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Publication Date

1984-12-01



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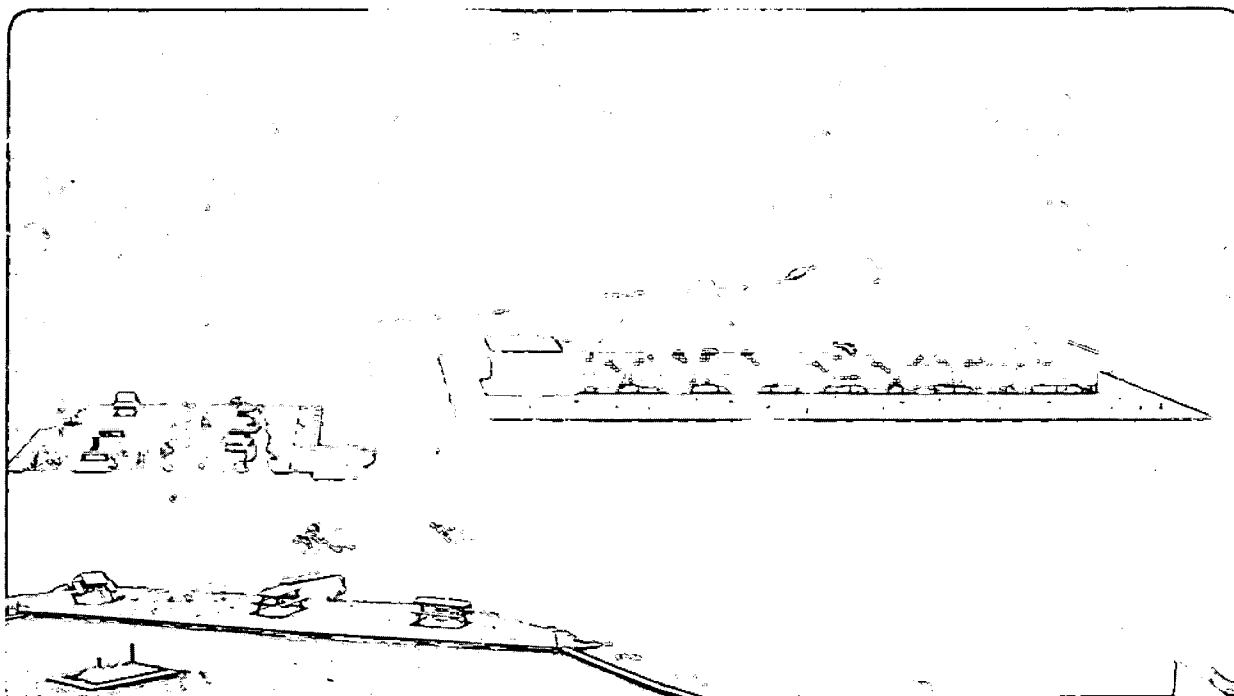
CATALYTIC GASIFICATION OF GRAPHITE OR CARBON
Quarterly Report: October 1 - December 31, 1984

H. Heinemann

December 1984

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Quarterly Report

October 1 - December 31, 1984

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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Berkeley, CA 94720

This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Research Gasification Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098, through the Morgantown Technology Center, Morgantown, West Virginia.

TABLE OF CONTENTS

I. TASK DESCRIPTION FOR FY 1985. 1

II. HIGHLIGHTS. 2

III. PROGRESS OF STUDIES 3

I. TASK DESCRIPTION FOR FY 1985

This program is designed to look at the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Much of the work is being carried out with graphite as a carbon source to insure that hydrogen or hydrogen in hydrocarbons is derived from water. Relatively low temperatures are being used to favor the equilibrium $C+2H_2O \rightarrow CH_4+CO_2$, which is almost thermally neutral. Our earlier work has shown that, in the presence of KOH as catalyst, higher hydrocarbons up to C_6 can be formed. This raises the question whether hydrocarbons are a primary product and syngas a secondary one formed by steam reforming. The formation of hydrocarbons is a stoichiometric reaction in which each H_2 in water reacts to form a phenolate and a hydrocarbon: $5C+4KOH \rightarrow 4COK+CH_4$. We have shown the presence of phenolate by surface spectroscopy and have found that it can be decomposed over metal oxides to make the reaction truly catalytic: $4COK \xrightarrow{MeOx} 2K_2O+2C+2CO$; $2K_2O+2H_2O \rightarrow 4KOH$. Future work is directed toward combining flow reactor studies with ultrahigh vacuum surface studies to follow the mechanism, to find the best catalysts for phenolate decomposition, to measure and improve kinetics, and to study the effect of added gases, such as CO or COS.

