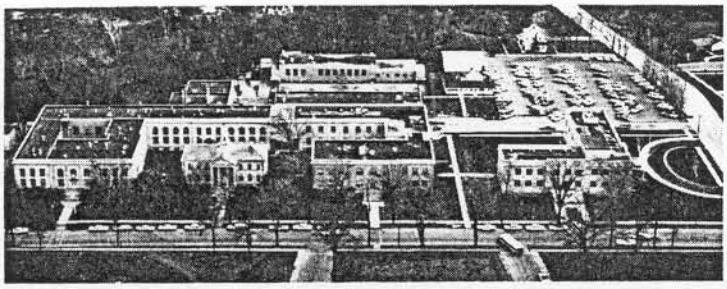

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REACTIONS OF HYDROGEN WITH ALKALI CARBONATE/SULFATE SMELT

JOHN H. CAMERON

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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.

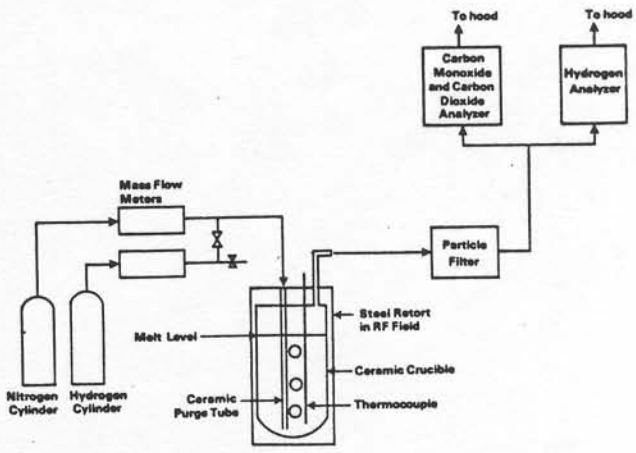

Figure 1. Experimental system with gases introduced below melt's surface.

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