Task 3.17 - Hot-Gas Cleanup

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SUBTASK 3.17 – HOT-GAS CLEANUP

1.0 INTRODUCTION

Emerging power systems, including pressurized fluidized-bed combustion (PFBC) and integrated gasification combined cycle (IGCC), being demonstrated under the U.S. Department of Energy (DOE) Clean Coal Technology Program and other technologies at earlier stages in their development will, over time, present opportunities for achieving generating efficiencies of 50% or higher, with stringent control of SO₂, NO_x, and particulate emissions. At their present stage of development and demonstration, these coal-fired technologies offer superior environmental performance for repowering, cogeneration, and greenfield projects at costs comparable to pulverized fuel firing with full stack gas cleaning, but at a considerably higher technical and financial risk. The development of hot-gas cleaning technologies that are less expensive and capable of operating at higher temperatures and pressures will greatly reduce the risks associated with PFBC and IGCC.

Catalytic tar cracking is another issue that advanced power systems are facing at this time. Tars and oils produced during combustion or gasification of coal result in a contaminated gas stream that fouls equipment and makes direct utilization of the stream impractical. Tar production in the gasification of coal is deleterious to the operation of downstream equipment, including fuel cells, gas turbines, hot-gas filters, and pressure-swing adsorption systems, all of which are candidate technologies for use as or in small power generation systems. Cracking of these tars into smaller hydrocarbons is a very important technical issue to be addressed. The oils tend to coat surfaces and enter pores and voids in hot-gas filters and pressure-swing sorbents, causing reduction in efficiencies during hot-gas cleanup. In addition to the problems caused by the oils, the tars, with their high dew points, condense on the surfaces of power generation equipment. Turbine blades can become coated with this condensate, resulting in deviation from acceptable aerodynamics and in metal corrosion. Deposits of tars on fuel cell components result in loss of cell efficiency. Tar coatings on gas separation equipment such as membranes, molecular sieves, and filters reduce gas cleanup efficiency. These are some of the operational complications that need to be addressed by this subtask on hot-gas cleanup.

2.0 **OBJECTIVES**

The programmatic goal in advanced power systems is to develop advanced methods for gas stream cleanup in combustion and gasification systems, using in situ and back-end technologies. The characteristics of the fuel, its ash, and sorbents are evaluated to determine their impact on overall performance, including the reduction of gas stream contaminants. Objectives for the work performed under this subtask included the following:

- Identify effective means for hot-gas cleanup and testing in-bed sorbents for accomplishing 99% alkali capture as well as effective capture of sulfur and chlorine during PFBC.
- Develop catalysts and effective operating ranges for removing tar from gasification process streams.

The two activities outlined below correspond to the above-stated objectives for Subtask 3.17.

2.1 Alkali Sorbents

PFBC has been identified as a promising technology for the future. The objective of this task was the development of sorbents for in-bed alkali, sulfur, and chlorine capture to reduce or eliminate problems on back-end equipment. Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (1400° to 1850°F). The alkalies are absorbed on the surface and diffuse into the bulk of the alkali getter. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a getter to capture alkali in the bed reduces the need for downstream alkali capture devices. Sulfur capture on the getter also reduces the amount of dolomite needed to meet sulfur emission standards. Chlorine can also be captured by certain types of sorbent. These systems are not without potential problems, however. Modification of the aluminosilicate matrix will lower melting points and could cause sintering and agglomeration problems. This and other potential complications were addressed.

During FY95, a limited number of alkali sorbent tests were performed. A capture of vapor-phase alkali of 93% was accomplished using kaolin. The final sodium level of 270 ppb is still higher than the 24 ppb recommended by turbine manufactures. The kaolin was also found to significantly reduce agglomeration. This and other promising sorbents were tested in the pressurized fluid-bed reactor.

The fundamental question to be answered by this task is whether in-bed alkali sorbents are technically feasible for capturing alkali in PFBC systems. The impacts of in-bed sorbents on reducing convective pass fouling and blinding of ceramic filter elements were also investigated. Any related operating problems and improvements in sulfur capture were noted.

2.2 Catalytic Tar Cracking

Previous and current work has involved selecting and screening catalysts that are available and relatively inexpensive. Synthetic montmorillonite, a pillared laboratory-prepared clay impregnated with nickel, was initially tested in combination with the feed in the reactor bed and as a separate bed. In-bed catalysis proved to be less effective in cracking tars than tar contact with catalyst in a separate bed. A separate bed of either zeolite or dolomite was more effective in cracking tar than the Ni-impregnated synthetic montmorillonite. Although the dolomite cracked the tar, decrepitation of the hot solid resulted in loss of catalyst through gas steam entrainment. In this study, the effect of selected operating conditions for the chosen catalyst was addressed. The effect of catalyst-tar contact time at approximately 900 K and 100 psig on catalytic tar cracking by zeolite impregnated with < 1% Pt was determined. The results from the study provide an uncomplicated means of tar removal from gas streams with reduction in the size of the hydrocarbon content of the usable gas stream.

The work was carried out on the integrated bench-scale gasifier (IBG) and involved evaluating the effect of the catalyst on the cracking of tars. The tars that escaped the fluidized bed of the reactor were cracked in catalyst beds of depths designed to produce contact times of 0, 1, 2, and 3 seconds. The effect of contact time (bed depth) was determined.

3.0 ACCOMPLISHMENTS

3.1 Capture of Alkali During PFBC Using In-Bed Sorbents

The work for this task was performed by Michael Mann as his doctoral research for a Ph.D. in energy engineering. The outline of his work is presented here along with the conclusions from his work. Details are included in his dissertation which is presented as Appendix A to this project report.

3.1.1 Research Outline

PFBC has been identified as a promising technology for the future; however, there are a number of obstacles for maximizing its potential. These include removal of 1) fine particulates to eliminate erosion and deposition on turbine blades, 2) alkalies which can lead to corrosion of turbine blades and blinding of ceramic filters, 3) sulfur at very high sorbent utilization efficiencies, 4) halogens that can lead to corrosion, and 5) toxic metals that were specified in the 1990 Clean Air Act Amendments. The primary focus of this research was the removal of alkali from PFBC flue gases to a level specified by turbine manufactures. The target level was less than 24 parts per billion by weight (ppbw). Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (1400° to 1850°F). The alkalies are absorbed on the surface and diffuse into the bulk of the alkali getter. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a getter to capture alkali in the bed reduces the need for downstream alkali capture devices. Other goals were to investigate the potential for simultaneously removing SO₂ and Cl from the PFBC gas stream.

Several side benefits were anticipated, and the goal was to demonstrate these. A reduction in the amount of fine particulate was expected when alkali was removed from the bed, since condensation of volatile alkalies is one of the primary mechanisms for the formation of these difficult-to-remove particulates. Improved performance of ceramic filters was expected, since alkalies can lead to bridging, pore plugging, and other problems in ceramic filters. Deposition on the walls of the PFBC and on heat-transfer surfaces can reduce the performance of the PFBC and may be controllable by capture of the alkalies with in-bed sorbents. The propensity of certain fuels to sinter and/or agglomerate in the fluid bed was also expected to be reduced or eliminated with the introduction of alkali getters.

The work reported here focused primarily on one class of sorbents, sodalites. The goal will be to determine whether sodalites can be used as an in-bed sorbent to simultaneously remove alkali and sulfur. Some of the key reactions that were studied are listed below:

$$NaCl + 3 (NaAlSiO_4) \Rightarrow Na_4Al_3Si_3O_{12}Cl$$
[1]
(nepheline) (sodalite)

$$Na_{4}Al_{3}Si_{3}O_{12}Cl + 6 SiO_{2} \Rightarrow NaCl + 3 (NaAlSi_{3}O_{8})$$
(sodalite) (albite) [2]

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$$2 (Na_4Al_3Si_3O_{12}Cl) + Na_2SO_4 \Rightarrow 2 (NaCl) + Na_8Al_6Si_6O_{24}(SO_4)$$
(sodalite) (nosean) [3]

$$Na_{8}Al_{6}Si_{6}O_{24}(SO_{4}) + 12 (SiO_{2}) \Rightarrow Na_{2}SO_{4} + 6 (NaAlSi_{3}O_{8})$$
(albite)
$$[4]$$

$$2 (Na_4Al_3Si_3O_{12}Cl) + SO_2 + O_2 \Rightarrow Na_8Al_6Si_6O_{24}(SO_4) + Cl_2$$
(sodalite) (nosean) [5]

Reactions 1 and 3 are the primary mechanisms for the removal of sodium from the gas stream. In these reactions, nepheline and albite are removing sodium chloride from the gas stream to form sodalite. The fate of the sodalite is dependent upon the other constituents that make up the sorbent/ash bed and the gas stream. For systems high in silica, the potential exists for the silica to react with the sodalite or nosean by Reactions 2 and 4 to release the alkali. Sulfates, on the other hand, will replace the chlorine. In Reaction 3, sodium sulfate reacts to release sodium chloride with no net change in the amount of alkali captured. Provided there is sufficient nepheline, the released sodium chloride could react according to Reaction 1, with the overall result being a capture of both sulfur and chlorine. Reaction 5 shows the exchange of SO₂ for Cl₂. For most fuels, the expected concentration of SO₂ relative to chlorine is high. Therefore, Reaction 5 will likely proceed. The extent of Reactions 2 and 4 will probably depend upon the chemistry of the ash and bed material.

A pressurized thermogravimetric analyzer (PTGA) was used to study the mechanism of alkali capture outlined in Reactions 1 through 5. Further testing was performed on a 3-in.-diameter pressurized fluid-bed reactor. In addition to studying the gettering capability of the sorbent, the impact of the getter on operational performance was evaluated. This evaluation included examining potential agglomeration of bed particles, deposition on heat-transfer surfaces, and the bridging of ceramic candle filters.

3.1.2 Conclusions

The work performed as a part of the dissertation consisted of three main efforts: the literature survey, thermogravimetric testing, and bench-scale testing. Conclusions from each of these three efforts are presented below. Following the conclusions, recommendations are presented based on the findings of this work.

3.1.2.1 Conclusions from Literature Review

- Electricity-generating demands are expected to grow at a rate ranging from 1% to 2% per year in the United States, creating a need for over 200 GW of new generating capacity. PFBC is projected to capture up to 25% of the new market for advanced coal technologies, with much of its market penetration in the area of repowering. Therefore, PFBC is expected to be a major source of new power in the 21st century.
- A number of issues must be resolved for PFBC to capture its projected share of the market. These issues include reducing capital costs and improving reliability and environmental performance. Technical issues related to hot-gas particulate removal, alkali

and chlorine control, trace emissions, and the use of advanced cycles must also be resolved for PFBC to reach its full potential.

• The reactions of organically associated mineral matter are of importance in the operating regime of the PFBC. The alkalies, chlorine, and sulfur will vaporize and condense heterogeneously on the surfaces of other ash particles, condense homogeneously to form very fine aerosols, or remain in the vapor phase. These constituents can cause agglomeration and ash deposition, bridging and blinding of hot-gas filters, and corrosion and deposition of turbine blades and, therefore, must be controlled to allow proper operation of the PFBC.

- Measured gas-phase alkali concentrations of 500 to 4000 ppm, depending upon coal type, are high relative to turbine blade specifications of 24 ppb. Therefore, turbine manufacturer specifications for vapor-phase alkali are exceeded even though less than 1% of the total sodium in the fuel is present as vapor. Gas-phase alkali will be higher for those fuels higher in chlorine. The sodium sulfate concentration in the gas phase remains relatively constant because of condensation.
- When sorbents are used in the bubbling fluid bed for adsorption of components from the gas phase, the outlet concentration of the controlled gas will vary inversely to the amount of the sorbent utilized. Therefore, very high sorbent feed rates will be required for high removals of alkali from the gas phase. The capture efficiency will vary directly with sorbent particle size for a kinetically limited system and with the square of particle size for diffusion controlled, assuming there is no elutriation of fines from the bed.
- Aluminosilicates have the most potential for adsorbing alkali under PFBC conditions. Bauxite, kaolinite, and emathlite have been demonstrated to effectively remove alkali vapors when used in packed, moving, and fixed beds.
- Reactions leading to the formation of sodalites have the potential for combined alkali and chlorine removal.
- Alkali metals can be measured either on-line, producing instantaneous alkali values, or off-line, using batch sampling techniques. The accuracy of on-line methods is still not reliable enough for use in PFBC. Therefore, batch sampling procedures are recommended even though they provide only average values of alkali metal over a given period of time.

3.1.2.2 Conclusions from TGA Screening Tests

- The PTGA at the EERC could not be equipped to feed a continuous and controlled amount of sodium vapor without extensive modifications. Therefore, testing was performed at atmospheric pressure.
- The atmospheric TGA made a good tool for screening sorbents and determining reaction mechanisms. The TGA allows the impact of gas type, temperature, and alkali concentration to be evaluated and rate data extracted. Samples large enough for analysis

by scanning electron microscopy can be generated in the TGA, with these analyses used to help understand the reaction mechanisms.

- Nosean, a sulfur-bearing zeolite, was the favored reaction product when sorbents were used for combined alkali, chlorine, and sulfur under the conditions tested. Sodalite, the chlorine-bearing counterpart, would be favored at higher chlorine-to-sulfur ratios and/or higher oxygen partial pressures. Albite reacts with NaCl vapor in an SO₂-bearing gas to capture sodium. The primary mechanism is condensation of Na₂SO₄ on the surface of the albite followed by chemical reaction. The rate of sodium adsorption decreases with decreasing SO₂ concentration in the gas phase because of reductions in the amount of condensed sulfate.
- Albite, quartz, and kaolinite captured sodium by chemical reaction and were kinetically limited. Sodalite and bauxite use physical adsorption as the primary capture method and are diffusion-controlled. After being physically adsorbed, some reaction occurs to permanently bind the alkali.
- The sorbents identified from the TGA screening tests as having commercial potential include albite, kaolinite, and bauxite.
 - 3.1.2.3 Conclusions from Bench-Scale Testing
 - 3.1.2.3.1 General Observations from the Use of Alkali Sorbents
- The pressurized fluid-bed reactor at the EERC provides a good tool for determining the effectiveness of sorbents in controlling ash chemistry in the PFBC. The impacts of sorbents on bed agglomeration, ash deposition, ash distribution and chemistry, filter blinding and bridging, vapor-phase alkali, and sulfur and nitrogen oxide emissions can be determined.
- The use of bauxite and kaolinite as in-bed sorbents resulted in a decrease in NO_x over the base case without sorbent addition. This may be due to a catalytic effect of the sorbent on the NO_x formation and destruction reactions, similar to those reported for dolomite.

3.1.2.3.2 Impacts of Sorbents on Ash Distribution

- Tests with the Beulah coal, which is typical of fuels with high organically bound sodium, tended to show bed agglomeration, deposition on heat-transfer surfaces, and loosely bonded deposits that hung up in the reactor piping. Reduction of the vapor-phase sodium content using bauxite as an in-bed getter eliminated these problems.
- All sorbents increased the mass loading of ash to both the cyclone and the filter vessel. The fine sorbents (-30 mesh) caused a disproportionate increase in cyclone ash while the coarse sorbents (-1/8 inch) caused a disproportionate increase in filter vessel ash.
- The fine sorbents displayed a higher tendency to form loosely bonded deposits that hung up in the reactor.

3.1.2.3.3 Impacts of Sorbents on Vapor-Phase Alkali Concentration

- The vapor-phase alkali concentration is directly related to the quantity of organically bound alkali in the fuel. The vapor-phase sodium concentrations measured from the Beulah, Belle Ayr, and spiked Belle Ayr were approximately proportional to the initial sodium concentration in the starting fuel.
- Kaolinite and bauxite were effective and albite was not effective at reducing the vaporphase alkali concentration. Kaolinite and bauxite captured similar amounts of sodium at comparable add rates, indicating that both were equally effective at alkali capture.
- At a 10:1 sorbent-to-sodium add rate, kaolinite and bauxite reduced the vapor-phase sodium concentration to between 500 and 700 ppm. At a 30:1 add rate, the resulting sodium concentration was 270 ppm. Therefore, it is unlikely that the turbine specifications of 25 to 125 ppm total alkali can be reached using in-bed sorbents.
- In-bed sorbents have an increased capture efficiency for higher initial alkali concentrations. For example, 90% reduction in sodium from 3600 ppm was realized for tests with the Beulah lignite, but only 67% reduction from 1700 ppm using the Belle Ayr coal at the same sorbent add rate.
- The fine sorbents were more effective at reducing vapor-phase sodium concentrations than the coarser sorbents, indicating that the increases in surface area more than offset the shorter bed residence time experienced by the finer sorbents.

3.1.2.3.4 Impacts of Sorbents on Ash Deposition

- For fuels high in organically bound sodium (Beulah lignite for example), sodium calcium sulfates form dense, tenacious deposits. When alkali sorbents are utilized to capture sodium, the amount of deposition is reduced, and the form changes to loosely bonded, lightly sintered deposits that could easily be removed by sootblowing.
- The use of albite as a sorbent resulted in no change in deposition characteristics. When kaolinite was used, some reduction in deposition was noted; however, considerable amounts of fines deposited in the reactor piping. Bauxite effectively eliminated deposition at add rates of 10:1 bauxite-to-sodium and greatly reduced the deposition at lower add rates. This indicates that certain sorbents themselves have a propensity for deposition regardless of the vapor-phase sodium concentration, since the kaolinite and bauxite were equally effective at reducing the vapor-phase sodium concentration.
- Bed agglomeration was apparent when the Beulah lignite was used. Bauxite effectively controlled agglomeration while albite did not. No evaluation for kaolinite was available from this work.

3.1.2.3.5 Impacts of Sorbents on Filter Performance

- The vapor-phase sodium concentration directly impacts bridging of the ceramic filter used for hot-gas particulate removal. Severe filter blinding was noted when the Beulah lignite, with a vapor-phase sodium concentration of 3600 ppm, was used. When using the asreceived and sodium-spiked Belle Ayr (900 and 1700 ppm vapor-phase sodium), no blinding occurred. Analyses indicate the blinding is caused by condensation and freezing of Na₂SO₄ on the surface of the filter, forming a relatively impervious layer that cannot be removed by backpulsing.
- For the Beulah lignite with a baseline vapor-phase alkali concentration of 3600 ppm, the addition of bauxite at a 10:1 sorbent-to-sodium ratio effectively controlled pressure drop in the filter vessel. An add rate of 3:1 was not effective at controlling pressure drop, while a 5:1 add rate of bauxite was only marginally effective.
- For the sodium-spiked Belle Ayr subbituminous with a baseline vapor-phase alkali concentration of 1700 ppm, the pressure drop in the filter vessel never exceeded 10 in. H₂O for the entire duration of the tests using both the kaolinite and bauxite as sorbents at the 10:1 add rate. The pressure drop without the use of sorbents approached 15 in. H₂O, indicating that the sorbents were effectively reducing filter pressure drop.
- The size of the sorbent utilized had no apparent effect on filter pressure drop at similar add rates. Bridging was noted after the test with Beulah coal with bauxite at a 10:1 add rate and only a moderate reduction in vapor-phase sodium concentration. Sodium calcium sulfate was the major component of the bridging material. High sorbent add rates may be effective at eliminating bridges by facilitating high vapor-phase sodium removal, thereby reducing the amount available for homogeneous and heterogeneous condensation to form sticky sulfates.
- During the test program, one of the ceramic filters experienced degradation in the form of spalling from the exterior of the filter. While the filter itself did not fail during the test program, it is speculated that over time this spalling would result in a filter failure. The sodium and sulfur appear to be attacking the protective yttrium coating on certain ceramic filters. Yttrium sulfate appears to be the reaction product. The more mobile phases such as sodium, sulfur, and calcium were found impregnated deep within the surface of the candle.

The overall conclusion from this work is that in-bed alkali sorbents can effectively reduce the vapor-phase alkali concentration. This reduction is of a magnitude great enough to control ash deposition and agglomeration and filter blinding but not to a level low enough to meet current turbine manufacturer recommendations for vapor-phase alkali. Bauxite was the best sorbent tested based on its ability to control all of the above-mentioned problems. Kaolinite is less effective because of its tendency to form sintered deposits from its fine fraction. Finally, although sodalite and nosean can be formed and result in combined sodium and chlorine or sulfur capture, they do not form at a rate high enough to make them effective getters under PFBC conditions.

