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**SIMULTANEOUS HIGH-TEMPERATURE REMOVAL OF ALKALI
AND PARTICULATES IN A PRESSURIZED GASIFICATION SYSTEM**

Final Technical Progress Report Covering the Period April 1981—July 1983

By
P. R. Mulik
M. A. Alvin
D. M. Bachovchin

September 1983

Work Performed Under Contract No. AC21-81MC16372

Westinghouse Electric Corporation
Research and Development Center
Pittsburgh, Pennsylvania

Technical Information Center
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United States Department of Energy

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M. A. Alvin
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September 1983

**Westinghouse Electric Corporation
Research and Development Center
1310 Beulah Road
Pittsburgh, PA 15235**

**Prepared for
U. S. Department of Energy
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ABSTRACT

This program is directed at performing experimental and analytical investigations, deriving system designs, and estimating costs to ascertain the feasibility of using aluminosilicate-based getters for controlling alkali in pressurized gasification systems. Its overall objective is to develop a plan for evaluating a scaled-up version of the gettering process as a unit operation or as an integral part of a particulate removal device.

This report describes work completed on the four technical program tasks: Thermodynamic Projections; Getter Selection and Qualification; System Performance Projections; and Program Definition for Concept Scale-up during the 27-month contract performance period. Work completed on the thermodynamic projections includes a data base update, development of alkali phase diagrams, and system performance projections. Getter selection and qualification efforts involved over 70 kinetic studies in which a leading candidate getter -- emathlite -- was selected and characterized. System performance projections identified a packed-bed configuration containing relatively large getter pellets as the preferred contacting device for a full-scale unit. For emathlite, we concluded that full-scale unit bed heights of 2 m or less would be required if we assume annual replacement on the basis of bed saturation capacity. Concept scale-up work involved defining the hardware and test program requirements for further development of the emathlite packed-bed system.

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NOMENCLATURE

AA	atomic absorption
ANL	Argonne National Laboratory
BSE	backscattering electron microscopy
C_p	heat capacity
DTA	differential thermal analysis
EPR	electron paramagnetic resonance
ESCA	electron spectroscopy for chemical analysis
GE	General Electric Company
HTHP	high temperature, high pressure
K	degrees Kelvin or potassium content as indicated in text
PDU	process development unit
PFBC	pressurized fluidized-bed combustion
SXM	scanning electron microscopy
TGA	thermogravimetric analysis (-zer)

1. INTRODUCTION

An advanced, low-Btu gasification system, when integrated with a combined-cycle power plant, results in one of the most promising processes utilizing fossil energy in an environmentally acceptable manner and, hence, permits the use of high-sulfur coal. Using this coal to generate a fuel gas requires the removal of contaminants (especially alkali and particulates) that could lead to corrosion, erosion, and deposition problems on turbine materials. A cleanup system, therefore, is obligatory. In the current study Westinghouse is examining the feasibility of a hot-gas cleaning process to minimize the concentration of alkali in a high-temperature fuel gas, with possible simultaneous particulate removal by aluminosilicate materials (getters).

Westinghouse initiated work on the alkali gettering concept in October 1978 as part of DOE contract DE-AC21-78ET10026. The program continued through October 1980. It consisted of seven tasks: 1) Test Plan, 2) Test Facility Assembly, 3) Getter Selection and Fabrication, 4) Getter Material Characterization, 5) Bench-Scale Evaluation of Getter Performance, 6) System Performance Projections, and 7) Program Definition for Concept Scale-up.

Task 1 was completed early in the program and approved by DOE. The Task 2 effort centered on the design and fabrication of two systems for obtaining kinetic data as a function of pertinent parameters such as getter material, temperature, pressure, extent of conversion, concentration of alkali in the bulk gas stream, composition of the alkali-laden gas, and bulk gas velocity. One of these systems was a batch-type, bench-scale reactor to be used for preliminary bench-scale studies. This reactor was completed early in the program and was used to screen three candidate getter materials - kaolin, ash from a low-temperature

coal char, and ash from a high-temperature gasifier. The second unit, consisting of a double-balance thermogravimetric analysis (TGA) system designed to continuously monitor the weight loss of the alkali source and the weight gain of a candidate getter, was designed and built during the course of the program. This system was used extensively in our second DOE contract (DE-AC21-81MC16372), reported here.

Getter fabrication (Task 3) efforts involved the development of procedures for producing sufficient quantities of the cylindrical pellets (1/8 in. dia $\times$ 1/4 in. long) used for both the analytical and kinetic investigations performed during the course of the program. Getter material characterization (Task 4) involved detailed chemical and physical analyses of both unreacted and reacted getter materials. Getter performance evaluation (Task 5) involved exposure of all three candidate getters for periods up to six hours at a system pressure of 11 atm absolute and at temperatures of 1123 and 1173 K in an inert gas (argon), $N_2/10\% H_2$, and a simulated fuel gas. All three gases contained approximately 80 ppm sodium chloride (NaCl). Work on Task 6 included preliminary estimates of the costs associated with alkali gettering in combined-cycle applications.

The experimental and analytical investigations, preliminary designs, and cost estimates completed under the previous contract provided a substantial basis for demonstrating the feasibility of utilizing aluminosilicate-based getters as agents for controlling alkali in a pressurized gasification system environment. These studies identified selected aspects of the problem that have been pursued in the work reported here.

Under our second contract we have developed a basis for evaluating the alkali removal unit operation. The results are also directly applicable to pressurized fluid-bed combustion (PFBC) systems. To accomplish this objective, the work under the current contract was comprised of four technical tasks: Process Thermodynamic Projections, Getter Selection and Qualification, System Performance Projections, and

Program Definition for Concept Scale-up. The overall objective of the program was to develop a plan for evaluating a scaled-up version of the gettering process as a unit operation or as an integral part of a particulate removal device. Realization of the primary objective required that the following interrelated aspects of the problem be taken into consideration: identification of a suitable candidate getter by additional bench-scale and TGA studies; utilization of the experimental data to provide a technical, economic, and environmental assessment of the gettering process; specification of appropriate design details for the scale-up studies; and delineation of key tests, operating conditions, and so on, for the conduct of the scale-up studies.

This report summarizes work completed on all four tasks during the 27 months of the project, from April 9, 1981 through July 9, 1983. In summary, work on the thermodynamic projections has been completed and includes an update of the data base, development of alkali phase diagrams, and projections for several gasification processes. Getter selection and qualification efforts involved over 70 kinetic tests on our bench-scale reactor and our TGA system. A key series of tests on both units involved comprehensive getter screening tests in which over 20 alternative getters were evaluated and the leading candidate getter — emathlite — was selected and evaluated in detail. Our system performance projection work involved using the available kinetic data from both experimental systems to evaluate the feasibility of gettering system concepts. These studies showed that packed beds containing relatively large sorbent particles are the preferred contacting device. For emathlite, we concluded that full-scale unit bed heights of 2 m or less would be required if we assume annual replacement on the basis of bed saturation capacity. Concept scale-up efforts focused on the nature of a pilot- or bench-scale reactor and an associated test program that would be required to ensure an orderly transition from our TGA and bench-scale units to the commercial-sized equipment.

2. PROJECT SUMMARY

The Westinghouse Electric Corporation initiated work on the alkali-gettering concept in October 1978 under DOE contract DE-AC21-78ET11026. The program extended through October 1980 and consisted of seven tasks: 1) Test Plan, 2) Test Facility Assembly, 3) Getter Selection and Fabrication, 4) Getter Material Characterization, 5) Bench-Scale Evaluation of Getter Performance, 6) System Performance Projections, and 7) Program Definition for Concept Scale-up. Extensive work was completed on six of the seven tasks. Specifically, work completed included the DOE-approved test plan (Task 1); design and construction of a high-temperature, high-pressure (HTHP), bench-scale reactor and a unique dual balance HTHP TGA system for detailed investigation of gettering kinetics (Task 2); selection of three getters (kaolin, char ash,* and gasifier ash*) and development of pellet fabrication techniques for the bench-scale reactor studies (Task 3); getter material characterization associated with the bench-scale reactor studies (Task 4); the scheduled bench-scale reactor studies using the three candidate getters listed above (Task 5); and preliminary system performance projections based on the bench-scale kinetic studies (Task 6).

The experimental and analytical investigations, preliminary systems design, and cost estimates completed under this program demonstrated the feasibility of using aluminosilicate-based getters for controlling alkali in pressurized gasification systems. On this basis this work was extended to the contract (DE-AC21-81MC16372) summarized in this report, which began in April 1981 and was completed in July 1983. The work under this contract was comprised of four technical tasks:

*Obtained from the Westinghouse gasifier process development unit.

1) Process Thermodynamic Projections, 2) Getter Selection and Qualification, 3) System Performance Projections, and 4) Program Definition for Concept Scale-up. Tasks 1, 3, and 4 were basically analytical investigations that depended on the experimental kinetic studies conducted in conjunction with Task 2. Task 1 input to the existing thermodynamic data base included phases and compounds identified by x-ray diffraction analysis of reacted getter pellets. The quantity of volatile alkali in the coal-derived fuel gas was then predicted thermodynamically. Task 3 was directed toward analysis of the experimental data in three areas: kinetic modeling studies using the bench-scale and TGA system data; process modeling; and an engineering assessment of the alkali gettering system. In Task 4 input from the other tasks was used to define a preliminary plan for concept scale-up.

Work completed on Task 1 includes a data base update, development of alkali phase diagrams, and gasification process projections. The data base update involved a literature review and subsequent updating of the thermodynamic data base to include aluminosilicate complexes that have been identified experimentally as resulting in gettered species. Phase diagrams were then generated to demonstrate the various interactions of the mineral constituents of the feedstock during gasification, the chemical transformations of the released volatile alkali with effluent gas constituents, and the chemical stabilities of potential getter materials.

The thermodynamic model was used to rank the Lurgi, Shell Koppers, Texaco, Winkler, and Westinghouse gasification systems on the basis of released alkali concentrations at process conditions. In the order of increasing released alkali concentrations for the gasification of Illinois No. 6 coal, the following series applies: Lurgi (0.028-0.035 ppm Na, 0.013-0.016 ppm K), Texaco (8.70-12.3 ppm Na, 4.5-6.4 ppm K), Westinghouse (19-23 ppm Na, 4.3-12 ppm K), and Shell Koppers (37.2-45.6 ppm Na, 983 ppm K). Gasification of eastern Kentucky coal in the Winkler process (15.5-132.2 ppm Na, 7.7-101 ppm K) or Wyoming subbituminous coal in the Westinghouse fluidized bed (34-51 ppm Na,

20-32 ppm K) is not projected to emit as much potassium as the Shell Koppers process but borders on, if not exceeds, emissions of sodium.

Work on Task 2 consisted of a number of bench-scale unit and TGA tests. The bench-scale studies involved runs with activated bauxite in an inert carrier gas containing NaCl, KCl, and NaCl/water vapor. In addition, a series of screening tests were conducted to evaluate 20 candidate getter materials. The final test series involved the leading candidate getter -- emathlite -- in various reactant gas compositions, including an inert gas with water vapor, an inert gas with water vapor and NaCl, and a simulated fuel gas containing water vapor and NaCl. The NaCl and KCl exposures at 11 atm with activated bauxite were conducted at 1123 K and 1153 K in an argon environment containing 80 ppmv NaCl or KCl for durations of 1, 3, and 6 hours. For both temperatures studied, potassium was gettered at approximately ten times the rate for sodium. Likewise, the presence of water vapor (4.6 mol% at 1123 K and 11 atm) enhanced the NaCl gettering by activated bauxite by a factor of about 2.

The limited rate, capacity, and other problems -- primarily, potassium release -- associated with the getters tested initially led us to direct part of our bench-scale efforts to evaluating new candidate getters. Several of the 20 candidates tested had gettering capacities higher than activated bauxite. At this point in the program, activated bauxite was considered to be the leading candidate getter, based on our work and that of Argonne National Laboratory (ANL). The other getters included Vansil,[®] Ebony Novacite,[®] zeolite, emathlite, and diatomaceous earth. Test conditions for these screening tests were 1123 K, 6 hour exposures, 11 atm pressure, and 80 ppmv NaCl.

