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**HOT-GAS CLEANUP FOR MOLTEN CARBONATE
FUEL CELLS-DECHLORINATION AND SOOT
FORMATION**

Final Report
For the Period May 19, 1981-July 19, 1983

By
**D. Ham
A. Gelb
G. Lord
G. Simons**

January 1984

Work Performed Under Contract No.: DE-AC21-81MC16242

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Physical Sciences, Inc.
Andover, Massachusetts

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ABSTRACT

Two separate aspects of hot-gas conditioning for molten carbonate fuel cells (MCFC) were investigated under this contract: potential high temperature chloride sorbent materials were screened and tested and carbon deposition on MCFC components was studied experimentally to determine guidelines for maximizing MCFC efficiency while avoiding carbon fouling.

Natural minerals containing sodium carbonate were identified as the most promising candidates for economical removal of chlorides from coal gasifier effluents at temperatures of about 800 K (980°F). The mineral Shortite was tested in a fixed bed and found to perform remarkably well with no calcination. Using Shortite we were able to achieve the program goal of less than 1 ppmV chlorides at 800 K. Shortite is an abundant mineral with no competing commercial demand, so it should provide an economical chloride cleanup sorbent.

Measurements showed that carbon deposition can occur in the equilibrium carbon free region because of the relative rates of the relevant reactions. On all surfaces tested, the Boudouard carbon formation reaction is much faster than the water-gas shift reaction which is much faster than the methanation reaction. This means that the normal practice of adding steam to prevent carbon formation will only succeed if flows are slow enough for the water shift reaction to go substantially to completion. More direct suppression of carbon formation can be achieved by CO₂ addition through anode recycle to force the Boudouard reaction backward. Addition of steam or CO₂ must be minimized to attain the highest possible MCFC efficiency.

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EXECUTIVE SUMMARY

The objectives of this program comprised steps toward solutions to two hot gas cleanup problems in molten carbonate fuel cell (MCFC) power plants: 1) cleanup of chlorides from the fuel gas stream; and 2) carbon deposition from the fuel gas on MCFC anodes and other cell materials. Both efforts involved a combination of experimental measurements using simulated gasifier effluent compositions and analysis based on thermodynamic calculations and application of a previously developed sorbent reactivity model.

The objective of the chloride cleanup part of this program was to screen and test potential hot gas chloride sorbents for possible use as part of a hot gas cleanup process in a combined MCFC/coal gasifier power plant. An effective sorbent can provide one stage of two or three fixed absorption beds between the gasifier and the MCFC for cleanup of sulfide species (primarily H_2S and COS), chlorides (essentially HCl) and trace contaminants (NH_3 , AsH_3 , H_2Se , H_2Te , Hg , Cd , Pb , etc.). We are aware of no investigations prior to this contract of candidates for chloride sorbents that will reduce total chloride concentrations to the ppmV range in gasifier effluent mixtures above 800 K (980°F).

The first phase of our investigation of potential chloride sorbents was an evaluation and screening of all candidate materials. Potential chloride absorption effectiveness was determined using equilibrium thermodynamics to obtain lower limits on chloride vapor pressures over potential sorbents in contact with a gas having the appropriate composition. Results of this screening show that alkali carbonates are the only substances that can reduce the total chloride concentration below ppmV levels at temperatures up to 800 K and that above 800 K the chloride concentration cannot be reduced below ppmV levels at equilibrium. Thus alkali carbonate sorbents provide a suitable match for use with MCFC's which are expected to have inlet temperatures of about 800 K.

Our search for economical, alkali-containing sorbents emphasized naturally occurring minerals due to their relatively low costs. Availability became a key consideration that narrowed the field of candidates to only a few minerals. Potentially useful minerals were tested by reacting them in a hot flow reactor with HCl contained in simulated coal gasifier effluent and deducing reaction rates as a function of sorbent capacity. These tests indicate that the naturally occurring mineral Shortite is the leading candidate for a hot gas HCl cleanup sorbent. Shortite is an abundant mineral, found with other commercially mined minerals, but not used commercially at this time. These features indicate that Shortite will be available at an advantageous price. Thermochemical estimates of bed capacities and melting temperatures were made for Shortite saturated with chloride to show that no problems should be encountered with bed melting over the 800-850 K temperature range anticipated for hot gas cleanup. We have demonstrated that Shortite meets the program goal of reducing chlorides to less than 1 ppmV of the gasifier effluent at 800 K with high potential utilization in a fixed bed configuration. Further study is required to evaluate the performance of full sized beds and extrapolate this performance to maximum utilizations.

The objective of our carbon deposition studies was to gain sufficient understanding of the qualitative mechanisms involved in carbon fouling to recommend a method for avoiding this problem. Detailed deposition rate measurements will be required beyond these results to quantitatively define optimal conditions for implementation of the recommendations.

The approach employed in these carbon fouling investigations was to perform bench scale experiments in which MCFC anode materials, or other materials used in MCFC construction, were exposed to simulated gasifier effluent compositions. The gas compositions were chosen to approximate, or deviate slightly from, equilibrium carbon deposition boundaries at relevant temperatures and pressures. Inlet and exit gas compositions were measured continually throughout a run and carbon formation was detected optically after the system was cooled. Data were obtained at three temperatures (875 K, 925 K and

975 K) for two total pressures (1 and 5 atmospheres). Three metal surfaces used in MCFC power plants were studied; stainless steel, nickel, and nickel-chromium Ni(Cr) anode material. Two different samples of Ni(Cr) material were tested, new and previously used in an MCFC. Partial equilibrium analysis of the measured exit gas compositions was used to deduce a global mechanism for carbon formation.

Our measurements showed that carbon deposition boundaries are determined by chemical kinetics such that carbon fouling can occur in the equilibrium carbon free region. On all surfaces tested the Boudouard carbon formation reaction is faster than the water-gas shift reaction which is much faster than the methanation reaction. This means that the normal practice of adding steam to prevent carbon formation will only succeed if flows are slow enough for the water gas shift reaction to go substantially to equilibrium. If equilibrium is not maintained, that is reaction kinetics are important, more direct suppression of carbon formation can be achieved by CO₂ addition to force the Boudouard reaction backward. CO₂ can be added most economically via anode gas recycle.

Ni(Cr) anode material that had been used in an MCFC was found to have a higher catalytic activity than other materials tested. Carbon fouling is most likely to occur on stainless steel or nickel inlet hardware or on new anode material, during the first few hundred hours of operation, because the water-gas shift reaction will not proceed to prevent the faster carbon deposition reaction on these surfaces. Partial equilibrium calculations provide a good approximation to the chemistry for these cases.

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1. INTRODUCTION

1.1 Motivation for Hot Gas Cleanup in MCFC Power Plants

Generation of electrical power using molten carbonate fuel cells (MCFC's) offers the possibility of power plants with potential efficiencies greater than fifty percent combined with environmentally acceptable operation. MCFC's operate well at an average temperature of about 925 K (1200°F) on low-to-medium Btu gas mixtures containing hydrogen and carbon monoxide as the fuel. These MCFC characteristics couple naturally to fuel gases produced by gasification of coal to provide a clean, quiet and efficient process for implementation of the national goal of increasing our use of coal.

However, reactivities of catalytic electrodes in MCFC's are quite sensitive functions of several impurities in coal gasifier effluent, the most serious problem species being H_2S , COS and HCl . MCFC anodes tolerate these species and retain sufficient reactivity only at concentrations such that $\text{H}_2\text{S} + \text{COS}$ is less than about 1 ppmV and HCl is below an uncertain value in the range 0.2-10 ppmV. Highly effective gas cleanup systems are necessary to achieve these low levels since untreated gasifier effluent contains concentrations of $\text{H}_2 + \text{COS}$ in the range 3500-6000 ppmV and HCl in the range 10-200 ppmV.

In addition to being poisoned by impurities, reaction at the catalytic anode can be inhibited by deposition of carbon from the fuel gas stream. The effect of this fouling is to clog the surface of the porous electrode material, restricting transport of the reactant fuel gas into the electrolyte and thus reducing the rate of the electrochemical reaction. Carbon fouling can reduce fuel transport into the cell sufficiently to cause failure of the MCFC even for the typical case that catalytic activity of the anode is not significantly reduced by the carbon deposit. Steam addition is usually recommended to prevent carbon deposition. High efficiencies can be maintained only by minimizing addition of any gas due to dilution of the heating value by the gas and the requirement to heat the gas to the operating temperature.

Gas treatment systems for removing impurities and preventing carbon fouling offer the highest overall systems efficiencies if they operate between the optimal MCFC anode inlet temperature and a higher gasifier exit temperature. Such hot gas cleanup processes retain the sensible heat from the gasifier to avoid the cost of gas reheat prior to the fuel cell as well as eliminate capital costs required in proposed low temperature systems for heat exchangers, water quench processes and sour water treatment. Several percentage points of potential power plant efficiency will be sacrificed if the gas must be cooled for treatment and subsequently reheated.

1.2 Chloride Levels in Gasifier Effluent

Concentrations of minor species in coal gasifier product gas have been reasonably well established. Gas phase species considered as minor species include NH_3 , H_2S , COS , HCN , HCl , and C_xH_y . Much more information exists on concentrations of these species than on concentrations of trace species. No data are available on the chemical forms of the trace species in the product gas since most of the existing data on levels of trace species resulted from concerns about contamination in waste streams (water, ash, slag) with little emphasis on product gas purity.

Measured values of minor species concentrations from three gasifiers are presented in Table 1.1 which was taken from a presentation by Anderson et al.^{1.1} The values for HCl range from 20 to 100 ppm. HCl results from reactions which release chlorine from the coal. The range of total chlorides found in a study of 101 American coals^{1.2} was from 0.01% to 0.54% with a mean value of 0.14%. This range implies that the range of HCl concentrations in gasifier effluents could span the approximate range from 10 to 200 ppm depending upon what coal is used in the gasifier.

1.3 Optimal Temperature Considerations

An optimal hot gas cleanup system would operate close to the MCFC inlet temperature. The freezing point of the binary alkali carbonate electrolyte restricts this temperature to a value greater than 800 K (980°F). The exothermicity of the electrochemical reaction is expected to cause temperature increases of 200-300 K (360-540°F) across realistically sized commercial

TABLE 1.1

OPERATING CHARACTERISTICS OF THE KOPPERS-TOTZEK, LURGI and HYGAS STEAM-OXYGEN GASIFIERS USING SUBBITUMINOUS COAL (from Anderson et al., Ref. 1.1)

	<u>Koppers-Totzek</u>	<u>Lurgi</u>	<u>Hygas</u>
Pressure, atm	2-3	20-32	69-100
Temperature K	1800-2000	590 (top) 1260 (bottom)	590 (top) 920-1060 (1st stage) 1030-1170 (2nd stage) 1170-1280 (SOG)
<u>Product Gas,</u> mole fraction			
H ₂ O	0.0801*	0.4659	0.4265†
H ₂	0.3039	0.2172	0.1500
CO	0.5428	0.0800	0.0843
CO ₂	0.0651	0.1638	0.1950
N ₂	0.0052	0.0005	0.0003
CH ₄	--	0.0591	0.1248
C ₂ -C ₅	--	0.0045	0.0064
BTX	--	0.0023	0.0068
H ₂ S	0.0026	0.0026	0.0023
COS	0.0002	0.0002	0.0001
NH ₃	0.00003	0.0032	0.0034
HCN	0.00002	0.000002	0.00006
HCl	0.0001	0.00002	0.00002
C ₆ H ₅ OH	--	0.0004	0.0005
Tar	--	0.1660 g/g-mol	--
Fatty Acids	--	0.0167 g/g-mol	--
g-mol/g-coal	0.0778	0.1165	0.0969

*Product gas does not include water added from water sprays.

†Product gas does not include oil or water used for a slurring coal.

cells,^{1,3} so that even with inlet temperatures of 800 K, high peak temperatures cause problems in the cells. Increasing the anode gas stream inlet temperature above 800 K causes even higher peak temperatures, causing increased corrosion, electrolyte evaporative losses and materials problems. These considerations delineate 800-850 K (980-1070°F) as the optimal temperature range for a hot gas cleanup system.

1.4 Program Objectives and Approach

The objectives of this program comprised steps toward solutions to two of the hot gas cleanup problems discussed above: 1) cleanup of chlorides from the fuel gas stream; and 2) carbon deposition on MCFC anodes and other cell materials. Both efforts involved a combination of experimental measurements using simulated gasifier effluent compositions and analysis based on thermodynamic calculations and application of a previously developed sorbent reactivity model.

The objective of the chloride cleanup part of this program was to screen and test potential hot gas chloride sorbents for possible use as part of a hot gas cleanup process in a combined MCFC/coal gasifier power plant. An effective sorbent can provide one stage of two or three fixed absorption beds between the gasifier and the MCFC for cleanup of sulfide species (primarily H_2S and COS), chlorides (essentially HCl) and trace contaminants (NH_3 , AsH_3 , H_2Se , H_2Te , Hg , Cd , Pb , etc.). We are aware of no investigations prior to this contract of candidates for chloride sorbents that will reduce total chloride concentrations to the ppmV range in gasifier effluent mixtures above 800 K.

The first phase of our investigation of potential chloride sorbents was an evaluation and screening of all candidate materials. Potential chloride absorption effectiveness was determined using equilibrium thermodynamics to obtain lower limits on chloride vapor pressures over potential sorbents in contact with a gas having the appropriate composition. Results of this screening show that alkali carbonates are the only substances that can reduce the total chloride concentration below ppmV levels at temperatures up to 800 K and that above 800 K the chloride concentration cannot be reduced below ppmV levels at equilibrium.

Our search for economical, alkali-containing sorbents emphasized naturally occurring minerals due to their relatively low costs. Availability became a key consideration that narrowed the field of candidates to only a few minerals. Potentially useful minerals were tested by reacting them in a hot flow reactor with HCl contained in simulated coal gasifier effluent and deducing reaction rates as a function of sorbent capacity. These tests indicate that the naturally occurring mineral Shortite is the leading candidate for a hot gas HCl cleanup sorbent. Shortite is an abundant mineral, found with other commercially mined minerals, but not used commercially at this time. Thermochemical estimates of bed capacities and melting temperatures were made for Shortite saturated with chloride to show that no problems should be encountered with bed melting over the temperature and composition ranges anticipated for hot gas cleanup.

The objective of our carbon deposition studies was to gain sufficient understanding of the qualitative mechanisms involved in carbon fouling to recommend a method for avoiding this problem. Detailed deposition rate measurements will be required beyond these results to quantitatively define optimal conditions for implementation of the recommendations.

The approach employed in these carbon fouling investigations was to perform bench scale experiments in which MCFC anode materials, or other materials used in MCFC construction, were exposed to simulated gasifier effluent compositions. The gas compositions were chosen to approximate, or deviate slightly from, equilibrium carbon deposition boundaries at relevant temperatures and pressures. Inlet and exit gas compositions were measured continually throughout a run and carbon formation was detected optically after the system was cooled. Partial equilibrium analysis of the measured exit gas compositions was used to deduce a global mechanism for carbon formation and a recommended method for economically suppressing carbon deposition using CO₂ addition via anode gas recycle.

Details of the work accomplished in this program are presented in the following sections, organized according to the contract task descriptions as outlined in the Table of Contents. An interim report of this work is contained in reference 1.4.

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2. SCREENING AND IDENTIFICATION OF CANDIDATE SORBENT MATERIALS: TASKS 1, ITEMS A AND B

2.1 Criteria and Approach for Material Evaluation

The purpose of these tasks was to screen potential hot gas chloride sorbent materials and recommend candidate species for further studies. Consideration was given to all materials that exist as stable solids at the gasifier effluent conditions under consideration. A thermodynamic analysis was used to evaluate the potential of materials for reducing total chloride vapor pressures to the ppmV range required by MCFC's at these conditions.

Measured thermochemical data from various literature sources were used to calculate, or estimate, chloride vapor pressures and thus identify non-volatile compounds that can react to remove HCl from a gas stream at temperatures between 800 and 1100 K (980-1520°F) and maintain a low level of chloride in the vapor phase. The two most important criteria that must be met by a successful hot gas chloride cleanup candidate are:

- 1) reduction of HCl level in gas stream to a low level
and
- 2) the reaction product must be non-volatile.

The level required in the first criterion depends on the proposed use of the coal gasifier effluent. Theoretical studies have indicated that substantial equilibrium chloride buildup in the MCFC electrolyte will occur even with sub ppm HCl levels in the gas phase.^{2.1} The effect of this buildup on the MCFC performance cannot be assessed presently, however, some relevant bench scale results are available.^{2.2} They indicate that a level of 100 ppm of HCl in the cathode gas stream causes severe cell deterioration due to corrosion of cell components. At the anode, a level of 10 ppm did not cause observable cell performance loss although some corrosion was noted. Tolerance levels of 10-100 ppm at the anode and less than 10 ppm at the cathode were concluded.^{2.2}

The second requirement is that the cleanup reaction removes the Cl from the gas stream by producing a non-volatile product. (The symbol Cl refers to chlorine atoms in all forms. In the untreated gasifier effluent

most Cl is present as HCl.) As will readily be seen later this requirement puts a severe constraint on the choice of reactants. Other obvious requirements are that the reactant not be toxic or unduly expensive.

Our approach was to compute the equilibrium compositions of gases above different reactant beds. The thermodynamic data base required for these calculations came from several sources. Most of the data were from the JANAF tables^{2,3} and their supplements. Thermodynamic quantities for the alkaline earth carbonates were from the Barin and Knacke tables.^{2,4} Values for KSH, which is a species included in calculations for cases involving H₂S, were estimated as in Ref. 2.5.