3.1.3 Recommendations

Bauxite and kaolinite are both effective in reducing the vapor-phase sodium concentration. The increased loading to the cyclone and filter vessel indicate that they have a limited residence time in the bed. These tests also indicated that the high surface area of finer sorbents enhanced alkali removal. Therefore, alkali capture could be improved by changing the form of the sorbent to keep the high surface area, but increasing its size and physical strength to give the sorbent a longer in-bed residence time. This could be accomplished by pelletizing a fine sorbent to a size approaching the mean size of the bed material. It is recommended that pelletization techniques be examined to determine if they can be utilized for kaolinite and bauxite. If not, other aluminosilicate materials should be researched to find a selection that has a propensity to adsorb alkalies and can form good, strong pellets. Even if these alternative sorbents may not be as effective as bauxite and kaolinite in their raw form, they could prove to be more effective overall if pelletizing can substantially increase their residence time in the bed.

If bauxite is chosen as a sorbent, consideration should be given to capturing the cyclone and filter ash and recycling the material back to the PFBC. This should improve the overall efficiency of both the bauxite and the dolomite. Pelletizing the material prior to reintroducing it to the combustor would help stabilize the recycled ash and increase its residence time. The presence of the dolomite in the ash may improve the pelletizing characteristics. This process has been demonstrated for the recycle of fly ash from the circulating FBC of petroleum coke and increased the utilization of the limestone from approximately 35% to over 70%.

For future testing on the PFBR for screening alkali sorbents, consideration should be given to sampling from the outlet of the filter vessel in addition to the top of the reactor. This would provide an indication of how much, if any, alkali is captured by the entrained ash and the ash that builds up on the filters. Results of other work have shown that SO_2 is captured on the filters as the flue gas passes through the filter cake. These measurements would be a better indication of the final vapor-phase concentration that the turbine blades would see. Tests at various filter vessel temperatures could provide information to determine how much cooling of flue gas is required to lower the alkali content from the nominal 500 to 700 ppb measured during this work to the 25 to 125 ppb recommended by turbine manufacturers.

Testing should continue to find effective in-bed sorbents for PFBC. If the PFBC is to realize high coal-to-electricity conversion efficiencies, inexpensive methods of capturing alkali are required. In-bed sorbents offer the capability to accomplish this goal.

3.2 Catalytic Tar Cracking

3.2.1 Experimental

Steam gasification tests were carried out on a high-volatile Illinois bituminous coal (IBC-101) at $1380^{\circ}F(1023 \text{ K})$ and 100 psig in an integrated bench-scale gasifier (IBG) fitted with a catalyst module at the outlet. The catalyst module was attached to the outlet of the reactor to take advantage of the excess reactor heat to keep the catalyst at elevated temperature and to crack the tars before they condensed.

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3.2.1.1 Integrated Bench-Scale Gasifier

The IBG is a small batch process gasifier, with a charge capacity of nominally 70 g of coal. This unit provides data on the effects of bed fluidization, conversion of feedstock, reaction rate response to temperature, pressure, catalyst and feed gas composition and flow rate, and gaseous products, while providing sufficient quantities of conversion products for subsequent analysis. The top of the reactor was fitted with a catalyst module through which the hot exhaust gas passed before entering the series of two condensers. Although the catalyst module had no heaters of its own, it received heat from the reactor and tended to remain predictably within $122^{\circ}-212^{\circ}F$ (323-373 K) of the reactor. A typical catalyst charge to the module was approximately 90–300 g. Gas flowed uninterrupted through the system. Gas exiting the second condenser was collected in gas bags at 12-minute intervals. The gas was analyzed by a refinery gas analyzer. The effect on the tar was determined by measuring the levels of methane and other hydrocarbons in the gas stream and the weight of the tar recovered from the system. In this study, EMcat Elite S-3699 was tested for its tar-cracking effect.

3.2.1.2 Gasification Tests

Four tests were carried out on identical quantities of coal under the same conditions of time, temperature, pressure, fluidization gas (N_2) velocity, and steam injection with approximately 0, 90, 180, and 270 g (module full) of Engelhard EMcat Elite S-3699. This zeolite catalyst was impregnated by the manufacturer with <1% Pt. One test at 1380°F (1023 K) and 100 psig was carried out with dolomite as the catalyst and one test at the same conditions with commercial CoO-MoO-on-alumina catalyst.

Gasification conditions were $1380^{\circ}F(1023 \text{ K})$ and 100 psig in a fluidized bed with fluidization gas (N₂) flow at (nominally) 20 scfh (550 liters per hour). The gas stream was passed through a catalyst bed that was contained in a module immediately downstream from the reactor and spontaneously heated by convection and conduction from the reactor. The temperature during gasification was 1110–1170°F (875–905 K). Each 60-minute test was carried out on 75 g of feed, with gas samples drawn each 12 minutes. Fluidization of the -60-mesh coal was achieved with nitrogen carrier gas flow of approximately 9.4 L/min, and steam was injected at approximately 11 g per minute. Gas-catalyst contact times were 0, 1, 2, and 3 seconds except in the single tests with dolomite and CoO-MoO-on-alumina, in which the contact time was 2 seconds. Solids and tar recoveries were obtained, and gas was collected and analyzed.

3.2.2 Results

Production of heavy tar always accompanies steam gasification of coal. This tar is detrimental to the process for several reasons, including environmental, operational, and product economics. Aerosols that escape into the atmosphere degrade air quality as well as surfaces on which they condense. Condensed droplets result in equipment fouling. This is particularly undesirable in processes such as cogeneration that utilize turbines. In addition, tar formation seriously affects the energy per pound of coal available as gaseous fuel. Conversion of this tar to additional gas and at the same time removing the fouling problems would favorably impact the economics of the process. Catalytic tar cracking is one solution to the problem. The search for an inexpensive, efficient catalyst is a necessary part of this solution.

Engelhard EMcat Elite S-3699 was tested for tar cracking of coal tar produced during steam gasification of Illinois No. 6 Bituminous Coal (IBC-101). The proximate analysis of the feed coal is given in Table 1.

TABLE 1

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Proximate Analysis of IBC	-101 Bituminous Coal
Sample: Treatment:	IBC-101 Raw
Moisture, wt%, ar*	7.64
Volatiles, wt%, mf**	43.10
Fixed C, wt%, mf	49.27
Ash, wt%, mf	7.62
* As received.	

**Moisture-free.

The effect of this catalyst in cracking heavy tar produced during steam gasification of IBC-101 is demonstrated by the total gas production and coincident total heavy tar yield as a percent of feed with increasing Pt-zeolite-tar contact time, shown in Figure 1.

The changes in tar and gas yields in weight percent with contact time are shown in Figure 2. A contact time of 3 seconds cracked nearly 80% of the tar. Tar conversion increased linearly as contact time increased over the conditions of this test series as shown in Figure 3. With the current catalyst module full and the gas flow rates set as above, tar-catalyst contact time was 3 seconds. At those conditions, 80% of the tar was cracked. Hydrogasification occurred using only the hydrogen produced by the gasification reaction.

Tests carried out with < 1% Pt on Zeolite, CoO-MoO on alumina, and natural dolomite as catalysts with a contact time of 2 seconds were carried out. The CoO-MoO cracked the tar as effectively with 2-second contact time as the Pt-zeolite did in 3 seconds. The conversion of tar by each of the three catalysts at similar conditions are shown in Table 2. The dolomite was as effective as the Pt-Zeolite but, as mentioned above, the loss of catalyst through decrepitation and gas entrainment was objectionable as shown in Table 2.

Hydrogen gas in the product gas stream decreases as a function of contact time with the catalyst as shown in Figure 4. As hydrocarbon production increases, hydrogen in the gas stream decreases.



Figure 1. Quantities of tar and gas products from catalytic cracking of tar produced during gasification of Illinois bituminous coal by different amounts of 1% Pt on zeolite.



Figure 2. Weight percent decrease in tar and weight percent increase in gas collected following catalytic cracking of tar by 1% Pt on zeolite.



Figure 3. Gasification tar converted to product gas stream after contact with 1% Pt on zeolite at approximately 600°C.

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Comparison of Catalyst on Tar Cracking and Subsequent Catalyst Recovery					
Catalyst	Conversion of Tar, %	Recovery of Catalyst, %			
<1% Pt on Zeolite	55	96			
CoO-MoO on Alumina	82	92			
Dolomite	58	75			

3.2.3 Conclusions

- In initial tests where catalyst temperature was in excess of 1110°F (875 K), dolomite decrepitated and became entrained in the gas stream, resulting in loss of catalyst and contamination of tar, introducing error into tar measurements.
- Emcat Elite S-3699, which is < 1% Pt on zeolite, withstood the high temperature and cracked coal tar.



Figure 4. Hydrogen content of product gas as a function of contact time with catalyst.

- Tar cracking increased linearly with tar-catalyst contact time for 0-3 seconds. Three seconds was the upper contact time limit since the module was full of catalyst and the fluidization gas which served as a carrier gas for the product gas was flowing as slowly as possible for maintaining fluidization.
- Tar-catalyst (EMcat Elite S-3699) contact time of 3 seconds cracked 80% of the tar entrained in the hot-gas stream. Since the curve produced by plotting tar cracked versus contact time up to 3 seconds is linear, it is expected that additional contact time would produce additional cracking.
- CoO-MoO on alumina was more effective in cracking the IBC-101 tar at the conditions of this study than either <1% Pt on zeolite or natural dolomite.

3.2.4 Recommendations

- Construct a larger catalyst module to increase contact time.
- Determine the effective life of the catalyst.
- Perform a similar suite of tests with dolomite in which the catalyst module is held at lower temperatures.
- Perform a similar suite of tests on other commercial catalysts.

APPENDIX A

CAPTURE OF ALKALI DURING PRESSURIZED FLUIDIZED-BED COMBUSTION USING IN-BED SORBENTS

Ph.D. Dissertation by Michael D. Mann

CAPTURE OF ALKALI DURING PRESSURIZED FLUIDIZED-BED

COMBUSTION USING IN-BED SORBENTS

by

Michael D. Mann

Masters of Science, University of North Dakota, 1981

A Dissertation

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Grand Forks, North Dakota May 1997

Copyright by Michael D. Mann 1996 This dissertation, submitted by Michael D. Mann in partial fulfillment of the requirements for the Degree of Doctor of Philosophy from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

(Chairperson)

This dissertation meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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Title Capture of Alkali During Pressurized Fluidized-Bed Combustion Using In-bed Sorbents

Department School of Engineering and Mines

Degree Doctor of Philosophy

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ABSTRACT

Pressurized fluidized-bed combustion (PFBC) has been identified as a promising technology for the future; however, there are a number of obstacles that must be overcome to maximize the potential of PFBC. These include removal of 1) fine particulates to eliminate erosion and deposition on turbine blades, 2) alkalies that can lead to corrosion of turbine blades and blinding of ceramic filters, 3) sulfur at very high sorbent utilization efficiencies, 4) halogens that can lead to corrosion, and 5) toxic metals that were specified in the 1990 Clean Air Act Amendments. The primary focus of this research was the removal of alkali from PFBC flue gases to a level specified by turbine manufacturers. The target level was less than 24 ppbw. Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (760° to 1010°C [1400° to 1850°F]). The alkalies are adsorbed onto the surface and diffuse into the bulk of the alkali sorbent. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a sorbent to capture alkali in the bed reduces the need for downstream alkali capture devices. Other goals of this work were to investigate the potential for simultaneously removing SO₂ and Cl from the PFBC gas stream.

Several side benefits were anticipated, and the goal was to demonstrate these during this work. A reduction in the amount of fine particulate was expected when alkali is removed in the bed, since condensation of volatile alkalies is one of the primary mechanisms for the formation of these difficult-to-remove particulates. Improved performance of ceramic filters was expected, since alkalies can lead to bridging, pore plugging, and other problems in ceramic filters. Deposition on the walls of the PFBC and on heat-transfer surface can reduce the performance of the PFBC and may be controllable by capture of the

alkalies with in-bed sorbents. The propensity of certain fuels to sinter and/or agglomerate in the fluid bed was also expected to be reduced or eliminated with the introduction of alkali sorbents.

The initial work focused primarily on one class of sorbents, sodalites, with the goal of determining whether sodalites can be used as an in-bed sorbent to simultaneously remove alkali and sulfur. Thermal gravimetric analysis was used to study the mechanism of alkali capture using sodalite. Further testing was performed on a 3-in.-diameter pressurized fluid-bed reactor. Early results indicated that simultaneous removal of alkali and sulfur and/or chlorine was not practical under the conditions for commercial PFBC operations. Therefore, the focus of the later part of this work was on sorbents that have been shown to capture alkali in other systems. The effectiveness of bauxite and kaolinite to reduce vapor-phase alkali concentrations was determined. In addition to studying the capture capability of the sorbent, the impact of the sorbent on operational performance was evaluated. This evaluation included examining potential agglomeration of bed particles, deposition on heat-transfer surfaces, and the bridging and blinding of ceramic candle filters.

The overall conclusion from this work is that in-bed alkali sorbents can effectively reduce the vapor-phase alkali concentrations. This reduction is of a magnitude great enough to control ash deposition and agglomeration and filter blinding, but not to a level low enough to meet current turbine manufacturer recommendations for vapor-phase alkali. Bauxite was the best sorbent tested based on its ability to control all of the above-mentioned problems. Kaolinite is less effective because of its tendency to form sintered deposits from its fine fraction. Finally, although sodalite and nosean can be formed and result in combined sodium and chlorine or sulfur capture, they do not form at a rate high enough to make them effective sorbents under PFBC conditions.

The effectiveness of in-bed alkali sorbents could be improved by pelletizing the material prior to feeding it into the PFBC. The production of a porous pellet from fine material would capture both the advantage of high sorbent surface area (small particle size) and long residence time in the bed (large particle size). Recycle of the fly ash back to the combustor should also improve the overall effectiveness of the sorbents for capturing alkalies and, if coupled with pelletization, should decrease deposition

problems associated with the fine ash. Testing should continue to find effective in-bed alkali sorbents for PFBC. If the PFBC is to realize cost-effective, high coal-to-electricity conversion efficiencies, inexpensive methods of capturing alkali are required. In-bed sorbents offer the capability to accomplish this goal.
CHAPTER 1

BACKGROUND

As the demand for electricity grows, pressurized fluidized-bed combustion (PFBC) is poised to capture a significant share of the market, especially for repowering older coal-fired units. This is due in part to the PFBC's inherent ability to achieve high efficiencies and low emissions. A number of obstacles hinder maximizing the potential for PFBC. These include the removal of fine particulates to eliminate erosion and deposition on turbine blades, alkalies which can lead to corrosion of turbine blades and blinding of ceramic filters, sulfur at very high sorbent utilization efficiencies, halogens that can lead to corrosion, and toxic metals that were specified in the 1990 Clean Air Act Amendments. The primary focus of this research is on the removal of alkalies from the gas stream of the PFBC. Current methods for alkali removal are either capital-intensive or result in a loss in overall system efficiency. The goal of this research was to identify sorbents that could be used to capture alkalies without impacting the overall capital costs or system efficiency.

1.1 Electricity Demand

Electricity demand is projected to grow as the U.S. economy grows. Estimates of new capacity requirements over the next 15 years differ widely, with predictions varying from 0.9% to 2.0% per year (IEA [International Energy Agency], 1992, 1994; Makovich and Smalley, 1993; Alliance to Save Energy, 1992). Estimated trends from various groups are shown in Figure 1. There appears to be significant markets for retrofit and repowering options, as well as new capacity construction as indicated in Figure 2 (Bdar, 1996; Longwell et al., 1995; Makovich and Smalley, 1993).

Changes in the regulatory structure and practice in the electric utility industry since 1979 have contributed to a trend toward more widely distributed, smaller-scale power generation facilities that have



Figure 1. Projected U.S. electricity generating demand (Energy Information Agency [EIA], Wharton Economic Forecasting Association [WEFA], Gas Research Institute [GRI], Data Research Institute [DRI], North American Electric Reliability Association [NERC], Edison Electric Institute [EEI], and National Economic Research Association [NERA])



Figure 2. U.S. power plants over 40 years old that are candidates for repowering (Bdar, 1996)

relatively low risk and capital costs. In addition, increased competition is reducing the willingness of the utility industry to develop and deploy advanced power generation technologies that are perceived as having higher risk.

In the near term, natural gas-fired systems will likely be the primary source of new capacity additions, driven by demands for peak and intermediate power, low gas prices, and low capital costs. However, coal is expected to remain the largest single energy source for power generation (IEA, 1993; EIA, 1994; Longwell et al., 1995), and resource limitations for domestic natural gas are expected to result in price increases (EIA, 1994; GRI, 1994). Combining this with a substantial need for new baseload generating capacity between 2006 and 2040 (Makovich and Smalley, 1993), a resurgence of coal-based power generation is expected.

Environmental concerns will probably have the most significant influence on future coal use in the United States, and requirements to reduce the environmental and health risks of waste streams from coal technologies are expected to be more stringent (Rubin, 1989; NRC [National Research Council], 1992). Control of SO_2 , NO_x , and fine particulate air pollutant, solid wastes, and air toxics will continue to determine the acceptability of coal-based systems with state and local regulators placing the most restrictive demands on power plant emissions. Among these, concern over global warming could present the greatest long-term threat to coal use because of the CO_2 emissions from coal combustion.

Expansion of coal-based power generation is anticipated in the developing nations, notably China, and major international markets exist for coal utilization technologies (EIA, 1993, 1996). The projected global demand is depicted in Figure 3. In the near term, capital investment requirements are expected to be a controlling consideration in most foreign markets. Foreign requirements to minimize conventional pollutant and greenhouse gas emissions will lag those imposed in the United States, but their introduction is expected to have a large impact on international sales of coal-based technologies (*Coal and Synfuels Technology*, 1993; U.S. DOE [Department of Energy], 1993; Longwall et al., 1995).



World Electricity Consumption



Non-OECO Electricity Consumption

Figure 3. Projected global demand for electricity (EIA, 1993, 1996)

1.2 PFBC: An Attractive Alternative

Fluidized-bed combustion (FBC) is the combustion of fuel in a bed of particles made up of fuel ash, limestone, and fuel suspended by an upward flow of air. The bed of suspended particles behaves similarly to a fluid. The minimum air velocity required to fluidize the coal is defined by the balance between the aerodynamic drag force on the particles and the gravitational force. The degree of fluidization in an FBC system is typically controlled by the air/gas velocity for a specific particle-size distribution. At velocities below the terminal velocity, the material is retained within a given height, and the fluid bed is said to be bubbling. A circulating fluid bed is operated at velocities above the terminal velocity, where particles are carried out of the reactor, captured in a high-efficiency cyclone, and returned to the reactor.

Uniform bed conditions are important in the performance of a fluid-bed combustion system as controlled gas-to-solid reactions are necessary. Indications of good fluidization quality are even temperature distribution across the bed and, essentially, a constant overall pressure drop with consistent low-amplitude pulsations in pressure. Large pressure fluctuations and/or low pressure drops, compared with the total bed weight, indicate poor fluidization.

In a fluidized bed, combustion takes place at low temperatures of $760^{\circ}-980^{\circ}C$ ($1400^{\circ}-1800^{\circ}F$) compared to $1370^{\circ}-1900^{\circ}C$ ($2500^{\circ}-3450^{\circ}F$) in conventional coal combustion systems (Singer, 1981). The lower temperature of the fluid bed substantially reduces the potential emissions of SO₂ and NO_x compared to a conventional system. The bed serves as an excellent media for heat and mass transfer and has a high thermal capacity. This results in good carbon burnout, even at the relatively low operating temperatures. The action of the bed also generates very high heat-transfer coefficients, typically three to five times those experienced in convective tubes of a conventional boiler.