The improved gettering capacity of emathlite, based on our bench-scale studies and TGA results (discussed below) and relative to the other leading candidates, warranted further study of its gettering capacity in various reactant gas compositions. A total of eight tests were made at 11 atm and 1123 K for exposure periods ranging from 2 to 24 hours. Gas compositions evaluated included an inert gas containing

4.6% H₂O, an inert gas containing 4.6% H₂O and 80 ppmv NaCl, and a simulated fuel gas (7.49% CO₂, 23.03% CO, 13.9% H₂, 4.6% H₂O, 0.2725% H₂S, 0.0025% HCl, 50.705% N₂, and 80 ppmv NaCl). We found that the simulated fuel gas environment did not interfere with the gettering process, but it did produce a black coating on the reacted pellet at the glass-pellet interface. Analysis suggests that this material was carbon, most likely formed through the Boudouard reaction of the simulated fuel gas constituents. Further discussion regarding the glass phase is presented below.

Initial TGA studies focused on: ancillary tests needed to define a good operating procedure, preliminary tests with a number of getters (activated bauxite, shattered activated bauxite, boiler ash, char ash, and gasifier ash), and tests involving a detailed evaluation of activated bauxite. The activated bauxite series involved tests at 1123 K and 1173 K at atmospheric pressure, with salt concentrations (NaCl) of approximately 0.8, 3, and 10 ppmv. Six of the tests were terminated when pellets were saturated with NaCl, while two tests were continued by terminating the salt flow to permit desorption to occur. Results of the activated bauxite series indicated that:

- Capacity is higher at 1123 K than at 1173 K at each gas phase concentration.
- Capacity is greater at high gas phase concentrations at each temperature.
- The desorption is not completely reversible at either temperature level studied.

In addition, the TGA system was used for eight screening tests of the most promising alternative getters identified in the bench-scale unit screening tests. This series involved tests at 1073 to 1173 K, atmospheric pressure, and a nominal NaCl concentration of 10 ppmv. The results revealed that three of the candidates -- Ebony Novacite®, emathlite, and diatomaceous earth -- have substantially better gettering capacity than does activated bauxite. Ebony Novacite® and diatomaceous earth were eliminated on the basis of several factors, including the TGA

results, cost considerations (raw material and processing), and their initial chemical compositions. After completion of the screening tests, the TGA system was modified to permit the addition of several percent of water vapor to the carrier gas stream. The gettering capacity of bauxite in the presence of water vapor was found to be greater, by a factor of two to three, than that observed without moisture in the system. These results were in agreement with those obtained earlier on the bench-scale unit.

The final TGA test series involved the leading candidate getter, emathlite. This test series involved 17 experiments at 1123 and 1173 K, atmospheric pressure, 1 and 4 mol% H₂O in the carrier gas, and NaCl concentrations ranging from ~2 to more than 50 ppmv. These tests proved emathlite to have a high capacity but a lower sorption rate.

Since capacity is more relevant than rate for system performance, our initial assessment of emathlite remained unchanged - that is, the relatively high gettering capacities observed in the runs can be achieved but require a longer exposure period at a given NaCl bulk gas concentration. This conclusion was experimentally verified in the last test of the emathlite TGA series.

Another aspect of our Task 2 effort involved an attempt to understand the reaction mechanism for emathlite. For this purpose we subjected a number of reacted pellets from both the bench-scale and TGA systems to detailed chemical and physical analyses. We found that a partially reacted pellet is comprised of three distinct reaction zones. The outer, glasslike layer is rich in sodium and silicon and composed principally of Na₂SiO₅. The next, innermost layer is somewhat lower in sodium concentration than the external glass phase, while both silicon and aluminum coexist as the principal and secondary elemental constituents. The most prominent feature of the center is the virtual absence of sodium. The data obtained indicate that the principal gettering reaction stoichiometry is:

In Task 3 (System Performance Projections), gettering data for activated bauxite from several runs were used to determine kinetic expressions. Intrinsic rates were low, so the overall rate would not be significantly increased by using fine particles. Furthermore, long solids residence times must be provided, so the batch packed bed proved to be the best choice. Bed depths of about 10 m for bauxite (based on a 1000 m/h velocity) with beds replaced after 4000 hours, were estimated on the basis of saturation capacity.

Our efforts on this task were then directed to evaluating the available data for emathlite. For this getter we assumed that the rate-controlling step was diffusion through the glass coating produced on the pellet surface. Under these conditions long solids residence times are still required, so packed beds, containing relatively large sorbent particles, are still the preferred contacting device. We therefore concluded that full-scale unit bed heights of 2 m or less (again based on a 1000 m/h gas velocity) will be required for 4000 h replacement. Furthermore, systems considerations indicated that the getter bed should be placed downstream of the final particulate filter. In addition, the low initial cost of the getter, coupled with the insoluble nature of the reaction product, led us to conclude that regeneration of the sorbent was not a satisfactory approach.

Work on Task 4 (Program Definition for Concept Scale-up) focused on the nature of a pilot or bench-scale reactor and the associated test program that would be required to ensure an orderly transition from our TGA and bench-scale units to the commercial-sized equipment.

3. PROJECT STATUS

3.1 TASK 1: PROCESS THERMODYNAMIC PROJECTIONS

The objective of task 1 is to develop a thermodynamic gettering model that predicts the equilibrium phase and concentration of alkali retained in alumina, silica, and aluminosilicate additives in gasification systems in relation to data obtained by atomic absorption and x-ray diffraction analysis on reacted getter pellets from the bench-scale and TGA studies. The three subtasks are:

- 1.1 Revision of the Thermodynamic Data Base
- 1.2 Gasification Process Projections
- 1.3 Development of Alkali/Aluminosilicate Phase Stability Diagrams.

The results obtained in each of these areas are detailed in Sections 3.1.1 through 3.1.3, respectively. Section 3.1.1 details the updated thermodynamic data base used in the calculations, and Section 3.1.2 describes the results of applying the equilibrium model to three types of feedstock-- Illinois No. 6 coal (3.1.2.1), Pittsburgh seam coal (3.1.2.2), and Wyoming subbituminous coal (3.1.2.3) - for both the air-blown and oxygen-blown Westinghouse single-stage gasifiers. The projected alkali reactions and equilibrium feedstock release concentrations in various gasification processes are then presented in Section 3.1.2.4. Alkali aluminosilicate phase diagrams developed from the model are described in Section 3.1.3 in terms of feedstock stability (3.1.3.1) and getter stability (3.1.3.2).

3.1.1 Revision of the Thermodynamic Data Base

The literature has been reviewed in an attempt to obtain molecular constants, heats of formation, entropy, and heat capacity (C_p)

values for alkali aluminosilicate complexes that are likely to result during the gettering reactions. Table 1 illustrates the current data file of alkali phases that can be accessed for use in the thermodynamic equilibrium program. Table 2 illustrates the reported¹ entropy (S), enthalpy (H), free energy (G), and equilibrium constant logarithmic value ($\log K_f$) for new candidate compounds in addition to those reported for the feldspars (KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$) already incorporated into the data base. A review of this listing indicates that the feldspar structure is generally the phase favored more than nepheline (NaAlSiO_4) on the basis of the net negative free energy of formation values. Nepheline, however, had been identified by x-ray diffraction analysis in previous studies to result from the reaction of sodium with the aluminosilicate lattice.² Heat capacity data as a function of temperature for nepheline are not reported in the literature. In order to model this compound, we estimated the C_p values for the solids involved in forming nepheline by summing across the reaction of the standard states for the oxides of sodium, aluminum, and silicon (Na_2O , Al_2O_3 , SiO_2). The generated reaction C_p equation, in addition to the entropy, enthalpy, and free energy data reported by the Geological Survey¹ was used to project the alkali stability at equilibrium conditions. Once experimental data become available, the molecular constants and C_p values can be modified. Similarly to nepheline, jadeite [$\text{NaAl}(\text{SiO}_3)_2$] is a candidate phase in the alkali aluminosilicate reaction. The required thermodynamic data for jadeite again are unavailable in the literature. We assume, however, that it may form when nepheline and albite ($\text{NaAlSi}_3\text{O}_8$) are projected at equilibrium. Phase identification by x-ray diffraction analysis is required to support this conjecture.

3.1.2 Gasification Process Projections

The complex chemistry of the various elemental and mineral reactions that occur during gasification is reflected in the composition of the resulting raw gas and solid products. Low partial pressures of oxygen (10^{-15} to 10^{-17} atm) and sulfur (10^{-6} to 10^{-7} atm) are projected

Table 1
CURRENT DATA FILE

Gases	Solids, Liquids, Condensed Phases	
(NaCN) ₂	NaHCO ₃	K ₂ O ₂
(KCN) ₂	NaCN	KAlO ₂
NaCN	KCN	KO ₂
KCN	Na ₂ CO ₃	Na ₂ O
Na ₂ O ₂ H ₂	K ₂ CO ₃	K ₂ O
K ₂ O ₂ H ₂	KAl(SO ₄) ₂ · 12H ₂ O	Na ₂ S ₄
NaOH	NaOH	K ₂ S ₄
KOH	KOH	Na ₂ S ₃
NaH	NaH	K ₂ S ₃
KH	KH	Na ₂ S ₂
Na ₂ SO ₄	KAl(SO ₄) ₂	K ₂ S ₂
K ₂ SO ₄	NaAlSi ₃ O ₈	Na ₂ S
Na ₂ O	KAlSi ₃ O ₈	K ₂ S
KO	3Na ₂ O · 2SiO ₂	K ₃ Al ₂ Cl ₉
Na ₂ Cl ₂	KAlSi ₂ O ₆	Na ₃ AlCl ₆
K ₂ Cl ₂	Na ₂ Si ₂ O ₅	K ₃ AlCl ₆
NaCl	K ₂ Si ₂ O ₅	NaAlCl ₄
KCl	Na ₂ SO ₄	KAlCl ₄
Na ₂	K ₂ SO ₄	NaCl
NaK	NaClO ₄	KCl
Na	KClO ₄	Na
K ₂	2Na ₂ O · SiO ₂	K
K	KAlSiO ₄	
	Na ₂ SiO ₃	
	K ₂ SiO ₃	
	Na ₂ O ₂	
	AlNaO ₂	
	NaO ₂	

Table 2
THERMODYNAMIC PROPERTIES OF MINERALS

Compound	S°_{298} (cal deg-gtw ⁻¹)	$\Delta H^{\circ}_{298.15}$ (cal gtw)	$\Delta G^{\circ}_{298.15}$ (cal gtw)	Log $K_{f298.15}$	Comment
NaAlSiO ₄ (nepheline)	29.72 ± 0.30	-497029 ± 1000	-469664 ± 1010	344.273 ± 0.740	New phase
Na _{0.8} K _{0.2} AlSiO ₄ (nepheline)	N.A.	-500993 ± 450	N.A.	N.A.	—
K ₂ Al ₆ (OH) ₁₂ (SO ₄) ₄ (alunite)	156.8 ± 0.9	N.A.	N.A.	N.A.	—
NaAl(SiO ₃) ₂ (jadeite)	31.90 ± 0.30	-719871 ± 1000	-677206 ± 1010	496.405 ± 0.740	*
KAlSi ₃ O ₈ (microcline)	52.47 ± 0.80	-946265 ± 930	-892817 ± 970	654.452 ± 0.711	Previous Data File
KAlSi ₃ O ₈ (high sanidine)	56.94 ± 1.00	-944378 ± 930	-892263 ± 980	654.046 ± 0.718	
KAlSi ₃ O ₈ (andalusite)	55.99 ± 1.00	-945000 ± 1200	-892602 ± 1240	654.294 ± 0.909	
KAlSi ₃ O ₈ (glass)	63.28 ± 1.00	-933276 ± 910	-883051 ± 960	647.293 ± 0.704	
KAlSiO ₄ (kaliophilite)	31.85 ± 0.30	-503926 ± 420	-476230 ± 430	349.086 ± 0.315	
KAlSi ₂ O ₆ (leucite)	44.05 ± 0.40	-721650 ± 750	-681642 ± 760	499.657 ± 0.557	
NaAlSi ₃ O ₈ (low albite)	50.20 ± 0.40	-937146 ± 740	-883988 ± 760	647.980 ± 0.557	
NaAlSi ₃ O ₈ (analcite)	54.67 ± 0.45	-934513 ± 770	-882687 ± 790	647.026 ± 0.519	
NaAlSi ₃ O ₈ (glass)	62.95 ± 0.60	-922609 ± 760	-873252 ± 790	640.110 ± 0.579	

N.A. (not available)

Nepheline:

$$C_{p298-847K} = 32.124 + 16.299 \times 10^{-3}T - 7.520 \times 10^{-5}T^{-2} - 1.684 \times 10^{-6}T^2$$

$$C_{p847-1400K} = 35.708 + 9.422 \times 10^{-3}T - 5.207 \times 10^{-5}T^{-2} - 1.684 \times 10^{-6}T^2$$

*Jadeite:

to exist in equilibrium with solid and condensed phases in the Westinghouse single-stage gasifier operating at 1300 K and 15 atm.