2.2 Equilibrium Thermodynamic Analysis

We begin the assessment by considering the volatility of chlorides. Melting and boiling points of several chlorides are listed in Table 2.1. Of the compounds listed only the alkali chlorides, alkaline earth chlorides, and CuCl have boiling points above 1500 K. We use the value of 1500 K for the minimum permissible boiling point in order to assure relatively non-volatile chloride products between 800 and 1100 K. The elements that pass this test are: Li, Na, K, Cs, Mg, Ca, Sr, Ba and Cu. For economic reasons we exclude Cs. Copper compounds are eliminated since they will react with hydrogen according to the reaction: $\text{Cu}_2\text{O} + \text{H}_2 = 2\text{Cu} + \text{H}_2\text{O}$. We consider reactions of compounds of these elements with HCl. The stable compounds of these elements in the gasifier environment are:

Li:	Li ₂ CO ₃	(m.p. 996 K)	
Na:	Na ₂ CO ₃	(m.p. 1124 K)	
K:	K ₂ CO ₃	(m.p. 1164 K)	
Mg:	MgO	(m.p. 3073 K)	
Ca:	CaCO ₃	(d. 1171 K)	T < 1171 K
	CaO	(m.p. 3073 K)	T > 1171 K
Sr:	SrCO ₃	(d. 1613 K)	
Ba:	BaCO ₃	(m.p. 2013 K, 90 atm)	

We note at this point that ZnCl₂ and FeCl₃ are gaseous above 800 K. Both Fe₂O₃ and ZnO have been proposed for hot gas S-cleanup from gasifier

TABLE 2.1

MELTING AND BOILING POINTS OF INORGANIC CHLORIDES

	<u>m.p. (K)</u>	<u>b.p. (K)</u>
AlCl ₃	467	456 (subl.)
BaCl ₂	1198-1235	1833
BeCl ₂	713	820
CdCl ₂	841	1233
CaCl ₂	1045	>1873
CrCl ₂	~1420	~1475 d
CsCl	919	1563
FeCl ₂	943-947	d 1347
FeCl ₃	555	588
PbCl ₂	744	1227
LiCl	887	1633
MgCl ₂	985	1685
MnCl ₂	923	1463
NiCl ₂	1274	1246 (subl.)
KCl	1049	1773
NaCl	1073.4	1686
SrCl ₂	1146	--
ZnCl ₂	556	1005
SbCl ₃	370	553
AsCl ₃	255	403
BiCl ₃	503	720
CeCl ₃	1095	11
CoCl ₂		1322
CuCl ₂	771	1266 (d to CuCl)
CuCl	695	1639
HgCl ₂	550	577

effluent. The presence of HCl in the gas stream during this process would result in the formation of gaseous chlorides which would be carried along in the gas stream. These gas producing reactions may interfere with S-cleanup as well as add metals to the gas flow. Note that ZnCl_2 and FeCl_3 are in addition molten at the temperatures of interest and would cause structural changes in the sorbent (e.g., pore plugging).

The possible cleanup reactions for the above alkali and alkaline earth compounds are:

The standard free energies for these reactions are shown in Figs. 2.1 and 2.2 as a function of temperature. The order of the propensity of alkali carbonates for reaction with HCl is

Note that (1) Li compounds are considerably more expensive than those of Na or K and (2) Li_2CO_3 is considerably less reactive than Na_2CO_3 or K_2CO_3 . We therefore eliminate Li from further consideration.

The standard free energies for reactions of alkaline earth compounds with HCl are shown in Fig. 2.2. The situation is more complicated than for the alkali compounds. Magnesium compounds (MgO) are not reactive and Mg is therefore eliminated and excluded from further discussion. Ca, Sr and Ba compounds show negative free energies for reactions with HCl. However, the values are substantially more positive than those for the alkali carbonates. Therefore the alkali carbonates are expected to be more efficient than alkaline earth carbonates for Cl cleanup.

Fig. 2.1 Free energies of reactions of alkali carbonates with HCl.

Fig. 2.2 Free energies of HCl reaction with alkaline earth compounds.

Calculations were performed to determine the equilibrium composition of gasifier effluent equilibrated over beds of CaCO_3 , SrCO_3 , BaCO_3 , Na_2CO_3 and K_2CO_3 . The pressures of significant chloride and alkali (or alkaline earth) compounds are shown in Figs. 2.3 through 2.7 as functions of temperature. The compositions of the mixtures were chosen in order to simulate typical coal gasifier effluents. These compositions correspond to oxygen/steam fed gasifiers. For these equilibrium calculations the atom ratios determine the compositions of the important species independent of nitrogen added in air/steam gasifiers. The total pressure for these calculations is 1 atmosphere. Since the equilibrium constants for the carbonate sorbent reactions (reactions 1-3 and 5-7) are independent of total pressure, conclusions based on these calculations may be extrapolated to higher pressures for determination of relative compositions. The equilibrium constants for oxide sorbent reactions (reactions 4 and 5) depend upon total pressure causing increased chloride sorption at higher pressures.

We discuss below the specific results for each reactant in order to assess the degree of Cl cleanup and the possibility that Cl containing species will be introduced into the gas flow from the bed.

Na

Vapor pressures above equilibrated Na_2CO_3 /coal gas effluent mixtures are shown in Fig. 2.3. At temperatures between 800 and 1100 K, HCl pressures are between 5×10^{-7} and 10^{-5} atm (0.5 and 10 ppm), respectively. However, above 870 K the primary chloride gas phase species is NaCl . At higher temperatures NaCl vaporization is the limiting factor in Cl cleanup.

K

Vapor pressures above equilibrated K_2CO_3 /coal gas effluent mixtures are shown in Fig. 2.4. Between 800 and 1100 K equilibrium HCl equilibrium vapor pressures are reduced to 5×10^{-8} and 10^{-6} atm (0.05 ppm and 1 ppm). However, the limiting chloride vapor species over this temperature range is KCl . KCl vapor pressures are more than an order of magnitude greater than HCl over most of the temperature range of interest. At 800 K the total chloride

Fig. 2.3 $\text{CH}_{0.8} \text{N}_{0.01} \text{Cl}_{0.03} + 0.05 \text{Na}_2\text{CO}_3 + 1/2(\text{O}_2 + \text{H}_2\text{O})$.

Fig. 2.4 $\text{CH}_{0.8} \text{N}_{0.01} \text{Cl}_{0.03} + 0.05 \text{K}_2\text{CO}_3 + 0.5 \text{O}_2 + 0.5 \text{H}_2\text{O}$.

Fig. 2.5 $\text{CH}_{0.08} \text{N}_{0.01} \text{Cl}_{0.03} + 0.5 \text{BaCO}_3 + 1/2 (\text{O}_2 + \text{H}_2)$.

Fig. 2.6 $\text{CH}_{0.8} \text{N}_{0.01} \text{Cl}_{0.03} + 0.05 \text{CaCO}_3 + 1/2 (\text{O}_2 + \text{H}_2\text{O})$.

Fig. 2.7 $\text{CH}_{0.8} \text{N}_{0.01} \text{Cl}_{0.03} + 0.05 \text{SrCO}_3 + 1/2 (\text{O}_2 + \text{H}_2\text{O})$.

species vapor pressures are about 2.5×10^{-7} atm (0.25 ppm). Due to the rapid increase of KCl vapor pressure with temperature, the degree of Cl cleanup diminishes rapidly as the system temperature is increased.

Ba

Vapor pressures above a $BaCO_3$ bed equilibrated with gasifier effluent are shown in Fig. 2.5. The HCl pressure varies between 8×10^{-6} atm (8 ppm) at 800 K and 9×10^{-5} (90 ppm) at 1100 K. $BaCl_2$ vapor pressures are also shown. The $BaCl_2$ pressure is much less than that of the HCl between 800 and 1100 K.

Ca

Vapor pressures of the significant impurity species above an equilibrated $CaCO_3$ /coal gasifier effluent mixture are shown in Fig. 2.6. The only important vapor species is HCl which varies between 5.6×10^{-4} atm (560 ppm) at 800 K and 2.6×10^{-3} atm (2600 ppm) at 1100 K. $CaCl_2$ vapor pressures are on the order of 10^{-12} - 10^{-6} atm in this temperature range.

Sr

Vapor pressures above an equilibrated $SrCO_3$ /coal gasifier effluent mixture are shown in Fig. 2.7. The only significant chlorine-containing species is HCl which varies between 7.9×10^{-5} atm (79 ppm) at 800 K and 3.6×10^{-4} atm (360 ppm) at 1100 K.

2.3 Comparison of Promising Materials

A general comparison of the Cl cleanup capabilities of alkali and alkaline earth compounds can be made. Alkali carbonates are more reactive (at equilibrium) with HCl than the alkaline earth carbonates or oxides. Therefore, the alkalis reduce the HCl concentration to lower levels. However, the alkali chlorides have significant vapor pressures which are the limiting factor in removing Cl from the gas phase at these temperatures. Additionally, at higher temperatures alkali hydroxide and metal atom concentrations become significant. Alkaline earth chlorides are much less volatile and do not interfere appreciably with Cl cleanup. Concentrations of alkaline earth metal atoms and

hydroxides are insignificant in the 800-1100 K temperature range. Hence, the alkali compounds Cl-cleanup capacity is limited by the volatility of alkali species whereas that of the alkaline earth's capacity is limited by reactivity with HCl. Total equilibrium gas phase chloride concentrations are listed in Table 2.2 for each cleanup scenario.

Gas inlet temperatures of 800 K are considered for use in commercial size MCFC (1 m² size cells)^{1,1} At this temperature Cl levels are reduced below the 10 ppm limit by Na, K and Ba. At 900 K only Na and K reduce Cl below 10 ppm and above 900 K none of the cleanup procedures reduce the Cl levels below 10 ppm. We therefore conclude that for gas flows at temperatures between 800-900 K only alkali carbonate cleanup with Na₂CO₃ or K₂CO₃ is capable of reducing Cl levels below the 10 ppm maximum tolerance level for MCFC application.

2.4 Interference by Chlorides with Sulfide Cleanup

We have also computed equilibrium species for the simultaneous cleanup of S and Cl by K₂CO₃, BaCO₃, SrCO₃, and CaCO₃, respectively. The equilibrium thermodynamic calculations for Cl cleanup are unaffected by the addition of S. The Cl levels are the same as presented earlier. Equilibrium H₂S pressures are presented in Table 2.3 for each reactant. Ba, Ca and Sr are not particularly effective in S removal. The degree of cleanup increases with temperature but even at 1100 K the equilibrium concentrations of H₂S are 500, 210, and 250 ppm for Ba, Ca, and Sr, respectively. At 800 K BaCO₃ does not react with H₂S. K cleans S to below levels of 2 ppm throughout the considered temperature range. These results are virtually identical to those obtained earlier for S cleanup by K without Cl.

2.5 Conclusions of Materials Screening

The primary conclusion of the above thermodynamic analysis is that at 800 K only alkali carbonates, i.e., Na₂CO₃ and K₂CO₃, will reduce Cl levels to the sub-ppm concentrations. Another result of practical importance is that chlorine may interfere with several candidate sulfur sorbents (e.g., ZnO and Fe₂O₃) by reacting to form volatile chlorides. This clearly implies that chloride cleanup should precede sulfur cleanup by these sorbents.

TABLE 2.2

TOTAL EQUILIBRIUM GAS PHASE CHLORIDE CONCENTRATIONS (ppm)
AT DIFFERENT TEMPERATURES

Cleanup Species	Temperature (K)			
	800	900	1000	1100
Na	0.60	5.3	66	610
K	0.30	8.2	120	990
Ca	560	970	1400	2600
Sr	79	170	260	360
Ba	7.6	24	54	95

TABLE 2.3

COMPUTED EQUILIBRIUM H_2S PRESSURES ABOVE GASIFIER
EFFLUENT (atm) AT DIFFERENT TEMPERATURES

Cleanup Species	T(K)			
	800	900	1000	1100
K	1.8×10^{-6}	1.7×10^{-6}	1.6×10^{-6}	1.5×10^{-6}
Ba	NR	6.5×10^{-3}	1.7×10^{-3}	5.0×10^{-4}
Ca	3.9×10^{-3}	9.0×10^{-4}	2.6×10^{-4}	2.1×10^{-4}
Sr	1.8×10^{-2}	3.7×10^{-3}	8.8×10^{-4}	2.5×10^{-4}

3. CANDIDATE SORBENT MINERAL SELECTION AND PREPARATION

3.1 Mineral Screening

Our approach in searching for an inexpensive, alkali containing sorbent has been to consider first naturally occurring minerals which are readily available. We believe these may provide the least expensive solution for the hot gas chloride cleanup problem just as limestone provides viable solutions to SO_2 and H_2S cleanup problems. A useful sorbent mineral was expected to be a stable, porous structure at the temperature of interest, 800 K, in which sodium or potassium can react rapidly with HCl . Only minerals which are readily available in large quantities in the continental United States are worth serious consideration as gas cleanup sorbents. If inexpensive, naturally occurring minerals cannot be found our second approach is to consider synthesizing mixed salts. These mixed crystals or pellets could be made from sodium carbonate or bicarbonate and a second substance such as calcium or magnesium carbonate to provide a porous support for the sodium compound. This second approach is likely to involve an expensive synthesis process not required if a natural mineral is available.

Our initial expectation was that calcination was necessary for rapid reaction of HCl with any sorbent. Calcination, decomposition of a carbonate with evolution of CO_2 , increases the porosities and surface areas of carbonate stones with resulting increases in reaction rate and maximum utilization. As our tests reported in Section 4 show, though calcination improves performance slightly, reaction rates are so fast with Shortite and Trona that calcination is unnecessary and therefore not desirable due to the added cost involved as well as problems associated with sintering and fragility of calcined products.

A thorough search of available alkali containing, carbonate minerals was completed. Many books and lists were surveyed as part of this search, but our most useful source of information was consulting with five geologists and mineralogists. The result of this search is that Shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) has been identified as the most promising candidate for a hot gas chloride sorbent. Information on Shortite occurrence and properties will be presented after a discussion of other minerals we considered.

The leading candidates on our initial list of possible sorbents were Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), Nahcolite (NaHCO_3) and Wegscheiderite ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$). We expected these minerals to calcine forming porous, sodium oxide structures suitable for chloride sorption. Several attempts to produce porosity in Trona at temperatures of interest failed. Communication with Dr. Harvey Ness at Grand Forks Energy Technology Center confirmed our negative results. Dr. Ness and his group have found that Trona and Nahcolite both calcine to become porous but sinter and lose their porosity at temperatures above 575-625 K (572-662°F). Thus none of these three minerals was initially considered useful for our purpose. In addition we learned that the availability of Wegscheiderite is extremely limited. Subsequently Trona reactivity was measured for comparison with that of Shortite when we discovered that calcination was unnecessary.

Our next approach was to search for sodium containing minerals which also contain salts with decomposition and melting temperatures higher than those of sodium carbonate. Our guideline in this search was the rule of thumb that the Tammann temperature, below which sintering is negligibly slow, is usually about one-half of the melting point in degrees kelvin. The most promising candidates contain calcium and magnesium carbonates, but many other minerals were considered.

Three possible sorbents containing alkaline earths are Gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$), Pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and Eitelite ($\text{Na}_2\text{Mg}(\text{CO}_3)_2$). Gaylussite may be a possibility. Its occurrence in Wyoming and Utah is widespread^{3.1} but nowhere in sufficient abundance for economical commercial mining. However, it is possible that commercially economical deposits exist in dried saline lakes in California which are mined for other minerals.^{3.2} We were not able to find any information on the abundance of Gaylussite in California. Pirssonite occurs over large areas in Wyoming and Utah but is not abundant in any locality.^{3.1} Eitelite occurs in several feet thick layers in a few places but the total known quantity is too small to be of interest.^{3.1} Eitelite can be synthesized fairly easily.^{3.3}

Other minerals considered included Dawsonite ($\text{NaAl}(\text{CO}_3)(\text{OH})_2$), Alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and Cancrinite ($\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$). Samples of these were obtained and examined. They were considered too hard and impure to be promising sorbent candidates.

Our leading candidate, Shortite, occurs almost solely in the Green River region in south-western Wyoming. There is no accurate way to estimate the exact amount of Shortite, but it is known to be "ubiquitous and abundant"^{3.1} in the Green River Formation and estimates based on examining many cores indicate amounts on the order of billions of tons.^{3.4} In fact, millions of tons of Shortite are currently being dumped at the sites of five commercial Trona mines near Westvaco, Wyoming, as an unused byproduct of those mines.^{3.5} Shortite availability certainly does not seem to be a limitation in its potential commercial use.

Shortite occurs as roof shaped crystals embedded in a heavy shale which contains low levels of oil. The 1-2 millimeter crystals occur in densely packed layers about 1/2 cm thick separated by shale layers that are about 1 cm thick. Layered beds of this material occur over thousands of feet at depths of 1500-2000 ft over thousands of square miles in Wyoming and Utah.

Shortite is the most promising candidate chloride sorbent. The major problem with this mineral is extracting it in a relatively clean state from the shale in which it naturally occurs. Our approach to this problem is discussed in the next section.

3.2 Preparation of Shortite for use as a Sorbent

It is necessary to extract the Shortite crystals from the shale in which it is found in order to use it as a sorbent or to test it experimentally. Several grinding and sieving methods were tried before settling on a standard mineralogical technique for laboratory use. High density flotation was also tried but the densities of Shortite and its surrounding shale were so nearly equal that clean separation could not be achieved.