Advantages offered by fluid-bed combustion technology compared to that in conventional coal combustion are due to the intense turbulence in the bed and to the comparatively long solid residence times in the bed without a long, linear-flow path requirement. The advantages are as follows:

- At FBC operating temperatures, SO₂ produced by the combustion of coal-bound sulfur can be adsorbed by alkaline components within the fuel (ash) or by added sorbents in the well-mixed combustion zone, thereby eliminating the need for additional SO₂ control equipment.
- At the lower combustion temperature in the FBC, NO_x is substantially lower than in conventional combustion systems. Very few of the trace metals are mobilized at these temperatures, minimizing concerns over air toxics.
- Because of mixing and intimate contact of hot solids, the FBC can fire fuels of low and varying quality. The long residence time allows nearly complete burnout of the solid carbon and allows virtually complete destruction of the volatile organic compounds.
- Because of the solids contact and radiation from the suspension of hot particles, the heat-transfer rates to in-bed tubes in FBCs are approximately three to five times that in the convective section of a conventional combustion system, thereby reducing overall combustor size.
- Because of the FBC's capability to accept larger and less uniform fuel particle sizes, the fuel preparation costs are lower than those for pulverized-coal-fired systems.
- Waste products from the FBC process are dry solids and have been shown to be relatively harmless compared with wastes from conventional wet scrubbing processes.
- Tube fouling is reduced because of the lower combustion temperature.
- The smaller size facilitates modular units with package construction.

FBC systems can be operated at atmospheric or elevated pressure, hence the designations of atmospheric (AFBC) and pressurized (PFBC) fluidized-bed combustion. PFBC typically operates at pressures ranging from 10 to 16 atmospheres. Operation in this manner allows the pressurized gas stream from a PFBC unit to be cleaned and fed to a gas turbine. The exhaust gas from the turbine is then passed through a heat recovery boiler to produce steam. The steam from the PFBC unit and that from the heat recovery boiler are then fed to a steam turbine. This combined-cycle mode of operation significantly increases PFBC system efficiency over AFBC systems. If the PFBC exhaust gas can be cleaned sufficiently without reducing its temperature, additional cycle efficiency can be achieved. Figure 4 depicts a first-generation (nontopped) PFBC system.



Figure 4. Schematic of a PFBC plant (Bdar, 1996)

When operating under pressure, the PFBC offers significant advantages over atmospheric units,

including:

- Power output similar to an AFBC but with a unit that has a smaller "footprint" because of the higher pressure and increased efficiency of the PFBC.
- Steam flows for PFBC units that are compatible with steam turbines at existing power plants making the technology especially attractive for repowering existing units at existing sites, avoiding the need and difficulty of developing new sites.
- Reduced equipment size and higher efficiencies which help offset the higher equipment costs related to the pressurized operation.
- Efficiencies of 39% to 42% (HHV [higher heating value]) with first-generation PFBC compared with 34% efficiency for AFBC.
- Emissions of CO₂ are 20% lower than AFBC for first-generation PFBC due to the higher overall efficiency. Advanced PFBCs can reduce CO₂ by over 30% as compared to AFBCs.

Hybrid PFBC systems (topped PFBC in Figure 4) offer substantial improvements in efficiency by afterburning with coal gas or natural gas to raise gas temperatures and efficiencies up to the limits imposed by the gas turbine (Dellefield and Reed, 1992). This decoupling of the gas turbine temperature allows flexibility for reducing PFBC temperatures when operating on high-alkali fuels to reduce the risk of alkali vapor carryover to the turbine and agglomeration of the bed.

In a hybrid PFBC system, sulfur control in the fluidized-bed gasifier supplying the gas for afterburning is proved by adding limestone or dolomite to capture H_2S as calcium sulfide (CaS). Achieving high levels of sulfur capture (e.g., 90%) in the gasifier requires operation at temperatures above 1650°F to calcine CaCO₃ to CaO (Pitrolo and Bechtel, 1988). The reaction of calcined limestone or dolomite is rapid, and H_2S removals approach equilibrium (Abbasian and Rehmal, 1990). However, high gasification temperatures intensify concern over alkali release and bed agglomeration when high alkali fuels are used. Efficiencies from 45% to 48% are expected from second-generation (hybrid) PFBC.

1.3 Projected PFBC Market

AFBC technology has achieved commercial acceptance, while PFBC technology is currently undergoing commercial demonstration. The *1995 U.S. Fluid Bed Directory* lists over 600 AFBC operating units with an average steam capacity of 235,000 lb/hr (72 MWe equivalent) (Stephens' Utility and Cogeneration Services, 1995). PFBC, meanwhile, is projected to see a strong demand over the next 50 years. Figure 5 shows a projection of the coal-fired technology market through 2050 (Guha and McCall, 1990). The U.S. utility market for all coal technologies, the penetration of first-generation PFBC systems, and the penetration of advanced PFBC systems are shown. The market penetrations shown in Figure 5 are similar to those developed by DOE (Dellefield and Reed, 1992). The projection recognizes that after an initial spurt of first-generation PFBC installations, the trend starting in the 2005 time frame will be toward utilities installing more efficient advanced PFBC systems. DOE's assessment of PFBC's ability to capture a significant share of the future coal generated electricity market warrants additional research to develop more efficient and environmentally superior PFBC systems, as well as to conduct



Figure 5. Advanced coal technology market penetration (Guha and McCall, 1990)

large-scale commercial demonstrations of PFBC systems in the Clean Coal Technology Programs (Dellefield and Reed, 1992; Bdar, 1996).

Evidence of PFBC's ability to penetrate the power generation market is given in Figure 6. Thirteen PFBC units greater than 50 MWe have either been built or are planned. Japan has made the biggest commitment to PFBC, with four commercial units in various stages of construction and/or operation and two additional units planned (Takahashi et al., 1995). PFBC will most likely be used for the retrofit/repowering projects at the unit size of 300 to 400 MW. Bubbling beds will dominate the PFBC systems in the beginning, with advanced designs competing by the year 2005. While further improvements in environmental and thermal performance will be required to maintain PFBC technology as a competitive option to gasification-based power systems in the 2000s, PFBC appears to be a strong contender for capturing a significant share of the power industry over the next 50 years.



Figure 6. PFBC projects around the world (Bdar, 1996)

1.4 Barrier Issues

There are several areas where PFBC systems need to improve their competitiveness in order to succeed in the year 2000 and beyond. Market-based issues that must be resolved to achieve the penetration projected in Figure 5 include (Dellefield and Reed, 1992; Longwell et al., 1995):

- Capital costs must be lowered.
- Reliability of the components and major subsystems must be demonstrated to the degree necessary to satisfy the owner's operating staffs.
- Environmental performance must be made to exceed any standards that could be placed upon the utility industry during the next several decades.
- The bottom line cost of electricity (COE) must not only be better than current solid fuel technology, but must also be comparable to future electricity options, including nuclear power, coal gasification, and renewable energy sources.

In addition to these market-based issues, a number of technical barriers must also be overcome if PFBC is to achieve a reasonable market status. The major issues identified by DOE requiring additional development work are shown in Figure 7 (Bdar, 1996). The commercialization of topping combustors are needed to take advantage of present state-of-the-art gas turbines. Work needs to continue to push the gas turbine inlet temperature as high as possible to match developments in the turbine industry. Development must also occur to produce higher efficiency, higher inlet temperature gas turbines to help the competitive position of PFBC units. Figure 8 shows the potential that gas turbines with higher inlet temperatures offer PFBC systems (Jansson, 1991). This figure compares the efficiency of PFBC and integrated gasification combined cycle (IGCC) systems employing gas turbines with increasing inlet temperatures, showing that the possible gains are dramatic. It is interesting to note that the hybrid PFBC will have higher efficiencies than the IGCC until the gas turbines reach the capability to have ISO (International Organization for Standardization) inlet temperatures in the 1250°C (2280°F) range. This compares to a U.S. gas turbine inlet temperature of 1340°C (2450°F). Advanced steam cycles and the use of a Kalina bottoming cycle should push the efficiency of the hybrid PFBC to over 50% based on the higher heating value.



Figure 7. PFBC research and development issues (Bdar, 1996)



Figure 8. Thermal efficiencies for PFBC and IGCC plants (Jansson et al., 1992)

While overall system efficiency should be improved, the environmental performance of the PFBC must also improve. PFBCs must prove that they are long-term viable alternatives to other low-emission coal systems such as IGCCs. Key areas of environmental performance include increasing the sulfur capture to above 95%, controlling NO_x to meet stringent local and state regulations (as low as 25 parts per million by weight [ppmw]), and ensuring hazardous air pollutants (HAPs) are controlled. This must be accomplished while minimizing solid wastes. For second-generation PFBCs, conversion of the CaS produced during the pyrolysis/gasification step to CaSO₄ is also a major environmental concern.

Boiler vendors and turbine vendors must design the system that allows essentially off-the-shelf turbines or advanced designs to be used. Hot-gas particulate filtration is the key component to making this a reality. Hot-gas filtration is needed to meet the stringent particulate requirements placed upon PFBC systems by gas turbine manufacturers to prevent erosion of turbine blades. Another issue that the hot-gas cleanup system must deal with is removal of alkalies. Current technology allows for cooling the gas to condense the alkalies which are then removed as particulates. Possible penalties in the overall efficiency

can be 1% to 3% (Longwell et al., 1995). The ability of hot-gas cleanup systems to reduce contaminants to levels acceptable for high-temperature advanced turbines has not yet been demonstrated.

1.5 Issues with Alkali

In PFBC combined-cycle systems, the alkalies, particularly those whose boiling point is less than the turbine blade temperature, act vigorously on the blade material. This alkali-induced corrosion can greatly reduce the life of the turbine. For example, an increase in sodium content of 2 to 4 ppmw reduces the service life of a turbine by half (Pintsch and Gudenau, 1991a). Therefore, special demands are made on the purity of the coal-derived gas if it is to be used in a combined-cycle process. Specifications for the purity of the gas entering the turbine are set to provide an economic life of at least 50,000 operating hours. The specifications for three turbines manufactured by Westinghouse and the operating characteristics are shown in Table 1. General Electric specifies a limit value of a maximum of 24 ppbw (parts per billion by weight) for alkalies (Radhakrishman et al., 1986). Foreign manufacturers and authors have proposed higher limits. Cramer (1986) mentions a study on alkalies with a limit of 500 ppbw, while the Federal Ministry for Research and Technology in Germany recommends alkali levels below 0.125 mg/m³

Table 1

Model	W501B12	W501D5	501F
Power Rating, MW	50	100	150
Inlet Gas Temp., °F	2065	2070	2300
Pressure Ratio	14.2	14.2	14.2
Thermal Eff. Single Cycle	32	33	36
Thermal Eff. Combined Cycle	46	48	50-52
Operating Life, hr	100,000	100,000	40,000
Particulate Spec.	10 ppm @ 5µm	10 ppm @ 5 μm	10 ppm @ 5 μ m
Alkali Spec.	l ppm fuel	20 ppb @ blade	20 ppb @ blade
Mass Flow, lb/sec	Not available	813	935
Exhaust Temp., °F	Not available	965	1060

Operating Characteristics of Westinghouse Gas Turbines

(approximately 113 ppbw) (Pintsch and Gudenau, 1991). The recommended purity of clean gas for turbine applications in the Federal Republic of Germany (FRG) is given in Table 2.

Table 2

Permissible Impurities in	Coal Gas (clean gas) (Pintsch and Gu	udenau, 1991)

Toxic Matter	Limit	Permissible concentration in clean gas ($H_u = 11,000 \text{ kJ/kg}$)
Sulfur	Emission	Depending on limit value
Nitrogen (chemically bound)	Emission	Depending on limit value and thermic NO_x
Chlorine	Emission Corrosion	400 mg/m ³ (STP ¹) (= 30 mg/m ³ in exhaust gas) Unknown, present limit 0.5 mg/m ³ (STP)
Fluorine	Emission Corrosion	70 mg/m ³ (STP) (= 5 mg/m ³ in exhaust gas) Unknown
Sodium and Potassium	Corrosion	0.125 mg/m ³ (STP)
Lead	Corrosion	0.25 mg/m ³ (STP)
Zinc	Corrosion	0.5 mg/m ³ (STP)
Calcium	Deposits	2.5 mg/m ³ (STP)
Particle Total	Emission	275 mg/m ³ (STP) (= 20 mg/m ³ in exhaust gas)
Particle <2 μ m	Deposits	140 mg/m ³ (STP)
Particles 2 to 5 μ m	Erosion	5.5 mg/m ³ (STP)
Particles 5 to 10 μ m	Erosion	0.4 mg/m ³ (STP)
Particles >10 μ m	Erosion	Impermissible

¹ Standard temperature and pressure.

The alkali vapor concentration resulting from the PFBC of a variety of fuels has been measured over a wide range of PFBC operating conditions. The measured values have been reported on the order of 60 to over 4000 ppbw sodium and 7 to 800 ppbw potassium (Lee and Carls, 1988; Lee et al., 1987, 1989, 1991, 1993; Lee and Swift, 1991; Laatikaninen et al., 1993; Mann et al., 1995; Mojtahedi and Backman, 1989). High-temperature operation and the use of high-alkali fuels will result in vapor-phase alkali concentrations well above even the least conservative recommended levels for turbine safety. Therefore, alkali capture must be developed to advance the efficiency of the PFBC. Thus far, the jury is still out on the verdict of a solution. Westinghouse is investigating filtering the hot gas through a bed of emathlite, a clay that will remove virtually all of the alkali by adsorption (Cuenca and Anthony, 1995). This option requires the addition of a packed, moving, or granular bed into the overall system, resulting in an increased capital cost. Foster Wheeler has currently chosen the path of cooling the gas below the dew point of the alkalies, 760 °C to 815 °C (1400° to 1500°F), and removing them with the particulates in the hot-gas cleanup step (Abdulally, 1996). This option is effective at removing the alkalies and eliminates the capital expense of adding an alkali-contacting vessel; however, a loss in overall efficiency results from this approach. The impact of the lower efficiency on the COE is less than that experienced by adding an alkali sorbent-contacting vessel. ABB Carbon, on the other hand, appears to be deferring the decision on alkali removal. While observing the response of its rugged turbines to hot high-pressure flue gas that has been cleaned of particulates only by passage through two stages of cyclones at two demonstration and one commercial plant, ABB Carbon is monitoring the alkali concentrations in the flue gas but making no attempt to reduce it (Jansson, 1991). Only after sufficient hours of operation are logged will ABB Carbon be able to gauge the effectiveness of this approach.

A number of researchers and developers have been working with various alkali sorbents to remove alkali from the hot-gas stream. Since contacting the alkali with the sorbent is critical, various packed-bed and granular bed filters have been used. Westinghouse (Bachovicn et al., 1986), Argonne National Laboratory (Lee and Swift, 1991), and the Coal Research Establishment (Scandrett and Clift, 1984) have all looked at alkali sorbents in a packed bed, while work done at Combustion Power Company (Goldback and Haas, 1991; Wilson, 1985) and New York University (NYU) (Radhakrishnan et al., 1986; Zakkay et al., 1989) utilized a granular bed filter design (moving bed). The University of Arizona considered using the sorbent in situ with the combustion process (Punjak et al., 1989; Uberoi et al., 1990). Data generated from these facilities have identified a number of good alkali sorbents, including bauxite, diatomaceous earth, emathlite, and kaolinite. Alkali capture exceeding 99% has been achieved in pilot-scale combustion testing at NYU, with the average capture at 90% to 96%. The main barrier to implementing any of these

systems is the optimization of the filter system packing to facilitate scaleup in a cost-effective manner. Other systems investigated include a tailing dry plate washer by Air Pollution Control Technology (Calvert et al., 1981), a traveling bed ceramic filter by Rockwell International (Giliberti, 1982), and a magnetically stabilized cross-flow filter bed by Exxon R&D (Research and Development) Company (Golan et al., 1982).

1.6 Research Outline

PFBC has been identified as a promising technology for the future; however, there are a number of obstacles for maximizing the potential of PFBC. These include removal of 1) fine particulates to eliminate erosion and deposition on turbine blades, 2) alkalies which can lead to corrosion of turbine blades and blinding of ceramic filters, 3) sulfur at very high sorbent utilization efficiencies, 4) halogens that can lead to corrosion, and 5) toxic metals that were specified in the 1990 Clean Air Act Amendments. The primary focus of this research was the removal of alkali from PFBC flue gases to a level specified by turbine manufactures. The target level was less than 24 ppbw. Several of the aluminosilicate minerals have the potential to capture alkalies, especially sodium and potassium, under conditions typical of fluid-bed operation (1400° to 1850°F). The alkalies are absorbed on the surface and diffuse into the bulk of the alkali sorbent. In addition, the nonbridging oxygen atoms released when alkalies modify the aluminosilicate mineral structure are potential sites for sulfur capture. The use of a sorbent to capture alkali in the bed reduces the need for downstream alkali capture devices. Other goals of this work were to investigate the potential for simultaneously removing SO₂ and Cl from the PFBC gas stream.

Several side benefits were anticipated, and the goal was to demonstrate these benefits during this work. A reduction in the amount of fine particulate was expected when alkali is removed in the bed, since condensation of volatile alkalies is one of the primary mechanisms for the formation of these difficult-to-remove particulates. Improved performance of ceramic filters was expected, since alkalies can lead to bridging, pore plugging, and other problems in ceramic filters. Deposition on the walls of the PFBC and on heat-transfer surface can reduce the performance of the PFBC and may be controllable by capture of the alkalies with in-bed sorbents. The propensity of certain fuels to sinter and/or agglomerate in the fluid bed was also expected to be reduced or eliminated with the introduction of alkali sorbents.

The work reported here was initially focused primarily on one class of sorbents, sodalites. The goal was to determine whether sodalites could be used as an in-bed sorbent to simultaneously remove alkali,

sulfur, and chlorine. Some of the key reactions that were studied are listed below:

$$NaCl + 3 NaAlSiO_4 = Na_4Al_3Si_3O_{12}Cl$$
[1]

(nepheline) (sodalite)

$$NaCl + 3 NaAlSi_{3}O_{8} - Na_{4}Al_{3}Si_{3}O_{12}Cl + 6 SiO_{2}$$
[2]

(albite) (sodalite)

$$2 \text{ NaCl} + \text{Na}_{8}\text{Al}_{6}\text{Si}_{6}\text{O}_{24}(\text{SO}_{4}) \leftarrow 2 \text{ Na}_{4}\text{Al}_{3}\text{Si}_{3}\text{O}_{12}\text{Cl} + \text{Na}_{2}\text{SO}_{4}$$
[3]

(nosean)

$$Na_{8}Al_{6}Si_{6}O_{24}(SO_{4}) + 12SiO_{2} - Na_{2}SO_{4} + 6 NaAlSi_{3}O_{8}$$
[4]

(sodalite)

(albite)

(nosean)

$$2 \operatorname{Na}_{4}\operatorname{Al}_{3}\operatorname{Si}_{3}\operatorname{O}_{12}\operatorname{Cl} + \operatorname{SO}_{2} + \operatorname{O}_{2} \rightleftharpoons \operatorname{Na}_{8}\operatorname{Al}_{6}\operatorname{Si}_{6}\operatorname{O}_{24}(\operatorname{SO}_{4}) + \operatorname{Cl}_{2}$$
(sodalite) (nosean) [5]

Reactions 1 through 3 are the primary mechanisms for the removal of sodium from the gas stream. In these reactions, nepheline, albite, and nosean are removing sodium chloride from the gas stream to form sodalite. The fate of the sodalite is dependent upon the other constituents that make up the sorbent/ash bed and the gas stream. For systems high in silica, the potential exists for the silica to react with the sodalite or nosean by Reactions 2 and 4 to release the alkali. Sulfates, on the other hand, will replace the chlorine. In Reaction 3, sodium sulfate reacts to release sodium chloride with no net change in the amount of alkali captured. Provided there is sufficient nepheline, the released sodium chlorine. Reaction 5 shows the exchange of SO₂ for Cl₂. For most fuels, the expected concentration of SO₂ relative to chlorine is high. Therefore, Reaction 5 will likely proceed to the right. The direction and extent of Reactions 2 and 4 will probably depend upon the chemistry of the ash and bed material.

Thermal gravimetric analysis was used to study the mechanism of alkali capture outlined in Reactions 1 through 5. Further testing was performed on a 3 in.-diameter pressurized fluid-bed reactor. Early results indicated that simultaneous removal of alkali and sulfur and/or chlorine was not practical under conditions for commercial PFBC operations. Therefore, the focus of the later part of this work was on sorbents that have been shown to capture alkali in other systems. The effectiveness of kaolinite and bauxite to reduce the vapor-phase alkali concentrations was determined while the impact of the sorbent on operational performance was evaluated. This evaluation included examining potential agglomeration of bed particles, deposition on heat-transfer surfaces, and the bridging and blinding of ceramic candle filters.