Depending on the initial feedstock composition and system operating parameters, the volatile alkali concentration is estimated to range between 8 and 83 ppm in the 1300 K gasifier effluent. In equilibrium with gaseous CO , CO_2 , CH_4 , H_2 , H_2O , NH_3 , H_2S , and the alkali phases, anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), ferrous sulfide (FeS), silica (SiO_2), potassium feldspar (KAlSi_3O_8), and carbon (C) are projected to form as principal solid or condensed constituents at these temperatures under oxygen-blown gasifier conditions. Sodium silicate (Na_2SiO_3) and feldspar ($\text{NaAlSi}_3\text{O}_8$), magnesium aluminate (MgAl_2O_4), and aluminum, iron, and calcium titanates ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, $\text{FeO} \cdot \text{TiO}_2$, $4\text{CaO} \cdot 3\text{TiO}_2$) are projected as minor and trace solids in the 1300 K gasifier. Minor variations in the above equilibrium gas and condensed phases are projected for the air-blown single-stage Westinghouse gasifier.

Reducing the maximum gasifier operating temperature minimizes the concentration of potentially corrosive volatile alkali complexes released into the gasifier effluent while enhancing the stability of the alkali within the resulting ash matrix. Although the ash may initially be chemically inert, if it is deposited with char and condensed volatiles along metal surfaces, subsequent phase interactions may lead to the production of corrosive species at the deposit/metal interface. The kinetics of these phase transitions and the interactions of the deposits with the underlying alloy remain to be evaluated.

The technique used in projecting the equilibrium product distribution of the major and minor trace constituents in coal (carbon, hydrogen, nitrogen, oxygen, sulfur, chlorine, silicon, aluminum, potassium, sodium, iron, calcium, magnesium, and titanium) in the resulting solid, condensed, or volatile gasification products is based on minimizing the total free energy of the polyphase system while satisfying the mass conservation equations. The equilibrium distribution estimates for the gasification of Illinois No. 6,³ Pittsburgh seam,⁴ and Wyoming subbituminous⁵ coals in the single-stage Westinghouse gasifier are considered in the following sections for oxygen-blown and air-blown operations.

Table 3 illustrates the three initial feedstock compositions and the coal feed oxidant and steam flow rates into the gasifier. A temperature of 1300 K is assumed as the maximum operating temperature for this design, with a typical pressure of 15 atm. The equilibrium projections in the following sections emphasize the stability of the solid or condensed phases formed in the 1300 K and 15 atm gasifier and demonstrate compositional changes that may occur within the solid or condensed phases as the system temperature decreases to 298 K.

3.1.2.1 Gasification of Illinois No. 6 Coal

During gasification feedstock carbon reacts with hydrogen, leading to the formation of methane, as shown in reaction 1. Simultaneous partial oxidation is accomplished by the reaction of carbon with water vapor, forming carbon monoxide and hydrogen (reaction 2). After preliminary oxidation of the coal has taken place, the shift reaction occurs (reaction 3):

At equilibrium the raw gas product composition resulting from the oxygen-blown gasification of Illinois No. 6 coal at 1300 K and 15 atm consists of 48.86% CO,* 40.24% H₂, 4.98% H₂O, 3.49% CO₂, 0.95% CH₄, 0.72% N₂, 0.68% H₂S, 0.03% HCl, 0.03% COS, and various trace gaseous hydrocarbon constituents. As shown in the solids profile of Table 4, complete devolatilization of the carbon matrix is expected at 1300 K operating temperatures, while the formation of carbon deposits is expected at temperatures of 1200 K and below. The effect of temperature on the resulting partial pressures for the various hydrocarbon constituents formed in this system over solid carbon and ash deposits is illustrated in Figure 1. Estimates

* Values reported as mol%.

Table 3

FEEDSTOCK COMPOSITION AND FEED RATES INTO
THE SINGLE-STAGE WESTINGHOUSE GASIFIER

Element, wt%	Illinois No. 6 ³		Pittsburgh Seam ^{4,5*}		Wyoming Subbituminous ^{3,4,6**}	
C	70		75.21		51.28	
H	5		5.20		6.44	
N	1.3		1.53		0.75	
O	8.2		8.19		34.83	
S	3.6		2.17		0.51	
Cl	0.14		0.113		0.03	
Si	2.4		1.65		0.75	
Al	1.2		1.06		0.18	
K	0.17		0.062		0.013	
Na	0.05		0.078		0.03	
Fe	2.0		0.72		0.08	
Ca	0.67		0.16		1.06	
Mg	0.05		0.012		0.26	
Ti	0.06		0.056		0.05	
Feed Rate, lb/hr	Oxygen Blown	Air Blown	Oxygen Blown	Air Blown	Oxygen Blown	Air Blown
Coal	100,000	100,000	100,000	100,000	100,000	100,000
Oxidant	58,420	294,650	62,970	324,910	55,040	267,960
Steam	50,000	25,000	50,000	25,000	50,000	25,000

* Pittsburgh Seam: C, H, N, O, S from (4); Cl, Si, Al, K, Na, Fe, Ca, Mg, Ti from (5)

** Wyoming Subbituminous: C, H, N, O, S from (4); Cl, Ti from (3); Si, Al, K, Na, Fe, Ca, Mg, from (6)

Table 4

COMPOSITION OF ASH PRODUCTS FORMED DURING THE GASIFICATION
OF ILLINOIS NO. 6 COAL UNDER OXYGEN-BLOWN CONDITIONS AS A
FUNCTION OF TEMPERATURE AT 15 atm

TEMP., K	300	400	500	600	700	800	900	1000	1100	1200	1300
C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
S	✓										
H ₂ O	✓										
MgCO ₃	✓	✓									
CaSO ₄ ·2H ₂ O	✓										
CaCO ₃		✓									
Al ₂ SiO ₅	✓	✓	✓								
Al ₂ O ₃ ·TiO ₂	✓	✓	✓						✓	✓	✓
FeO·TiO ₂				✓	✓	✓	✓	✓			✓
FeO·Al ₂ O ₃				✓	✓	✓	✓	✓			
FeS ₂	✓	✓	✓	✓							
FeS					✓	✓	✓	✓	✓	✓	✓
K ₂ SO ₄	✓	✓									
KCl	✓	✓	✓	✓	✓	✓					
KAlSi ₃ O ₈			✓	✓	✓	✓	✓	✓	✓	✓	✓
NaCl	✓										
NaAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CaO·Al ₂ O ₃ ·2SiO ₂			✓	✓	✓	✓	✓	✓	✓	✓	✓
CaO·MgO·2SiO ₂				✓	✓	✓	✓	✓			
MgSiO ₃									✓	✓	
MgAl ₂ O ₄									✓	✓	✓

of the resulting oxygen and sulfur partial pressures as a function of temperature that are obtained using the equilibrium model are shown in Table 5.

The carbon-free solid phase composition projected to form at equilibrium within the single-stage Westinghouse gasifier under oxygen-blown conditions at temperatures of 1300 K and pressures of 15 and 35 atm is illustrated in Table 6. On a weight percent basis $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and KAlSi_3O_8 are the principal constituents in the solid complex, with $\text{NaAlSi}_3\text{O}_8$, MgAl_2O_4 , $\text{FeO} \cdot \text{TiO}_2$, and $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ present as minor and trace phases. The composition is virtually constant in both pressurized gasifiers, but the equilibrium major raw gas products vary.

Figure 2 illustrates the effect of temperature on the stable solid formation within the 15 atm oxygen-blown gasifier. As previously indicated, carbon is the major constituent in the solids formed below temperatures of 1200 K. Silica is relatively stable between 298 and 1300 K, while the low-temperature $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ converts into a $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ structure between operating temperatures of 400 and 500 K. The pyrite or marcasite (FeS_2) phase present within the feedstock between 298 and 600 K releases sulfur at higher temperatures, forming predominantly FeS with solid $\text{FeO} \cdot \text{Al}_2\text{O}_3$ present as a minor constituent phase.

Thermodynamically, minor transitions between solid $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ and solid $\text{FeO} \cdot \text{TiO}_2$ are projected to occur below 1000 K, with a final reconversion of titanium into the $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ complex at elevated gasification temperatures. Analogous to these reactions are the interconversions of calcium magnesium silicate ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), magnesium metasilicate (MgSiO_3), and magnesium aluminate (MgAl_2O_4). The pressure dependency on the stability of these phases influences the transition temperatures between the various constituents to change slightly and to alter their weight percent contribution within the ultimate ash composition by less than 1 weight percent.

Figure 1 - Volatile hydrocarbon partial pressures formed in a Westinghouse single-stage gasifier as a function of temperature at 15 atm total pressure over solid carbon and ash deposits.

Table 5
PARTIAL PRESSURES OF MAJOR VOLATILE COMPLEXES FROM
THE GASIFICATION OF ILLINOIS NO. 6 COAL AS A FUNCTION
OF TEMPERATURE (OXYGEN BLOWN)

15 atm		
Temperature	P _{O₂} (atm)	P _{S₂} (atm)
300K (81°F)	--	1.29-14
400K (261°F)	--	2.27-15
500K (441°F)	--	4.38-13
600K (621°F)	1.64-34*	2.82-11
700K (801°F)	1.39-29	8.25-10
800K (981°F)	6.78-26	5.59-9
900K (1161°F)	4.68-23	2.64-8
1000K (1340°F)	7.35-21	9.62-8
1100K (1520°F)	3.33-19	2.59-7
1200K (1700°F)	5.22-18	7.69-7
1300K (1881°F)	1.20-16	2.44-6

* 1.64-34 $\equiv$ 1.64 $\times$ 10⁻³⁴

Table 6

INFLUENCE OF TOTAL SYSTEM PRESSURE ON
RAW GAS PRODUCTS AND ASH COMPOSITION

Illinois No. 6 Coal

Oxygen Blown

15 atm, 1300 K

Raw Gas Composition (mole %)	Moles x 10 ⁶ (lb/hr) Solids	
48.86% CO	0.1951-2* KAlSi_3O_8	(1197.2)
40.25% H ₂	0.8900-3 $\text{NaAlSi}_3\text{O}_8$	(514.5)
4.98% H ₂ O	0.7583-2 $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	(4651.0)
3.49% CO ₂	0.1511-3 $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	(60.6)
0.95% CH ₄	0.4171-3 $\text{FeO} \cdot \text{TiO}_2$	(139.5)
0.72% N ₂	0.1507-1 SiO_2	(1996.2)
0.68% H ₂ S	0.9329-3 MgAl_2O_4	(292.6)
0.03% HCl	0.1583-1 FeS	<u>(3068.0)</u>
0.03% COS		(11919.6 lb/hr)

35 atm, 1300 K

Raw Gas Composition (mole %)	Moles x 10 ⁶ (lb/hr) Solids	
47.77% CO	0.1961-2 KAlSi_3O_8	(1203.3)
36.71% H ₂	0.9334-3 $\text{NaAlSi}_3\text{O}_8$	(539.6)
6.23% H ₂ O	0.7583-2 $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	(4651.0)
4.68% CO ₂	0.1246-3 $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	(49.9)
3.07% CH ₄	0.4436-3 $\text{FeO} \cdot \text{TiO}_2$	(148.4)
0.75% N ₂	0.1491-1 SiO_2	(1975.0)
0.70% H ₂ S	0.9328-3 MgAl_2O_4	(292.6)
0.40% HCl	0.1580-1 FeS	<u>(3062.2)</u>
0.03% COS		(11922.0 lb/hr)

* $0.1961-2 \equiv 0.1951 \times 10^{-2}$

Figure 2 - Effect of temperature on the stability of solids formed during gasification

The thermodynamic projections indicate that Illinois No. 6 coal contains potassium as both an alkali chloride and a sulfate (KCl , K_2SO_4). Gasification enhances the migration of potassium into the aluminosilicate lattice, forming the relatively stable KAlSi_3O_8 structure. Similarly, sodium is present as the alkali chloride in the feedstock and converts into the feldspar ($\text{NaAlSi}_3\text{O}_8$) structure as gasification temperatures are increased.