The technique we have adopted in the laboratory starts by crushing large pieces down to less than 1/4 inch sizes. We accomplish this by pressing the large pieces hydraulically between two plates but any standard crusher would be preferable. The small pieces are then tumbled in a standard rock polishing tumbler in a dilute aqueous solution of sodium hexametaphosphate ($(\text{Na}_3\text{PO}_4)_6$). The hard, insoluble Shortite crystals act as a grinding agent to disperse the shale. Sodium hexametaphosphate is a standard defloculant that softens the shale for easy grinding. One to two days of this tumbling allows the Shortite crystals to be separated relatively cleanly from the shale using a number 30 sieve.

Of course the crystals obtained by this procedure are not a chemically pure compound. However, they are relatively clean with only small traces of shale adhering. Several determinations have yielded similar results that the naturally occurring rocks contain about 20% Shortite by weight. The Shortite looks like clear, transparent crystals of a pure substance, but we have not analyzed these crystals for impurity levels. Our experiments all use crystals prepared in this way for a close simulation to the substance we expect would be used as a sorbent in a full scale process. The natural size range of 1-2 mm may prove to be suitable for a process with no comminution.

This procedure is suitable and convenient for laboratory use but is not expected to be acceptable on a commercial scale in Wyoming due to the large amount of water that would be required. Not only is the water not readily available but dewatering and back filling with wet materials are expensive and strictly regulated. Recently developed dry ore dressing processes can probably be adopted to extraction of Shortite from shale. Perhaps the petroleum content of the shale can be used as an aid in the separation, using pyrolytic blackening to enhance heating and subsequent sticking to a temperature sensitive adhesive, or oil extraction can provide an economic incentive for another process. Consideration of details of this practical problem is beyond the scope of this contract.

3.3 Calcination of Shortite and Trona:

Task 1, Item C

Calcination of carbonate stones produces porosity and thus enhances the surface area, typically by a factor of 100-1000. Since heterogeneous reaction rates occur on the surface, these rates are greatly enhanced by calcination. We studied calcination of both Trona and Shortite. Calcined Shortite was used in reactivity tests described in the next section.

Our calcination studies were done by heating the stone in a flow of nitrogen in the flow reactor described in the next section. Samples sieved to -16, +20 mesh (mean particle size about 1.0 mm D) were used in all experiments. The furnace was slowly heated until CO₂ evolution was detected by a GC monitor of the exit gas. The temperature was then held constant, or increased by a predetermined amount, until CO₂ evolution ceased. After cooling, pore size distributions of the calcined material were measured with a Micromeritics Model 9300 Pore Sizer. Initial and final weights were always determined for weight loss calculations.

Measurements with Trona and several pure sodium carbonate compounds all gave the result that no porosity was obtained at temperatures above 700 K in spite of loss of CO₂ and H₂O. These results were consistent with results of Dr. Harvey Ness at GFETC that pure sodium oxide compounds sinter and lose their porosity above temperatures in the range 575-625 K (572-662°F).

Shortite has a much higher melting temperature than pure sodium compounds and is expected to have a correspondingly higher sintering temperature. Our tests showed that Shortite calcines above 1025 K with a mass loss of about 29 percent. This decrease in mass corresponds to evolution of 2/3 of the CO₂ as indicated by the reaction

Heating the calcined Shortite to higher temperatures produced no further CO₂ evolution. We sent a sample of our cleaned Shortite to Dr. Ness who obtained

results very similar to ours using TGA. Figure 3.1 shows the TGA results obtained at GFETC.

Upon heating to temperatures above 1075 K (1472°F) the calcined Shortite began to sinter. This was apparent from the observation that Shortite particles were partially stuck together after the run. Sintering is also apparent in the pore size distributions shown in Fig. 3.2. An increase in the calcination temperature from 1050 to 1075 K caused a decrease in the mean pore diameter from about 2 μm to about 0.5 μm . We interpret this to be the result of sintering as surface liquid flows to fill in the pores. The 1050 K curve in Fig. 3.2 corresponds to a total porosity of about 15% with a mean pore diameter of about 2 μm in the 1.0 mm D particles. It was this calcined Shortite that was used for experiments described in the next section.

Another important feature of calcined Shortite is that it is a fragile material. It was impossible to remove the calcined material from the reactor holder without breaking many of the particles into much smaller particles. Unbroken particles could be easily crushed with a slight pressure from a finger. This fragility would be a problem in any fixed or fluidized bed application but may prove to be an advantage for an entrained flow cleanup process. The very small particles required for high reactivity in an entrained flow process could be achieved easily and cheaply from such a fragile material.

Sample:
Size: 48.27 mg
Rate: 20 DEG/MIN
Program: TGA Analysis V1.0

TGA

Date: 28-Dec-82 Time: 14:10:34
File: TGA PROX 1
Operator: RINDT
Plotted: 28-Dec-82 15:38:50

DuPont 1090

Fig. 3.1 TGA measurement of Shortite calcination provided by Grand Forks Energy Technology Center.

Fig. 3.2 Measured pore size distributions for Shor-lite calcined at two temperatures.

4. HCl ABSORPTION EXPERIMENTS: TASKS 1C AND 1E

4.1 Apparatus and Procedures

Reactivity of both Shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) and Trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) with HCl were measured in a fixed bed reactor at 800 K (980°F) as a function of sorbent utilization. Shortite was tested in both raw and calcined forms. HCl was included at impurity levels in a gas flow mixed to simulate the major species concentrations of the effluent of an air blown, coal gasifier. The total flow was as large as possible, consistent with a controlled experiment, to decrease the amount of reaction since preliminary experiments indicated that reaction rates were much larger than anticipated. It was also necessary to reduce the HCl concentration below typical impurity levels, and use small masses of sorbent material to further reduce the reaction rate and obtain data at sufficiently small fractions of HCl reacted that rates could be reduced from the data. An experiment consisted of flowing known mixtures of preheated gases into a sorbent bed of known mass and measuring the exit gas composition, emphasizing HCl, as a function of time.

A diagram of the hot flow reactor used is shown in Fig. 4.1. The hot parts of the flow system were all constructed from 1/4" stainless steel tubing and Swagelok® fittings. The catalyst/sorbent holder in the center of the furnace heated zone was made from 1/2" stainless steel Swagelok® fittings. The temperatures of the inlet gas lines and the tube furnace were controlled to within ± 2 K of preset values. All of the experiments reported here were run with preheat temperatures of 575 K and the furnace temperature at 800 K. Calculations of the thermal accommodation of the gas showed that the gas was heated to within a few degrees Kelvin of the furnace control temperature by the time it reached the sorbent for the temperatures and flows used.

Individual gas flows were measured with Matheson rotameters. Absolute calibrations for one flow rate of N_2 was accurately established by several determinations with a wet test meter. Flows of other gases were measured relative to this known flow using the gas chromatograph, a Carle Analytical GC with H_2 transfer tube integrated and normalized by a Shimadzu Model C-RIA Cromatopac. The GC includes three columns: (1) an 8' 80% Porapak N + 20% Porapak Q (50/80 mesh); (2) an 8' 90% Molecular Sieve 13X, 10% Molecular Sieve 5A and (3) a 3' Molecular Sieve 5A column. A column temperature of 80°C was used with

Fig. 4.1 Diagram of hot flow reactor used for HCl absorption measurements.

26 ml/min of He flow and a TCD detector. This approach gave the most accurate comparison of inlet and outlet compositions since the same instrument was used for both determinations. The GC calibration factors were determined using several different analyzed gas mixtures. The inlet gas mixture was measured for every run with the rotameters set at the correct values and all heaters off so that no reaction could occur.

The inlet gases, controlled by needle valves and measured with rotameters, included only H_2 , CO_2 , N_2 , and N_2 containing a known fraction of HCl. The other gases required to simulate an air blown gasifier composition, H_2O and CO , were formed from H_2 and CO_2 on a catalyst via the reverse of the water-gas shift reaction, $H_2 + CO_2 \rightarrow H_2O + CO$. This approach was adopted to avoid other difficult, inaccurate methods for quantitative addition of steam. The catalyst used was an Engelhard Industries noble metal catalyst supported on an alumina monolithic structure. It was located directly above the sorbent in the same holder. The inlet flows of CO_2 and H_2 were predetermined to give the correct equilibrium mixture to correspond to the gasifier composition.

This approach for preparation of an appropriate gas composition caused an unexpected problem in attaining a good simulation. Since the rate of HCl reaction with the sorbents was much faster than anticipated, it was necessary for the total flow to be so fast that water gas shift equilibrium was not achieved on the noble metal catalyst. The actual composition was measured with the GC for each run. Typical experimental parameters are shown in Table 4.1. Though the H_2O and CO concentrations were well below equilibrium values, we do not believe this difference affects our HCl absorption measurements. This problem emphasizes our conclusion that HCl absorption is extremely fast. The reactions with both Shortite and Trona are faster than the reverse of the water-gas shift on an active noble metal catalyst.

Sorbents to be tested were prepared as described in the preceding sections and supported on a fine mesh stainless steel screen just below the catalyst. All experiments were performed with uniformly sized sorbent particles, sieved to - 16, + 20 mesh or about 1.0 mm diameter. Accurate weights of the sorbent were recorded before and after a test. This information cannot be used, however, to provide a check on the accumulated amount of reaction product

TABLE 4.1

EXPERIMENTAL PARAMETERS

T : 798 K = 525°C = 977°F

Sorbent mass : 0.15 - 1g

Total flow rate : 87, 16 cm³/s

Space velocity : $1.2 \times 10^3 - 50 \text{ s}^{-1}$

$4.4 \times 10^6 - 1.8 \times 10^5 \text{ h}^{-1}$

Gas composition :

H₂ 46%

CO₂ 41%

N₂ 7.8%

CO 2.5%

H₂O 2.7%

CH₄ 0.1%

HCl 66, 356 ppm

since the extent of conversion of carbonate to oxide in the sorbent is unknown. A sensitive test for chloride closure was performed for each run by dissolving a known mass fraction of the used sorbent in nitric acid and using AgCl gravimetric determinations to measure total chloride content.

The inlet HCl flow was the same in all runs, 5.3×10^{-6} moles per minute, carried in a constant, calibrated N₂ flow. This practice leads to the most accurate comparisons between runs and allows exactly the same chloride measurement procedure for each case.

The exit flow of HCl was monitored continuously during a run. The exit flow from the reactor was bubbled through a basic solution in a pyrex flask, as shown in Fig. 4.1, to dissolve all of the unreacted HCl. Measurement of the total chloride concentration accumulated since the start of the experiment was obtained from a chloride ion selective electrode immersed in the flask and read out on an Orion Research Model 701A/digital Ionalyzer. An initial chloride concentration of 5×10^{-5} M in 400 ml was used to start the measurement on a sensitive part of the electrode response curve. A calibration curve was determined with accurately prepared solutions to convert the measured voltage of the electrode to chloride ion concentration. The initial concentration for each run served also to verify that we were on this calibration curve. Solutions were stirred constantly and their temperatures recorded during all measurements.

The ionic strength of the solution was controlled and held constant during calibrations and experiments by adding enough sodium bicarbonate to the solution to make it nearly saturated in CO₂. A 0.5 M NaHCO₃ was used to provide a basic solution for dissolution of the HCl while preventing CO₂ from dissolving. If CO₂ dissolves in the solution, it causes changes in the pH of the solution and consequent drifts in the chloride electrode potential. Some drifts occurred during our measurements but this procedure minimized them. A small amount of Ni(NO₃)₂ was also added to the chloride measurement solution to saturate it with nickel carbonate. The nickel protected the chloride ion electrode from any sulfide impurities in the sorbent by precipitating nickel sulfide.

Chloride concentrations could be measured with a sensitivity of about $1-2 \times 10^{-5}$ M using this technique. This concentration corresponds to 1 ppmV of HCl in the exit gas accumulating for about 12 minutes. Sudden jumps in the chloride concentrations were a serious problem in our initial experiments. This inaccuracy was eliminated by adding the filter containing pyrex wool to the apparatus as shown in Fig. 4.1. This filter trapped very small pieces of used sorbent which broke off and were entrained in the rapid gas flow. Chloride balance determinations showed that these particles contained a very small fraction of the total chloride but still contributed significantly to the chloride carryover if not trapped.

Prior to each set of experiments, it was necessary to passivate the reactor to prevent reaction of HCl with the stainless steel. This was accomplished by filling the sorbent holder with stainless steel balls and flowing 0.1% HCl in N_2 through the reactor at operating temperature for more than two hours. Passivation was established by measuring the exit chloride concentration and verifying that it was constant and equal to the value determined from the flow rate and the analyzed HCl concentration in nitrogen.

4.2 Reduction of Raw Data

The output obtained using the above procedures is a record of the chloride ion electrode potential as a function of time since the HCl flow was turned on. Examples of the raw data from runs using two different amounts of Shortite as sorbent are shown in Fig. 4.2. The constant potential in the 0.9276 gm case over the initial 30 minutes of the run indicates that less than 1 ppmV was coming through the bed. Even this small bed in a rapid flow absorbs sufficient HCl to meet the stated program goal.

The curves shown in Fig. 4.2 are determined by the Nernst equation for the chloride ion electrode. If the chloride flow into the analyzing solution is constant with time, this plot will give a straight line for chloride concentrations above 10^{-4} M with a slope of about 58 mV/decade which depends only on the temperature of the solution. The amount of chloride dissolved in the solution in any time interval can be calculated from the two points on the curve corresponding to that time interval. The equations used in this calculation are presented in Table 4.2. Using the value of 1.32×10^{-5} Molar per minute which would result if none of the HCl reacted we obtain our working equation

Fig. 4.2 Raw data from tests with two masses of Shortite.

TABLE 4.2 HCl ABSORPTION DATA REDUCTION

$$f = \frac{[Cl]_{OUT}}{[Cl]_{IN}} = \text{FRACTION OF HCl } \underline{\text{NOT}} \text{ ABSORBED} = \text{FRACTIONAL CARRYOVER}$$

$$E - E_0 = - \frac{RT}{nF} \ln \frac{[Cl]}{[Cl]_0} \quad (\text{NERNST EQUATION})$$

$$\begin{aligned} \Delta(mv) &= (mv)_2 - (mv)_1 = - 25.68 \ln \frac{[Cl]_2}{[Cl]_1} \\ &= - 25.68 \ln \frac{[Cl]_1 + f \times \text{FLOW (M/MIN)}(t_2 - t_1)}{[Cl]_1} \end{aligned}$$

(FLOW = 1.32×10^{-5} (M/MIN) FOR ALL EXPERIMENTS)

$$f = \frac{[Cl]_1}{1.32 \times 10^{-5} (t_2 - t_1)} \left[e^{\frac{-\Delta(mv)}{25.68}} - 1 \right]$$

$$\text{PERCENT UTILIZATION} = \frac{\text{MOLES Cl REACTED}}{\text{MOLES NO IN SORBENT}} \times 100$$

$$\% U = 100 \times \frac{\left\{ 1.32 \times 10^{-5} t(\text{MIN}) - ([Cl] - [Cl]_0) \right\} V_{\text{SOLN}}}{\# \text{ NO PER FW OF SORBENT} \times \text{SORBENT MASS/FW}}$$

for calculation of f , the fractional HCl carryover. The constant number -25.68 was calculated for $T = 297$ K which is within 2 K of the solution temperatures for all cases.

Equations used to calculate percent utilization are also shown in Table 4.2. Utilization is defined for each sorbent as moles of chloride reacted with the sorbent per mole of sodium in the sorbent. This definition is based on the assumption that the HCl reacts with Na but not Ca. In a mixed crystal such as Shortite there is no way to ascribe any physical significance to this assumption, but it is convenient for consistent comparison of the sorbents based on our conclusions about sodium reactivity. A more significant comparison for a practical process is the mass of chloride reacted per unit mass of sorbent. This can be calculated from the utilization by multiplying $\% U/100$ by the number of sodium ions per formula weight (FW) of sorbent and by the ratio of the chlorine atomic weight to the formula weight of the sorbent.

4.3 Results for Shortite and Trona Performance

Data like those in Fig. 4.2 were used in the equations displayed in Table 4.2 to obtain plots of HCl carryover versus sorbent utilization. This form of data presentation is appropriate for evaluation of a fixed bed application. Further reduction of these data using a model for reactivity of a porous sorbent leads to a more fundamental interpretation of these results as described in the following section.

Results of reduction of the data plotted in Fig. 4.2 for 0.15 grams of raw (i.e., uncalcined) Shortite are displayed in Fig. 4.3. The bed depth of this 0.15 g sample was only about 3 mm, the minimum amount to obtain optical opacity. This extremely thin bed was chosen to allow extraction of rate information for the extremely fast reaction. Preliminary experiments showed that the reaction was so fast that within a reasonable experimental time no measurable HCl came through a bed which filled the holder.

The results shown in Fig. 4.3 are very encouraging. In addition to demonstrating the surprisingly fast reaction with uncalcined Shortite, they show reactivity continuing above 25% utilization. This utilization compares

Fig. 4.3 HCl carryover versus percent utilization for uncalcined Shortite sorbent.

favorably with values for SO_2 absorption by calcined limestone. Both the rapid rate and high utilization were unexpected for an uncalcined sorbent. Relatively small surface area (0.1-1% of the calcined sorbent) and transport restrictions through a product layer were expected to cause severe limitations on the performance of an uncalcined sorbent. High reactivity of raw Shortite is a fortuitous advantage for any application since it allows the elimination of the expensive calcination process as part of sorbent preparation. Observation of such highly reactive solids is unprecedented in any literature we have reviewed. Explanation of this behavior in terms of fundamental physical phenomena will be highly interesting and may lead to other systems with other applications based on the same phenomena.

The effect of bed depth on the HCl carryover can be seen in the results plotted in Fig. 4.4 for beds of 0.15 gm and 0.93 gm of uncalcined Shortite. These samples correspond to thicknesses of about 3 mm and 18 mm contained in the same 1/2" ID holder. It should be emphasized that both of these beds are in a very thin limit in accordance with our goal of obtaining rate information.