CHAPTER 2

LITERATURE REVIEW

The goal of this research was to investigate methods to reduce the level of alkalies in the exit gas from the PFBC to meet the current and proposed design standards for high-efficiency gas turbines. Understanding all aspects of the process was necessary, beginning with the evolution of the alkali from the coal and its formation of gaseous species, capture by the alkali sorbent and, finally, determining the quality of the gas that enters the turbine. Therefore, a basic understanding of these processes was extracted from the literature and is presented in this chapter. The chapter first discusses the transformation of the mineral matter in coal to gaseous, liquid, and solid species. Since direct measurement of the alkali components of the flue gas is difficult and many times inaccurate, thermochemical modeling is often used to predict the fate of the alkali in the flue gases and to predict the impact of changes in operating conditions and fuel properties on the gas quality. Results from several modelers are reported here, along with measurements taken to determine the validity of the models. Sorption theory is reviewed, with an emphasis on sorbent behavior in a fluidized bed and on the interactions of alkalies with aluminum silicates. Other researchers' success with various alkali sorbents is presented to provide a baseline with which to compare results from my work. Their experimental techniques are also presented, especially as they relate to my choice of experimental techniques. The various measurement techniques utilized are reviewed, since the accurate measurement of the alkalies leaving the PFBC is an essential component in demonstrating the success of my work. Some conclusions from the literature review are presented in this chapter. The material presented in this chapter will be referenced heavily in the remainder of this dissertation as it is used to justify choices made for the experimental approach and interpretation of the results generated from my work.

2.1 Transformation of Mineral Matter in Coal

The purpose of this subsection is to provide the background necessary to understand which coals are potentially high emitters of alkali and how that alkali is released during the combustion process. This knowledge was used in designing the original fundamental experiments to ensure that useful real-world information could be extracted. This understanding will also be important as one tries to apply the experience gained during this work to other fuels and applications.

2.1.1 The Nature of the Inorganic Constituents

Coal is a primarily organic sedimentary rock that contains small amounts of inorganic constituents. Although comprising only a small fraction of the total weight of the coal, the inorganic constituents affect every facet of coal preparation and usage. The inorganics have three principal origins: they existed in the original plant material whose remains make up the organic fraction of the coal; they were carried into the coal-forming environment by water or wind as detrital mineral matter; or they were deposited from solution through ion-exchange or precipitation (authigenic formation). Whatever the origin, the inorganic constituents of coals exhibit two modes of occurrence: as discrete mineral particles or, most importantly with low-rank coals, as cations associated with organic acids or other organic complexation sites.

The ash particulate and alkali concentrations in the hot gases leaving a PFBC depend on the mode of occurrence of inorganic elements in the coal and their high-temperature reaction chemistry. The size and morphology of the minerals found within coal vary greatly, but depend on the type and origin of the mineral inclusion. The clay minerals often occur as layers within the coal seam, but can also occur as finely dispersed inclusions. In pulverized coal, the clay particles vary from masses as large as the largest coal particles to individual particles less than 10 nanometers in diameter (Stach et al., 1982). Quartz particles most often occur as partially rounded grains of probable detrital origin, but can also exist as massive cryptocrystalline bodies that formed authigenically (Miller and Given, 1979). Pyrite can also exist in such forms, but in addition may occur as raspberrylike agglomerations of smaller particles, termed framboids. The carbonate and sulfate minerals most often occur as precipitates that fill cracks or fissures in the coal (Stach et al., 1982). The size range of the mineral matter in pulverized coal varies from the largest size that will pass the pulverizer to particles 2 nanometers in diameter that contain only a few hundred atoms

(Hurley, 1990). A typical mass median diameter for the mineral matter in a pulverized western U.S. lowrank coal is approximately 20 microns. In a PFBC, since the coal is typically crushed to only -1/8 in., larger mineral grains typically are seen.

In addition to association as discrete mineral matter, the inorganic constituents can exist as cations associated with organic acids or other organic complexation sites. Miller and Given (1979) list eight oxygen or nitrogen functional groups that are known to exist in peats and lignites that could participate in complexing metal ions. This is the major mode of occurrence of the alkalis in most western U.S. coals.

One method of determining whether the elements are organically associated or present in discrete mineral particles is to extract the elements from the coal using different aqueous reagents. Using techniques modified from those used by Miller and Given (1979), Benson and Holm (1985), and Hurley and others (1986), 14 western U.S. coals, lithotypes, and size-fractionated coal samples were extracted in an effort to delineate the associations of the inorganic elements in the coals. Table 3 lists the ranges of concentrations of the major inorganic elements in the 14 coals studied and the percentages of each element removed by the one molar NH₄OAc extractions. Table 4 lists the ranges in the percentages of the elements extracted from the NH₄OAc-extracted residues by one molar HCl and the percentages of the elements remaining. The data for Tables 3 and 4 were taken from a series of DOE quarterly technical progress reports (Benson and Hurley, 1983; Benson et al., 1984ab; Karner et al., 1984).

The elements removed from the coals by the NH₄OAc extractions exist in the coals predominantly as cations associated as the salts of organic acids, although small amounts may be present as soluble minerals such as gypsum. Morgan (1980), however, showed that greater than 90% of the elements that could be extracted with one molar NH₄OAc from the western U.S. lignites that he studied were ion-exchanged from organic associations. In general, the majority of sodium and calcium in the coals was organically associated. In addition, large fractions of potassium and magnesium may be organically associated, although these percentages are much more variable. Potassium is most often not highly exchangeable and, therefore, assigned to clay minerals. As will be discussed later, the organically bound cations are of the most importance in PFBC since they are the most likely to volatilize during combustion and cause problems elsewhere in the combustion system.

Ranges in Concentrations of Inorganic Elements and Percents Extracted by 1 Molar Ammonium Acetate from 14 Western U.S. Low-Rank Coals

Element	Initial, ppm	Removed by NH₄OAc, %
Na	960-6200	76–100
Mg	980-20,540	17–100
Al	2180-11,480	0–23
Si	2050-33,060	0-12
K	390-1530	2-89
Ca	7500-22,790	39-85
Ti	104-1180	05
Fe	1450-11,090	0

Table 4

Ranges of Inorganic Elements Extracted by 1 Molar HCl and Remaining in the Residues from the Extractions of 14 Western U.S. Low-Rank Coals

Element	Removed by HCl, %	Remaining, %
Na	0-2	0-24
Mg	0-17	0-82
Al	29-81	19-58
Si	2-17	72–97
K	0–30	11–97
Ca	11–29	1–49
Ti	2–57	43–98
Fe .	14-73	27–79

The sources of the elements extracted by one molar HCl are less clear than the sources of the elements extracted by one molar NH₄OAc. Like the NH₄OAc extractions, the HCl extractions also remove elements associated with the organic fraction of the coal, principally those associated with coordination complexes. However, they also remove some elements present in mineral forms such as carbonates, sulfates, and oxides. Therefore, the amounts of elements extracted by one molar HCl indicate the maximum amount of the element that is organically complexed in the coal. Additional information about the concentrations of acid-soluble mineral matter is needed in order to calculate from the acid extraction data the actual concentrations of organically associated elements present in the coal.

2.1.2 Ash Formation and Partitioning During Combustion and Gasification

During combustion or gasification, the inorganic constituents of coal can undergo a variety of physical and chemical transformations. The transformations depend on the original mode of occurrence of

the constituent, the time-temperature history of the constituent during combustion or gasification, and the degree of the interaction with other constituents. The transformations are usually so extensive that the mineralogy and size distribution of the ash produced from the utilization of coal are quite different from the inorganic particles in the coal. Of critical importance to this work are the transformations that influence the partitioning of the ash among solid, liquid, and vapor phases.

Tracing the reactions that lead to the formation of the different species in the ash is a difficult process. There are, however, two main reaction paths: that encountered by the inorganics present in the coal as discrete particles of mineral matter and that followed by the organically associated inorganic species.

Several types of changes can occur in the discrete mineral matter present in coal during combustion. The main changes include:

- Vaporization and condensation.
- Fragmentation of inorganic grains.
- Convective transport of ash during rapid organic reaction (release of ash particles from burning char).
- Structural disintegration of char during the combustion process.
- Shedding of ash during receding of the surface of char particles.
- · Coalescence of ash particles.
- Cenosphere formation.

All of these mechanisms will be discussed briefly here for completeness; however, it should be recognized that many of these will not occur at the relatively low temperatures of the PFBC.

The initial reactions of the discrete mineral matter can begin at relatively low temperatures compared to those ultimately reached within the coal flame. Unfortunately, knowing at exactly what temperatures certain reactions or physical processes occur is complicated by the rapid heating rate experienced by the coal as it enters the combustor. The high heating rates and comparatively slow reaction rates cause initiation and completion temperatures to be different from those determined at slow heating rates, such as those obtained with laboratory analytical equipment. In addition, the high heating rates may cause some

reactions to occur concurrently, whereas at low heating rates they may occur sequentially. Therefore, the temperatures at which various reactions occur as determined by laboratory equipment operating at relatively low heating rates should be used only as a guide when attempting to delineate the reactions undergone by the mineral matter in coal during combustion.

Using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), O'Gorman and Walker (1973) studied the thermally induced decomposition and oxidation reactions in commonly occurring coal minerals as a function of temperature. When heating a mixture of pure minerals in air, O'Gorman and Walker showed that loss of adsorbed and interlayer water from clays occurs between 50° and 150°C (125° and 300°F). Gypsum (CaSO₄·2H₂O) also dehydrates in this temperature range, converting to bassanite (CaSO₄·½H₂O) and finally to anhydrite (CaSO₄) at 175°C (350°F). From 325° to 620°C (617° to 1150°F), loss of hydroxyl water from clays occurs as well as oxidation of pyrite (FeS₂). Between 700° and 830°C (1300° and 1525°F), the decomposition of calcite (CaCO₃) takes place, with no other weight losses occurring up to 1090°C (2000°F). In a simulated flue gas atmosphere, the weight loss curve was similar, except that the decomposition of calcite occurred about 150°C (270°F) higher than in air due to the presence of CO₂, along with a possible decomposition of anhydrite to calcium oxide above 800°C (1475°F). No significant solid-phase interactions between the minerals were noted below 1090°C (2000°F) (O'Gorman and Walker, 1973).

Manzoori (1990) focused his work primarily on the interactions of sodium and chlorine during fluidbed combustion. As a result of his work, he concluded that the inherent moisture in the coal evaporates as the coal is heated. The evaporation is complete when the particle temperature reaches 200°C (390°F). Sodium chloride and other salts dissolved in the inherent water crystallize within the coal particles. The crystals are likely to be finely distributed in the coal matrix. At temperatures between 400° and 900°C (705° and 1650°F), the coal devolatilizes, releasing the organic volatiles. During pyrolysis, the functional groups containing the inorganics decompose resulting in the formation, inside the coal particles, of reactive inorganic species. Some of these species are volatile (i.e., those from Na, S, and Cl) and may be released into the gas phase. Those species remaining in the coal are finely distributed in the coal matrix. Sodium carbonate, calcium oxide, magnesium oxide, alkali sulfates, iron oxide, and alumina phases may be formed.

Sodium chloride melts at about 815°C (1500°F) and has a significant vapor pressure at temperatures found in an FBC. At these temperatures, however, it reacts with other compounds inside and/or at the char's surface, resulting in a disproportionate release of sodium and chloride. Direct vaporization of sodium chloride increases with increasing temperatures. The volatilized alkali species can react with sulfur, silica, and clay to form sulfates, silicates, and aluminum silicates (Erickson et al., 1991). Above the temperatures typical in the FBC (900°C [1650°F]), significant reactions can occur between the acidic and basic oxides with the resultant formation of low melting eutectics. Sodium chloride and the species formed from the alkali elements, however, can form solid solutions with melting temperatures often below those found in FBC systems.

In pc (pulverized coal)-fired systems, fragmentation of some minerals has been shown to occur. Raask (1984) reports that under rapid heating conditions, pyrite fractures and fragments upon partial oxidation to FeS and before the FeS melts at 1075°C (1970°F). Raask (1984) also reports that significant portions of the carbonate minerals calcite, siderite (FeCO₃), and ankerite (CaFeCO₃) also fragment upon decomposition to form fume particles. Unlike the carbonate minerals, the silicate minerals do not undergo fragmentation during combustion or gasification. Instead, silicate and aluminosilicate particles tend to fuse into glassy spheres. In drop-tube furnace tests, aluminosilicate particles were found to spheroidize between 1300° and 1450°C (2375° and 2650°F), while larger quartz particles required temperatures above 1450°C (2650°F) (Raask, 1985). Fragmentation and melting will not typically occur at the temperatures seen in a PFBC (Erickson et al., 1992).

Of more importance to the temperatures experienced in the PFBC, and essential to this project, are the reactions of the organically associated mineral matter. The initial step in the release of alkali and alkaline earth metals from carboxylate groups in low-rank coal during combustion is decomposition of the carboxylate to form the metal carbonate. In DTA and TGA studies of sodium and potassium benzoates, Stewart and others (1982) described the formation of sodium and potassium carbonates in the temperature range of 400° to 600°C (750° to 1110°F). The formation of the carbonates was independent of the atmosphere used.

At higher temperatures, decomposition of the carbonates occurs. The exact mode of decomposition is not always clear and may vary with the metal in question. The general route of the decomposition of alkali metal carbonates is believed to be decomposition of the alkali metal carbonate to the metal oxide, followed by reduction of the oxide to metal vapor by carbon monoxide or char. The metal vapor then diffuses through the porous char to the surface of the char where it can react with ash particles or escape to the gas surrounding the burning char particle. In quadrupole mass spectrometry studies of the gas species present in a pulverized low-rank coal-air flame, Greene and O'Donnell (1987) demonstrated the appearance and disappearance of sodium atoms in the gas phase within 5 milliseconds of the time the coal entered the flame. After 5 milliseconds, sodium hydroxide appeared to be the dominant sodium species. However, the concentrations of all of the sodium species present in the flame after the disappearance of the atomic sodium were not enough to account for the disappearance of the atomic sodium from the gas phase, indicating condensation reactions had occurred. Neville and others (1981) have found that up to 60% of the sodium in a Montana lignite can escape the char during combustion in an entrained-flow reactor. Quann and Sarofim (1986) found that up to 20% of the magnesium, a small percentage of the calcium, and less than 1% of the aluminum found in the western U.S. low-rank coals that they studied were vaporized from the char during combustion in an entrained-flow reactor. Knudsen cell mass spectroscopy work on lowtemperature ashed sample of Illinois No. 6 and Wyodak coals was conducted by SRI (Southern Research Institute) International (SRI International, 1989). In the work with the Wyodak subbituminous coal, NaCl and KCl vapor species were observed above the coal ash, but these species were not detected above the Illinois No. 6 coal ash. The chlorine levels in the Wyodak were approximately three times higher than in the Illinois No. 6 sample.

As the metal vapors leave the burning char particle, they diffuse through the boundary layer of gas surrounding the char. The boundary layer is a region surrounding the oxidizing char within which gas concentrations and temperatures make the transition from conditions at the surface of the burning char to the conditions in the main combustor or gasifier atmosphere. In diffusing outward, the metal vapors encounter decreasing gas temperature and increasing compositions of gases, such as oxygen, that promote the condensation of the alkali.

In his work, Manzoori (1990) focused on the physicochemical transformations experienced by the inorganic mineral matter during AFBC. He analyzed the residual char and/or ash residues at various stages during combustion and attributed any loss of a specific component to vaporization. In his work with a high-sodium (12.4% Na₂O in the ash) Australian coal from the Lochiel trial pit, Manzoori found that the extent of vaporization of the sodium species including the sodium chloride was small. Most of the species formed from the organically bound sodium remain in the char and are likely to participate in ash formation on the char's surface. Chlorine was released at a disproportionately higher level than the sodium, suggesting that sodium chloride reacts with other compounds inside the char and/or on the char's surface. Sodium species formed as a result of these reactions can also participate in the ash formation mechanism. The presence of organic sulfur and sodium in low-rank coals resulted in a formation of a molten ash matrix on the char's surface. The ash matrix retains some of the solid species formed during the transformations of the organically bound elements such as Ca, Mg, and Al as well as some of the mineral inclusions in the coal including submicron silica particles which are intimately distributed in the coal matrix. Although the molten phase is likely to include sodium species formed from NaCl transformations, it contains only minute quantities of Cl. Figure 9 reviews the mechanisms of mineral matter release under FBC conditions.



Figure 9. Mechanisms of mineral matter release under FBC conditions

Cooling of the combustion gas has been utilized as one method for limiting the alkali content in the flue gas entering the turbine. The temperature and gas compositions necessary for the metals to condense depend on the metal and gas species, with alkali metals requiring cooler temperatures and greater reactant gas partial pressures than the alkaline earth metals. Consequently, the alkaline earth metals are predominantly in a condensed form in both combustion and gasification systems. The alkali metals, however, are present in much higher concentrations in the vapor phase. The most common vapor forms of the alkali metals are sulfate, hydroxide, and chloride. The saturation partial pressures of the potassium salts are slightly higher than those of the sodium salts, although they are generally similar.

In combustion systems, where SQ₂ is available, condensed sulfates and silicates are the thermodynamically favored forms of sodium and potassium, so most, but not all, of the alkalies are present in those forms. The vapor pressure of the sulfate forms is high enough that a portion of the alkali sulfates can exist in vapor form. Therefore, some alkali exists as vapor, with sulfates and hydroxides as the dominant forms. Although the saturation vapor pressures of the alkali hydroxides are higher than those of the sulfates, the sulfates are more thermodynamically stable and so usually make up the larger fraction of the vapor-phase alkali. Only a small proportion of the other more volatile trace elements leave the PFBC in the vapor phase. Emissions range from 0.5% to 1.2% for Cu, 7.5% to 16% for Hg, 1% to 3% for Pb, 5% for Cd, and 4% for As (Mojtahedi et al., 1990).

2.2 Modeling of Gas-Phase Alkali Composition

While the previous discussion focused on the mechanisms by which sodium, potassium, and chlorine are initially released in a coal conversion process, equally important are the chemical interactions that occur in the gas phase. These interactions subsequently alter the chemical compositions and the resultant phase equilibria of the alkali and halogen compounds. The gas composition is important in determining the exact methods by which the alkali and halogen compounds can be removed from the gas stream or in evaluating their effect on material corrosion. Recent studies to evaluate these aspects have assumed two formats: thermodynamic studies where thermochemical equilibrium models have been used to predict the composition and nature of the chemical species present in various reactant systems (Scandrett, 1983; Scandrett and Clift, 1984; Spacil and Luthra, 1982; Mulik et al., 1983; and Pintsch and Gudenau, 1991) and experimental studies where measurements are performed to determine the same parameters (Bachovchin et

al., 1986; Bachovchin and Alvin, 1987; Lee and Johnson, 1980; Lee and Myles, 1987; Lee and Swift, 1991; Scandrett and Clift, 1984; Radhakrishnan et al., 1986; Pintsch and Gudenau, 1991b; Zakkay et al., 1989; Punjak et al., 1989; Uberoi et al., 1990). This subsection will review the thermochemical equilibrium studies, while the next section will present experimental results. Understanding the processes affecting the composition, phase equilibria, and unit operations for the removal of the alkali and halogen compounds formed in the PFBC is an important step toward developing methods to clean the product gas to a level that can meet current turbine manufacturer standards.

A number of different thermochemical equilibrium models have been used to calculate the distribution of alkali species both with and without alkali sorbents. Most of these models are based on calculating the equilibrium composition by minimizing the Gibbs free energy of the system. Similar results have been obtained by various researchers using these types of models. When using results from these calculations, it is important to remember that all calculations based on thermochemical data are subject to limitations. First, they are dependent upon the accuracy of the data on which they are based. Second, thermochemical data can be difficult to obtain for all of the relevant species at high temperatures. Third, these calculations estimate the conditions at thermodynamic equilibrium only and do not take kinetic limitations into account. However, thermodynamic equilibrium represents a composition toward which chemical reactions proceed. This type of calculation can be used to distinguish between reactions that can and cannot proceed under given conditions of temperature, pressure, and composition. The rates of approach to this thermodynamic equilibrium (chemical kinetics), however, must normally be investigated experimentally.