Volatile alkali chloride complexes, however, are projected to exist as major phases in equilibrium with the stable aluminosilicates formed at gasification temperatures. The partial pressures exerted by these phases are shown in Table 7. The maximum alkali release at 1300 K of 9.79 percent of the background sodium content and 1.08 percent of the background potassium content in Illinois No. 6 coal represents 19 ppm NaCl and 4.3 ppm KCl present as volatile chlorides in the gasifier outlet stream.

Although the system temperature and the partial pressure of various buffer gas constituents determine the stability of various complexes formed during gasification, modification of the process conditions, for example, oxidant composition, provides another means by which alternative stable products can be formed. The equilibrium raw gas composition and solid phases shown in Table 8 are projected to result during the gasification of Illinois No. 6 coal in air. Unlike gasification with oxygen, the air-blown Illinois No. 6 system contains solid carbon at 1300 K and 15 atm. At equilibrium the calculated percentage of carbon within the ash solids is approximately 35 weight percent (Table 9). Minor variation is observed in the ash composition transitions over the considered temperature range. For example, in the air-blown system, potassium as KCl coexists at low temperatures with KAlSi_3O_8 . In the oxygen-blown system, however, both K_2SO_4 and KCl are stable low-temperature solids, with formation of the feldspar complex occurring as the solid sulfate is removed from the system. Similarly, the stability of the solid

Table 7

PARTIAL PRESSURES AND PERCENT FEEDSTOCK CONCENTRATION OF
VOLATILE ALKALIS FORMED IN THE GASIFIER FROM
ILLINOIS NO. 6 COAL (OXYGEN BLOWN, 15 atm)

Temp., K	P _{NaCl}	Percent Feedstock, Na	P _{KCl}	Percent Feedstock, K
300	0.1728-31	0.4078-28	0.3293-30	0.3988-27
400	0.2944-24	0.5460-20	0.1413-20	0.1311-16
500	0.1287-17	0.2396-13	0.7713-15	0.7183-11
600	0.6041-13	0.1130-8	0.4803-11	0.4496-7
700	0.1279-9	0.2433-5	0.2336-8	0.2221-4
800	0.3938-7	0.7738-3	0.2315-6	0.2276-2
900	0.5230-6	0.1098-1	0.1243-5	0.1305-1
1000	0.3246-5	0.7654-1	0.3658-3	0.4315-1
1100	0.1625-4	0.4489	0.9773-5	0.1351
1200	0.7752-4	0.2471+1	0.2724-4	0.4343
1300	0.2908-3	0.9790+1	0.6398-4	0.1077+1

Table 8

COMPOSITION OF ASH PRODUCTS FORMED DURING THE
GASIFICATION OF ILLINOIS NO. 6 COAL UNDER AIR-
BLOWN CONDITIONS AS A FUNCTION OF TEMPERATURE
AT 15 atm

TEMP., K	300	400	500	600	700	800	900	1000	1200	1300
CaCO_3	✓	✓								
MgCO_3	✓	✓								
C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
$\text{H}_2\text{O}(l)$	✓									
KAlSi_3O_8	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
$\text{Al}_2\text{Si}_2\text{O}_5$	✓	✓	✓							
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓	✓	✓						
S	✓									
KCl	✓	✓	✓	✓						
NaCl	✓	✓	✓	✓	✓					
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$		✓	✓						✓	✓
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓			
$\text{FeO} \cdot \text{Al}_2\text{O}_3$				✓	✓	✓	✓			
$\text{FeO} \cdot \text{TiO}_2$				✓	✓	✓	✓	✓		
FeS					✓	✓	✓	✓	✓	✓
$\text{NaAlSi}_3\text{O}_8$						✓	✓	✓	✓	✓
MgAl_2O_4								✓	✓	✓
MgSiO_3									✓	✓

Table 9

PROJECTED RAW GAS COMPOSITION AND SOLIDS
FORMED DURING THE AIR-BLOWN GASIFICATION
OF ILLINOIS NO. 6 COAL AT 1300 K AND
15 atm

Raw Gas Composition (mole %)	Moles x 10 ⁶ (lb/hr) Solids		
29.49% CO	0.2407	C	(6373.0)
20.05% H ₂	0.1877-2	KAlSi ₃ O ₈	(1151.8)
0.80% H ₂ O	0.7583-2	CaO·Al ₂ O ₃ ·2SiO ₂	(4651.0)
0.68% CO ₂	0.5682-3	Al ₂ O ₃ ·TiO ₂	(227.8)
0.44% CH ₄	0.5963-3	MgAl ₂ O ₄	(187.0)
48.06% N ₂	0.3365-3	MgSiO ₃	(74.5)
0.42% H ₂ S	0.1522-1	SiO ₂	(2016.1)
0.02% HCl	0.8026-3	NaAlSi ₃ O ₈	(463.9)
0.02% COS	0.1624-1	FeS	<u>(3147.4)</u>
			(18292.5 lb/hr)

NaCl phase is extended to between 700 and 800 K in air, while temperatures not exceeding 400 K are required to maintain the alkali chloride in the oxygen-blown system. In the gasifier that utilizes Illinois No. 6 coal under air-blown conditions and operates at temperatures below 700 to 800 K, sodium is projected to exist primarily as the solid chloride. At temperatures above 800 K the $\text{NaAlSi}_3\text{O}_8$ formation is enhanced through the reaction of the volatile or alkali chloride phase within the ash lattice. The alkali will then remain bound within the claylike structure of the ash fines and will be transported in the effluent gas stream through the heat exchanger, particle removal gas-cleaning systems, and ultimately through the combustor flame at the turbine inlet. Within the hot turbine flame the alkali may be released from the ash and may react with chloride ions or sulfur oxides present in the combustion gases. Under these conditions gaseous sodium chloride or sulfate may form, condense, and deposit within the turbine.

Alkali released from Illinois No. 6 coal under air-blown conditions into the effluent stream at the gasifier outlet may be transported in the carrier gas to cooler regions within the system where deposition of potentially corrosive phases (alkali sulfates, chlorides, eutectic melts, vanadates) may occur. Projected release of sodium and potassium from the feedstock as a function of temperature is shown in Table 10, and it appears that the gasification of Illinois No. 6 coal in air at 1300 K releases 23 ppm NaCl, but only 12 ppm KCl.

Table 10

PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF VOLATILE ALKALIS FORMED
IN THE GASIFIER FROM ILLINOIS NO. 6 COAL
(AIR BLOWN, 15 atm)

Temp, K	P_{NaCl}	Percent Feedstock Na	P_{KCl}	Percent Feedstock K
300	0.1728-31	0.4897-27	0.3293-30	0.4668-26
400	0.1604-21	0.6412-17	0.1413-20	0.2824-16
500	0.1394-15	0.5583-11	0.7713-15	0.1545-10
600	0.1186-11	0.4764-7	0.4151-11	0.8337-7
700	0.7222-9	0.2925-4	0.3312-9	0.6708-5
800	0.3561-7	0.1468-2	0.1569-7	0.3237-3
900	0.3672-6	0.1569-1	0.1711-6	0.3657-2
1000	0.2797-5	0.1270	0.1356-5	0.3079-1
1200	0.8613-4	0.4466+1	0.4383-4	0.1137+1
1300	0.3499-3	0.1865+2	0.1807-3	0.4817+1

3.1.2.2 Gasification of Pittsburgh Seam Coal

Variation in the trace and minor constituent concentration in the feedstock source provides another means in which the composition of the resulting raw gas and ash products can be modified. This is evident when the projected solid composition formed in a gasifier using Illinois No. 6 coal is compared to the solid composition formed in a gasifier using Pittsburgh seam coal. At 1300 K and 15 atm in oxygen, Illinois No. 6 forms an ash containing 10% KAlSi_3O_8 , 39% $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 0.5% $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, 1.2% $\text{FeO} \cdot \text{TiO}_2$, 16.7% SiO_2 , 2.5% MgAl_2O_4 , 4.3% $\text{NaAlSi}_3\text{O}_8$, and 25.7% FeS on a weight percent basis, while under similar gasification conditions Pittsburgh seam coal forms an ash consisting of 6% KAlSi_3O_8 , 15.9% $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, 3% $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, 28.7% $\text{FeO} \cdot \text{Al}_2\text{O}_3$, 1% MgAl_2O_4 , 31% SiO_2 , 12.4% $\text{NaAlSi}_3\text{O}_8$, and 1.6% FeS (Tables 6 and 11). Although the major constituents within the ash matrix of Illinois No.6 and Pittsburgh seam coals are chemically similar, minor variations are detected in the projected solid transitions as a function of temperature (Table 4 and Table 12). What is apparent, however, is that operating the gasifier at 1300 K and 15 atm in oxygen prevents the equilibrium formation of solid carbon compounds from both feedstock materials.

Table 13 illustrates the projected alkali partial pressure and the corresponding percentage of the feedstock concentration that is released at equilibrium as a function of temperature from the Pittsburgh seam coal, oxygen-blown gasifier. Maximum alkali release at 1300 K of 2.6 percent of the background sodium content and 2.9 percent of the background potassium content in Pittsburgh seam coal represents 8 ppm NaCl and 4 ppm KCl present as volatile chlorides in the gasifier outlet stream.

