions of H_2 was studied by varying the mixing rate once the reaction reached approximately steady state and by monitoring changes in off-gas composition. The effect of the level of mixing on the off-gas composition is shown in Fig. 9. The mixing rate was changed over approximately 15 min. During this time, there was some change in the melt composition, which affected these reactions. The duplicate points at a stirring rate of 0 RPM were taken before and after this period. From these duplicate points, it is evident that the effect of composition changes during this time period is small relative to the effect of stirring rate.

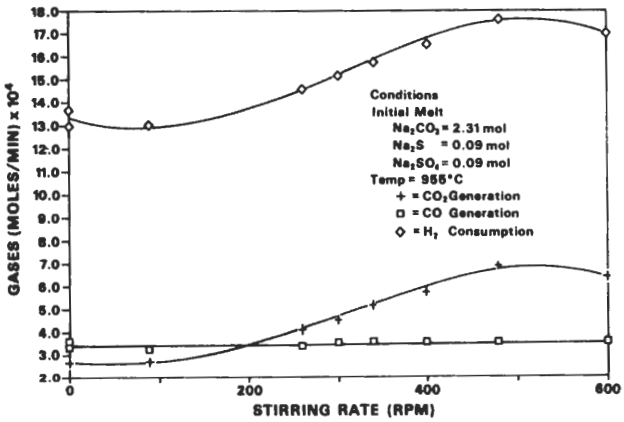

Figure 9. Effect of mixing on hydrogen reactions.

As shown in Fig. 9, the degree of mixing has only a small effect on the reactions of H_2 with a Na_2CO_3-Na_2SO_4 melt. The CO generation rate remained constant and there were slight increases in the CO_2 generation rate and the H_2 consumption rate as mixing rate was increased. The increases in the H_2 consumption rate and the CO_2 generation rate were approximately equal. The increase in the H_2 consumption rate then resulted only from the reaction of H_2 with Na_2CO_3, producing CO-CO_2, and the reaction of H_2 with Na_2SO_4 remained constant.

CO/CO_2 ratio in the off-gas from the reactor is controlled by the equilibrium reaction described by Eq. (3). The nearly constant level of CO in Fig. 9 results from the levels of CO_2 and H_2 in the off-gas being nearly equal.

$$H_2O + CO = H_2 + CO_2 \qquad (3)$$

Effect of Surface Area

The effect of gas-melt interfacial area was studied by using two reactors of different cross-sectional areas. Both these reactors were charged with the same amount of melt, and the rate of H_2 consumption was measured with different levels of mixing. The reaction rates for these reactors are compared in Fig. 10.

Although the consumption of H_2 in both reactors increased as the stirring rate increased, the relative rates of H_2 consumption in the two reactors remained approximately constant. For the stirring

rates in Fig. 10, the average rate of H_2 consumption in reactor 1 was 80.6 ± 2.7% of the rate of H_2 consumption in reactor 2, while the surface area of reactor No. 1 was 75% of the surface area of reactor No. 2. This indicates that the rate of H_2 consumption is nearly proportional to the gas-melt interfacial area.

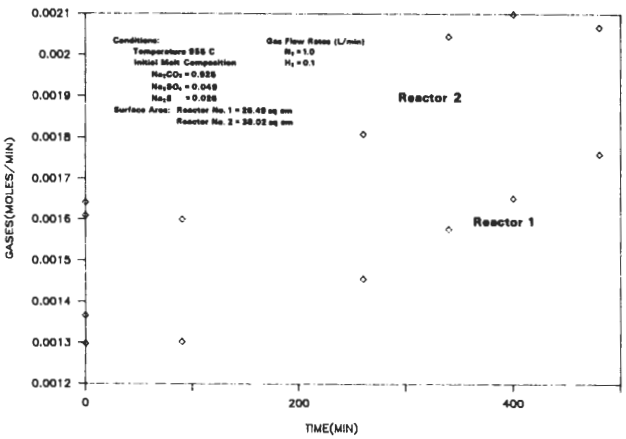

Figure 10. Effect of surface area on hydrogen reactions with melt.