Mojtahedi and Backman (1989) utilized a computer program (SOLGASMIX) developed by Erickson (1975) to predict the gas-phase composition of alkali species as a function of temperature, pressure, and the relative content of sodium, potassium, chlorine, and sulfur. The 64 chemical species listed in Table 5 were included in model predictions. Equilibrium compositions were calculated assuming that gas mixtures are ideal and that all solid condensed phases are immiscible. This is a reasonable assumption for the relatively low temperatures and pressures under which the PFBC operated. For the liquid phase, a nonideal subregular model was used for alkali carbonates and sulfates.

Table 5

Chemical Species Considered in the Equilibrium Calculations (Mojtahedi and Backman, 1989)

Gas Phase:	CO ₂ , H ₂ O, O ₂ , OH, N ₂ , H ₂ , CH ₄ , HCO, H, O, N, HCN, C, NH ₃ , HCl, Cl, Cl ₂ , SO ₃ , SO ₂ , S, S ₂ , H ₂ ,S, COS, HS, CS, CS ₂ , S ₂ O, H ₂ SO ₄ , Na, Na ₂ , NaCl, Na ₂ Cl ₂ , NaOH, NaH, NaO, Na ₂ SO ₄ , K, K ₂ , KCl, K ₂ Cl ₂ , KOH, KH, KO, K ₂ ,SO ₄
Liquid Phase:	Na ₂ CO ₃ , Na ₂ SO ₄ , Na ₂ S, NaCl, NaOH, K ₂ CO ₃ , K ₂ SO ₄ , K ₂ S, KCl, KOH
Solid Phases:	Na ₂ CO ₃ , Na ₂ SO ₄ , Na ₂ S, NaCl, NaOH, K ₂ CO ₃ , K ₂ SO ₄ , K ₂ S, KCl, KOH
Feedstock Composition	n, wt% on a dry basis
Carbon	55
Hydrogen	5.5
Oxygen	32.6
Nitrogen	1.7
Sodium	0.005–0.16
Potassium	0.014-0.448
Chlorine	0.005–0.8
Sulfur	0.01-0.26
(40 wt% H_2O in the as-	received fuel)

Figure 10 shows the predicted phase distribution of sodium, potassium, and chlorine for the case with a pressure of 10 bar; a stoichiometric air ratio of 1.2; and potassium, sodium, and chlorine concentrations of 400, 100, and 400 ppmw, respectively. The liquid phase consists almost entirely of the sulfates of sodium and potassium. Solid sodium sulfate seems to form below 740°C (1364°F), but solid potassium sulfate could be present even at 900°C (1650°F). The total alkali content in the vapor phase was predicted to be 0.06 ppmv (parts per million by volume) (0.01 Na and 0.05 K) at 800°C (1472°F) under these PFBC conditions. These values represent about 0.1% of the sodium and 0.16% of the potassium in the system. The corresponding values at 900°C (1650°F) are 0.83 ppmv for the total volatilized alkali (Na = 0.14; K = 0.69), an increase of 10-fold. This represents about 1.2% of the total sodium and 2.5% of the potassium entering the system.



Figure 10. Distribution of Na, K, and Cl in three phases under PFBC conditions (Mojtahedi and Backman, 1989)

The predicted gas-phase composition is presented in Figure 11. This figure shows a dominance of HCl in the gas phase. Of the alkalies, the chlorides exist in significantly higher quantities than do the corresponding sulfates and hydroxides. The alkali chlorides are 1 to 3 orders of magnitude higher in the PFBC operating range. The effect of the chlorine content of the fuel on the distribution of the two metals is interesting to note. Because the HCl(g) concentration is much higher than that of the alkali chlorides, its formation would be expected to have a negligible effect upon the latter's concentration in the gas. However, Figure 12 shows that the volatilization of both sodium and potassium can be strongly dependent on the chlorine content of the in-going fuel. The higher the Cl content is, the higher the vapor-phase alkali chlorides in the flue gas. At 900°C (1650°F), the alkali content in the vapor phase more than doubles with a corresponding doubling of the chlorine content in the fuel.

The dependency of alkali vapor concentrations on the fuel's chlorine concentration is reinforced in Figure 13. Here, the chlorine content of the feedstock was varied between 50 and 800 mg/kg which represents the two extremes in the chlorine studied. Both vapor-phase chlorides of sodium and potassium



Figure 11. Variation of the partial pressure of the gaseous alkali species with temperature (Mojtahedi and Backman, 1989)



Sodium in Vapor Phase

Figure 12. Variation of the vapor-phase Na and K concentrations in the flue gas with temperature for three different Cl contents (Mojtahedi and Backman, 1989)



Figure 13. Variation of the partial pressure of the gaseous alkali species with (Na + K)/Cl ratio (Mojtahedi and Backman, 1989)

show a decrease of almost an order of magnitude in their concentration when the chlorine content is reduced by about 90%. The total alkali (Na + K) content in the vapor phase decreases from 0.5 to 0.04 ppmv. This indicates the importance of the chlorine concentration of the fuel used in a PFBC. The flue gas composition with respect to the volatilized alkali compound (principally chlorides), the necessity to remove these compounds, and the removal mechanisms selected would depend to some extent on the type of fuel combusted, i.e., the initial chlorine and alkali content.

One of the attributes of the PFBC is the ability to remove sulfur in the bed using sulfur sorbents. The effect of sulfur removal on vapor-phase alkali concentrations is demonstrated in Figure 14. The sulfur content of the fuel was varied between 100 and 2600 mg/kg, while the alkali content, chlorine content, and Na/K ratio were maintained. The operating conditions, temperature of 850°C (1560°F), and pressure of 10 bar were also kept constant. The concentration of chlorides shows a steady increase with decreasing sulfur content. This is due to the fact that the percentage of condensed alkali sulfates decreases when the alkali/sulfur ratio increases, releasing more alkali to form alkali chlorides in the gas phase. The presence of condensed alkali sulfates causes the concentrations of vapor-phase alkali sulfates to be constant in the whole



Figure 14. Variations of the partial pressure of gaseous alkali species with (K + NA)/S ratio (Mojtahedi and Backman, 1989)

alkali/sulfur range considered. Use of low-sulfur fuel or an efficient sulfur removal sorbent seems to result in increased vapor-phase alkali content in the flue gas. The curves corresponding to the volatilized sulfates show no change in concentration with changing (Na+K)/S ratios.

Calculations were also performed by Mojtahedi and Backman (1989) at operating conditions corresponding to AFBC (1 bar). As with the pressurized case, the higher chlorine content of the fuel enhances alkali metal volatilization in the form of alkali chlorides. The effect of increasing the operating pressure of the system on the concentration of alkali metals released in the gas phase at equilibrium is shown in Figure 15. At 850°C (1560°F), the equilibrium concentration of sodium in the gas-phases increases from almost 0.04 to about 0.67 ppmv when the pressure is reduced from 10 to 1 bar. Similar calculations with potassium show an increase of more than 10-fold (0.19 to 2.76 ppmv) in the concentration of volatilized potassium released into the flue gas.

Sinha and others (1987) have also performed equilibrium calculations to estimate the most likely compounds and phases formed during PFBC. They used a high-sulfur eastern U.S. bituminous coal as the basis of their calculations. Figure 16 presents a summary of the calculated molar concentrations for the



Figure 15. Na and K concentration in the vapor phase in the flue gas at 1 to 25 bar pressure range under combustion conditions (Mojtahedi and Backman, 1989)



Figure 16. Composition of condensed mineral phases formed under oxidizing conditions when burning an eastern bituminous coal (Sinha et al., 1987)
relatively large number of sodium- and nonsodium-based liquid species formed in a combustion environment. At high gas temperatures outside of the PFBC range (above $1327^{\circ}C$ [2420°F]), the equilibrium concentration of the condensed liquid species formed are dominated by the presence of Na₂·2SiO₂ and FeO·SiO₂ compounds. At PFBC temperatures below 977°C (1790°F), the condensed phases were predicted to consist mainly of Na₂SO₄. This is in agreement with the work reported by Mojtahedi and Backman (1989). However, the studies by Mulik and others (1983) and Scandrett and Clift (1984) suggest that the vapor-phase alkali chlorides may react to form alkali aluminosilicates. Some of the glassy phase aluminosilicate compounds that were predicted to exist at equilibrium conditions can only be formed by very slow reactions that rely on the intimate contact between the Na₂SO₄ liquid and an ash-based aluminosilicate phase, and these reactions are unlikely to proceed to completion in a practical system. Therefore, the liquid phase compositions which were calculated by Sinha and others (1987) at temperatures lower than 1117°C (2040°F) represent higher nonequilibrium concentrations of these compounds (shown as dotted lines in Figure 16).

Even though the reactions with the aluminosilicates are slow and do not proceed to equilibrium, aluminosilicate phases have been observed in PFBC fly ashes and bed material (Mann, 1994) and should be included in modeling efforts. When Sinha included the aluminosilicate phases in his modeling efforts, the Na₂SO₄ liquid phases practically disappeared at temperatures below 1117°C. In reality, it is anticipated that the Na₂SO₄ will be the major phase, but aluminosilicates will also be present. However, within this temperature range, the sodium silicates are not expected to be formed as indicated by the results of Sinha's modeling. Vapor pressures of the chlorine compounds calculated under equilibrium and nonequilibrium conditions are reported in Figure 17 and show NaCl and HCl are the major carries of the chlorine in the system. They also show a predominance of the alkali chlorides versus the sulfates and hydroxides. These results are again similar to those of Mojtahedi and Backman (1989) and others who have performed thermochemical equilibrium calculations under PFBC or gasification conditions (Scandrett, 1983; Scandrett and Clift, 1984; Spacil and Luthra, 1982; Mulik et al., 1983; Pintsch and Gudenau, 1991b).

The thermochemical equilibria calculations of the alkali compounds show that when coals are burned in a PFBC, condensed alkali sulfates are formed in the flue gas. The alkali sulfates will most likely



Figure 17. Partial pressures of important gaseous species formed during the combustion of an eastern bituminous coal (Singh et al., 1989)

deposit on the fly ash particles and be removed from the gas phase by filtration in a dust suppression system. Some may condense to form fine particulate that would be more difficult to collect in conventional filter devices. Alkali sulfate deposition in the fly ash would be expected to improve the cohesivity and retention properties of the PFBC fly ash and lower the sintering temperatures. The calculations also show that a substantial residual fraction of the alkalies will remain in the gas phase, primarily as alkali chlorides for higher-chlorine coals. In theory, the condensation and removal of alkali sulfates by particulate filtration alone can remove all of the alkali contaminant released when a coal is burned with negligible or zero chlorine content. However, virtually all coals have enough chlorine where particulate filters alone will not be able to remove the higher residual concentrations of the volatile alkali chlorides present in the PFBC environment, and combined alkali and chlorine removal may prove to be an essential element in effectively controlling alkalies.

2.3 Adsorption Theory

Removal of a vapor from a gas can be accomplished either physically by absorption in a liquid or adsorption on a solid surface or by chemical reaction. Physical adsorption, or "van der Waals" adsorption,

a readily reversible phenomenon, is the result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed. When, for example, the intermolecular attractive forces between a solid and a gas are greater than those existing between molecules of the gas itself, the gas will condense upon the surface of the solid even though its pressure may be lower than the vapor pressure corresponding to the prevailing temperature. Such a condensation will be accompanied by an evolution of heat, in an amount usually somewhat larger than the latent heat of vaporization and of the order of the heat of sublimination of the gas. The adsorbed substance does not penetrate within the crystal lattice of the solid and does not dissolve in it but remains entirely upon the surface. If, however, the solid is highly porous, containing many fine capillaries, the adsorbed substance will penetrate these interstices if it wets the solid. At equilibrium, the partial pressure of the adsorbed substance equals that of the contacting gas phase, and by lowering the pressure of the gas phase or by raising the temperature, the adsorbed gas is readily removed or desorbed in unchanged form.

Chemisorption, or activated adsorption, is the result of chemical interaction between the solid and the adsorbed substance. The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form, but the adhesive force is generally much greater than that found in physical adsorption. The heat liberated during chemisorption is usually large, of the order of the heat of chemical reaction. The process is frequently irreversible, and on desorption the original substance will often be found to have undergone a chemical change. The same substance which, under conditions of low temperature, will undergo substantially only physical adsorption upon a solid will sometimes exhibit chemisorption at higher temperatures, and both phenomena may occur at the same time.

Some of the attributes of sorbents whose primary removal mechanisms are either physical or chemical adsorption are listed in Table 6. For most parameters, the sorbent characteristics are very different depending upon its adsorption mechanism. It is critical to understand these differences to ensure selection of a sorbent with the characteristics required for use as an in-bed capturing agent. The characteristics of a good sorbent for this application include the following:

- High-temperature compatibility
- Rapid rate of adsorption

- High loading capacity
- Transformation of alkali into a less corrosive form
- Irreversible adsorption
- Physical stability
- Solid at system temperature
- No toxicological effects
- Low cost

Table 6

Characteristics of Physical and Chemical Adsorption

Parameter	Physical Adsorption	Chemical Adsorption		
Adsorbent	All solids	Some solids		
Adsorbate	All gases below critical temperature	Some chemically reactive gases		
Temperature Range	Low Temperature	High Temperature		
Heat of Adsorption	Low	High (order of heat of reaction)		
Rate, Activation	Very rapid, Low E	Nonactivated, low E; Activated, high E		
Coverage	Multilayer possible	Monolayer		
Reversibility	Highly reversible	Often irreversible		

This subsection will discuss the mechanism of adsorption theory to identify the importance of gas-solid adsorption. Subsection 2.4 will discuss aluminosilicate adsorbents to show specific attributes required for adsorption of alkali gases.

2.3.1 Mass Transfer in Batch Operations

The adsorption process in fluid beds is rather complex. The approach taken here is first to describe mass transfer in general for fluid-bed operations using a general rate equation for adsorption. This analogy will present some limitations on the maximum effectiveness of the FBC for removing specific vapor components from the flue gas. Following will be a discussion of the various rate-limiting steps and how each of these impacts the conversion efficiencies and residence time requirements for the adsorption process. The impact of operating parameters will also be discussed. The general theory discussed is taken from Kunii and Levenspiel, 1991.

Figure 18 defines the system where a batch of solids is fluidized with an inert carrier gas containing dilute A of mass concentration C_{Ai} (kg/m³), which is adsorbed isothermally by the solids. Let Q be the weight fraction of adsorbed vapor (adsorbate) on the solids, and let C_A^* be the vapor concentration of A in equilibrium with solids having a vapor fraction Q. Figure 19 shows the equilibrium relationships found by experiment for various adsorbent systems with Q_i and Q_i representing the weight fraction of volatiles, initially in the solids and in equilibrium with the entering gas, respectively. The y-axis is the amount of solute adsorbed by the solids divided by the maximum that could be adsorbed. The time required to reach zero (full adsorbance) indicates long solids residence times are required for efficient use of adsorbents in a fluid bed.

For this preliminary analysis, it is assumed that the difference in concentration of diffusing vapor between the center and surface of adsorbent particles is negligibly small except for an extremely fast change in vapor composition with the time in the bed. Also, for normal fluidizing conditions such as particle diameter, $d_p < 1$ mm and bed depth, $L_m > 0.2$ to 0.3 m, the exiting gas can be taken to be in equilibrium with the solids in the bed, or:

$$C_{Ae} = C_A^*$$
 [6]



Figure 18. Adsorption of vapor by a batch of solids. The calculated lines are for theoretical adsorption of water vapor from air by activated alumina at 25°C



Figure 19. Examples of equilibrium isotherms between water vapor on the solid and in air, Q (kg adsorbed/kg solid) for 1) silica gel, 2) molecular sieve, and 3) activated alumina

A material balance about the whole bed gives:

$$\begin{pmatrix} vapor lost \\ by gas \end{pmatrix} = \begin{pmatrix} vapor adsorbed \\ by solids \end{pmatrix}$$

From Eq. 6 this expression becomes:

$$A_{\mu}u_{o}(C_{A_{\mu}}-C_{A}) dt = A_{\mu}(1-\varepsilon_{m})\rho_{s}dQ, \quad [kg]$$
^[7]

where A_i is the bed cross-sectional area, u_o is the superficial gas velocity, ρ_s is the solids density, and ϵ_m is the void fraction in the bed. Separating and integrating for an initial vapor content on the solids Q_0 gives:

$$\int_{Q_0}^{Q} \frac{dQ}{C_{A_i} - C_A^*} = \frac{u_o t}{\rho_s L_m (1 - \varepsilon_m)}$$
[8]

Given the relationship between C_A^* and Q for the system on hand, we can then find how Q changes with time. For example, for the adsorption of water vapor from air by activated alumina, as shown in Figure 19, we have approximately:

$$C_A^* = b_1 + b_2 Q$$
 [9]

where b_1 and b_2 are arbitrary constants. Substituting Eq. 9 in Eq. 8 and solving gives:

$$\frac{Q_i^* - Q}{Q_i^* - Q_0} = \exp\left[-\frac{b_2 u_0 t}{\rho_s (1 - \varepsilon_m) L_m}\right]$$
[10]

where Q_1^* is the vapor fraction of the solid that would be in equilibrium with the incoming gas, or

$$C_{Ai} = b_1 + b_2 Q_i^*$$
 [11]

With $b_2 = 0.1$ kg/m³ and $\rho_s = 2000$ kg/m³, and Em = 0.5 for alumina, Eq. 10 can be written as:

$$\frac{Q_i^* - Q}{Q_i^* - Q_0} = \exp\left[-\exp\left[-\exp\left[\frac{1 \times 10^{-4}t}{L_m/u_o}\right]\right]$$
[12]

Eq. 12 shows that the moisture fraction in the solids rises exponentially with time with rate proportional to gas velocity and inversely proportional to bed height. This result is presented in Figure 18 and shows that the approach to equilibrium for the solids is rather slow under normal fluidizing conditions.

For desorption of volatile matter from porous adsorbed solids, a similar analysis gives:

$$-\int_{Q=Q_0}^{Q} \frac{dQ}{C_A^* - C_{A_I}} = \frac{u_o t}{\rho_s (1 - \varepsilon_m) L_m}$$
[13]

With the linear equilibrium relationship of Eq. 11, this integrates to:

$$\frac{Q-Q'}{Q_0-Q'} = \exp\left[-\frac{b_2 u_o t}{\rho_s (1-\varepsilon_m) L_m}\right]$$
[14]

Again, Q_0 and Q_i are the weight fractions of volatiles initially in the solid and in equilibrium with the entering gas, respectively.

2.3.2 Mass Transfer in Continuous Operations

A similar analogy can be done for a continuous operation. This section considers only reversible mass transfer. Irreversible transfer or adsorption followed by reaction with solid will be discussed in the next subsection. A rigorous treatment of continuous operations is quite complicated; however, a great simplification can be made with the fairly good assumption, suggested from batch operations, that the bed solids are in equilibrium with the leaving gas. Thus for beds that are not too shallow, $L_m/d_p > 100$ to 200, assume an equilibrium operation, and take a mass balance. Referring to Figure 20, a mass balance for the transferring vapor gives:

$$A_i u_o (C_{Ai} - C_A^*) = F_0 (Q - Q_i) \quad [\text{kg moisture/s}]$$
[15]

where each gas-solid system has its own particular equilibrium relationship, such as given by Eq. 11. In general, Eqs. 11 and 15 can then be solved simultaneously and directly without integration.