Reevaluation of the Pittsburgh seam coal in which gasification is performed under air-blown conditions indicates that 11 ppm NaCl and 5.5 ppm KCl are released into the effluent stream at 1300 K and 15 atm (Table 14). Approximately 6.5 weight percent of the resulting ash is composed of $\text{NaAlSi}_3\text{O}_8$ and

Table 11

PROJECTED RAW GAS COMPOSITION AND SOLIDS FORMED
DURING THE OXYGEN-BLOWN GASIFICATION OF PITTSBURGH
SEAM COAL AT 1300 K AND 15 atm

Raw Gas Composition (mole %)	Moles x 10 ⁶ (lb/hr) Solids	
50.47% CO	0.6973-3 KAlSi ₃ O ₈	(427.9)
39.74% H ₂	0.1808-2 CaO·Al ₂ O ₃ ·2SiO ₂	(1108.9)
4.02% H ₂ O	0.5296-3 Al ₂ O ₃ ·TiO ₂	(212.3)
3.08% CO ₂	0.5237-2 FeO·Al ₂ O ₃	(2006.7)
1.12% CH ₄	0.2236-3 MgAl ₂ O ₄	(70.1)
0.78% N ₂	0.1641-1 SiO ₂	(2173.7)
0.56% H ₂ S	0.1496-2 NaAlSi ₃ O ₈	(864.8)
0.03% HCl	0.6029-3 FeS	(116.8)
0.02% COS		(6981.2 lb/hr)

Table 12

SOLIDS FORMED AS A FUNCTION OF TEMPERATURE AT
15 atm DURING THE GASIFICATION OF PITTSBURGH
SEAM COAL (OXYGEN BLOWN)

Pittsburgh Seam Coal: 100,000 lb/hr

Oxidant: 62,970 lb/hr

Steam: 50,000 lb/hr

Temp, K	300	400	500	600	700	800	900	1000	1100	1200	1300
MgCO ₃	✓	✓									
C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
CaSO ₄ ·2H ₂ O	✓										
H ₂ O	✓										
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Al ₂ SiO ₅	✓	✓	✓	✓							
Al ₂ O ₃ ·TiO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Na ₂ SO ₄	✓										
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓	✓								
S	✓										
NaCl	✓	✓	✓	✓	✓						
CaCO ₃		✓	✓								
NaAlSi ₃ O ₈		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CaO·MgO·2SiO ₂			✓		✓	✓	✓				
CaO·Al ₂ O ₃ ·2SiO ₂				✓	✓	✓	✓	✓	✓	✓	✓
FeO·Al ₂ O ₃				✓	✓	✓	✓	✓	✓	✓	✓
MgAl ₂ O ₄				✓				✓	✓	✓	✓
FeO·TiO ₂						✓	✓	✓			
FeS										✓	✓

Table 13

PARTIAL PRESSURES AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALIS FORMED IN THE
GASIFIER FROM PITTSBURGH SEAM COAL
(OXYGEN BLOWN, 15 atm)

Temp, K	P _{NaCl} (atm)	Percent Feedstock Na	P _{KCl} (atm)	Percent Feedstock K
300	0.1728-31	0.3061-28	0.6974-31	0.2644-27
400	0.1604-21	0.1979-17	0.3614-22	0.9539-18
500	0.1394-15	0.1722-11	0.4198-16	0.1109-11
600	0.1186-11	0.1474-7	0.4283-12	0.1138-7
700	0.7273-8	0.9094-5	0.2937-9	0.7912-5
800	0.3178-7	0.4135-3	0.1401-7	0.3899-3
900	0.3320-6	0.4615-2	0.1547-6	0.4603-2
1000	0.2234-5	0.3487-1	0.1083-5	0.3617-1
1100	0.1233-4	0.2255	0.6147-5	0.2406
1200	0.4195-4	0.8856	0.2135-4	0.9644
1300	0.1175-3	0.2645+1	0.6067-4	0.2923+1

Temp, K	P _{NaOH} (atm)	Percent Feedstock Na	P _{KOH} (atm)	Percent Feedstock K
1100	0.2959-8	0.5413-4	0.1443-8	0.5648-4
1200	0.1972-7	0.4162-3	0.9668-8	0.4367-3
1300	0.1152-6	0.2594-2	0.5662-7	0.2728-2

Temp, K	Percent Feedstock Na as NaAlSi ₃ O ₈ (s)	Percent Feedstock K as KAlSi ₃ O ₈ (s)
1100	~100	~100
1200	99.11	99.03
1300	97.35	97.08

Table 14

PARTIAL PRESSURE AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALIS FORMED IN THE
GASIFIER FROM PITTSBURGH SEAM COAL
(AIR BLOWN, 15 atm)

Temp, K	P_{NaCl} (atm)	Percent Feedstock Na	P_{KCl} (atm)	Percent Feedstock K
300	0.1728-31	0.3504-27	0.1320-31	0.5729-27
400	0.1604-21	0.4483-17	0.3614-22	0.2161-17
500	0.1394-15	0.3899-11	0.4198-16	0.2512-11
600	0.1186-11	0.3327-7	0.4283-12	0.2570-7
700	0.7222-9	0.2040-4	0.2937-9	0.1775-4
800	0.2479-7	0.7124-3	0.1092-7	0.6719-3
900	0.2709-6	0.8063-2	0.1263-6	0.8041-2
1000	0.1969-5	0.6219-1	0.9545-6	0.6451-1
1200	0.3926-4	0.1415+1	0.1998-4	0.1540+1
1300	0.1592-3	0.5891+1	0.8223-4	0.6511+1

Temp, K	P_{NaOH} (atm)	Percent Feedstock Na	P_{KOH} (atm)	Percent Feedstock K
1200	0.9019-8	0.3249-3	0.4423-8	0.3410-3
1300	0.4972-7	0.1840-2	0.2444-7	0.1935-2

Temp, K	Percent Feedstock Na as $\text{NaAlSi}_3\text{O}_8$ (s)	Percent Feedstock K as KAlSi_3O_8 (s)
1200	98.59	98.46
1300	94.11	93.49

3.2 weight percent of KAlSi_3O_8 (Table 15). The stability of the solid complexes formed as a function of temperature in the Pittsburgh seam coal, air-blown gasifier is shown in Table 16.

3.1.2.3 Gasification of Wyoming Subbituminous Coal

Although the previous discussion illustrated that the gasification products are dependent on such operating conditions as temperatures and pressure, feedstock composition, and oxidant sources, a dramatic change is not evident in the estimated solid composition projected to form when Illinois No. 6 and Pittsburgh seam coals are subjected to identical gasifier operating conditions. Gasifying a Wyoming subbituminous coal produces numerous solid phases not encountered with the Illinois No. 6 or Pittsburgh seam feedstocks. Table 17 defines the stability of these solid species as a function of temperature. For the 0.5 weight percent sulfur coal under oxygen-blown conditions, carbon is not projected to form at operating temperatures of 1300 K and 15 atm. Iron, previously projected to form pyrite at this temperature, preferentially oxidizes to form FeO . Spinel and oxides are also found in the ash matrix, resulting from the presence of the trace and minor mineral constituents.

Sodium in the Wyoming subbituminous coal undergoes a series of complex reactions during gasification. As shown in the thermodynamic calculations, sodium is initially present in the feedstock material as either solid sodium chloride or sulfate. The alkali chloride phase preferentially exists as the major solid phase when gasification temperatures approach 800 K. As secondary sodium complexes, the alkali feldspar, $\text{NaAlSi}_3\text{O}_8$, is projected to form between 300 and 700 K while nepheline, NaAlSiO_4 , is defined as a stable phase only between temperatures of 700 and 800 K. At higher temperatures sodium carbonate is projected to form as the major phase, with chloride present only as a minor phase, prior to conversion into an alkali silicate, Na_2SiO_3 , at temperatures above 1200 K.

Potassium is present as the feldspar complex between operating temperatures of 300 and 800 K, whereupon the alkali is released from the

Table 15.

PROJECTED RAW GAS COMPOSITION AND SOLIDS
FORMED DURING THE AIR BLOWN GASIFICATION
OF PITTSBURGH SEAM COAL AT 1300 K AND
15 atm

Raw Gas Composition (mole %)	Moles $\times 10^6$ (lb/hr) Solids		
29.63% CO	0.2161	C	(5722.2)
19.19% H ₂	0.6715-3	KAlSi ₃ O ₈	(412.0)
0.77% H ₂ O	0.1808-2	CaO·Al ₂ O ₃ ·23H ₂ O	(1108.9)
0.69% CO ₂	0.5275-2	Al ₂ SiO ₅	(1884.5)
0.41% CH ₄	0.5296-3	Al ₂ O ₃ ·TiO ₂	(212.3)
48.99% N ₂	0.2236-3	MgAl ₂ O ₄	(70.1)
0.28% H ₂ S	0.1137-1	SiO ₂	(1506.1)
0.02% HCl	0.1446-2	NaAlSi ₃ O ₈	(835.9)
0.02% COS	0.5840-2	FeS	(1131.8)
			(12883.9 lb/hr)

Table 16

SOLIDS FORMED AS A FUNCTION OF TEMPERATURE AT
15 atm DURING THE GASIFICATION OF PITTSBURGH
SEAM COAL (AIR BLOWN)

Pittsburgh Seam Coal: 100,000 lb/hr

Oxidant: 324,910 lb/hr

Steam: 25,000 lb/hr

Temp., K	300	400	500	600	700	800	900	1000	1200	1300
CaCO_3	✓	✓								
MgCO_3	✓	✓								
C	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
H_2O	✓									
KAlSi_3O_8	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Al_2SiO_5	✓	✓	✓	✓					✓	✓
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Na_2SO_4	✓									
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓	✓							
NaCl	✓	✓	✓	✓	✓					
$\text{NaAlSi}_3\text{O}_8$		✓	✓	✓	✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓		✓	✓	✓			
$\text{FeO} \cdot \text{Al}_2\text{O}_3$				✓	✓	✓	✓	✓		
MgAl_2O_4				✓				✓	✓	✓
$\text{FeO} \cdot \text{TiO}_2$						✓	✓	✓		
FeS									✓	✓

Table 17

SOLIDS FORMED AS A FUNCTION OF TEMPERATURE AT
15 atm DURING THE GASIFICATION OF WYOMING SUB-
BITUMINOUS COAL (OXYGEN BLOWN)

Wyoming Subbituminous Coal: 100,000 lb/hr

Oxidant: 55,040 lb/hr

Steam: 50,000 lb/hr

Temp., K	300	400	500	600	700	800	900	1000	1100	1200	1300
CaCO_3	✓	✓	✓	✓	✓	✓					
MgCO_3	✓	✓									
C	✓	✓	✓	✓	✓	✓	✓	✓			
H_2O	✓										
KAlSi_3O_8	✓	✓	✓	✓	✓						
Al_2SiO_5	✓	✓	✓								
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	✓	✓	✓	✓							
Na_2SO_4	✓										
SiO_2	✓	✓	✓								
FeS_2	✓	✓	✓								
NaCl	✓	✓	✓	✓	✓	✓	✓	✓			
$\text{NaAlSi}_3\text{O}_8$		✓	✓	✓							
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓	✓	✓					
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$				✓							
$\text{FeO} \cdot \text{Al}_2\text{O}_3$				✓	✓	✓					
CaSiO_3				✓	✓	✓	✓	✓	✓	✓	
MgAl_2O_4					✓	✓	✓	✓	✓	✓	✓
NaAlSiO_4					✓						
$\text{CaO} \cdot \text{TiO}_2$					✓	✓					
KCl						✓	✓	✓			
Na_2CO_3						✓	✓	✓	✓		
FeS							✓				
$4\text{CaO} \cdot 3\text{TiO}_2$							✓	✓	✓	✓	✓
Ca_2SiO_4							✓	✓	✓	✓	✓
Mg_2SiO_4							✓	✓	✓	✓	✓
FeO								✓	✓	✓	✓
Na_2SiO_3										✓	✓

clay lattice and reacts with chlorine to form KCl. At temperatures above 1100 K, potassium is projected to completely devolatilize from the ash residue. The projected percent release of the alkali from the feedstock as a function of temperature is shown in Table 18. The maximum alkali release at 1300 K of 40.5 percent of the background sodium content and 100 percent of the background potassium content from Wyoming subbituminous coal represents 44 ppm NaCl, 7.2 ppm NaOH, 28 ppm KCl, and 4.3 ppm KOH present as volatile chlorides and hydroxides in the gasifier outlet stream.

The projected raw gas and solid composition formed in the gasification of Wyoming subbituminous coal in oxygen at 1300 K and 15 atm is shown in Table 19. Calcium metasilicate, CaSiO_3 , is projected to form as the principal solid constituent in the ash. The stability of the solid phases as a function of temperature, the composition of the 1300 K ash, the partial pressure of oxygen and sulfur, and the percentage of alkali released during the gasification of the Wyoming subbituminous coal using air as the oxidant are similar to the projections made for the oxygen-blown gasifier (Tables 20-22).