No HCl carryover was detected coming through the thicker bed until the utilization exceeded 2% as shown in Fig. 4.4. This result shows that even for this thin bed case the exit concentration of HCl was less than 1 ppmV which is a goal of this program. The inlet HCl concentration was 66 ppmV for both experiments plotted in Fig. 4.4, on the low end of the 50-200 ppmV range expected for gasifier effluents. This low value was necessary to decrease the reaction rate into a measurable range. We expect the rate is proportional to the HCl concentration, so higher inlet levels would increase the fractional fall-off distance in the bed. Higher HCl levels require a thicker bed to maintain the exit concentration below 1 ppmV. Our results indicate that the program goal of 1 ppmV HCl concentrations can be accomplished with a realistic bed thickness.

Our understanding of HCl absorption characteristics in a Shortite bed thick enough for any application is based on the qualitative results that reaction is very fast and goes substantially to completion. We have deduced from the data in Fig. 4.4 that the exponential decay length in a bed is of the order

of a millimeter or two, and, as seen in Fig. 4.3, absorption continues well above 25% utilization. Thus, most absorption will initially occur near the inlet of a bed, leaving most of the bed thickness to act as a trimming bed to achieve very low concentrations. As operation continues, the thin reaction zone will move through the bed, absorbing most of the HCl so that a clean length of sorbent remains for trimming at the exit until just before breakthrough when the whole bed becomes saturated. The inlet region of the bed can continue to function as a low reactivity prefilter until high utilizations are obtained.

Used sorbent particles removed from the holder were routinely examined under an optical microscope. Prior to a run Shortite crystals appeared glossy and transparent. After absorbing HCl they looked somewhat like small clusters of loosely packed snow. In a couple of cases we were able to remove the used sorbent sufficiently carefully that very fine needles remained projecting from the surface. These needles appeared to be about 0.07 mm long with an aspect ratio of about 10. We cannot determine how many needles were knocked off in removing the used sorbent from the holder. It is possible that the chloride product of the absorption reaction is formed mostly as needles, which can explain why the reaction rate remains high even after significant utilizations of an uncalcined sorbent.

A comparison of the performances of calcined and uncalcined Shortite is shown in Fig. 4.5. The HCl carryover is about twice as great with the raw sorbent as with the calcined stone, up to about 30% utilization. Above 30%, the calcined stone seems to lose reactivity very rapidly. This enhanced reactivity due to calcination is explained quantitatively in the next section as resulting from enhanced surface area and porosity. The intrinsic reaction rate is so fast that the HCl transport to an unreacted surface limits the overall reaction rate so that the increased reactivity of calcined Shortite is small compared to the increase in internal surface area. Due to the extremely rapid rate in both cases, the difference between calcined and uncalcined sorbents will be insignificant for any realistic bed depth. The conclusion of this comparison is that raw, uncalcined Shortite reacts so rapidly with HCl that the extra cost of calcination should not be seriously considered for fixed bed applications.

Fig. 4.4 HCl carryover versus utilization for two bed depths of uncalcined Shortite.

Fig. 4.5 HCl carryover versus utilization for calcined and uncalcined Shorttite.

Our measurements emphasized Shortite as it was identified as the most promising candidate sorbent. Measurements were made for Trona under identical conditions to provide a direct comparison with another available mineral. Results of these measurements for uncalcined Trona sieved to -16, +20 mesh are shown in Fig. 4.6. It is clear that reactivity decreases much more rapidly with increasing utilization in this case than it did with Shortite. Our definition of utilization based on HCl reacted per sodium atom gives an advantage in this comparison to Shortite, which has two Na's per formula weight as opposed to three for Trona. However, when compared on the basis of HCl absorbed per gram of sorbent, the relevant comparison for most applications, Shortite still has a significant performance advantage over Trona. This measurement strengthens our conclusion that Shortite is the leading candidate for a hot gas chloride cleanup sorbent.

After each of our performance tests, a sample of the used sorbent was analyzed to determine chloride closure and provide a cross check on our direct carryover measurement. In all cases, we accounted for from 85%-97% of the chloride. The chloride contained in small pieces broken from the sorbent and trapped in the pyrex wool filter were included in these measurements in only one case. Our closure would be improved by including this contribution, but we consider these results provide an adequate check of the validity of the measurements.

In our early planning, we anticipated that alkali containing sorbents would be so expensive that it would be necessary to minimize the quantities required by using a first stage bed of limestone. The limestone bed would absorb some of the HCl at a slower rate than the alkali containing bed and cannot reduce the total chloride level to the required values. While this approach may yet prove advantageous, the amazing reactivity of Shortite and its anticipated low price indicate that limestone will not improve the chloride cleanup. We therefore devoted our efforts to a more complete study of Shortite performance rather than spending effort on tests of a combined bed.

Fig. 4.6 HCl carryover versus utilization for a sorbent bed of 1.2 mm D, uncalcined Trona.

4.4 Summary of Chloride Sorbent Tests

Performance tests have shown that the naturally occurring mineral Shortite is a promising candidate for a hot gas chloride cleanup sorbent. Our measurements have demonstrated that the program goal of reducing the chloride concentration from gasifier effluent values to below 1 ppmV can be attained with Shortite, even in a thin bed. Significant reactivity persisted even at utilizations of about 30% for thin beds. In a thick bed, we expect greater than 50% utilization to be attainable. The most amazing result is that this outstanding performance was achieved with uncalcined stones. These results together indicate Shortite can be an effective, economical chloride sorbent for hot gas cleanup applications.

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5. ANALYSIS OF EXPERIMENTAL RESULTS: TASK 1, ITEM D

5.1 Sorbent Modeling Background

The practical utility of the absorption of HCl by a porous stone cannot be evaluated on the basis of chemical kinetics alone. For example, in the well studied case of SO_2 removal by calcined limestone, there is clear evidence^{5.1,5.2} that the diffusion of SO_2 through porous CaO may be rate controlling. In addition, it has been proposed^{5.3,5.4} that the diffusion of the reactant gas through the solid sulfur deposits within the porous structure is, under some circumstances, rate limiting. The whole process is complicated by the fact that the porous structure itself is dependent upon the degree of calcination and sulfation. These complicated processes must be described in order to predict sulfur or HCl removal rates in diffusion-controlled environments.

Transport theories have been developed to describe diffusion-limited processes in SO_2 cleanup. Hartman and Coughlin^{5.3,5.4} represent the porous CaO by a pattern of small spherical grains surrounded by pores. The SO_2 diffuses through the pores to the grain where it reacts with the CaO . As the CaO reacts, CaSO_4 is formed on the outside of the grain and further reaction requires that the SO_2 must diffuse through the solid phase CaSO_4 . The net reaction is then limited by both the diffusion of SO_2 through solid CaSO_4 and by the diffusion of SO_2 through the pores. The reaction ultimately terminates because the porosity of the stone is reduced to zero and prevents SO_2 from reaching the grain.

In order to develop a theory capable of predicting the rate of gas removal by a porous sorbent stone, we must fully understand the porous structure, the kinetics of the reaction, the diffusion of the reactant gas to and through the porous stone, and the diffusion of the reactant gas through the product deposits. As a first step in the development of such a theory, we have concentrated on the kinetics and gas phase diffusion through the porous sorbent. The theory is valid only at early time, before deposits become appreciable. A clear evaluation of the kinetics for the reaction of CaO with both SO_2 and H_2S was established by Simons and Rawlins^{5.5} and that theory is presently applied to evaluate the performance of Shortite in HCl removal. Below, the model is

described and applied to eliminate the effects of particle size, porosity and bed depth in determining the intrinsic first order reaction rate of HCl with Shortite. It is shown that an HCl molecule is absorbed by Shortite after about 50 collisions with the sorbent stone. Thus, for all practical purposes, Shortite can absorb HCl just as fast as the fluid mechanics can transport HCl to the Shortite.

5.2 Model Description and Data Reduction

The intrinsic rate constant (k) is assumed to be first order in the HCl concentration and measures the grams of HCl gas removed per cm^2 of Shortite surface area per second per atm of HCl partial pressure:

$$k \text{ (grams HCl/cm}^2 \cdot \text{s} \cdot \text{atm HCl) .}$$

Since the number flux of HCl molecules to the Shortite surface is $\bar{n}\bar{V}/4$ ($\bar{n}$ is the number density and $\bar{V}$ is the mean thermal speed), k is readily seen to be

$$k = \rho_G \bar{V} f / 4 p_G$$

where ρ_G and p_G are the gas density and pressure, respectively, and f is the probability of reaction in a single collision. In the units expressed above,

$$k = 10f \text{ gram/cm}^2 \cdot \text{s} \cdot \text{atm} .$$

A typical value of k for sulfur sorption is 10^{-4} or $f = 10^{-5}$. Hence, SO_2 must collide with CaO 10^5 times per reaction. HCl reaction with Shortite will be shown to occur in 50 collisions.

The intrinsic rate constant k , the particle radius a , porosity θ , internal surface area S_p and the mass fraction (C_∞) of HCl in the gas stream are input to the single particle sorption model discussed above and included as Appendix 1.5.5. The single particle model yields the rate of HCl removal (g/s) per gram of sorbent stone ($\dot{M}/M$). Considering a bed of sorbent stones, the rate of change of C_∞ with the coordinate x is written as

$$\rho_G \dot{Q} \frac{dC_\infty}{dx} = - \left(\frac{\dot{M}}{M} \right) \frac{dM_{\text{stone}}}{dx}$$

where $\dot{Q}$ is the volume flow rate through the bed and M_{stone} is the mass of sorbent stone in the bed.

The geometry of the bed enters only through the gas flow velocity in $\dot{Q}$ and the coordinate x is eliminated to yield

$$\frac{dC_{\infty}}{dM_{\text{stone}}} = - \frac{(\dot{M}/M)}{\rho_G \dot{Q}}$$

Numerical integrations yield the fall off of C_{∞} with increasing M_{stone} as illustrated by the example in Fig. 5.1. The results are parametric in k for fixed values of particle size, porosity and volume flow rate. Reactivity data are cross plotted on Fig. 5.1 to infer the intrinsic rate. The intrinsic rate is illustrated in Fig. 5.2. Note the reduction in the rate with increased utilization. This is due to surface deposits of products or depletion of reactants near the surface which are not considered here. The true intrinsic rate is valid only in the limit of zero utilization. Available data lead to the value

$$k = 0.2 \text{ g/cm}^2 \text{ s atm HCl}$$

or

$$f = 0.02$$

which indicates that only 50 collisions are required per reaction. The intrinsic chemistry is rapid and the rate of HCl sorption by Shortite is limited by fluid transport. Hence, HCl will react on virgin Shortite as fast as the gas can flow through the bed.

As shown in Fig. 5.2, data for both raw and calcined Shortite yield the same intrinsic rate constant when reduced by the model. This result shows that the model correctly accounts for the 15% porosity of the calcined Shortite and that the increased reactivity of the calcined stones shown in the last sections is a result of a larger internal surface area, not a change of intrinsic rate constant.

Fig. 5.1 HCl absorption by Shortite.

Fig. 5.2 Rate constant for reaction of Shortite with HCl.

The intrinsic rate constant plotted in Fig. 5.2 can be considered as an effective rate constant at any utilization. This effective rate constant is seen to decrease by a factor of ten as HCl absorption increases the utilization to 12%. At this degree of completion reaction is still occurring in one of every 500 collisions of an HCl with the 12% reacted Shortite, or about 100 times as fast as SO₂ reacts with a typical virgin, calcined limestone. This comparison emphasizes the rapidity of the transport of reactants through any reacted surface layer on the Shortite and leads us to expect useful utilizations that are much larger than those demonstrated in our experiments so far. For comparison, typical maximum utilizations for useful calcined limestone sorbents are about 30%.

6. BED CAPACITIES FOR ALKALI CONTAINING SORBENTS: TASK 1, ITEM D

6.1 Method of Thermochemical Analysis

We have calculated melting points of binary and some ternary reciprocal mixtures containing alkali, carbonate and chloride ions. The purpose of these calculations is to establish ultimate chloride capacities at bed melting for candidate chloride sorbents. In particular, we are interested in the capacities of chloride sorbent beds containing sodium and calcium carbonates. We first discuss the potential melting of beds containing one cation, i.e., mixtures of $\text{CaCO}_3\text{-CaCl}_2$ or $\text{Na}_2\text{CO}_3\text{-NaCl}$. The treatment is then extended to beds containing mixtures of CaCO_3 , Na_2CO_3 and NaCl . This system gives a reasonable simulation of Shortite in a chloride absorption process.

We will illustrate the calculation of the melting temperature for a mixture of x moles of compound AB and y moles of compound A_2C . We assume that the mixture does not form solid solution. The net melting process may be written as:

and the free energy for the process denoted as ΔG_T . At the melting temperature of the mixture, the free energy change is zero, i.e., $\Delta G_T = 0$. This temperature is clearly a function of the mixture composition. For computational purposes the above reaction is divided into two steps:

- a) melting of AB(s) and $\text{A}_2\text{C(s)}$ separately,
- b) mixing of molten AB and A_2C

with respective free energies of ΔG_1 and ΔG_2 . Obviously,

$$\Delta G_T = \Delta G_1 + \Delta G_2.$$

The quantity ΔG_1 is given by:

$$\Delta G_1 = x \Delta G_{\text{AB}} + y \Delta G_{\text{A}_2\text{C}}$$

where ΔG_{AB} is the free energy of melting for AB and $\Delta G_{\text{A}_2\text{C}}$ the same quantity for A_2C . The mixing term ΔG_2 is the sum of an ideal mixing term given by

$$\Delta G_{\text{IDEAL}} = xRT \ln \frac{x}{x+y} + yRT \ln \frac{y}{x+y}$$

and an excess free energy of mixing term $(x+y) \Delta G_{A/B,C}^E$.

The magnitude of ΔG^E is often considerably smaller than the ideal solution free energy of mixing term (for the systems of interest) and in many calculations is safely omitted without appreciable error. In the present calculation of binary systems we retain these terms. We discuss first the $\text{Na}^+/\text{CO}_3^{2-}, \text{Cl}^-$ and then give a modification of the theory applicable to $\text{Ca}^{++}/\text{CO}_3^{2-}, \text{Cl}^-$ systems.

6.2 Calculations for the $\text{Na}^+/\text{CO}_3^{2-}, \text{Cl}^-$ System

Free energy changes for the melting of pure NaCl and Na_2CO_3 are listed in Table 6.1 as a function of temperature. These data are from the JANAF Tables.^{6.1}

Data on excess free energies of mixing for molten salts are not generally available. Amadori^{6.7} measured excess partial molar free energies of NaCl in Na_2CO_3 and deduced the following relation:

$$RT \ln \gamma_{\text{NaCl}} = -0.4 (1 - x_{\text{Cl}^-})^2 / (2 - x_{\text{Cl}^-})^2 \text{ (kcal/mole)} \quad (1)$$

where x_{Cl^-} denotes the anion fraction of chloride ions and is equal to the mole fraction of NaCl in a $\text{Na}^+/\text{Cl}^-, \text{CO}_3^{2-}$ mixture. To convert this quantity to an integral excess free energy, as needed for the calculation of melting temperatures, we use the following equation

$$\Delta G_m^E = x_{\text{NaCl}} RT \ln \gamma_{\text{NaCl}} + x_{\text{Na}_2\text{CO}_3} RT \ln \gamma_{\text{Na}_2\text{CO}_3} \quad (2)$$

where $RT \ln \gamma_{\text{Na}_2\text{CO}_3}$ is computed from the Gibbs-Duhem relation

$$x_{\text{Na}_2\text{CO}_3} \frac{\partial \ln \gamma_{\text{Na}_2\text{CO}_3}}{\partial x_{\text{Na}_2\text{CO}_3}} + x_{\text{NaCl}} \frac{\partial \ln \gamma_{\text{NaCl}}}{\partial x_{\text{NaCl}}} = 0 \quad (3)$$

TABLE 6.1

Free energies of melting for Na_2CO_3 and NaCl (kcal/mole)

T(K)	$\Delta G_m(\text{Na}_2\text{CO}_3)$	$\Delta G_m(\text{NaCl})$
700	2.277	2.185
800	1.857	1.637
900	1.338	1.066
1000	0.756	0.460
1100	0.149	-0.164
1200	-0.452	-0.792

As an example of this procedure we consider fairly dilute chloride solutions so that

$$RT \ln \gamma_{\text{NaCl}} \approx -0.1 (1 - x_{\text{Cl}^-})^2 \quad (\text{kcal/mole}). \quad (4)$$

The solution for for $RT \ln \gamma_{\text{Na}_2\text{CO}_3}$ is written as:

$$RT \ln \gamma_{\text{Na}_2\text{CO}_3} = + \int_0^{x_{\text{NaCl}}} \frac{x_{\text{NaCl}}}{1 - x_{\text{NaCl}}} RT \frac{\partial \ln \gamma_{\text{NaCl}}}{\partial x_{\text{NaCl}}} dx_{\text{NaCl}} \quad (5)$$

which yields

$$RT \ln \gamma_{\text{Na}_2\text{CO}_3} = -0.1 (1 - x_{\text{Na}_2\text{CO}_3})^2 \quad (\text{kcal/mole}). \quad (6)$$

Inserting Eqs. (4) and (6) into (2) yields finally

$$\Delta G_{\text{Na}^+/\text{Cl}^-, \text{CO}_3}^E = -0.1 x_{\text{NaCl}} x_{\text{Na}_2\text{CO}_3} \quad (\text{kcal/mole}), \quad (7)$$

which is in the form of regular solution theory free energy of mixing.^{6.3}

Using Eq. (1) for ΔG^E requires a bit more algebra. The calculations yield:

$$\Delta G_{\text{Na}^+/\text{Cl}^-, \text{CO}_3}^E = - \frac{0.2 x_{\text{NaCl}} x_{\text{Na}_2\text{CO}_3}}{(2 - x_{\text{NaCl}})} \quad (\text{kcal/mole}) \quad (8)$$

which in the limit considered before, $x_{\text{NaCl}} \rightarrow 0$, reduces to the regular solution result, Eq. (7).