Again, using the adsorption of water vapor on activated alumina for example, the relationship of bed solids and exit gas becomes:

$$C_{A}^{*} = b_{1}^{*} + b_{2}^{*}Q$$
 [16]

For gas in equilibrium with entering solids:

$$C_{A_{i}}^{*} = b_{1} + b_{2}Q_{i}$$
 [17]

and for solids in equilibrium with entering gas:

$$C_{A_{1}} = b_{1} + b_{2}Q_{1}^{*}$$
 [18]

Rearranging Eq. 15 allows the following efficiency measures to be defined:

$$\eta'_{g} = \begin{pmatrix} \text{amount of solute} \\ \frac{\text{actually given up by gas}}{\text{maximum that could}} \\ \text{be given up} \end{pmatrix} = \frac{C_{Ai} - C_{Ae}}{C_{Ai} - C_{Ai}^{*}} = \frac{1}{1 + \phi'}$$
[19]

and:

$$\eta'_{s} = \begin{pmatrix} \text{amount of solute} \\ \frac{\text{adsorbed by solids}}{\text{maximum that could}} \\ \text{be adsorbed} \end{pmatrix} = \frac{Q - Q_{i}}{Q_{i}^{*} - Q_{i}} = \frac{\Phi}{1 + \Phi} = 1 - \eta'_{g}$$
[20]

where:

1

$$\phi' = \frac{A_i u_o b_2}{F_0}$$
[21]

These equations show that a 99% efficiency in removing solute from the gas is possible only at the expense of a 1% efficiency in the use of solids as an adsorbent. This requires using large amounts of solids and illustrates the general finding that single-stage contacting is accompanied by low efficiencies. This may be a concern for finding an economical in-bed sorbent capable of meeting the stringent turbine manufacturer guidelines.



Figure 20. Continuous mass transfer operations between solids and gas in a single fluidized bed, for gas in equilibrium with entering solids

2.3.3 Kinetic Models for the Conversion of Solids

The conversion of solids can follow one of two extremes of behavior. At one extreme, the diffusion of gaseous reactant into a particle is rapid enough compared to chemical reaction so that solid reactant B is consumed more or less uniformly throughout the particle. This is the *uniform-reaction model* (Figure 21). At the other extreme, diffusion into the reactant particle is so slow that the reaction zone is restricted to a thin front that advances from the outer surface into the particle. This model is called the *unreacted-* or *shrinking-core model* (Figure 22). Real situations lie between these extremes; however, because these extremes are easy to treat, they are used to represent the real situation. The first and most important consideration to applying these models is to select the model that most closely represents reality, and only then should the detailed mechanism and the rate constants be evaluated.

2.3.3.1 Uniform-Reaction Model for Porous Solids of Unchanging Size

As shown in Figure 21, gaseous reactant A is present evenly, or close to evenly, throughout the particle and reacts with solid reactant B everywhere. Although further analysis in terms of a detailed



Figure 21. Uniform-reaction model. Here the reaction proceeds throughout the particle



Figure 22. Shrinking-core model. Here the reaction proceeds at a narrow front that advances into the particle

mechanism may lead to a more complicated reaction rate expression, it can be assumed that

$$\begin{pmatrix} \text{rate of consumption} \\ \text{of B} \end{pmatrix} \propto \begin{pmatrix} \text{concentration of A} \\ \text{bathing the particle} \end{pmatrix} \begin{pmatrix} \text{amount of reactant} \\ \text{B left unreacted} \end{pmatrix}$$

as a first approximation. In terms of the fraction of B converted, $X_{\rm B}$, and for a uniform concentration of gaseous reactant, $C_{\rm A}$, the rate expression becomes

$$\frac{dX_B}{dt} = k_r C_A (1 - X_B)$$
[22]

Since C_A is a constant, integration gives the progress of conversion with time, or

$$1 - X_B = \exp\left(-k_{c}C_{d}t\right)$$
[23]

where k_r (m³ gas/mol A · s) is the rate coefficient based on unit volume of solid.

2.3.3.2 Shrinking-Core Model for Solids of Unchanging Size

Figure 22 shows that the reaction front advances from the outer surface into the particle leaving behind a layer of completely converted and inert material. At the same time, the core of unreacted solid shrinks and finally disappears. For a reacting particle at some intermediate stage of conversion, the following steps can occur in series:

Step 1. Gaseous A diffuses through the film surrounding the particle to its surface.

Step 2. Gaseous A penetrates and diffuses through the blanket of product solid to reach the reaction front.

Step 3. Gaseous A reacts with reactant B in the narrow reaction zone.

Step 4. Gaseous reaction products diffuse through the product layer from the reaction zone to the surface of the particle.

Step. 5 Gaseous reaction products diffuse into the main gas stream.

A reaction need not involve all these steps. For example, if no gaseous product forms, only the first three steps occur.

The kinetic expressions and integrated conversion equations are given when one of the above resistance controls. The detailed derivations of these expressions are given elsewhere (Levenspiel, 1972) and are based on the assumptions that reaction is irreversible, that particles are spherical, and that the thickness of reaction zone is small compared with the dimensions of the particle. This last assumption allows us to use the shrinking-core model. This model may reasonably represent large particles while the uniform-reaction model better represents small particles in the same environment.

Finally, the distinguishing feature of the conversion equations that follow is that they are expressed in terms of a characteristic time τ , the time required to completely convert an unreacted particle into product. This differs from what usually is encountered in other areas of kinetics. This analogy was used since τ is a critical design parameter that can be used to evaluate the effectiveness of the sorbent.

<u>Chemical Reaction Controls</u>. Here the rate of conversion of solid is proportional to the area of reaction front. Thus for an unreacted core of radius r_c in a particle of radius R, the rate of reaction of A can be reasonably be represented by:

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = -\frac{1}{4\pi r_c^2 b} \frac{dN_B}{dt} = k_c C_A$$
[24]

where k_c (m³ gas/m² solid \cdot s) is a rate constant for the chemical reaction, but is proportional to the volume fraction of *B* in the solid.

The progress of reaction in a single particle, in terms of the core size or conversion, is:

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}$$
[25]

where the relation between conversion and radius of shrinking core is:

$$\left(\frac{r_c}{R}\right)^3 = 1 - X_B$$
 [26]

In Eq. 25 the time for complete conversion is:

$$\tau = \frac{\rho_B R}{bk_c C_A} = \frac{\rho_B d_p}{2bk_c C_A}$$
[27]

where τ is independent of the volume fraction of *B* in the solid and ρ_B (mol/m³) is the molar density of *B* in the solid (Kimura et al., 1982).

<u>Diffusion Through Gas Film Controls</u>. This mechanism can only control in the early stages of conversion when no product layer is present. As soon as a product layer forms, its resistance dominates; consequently, for engineering applications, the resistance to diffusion through the gas film surrounding the particle can safely be ignored whenever a product layer remains on the particle.

<u>Diffusion Through the Product Layer Controls</u>. The direct application of Fick's law for diffusion of reactant *A* through the product layer gives the progress of reaction with time as:

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3$$
[28]

where τ is the time for complete conversion of a fresh particle and is given by:

$$\tau = \frac{\rho_B R^2}{6b D_s C_A} = \frac{\rho_B d_p^2}{24 b D_s C_A}$$
[29]

where D_s is the effective diffusivity of gaseous reactant through the product blanket and ρ_B is the molar density of B in the unreacted solid.

<u>Combination of Resistances</u>. When the resistances of the chemical reaction and diffusion steps are comparable, we can approximately represent the overall progress of the reactions by Eqs. 24 and 27, where the reaction rate constant k_c is replaced by \overline{K} , defined by:

$$\frac{1}{\overline{k}} \approx \frac{1}{k_c} + \frac{d_p}{12D_s}, \qquad [\text{m}^2 \text{ solid} \cdot \text{s/m}^3 \text{gas}] \qquad [30]$$

For completely porous spherical particles, we can define a Thiele-type modulus:

$$M_T = R \sqrt{\frac{K_r}{D_s}} \quad \text{with} \quad K_r = \frac{\left(3 \ to \ \frac{1}{3}\right)k_c}{R} = \frac{K_r \times \rho_B}{b} \quad [\text{m}^3\text{gas/m}^3\text{solid}\cdot\text{s}]$$
[31]

to represent the relative rates of diffusion of A into the particle and the reaction of A in the particle. Then, as shown by Kimura, 1981):

When $M_T \le 1$, gaseous reactant A can easily penetrate the particle and is close to evenly distributed therein, thus the uniform-conversion model of Eq. 23 applies.

When $M_T > 20$, the progression of reaction of the particle follows the shrinking-core model with diffusion through the product layer controlling, as given by Eq. 29.

2.3.3.3 Intermediate Models for Particles of Unchanging Size

Numerous models have been developed to account for particle behavior between the extremes of the uniform-conversion and the shrinking-core models. These intermediate models fall into two classes: those for porous particles and those for particles that start as nonporous but then become porous on reaction. For porous particles, the porous-pellet model of Ishida and Wen (1968) and the grain model of Sohn and Szekely (1972) are applicable. The conversion-versus-time curves for these models are closely

similar to the curves for the shrinking-core model—high rate of conversion at the beginning, slowing progressively as conversion rises. For particles that start as nonporous, we have the crackling-core model of Park and Levenspeil (1975). By action of reactant gas, the pellet transforms progressively from the outside in, by crackling and fissuring, to form an easily penetrated (no diffusional resistance) porous structure consisting of grain material that then reacts away to the final product according to the shrinking-core model. Of special interest is that this model can account for the sometimes observed S-shaped conversion-versus-time curves—thus, slow conversion at the start, then fast, and finally slow.

Finally, in any particular reacting system, the controlling resistance not only may shift from diffusion to reaction, but it may even change from the shrinking-core model to the uniform-reaction model as particle size and temperature of operations are changed.

2.3.4 Applying the Models to a Dynamic System

In a real fluid bed, there is a constant feed rate of both solids and gas. Figure 23 represents a simple system where the particles are of uniform size and there is no carryover of material from the fluid bed.

The conversion $X_{\rm B}$ of an individual particle of solid depends on its length of stay in the bed. For the appropriate controlling resistance, this conversion is given by Eq. 23, 25, or 29. However, the individual particles have different residence times in the bed. For this reason, the conversion level varies from particle to particle, and on accounting for this, the mean conversion of the exit stream of solids \overline{X}_{B} is:

$$\begin{pmatrix} \text{fraction of B} \\ \text{unconverted in} \\ \text{the leaving solids} \end{pmatrix} = \sum_{\substack{\text{particles} \\ \text{of all ages}}} \begin{pmatrix} \text{fraction of B} \\ \text{unconverted in} \\ \text{particles staying} \\ \text{in the reactor} \\ \text{for time between} \\ \text{t and t + dt} \end{pmatrix} \begin{pmatrix} \text{fraction of exit} \\ \text{stream that stays} \\ \text{this length of time} \\ \text{in the reactor} \end{pmatrix} [32]$$

In symbols:

$$1 - \overline{X}_B = \int_{t=0}^{\infty} (1 - X_B)_{\text{particle}} \boldsymbol{E}(t) dt \qquad [32]$$

52

where the exit age distribution for the solids in a single fluidized bed is:

$$E(t) = \frac{1}{t} e^{-t/t}$$
[33]

and where the mean residence time of these solids is:

$$\overline{t} = \frac{W}{F_1}$$
[34]

This allows us to give the conversion expressions for a fluidized bed for the various controlling resistances. For the *uniform-reaction model* and first-order reaction with respect to the reactant gas, substitution of Eqs. 23 and 33 in Eq. 32 gives:

$$1 - \bar{X}_{B} = \int_{t=0}^{\infty} \exp(-k_{r}C_{A}t) \frac{e^{-t/\bar{t}}}{\bar{t}} dt = \frac{1}{1 + k_{r}C_{A}\bar{t}}$$
[35]

For shrinking-core reaction-controlling kinetics, substitution of Eqs. 25 and 33 in Eq. 32 gives

$$1 - \overline{X}_B = \int_0^\tau \left(1 - \frac{t}{\tau}\right)^3 \frac{e^{-t/\overline{t}}}{\overline{t}} dt$$
 [36]



Figure 23. Variables for a fluidized-bed reactor treating particles of uniform size using the shrinking-core model

The range of integration is from 0 to τ rather than from 0 to ∞ , because a particle that stays in the bed longer than time τ does not contribute to $1 - X_{\rm B}$. Integrating this expression gives:

$$1 - \overline{X}_{B} = 1 - 3\left(\frac{\overline{t}}{\tau}\right) + 6\left(\frac{\overline{t}}{\tau}\right)^{2} - 6\left(\frac{\overline{t}}{\tau}\right)^{3} \left(1 - \overline{e^{\tau/t}}\right)$$
[37]

or, in equivalent expanded form, useful for $\overline{t}/\tau > 1$:

$$1 - \overline{X}_B = \frac{1}{4} \left(\frac{\tau}{\overline{t}}\right) - \frac{1}{20} \left(\frac{\tau}{\overline{t}}\right)^2 + \frac{1}{120} \left(\frac{\tau}{\overline{t}}\right)^3 - \cdots$$
[38]

or for $\overline{t}/\tau > 5$

$$1 - \bar{X}_B \approx \frac{1}{4} \frac{\tau}{\bar{t}}$$
[39]

In all these expressions, τ is given by Eq. 27.

For shrinking-core diffusion in product-layer-controlling kinetics, replacing Eq. 29 in Eq. 32 and integrating gives an expression that, on expansion, reduces to:

$$1 - X_B = \frac{1}{5} \left(\frac{\tau}{t}\right) - \frac{19}{420} \left(\frac{\tau}{t}\right)^2 + \frac{41}{4620} \left(\frac{\tau}{t}\right)^3 - 0.00149 \left(\frac{\tau}{t}\right)^4 + \cdots$$
 [40]

Again, for high conversions, or where $t/\tau > 5$:

$$1 - \overline{X}_B = \frac{1}{5} \left(\frac{\tau}{t} \right)$$
 [41]

In these expressions τ is given by Eq. 29.

2.3.4.1 Conversion of Both Gas and Solids

Until now, it has been assumed that the reacting solids are bathed by gas of the same mean composition, no matter what changes are made in the operating conditions. Often this approximation is reasonable, such as when reaction is slow and the concentration of gaseous reactant does not change much in passing through the bed. In this case, the conversion equations given so far can reasonably be expected to apply. This assumption also applies when solids are transformed into product without the action of gaseous reactant, such as in the calcination of limestone. In the general case, however, the mean gas-phase driving force in the bed is a variable that changes with operating conditions. For example, if the feed rate of solid is lowered, then the concentration of gaseous reactant in the bed rises. Thus the conversion of solid and the concentration of gaseous reactant leaving and within the bed are interdependent, and a proper analysis of the bed behavior requires accounting for both these changes. This can be dealt with by a three-step calculation that is applicable to solids of constant size and of changing size:

- Step 1: Conversion of gas. Write expressions for the conversion of gaseous reactant A in terms of a mean first-order reaction rate constant K_r , and for the mean concentration of A encountered by the bed solids.
- Step 2: Conversion of solids. Write an expression for the conversion of B in the particles that are bathed by gas of mean composition C_A . This would be one of the models developed for particles of constant size or of changing size.
- Step 3: Overall material balance. Then relate the conversion of gaseous reactant A with that of solid reactant B.

As examples of the calculation procedure, the equations for the reactions of small and large sorbent particles in a bed of large particles is given. This analogy is chosen since it represents the expected conditions in a PFBC.

2.3.4.2 Performance Calculations for the Large-Particle Bed

Figure 23 illustrates the situation when large sorbent particles are used. The three-step procedure is outlined below.

Step 1. Assume a first-order reaction for the disappearance of A:

$$-\frac{1}{V_{\text{solid}}}\frac{dN_A}{dt} = \bar{K}_r C_A$$
[42]

where K_r is the mean value of the rate constant for the reaction of A with all the solids in the bed, some fresh, others highly converted. This constant depends, in general, on the extent of conversion of the solids in the bed. Kunii and Levenspiel (1991) have developed the equations that can be used for the large particle conversion expressions. The conversion of gaseous reactant A leaving the reactor utilizing these expressions becomes:

$$X_{A} = 1 - \exp\left[-\overline{K_{r}} \frac{L_{mf}(1 - \varepsilon_{mf})u_{mf}(1 - \delta)}{u_{o}^{2}}\right]$$
[43]

where u_{mf} is the minimum fluidization velocity and δ is the fraction of bubbles in the bed.

In addition, the mean concentration of A which bathes the solids must be calculated. Since the gas passes in a combination of bypass and plug flow through the bed in this flow regime, we can write, with Eq. 43:

$$\overline{C}_{A} = \frac{1}{L_{f}} \int_{0}^{L_{f}} C_{A}(z) dz = \frac{1}{L_{f}} \int_{0}^{L_{f}} C_{Ai} \exp\left[-\overline{K}_{r} \frac{L_{m}(1 - \varepsilon_{mf})u_{mf}(1 - \delta)}{u_{o}^{2}}\right] dz$$

$$= \frac{C_{Ai}X_{A}u_{o}^{2}}{\overline{K}_{r}L_{mf}(1 - \varepsilon_{mf})u_{mf}(1 - \delta)} = \frac{C_{Ai}X_{A}}{\overline{K}_{r}\pi} \frac{u_{o}}{u_{mf}(1 - \delta)}$$
[44]

Step 2. For the shrinking-core model with diffusion through the ash layer controlling (for example) and one size of particle, we write:

$$\overline{X}_{B} = 1 - \frac{1}{5} \frac{\tau}{\overline{t}} + \frac{19}{420} \left(\frac{\tau}{\overline{t}}\right)^{2} - \cdots$$
[45]

where, in the $\overline{C_A}$ environment:

$$\tau = \frac{\rho_B d_P^2}{24b D_s \bar{C}_A}$$
[46]

Step 3. Here:

$$\begin{pmatrix} disappearance \\ of B from solids \\ (mol/s) \end{pmatrix} = b \begin{pmatrix} disappearance \\ of A from gas \\ (mol/s) \end{pmatrix}$$
[47]

With $M_{\rm B}$ as the molecular weight of B and $F_{\rm O}$ (kg/s) as the feed rate of B to the reactor, Eq. 47 becomes:

$$\left(\frac{F_0}{M_B}\right) \bar{X}_B = b(A_I u_o C_{AI} X_A)$$
[48]

2.3.4.3 Performance Calculations for the Fine-Particle Bed

When a small sorbent particle is used, the kinetic limiting model for gas and the uniform-reaction model for solids are likely to apply. Hence, the three-step procedure is as follows.

Step 1. Using the mean value of the first-order reaction rate constant \overline{K} (as done previously) we have:

$$X_{A} = 1 - \exp\left[-K_{f} \frac{\delta L_{f}}{U - o}\right]$$
[49]

where:

$$K_{f} = \begin{bmatrix} \gamma_{b}\bar{K}_{r} + \frac{1}{\frac{1}{K_{bc}} + \frac{1}{\gamma_{c}\bar{K}_{r}} + \frac{1}{\frac{1}{K_{ce}} + \frac{1}{\gamma_{e}\bar{K}_{r}}} \end{bmatrix}$$
[50]

In addition, the mean concentration of A bathing the solids can be expressed by the simple plug flow expression (Kunii and Levenspiel, 1991):

$$\bar{C}_{A} = \frac{C_{A}X_{A}u_{o}}{\bar{K}_{L}L_{m}(1 - \varepsilon_{m})} = \frac{C_{A}X_{A}}{K_{L}\tau}$$
[51]

This type of expression results because gaseous reactant reacts away by a first-order reaction. Step 2. Applying the uniform-reaction model, we have for the conversion of solids:

$$\bar{X}_{B} = 1 - \frac{1}{1 + k_{r}\bar{C}_{A}W/F_{0}}$$
[52]

For the shrinking-core models, $\overline{X_B}$ is given by Eqs. 37–41. Eqs. 38 and 40 can reasonably be approximated by Eq. 35 whenever $\overline{X_B} > 0.80$.

Step 3. Here Eq. 48 applies.

2.3.5 Model Implications

The models developed in this section provide the design equations for an adsorption system in a fluid bed. It also provides the relationships necessary to qualitatively assess the impacts of changing sorbent size and type as well as operating conditions on the sorbent efficiency. This last section will perform such an assessment for the three models: the uniform reactant model, the kinetically controlled shrinking-core model, and the diffusion-controlled shrinking-core model.