II. HIGHLIGHTS

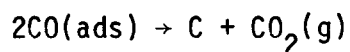
Adsorption experiments with CO or CO₂ on graphite using labelled carbon have shown an exchange of carbon between graphite and CO at very high temperatures, but not between graphite and CO₂. Since ¹³CO₂ is desorbed from adsorbed ¹³CO at 730K (437°C) and below, it must be formed by disproportionation, leaving some carbon on the graphite surface.

In the gasification of graphite over KOH/NiO catalysts at 860K (567°C) more hydrogen and less CO and methane are observed than corresponds to equilibrium. CO₂ is a major product along with hydrogen. To determine whether methane is a major primary product which is then decomposed by steam reforming, methane was added to the steam feed. The vast majority (95+%) of the added methane was recovered in the product, showing that steam reforming plays at most a minor role. However, in the presence of added methane the gasification rate declined. While the reasons for this are not yet clear, they must lie in a surface poisoning by some decomposition product of the small amounts of methane disappearance.

III. PROGRESS OF STUDIES

A. Thermal desorption of ^{13}CO and $^{13}\text{CO}_2$ from graphite at low pressures.

Thermal desorption experiments using ^{13}C labelled ^{13}CO and $^{13}\text{CO}_2$ were carried out from the clean graphite surface to determine the nature of the intermediates formed on the surface when either of these two gases is adsorbed. Adsorption of either CO or CO_2 on polycrystalline graphite followed by heating at a rate of $5^\circ/\text{sec}$, gives rise to CO_2 desorption at 730K and CO desorption at 1250K. In order to determine if the carbon in the desorbed gaseous molecules is derived from graphite or from the adsorbed gases, labelled ^{13}CO and $^{13}\text{CO}_2$ were used. The results indicate that regardless of whether ^{13}CO or $^{13}\text{CO}_2$ was adsorbed, CO_2 desorbed at 730K contained only ^{13}C and therefore the carbon in desorbing CO_2 comes from the adsorbed gas. Thus, we have clear evidence for the disproportionation of adsorbed CO on clean graphite according to the Boudouard reaction,



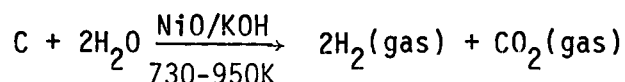
CO desorbed at 1230K contained only ^{12}C and therefore, must derive from graphite. It appears that the oxygen atom produced from the dissociation of adsorbed ^{13}CO or $^{13}\text{CO}_2$ can also react with the graphitic

carbon to produce a strongly adsorbed species that desorbs as CO only at high temperatures, such as 1230K.

B. Catalytic studies of the graphite-steam reaction using a flow reactor.

We have found that a combination of KOH and NiO is a good catalyst for the gasification of graphite with steam in the temperature range of 730-950K. With KOH alone the reaction was stoichiometric below 850K and stopped after one turnover. With KOH/NiO catalyst H₂ and CO₂ were the major products and their yield and concentration are displayed in Figure 1A. CH₄ and CO are also produced but in small amounts.

The dominant net reaction appears to be



The formation of CO₂(gas) instead of CO(gas) can be readily explained using the results of our CO thermal desorption studies that indicate that it disproportionates to C and CO₂. If CO formation is the first step in the C/H₂O reaction (along with H₂ formation), followed by its disproportionation, only CO₂ will be detected. It is interesting that gas production is detected only above the desorption temperature of CO₂, 730K. The possibility that CO is converted to CO₂ by the watergas shift reaction cannot fully be excluded at this time.