3.1.2.4 Projected Alkali Release Concentrations for Various Gasification Processes

Estimates of the alkali phase stability for gasification processes shown in Table 23 are presented in this section. In addition to the pressure range indicated for each system, a 15 atm calculation has been included so that comparison of these systems with the 15 atm Westinghouse single-stage gasifier can be made. Although the alkali, chloride, and mineral concentrations are not shown in Table 23, concentrations comparable to those shown in Table 3 are considered for the Illinois No. 6 solids projections, while a reduced chlorine content (0.01%) was used in the eastern Kentucky coal projections. Table 24 illustrates that the resulting solid complexes as a function of temperature for the Lurgi moving-bed gasifier are virtually unaffected by variation in operating pressure. Solid carbon, which is initially present, is depleted below temperatures of 700 K.

Table 18

PARTIAL PRESSURE AND PERCENT FEEDSTOCK
CONCENTRATION OF ALKALIS FORMED IN THE
GASIFIER FROM WYOMING SUBBITUMINOUS COAL
(OXYGEN BLOWN, 15 atm)

Temp., K	P _{NaCl} (atm)	Percent Feedstock Na	P _{KCl} (atm)	Percent Feedstock K
300	0.1728-31	0.1100-27	0.1989-30	0.4974-26
400	0.1604-21	0.5905-17	0.3614-22	0.5220-17
500	0.1394-15	0.5151-11	0.4198-16	0.6087-11
600	0.1186-11	0.4403-7	0.4283-12	0.6239-7
700	0.7222-9	0.2717-4	0.2289-8	0.3380-3
800	0.8483-7	0.3296-2	0.2315-6	0.3532-1
900	0.3332-5	0.1384	0.7962-5	0.1298+1
1000	0.6082-4	0.2815+1	0.1305-3	0.2370+2
1100	0.5518-3	0.2799+2	0.5024-3	0.9904+2
1200	0.5597-3	0.2929+2	0.4697-3	0.9647+2
1300	0.6619-3	0.3482+2	0.4195-3	0.8661+2

Temp., K	P _{NaOH} (atm)	Percent Feedstock Na	P _{KOH} (atm)	Percent Feedstock K
1100	0.5421-5	0.2749	0.4826-5	0.9607
1200	0.2125-4	0.1112+1	0.1718-4	0.3529+1
1300	0.1076-3	0.5658+1	0.6489-4	0.1340+2

Temp., K	Percent Feedstock Na as Solid Complexes		Percent Feedstock K as Solid Complexes
1100	Na ₂ CO ₃	0.7202+2	0.0000
1200	Na ₂ SiO ₃	0.6960+2	0.0000
1300	Na ₂ SiO ₃	0.5953+2	0.0000

Table 19

PROJECTED RAW GAS COMPOSITION AND SOLIDS FORMED
DURING THE OXYGEN-BLOWN GASIFICATION OF WYOMING
SUBBITUMINOUS COAL AT 1300 K and 15 atm

Raw Gas Composition, mole %	Moles $\times 10^6$ (lb/hr) Solids		
27.9% CO	0.1511-2	MgAl ₂ O ₄	(473.9)
31.4% H ₂	0.1576-3	4CaO·3TiO ₂	(161.2)
26.4% H ₂ O	0.1096-2	Ca ₂ SiO ₄	(416.2)
13.5% CO ₂	0.1667-2	Mg ₂ SiO ₄	(517.1)
0.05% CH ₄	0.1759-3	Na ₂ SiO ₃	(47.3)
0.56% N ₂	0.9157-2	CaSiO ₃	(2026.7)
0.15% H ₂ S	0.6489-3	FeO	(204.4)
0.001% HCl			(3846.8 lb/hr)
0.005% COS			

Table 20

SOLIDS FORMED AS A FUNCTION OF TEMPERATURE
AT 15 atm DURING THE GASIFICATION OF WYOMING
SUBBITUMINOUS COAL (AIR BLOWN)

Wyoming Subbituminous Coal: 100,000 lb/hr

Oxidant: 267,960 lb/hr

Steam: 25,000 lb/hr

Temp., K	300	400	500	600	700	800	900	1000	1100	1200	1300
CaCO_3	✓	✓	✓	✓	✓	✓					
MgCO_3	✓	✓									
C	✓	✓	✓	✓	✓	✓	✓				
H_2O	✓										
KAlSi_3O_8	✓	✓	✓	✓							
Al_2SiO_5	✓	✓	✓								
$\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$	✓	✓	✓	✓							
Na_2SO_4	✓										
SiO_2	✓	✓									
FeS_2	✓	✓	✓								
NaCl	✓	✓	✓	✓	✓	✓	✓	✓			
$\text{NaAlSi}_3\text{O}_8$		✓	✓	✓							
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓							
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓	✓	✓					
$\text{FeO} \cdot \text{Al}_2\text{O}_3$				✓	✓						
CaSiO_3				✓	✓	✓	✓	✓	✓	✓	✓
MgAl_2O_4					✓	✓	✓	✓	✓	✓	✓
NaAlSiO_4					✓						
KCl					✓	✓	✓	✓			
$\text{CaO} \cdot \text{TiO}_2$					✓						
FeS						✓	✓				
Na_2CO_3						✓	✓	✓			
$4\text{CaO} \cdot 3\text{TiO}_2$						✓	✓	✓	✓	✓	✓
Ca_2SiO_4							✓	✓	✓	✓	✓
Mg_2SiO_4							✓	✓	✓	✓	✓
FeO								✓	✓	✓	✓
Na_2SiO_3									✓	✓	✓

Table 21

PROJECTED RAW GAS COMPOSITION AND SOLIDS
FORMED DURING THE AIR-BLOWN GASIFICATION
OF WYOMING SUBBITUMINOUS COAL AT 1300 K
AND 15 atm

Raw Gas Composition (mole %)	Moles $\times 10^6$ (lb/hr) Solids		
19.2% CO	0.1511-2	MgAl ₂ O ₄	(473.9)
17.2% H ₂	0.1576-3	4CaO·3TiO ₂	(161.2)
10.5% H ₂ O	0.1089-2	Ca ₂ SiO ₄	(413.5)
6.8% CO ₂	0.1667-2	Mg ₂ SiO ₄	(517.1)
0.01%CH ₄	0.1686-3	Na ₂ SiO ₃	(45.4)
46.2% N ₂	0.9171-2	CaSiO ₃	(2029.8)
0.09%H ₂ S	0.6489-3	FeO	(204.4)
			(3845.4 lb/hr)

Table 22

PARTIAL PRESSURE AND PERCENT FEEDSTOCK CONCENTRATION
OF ALKALIS FORMED IN THE GASIFIER FROM WYOMING SUB-
BITUMINOUS COAL (AIR BLOWN, 15 atm)

Temp., K	P _{NaCl} (atm)	Percent Feedstock Na	P _{KCl} (atm)	Percent Feedstock K
300	0.1728-31	0.7825-27	0.1108-31	0.1969-26
400	0.1604-21	0.1099-16	0.3614-22	0.9720-17
500	0.1394-15	0.9576-11	0.4198-16	0.1132-10
600	0.1186-11	0.8170-7	0.4283-12	0.1158-6
700	0.7222-9	0.5015-4	0.2336-8	0.6366-3
800	0.8483-7	0.6008-2	0.2315-6	0.6437-1
900	0.3332-5	0.2457	0.7962-5	0.2304+1
1000	0.6082-4	0.4819+1	0.1305-3	0.4058+2
1100	0.3316-3	0.2750+2	0.3072-3	0.9944+2
1200	0.3802-3	0.3190+2	0.3037-3	0.9663+2
1300	0.4432-3	0.3723+2	0.2646-3	0.8725+2

Temp., K	P _{NaOH} (atm)	Percent Feedstock Na	P _{KOH} (atm)	Percent Feedstock K
1100	0.1899-5	0.1575	0.1721-5	0.5600
1200	0.1329-4	0.1115+1	0.1023-4	0.3367+1
1300	0.6798-4	0.5711+1	0.3862-4	0.1274+2

Temp., K	Percent Feedstock Na as Solid Complexes		Percent Feedstock K as Solid Complexes
1100	Na ₂ SiO ₃	0.7250+2	0.0000
1200	Na ₂ SiO ₃	0.6699+2	0.0000
1300	Na ₂ SiO ₃	0.5705+2	0.0000

Table 23
PROCESS SYSTEMS

Technology		Lurgi		Shell Koppers	Texaco		Winkler	
Gasifier Type		Moving Bed, Pressurized, Dry Ash		Entrained Flow, Pressurized	Entrained Flow, Pressurized		Fluidized Bed, Atmospheric	
Oxidant	Composition	Air	98% O ₂	99% O ₂	Air	98% O ₂	Air	98% O ₂
	Temp., °C	171	160	?	537.8	148.8	248.9	37.8
	Pressure, atm	23.8	27.2	18.4	40.8	48.9	3.4	3.4
Coal	Type	Illinois No.6		Illinois No.6	Illinois No.6		East Kentucky	
	Btu/lb	12,235		11,961	12,235		10,667	
	Wt% C	66.6		66.72	66.1		60.47	
	H	5.1		4.70	5.1		3.70	
	O	9.6		9.31	9.6		5.96	
	N	1.2		1.03	1.2		1.49	
	S	3.7		3.67	3.7		0.96	
	Ash	9.6		12.57	9.6		22.42	
	Moisture	4.2		2.00	4.2		5.00	
Steam	Temp., °C	282.2	282.2	132.0	None		265.6	213.3
	Pressure, atm	23.8	27.2	?	None		~1.4	~1.4
Range Outlet Temp., °C		371 - 538		~1482	Above 1093		816 - 1093	
Range Pressures, atm		20.4 - 30.6		20.4 - 30.6	40.8 - 81.6		0.5 - 2.1	
Oxygen Feed, lb/lb coal		0.3		0.95	0.84		-	
Steam Feed, lb/lb coal		0.7		0.07	0		-	
Contaminants to Be Removed from Gas		S compounds, tar, phenols, NH ₃ , trace metals		S compounds, trace metals	S compounds, trace metals		S compounds, trace metals	

Table 24

PROJECTED EQUILIBRIUM SOLIDS FORMED IN THE LURGI GASIFICATION OF
ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 15 atm

Temp. (K) Compound (s)	300	500	700	900	1100	1300	1500
CaCO_3	✓	✓					
C	✓	✓					
H_2O	✓						
KAlSi_3O_8	✓	✓	✓	✓	✓	✓	
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	✓		✓				
Al_2SiO_5	✓	✓					
SiO_2	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓					
KCl	✓	✓					
NaCl	✓	✓	✓				
MgCO_3		✓					
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓
$\text{FeO} \cdot \text{Al}_2\text{O}_3$			✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓ (l)
$\text{NaAlSi}_3\text{O}_8$				✓	✓	✓	
MgAl_2O_4				✓	✓	✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓
K_2SiO_3							✓

Table 24 (Continued)

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 20.4 atm

Temp. (K)	300	500	700	900	1100	1300	1500
Compound (s)							
C	✓	✓					
H ₂ O	✓						
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	
CaO·Al ₂ O ₃ ·2SiO ₂	✓		✓	✓	✓	✓	✓
CaO·MgO·2SiO ₂	✓		✓				
Al ₂ SiO ₅	✓	✓					
SiO ₂	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓					
KCl	✓	✓					
NaCl	✓	✓	✓				
CaCO ₃		✓					
MgCO ₃		✓					
FeO·Al ₂ O ₃			✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓ (l)
NaAlSi ₃ O ₈				✓	✓	✓	
MgAl ₂ O ₄				✓	✓	✓	✓
Na ₂ Si ₂ O ₅							✓
K ₂ SiO ₃							✓

Table 24 (Continued)

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 30.6 atm

Temp. (K) Compound (s)	300	500	700	900	1100	1300	1500
C	✓	✓					
H ₂ O	✓						
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓	
CaO·Al ₂ O ₃ ·2SiO ₂	✓		✓	✓	✓	✓	✓
CaO·MgO·2SiO ₂	✓		✓		✓		
Al ₂ SiO ₅	✓	✓					
SiO ₂	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓					
KCl	✓	✓					
NaCl	✓	✓	✓				
CaCO ₃		✓					
MgCO ₃		✓					
FeO·Al ₂ O ₃			✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓ (l)
NaAlSi ₃ O ₈				✓	✓	✓	
MgAl ₂ O ₄				✓		✓	✓
Na ₂ Si ₂ O ₅							✓
K ₂ SiO ₃							✓

At Lurgi gasifier outlet temperatures of 644 and 800 K both sodium and potassium are partitioned between the chloride and feldspar phases. At the higher outlet temperature conversion of the chloride into the feldspar solid is the predominant chemical reaction.