The free energy of mixing ΔG_2 is therefore given by

$$\Delta G_2 = RT(x_{\text{NaCl}} \ln x_{\text{NaCl}} + x_{\text{Na}_2\text{CO}_3} \ln x_{\text{Na}_2\text{CO}_3}) - \frac{0.2 x_{\text{NaCl}} x_{\text{Na}_2\text{CO}_3}}{(2 - x_{\text{NaCl}})} \quad (9)$$

(kcal/mole) .

The maximum value of the excess free energy of mixing (Eq. (8)) is approximately - 0.034 kcal/mole, whereas the first term of Eq. (9), the ideal mixing free energy, has a maximum value of - 1.1 kcal/mole at 800 K. Hence we expect $\text{Na}^+/\text{CO}_3^{2-}, \text{Cl}^-$ to behave nearly as an ideal solution. Note again that we have not included the possibility of solid solution formation. No experimental evidence for such compounds was found.

Computed melting points of mixtures of NaCl and Na_2CO_3 are shown in Fig. 6.1 as a function of NaCl mole fraction. The end points correspond to the pure components; $X_{\text{NaCl}} = 0$ is pure Na_2CO_3 and $X_{\text{NaCl}} = 1$ is pure NaCl. This figure clearly shows a large melting point depression. The minimum melting temperature mixture is 0.5 NaCl/0.5 Na_2CO_3 and melts at 890 K which is 184 K below the melting point of pure NaCl. It seems quite clear that a Na_2CO_3 sorbent must be kept below 890 K to prevent sorbent melting. A practical temperature is probably 800 K.

6.3 Calculations for the $\text{Ca}^{++}/\text{CO}_3^{2-}, \text{Cl}^-$ System

We now consider the melting of mixtures of CaCO_3 and CaCl_2 . In this case the free energy of mixing of the pure solids to form a molten salt mixture is given by:

$$\Delta G_2 = RT (X'_{\text{CO}_3} \ln X'_{\text{CO}_3} + X'_{\text{Cl}^-} \ln X'_{\text{Cl}^-}) + \Delta G^E \quad (10)$$

where X'_{CO_3} and X'_{Cl^-} denote anion fractions of carbonate and chloride in the molten mixture and ΔG^E is the excess free energy of mixing. The anion fractions may be written in terms of mole fractions of CaCO_3 and CaCl_2 , X_{CaCO_3} and X_{CaCl_2} , respectively:

$$X'_{\text{CO}_3} = \frac{X_{\text{CaCO}_3}}{2X_{\text{CaCl}_2} + X_{\text{CaCO}_3}}$$

and

$$X'_{\text{Cl}^-} = \frac{2X_{\text{CaCl}_2}}{2X_{\text{CaCl}_2} + X_{\text{CaCO}_3}} \quad (11)$$

Fig. 6.1 Melting points of $Na^+/CO_3^{2-}, Cl^-$ as function of mole fraction NaCl.

The ideal free energy of mixing therefore becomes

$$\Delta G_2 = RT \left[\left(\frac{x_{\text{CaCO}_3}}{2x_{\text{CaCl}_2} + x_{\text{CaCO}_3}} \right) \ln \left(\frac{x_{\text{CaCO}_3}}{2x_{\text{CaCl}_2} + x_{\text{CaCO}_3}} \right) + \left(\frac{2x_{\text{CaCl}_2}}{2x_{\text{CaCl}_2} + x_{\text{CaCO}_3}} \right) \ln \left(\frac{2x_{\text{CaCl}_2}}{2x_{\text{CaCl}_2} + x_{\text{CaCO}_3}} \right) \right] .$$

Note that the maximum value of this term occurs for $x_{\text{CO}_3} = x_{\text{Cl}^-}$ or equivalently $x_{\text{CaCl}_2} = 0.5 x_{\text{CaCO}_3}$.

Empirical values of ΔG^E are not available for $\text{Ca}^{++}/\text{CO}_3^{=}$, Cl^- mixtures. We, therefore, have adopted the same form as for $\text{Na}^+/\text{CO}_3^{=}$, Cl^- mixtures. This is a reasonable procedure since both mixtures involve mixing of carbonate and chloride ions in the presence of a common cation. When this procedure was tested for other mixtures reasonable results were obtained.

Free energies of melting of pure CaCl_2 and CaCO_3 are listed in Table 6.2 as a function of temperature. Values for CaCl_2 were obtained from the JANAF Tables. The values for CaCO_3 were derived from the work of Baker.^{6.4} From those data Lumsden^{6.5} computed the melting point of pure CaCO_3 to be 1613 K. He also gives free energies of melting at several temperatures in the range 1106-1613 K. We have linearly extrapolated those values to lower temperatures. Note that we consider only pure CaCO_3 and do not include the possible formation $\text{Ca}^{++}/\text{CO}_3^{=}, \text{O}^{=}$ mixtures. This is a reasonable assumption since the melting point CaO is substantially higher than that of either CaCO_3 or CaCl_2 and mixtures containing substantial amounts of CaO would have considerably higher melting points.

The results of our calculations are shown in Fig. 6.2 where the melting points of CaCl_2 - CaCO_3 mixtures versus mole fraction of CaCl_2 are plotted. Two features are readily seen: (1) the minimum melting mixture melts at just below 1000 K which is 55 K below the melting point of pure CaCl_2 ; and (2) the melting point curve is quite asymmetric due to the large difference between the melting points of CaCO_3 and CaCl_2 .

TABLE 6.2

Free energies of melting for CaCO_3 and CaCl_2 (kcal/mole)

T(K)	$\Delta G_m(\text{CaCO}_3)$	$\Delta G_m(\text{CaCl}_2)$
700	3.84	1.962
800	3.42	1.465
900	3.00	0.902
1000	2.58	0.287
1100	2.16	-0.367
1200	1.73	-1.051

Fig. 6.2 Melting points of $\text{Ca}^{++}/\text{Cl}^{-}$, $\text{CO}_3^{=}$ as function of mole fraction CaCl_2 .

From a practical point of view, sorbent beds of CaCO_3 may be maintained in the solid phase by restricting maximum temperatures below 1000 K. This is a considerably higher temperature than the melting temperatures of Na_2CO_3 - NaCl mixtures.

6.4 Calculations for CaCO_3 - Na_2CO_3 - NaCl Reciprocal Mixtures

We have simulated the melting of a mixed CaCO_3 - Na_2CO_3 chloride sorbent bed by computing melting temperatures for mixtures containing CaCO_3 , Na_2CO_3 and NaCl . The motivation for these calculations is to estimate the capacity of Shortite ($\text{Ca}_2\text{Na}_2(\text{CO}_3)_3$) as a chloride sorbent. Two points should be made here. Our calculations do not account for the formation of mixed solid solutions and are therefore treated as CaCO_3 - Na_2CO_3 physical mixtures rather than the mixed crystal. We feel, however, this should not be a major problem and will not lead to serious errors. The other point is that in the pretreatment of Shortite it is calcined. The resulting mineral has the composition $2\text{CaO} \cdot \text{Na}_2\text{CO}_3$. We will, however, treat mixtures of $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$. In a gas cleanup environment there is an excess of CO_2 and at ambient temperatures in the range of 800 K CaO will react to form some CaCO_3 . Additionally, the melting temperature of CaO is 3223 K so that it is quite unlikely to melt in the hot gas cleanup environment.

We therefore treat mixtures of CaCO_3 - Na_2CO_3 - NaCl and compute temperatures for which the solid mixtures (of given composition) will melt to form reciprocal molten salt mixtures, $\text{Na}^+, \text{Ca}^{++}/\text{CO}_3^=, \text{Cl}^-$. Note that such a molten salt mixture has three independent components and thus a mixture of x-moles CaCO_3 , y-moles Na_2CO_3 and z-moles NaCl uniquely specifies the composition of the molten salt.

The calculation of the melting temperature proceeds in a similar fashion as for the binary mixtures. The melting process is written in two steps

where in the first step the pure solids are melted separately and in the second the pure molten salts are mixed. The free energy change for the first step, ΔG_1 , is given by

$$\Delta G_1 = x\Delta G_{\text{CaCO}_3} + y\Delta G_{\text{Na}_2\text{CO}_3} + z\Delta G_{\text{NaCl}}$$

and the free energy for the second step, ΔG_2 , is written as

$$\begin{aligned} \Delta G_2 = RT(x_{\text{Na}^+} \ln x_{\text{Na}^+} + x_{\text{Ca}^{++}} \ln x_{\text{Ca}^{++}} + x_{\text{CO}_3} \ln x_{\text{CO}_3} \\ + x_{\text{Cl}^-} \ln x_{\text{Cl}^-}) + \Delta G^E, \end{aligned}$$

where

$$x_{\text{Na}^+} = \frac{2n_{\text{Na}_2\text{CO}_3} + n_{\text{NaCl}}}{2n_{\text{Na}_2\text{CO}_3} + n_{\text{NaCl}} + n_{\text{CaCO}_3}} = \frac{2y + z}{2y + z + x}$$

$$x_{\text{Ca}^{++}} = \frac{n_{\text{CaCO}_3}}{2n_{\text{Na}_2\text{CO}_3} + n_{\text{NaCl}} + n_{\text{CaCO}_3}} = \frac{x}{2y + z + x}$$

$$x_{\text{Cl}^-} = \frac{n_{\text{NaCl}}}{n_{\text{NaCl}} + n_{\text{CaCO}_3} + n_{\text{Na}_2\text{CO}_3}} = \frac{z}{x + y + z}$$

$$x_{\text{CO}_3} = \frac{n_{\text{Na}_2\text{CO}_3} + n_{\text{CaCO}_3}}{n_{\text{NaCl}} + n_{\text{Na}_2\text{CO}_3} + n_{\text{CaCO}_3}} = \frac{y + z}{x + y + z}$$

are ion fractions and ΔG^E is the excess free energy of mixing. We adopt for this term the conformational ionic solution theory form for ternary reciprocal mixtures of unequally charged ions^{6,6}:

$$\begin{aligned} \frac{\Delta G^E}{n_{eq}} = & Y_{Ca^{++}} Y_{Cl^-} \Delta G^O + Y_{Ca^{++}} \Delta G^E_{Ca^{++}/CO_3^=, Cl^-} \\ & + Y_{Na^+} \Delta G^E_{Na^+/CO_3^=, Cl^-} + Y_{CO_3^=} \Delta G^E_{Na^+, Ca^{++}/CO_3^=} \\ & + Y_{Cl^-} \Delta G^E_{Na^+, Ca^{++}/Cl^-} + Y_{Na^+} Y_{Ca^{++}} Y_{Cl^-} Y_{CO_3^=} \Lambda \end{aligned}$$

where the Y's are ionic equivalence fractions:

$$\begin{aligned} Y_{Na^+} &= \frac{x_{Na^+}}{2x_{Ca^{++}} + x_{Na^+}}, \quad Y_{Ca^{++}} = \frac{2x_{Ca^{++}}}{2x_{Ca^{++}} + x_{Na^+}} \\ Y_{CO_3^=} &= \frac{2x_{CO_3^=}}{2x_{CO_3^=} + x_{Cl^-}}, \quad \text{and } Y_{Cl^-} = \frac{x_{Cl^-}}{2x_{CO_3^=} + x_{Cl^-}} \end{aligned}$$

$\Delta G^E_{A,B/C}$ is the excess free energy of mixing of binary mixture A,B/C, n_{eq} is the number of equivalents in the mixture given by

$$n_{eq} = n_{NaCl} + 2n_{Na_2CO_3} + 2n_{CaCO_3}$$

Λ is given by the relation

$$\Lambda = - (\Delta G^O)^2 / 12RT$$

where ΔG^O is the free energy change for the hypothetical liquid phase reaction:

The excess free energy of mixing of $\text{Ca}^{++}, \text{Na}^{+}/\text{CO}_3^{-}$ is available from Lumsden's book^{6.5} and given by:

$$\Delta G_{\text{Ca}^{++}, \text{Na}^{+}/\text{CO}_3}^E = - \frac{1.25 X_{\text{Ca}^{++}} X_{\text{Na}^{+}}}{2 - X_{\text{Na}^{+}}} \quad (\text{kcal/equivalent}) .$$

Pelton et al.^{6.7} have listed excess free energies of mixing for several binary chloride molten salts including $\text{Ca}^{++}, \text{Na}^{+}/\text{Cl}^{-}$ which they give as:

$$\begin{aligned} \Delta G_{\text{Na}^{+}, \text{Ca}^{++}/\text{Cl}^{-}}^E = & (-4.4814 + 0.0013289 T) X_{\text{Na}^{+}} X_{\text{Ca}^{++}} \\ & + (1.6014 - 0.001544 T) X_{\text{Na}^{+}} X_{\text{Ca}^{++}}^2 \quad (\text{kcal/mole}) . \end{aligned}$$

Calculations have been performed over all variations of the three components. The minimum melting mixture is one of 0.45 NaCl, 0.50 Na_2CO_3 and 0.05 CaCO_3 which melts at 879.5 K. Our previous results indicate a minimum melting binary mixture of NaCl- Na_2CO_3 to be 0.5 NaCl and 0.5 Na_2CO_3 melting at 890 K. Clearly the presence of CaCO_3 is of relatively little importance. This is a quite reasonable result because of the much higher melting point of CaCO_3 . Note that if CaO- Na_2CO_3 -NaCl mixtures were considered, the influence of calcium would be further diminished since the melting point of CaO is much higher than that of CaCO_3 .

Thus far we have considered that only the sodium compounds react to form chlorides. This is a reasonable assumption based on the free energies of reaction for reaction of CaCO_3 and Na_2CO_3 with HCl. These values were presented in an earlier report. However, some possible interference could occur if the mixed chlorides $\text{CaCl}_2 \cdot \text{NaCl}$ formed a low melting eutectic. However, this is not the case. The minimum melting eutectic is of composition Na_4CaCl_6 and melts at 922.1 K (Ref. 6.7), well above the binary Na_2CO_3 -NaCl mixtures.

6.5 Summary of Sorbent Melting Point Results

Na_2CO_3 -NaCl sorbents - Minimum melting occurs at 890 K corresponding to 25 percent bed conversion of pure Na_2CO_3 .

CaCO₃ sorbents - Minimum melting occurs at 1000 K at 70 percent pure CaCO₃ bed conversion.

CaCO₃-Na₂CO₃ (Shortite) sorbents - Minimum melting occurs at 880 K at 25 percent conversion of Na₂CO₃ components.

7. CONTROL OF CARBON DEPOSITION ON MCFC ANODES: RATIONALE AND APPROACH:
TASK 2, ITEMS A, B, and C

7.1 Carbon Fouling Problem

Formation of carbon deposits on molten carbonate fuel cell (MCFC) anode materials and inlet hardware can possibly clog the electrode pores decreasing reactivity or completely clog the inlet blocking the fuel flow. Carbon deposition has been observed to occur for gas inlet conditions which would be carbon free if chemical equilibrium were attained.

A standard solution to this problem is to add sufficient steam to the inlet fuel gas to prevent carbon formation. Two penalties are incurred in diluting the fuel with steam. First, heat is required to generate the steam for addition at the MCFC inlet temperature of greater than 800 K (980°F). A more severe penalty is the loss in cell operating efficiency due to the decrease in cell voltage resulting from the change in fuel gas composition. Dr. Gerald Wilemski has used the PSI MCFC performance code to evaluate this loss. Performance curves were calculated for two separate cases; (1) typical compositions used for carbon free operation in experimental cells, and (b) compositions near the equilibrium carbon formation boundary. These calculations showed that a gain in efficiency of 2 to 3 percent (20 mV) can be achieved by operating closer to the boundary. How much of this improvement can be realized depends upon how close the equilibrium boundary can be approached while maintaining carbon free operation.

Practical operating composition boundaries for carbon free operation are necessary for MCFC power plant optimization. These boundaries determine the minimum conditioning of the hot fuel gas required to optimize performance while avoiding carbon deposition.

7.2 Task Objective

The goal of this task was to determine what conditions lead to carbon deposition on MCFC anodes and inlet hardware via the Boudouard reaction (reaction 3 below). Experiments were performed which allowed the formation or absence of carbon deposits to be determined for a large number of gas compositions, metal surfaces, temperatures and pressures similar to those expected in

MCFC power plants. Previously such data were available for only a few conditions from observations of operating cells in which carbon was determined only when catastrophic carbon buildup caused pressure increases in the inlet. Disassembly and cleaning of cells after carbon deposition is time consuming, limiting the amount of data that can be acquired in this way. By using an apparatus which allowed rapid disassembly for examinations we have accumulated a data base for comparison with and evaluation of various criteria for operational carbon deposition boundaries.

Additional experiments were used to establish the relative rates of the reactions involved. These observations provide an understanding that leads directly to recommendations for measures to avoid carbon deposition.