During the catalyzed C/H₂O reaction more hydrogen is detected than

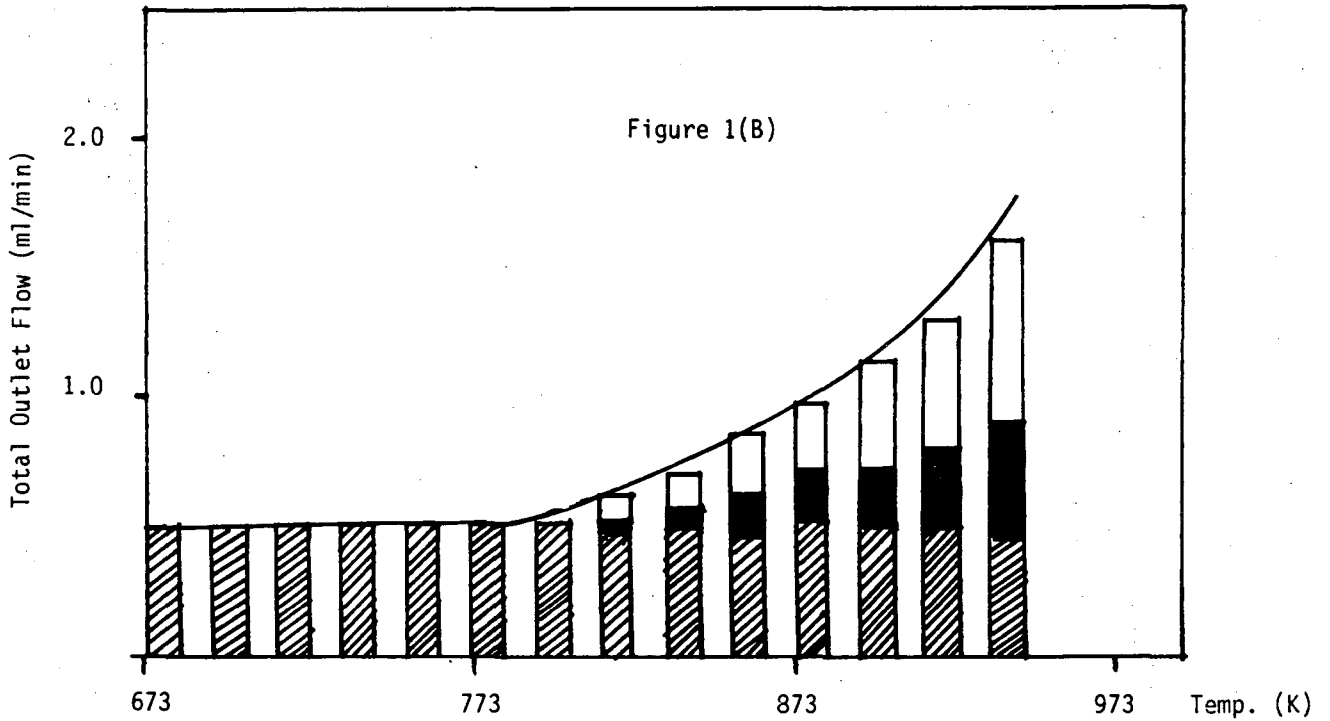
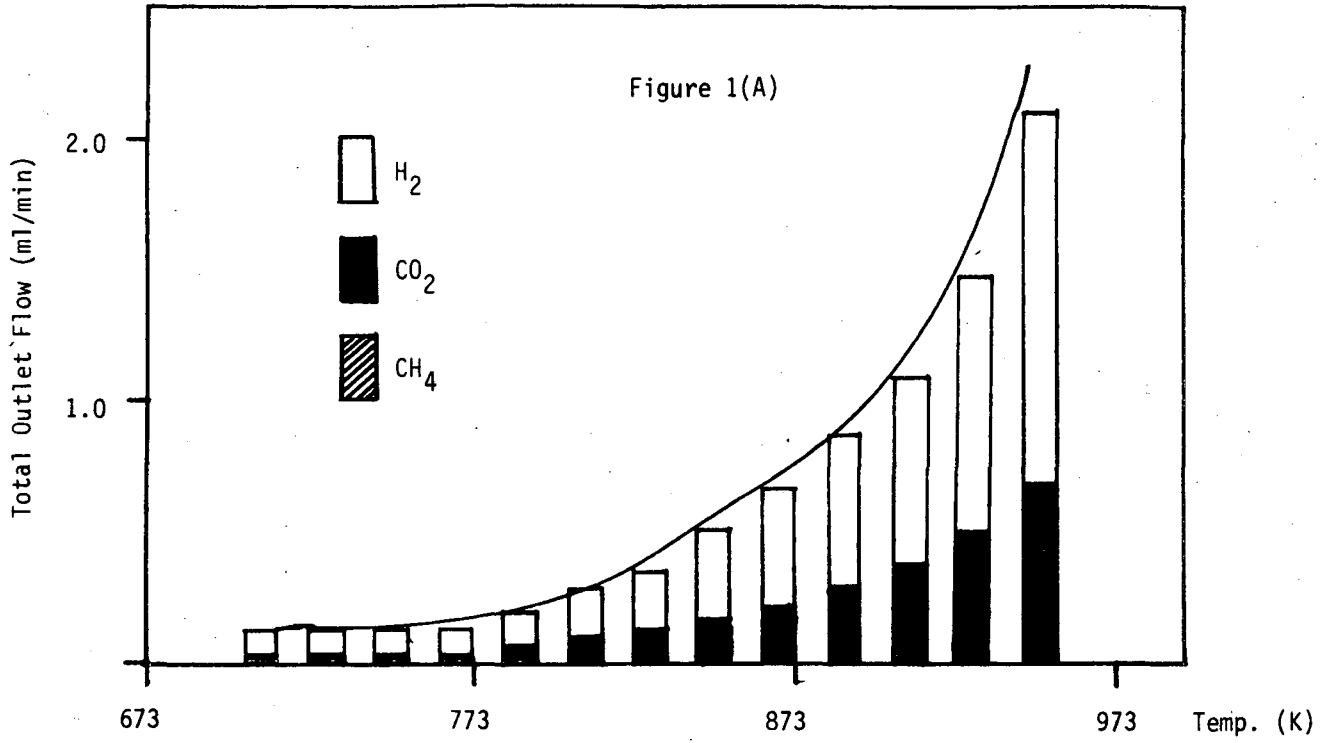
indicated by the stoichiometry of the net reaction ($C + 2H_2O \rightarrow CO_2 + 2H_2$). It was thought that if CH_4 is also produced, which is thermodynamically certainly feasible at the low gasification temperatures ($2C + 2H_2O \rightarrow CH_4 + CO_2$), its reactions with steam ($CH_4 + H_2O \rightarrow 3H_2 + CO$) could account for the increased amount of hydrogen. In order to obtain evidence for the presence of methane steam reforming, CH_4 was mixed with steam and the mixture was passed over graphite at a flow rate of 0.5 ml/min. in the presence of KOH/NiO catalyst. The results are shown in Figure 1B. The addition of CH_4 decreases the rate of gas production by a factor of two while only a small fraction (1-5%) seems to react with steam. The inhibition of gas production (H_2 and CO_2) by CH_4 may be due to the deposition of carbon from the disproportionation of CO that has been produced by the $CH_4 + H_2O$ reaction. While only a small fraction of the methane that was introduced reacted, this reaction could account for the observed larger than 2:1 $H_2:CO$ ratio which was detected in the catalyzed C/ H_2O reaction.