Reactions with Na_2CO_3

When H_2 is added to an alkali carbonate-sulfate melt, it reacts with both the sulfate to form sulfide and with the carbonate to form hydroxide. The nature of the reaction with sulfate appears to be similar to that reported by Atomics International (2). However, the reaction with carbonate was not reported by Atomics International. In the H_2 reduction experiments shown in Table 1, approximately 3% of the Na_2CO_3 was converted to NaOH.

Recently, Wensley (3), and Barna and Rogan (4) have implicated NaOH as the active agent in composite tube corrosion. Since the conversion of Na_2CO_3 to NaOH was unexpected and may be important in composite tube corrosion, this reaction was examined in greater detail. Experiments were conducted to determine the effects of the experimental variables on the reaction between H_2 and Na_2CO_3.

Hydrogen Reduction of Sodium Carbonate

The reaction of H_2 with a pure Na_2CO_3 melt is shown in Fig. 11. The major gaseous product in this reaction is CO, and analysis of the melt found that it contained 3.8% NaOH. In this experiment two moles of NaOH were generated for every mole of CO in the off-gas. This verifies that the overall reaction of H_2 with Na_2CO_3 is shown by Eq. (4). Since this experiment contained no Na_2SO_4, the H_2 consumption rate rapidly decreases after a few percent NaOH is formed.

$$H_2 + Na_2CO_3 = 2NaOH + CO \qquad (4)$$

The effects of the experimental variables on H_2 reduction of Na_2CO_3 were investigated and are described below.

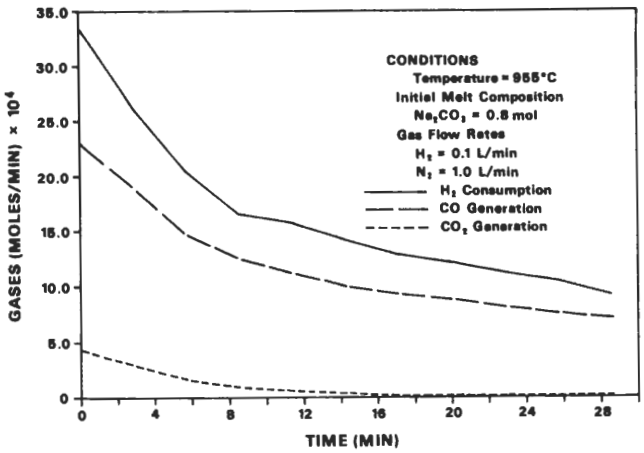

Figure 11. Hydrogen reduction of sodium carbonate.

1) Melt Volume:

It was previously found that H_2 reduction of a Na_2CO_3-Na_2SO_4 melt did not occur through the melt as a whole but that the reaction occurred at the melt-gas interface. To determine if this was also the situation for H_2 reduction of Na_2CO_3, the effect of melt volume on the consumption of H_2 was determined and is shown in Table 4. Table 4 shows the effect of melt volume on the H_2 consumption rate.

Table 4. Effect of melt volume on H_2 reduction of Na_2CO_3.

Conditions

Temperature = 955°C

Gas Flow Rates:

H_2 = 0.1 L/min
N_2 = 1.0 L/min

Melt Volume, cc	H_2 Consumption Rate, mol/min
22.1	0.00106
33.1	0.00109
44.2	0.00118
55.3	0.00117

To ensure the compositions of the melts in Table 4 were the same, the reaction rates were measured at the same relative level of H_2 consumed. Therefore the reaction rates were measured when each melt had the same NaOH/Na_2CO_3 ratio. As shown in this table, the melt volume had no effect on the rate of H_2 consumption. This demonstrates that the reaction is rapid and that the H_2 in the gas phase does not reach equilibrium with the melt.

2) Effect of Mixing and Surface Area:

The effects of mixing and surface area on the reaction of H_2 with Na_2CO_3 were studied by varying the level of mixing using different gas flow rates. While the total gas flow rate was varied, the H_2-N_2 ratio in the inlet gas was simultaneously adjusted to maintain the same H_2 concentration. The effect