7.3 Approach of These Studies

Understanding of the formation of carbon deposits by the Boudouard reaction requires consideration of the major species in the fuel, H_2 , H_2O , CO , CO_2 and CH_4 , as well as the solid carbon formed. The number of independent reactions required for consideration of equilibrium carbon deposition from the five major gaseous species is determined by Gibbs' phase rule. This rule states that the number of intensive variables required to specify the state of a system at equilibrium is given by $f = c - p + 2$, where c is the number of components required to prepare the system and p is the number of phases. For our case $c = 5$, the five gaseous species, since the solid carbon is formed from them is thus not an independent component. Two phases are present, gas and solid, so that $p = 2$. Therefore, $f = c - p + 2 = 5 - 2 + 2 = 5$. Temperature and pressure are two of the intensive variables that are controlled leaving three independent composition variables. Thus, three, and only three, independent reactions at equilibrium are necessary to completely describe equilibrium carbon formation boundaries.

Any set of three reactions among the six species being considered can be chosen as the three independent reactions. No detailed reaction mechanisms are known that can influence our choice of reactions. We have thus chosen the three simplest global reactions as our complete set of reactions for this discussion. These reactions along with their commonly used names are;

Any other reactions among these species are linear combinations of these three reactions and are not independent. All three reactions are reversible, heterogeneous reactions. Rates of these reactions will depend upon the surface on which they occur. Equilibrium constants for the reactions are independent of the metal surface but depend upon the form of carbon deposited which may be determined by the metal surface.

Our approach to studying this system has been to measure changes in gas compositions at relevant temperatures and pressures as the gases flow over various materials used in MCFC construction. These measurements have been interpreted in terms of progress of reactions (1), (2) and (3) in order to deduce relative rates of these three reactions. This level of qualitative understanding is useful if the reactions selected have very different rates as it leads to a simplified partial equilibrium analysis. In a partial equilibrium analysis we assume the fast reactions remain at equilibrium but the slow reactions do not proceed at all, that is, fast reactions are infinitely fast and slow reactions have zero rates.

The goal is to determine partial equilibrium boundaries on triangular C/H/O composition diagrams which will serve as criteria for carbon deposition in gas mixtures in which the molecular components are not in equilibrium. It should be emphasized that the triangle plot refers to atomic compositions only (C/H/O) and that a gas composition in the equilibrium carbon free region on this plot may have a molecular composition that is far from equilibrium so that carbon can deposit due to kinetic effects. If this approach is adequate it is by far the simplest way to treat a system which is not at full equilibrium. Determinations of detailed mechanisms, rate laws and associated rate constants is a much more ambitious undertaking and beyond the scope of these studies.

7.4 Summary of Carbon Deposition Results

A summary of the results presented in the following sections can be expressed in terms of reactions (1) through (3). On all surfaces tested the Boudouard carbon formation reaction is faster than the water shift reaction which is much faster than the methanation reaction. This result suggests a partial equilibrium correlation of our data in which reactions (1) and (3) remain at equilibrium while reaction (2) is frozen. These results also show that the usual recommendation of adding steam to prevent carbon formation will only succeed if flows are slow enough for the water-gas shift reaction to go substantially to completion. Carbon formation is suppressed when an increase in CO_2 concentration forces reaction (3) backward, whereas water addition increases CO_2 only if reaction (1) proceeds. More direct and reliable suppression of carbon formation can be achieved by CO_2 addition through anode recycle to force the Boudouard reaction backward.

Measurements were made for a range of gas compositions at 875 K (1116°F), 925 K (1206°F), and 975 K (1296°F) at both one and five atmospheres total pressure. Three metal surfaces used in MCFC power plants were studied; stainless steel, nickel and both new and used nickel chromium (Ni(Cr)) anode material. The qualitative kinetic results mentioned above imply that carbon formation is most likely to occur when reaction rates are slow enough that reactions (1) and (2) do not proceed fast enough to prevent excess CO from driving reaction (3) forward. This is more likely to happen on smooth stainless steel or nickel surfaces than on the Ni(Cr) anode material which has a much higher surface area and thus much higher reaction rates. Thus, carbon deposition is more likely to be a problem on inlet hardware than on the anode material. This expectation is enhanced by the realization that the CO concentration decreases as the fuel is consumed flowing across the cell so that the gas composition with the highest carbon forming tendency is at the cell inlet.

8. CARBON DEPOSITION EXPERIMENTS: TASK 2, ITEMS A, B and C

8.1 Apparatus and Procedures

Laboratory experiments were run in our hot flow reactor to determine conditions for carbon deposition on several materials found in MCFC's. With this reactor, different sets of conditions can be run on a two day experimental cycle which allows for disassembly to examine for carbon deposits. A diagram of the reactor is shown in Fig. 8.1.

The high temperature section of this apparatus is constructed from one-quarter inch stainless steel tubing and Swagelok® fittings. A catalyst holder is made from one-half inch Swagelok® fittings in which the catalyst is held by a stainless steel screen. The main reaction zone is heated by a temperature-controlled tube furnace. Temperature-controlled heating tapes are used to preheat all gases to about 300°C prior to mixing and entering the reaction zone. Flows are measured using rotameter flow tubes calibrated with a wet test meter. Flows for all gases except water were also calibrated relative to each other with the same gas chromatograph used in experimental runs. Absolute values were then determined by comparison with the nitrogen flow during the experiment since nitrogen does not react. Exactly the same nitrogen flow was used in all cases to improve accuracy in comparing different runs.

Thermal accommodation calculations showed that, over the range of temperatures and flows used, the gas was heated to within a few degrees Centigrade of the furnace control temperature before reaching the catalyst surface being tested. Thermal conductivity calculations showed that the materials under study remain at a constant temperature equal to the furnace temperature throughout the experiment. The experimental conditions are isothermal within about $\pm 5^\circ\text{C}$.

The effluent gas composition was measured three to five times for each set of conditions with the gas chromatograph. Carbon formation was detected by visual examination of the surfaces after disassembly. The major gas species with the exception of H_2O (H_2 , CO , CO_2 and CH_4) were measured quantitatively with a Carle Model 111-H, 158-A gas chromatograph (GC) the operating conditions for the GC were the same as those specified in Section 4.1. The output of the

Fig. 8.1 Small, high temperature reactor.

GC was recorded and integrated by a Shimadzu Model C-R1A Recording Data Processor. Standard calibration mixtures were used to calibrate the GC output for all gases used. Standard deviations were less than two percent for concentrations of five samples measured over a period of three hours while reactor conditions were held constant. Water was removed by a room temperature trap and calcium chloride drying tube before the gases entered the GC. Calibration runs were made for every set of conditions with the furnace and preheaters off to obtain accurate measures of the unreacted gas with the same instruments.

Attempts were made on several runs to detect hydrocarbon species larger than methane. A Hewlett-Packard Model 5990A Gas Chromatograph/Mass Spectrometer (GC/MS) was used for these measurements a Porapak N column was used in this instrument. This instrument provides an extremely sensitive diagnostic for the larger species which are not expected in measurable amounts based on equilibrium calculations. The experimental configuration including the GC/MS is shown in Fig. 8.2. No C_2 or larger species were detected.

Most of our experiments employed the nickel chromium (Ni(Cr)) material currently being used for MCFC anodes. Both new and used Ni(Cr) anode materials were tested. A new sample of anode material made by Gould was supplied to us by Dr. Charles E. Baumgartner of General Electric Corporate Research and Development Laboratory. Two samples of used Ni(Cr) material were provided by Dr. Dean Pierce of Argonne National Laboratory. Both samples of used anodes had been operated in experimental MCFC's; one was used for 460 hours and washed free of carbonates with distilled water and the other was used for 196 hours and was not washed. The Ni(Cr) was made into X-shaped vanes as shown in Fig. 8.3 for testing. Seven staggered vanes filled the catalyst holder during a run. The new material was tested at 875 K, 925 K and 975 K and at both one and five atmospheres. Tests with the used material were limited by the lack of availability of the material to 925 K and one atmosphere. A set of experiments at 925 K and 1 atm was also run to determine carbon deposition on smooth stainless steel and nickel surfaces. Both materials were tested in the form of one-eighth inch diameter balls held in the catalyst holder.

Fig. 8.2 Small flow tube system schematic.

Ni(Cr) Anode Material

Vanes made from Ni(Cr)
Anode material. Seven staggered
vanes were used in each run.
Note nonuniform carbon deposits.

Fig. 8.3 Vanes made from Ni(Cr) anode material.

Total room temperature flow rates of 11 cm³/s to 39 cm³/s were used. These values are larger than MCFC flows by factors ranging from 2.7 to 9.4 so that extrapolation is necessary before the measured results can be used directly.

8.2 Conditions and Results of Carbon Deposition Experiments

Experiments were run in several different ways with different specific approaches to achieve our overall goal of a qualitative kinetic understanding of realistic carbon deposition boundaries. Modifications of our detailed experimental plans were motivated by our improving understanding of the carbon deposition phenomenology as the work progressed and by our realization of limits imposed by experimental inaccuracies. Our objective throughout the project was to obtain data that seemed most likely to improve our understanding of the phenomenology and thus lead to recommendations for control of carbon deposition in operating MCFC environments.

Gas compositions used in our first few series of experiments were chosen to simulate gasifier effluent compositions on the carbon free side of equilibrium carbon formation boundaries. Our reference composition, on the boundary, had mole fraction ratios of $H_2/H_2O/CO/CO_2/CH_4 = 0.36/0.13/0.33/0.17/0.01$. Gas compositions were varied in experiments on each material in order to determine the relative importance of the reactions among the major species. After each experiment the flow reactor was disassembled to examine the test material for carbon deposits. These experiments on stainless steel, nickel and Ni(Cr) anode material gave the first evidence that the methanation and water gas shift reactions did not proceed significantly in many cases where carbon deposits showed that the Boudouard reaction was fairly fast. These experiments provide results for absence or presence of carbon for specific compositions which are shown compared with partial equilibrium carbon deposition boundaries in Section 10. However, measurements of the progress of individual reactions were limited by uncertainties in subtracting large final concentrations from large initial concentrations to obtain small changes in individual species concentrations.

These inaccuracies were overcome by using initial compositions that were well away from equilibrium to obtain large concentration changes. Methane

was omitted from the inlet gas in most experiments so the final methane concentration became a measure of progress of the methanation reaction. Methane production was very small in all experiments. Carbon dioxide was also omitted from the initial composition in many cases for which carbon deposition was not expected so that final carbon dioxide concentrations gave a direct measure of progress of the water gas shift reaction. In some cases this approach led to global rate measurements which are discussed in Section 10.

In addition to experimental inaccuracies due to subtraction of two large numbers, major problems in data analysis resulted from our inability to know the water concentration accurately. Water cannot be measured with the gas chromatograph so the final concentration was always unknown. Control of initial water flows was also very difficult due to our need to operate at the smallest possible flows to approach MCFC conditions. Uncertainties in initial and final water concentrations prevented accurate comparison of data for many runs with equilibrium calculations. This problem was eliminated in several series of runs by eliminating water from the initial flow altogether and compensating this by addition of extra hydrogen and carbon dioxide to obtain desired atomic mole fractions.

Series of experiments eliminating either steam or carbon dioxide from the initial gas mixture allowed qualitative, or semiquantitative, measurements of the separate reactions under consideration. These series of experiments lead to our unexpected conclusion that the Boudouard reaction is faster than the water gas shift reaction which is in turn faster than the methanation reaction. Data for initial and final compositions as well as carbon formation are presented in the tables in this section which provide a catalogue of conditions for all experiments. Analysis and interpretation of these results are presented in Section 10 after discussion of equilibrium and partial equilibrium carbon deposition criteria in Section 9. The initial reactant flows, temperatures and pressures of the experiments carried out on the various materials are presented in Tables 8.1, 8.3 and 8.5 along with a qualitative indication of the carbon deposit formed. The unit of flow in these tables is cm^3/s of gas measured at 22°C , the calibration condition. Results of the GC analysis of the runs in Tables 8.1, 8.3 and 8.5 are shown in Tables 8.2, 8.4 and 8.6, respectively. The concentrations reported are mole fractions of the effluent gas

TABLE 8.1

EXPERIMENTAL CONDITIONS: STAINLESS STEEL SURFACE

All experiments at 1 atmosphere total pressure

Run	T(K)	Initial Flow (cm ³ /s)						Carbon Deposit
		H ₂	H ₂ O	CO	CO ₂	CH ₄	Total	
7/6	925	10.7	3.8	9.9	5.1	0.32	29.8	Slight
7/10	925	10.9	3.4	9.9	5.1	0	29.3	Lots
7/21	975	10.7	3.8	9.9	5.1	0.30	29.8	Slight
7/27	925	6.7	3.9	6.1	3.2	0.24	20.1	No
8/4	925	6.7	3.9	6.1	3.2	0	13.9	No

Atom Mole Fractions

Run	X _C	X _H	X _O
7/6	0.220	0.436	0.344
7/10	0.224	0.426	0.350
7/21	0.220	0.435	0.344
7/27	0.200	0.459	0.341
8/4	0.198	0.452	0.350

TABLE 8.2

EXPERIMENTAL RESULTS: STAINLESS STEEL

All experiments at 1 atmosphere total pressure

Normalized Concentrations; Dry Analysis					
Run	T(K)	H ₂	CO	CO ₂	CH ₄
7/6	925	0.390	0.403	0.192	0.015
7/10	925	0.401	0.415	0.184	0
7/21	975	0.391	0.407	0.186	0.0156
7/27	925	0.393	0.415	0.170	0.023
8/4	925	0.398	0.424	0.178	0

TABLE 8.3

EXPERIMENTAL CONDITIONS: NICKEL SURFACE

All experiments at 1 atmosphere total pressure

Run	T(K)	Initial Flow (cm ³ /s)						Carbon Deposit
		H ₂	H ₂ O	CO	CO ₂	CH ₄	Total	
7/8	925	10.7	3.4	9.9	5.1	0.28	29.4	Slight
7/14	925	10.9	3.8	9.9	5.1	0	29.7	No
7/23	975	10.7	3.8	9.9	5.1	0.30	29.8	No
7/29	925	6.7	3.8	6.1	3.2	0.24	20.0	No
8/14	925	10.6	3.6	9.1	5.1	0	29.2	Yes
8/21	925	10.7	3.4	9.8	0	0	28.9	Slight
8/27	925	10.6	3.4	0	5.0	0	29.0	No

Atom Mole Fractions

Run	X _C	X _H	X _O
7/8	0.224	0.431	0.345
7/14	0.220	0.430	0.350
7/23	0.220	0.435	0.344
7/29	0.200	0.459	0.341
8/14	0.224	0.423	0.353
8/21	0.191	0.551	0.258
8/27	0.108	0.603	0.289

TABLE 8.4

EXPERIMENTAL RESULTS: NICKEL

All experiments at 1 atmosphere total pressure

Normalized Concentrations; Dry Analysis					
Run	T(K)	H ₂	CO	CO ₂	CH ₄
7/8	925	0.389	0.404	0.182	0.015
7/14	925	0.402	0.413	0.185	0
7/23	975	0.396	0.402	0.187	0.015
7/29	925	0.395	0.411	0.173	0.021
8/14 calib.	925	0.394	0.411	0.195	0
		0.398	0.411	0.191	0
8/21	925	0.385	0.391	0.0006	0
8/27	925	0.393	0	0.188	N ₂ = 0.224
					0
					N ₂ = 0.419

TABLE 8.5

EXPERIMENTAL CONDITIONS: Ni(Cr)

All experiments at 925 K and 1 atmosphere total pressure

Run	Ni(Cr)	Initial Flow (cm ³ /s)						Carbon Deposit
		H ₂	H ₂ O	CO	CO ₂	N ₂	Total	
9/25	NEAT	10.6	3.4	9.9	5.1	0.7	29.7	Yes
9/28	NEAT	10.6	3.4	9.9	5.1	0.7	29.7	Yes
9/30	NEAT	10.6	7.6	9.9	5.1	0.7	33.9	Very slight
10/2	NEAT	10.6	9.4	9.9	9.2	0	39.1	Yes
10/8	NEAT	4.8	9.4	1.57	9.17	3.5	28.4	No
10/12	NEAT	10.6	3.4	9.9	5.1	0.7	29.7	Yes
10/14	NEAT	9.0	7.6	6.3	0	0.7	22.9	Light
10/20	NEAT	4.1	3.4	2.8	0	0.7	11.0	Very slight
10/22	Used unwashed	4.1	3.4	2.8	0	0.7	11.0	No
10/26	Used washed	4.1	3.4	2.8	0	0.7	11.0	No

TABLE 8.5 (Continued)

EXPERIMENTAL CONDITIONS Ni(Cr)

Atom Mole Fractions

Run	x_C	x_H	x_O
9/25	0.224	0.440	0.336
9/28	0.226	0.421	0.353
9/30	0.190	0.460	0.350
10/2	0.197	0.413	0.389
10/3	0.157	0.415	0.428
10/12	0.226	0.421	0.353
10/14	0.206	0.588	0.206
10/20	0.117	0.625	0.258
10/22	0.117	0.625	0.258
10/26	0.117	0.625	0.258

after water was removed. Each entry is an average of three to five values measured over a period of two to three hours. No variation in these concentrations was ever detected as carbon deposited.

No significant changes in the dry gas concentrations were detected for reaction on stainless steel and nickel surfaces; the numbers in Tables 8.2 and 8.4 are the same as the measurement with the furnace off within our two percent uncertainty so that no measurable reaction occurred. The entries in Table 8.4 for CO_2 on the 8/21 run and CO on the 8/27 run provide accurate evidence of this lack of reaction since these gases were not present in the inlet mixture for these runs. The surprising observation is that carbon deposits were formed in six out of these ten runs even though the gas compositions were unchanged. This is strong evidence that the Boudouard reaction is very fast and certainly much faster than the water-gas shift or methanation reactions on these surfaces at this temperature.