Table 25 shows the estimated volatile alkali mole fractions in either the chloride, the hydroxide, or the sulfate phase that are released during the Lurgi gasification of Illinois No. 6 coal as a function of temperature and pressure. At a maximum gasifier outlet temperature of 900 K in the 20.4 and 30.6 atm system, a total of less than 35 ppb sodium and 28 ppb potassium is released; the principal phase is the volatile chloride. Table 26 projects the background percent alkali released in the Lurgi gasifier if operating temperatures were comparable to those of the 1300 K Westinghouse single-stage gasifier. Although 3.64 percent of the background sodium (9.79 ppm NaCl) is released in the Lurgi and 9.79 percent (19 ppm NaCl) is released in the Westinghouse gasifier, only 0.94 percent (5.06 ppm KCl) of the background potassium is released in the Lurgi, as compared with the 1.08 percent (4.3 ppm KCl) from the Westinghouse gasifier. A somewhat different solids reaction chemistry results in the Shell Koppers gasification of Illinois No. 6 coal (Table 27). Again, the resulting solids are virtually unaffected by variation in system pressure. In the Shell Koppers process, carbon is projected to remain as a stable solid to temperatures below 1100 K. Potassium during gasification resides predominantly in the feldspar structure prior to its possible conversion into the silicate complex at temperatures between 1300 and 1500 K. Sodium, initially as the chloride, is converted into the feldspar and finally into the silicate phase as the temperature increases from 300 to 1700 K. The Shell Koppers operating conditions promote release of 11 to 12 percent background sodium and 5 to 6 percent background potassium in the 1700 K, 20.4 and 30.6 atm gasification system (Table 28). This release corresponds to 37 to 46 ppm sodium as NaCl and NaOH, and 983 ppm potassium as KCl and KOH emitted into the effluent system at the outlet of the Shell Koppers gasifier (Table 29).

Table 25

ESTIMATED VOLATILE ALKALI MOLE FRACTIONS RELEASED DURING THE LURGI
GASIFICATION OF ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE
AND PRESSURE

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 15 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.1152-32	0.2196-31	-	-	-	-
500	0.9295-17	0.5142-16	0.5168-26	0.3435-25	-	0.4184-35
700	0.4815-10	0.1518-10	0.5544-17	0.1888-17	0.5538-31	0.8553-30
900	0.4035-7	0.1881-7	0.1771-12	0.8392-13	0.1518-26	0.1189-25
1100	0.8908-6	0.4442-6	0.8919-10	0.4349-10	0.2485-25	0.8741-25
1300	0.9799-5	0.5061-5	0.1035-7	0.5086-8	0.9646-22	0.1895-21
1500	0.2081-4	0.3224-3	0.2852-5	0.4122-4	0.3356-17	0.3665-14

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 20.4 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.8471-33	0.1614-31	-	-	-	-
500	0.6835-17	0.3781-16	0.4431-26	0.2946-25	-	0.5689-35
700	0.3540-10	0.1302-10	0.4077-17	0.1619-17	0.5533-31	0.1163-29
900	0.3460-7	0.1613-7	0.1519-12	0.7196-13	0.2064-26	0.1619-25
1100	0.7639-6	0.3809-6	0.7648-10	0.3729-10	0.1827-25	0.6428-25
1300	0.8403-5	0.4339-5	0.8873-8	0.4362-8	0.7092-22	0.1393-21
1500	0.2081-4	0.3224-3	0.2445-5	0.3534-4	0.2467-17	0.2695-14

Table 25 (Continued)

System: Lurgi

Gasifier Type: Moving Bed

Pressure: 30.6 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.5647-33	0.1076-31	-	-	-	-
500	0.4556-17	0.2520-16	0.3618-26	0.2405-25	-	0.8535-35
700	0.2360-10	0.1063-10	0.2718-17	0.1322-17	0.5533-31	0.1745-29
900	0.2825-7	0.1317-7	0.1240-12	0.5876-13	0.3097-26	0.2425-25
1100	0.7242-6	0.3611-6	0.2849-9	0.1389-9	0.3049-22	0.1073-21
1300	0.3543-5	0.6861-5	0.7245-8	0.3561-8	0.4728-22	0.9288-22
1500	0.2081-4	0.3224-3	0.1997-5	0.2886-4	0.1645-17	0.1797-14

Table 26

PROJECTED PERCENT BACKGROUND ALKALI RELEASE IN THE LURGI
GASIFICATION OF ILLINOIS NO. 6 COAL AT 1300 K

Volatile Species	Pressure		
	15 atm	20.4 atm	30.6 atm
NaCl(g)	3.64	3.12	2.53
NaOH(g)	3.34-3	3.12-3	2.89-3
Na ₂ SO ₄ (g)	2.05-17	2.54-17	3.89-17
KCl(g)	0.94	0.80	0.65
KOH(g)	8.18-4	7.64-4	7.09-4
K ₂ SO ₄ (g)	2.01-17	2.49-17	3.81-17

Table 27

PROJECTED EQUILIBRIUM SOLIDS FORMED IN THE SHELL KOPPERS GASIFICATION
OF ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 15 atm

Temp. (K) Compound (s)	300	500	700	900	1100	1300	1500	1700
NaHCO ₃	✓							
CaCO ₃	✓	✓						
MgCO ₃	✓							
C	✓	✓	✓	✓				
H ₂ O	✓							
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓		
Al ₂ SiO ₅	✓	✓						
FeO·Al ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓						
NaCl	✓	✓	✓					
CaO·MgO·2SiO ₂		✓	✓	✓				
NaAlSi ₃ O ₈		✓	✓	✓	✓	✓		
CaO·Al ₂ O ₃ ·2SiO ₂			✓	✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓ (ℓ)	✓ (ℓ)
MgAl ₂ O ₄					✓	✓	✓	✓
Na ₂ Si ₂ O ₅							✓	✓
K ₂ SiO ₃							✓	✓

Table 27 (Continued)

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 20.40 atm

Temp. (K) Compound (s)	300	500	700	900	1100	1300	1500	1700
NaHCO ₃	✓							
CaCO ₃	✓	✓						
MgCO ₃	✓							
C	✓	✓	✓	✓				
H ₂ O	✓							
KAlSi ₃ O ₈	✓	✓	✓	✓	✓	✓		
Al ₂ SiO ₅	✓	✓						
FeO·Al ₂ O ₃	✓	✓	✓	✓	✓	✓	✓	✓
SiO ₂	✓	✓	✓	✓	✓	✓	✓	✓
FeS ₂	✓	✓						
NaCl	✓	✓	✓					
NaAlSi ₃ O ₈		✓	✓	✓	✓	✓		
CaO·MgO·2SiO ₂		✓	✓	✓				
CaO·Al ₂ O ₃ ·2SiO ₂			✓	✓	✓	✓	✓	✓
FeS			✓	✓	✓	✓	✓ (l)	✓ (l)
MgAl ₂ O ₄					✓	✓	✓	✓
Na ₂ Si ₂ O ₅							✓	✓
K ₂ SiO ₃							✓	✓

Table 27 (Continued)

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 30.60 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
NaHCO_3	✓							
CaCO_3	✓	✓						
MgCO_3	✓	✓						
C	✓	✓	✓	✓				
H_2O	✓							
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
Al_2SiO_5	✓	✓						
$\text{FeO} \cdot \text{Al}_2\text{O}_3$	✓	✓	✓	✓	✓	✓	✓	✓
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓						
NaCl	✓	✓	✓					
$\text{NaAlSi}_3\text{O}_8$		✓	✓	✓	✓	✓		
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓				
FeS			✓	✓	✓	✓	✓ (L)	✓ (L)
MgAl_2O_4					✓	✓	✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	✓
K_2SiO_3							✓	✓

Table 28

CALCULATED PERCENT BACKGROUND ALKALI RELEASE DURING THE SHELL KOPPERS
GASIFICATION OF ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE AND
PRESSURE

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure Temp. (K)	15 atm		20.4 atm		30.6 atm	
	Na	K	Na	K	Na	K
300	-	-	-	-	-	-
500	-	-	-	-	-	-
700	-	-	-	-	-	-
900	-	-	-	-	-	-
1100	-	-	-	-	-	-
1300	2.77	0.71	2.38	0.61	1.95	0.50
1500	6.14	4.73	6.02	4.64	5.86	4.51
1700	12.66	6.34	11.97	6.01	11.18	5.63

Table 29

ESTIMATED VOLATILE ALKALI MOLE FRACTIONS RELEASED DURING THE SHELL KOPPERS
GASIFICATION OF ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 15 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.1152-32	0.3617-32	-	-	-	-
500	0.9295-17	0.2799-17	0.7555-25	0.2734-25	-	0.1334-36
700	0.4815-10	0.1958-10	0.1851-16	0.8129-17	0.1719-29	0.4417-28
900	0.5109-7	0.2381-7	0.7285-12	0.3452-12	0.4977-25	0.3898-24
1100	0.1254-5	0.6253-6	0.1096-9	0.5345-10	0.2942-24	0.1035-23
1300	0.1379-4	0.7124-5	0.2215-7	0.1089-7	0.1051-19	0.2065-19
1500	0.3022-4	0.4683-3	0.4131-5	0.5971-4	0.8844-15	0.9660-12
1700	0.2419-4	0.4682-3	0.2899-4	0.5152-3	0.2354-13	0.2793-10

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 20.4 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.8471-33	0.3617-32	-	-	-	-
500	0.6835-17	0.2058-17	0.6478-25	0.2344-25	-	0.1679-36
700	0.3540-10	0.1439-10	0.1587-16	0.6971-17	0.2338-29	0.6007-28
900	0.4381-7	0.2042-7	0.6247-12	0.2959-12	0.6768-25	0.5301-24
1100	0.1075-5	0.5362-6	0.9398-10	0.4583-10	0.2163-24	0.7609-24
1300	0.1183-4	0.6109-5	0.1899-7	0.9335-8	0.7729-20	0.1518-19
1500	0.3022-5	0.4683-3	0.3542-5	0.5119-4	0.6503-15	0.7103-12
1700	0.2074-4	0.4682-3	0.2486-4	0.5152-3	0.1733-13	0.2793-10

Table 29(Continued)

System: Shell Koppers

Gasifier Type: Entrained Bed

Pressure: 30.6 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.5647-33	0.3617-32	-	-	-	-
500	0.4557-17	0.1372-17	0.5294-25	0.1915-25	-	0.2266-36
700	0.2360-10	0.9597-11	0.1296-16	0.5692-17	0.3507-29	0.9011-28
900	0.3577-7	0.1667-7	0.5100-12	0.2417-12	0.1015-24	0.7951-24
1100	0.8779-6	0.4378-6	0.7673-10	0.3742-10	0.1442-24	0.5073-24
1300	0.9658-5	0.4988-5	0.1551-7	0.7622-8	0.5153-20	0.1012-19
1500	0.3022-4	0.4683-3	0.2892-5	0.4180-4	0.4335-15	0.4735-12
1700	0.1694-4	0.4682-3	0.2029-4	0.5152-3	0.1155-13	0.2793-10

At the 1700 to 1755 K Shell Koppers operating temperatures, the alkali silicates are projected to form with ash solids containing liquid iron sulfide (FeS). Agglomeration of the ash fines may prevent further release of the potentially volatile alkali species.