In order to carry out the steam gasification of graphite in the presence of CH_4 (or other gases), a time consuming modification of the flow reactor had to be undertaken. Work is now in progress studying the effect of added CO and/or CO_2 on steam gasification of graphite.

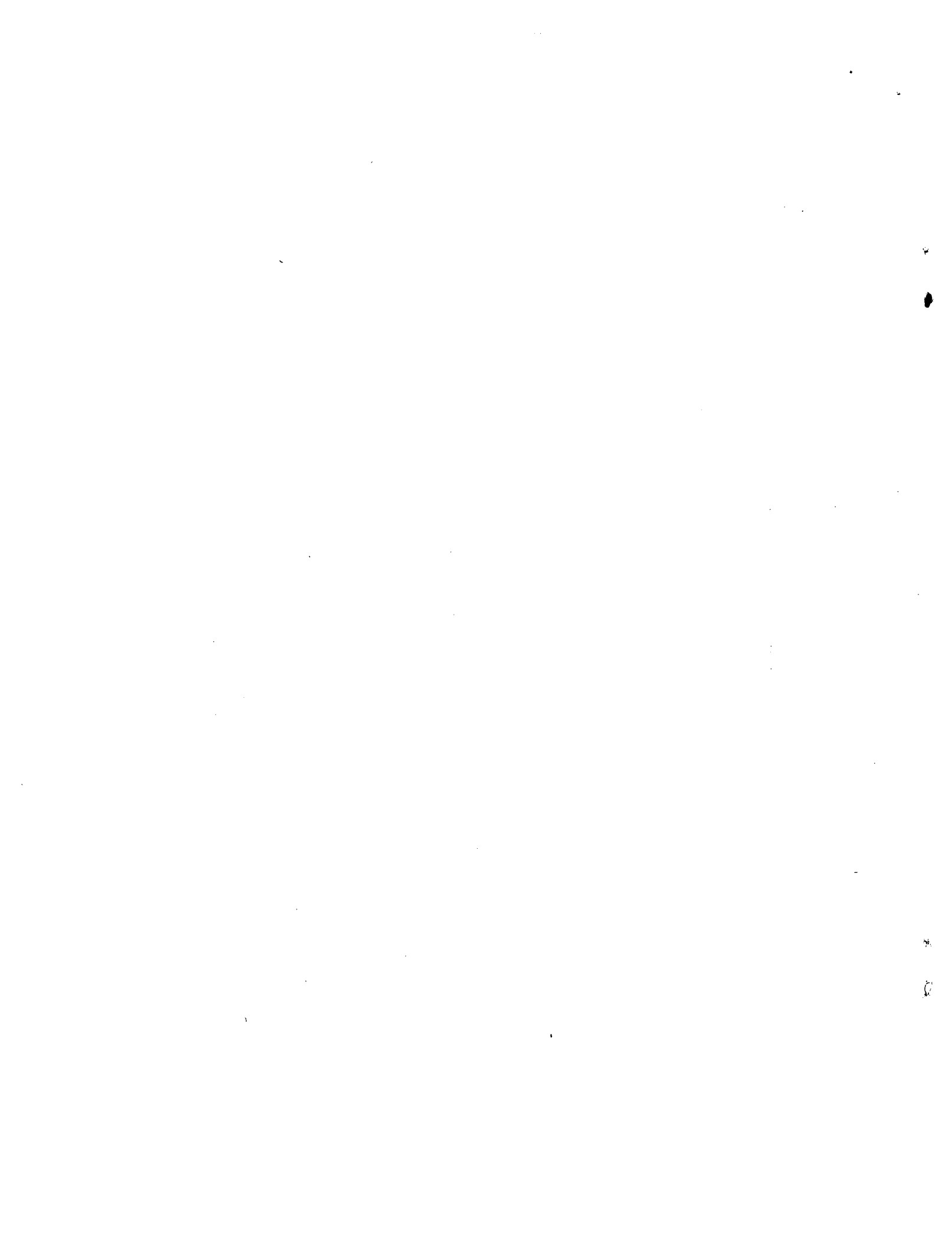
Figure Captions

Figure 1A: Total outlet flow when passing steam over a graphite sample loaded with .4% KOH and .4% NiO. Charge rate 1 ml water/min.

Figure 1B: Total outlet flow when passing steam and methane over a graphite sample loaded with .4% KOH and .4% NiO. Charge rate 1 ml water/min. Steam/methane ratio = 2.



XBL 851-733



This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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