Reaction was observed in all cases on $\text{Ni}(\text{Cr})$ anode material and this was the material of greatest initial interest, so most of our data were obtained using this material. The greater reactivity of $\text{Ni}(\text{Cr})$ is mostly due to its much greater surface area than the smooth stainless steel and nickel surfaces. Results of our early $\text{Ni}(\text{Cr})$ experiments are presented in Table 8.6. The corresponding cold furnace calibration is shown with each concentration value as a direct measure of the effect of reaction. The absence of CH_4 from the products of all of the $\text{Ni}(\text{Cr})$ runs, is evidence that the methanation reaction does not proceed even on this active surface since no CH_4 was included in the reactant mix for any of these runs. The changes in species concentrations result only from the water-gas shift and Boudouard reactions.

The $\text{Ni}(\text{Cr})$ runs 9/25 through 10/20 all used the same pieces of new anode material. During the course of these runs a total of 157 hours was accumulated for these pieces in hot reactive flows. The reactivity on this unused material was very low and did not measurably change over the course of all the runs. The 9/25, 9/28 and 10/12 runs were made using identical conditions and showed no significant activity after 142 hours of operation. The observation of carbon deposits on seven out of eight of these new $\text{Ni}(\text{Cr})$ runs shows that the Boudouard reaction is much faster than the water-gas shift reaction just as it is on smooth stainless steel and nickel.

TABLE 8.6

EXPERIMENTAL RESULTS: Ni(Cr)

All experiments at 925 K and 1 atmosphere total pressure

Normalized Concentrations; Dry Analysis					
Run	H ₂	CO	CO ₂	N ₂	CH ₄
9/25	0.397	0.397	0.132	0.074	0
cal.	0.371	0.396	0.158	0.071	0
9/28	0.386	0.389	0.151	0.071	0
cal.	0.371	0.396	0.158	0.071	0
9/30	0.366	0.377	0.187	0.069	0
cal.	0.371	0.396	0.158	0.071	0
10/2	0.356	0.374	0.269	-----	0
cal.	0.342	0.353	0.239	0.066	0
10/8	0.226	0.104	0.451	0.218	0
cal.	0.220	0.103	0.458	0.218	0
10/12	0.372	0.395	0.160	0.072	0
cal.	0.371	0.396	0.158	0.071	0
10/14	0.494	0.385	0.0064	0.114	0
cal.	0.488	0.401	0	0.111	0
10/20	0.226	0.457	0.027	0.290	0
cal.	0.213	0.489	0	0.298	0
10/22	0.310	0.279	0.151	0.260	0
cal.	0.231	0.489	0	0.298	0
10/26	0.339	0.242	0.169	0.247	0.00014
cal.	0.231	0.489	0	0.298	0

The last three runs in Tables 8.5 and 8.6 were made using identical conditions. The 10/20 run tested Ni(Cr) that had aged for about 155 hours but was never used in a fuel cell. The material used in the 10/22 run was used in an MCFC for 196 hours and that in the 10/26 run was used in an MCFC for 460 hours and subsequently washed free of carbonates with distilled water. The total flow used in these three runs was less than half that of the other runs which caused an increase in reactivity. No CO_2 was in the initial gas and negligible amounts of carbon were formed in these three runs so the final CO_2 concentrations are measures of the extents of the water-gas shift reaction.

Several conclusions are apparent in the results of the 10/20, 10/22 and 10/26 Ni(Cr) runs. The tendency to deposit carbon is removed when the water-gas shift reaction proceeds since the gas composition is well within the equilibrium carbon free zone, as will be shown in the next section. The catalytic activity for water-gas shift increases with increasing age and use of the material; it is unclear if the presence of the carbonates on the 10/22 sample had any effect. Even on the most active sample tested, in the 10/26 run, the methanation reaction was negligible.

The data presented in the remaining tables, 8.7 through 8.10, were all obtained using Ni(Cr) anode material that had not been exposed to a molten carbonate electrolyte. Conditions for most of the runs in these tables were chosen to be well away from carbon formation conditions with the intention of determining qualitative, relative reaction rates. The primary variable addressed in these experiments were temperature ($T = 875 \text{ K}$, 925 K and 975 K) and pressure ($p = 1 \text{ atm}$ and 5 atm). Some combination of methane, carbon dioxide and water were omitted in many of the runs to obtain rate information more directly as discussed above. With this goal total flow rate was also an important variable. Carbon formation on the inlet and outlet tubes of the 5 atm . runs forced us to use compositions far from the carbon formation region in most cases to obtain meaningful data.

The format in Tables 8.7 through 8.10 combines initial and final compositions in the same table. Initial and final flows are indicated by brackets with subscripts i or f. Ratios of final to initial flows are presented as a convenient first measure of what reaction occurred in each case. Comparisons with equilibrium calculations for some of these runs appear in Section 10.

TABLE 8.7

EXPERIMENTAL CONDITIONS AND RESULTS: Ni(Cr)

 $p = 1$ atm; no carbon formed in any run

Flows (std cm ³ /s)										
Run	T (°C)	(H ₂) _i	(H ₂) _f	(H ₂ O) _i	(CO) _i	(CO) _f	(CO ₂) _i	(CO ₂) _f	(CH ₄) _f	f _T
5/12	650	15.6	15.8	3.6	17.9	16.6	7.7	7.3	----	44.9
5/14	600	15.6	16.0	3.4	17.9	17.6	7.7	7.7	----	44.9
5/17	700	15.6	15.2	3.4	17.9	17.8	7.7	7.6	0.05	44.9
5/17	600	15.6	15.8	3.7	17.9	17.8	7.7	7.8	0.12	44.9
5/18	647	15.6	16.0	3.4	17.9	17.2	7.7	7.8	0.05	44.9

Final flow/initial flow				
Run	T (°C)	H ₂	CO	CO ₂
5/12	650	1.008	0.928	0.953
5/14	600	1.026	0.982	1.007
5/17	700	0.974	0.991	0.990
5/17	600	1.010	0.990	1.012
5/18	647	1.022	0.961	1.012

$$X_C = 0.254, X_H = 0.381, X_O = 0.366$$

TABLE 8.8

EXPERIMENTAL CONDITIONS AND RESULTS: Ni(Cr)

(runs with no initial CO₂)
 p = 1 atm; no carbon formed in any runs

Flows (std cm ³ /s)											
Run	T (°C)	(H ₂) _i	(H ₂) _f	(H ₂ O) _i	(N ₂)	(CO) _i	(CO) _f	(CO ₂) _i	(CO ₂) _f	(CH ₄) _f	f _T
5/25	703	2.3	4.3	3.5	2.3	5.2	3.2	----	2.1	----	13.4
5/25	650	2.3	4.2	3.6	2.3	5.0	3.2	----	1.9	0.01	13.3
5/25	600	2.5	3.8	3.6	2.3	5.2	3.8	----	1.4	0.02	13.6
5/28	700	1.75	4.63	3.9	2.4	4.65	3.74	----	0.91	----	12.7
5/28	650	1.75	4.00	4.0	2.4	4.65	3.84	----	0.81	----	12.8
5/28	600	1.75	3.37	4.0	2.4	4.65	4.22	----	0.44	----	12.8

Final flow/initial flow				
Run	T (°C)	H ₂	CO	CO ₂
5/25	703	1.91	0.619	---
5/25	650	1.82	0.641	---
5/25	600	1.52	0.729	---
5/28	700	2.65	0.80	---
5/28	650	2.29	0.83	---
5/28	600	1.93	0.91	---

TABLE 8.9

EXPERIMENTAL CONDITIONS AND RESULTS: Ni(Cr)

 $p = 1$ atm; (runs with no initial H_2O)

Flows (std. cm ³ /s)												
Run	T (°C)	(H ₂) _i	(H ₂) _f	(H ₂ O) _i	(N ₂)	(CO) _i	(CO) _f	(CO ₂) _i	(CO ₂) _f	(CH ₄) _f	f _T	C _S
6/3	700	7.51	6.53	---	2.32	4.54	5.51	3.63	2.56	0.051	18.0	(No)
6/3	650	7.42	6.49	---	2.32	4.54	5.43	3.57	2.63	0.10	17.9	(No)*
6/3	600	7.51	6.11	---	2.40	4.48	4.86	3.63	2.84	0.17	18.0	(No)
6/8	650	7.51	7.23	---	2.32	4.36	5.13	3.57	2.67	0.10	17.8	(No)*
6/23	650	7.54	6.70	---	15.6	4.60	5.41	3.64	2.91	----	31.4	Yes
12/10	645	3.20	3.12	---	2.4	---	0.55	1.1	0.39	0.055	----	(No)
12/10	702	3.20	3.24	---	2.4	---	0.63	1.1	0.34	0.009	----	(No)
12/11	601	3.20	3.23	---	2.4	---	0.54	1.2	0.57	0.028	----	(No)

*At the end of these runs no C_S was on the Ni(Cr) vanes but large amounts had formed in the stainless steel exit tube.

Final flow/initial flow				
Run	T (°C)	H ₂	CO	CO ₂
6/3	700	0.87	1.21	0.71
6/3	650	0.88	1.20	0.74
6/3	600	0.81	1.09	0.78
6/8	650	0.96	1.18	0.75
6/23	650	0.89	1.18	0.80

TABLE 8.10

EXPERIMENTAL CONDITIONS AND RESULTS: Ni(Cr)

p = 5 atm

Run	T. (°C)	Flows (std cm ³ /s)									
		(H ₂) _i	(H ₂) _f	(H ₂ O) _i	(N ₂)	(CO) _i	(CO) _f	(CO ₂) _i	(CO ₂) _f	(CH ₄) _f	f _T
11/2	650	12.6	12.4	3.3	4.8	7.2	5.5	----	1.0	0.31	27.9
11/12	658	16.2	12.9	1.9	4.9	----	1.46	4.94	3.24	0.036	26.0
11/12	600	16.2	14.6	1.6	4.8	----	1.22	4.94	3.51	0.071	25.9
11/12	700	16.2	12.7	2.8	4.8	----	2.49	4.86	2.21	0.084	25.8
11/16	649	4.0	2.85	----	4.8	----	0.81	2.2	1.41	0.02	11.0
11/17	650	4.3	3.22	----	4.8	----	1.00	2.3	1.40	0.05	11.4
11/17	708	4.2	2.98	----	4.8	----	1.00	2.2	1.07	0.01	11.2
11/17	649	32.0	28.0	----	4.8	----	3.14	8.9	5.71	0.21	45.7
11/17	704	32.1	25.4	----	4.8	----	3.87	8.8	4.47	0.18	45.7
11/18	605	4.2	3.30	----	4.9	----	0.71	2.2	1.36	0.04	11.3
11/18	604	32.1	27.2	----	4.8	----	2.92	8.8	5.74	0.21	45.7
11/22	650	16.2	12.2	----	4.9	----	1.75	4.94	3.01	0.13	26.1

9. CALCULATION OF EQUILIBRIUM AND PARTIAL EQUILIBRIUM CARBON BOUNDARIES: TASK 2, ITEMS B and C

9.1 Equilibrium Constant for Relevant Form of Carbon

Correlation and interpretation of the data presented in the last section require comparison with equilibrium calculations. Calculations of equilibrium compositions of the gaseous species indicate what values the various species concentrations are changing toward at any given temperature and pressure. Comparisons of species concentrations with equilibrium calculations are made in Section 10. Observations of carbon formation can be interpreted by comparison with calculated equilibrium carbon deposition boundaries. These boundaries provide a first cut criterion whether we expect carbon depositions for any specific conditions.

Carbon deposition boundaries (CDB) can be calculated in terms of atomic mole fractions for full equilibrium or for partial equilibrium for any specified set of reactions. Equations and results of calculations for these two cases are presented in the following two sections. Correct calculations for any case require correct equilibrium constants, or equivalently free energies of formation, for the form of solid carbon deposited. An extensive literature, for example reference 9.1 and references therein, has documented that carbon deposits on metals form as sub-micrometer diameter filaments of a variety of structures. The specific form of filamentous carbon depends on the nature of the metal surface and the conditions. The relevant form of carbon and its thermochemical values are not known for any of the MCFC materials of interest. Thermochemical differences between various filamentary carbon structures are expected to be small but the difference is significant between these values and values for graphite which are frequently used for equilibrium CDB calculations.

The only measurements of equilibrium constants for formation of filamentous carbon from carbon monoxide that we are aware of were reported by Rostrup-Nielsen.^{9.2} These measurements were made for carbon deposited on finely divided nickel supported on alumina. Though this material is not like any of the MCFC materials we tested, Rostrup-Nielsen's measurements provide the best values available and we believe they provide a good approximation to the carbon deposits we studied.

Equilibrium CDB's have been calculated using the equations from the next section for both graphite and filamentous carbon to demonstrate the differences that result for these two forms of carbon. Results of these calculations are shown in Fig. 9.1 for $T = 925$ K and $P = 1$ atm. The significant difference between the two curves in this figure demonstrates the importance of using the equilibrium constant for the relevant morphology of carbon. The difference between these two curves increases with decreasing temperature as shown in the inset of Fig. 9.1 taken from Ref. 9.2.

9.2 Equilibrium Carbon Deposition Boundaries

Calculations of carbon deposition boundaries (CDB) were made using Rostrup-Nielsen's data by using the relationships between mole fractions of the gas phase species involved. The equations can be derived using a simplified nomenclature for the major species: C, CO(1), CO₂(2), H₂(h), H₂O(w) and CH₄(m).

At equilibrium each of the three reactions among these species, (1)-(3), must be at equilibrium, with equilibrium constants defined in terms of mole fractions and total pressure:

$$K_s = \frac{x_2 x_h}{x_1 x_w} \quad (\text{for reaction (1)}) \quad (4)$$

$$K_m = \frac{x_m x_w}{x_1 x_h^3} \frac{1}{P^2} \quad (\text{for reaction (2)}) \quad (5)$$

$$K_B = \frac{x_2}{x_1^2} \frac{1}{P} \quad (\text{for reaction (3)}) \quad (6)$$

For the gaseous species the mole fractions are related by

$$x_1 + x_2 + x_h + x_w + x_m = 1. \quad (7)$$

Fig. 9.1 Equilibrium carbon deposition: Graphite and filamentary carbon on supported nickel catalyst.

Substitution of Eqs. (4) through (6) into Eq. (7) gives

$$1 = X_1 + PK_B X_1^2 + (1 + PK_B X_1 / K_S) X_h + P(K_m K_S / K_B) X_h^2. \quad (8)$$

Equation (8) can be solved for X_h in terms of X_1 as

$$X_h = \{ [1 + 4P(K_m K_S / K_B) + 2PK_B(K_S^{-1} - 2K_m K_S / K_B^2) X_1 + P^2 K_B^{+2} (K_S^{-2} - 4(K_m K_S / K_B^2)) X_1^2]^{1/2} - (1 + P(K_B / K_S) X_1) \} K_B / 2K_m K_S P \quad (9)$$

The physically acceptable values of X_1 , X_h pairs can be used to calculate the remaining X 's using Eqs. (4) through (6).

This procedure can be used to calculate any gas composition lying on the CBD for the particular pressure and temperature of interest. The CBD can be plotted on a standard C-H-O triangular diagram by using the additional relations between the molecule mole fractions (X_i) and atom mole fractions (X_I):

$$X = 2X_1 + 2X_h + 3X_2 + 3X_w + 5X_m \quad (10)$$

$$XX_C = X_1 + X_2 + X_m \quad (11)$$

$$XX_H = 2X_h + 2X_w + 4X_m \quad (12)$$

$$XX_O = X_1 + 2X_2 + X_w. \quad (13)$$

Values used for equilibrium constants in Eqs. (4) through (6) were all taken from Ref. 9.2 and are listed in Table 9.1. Examples of calculations using these equations and data are presented in Fig. 9.2 for three pressures which span the range of interest for MCFC's. Note that the difference between the 5 atm and 10 atm curves is not large. Because of this small difference we expect our qualitative results obtained at 5 atm to be applicable to the 10 atm conditions anticipated for MCFC operation.

TABLE 9.1

EQUILIBRIUM CONSTANTS USED IN CDB CALCULATIONS

T(K)	K_S	$K_m(\text{atm}^{-2})$	$K_B(\text{atm}^{-1})$
800	4.16	34.2	33.5
875	2.59	1.90	5.3
925	1.98	0.357	1.85
975	1.57	0.0792	0.71

Fig. 9.2 Full equilibrium carbon deposition boundary curves for filamentous carbon formed at three pressures.

CDB's calculated over an expected range of MCFC conditions show very little difference as long as full equilibrium is maintained. This conclusion is illustrated in Fig. 9.3 where the darkened area encompasses all full equilibrium curves between 875 K and 975 K and pressures between 1 atm and 5 atm. The narrow waist where all of these curves intersect is close to the region of normal operating compositions which minimizes these differences. The four X's in Fig. 9.3 represent the atom mole fraction compositions of six different coal gasifier exit compositions. The locations of these points with respect to the CDB zone emphasize the narrow parameter range spanned by the full equilibrium curves. Variation over such a small range is not true if full equilibrium is not maintained as shown in the following section.

9.3 Partial Equilibrium Carbon Deposition Boundaries

Our experimental results show that methane concentrations are significantly less than their equilibrium values in all runs. This indicates that a partial equilibrium calculation, with no methanation reaction allowed, is a more accurate approximation of the observed reactions than a full equilibrium calculation. This case corresponds physically to reactions (1) and (3) being fast enough that their equilibria are maintained while reaction (2) is so slow that it essentially does not proceed at all during the relevant residence time.