The uniform reactant model is represented by Eq. 35 as:

$$1 - \bar{X}_{B} = \int_{t=0}^{\infty} \exp(-k_{r}C_{A}t) \frac{e^{-t/\bar{t}}}{\bar{t}} dt = \frac{1}{1 + k_{r}C_{A}\bar{t}}$$
[35]

Since we are interested in reducing the concentration of the alkali vapor to a low level rather than maximizing conversion of the sorbent, this equation is rewritten as:

$$C_{A} = \left(\frac{1}{(1-\bar{X}_{B})} - 1\right) \left(\frac{1}{k_{r}}\right)$$
[53]

From this relationship, it is easily seen that the outlet vapor concentration is proportional to $[1/(1 - X_B) - 1]$. This relationship is shown generally in Figures 24 and 25. It becomes obvious that to obtain a reasonably low concentration of the vapor-phase alkali, a relatively large excess of sorbent will be required. It is also seen from Eq. 53 that the alkali vapor concentration will be inversely proportional to the rate constant. Therefore, the capture efficiency of the sorbent will be temperature-dependent, with that dependency a function of whether the reaction is endothermic or exothermic.

In examining the *shrinking-core model where the kinetic reaction rate is limiting*, the conversion of the adsorbent is given by Eq. 39 as:

$$1 - \bar{X}_B \approx \frac{1}{4} \frac{\tau}{\bar{t}}$$
[39]

where τ was defined in Eq. 27 as:



Figure 24. Relationship between alkali content and the percent utilization of the sorbent particle



Figure 25. Relationship between alkali content and the percent utilization of the sorbent particle plotted on a log scale

$$\tau = \frac{\rho_B R}{bk_c C_A} = \frac{\rho_B d_p}{2bk_c C_A}$$
[27]

Inserting Eq. 27 into Eq. 29, the expression becomes:

$$1 - \overline{X}_B = \frac{d_p}{4 k_c C_A t}$$
[54]

This can be rewritten as a function of the outlet adsorbate concentration as:

$$C_{A} = \frac{d_{p}}{4 k_{c} t (1 - \bar{X})}$$
[55]

The following conclusions can be made from this relationship. For a shrinking-core model where kinetics are the rate-limiting step, the outlet alkali vapor concentration will be directly proportional to the particle size of the adsorbent and inversely proportional to the rate constant. This provides a clear indication of the importance of sorbent particle size and the need to find an optimal size to maximize alkali capture (small particle) while being large enough not to be blown from the bed after only a short residence time. The form of the rate constant will dictate the impact of temperature on the conversion efficiency of the adsorbent and the relative outlet alkali concentration.

The shrinking-core model also shows that the outlet vapor phase concentration is inversely proportional to the conversion of the adsorbent $(1 - X_B)$. This relationship is shown graphically in Figures 24 and 25. As is the case with the uniform reactant model, it is not practical to achieve low outlet vapor concentrations while simultaneously achieving high adsorbent conversions. A comparison of the shapes of the curves for the uniform reactant and shrinking core also shows a more rapid decrease in adsorbent efficiency with decreasing outlet vapor concentration. Therefore, when the shrinking-core model is applicable, which is most likely the applicable model for the alkali vapor system being considered as a part of this research, even lower conversion efficiencies of the adsorbent can be expected to achieve a target outlet alkali vapor concentration.

When the *shrinking-core model is diffusion-limited*, the relationships shown in Eqs. 41 and 29 govern the behavior:

$$1 - \bar{X}_B = \frac{1}{5} \left(\frac{\tau}{\bar{t}} \right)$$
[41]

$$z = \frac{\rho_B R^2}{6b D_s C_A} = \frac{\rho_B d_p^2}{24b D_s C_A}$$
[29]

These can be combined to represent the conversion of the adsorbent as a function of the adsorbate concentration as follows:

$$1 - \bar{X}_{B} = \frac{d_{p}^{2}}{5 D_{s} C_{A}}$$
[56]

This relationship shows that the outlet alkali vapor concentration when limited by diffusion is given by:

$$C_{A} = \frac{d_{p}^{2}}{5 D_{s} (1 - \bar{X}_{R})}$$
[57]

The diffusion coefficient generally takes the form of:

$$D_s = \frac{aT^b}{p}$$
[58]

where a and b are constants depending upon properties of the adsorbent. From this it is seen that the outlet alkali concentration is proportional to adsorbent particle size, temperature, pressure, and adsorbent conversion by the following relationship:

$$C_{A} = \frac{d_{p}^{2}p}{5aT^{b}(1-\bar{X}_{B})}$$
[59]

A look at this relationship shows that the particle size of the sorbent now becomes very important for minimizing the outlet alkali concentration. Extremely poor conversions of the sorbent would be expected for larger particle sizes. The equation given in Eq. 57 shows an inverse relationship between outlet alkali concentration and diffusivity as expected. Therefore, any changes that effectively increase the diffusivity

will have the desired effect of reducing the outlet alkali vapor concentration. From Eqs. 58 and 59, it can be seen that increasing the system temperature and decreasing the system pressure would increase the overall efficiency of alkali capture. It should be noted that increasing the temperature and decreasing the pressure will also result in more alkali vapor being generated from the combustion of the coal. Therefore, even though the collection efficiency of the sorbent will improve, it is probably the outlet concentration of the alkali vapors will increase with this change in operating variables.

2.4 Mechanisms of Capture using Aluminosilicates

Silicon dioxide (SiO_2) is the building block of an important group of minerals for use in alkali capture. It has a molecular structure which, in the aggregate condition, is a solid body with a high melting point. Each oxygen atom combines with two silicon atoms in the crystallized or even amorphous condition (glass) of silicon dioxide. Thus each silicon atom is combined via four such oxygen bonds with four neighbors since no Si=O double bonds are formed. This allows the Si and O atoms to form a threedimensional atomic crystal, in which each Si atom is tetrahedrally surrounded by four O atoms.

Warren and Pincus (1940) pictured the atomic bonding in a glass as largely ionic and calculated the bonding energy from the equation:

$$E = (-z_1 z_2 e^2) / R_{12}$$
 [60]

where E is the bonding energy between an ion pair, z_1 and z_2 are the valences of the respective ions, e is the charge on the electron, and R_{12} is the separation between ions. The Si-O bond is extremely stable because of the high charge and small ionic radius of the silicon atom (Si = 4+, O = 2-, R_{12} = 1.62 A). By contrast, the Na-O bond is relatively weak (Na = 1+, O = 2-, R_{12} = 2.35A).

In the silicate system, silicon has the coordination constant of four. In quartz, tridymite, crystobalite and other modifications of SiO_2 , a tetrad bond results which fills up the entire crystal, which is held together in all directions without interruption of the solid Si-O bonds. The SiQ_4^{4-} ion with its tetrad structure has a large tendency for forming greater bonds of differing structures (Figure 26). This structure will differ depending upon the silicate structural units, which differ as a function of the oxygen-to-silicon ratio. Figure 27 shows this effect, with the structural units of some of the common silicate systems summarized in



Figure 26. Tetrad arrangement of silicic acids and silicates with chain-, tape- and leaf-type structures (Pintsch and Gudenau, 1991)

Table 7. The tendency for the silicates to form greater bonds of differing structure appears to be the reason for the preferred binding of alkalies.

Orthosilicates have largely the composition $Me_2^{+2} SiO_4$. The Si atoms are contained in the tetrad "hollow spaces" and the metal cations in the octahedric hollow spaces (Figure 28). The dimension and charge of the ions is important for the crystalline structure; ions of similar dimensions can be replaced in the crystal. Therefore, the orthosilicates have a composition which fluctuates within certain limits; i.e., they have a nonstoichiometric composition. This is apparently an important mechanism for alkali sorption.

Chain silicates contain chain-type lattice anions to which bonded SiQ₄ groups or bands made of several such SiO₄ chains are attached. The composition of these compounds becomes more complicated because aluminum and silicon atoms can be interchanged in the SiQ₄ tetrads due to their similar dimension. Therefore, they are called aluminosilicates. Although aluminum has the coordination number four in this case, it has only three outer electrons. Thus one part of the tetrad SI⁴⁺ ion is replaced by Al³⁺ ions. The total negative charge of the anion is raised by one unit because of the replacement of one silicon atom by



Figure 27. Effect of oxygen-to-silicon ratio on silicate structure (Kingery et al., 1976)

Table 7

Structural Units in Crystalline Silicates

Oxygen-Silicon Ratio	Silicon-Oxygen Groups	Structural Units	Examples
2	SiO ₂	3-Dimensional network	Quartz
3	SiO ₃	Chain-rings	Pyroxenes
3.5	Si ₂ O ₇	Tetrahedra sharing one oxygen	Pyrosilicates
4	SiO4	Isolated tetrahedra	Orthosilicates



Figure 28. Schematic representations of the atomic arrangement in soda-silica glass (Kingery et al., 1976)

one aluminum atom. Thus more cations like K^* , Na^{*}, or Ca^{2*} are necessary to build up one electrically neutral lattice; i.e., the charge is compensated by the binding of cations. The lattice structure, however, remains intact. For example, nepheline (Na[AlSiQ₄]) exhibits the same (hexagonal) tetrad structure as tridymite; carnegieite (Na[AlSiQ₄]) exhibits the same (cubic) lattice as crystobalite.

Sodium and other alkalies are incapable of building a continuous network. These "network modifiers" break up the network by adding oxygen to produce nonbridging oxygen. For example, when a network modifier is added to the silicate system, the Si-O bond is broken, and the added oxygen will join with one of the silicon atoms, producing a gap in the chain. The cation associated with the added oxygen will balance the charge produced by the breaking of the tetrahedra structure and the addition of another oxygen atom. Sodium, calcium, and magnesium oxides are good examples of network modifiers. If the silicates are present in the glass form, this breakup of the network will reduce the viscosity and, if enough is added, will result in crystallization of the glass.

The ability of the alkalies to modify the network of the aluminosilicates makes the aluminosilicates good candidates for alkali capture. The general reaction mechanism for alkali capture by the

aluminosilicates is given in Table 8. The characteristics of two of the more promising silicate groups for alkali capture are discussed in more detail in the next two subsections.

Table 8

Reaction Mechanisms of Vaporous Alkalies with Aluminosilicates to Form Alkali Alumina Silicates

Reactive Alkalies	Alumina Silica Additive	te Alkali Al Silicat	umina tes	By-Products
$\left.\begin{array}{c} \text{KOH/K}_2\text{O}\\ \text{NaOH/Na}_2\text{O}\\ \text{KCL}\\ \text{NaCl}\\ \text{K}_2\text{CO}_3\\ \text{Na}_2\text{CO}_3\\ \text{K}_2\text{SO}_4\\ \text{Na}_2\text{SO}_4 \end{array}\right\}$	+ $\left\{ xAl_2O_3 \cdot ySiO_3 \right\} -$	KAlSi $_{3}O_{8}$ NaAlSi $_{3}O_{8}$ KAlSi $_{2}O_{6}$ NaAlSi $_{2}O_{6}$ NaAlSiO $_{4}$ plus calcium and mixed alumina silicates	+	$ \begin{array}{ccc} H_2O & (g) \\ O_2 & (g) \\ HCl & (g) \\ SO_x & (g) \\ SiO_2 & (s) \\ 3Al_2O_3 \cdot 2SiO_2 & (s) \end{array} $
(gas/vapor and liquids)	(solids)	(solids)		(gases and/or solids)

2.4.1 Zeolites

The zeolite minerals constitute a large and important group within the network silicates. Like all network silicates, the zeolites have a primary frame made up of SiQ and AlO₄ tetrahedra that link together by corner sharing to form a connected, three-dimensional network. Like the feldspars and feldspathoids, the negative charge on the zeolite frame is balanced by cations that occupy the intraframe cavities.

The structural differences between the zeolites and the other network silicates are the dimensions of the intraframe cavities and the connecting channels between them. In the feldspar structure, the cavities are relatively small, and the cations occupying them are so strongly bonded to the primary frame that their substitution by other cations having different valences requires a change in the Al/Si ratio. The cavities are not connected and are occupied only by monovalent and divalent cations. The feldspathoid frame is more expanded than the felspar structure, and some connectivity exists between the intraframe cavities. Some of the cavities are occupied by cations, and the other cavities are large enough to accommodate molecular

water. In comparison with the feldspathoid frame, the primary frame of the zeolites is even more expanded, containing larger cavities that are connected by broad channels.

Upon heating, molecular water is readily driven out of the zeolite structure. The anhydrous material can then absorb other kinds of molecules, providing they are not larger than the channels through which they must pass. This special aspect of the structure makes zeolites useful as molecular sieves.

The sodalite group's structure consists of loops of six tetrahedra linked by loops of four tetrahedra to form complex polyhedral cages (see Figure 29). The sodalite minerals have a tetrahedral cation to oxygen ratio of 1:2, and within the tetrahedra, AI^{p+} may never be in excess of SI^{*+} . Depending on the ratio of AI^{p+} to SI^{4+} in tetrahedra sites, various amounts of Na, Ca, K, and Ba may occupy the intraframe cavities. The coupled substitution of $Ca^{2+} + AI^{3+} = Na^{1+} + SI^{4+}$ characteristic of other network silicates such as plagioclase feldspars does not apply to zeolites. Unlike the feldspars, zeolites, including sodalite, have so much intraframe volume that cations need not be exchanged on a one-to-one basis. For example, natrolite can be derived from sodalite by substituting 2 Na¹⁺ for Ca²⁺. In addition, this structure allows for the interchange of the major anion groups, such as SQ_4^{2-} for 2 Cl¹⁻ between sodalite and nosean. These properties are of interest for this study.



Figure 29. Structure of the sodalite mineral

2.4.2 Layered Silicates

The most important mineral groups within the layered silicates are micas and clays, with the most common clay minerals being kaolinite, illite, and montmorillonite. The clays are of interest for their potential to adsorb alkalies. The tetrahedral frame of all layered silicates is a two-dimensional network in which three of the four apical oxygens of every tetrahedron are shared with other tetrahedra (Type C in Figure 26). The resulting tetrahedral layer usually has a sharing coefficient of 1.75 compared to 2.00 for most network silicates, creating strong Si-O bonds with each layer.

The term "clay" has two meanings. The first usage refers to minerals that possess a claylike crystal structure, and the term is used without consideration of grain size. The second usage refers to any mineral with diameters less than 2 microns. Feldspars and quartz, for example, can be considered as clay-sized particles in many sedimentary rocks, but they are not true clays in the structural sense. Any reference to clays in this dissertation refers to those minerals that possess the claylike structure.

The basic structure of the common layer silicates (clays) consists of tetrahedral layers alternating with parallel layers of octahedrally coordinated cations. Two types of alternation occur: one referred to by the symbol TO to denote single tetrahedral, T, and octahedral layers, O, joined together by sharing oxygens, and the other referred to as TOT to denote a structural unit that consists of a single octahedral layer sandwiched between two tetrahedral layers. Kaolinite is of the first category (TO), and is the primary clay used for alkali capture.

The structure of kaolinite (Figure 30) shows that each apical oxygen of each tetrahedron is shared with the apical oxygen of three octahedra in an adjoining layer. The TO units of kaolinite are joined by relatively weak hydrogen bonds. Upon heating to 500°C (930°F), kaolinite will lose 2 H₂O to transform from Al₂Si₂O₃(OH)₄ to metakaolinite (Al₂O₃ · SiO₂). This opens up the crystal structure and makes it more readily accessible to mobile cations. This structure provides the good sorbing properties to kaolinite and other similar minerals.



Figure 30. Structure of kaolinite

2.5 Alkali Sorbents Tested

Many different potential alkali sorbents have been tested by various institutions (Bachovchin et al., 1986; Bachovchin and Alvin, 1987; Lee and Johnson, 1980; Lee and Myles, 1989; Lee and Swift, 1991; Scandrett and Clift, 1984; Radhakrishnan et al., 1986; Pintsch and Gudenau, 1991b; Zakkay et al., 1989; Punjak et al., 1989; Uberoi et al., 1990). Following these sorbents listed below the attributes of several of the more effective sorbents are discussed, including how their performance is affected by operating conditions and fuel properties:

- Diatomaceous earth (Celatom-MP-91)
- Activated bauxite
- Silica gel
- Burgess No. 10 pigment (kaolin clay)
- Limestone, alumina powder, and dolomite
- Bentonite and franconite (natural minerals based on montmorillonite)
- Feldspar and kyanite (not very effective)
- Talcum (Mg₆[OH]₄Si₈O₂₀) (effective to some extent)

- Calcium silicates
- Kaolinite $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$
- Montmorillonite (n[Ca, Mg]O Al₂O₂ · 4SiO₂ · nH₂O)
- Halloysite $(Al_2O_3 \cdot 2SiO_2 \cdot nH_2O) n = 2 \text{ to } 4$
- Allophane $(Al_2O_3 \cdot nSiO_2 \cdot nH_2O)$
- Sericite ([Na, K]₂ $O \cdot 3Al_2O_3 \cdot nH_2O$)
- Beidellite $(Al_2O_3 \cdot 3SiO_2 \cdot nH_2O)$
- Pyrophyllite ($Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$)
- Illite $(K_{1-15} Al_4 [Si_{7-65} Al_{1-1.5}O_{20}] [OH]_4)$
- Illite-montmorillonite ([Na, Ca]_{0.33} [Al, Mg]₂ Si₄O₁₀[OH]₂ · nH₂O)
- Mullite $(3Al_2O_3 \cdot 2SiO_2)$
- Sillimanite $(Al_2O_3 \cdot SiO_2)$
- Alundum
- Attapulgus clay
- Novacite
- Emathlite
- Vansil (CaSiO₃)
- Zeolite
- CaO impregnated in bauxite or kaolinite for SO₂ and alkali control
 - 2.5.1 Alkali Removal Performance

The three most successful sorbents tested are bauxite, kaolinite, and emathlite. Alkali is captured by bauxite primarily by physical adsorption. Some chemical fixation by the clay impurities also occurs. Bauxite has been tested as an alkali sorbent at temperatures ranging from 730° to 1010°C (1350° to 1850°F). The apparent activation energy for the bauxite is low, indicating that temperature has only a small impact on its ability to adsorb alkali. Since an adsorption process is exothermic, the amount of alkali adsorbed decreases with increasing temperature. In contrast, kaolinite and emathlite remove alkali by chemical reaction of the sodium and potassium with these silicate-based minerals. Kaolinite has a high activation energy, indicating it is sensitive to temperature, with alkali removal increasing with increasing temperature. Emathlite had a small activation energy, indicating its relative insensitivity to temperature.

The maximum temperature limitations will differ for these three sorbents. The emathlite reacts with the sodium to form albite, a sodium aluminosilicate compound. Albite has a melting temperature of 1000°C (1832°F). At temperatures above 1000°C (1832°F), a glass will form which could potentially cause sticking and agglomerating problems within the bed (Bachovchin et al., 1986). Kaolinite, on the other hand, will form nephelite and/or carnegieite, depending upon the temperature of the bed. The relative melting point of nephelite, which is the favored species at higher temperatures, is 1560°C (2840°F) (Uberoi et al., 1990). If a granular bed of nephelite proves an effective alkali sorbent, it would have the distinct advantage of operating at combustor exit temperatures, eliminating the costly steps of cooling, cleaning, and reheating the flue gas. Bauxite will not melt until 1982°C (3600°F); however, its adsorption capacity will decrease as the temperature increases.

Uberoi and others (1990) studied the kinetics and mechanisms of alkali removal from flue gases using a microgravimetric analyzer (modified TGA). The intent of their work was to identify solid sorbents for either in situ or downstream removal of alkali from high-temperature combustion systems. Typical weight gain profiles generated in the microbalance system for the three sorbents tested, bauxite, kaolinite, and emathlite, are shown in Figure 31. The results for all sorbents indicate a decrease in sorption rate as loading increases. On continued exposure to the alkali vapors, the sorbents reach their maximum capacity for alkali removal, and the rate of sorption drops to zero. At 800°C (1472°F), bauxite was observed to have the highest initial rate, while kaolinite had the largest increase in mass. Each sorbent was also tested for desorption by reducing the alkali vapor concentration to zero after the sorbent was saturated. Kaolinite and emathlite did not undergo any loss in weight, but bauxite lost approximately 10% of the original weight gain. Scanning Auger microprobe indicated that chlorine was not retained by kaolinite or emathlite. Bauxite did capture some chlorine; however, this chlorine was readily lost during desorption. Since the chlorine is desorbed from the bauxite, the weight loss during desorption could correspond to the release of physiosorbed NaCl.



Figure 31. Temporal profile of NaCl adsorption on sorbents at 800°C (Uberoi et al., 1990)

The effect of temperature on the rate constants of bauxite and kaolinite was also measured by Uberoi and others (1990) and is shown in Figure 32. The activation energy for kaolinite is higher than that for bauxite, indicating that alkali removal by kaolinite is more sensitive to temperature. This is consistent with the observation that sorption on kaolinite occurs by chemical reaction alone, while sorption on bauxite occurs by both physiosorption and chemical reaction.

Pilot-scale tests have been performed by Argonne National Laboratory (ANL) on its pilot-scale PFBC using bauxite as an alkali sorbent (Lee and Johnson, 1980; Lee and Myles, 1987; Lee and Swift, 1991). Tests were performed at 850°C and 875°C (1560° and 1610°F) using a Beulah, North Dakota, lignite. Flue gas concentrations of 1.4 to 1.5 ppmw sodium and 0.1 ppmw potassium were measured at the inlet to the filter device. Using a packed bed of bauxite with a particle size ranging from 2 to 2.4 mm, greater than 99% removal of the alkali was effected. The outlet alkali measurements were less than 10 ppbw. Adsorption data were collected that can be used for preliminary design scaleup.



Figure 32. Apparent rate constants for bauxite and kaolinite (Uberoi et al., 1990)

The Combustion Power Company (CPC) granular bed filter (GBF) was tested at NYU using Beulah lignite with 8.0% ash and 0.62% sodium (as Na₂O) in the coal as the fuel (Radhakrishnan et al., 1986; Zakkay et al., 1989). The PFBC pilot plant was operated at temperatures ranging from 810° to 870°C (1490° to 1600°F) and 6.9 to 9.2 atmospheres. Both 2-millimeter (mm) and 3-mm mullite particles were tested. The average alkali content in the flue gas entering the GBF was measured to be 1.25% of the sodium and 1.12% of the potassium in the coal. The measured alkali capture efficiency for all of the tests was between 90% and 96%, with a possible error of 5%. The outlet alkali concentration ranged from 3 to 20 ppbw, which is below the 24-ppmw recommended turbine tolerance limit. In that work, no attempt was made to determine the mechanism of capture, i.e., whether the alkali reduction was due to condensation on the filter media, capture of fine alkali sulfate dust and aerosol particles, physical adsorption, or chemical absorption and reaction. Therefore, although it was proven that the concept will simultaneously capture particulate and alkali in practice, no scaleup data were obtained.

A more practical study was performed by Westinghouse, focusing on emathlite as the sorbent material (Bachovchin et al., 1986). Results from their testing indicated that the concept of using a fixed bed
of emathlite pellets is a practical technique for alkali removal from hot flue gases. Process development tests included a 102-hour test where gas containing 10-ppmv NaCl was reduced to less than 0.2 ppmv (detection limits). In other studies, alkali removal of greater than 99% was demonstrated, with a reduction of sodium to below the 24-ppbw turbine tolerance level. A commercialized process has been identified for manufacture of the emathlite pellets. In their testing, the kinetics were found to be insensitive to temperature over the range of 775° to 900°C (1426° to 1651°F). The adsorption rate was proportional to the alkali gas-phase concentration, with no capacity limitations due to adsorption limitation at low gas-phase alkali concentrations. The Westinghouse research was based on a packed-bed design, and it was concluded that it would be necessary to install a particulate cleanup device ahead of the sorbent bed. The Westinghouse researchers had envisioned a long time between replacement of the bed material (one-half to one year) and had concerns about bed pluggage due to the fly ash. The use of a GBF would prevent this from happening. An important finding from the Westinghouse work was that no attrition of the emathlite pellets was noted during any of the testing. Six-mm pellets were recommended for the packed-bed.

All of these studies have been performed using combustion gases. In a combustion atmosphere, most of the alkali material is vaporized during combustion and will be present as a sulfate. At the typical filter temperatures (788° to 900°C [1450° to 1650°F]), a majority of the sulfates will have condensed on the surface of other ash particles or as fine particles and aerosols (Scandrett and Clift, 1984; Spacil and Luthra, 1982; Mojtahedi and Backman, 1989). The removal of the alkali in this form is difficult because of the need to capture the fine sulfate particles and either remove them as sulfates or provide the contact necessary to react the sulfates with the sorbent material. The good performance results by ANL, NYU, and Westinghouse indicated this is possible.

Less testing has been done for gasification systems. Thermodynamic calculations for a reducing atmosphere indicate that the alkali will be present as hydroxide vapors or chloride vapors for high-chlorine coals. In these cases, the alkali capture can be achieved by direct reaction of the vapor with the capture material to form a nonvolatile product. This type of capture is much more effective than the removal of the sulfates from the combustion gases (Scandrett and Clift, 1984; Spacil and Luthra, 1982; Mojtahedi and Backman, 1989) and is the preferred method of alkali removal for the current study. Some of the sorbents

tested in screening tests by McLaughlin (1990) are listed in Table 9. Typical nonsorbents identified in these tests are high silica, alumina, or aluminosilicate materials that were characterized by a tightly layered crystalline structure and which did not react to any significant extent with water vapor in the 400° to 1000°C (750° to 1832°F) temperature range. The effective sorbents had more open layered crystal structure, with a higher concentration of interlayer cations or other reaction sites that were rapidly rehydoxylated by reaction with water vapor. These hydroxylated groups subsequently acted as reactive sites for the adsorption of the vapor-phase alkalies. This is consistent with the previous discussions on the mechanisms of alkali removal using aluminosilicate minerals.

Table 9

Unreactive Adsorbent, nonsorbent	Reactive Adsorbent, sorbent
Alpha Al ₂ O ₃	Activated bauxite
Gamma Al ₂ O ₃	Attapulgus clay
Activated Alumina	Barytes
Andalusite	Burgess no. 10 pigment
Celestite	Calcium montmorillonite
Iron Oxide	Celetom
Kyanite	Diatomaceous earth
Olivine	Ebony novacite
Silicalite	Emathlite
Silicon Carbide	Kaolin
Sillimanite	Pumice
Talc	Pyrophillite
Zeolite 4A	Vansil
Zeolite ZSM-5	

Summary of Alkali Chloride Adsorbent Screening Tests (McLaughlin, 1990)

Significant work has also been performed to identify sorbents to capture other metals from flue or waste gases. At relatively low temperatures, mercury, cadmium, lead, and zinc have been removed from gas streams. At temperatures similar to PFBC, cadmium, lead, zinc, nickel, vanadium, and arsenic have been removed using sorbents. Some sorbents have also shown an affinity to chlorine. Finding a sorbent that is selective to trace metals and chlorine in addition to alkali will greatly enhance the effectiveness of that sorbent.

For the individual coal-bound trace metal species, Mojtahedi and others (1990) estimate that the vapor-phase emissions range from 0.5 to 1.2% for Cu, 7.5 to 16.0% for Hg, 1 to 3% for Pb, 5% for Cd, and up to 4% for As, with the balance tied up in either the bottom or fly ash. These results showed that the trace metal emissions from a PFBC unit can be controlled effectively with a barrier filter. The authors suggest that despite the initially high volatilization of the trace metals into the gas phase, the low levels of vapor emissions may be attributed to adsorption onto the high surface area and highly irregular, crystalline fly ash particles. Unless stringent standards are adopted, the need to control these trace metals is unlikely.

Work from previous researchers has demonstrated that alkali sorbents can be effective in removing alkali from both combustion and gasification gas streams. Both packed beds and GBFs have been utilized. Drawbacks include the need for a particulate removal device both before and after a packed bed and the expense of the added pressure vessels to contain the packed or granular bed. The granular bed may be costeffective if both particulate and alkali control can be achieved. However, because of the disadvantages associated with packed and granular beds, in situ removal of alkali may be preferred. A sorbent, used in the same manner as a sorbent is used to remove sulfur, would not add any significant cost to the system, would be easy to maintain, and could be used in both oxidizing and reducing atmospheres.

2.5.2 Effect of Operating Parameters on Sorbent Performance

Lee and Johnson (1980) investigated the impact of sorbent bed temperature, exposure time, superficial gas velocity, and gas hourly space velocity (GHSV) on alkali capture in a packed bed. The results show an increase in NaCl capture with increasing temperature for the diatomaceous earth and the opposite effect for the activated bauxite tested. This is expected since capture by diatomaceous earth is by chemical reaction, with the rate increasing with temperature according to the Arrhenius equation, while capture with bauxite is primarily through physical adsorption. Since physical adsorption is exothermic, the amount adsorbed should decrease with increasing temperature according to Le Chatelier's principle. In both cases, the amount of capture increases nonlinearly with time, indicating that under the experimental conditions, the rates of NaCl capture are not controlled by the mass transfer of NaCl vapor from the bulk of the flue gas to the external surfaces of the sorbent.

To further investigate the rate-controlling mechanism, tests were conducted at various superficial gas velocities while holding the GHSV constant. For mass-transfer-controlled reactions, an increase in superficial gas velocity increases the mass-transfer coefficient, thereby increasing the extent of reaction. Within the limits of experimental and analytical errors, the rate of NaCl capture was found to remain constant over the velocity range tests. This indicates that the rate of NaCl capture is not mass-transfer-controlled, but controlled by either the diffusion of NaCl vapor through the internal pores, the adsorption of NaCl on the active sites of the sorbent, or the chemical kinetics.

Work performed by Lippert and others (1991) investigated the use of sorbents for removing alkalies in GBFs. Most of their work was performed using nitrogen as the carrier gas for the alkali chloride. However, when several tests were performed adding water vapor to the gas stream, a marked improvement in sorbent performance was noted. The weight gains experienced during their TGA-based experiments were 3 to 5 times higher when water vapor was added versus those tests with no water added. McLaughlin (1990) also showed a significant improvement in sorbent effectiveness when the carrier gas stream contained 5% water vapor in his work with calcium montmorillonite.

The effect of chlorine on the performance of alkali sorbents has been reported by Singh and others (1986) under both PFBC and gasification conditions. Under both sets of operating conditions, the presence of HCl in the flue gas is expected to decrease the sorbent efficiency, although gasification operating conditions seem to be more significantly affected. Increasing pressure and decreasing temperature also seem to improve the sorbent efficiency. Potential sorbent reactions for alkali chloride compounds all form HCl in the product gas; therefore, if there is a high HCl concentration in the product gas, the "capture" reaction is limited because of the thermochemical equilibrium. Methods for the removal of HCl were studied (Krishnan et al., 1986), but they used a Na₂CO₃-based mineral at lower operating temperatures (535° to 650°C).

In their theoretical evaluation, Singh and others (1986) effectively estimated the impact of gas composition and operating conditions on the adsorption efficiency of sillimanite/silica. Figure 33 summarizes their results, expressed as reduced parameters relative to a baseline value. The critical influence of temperature and HCl concentration on alkali chloride adsorption is evident in this figure. A zero

dependence on the SO₂ concentration is shown because the formation of the condensed NaSO₄ phase has no effect on the capture reaction (Singh et al., 1987) or in the sulfation of the vapor-phase alkali chloride species in the temperature range of 800° to 1117°C (1472° to 2040°F). Clearly more work is necessary to identify the optimum process conditions and the alkali adsorbents that can be used in a PFBC cycle.

2.6 Measurement Techniques

Alkali metal components contained in coal are released during combustion into the exhaust gas as particulate material, vapor, and aerosol. In a PFBC, the hot offgas is expanded through a gas turbine. The amount of alkali material in the gas, as well as the condensation and/or accumulation of material on the turbine blades, may cause hot corrosion of these materials. The measurement of the levels of alkali in the exhaust gases is, therefore, of particular interest. Alkalies that are condensed on particulates or held within the particulate are collected on the ceramic barrier filter, while vapor-phase alkali and suspended aerosols can pass through these barrier filters and attack the turbine blades. It is, therefore, important to be able to differentiate between the form of alkali when determining its effect on PFBC turbine performance.



Figure 33. Effect of gas composition and conditions on the adsorption efficiency of sillimanite/silica in a combustion environment (Singh et al., 1986)

Design of an alkali-sampling probe is no trivial task. For accurate alkali measurement, the following design and operational criteria must be met:

- The sample gas must be cleaned of all particulate matter before it enters the sampling system.
- All surfaces of the sampling system in contact with the sample gas must be inert towards alkali; that is, they must neither react or emit alkalies.
- In order to avoid premature condensation of alkalies or salts from alkali, the gas must be kept at combustion temperatures until it has entered the sampling system.
- No alkali metal-or only negligible amounts-must be allowed to pass through the sampling train.
- The sampling system should be completely detachable in order to allow total recovery of alkali compounds on completion of sampling.
- The sampling system should be calibrated with a known amount of alkali salt under conditions similar to those during operation.
- Potential errors due to the sampling procedure should be considered, such as the accuracy of the techniques for measuring the alkalies in the extracted solution and measurement of the sampled gas.

Several techniques have been developed to measure the alkali levels in flue gases. These techniques include in situ techniques such as laser-induced fluorescence spectroscopy (LIFS); laser-induced photo and fluorescence (LIPF); laser-induced breakdown spectroscopy (LIBS); hot-extraction techniques, such as the Ames alkali monitor, the Federal Energy Technology Center (FETC) fiber-optic alkali monitor (FOAM) analyzer, and the Western Research Institute (WRI) condensing/electric conductance probe; and batch-type, condensation cold traps such as the alkali and particulate sampling train (APST) technique. One additional technique is the use of a fixed bed of alkali sorbent material in which a known amount of flue gas is passed through the bed for a given time, after which the bed material is regenerated and analyzed for its alkali content.

The Energy & Environmental Research Center (EERC) has performed some testing using a LIFS system to look at the concentration of sodium atoms in a small-scale burner (Benson et al., 1989). These tests looked at sodium in solution, solid-phase sodium compounds, sodium impregnated on carbon, and three different Beulah lignite coal samples: a demineralized Beulah lignite, a demineralized Beulah lignite with sodium acetate impregnated back into the sample, and a raw Beulah lignite. The form of the sodium in

solution was found to have no effect on the concentrations measured. The solid-phase sodium salts (benzoate, sulfate, and carbonate) gave signals similar to the solutions, while the sodium montmorillonite and chloride gave signals much less than those observed for solutions. The coal and char samples gave signals higher than the solutions, and there was a linear response of the coal samples with Na concentration in the sample. The thermodynamic code SOLGASMIX was used to predict how much Na would be in the atomic state. The code did agree with the general observations that NaCl and sodium montmorillonite liberated less Na atoms when combusted; however, the predictions were 30% to 70% in error, since the mole fraction values put into the program are that much in error. This system is no longer in operation.

Los Alamos National Laboratory has performed some laboratory testing with a photofragment fluorescence technique that is capable of identifying different anions of the same alkali (Oldenberg, 1989). This technique is based on the UV laser-induced photo dissociation of alkali-containing compounds. Sodium and potassium compounds can be distinguished by their characteristic emission wavelength (589 nm for Na+, 766 nm for K+). Variation of the threshold energy wavelength should allow good discrimination between alkali compounds with different anion groups. Research indicates that the instrument is sensitive down to 0.03 ppb NaCl and 0.4 ppb KCl, 0.1 ppb NaOH and 7 ppb KOH, and 0.01 ppb Na₂SO₄ and 0.3 ppb K₂SO₄. This research concluded that, in predominantly binary mixtures of the chloride anion with the hydroxide or sulfate anion, the photofragment fluorescence technique will be able to distinguish the concentration of each compound. However, in mixtures containing comparable amounts of the hydroxide and sulfate anions, the spectra are similar enough to make concentration measurements difficult. Research with the photo dissociation fluorescence technique is being continued at PSI Technologies Company in testing on its laminar flow drop-tube furnace (Helbe et al., 1990). Results have been obtained which indicate that chlorine is the species-limiting compound in the formation of NaCl. SOLGASMIX was used to validate the dependence of NaCl formation on the chlorine levels in the coal. Additional kinetic modeling was performed to determine that the NaCl equilibrium is approached in approximately 5 ms. There is little report of the use of this instrument in practical applications.

Argonne National Laboratory utilized several different approaches for measuring the amount of alkali in the process gas stream from the PFBC. One technique utilized a filter to remove particulate matter prior to passing the gas through a stainless steel cold trap followed by water bubblers. The intent was to

remove any particulate matter and aerosols from the gas stream using the filter and allow only the vaporphase material to pass into the cold trap. The alkali that did not condense in the cold trap was scrubbed out in the water bath. Argonne National Laboratory investigated several different filtering materials. The ideal filter is one that is effective in removing fine particulate matter, but is inert toward alkali vapor. A ceramic ultrafiber made by 3M, Nextel, was used in early tests. While effective in removing particulate matter, this material was shown to have some reactivity to alkali vapor (Lee and Myles, 1987).

As a part of its work for FETC, ANL investigated the reliability of various alkali measurement techniques. One technique investigated was the analytical alkali sorber bed (AASB). Clean gas (after candle filter) is passed through a packed bed of sorbent material such as activated bauxite or diatomaceous earth which captures the alkali vapor. After the designated sample time, the sorbent is removed and digested first in gently boiling water and then in acid. Atomic absorption spectrometry (AA) is used to quantify the amount of sodium and potassium in the solutions. The AASBs were placed directly in the pressure vessel to eliminate problems with condensation in the sample lines. Results were compared to those from the Ames on-line analyzer. The APST batch-type condensation train gave alkali levels between 0.6 to 1.0 ppm Na, while the sorbent bed technique gave values between 1.3 to 1.5 ppm Na. The discrepancies in the numbers have been attributed to the adsorption of the alkali on the heated sample lines, while the sorbent bed is right in the flow gas, so there is no sample line to change the concentrations. The sorbent bed numbers could be inflated because of some contamination by particulate.

One important result from the work at ANL was the discovery that the stainless steel (both 304 and 316) used for the sample lines capture both NaCl and KCl vapors and that the sodium and potassium captured by the steel showed reversible release to an alkali-vapor-free gas. This interaction with the stainless steel lines can lead to lower than expected readings as the actual alkali concentration increases from a baseline value or, conversely, higher than expected when the alkali concentrations decrease from the baseline value. Lee and Myles (1989) also observed condensation and vaporization of alkali vapors, primarily as Na₂SO₄ and K₂SO₄ in the sample lines. When the gas-sampling line was cooler than the PFBC gas stream, condensation in the sample line occurred, resulting in low alkali readings. Higher than expected readings were noticed when the sampling line was hotter than the PFBC flue gas. To minimize these

problems, Lee and Myles recommend using as short of a sample line as practical, using an inert (nonstainless steel) sample line, and maintaining the sample line at the system temperature.

A novel concept for an on-line alkali monitoring probe based on monitoring the vapor-phase alkali by condensing them on a sensing element held in a temperature gradient is being developed at WRI (Sethi, 1995). Portions of the element, which are at temperatures below the dew point, develop a condensate layer either as a solid deposit or as a liquid film. Areas of the probe where a solid layer of alkali compounds is present can then be detected by remote-sensing techniques based on differences in the electrical conductance between the liquid and the solid salt. Laboratory verification tests indicate that the concept can be made to work in furnace tests, and remote sensing of deposited salts is possible (Sethi, 1995).

A review of the literature used to design the carbonizer for the Foster Wheeler second-generation PFBC system (Boteler, 1973) indicates that the dry tar had ash levels ranging from 0.1 to 3.2 wt% ash (avg. 1.0 wt%). While some of the ash could be the result of fine fly ash carrying over out of the carbonizer, some of the ash is probably due to the volatilization of alkali metal compounds which would not be collectible by hot-gas cleanup device such as ceramic candle filters, etc. The presence of organic vapors in the gas stream will also make the sampling and identification of alkali compounds more difficult for carbonization (advanced PFBC) and gasification conditions. The organic vapors are known to absorb ultraviolet (UV) radiation which will preclude the use of any LIFS technique because they fluoresce in the UV wavelengths. Condensation cold trap sampling trains would also condense the organic tars, making the analyses for alkali compounds much more difficult. A fixed bed of sorbent material could potentially work as an alkali measurement device provided the bed is maintained at the same temperature as the gas-tar stream to prevent the condensation of tars on the sorbent material.

In summary, alkali metals can be measured either on-line producing instantaneous alkali values or off-line where a batch-sampling technique typically requiring several hours is used. Unfortunately, the accuracy of on-line methods is still not reliable enough for use in a PFBC (Lee and Swift, 1991; Fantom, 1993). Therefore, batch-sampling procedures are recommended even though they only provide average values of alkali metal over a given period of time.