CDB curves for the no methane partial equilibrium case can be calculated following the same procedure used in the previous section. The appropriate equation results from substitution of equations (4) and (6) into equation (7) with X_m set equal to zero. The resulting equation for X_h in terms of X_1 is

$$X_h = \frac{1 - X_1 - PK_B X_1^2}{1 + PK_B K_s^{-1} X_1} \quad (14)$$

Values for X_2 and X_w are obtained by using equations (6) and (4). Equations (10) through (13) are still correct with $X_m = 0$. Curves calculated for both full and no methane partial equilibrium cases are compared in Fig. 9.4 at

Fig. 9.3 Zone of full equilibrium CDB's for parameter range 875 K to 975 K and 1 atm to 5 atm. Four X's represent effluent compositions from six different gasifiers: Lurgi, Hygas, Gravitating Bed (air blown), Fluidized Bed (oxygen blown), Entrained (oxygen blown) and Molten Salt (air blown).

Fig. 9.4 Comparison of full equilibrium CDB's (solid curves) with CDB's calculated assuming no methane formation (dashed curves) for filamentous carbon at 875 K.

875 K. This comparison shows clearly that carbon depositions can occur over a much larger composition range if the methanation cannot proceed than if full equilibrium is maintained. In particular the partial equilibrium boundaries move into the range of gasifier effluent compositions shown in Fig. 9.3. Some of our experimental results are compared with no methane partial equilibrium calculations in Section 10.

In many of the experimental runs, in fact all of those on stainless steel and nickel, not only was the rate of the methanation reaction negligible but the extent of the water-gas shift reaction was also negligible. The partial equilibrium case which best approximates carbon deposition in this case, if the Boudouard reaction is still relatively fast, is equilibrium of the Boudouard reaction only. CDB's can be calculated for this case using only equation (6). Since X_H and X_W do not enter into equation (6) these calculations require values for these mole fractions from the unreacted inlet gas. The total range of compositions covered by this partial equilibrium case is shown by the two curves in Fig. 9.5 in which all of the H is in the form of H_2 or all H is present in H_2O . MCFC anode inlet gas has a ratio of $H_2/H_2O \cong 3$ so that we would expect a curve about one-quarter of the way from the H_2 curve to the H_2O curve to be a reasonable approximation for this partial equilibrium case.

Clearly, our data show that CDB's are determined by chemical kinetics, not equilibrium, and are thus dependent on total flow rate (space velocity) as well as temperature and pressure. The two partial equilibrium cases plotted in Figs. 9.4 and 9.5 are better approximations to the finite rate chemistry involved than is a full equilibrium calculation. It is important for the equilibrium constant for the correct morphological form of carbon, filamentary carbon, to be used in all of these calculations.

Fig. 9.5 Partial equilibrium boundaries for filamentary carbon deposition in which only Boudouard reaction occurs.

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10. ANALYSIS OF CARBON DEPOSITION EXPERIMENTS

10.1 Approach and Limitations of this Analysis

From a scientific point of view, the problem of carbon deposition from carbon monoxide presents a system of three simultaneous, heterogeneous reactions among six species, one of which is a solid. The fascinating morphological shapes of carbon formed on metallic surfaces affect the thermochemistry of the carbon deposits. For each form of carbon, determined by the metallic surface and conditions, five degrees of freedom are required to specify the equilibrium state for any initial gas composition. For normal MCFC operating conditions and residence times equilibrium is not established so that rates of each of the three reactions involved must be considered in addition. The large number of variables involved in a study of this phenomenon lead to complexity in analysis of experimental results. The qualitative, phenomenological nature of this investigation was determined by this complexity.

Our approach has been to make sufficient measurements of various types, guided by considerations of the underlying chemistry and physics, to enable determination of the most important phenomena that must be understood for controlling carbon deposition in an MCFC power plant. We have not reached our goal of a complete set of practical carbon deposition boundaries for conditions that span the operating parameter range of interest. However, analyses in this section of the extensive data presented in Section 8 lead to several new, qualitative understandings that suggest recommendations for practical, ameliorative approaches to cost effective carbon control.

Several inherent limitations in application of these results to MCFC's should be reiterated as a caution. None of our experiments used metals flooded with molten carbonate electrolyte as the anode exists in a cell. Two runs with used Ni(Cr) anode material showed that even after rinsing the material, use in a cell enhanced catalytic activity for the water gas shift reaction which moves the effective carbon deposition boundary toward the equilibrium boundary. Thus, carbon deposition is less likely on operating anode materials than on the Ni(Cr) materials in our study. Also, kinetic enhancement of Boudouard carbon deposition should be less on all surfaces in an MCFC than in our study due to

the lower gas flow rates. Our flow rates ranged from three to five times the values used in MCFC's, exaggerating non-equilibrium effects. This exaggeration has the compensating advantage of enabling more definite observations of carbon fouling phenomena within reasonable times.

10.2 Comparisons with Carbon Deposition Boundaries

Gas compositions used in our first few series of experiments contained all of the species, with the exception of methane in some runs, and were varied near the carbon free side of the equilibrium CDB. These inlet gases were prepared near their equilibrium compositions so very little change occurred in the concentrations of each species. Data for these runs are in Tables 8.1 through 8.6.

Observations of carbon deposition for the runs of Tables 8.1 through 8.6 are compared with both full equilibrium and no methane, partial equilibrium CDB's in Figs. 10.1 through 10.3 for the three metal surfaces studied. In these figures solid curves are full equilibrium carbon boundaries and dashed curves are the partial equilibrium boundaries. Filled symbols refer to carbon formation and open symbols indicate no carbon formation. The extra 5 atm curves in Fig. 10.2 are included to show the effect of pressure on the calculated curves. All data shown in Figs. 10.1 through 10.3 were taken at 1 atm.

It is obvious from the comparisons in Figs. 10.1 and 10.2 that the no methane, partial equilibrium curves correlate well with observed carbon formation on both smooth stainless steel and smooth nickel surfaces. Two points in the comparison for the Ni(Cr) case do not correlate with the partial equilibrium boundary prediction. The two points which do not agree with this prediction are for the 9/30 and 10/2 runs in Table 8.5. These two runs had the highest total flows of the runs in this series. Perhaps the water gas shift reaction rate involved is very close to maintaining a carbon free condition so that a small increase in flow rate prevents this reaction from removing CO fast enough. Since fuel cell flow rates are significantly slower than any flow rates in this series, these deviations may not be relevant to MCFC operating conditions.

Fig. 10.1 Comparison of carbon formation on stainless steel with CDB's. The solid curve is for full equilibrium and the dashed curve is for the no methane, partial equilibrium case. Both curves and all data points are for 925 K and 1 atm. Filled symbols mean carbon formed, open symbols mean no carbon.

Fig. 10.2 Comparison of carbon formation on nickel with CDB's. The solid curves are for all equilibrium and the dashed curves are for the no methane, partial equilibrium case. All curves and data points are for 925 K. The data were taken at 1 atm. Filled symbols mean carbon formed, open symbols mean no carbon.

Fig. 10.3 Comparison of carbon formation on Ni(Cr) with CDB's. The solid curve is for full equilibrium and the dashed curve is for the no methane, partial equilibrium case. Both curves and all data points are for 925 K and 1 atm. Filled symbols mean carbon formed, open symbols mean no carbon.

No methane was detected in any of the experiments of Tables 8.1 through 8.6 which had no initial methane. This observation combined with the good correlations in Figs. 10.1 through 10.3 suggest very strongly that the no methane, partial equilibrium carbon deposition boundaries are appropriate for predicting carbon fouling in MCFC's. This hypothesis seems valid particularly for smooth stainless steel and smooth nickel surfaces, where we expect the most severe carbon fouling problems to occur.

Attempts to obtain data similar to those of Tables 8.1 through 8.6 at 5 atm failed due to very rapid carbon deposition in our inlet tube when compositions were close to the CDB.

10.3 Comparisons with Equilibrium Species Concentrations

Results of the experiments in Tables 8.1 through 8.6 suggested that the Boudouard reaction is very fast and that the methanation reaction is too slow to proceed significantly. However, since the initial compositions were all close to equilibrium compositions, changes in species concentrations were mostly too small to be detected with our experimental accuracy so that the progress of individual reactions could not be determined.

The compositions of all of the runs listed in Table 8.7 were in the equilibrium carbon forming region yet carbon deposits were not observed in any of these runs, over the temperature range from 875 K to 975 K. The total flow rate for all of these runs was much larger than those for the experiments of Tables 8.1 through 8.6. Since no other variable was very different in this series, we suspect that this fast flow did not allow time for even the Boudouard reaction to occur. The implication of this is that the effective Boudouard reaction rate is faster, but not very much faster, than the water gas shift. But these results still do not allow determination of relative reaction rates.

The series of runs reported in Table 8.8 was carried out with no initial CO_2 or CH_4 and with carbon free compositions. For these conditions any CO_2 produced is a measure of progress of the water gas shift reaction and any CH_4 produced is a measure of the methanation reaction. All of these runs started

out rich in CO and H₂O while initial H₂ was varied in two similar series. Total flows were approximately constant for all of these runs. Results for the ratios of the final concentrations to the full equilibrium concentrations for each run are given in Table 10.1.

The comparisons of measured final concentrations to calculated equilibrium concentrations in Table 10.1 clearly show that progress of the methanation reaction, measured by the CH₄ concentration, was negligible. Progress of the water gas shift reaction, measured by the CO₂ concentration, was substantial in all cases, increasing with temperature, but did not reach equilibrium even at 975 K. The conditions for the 925 K experiments were very similar to runs listed in Table 8.5 for Ni(Cr) except that the total flows were lower by a factor greater than two. Yet in the Table 8.5 runs the Boudouard reaction proceeded. Boudouard carbon deposition did not occur in the Table 8.8 runs because the compositions were well within the carbon free zone. This comparison shows that the Boudouard reaction is faster than the water gas shift reaction on Ni(Cr). Clearly the methanation reaction is much slower than either of the other reactions on Ni(Cr).

No measurable chemical reactions occurred on the stainless steel and nickel surfaces other than the Boudouard reaction. The reactions on the used Ni(Cr) anode material can be compared with equilibrium calculations to assess the effect of being used. Table 10.2 shows the measured molecular compositions compared with full equilibrium values for three different Ni(Cr) samples run under identical conditions. None of the samples is sufficiently active to bring the gas close to equilibrium, but we see that the samples used in cells are more active. The measured values are not close to the values for the partial equilibrium case with methane excluded; these partial equilibrium values are only slightly different from the full equilibrium values for this case.

Similar comparisons can be made using results at 5 atm for Ni(Cr) anode material using the set of 11/12 runs in Table 8.10. In this case CO was omitted from the initial gas mixture instead of CO₂ due to problems with carbon formation on the stainless steel inlet tube. Thus the final concentration of CO is a measure of the water gas shift reaction in the reverse direction from

TABLE 10.1

MEASURED CONCENTRATIONS COMPARED TO EQUILIBRIUM CONCENTRATIONS

(Using 1 atm data from Table 8.8)

Final concentration/equilibrium concentration					
Run	T(K)	H ₂	CO	CO ₂	CH ₄
5/25	975	1.02	1.01	0.87	----
5/25	925	1.05	1.28	0.72	0.05
5/25	875	1.07	2.87	0.44	0.04
5/28	975	1.13	1.33	0.390	----
5/28	925	1.08	1.66	0.333	----
5/28	875	1.07	2.62	0.157	----

TABLE 10.2

MEASURED COMPOSITIONS COMPARED WITH EQUILIBRIUM CALCULATIONS

Ni(Cr) anode material, new and used

T = 925 K, P = 1 atm, flow velocity = 32 cm/s

Species	Equilibrium Composition		10/20 run Neat Ni(Cr)	10/22 run Used 196 hours	10/26 run Used 460 hours Washed
	Full	Dry			
H ₂	0.475	0.623	0.318	0.419	0.452
H ₂ O	0.238	-----	-----	-----	-----
CO	0.125	0.164	0.644	0.377	0.323
CO ₂	0.135	0.177	0.038	0.204	0.225
CH ₄	0.027	0.035	0	0	1.9x10 ⁻⁴
C ₂ H ₆	2.1x10 ⁻⁷	2.8x10 ⁻⁷			
C ₂ H ₄	1.8x10 ⁻⁸	2.4x10 ⁻⁸			
C ₂ H ₂	1.1x10 ⁻¹¹	1.4x10 ⁻¹¹			
C(s)	0	0	very slight	0	0

the way we have been writing it. The CH_4 concentration is still a measure of the methanation reaction or the equivalent reaction which produces CH_4 from CO_2 , $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$.

Clearly the results of this comparison, shown in Table 10.3, show that CO is produced by the reverse of the water gas shift reaction much faster than it can be consumed to produce methane. We conclude that at 5 atm the same result is true that we found at 1 atm, the water gas shift reaction is much faster than the methanation reaction.

10.4 Apparent Rate for Water Gas Shift Reaction

The qualitative behavior that has emerged from the discussion in Section 8.2 and the last two sections is that in most circumstances relevant to MCFC's the Boudouard reaction can be considered fast, the methanation reaction can be assumed not to proceed and the water gas shift reaction is in an intermediate region where its progress can vary considerably. Since the water gas shift reaction must remove CO to prevent carbon deposition, the kinetics of this reaction can be critical for carbon fouling. Several runs were designed to allow measurement of an effective rate for this reaction to provide a parameter that may be useful in future planning. No attempt was made to determine the rate law for the water gas shift reaction so the rate we extract from these data is useful in a semi-quantitative way only and only for compositions near those of the measurement. We have, however, observed a trend with temperature which indicates how rapidly problems develop as temperatures decrease.

CO_2 and CH_4 were omitted from the initial compositions and the composition of the remaining gases was not in a range where solid carbon was formed. This meant that CO_2 formation is a direct measure of progress of the water gas shift (wgs) reaction. If flows are fast enough that this progress is not too great, an initial rate can be extracted from the final CO_2 concentration using the method described at page 88 of reference 9.2.

We followed Rostrup-Nielsen's method for determining a rate of a reversible reaction approaching equilibrium and make the additional assumption that

TABLE 10.3

MEASURED COMPOSITIONS COMPARED WITH EQUILIBRIUM CALCULATIONS

(using 5 atm dta from Table 8.10)

		Final concentration/equilibrium concentration			
Run	T(K)	H ₂	CO	CO ₂	CH ₄
11/12	875	8.66	170	1.02	0.005
11/12	933	4.75	63.8	1.01	0.003
11/12	975	3.04	35.5	0.674	0.008

in the initial slope region of CO_2 production the wgs reaction is pseudo-first order if only the space velocity is varied. Even in complex catalytic systems it has been found that the rate of approach toward equilibrium can be expressed in terms of the degree of conversion of the reactant, in this case CO. Degree of conversion C is defined at any time for this case by

$$C = \frac{\text{CO}_2 + \text{CH}_4}{\text{CO} + \text{CO}_2 + \text{CH}_4} = \frac{(\text{CO}_2)_f}{(\text{CO})_i} \quad (15)$$

and a rate can be expressed in terms of catalyst weight W and inlet flow of CO as

$$\text{rate} = (\text{CO})_i \frac{dC}{dW} \cong k_a \left(1 - \frac{C}{C_{eq}} \right) \quad (16)$$

In this equation k_a is an apparent rate constant and C_{eq} is the equilibrium value of the conversion being approached by the reaction. With the rate set equal to $d(\text{CO}_2)/dt$ this equation can be integrated to give an expression for the apparent rate constant,

$$k_a = \frac{(\text{CO})_i C_{eq}}{W} \ln \left[1 - \frac{C}{C_{eq}} \right]^{-1} \quad (17)$$

We have used this equation to calculate apparent rate constants with the full awareness that the values obtained should only be used to compare relative rates for different catalysts or temperatures in the same composition range. The temperature dependence is assumed to have the usual Arrhenius form with activation energy E_a

$$k_a \propto \exp(-E_a/RT) \quad (18)$$

Analysis of the 6/3 runs from Table 8.9 and the 11/12 runs from Table 8.10 using this approach gives the results for the temperature dependence plotted on an Arrhenius plot in Fig. 10.4. Again we emphasize that these numbers should be used only to approximate rates on new Ni(Cr) anode materials.

Fig. 10.4 Temperature dependence of an apparent rate constants for the water gas shift reaction on new Ni(Cr) at 1 atm and 5 atm.

10.5 Summary and Conclusions of Carbon Deposition Experiments

Bench scale experiments have been used to gain a qualitative understanding of carbon fouling of MCFC hardware. Our measurements show that carbon deposition is determined largely by the kinetic behavior of the three reactions involved. A no methane, partial equilibrium carbon deposition boundary seems to be a useful criterion for carbon fouling. This is true because on all surfaces tested we found the Boudouard reaction is faster than the water gas shift reaction which is much faster than the methanation reaction at MCFC conditions.

Carbon deposition is not expected on Ni(Cr) anode materials, especially after initial stages of operation, because rates for the water gas shift reaction are adequate on this material to stay close to partial equilibrium. In addition, the reaction of the fuel gas as it traverses the fuel cell electrode reduces CO concentrations, moving the gas mixture away from the carbon forming zone. Carbon deposition is most likely to occur on the smooth metallic surfaces of the inlet hardware where reaction rates for the water gas shift reaction are slow.

Suppression of carbon deposition can be accomplished even if the water gas shift reaction is slow by CO₂ addition rather than the usual H₂O addition. CO₂ can be added economically as anode gas recycle in an MCFC power plant.

Improved catalytic activity of any of the surfaces in an MCFC will reduce the possibilities of carbon deposition. Catalysts in the cell for internal reforming of methane should be especially effective by enhancing the methanation reaction so that full equilibrium carbon deposition boundaries apply as opposed to no methane, partial equilibrium boundaries. Inclusion of a high surface area metallic catalyst coating on inlet hardware components may eliminate carbon deposition in this likely problem region.

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