In the Texaco gasifier the resulting solid phases formed during the gasification of Illinois No. 6 coal are again similar in composition to those previously shown in the Lurgi and Shell Koppers system. Subtle changes in phase stabilities such as the conversions and interconversions of phases, however, result as a function of temperature and pressure (Table 30). Carbon exists in the Texaco gasifier as a solid phase up to temperatures of 1500 K, somewhat higher than those calculated for either the Lurgi or Shell Koppers process. Both sodium and potassium initially exist as the chlorides and feldspars but are converted into the possible silicate phases as operating temperatures exceed 1500 K. At 1300 K between 9 and 12 ppm sodium are release as NaCl into the 40.8 and 81.6 atm Texaco gasifier effluent, corresponding to 1 to 2 percent of the background sodium content, while 4 to 6 ppm potassium are released as KCl, corresponding to 0.3 to 0.5 percent of the background potassium feedstock content (Tables 31 and 32).

A totally different solids chemistry is projected when eastern Kentucky coal is gasified in the Winkler fluidized-bed gasifier. In the Winkler system, carbides of iron and silicon are projected to result with solid carbon when the gasifier operates between temperatures of 300 to 1700 K (Table 33). Solid sulfides of calcium, iron, potassium, and sodium are also projected to form in the resulting ash solids. The effect of operating pressure on the stability of these solid phases is again insignificant. At Winkler operating temperatures of 1089 to 1366 K, potassium is bound predominantly within the feldspar lattice, while sodium is partitioned between the chlorides and feldspar phases. At 2.1 atm nepheline is projected to form at 1300 K, prior to conversion into the sulfide and subsequent volatilization.

Table 30

PROJECTED EQUILIBRIUM SOLIDS FORMED IN THE TEXACO GASIFICATION OF
ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 15 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
CaCO_3	✓	✓						
MgCO_3	✓							
C	✓	✓	✓	✓	✓	✓		
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	✓							
H_2O	✓							
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
Al_2SiO_5	✓	✓			✓			
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓						
KCl	✓	✓						
NaCl	✓	✓	✓					
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$		✓	✓	✓				
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓
$\text{FeO} \cdot \text{Al}_2\text{O}_3$			✓	✓				
FeS			✓	✓	✓	✓	✓ (l)	✓ (l)
$\text{NaAlSi}_3\text{O}_8$			✓	✓	✓	✓		
MgAl_2O_4					✓	✓	✓	✓
$\text{Al}_6\text{Si}_2\text{O}_{13}$						✓	✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	✓
K_2SiO_3							✓	✓

Table 30 (Continued)

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 40.80 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
CaCO_3	✓	✓						
MgCO_3	✓	✓						
C	✓	✓	✓	✓	✓	✓		
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	✓							
H_2O	✓							
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
Al_2SiO_5	✓	✓						
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓						
KCl	✓	✓						
NaCl	✓	✓	✓					
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓				
$\text{FeO} \cdot \text{Al}_2\text{O}_3$			✓	✓	✓			
FeS			✓	✓	✓	✓	✓ (ℓ)	✓ (ℓ)
$\text{NaAlSi}_3\text{O}_8$				✓	✓	✓		
MgAl_2O_4					✓	✓	✓	✓
$\text{Al}_6\text{Si}_2\text{O}_{13}$						✓	✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	✓
K_2SiO_3							✓	✓

Table 30 (Continued)

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 81.60 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
CaCO_3	✓	✓						
MgCO_3	✓	✓						
C	✓	✓	✓	✓	✓	✓	✓	
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	✓							
H_2O	✓							
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
Al_2SiO_5	✓	✓			✓			
SiO_2	✓	✓	✓	✓	✓	✓	✓	✓
FeS_2	✓	✓						
KCl	✓	✓						
NaCl	✓	✓	✓					
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$			✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$			✓	✓				
$\text{FeO} \cdot \text{Al}_2\text{O}_3$			✓	✓				
FeS			✓	✓	✓	✓	✓ (l)	✓
$\text{NaAlSi}_3\text{O}_8$				✓		✓		
MgAl_2O_4					✓	✓	✓	✓
$\text{Al}_6\text{Si}_2\text{O}_{13}$						✓	✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	✓
K_2SiO_3							✓	✓

Table 31

ESTIMATED VOLATILE ALKALI MOLE FRACTIONS RELEASED DURING THE TEXACO
GASIFICATION OF ILLINOIS NO. 6 AS A FUNCTION OF TEMPERATURE AND
PRESSURE

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 15 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.1152-32	0.2195-31	-	-	-	-
500	0.9295-17	0.5142-16	0.4249-26	0.2825-25	-	0.2779-36
700	0.4815-10	0.1866-10	0.1759-16	0.7364-17	0.1478-29	0.3450-28
900	0.4739-7	0.2209-7	0.6555-12	0.3106-12	0.3888-25	0.3045-24
1100	0.1252-5	0.2512-5	0.3839-10	0.1872-10	0.1674-26	0.5889-26
1300	0.2029-4	0.1048-4	0.5699-8	0.2802-8	0.3228-22	0.6341-22
1500	0.3064-4	0.4747-3	0.1913-5	0.2765-4	0.2794-17	0.3052-14
1700	0.2039-4	0.4746-3	0.1339-4	0.2864-3	0.7365-16	0.1262-12

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 40.80 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.4235-33	0.8072-32	-	-	-	-
500	0.3417-17	0.1890-16	0.2578-26	0.1714-25	-	0.7517-36
700	0.1770-10	0.1131-10	0.6468-17	0.4465-17	0.1478-29	0.9385-28
900	0.2874-7	0.1339-7	0.3975-12	0.1883-12	0.1057-24	0.8282-24
1100	0.7975-6	0.3977-6	0.9800-10	0.4779-10	0.6812-23	0.2397-22
1300	0.1231-4	0.6355-5	0.3456-8	0.1699-8	0.1187-22	0.2332-22
1500	0.3064-4	0.4747-3	0.1159-5	0.1676-4	0.1027-17	0.1122-14
1700	0.4608-4	0.4747-3	0.8149-5	0.7709-4	0.2756-16	0.9255-14

Table 31 (Continued)

System: Texaco

Gasifier Type: Entrained Bed

Pressure: 81.60 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.2118-33	0.4036-32	-	-	-	-
500	0.1709-17	0.9452-17	0.1823-26	0.1212-25	-	0.1503-35
700	0.8850-11	0.7999-11	0.3234-17	0.3157-17	0.1478-29	0.1877-27
900	0.2032-7	0.9471-8	0.2811-12	0.1332-12	0.2115-24	0.1656-23
1100	0.6533-6	0.3258-6	0.4017-10	0.1959-10	0.4559-23	0.1604-22
1300	0.8701-5	0.4494-5	0.2444-8	0.1201-8	0.5935-23	0.1166-22
1500	0.3064-4	0.4747-3	0.8201-6	0.1185-4	0.5137-18	0.5611-15
1700	0.4608-4	0.4747-3	0.5762-5	0.5451-4	0.1378-16	0.4627-14

Table 32

CALCULATED PERCENT BACKGROUND ALKALI RELEASE DURING THE TEXACO
GASIFICATION OF ILLINOIS NO. 6 COAL AS A FUNCTION OF TEMPERATURE
AND PRESSURE

System: Texaco

Gasifier Type: Entrained Bed

Pressure Temp. (K)	15 atm		40.8 atm		81.6 atm	
	Na	K	Na	K	Na	K
300	-	-	-	-	-	-
500	-	-	-	-	-	-
700	-	-	-	-	-	-
900	-	-	-	-	-	-
1300	4.68	1.21	1.96	0.52	1.11	0.29
1500	7.82	60.67	7.56	58.89	7.37	56.97
1700	14.93	70.43	13.65	65.22	13.30	62.53

Table 33

PROJECTED EQUILIBRIUM SOLIDS FORMED IN THE WINKLER GASIFICATION
OF EASTERN KENTUCKY COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 15 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
Fe_3C	✓	✓	✓	✓				✓
C	✓	✓	✓	✓	✓	✓	✓	✓
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
$\text{NaAlSi}_3\text{O}_8$	✓	✓	✓	✓	✓	✓		
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	✓	✓	✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	✓	✓	✓					
Al_2SiO_5	✓	✓	✓	✓	✓	✓		
SiO_2	✓	✓	✓	✓			✓	
CaS	✓	✓	✓	✓	✓	✓		
NaCl	✓	✓	✓	✓	✓			
FeSi	✓	✓	✓	✓		✓	✓	
MgAl_2O_4				✓		✓	✓	
MgSiO_3					✓			✓
FeS					✓	✓		
$\text{Al}_6\text{Si}_2\text{O}_{13}$							✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	✓
K_2S							✓	✓
SiC								✓

Table 33 (Continued)

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 0.5 atm

Temp. (K) Compound (s)	300	500	700	900	1100	1300	1500	1700
Fe_3C	✓	✓	✓	✓				✓
C	✓	✓	✓	✓	✓	✓	✓	✓
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
$\text{NaAlSi}_3\text{O}_8$	✓	✓	✓	✓	✓	✓		
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	✓	✓	✓	✓	✓	✓	✓	
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	✓	✓	✓					
Al_2SiO_5	✓	✓	✓	✓	✓			
SiO_2	✓	✓	✓	✓				
CaS	✓	✓	✓	✓	✓	✓		✓
NaCl	✓	✓	✓	✓				
FeSi	✓	✓	✓	✓	✓	✓	✓	
MgAl_2O_4				✓		✓	✓	✓
MgSiO_3					✓			
FeS					✓			
$\text{Al}_6\text{Si}_2\text{O}_{13}$						✓	✓	
SiC							✓	✓
$\text{Na}_2\text{Si}_2\text{O}_5$							✓	
K_2S							✓	
$\text{CaO} \cdot 6\text{Al}_2\text{O}_3$								✓
CaSiO_3								✓

Table 33 (Continued)

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 2.1 atm

Temp. (K)	300	500	700	900	1100	1300	1500	1700
Compound (s)								
Fe_3C	✓	✓	✓	✓				✓
C	✓	✓	✓	✓	✓	✓	✓	✓
KAlSi_3O_8	✓	✓	✓	✓	✓	✓		
$\text{NaAlSi}_3\text{O}_8$	✓	✓	✓	✓	✓			
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	✓	✓	✓	✓	✓	✓	✓	✓
$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	✓	✓	✓					
Al_2SiO_5	✓	✓	✓	✓	✓			
SiO_2	✓	✓	✓	✓			✓	
CaS	✓	✓	✓	✓	✓			✓
NaCl	✓	✓	✓	✓				
FeSi	✓	✓	✓	✓	✓	✓	✓	
MgAl_2O_4				✓			✓	✓
MgSiO_3					✓			
FeS					✓	✓		
$\text{Al}_6\text{Si}_2\text{O}_{13}$						✓	✓	
Mg_2SiO_4						✓		
NaAlSiO_4						✓		
K_2S							✓	
Na_2S							✓	
SiC								✓
$\text{CaO} \cdot 6\text{Al}_2\text{O}_3$								✓

Estimates of the volatile alkali mole fraction released as a function of temperature and pressure presented in Table 34 indicate that even though the chlorine concentration present in the original feedstock material is significantly lower than in the Illinois No. 6 feedstock, the principal released volatile alkali phases are those of the chloride. Between 15 and 132 ppm sodium and 7 to 100 ppm potassium are projected to be released into the 1089 to 1366 K effluent as a result of gasification of eastern Kentucky coal in the Winkler system.

3.1.2.5 Comment on the Equilibrium Projections and the Thermodynamic Model

Complex chemical phases and reactions were demonstrated in the previous sections to result as a function of the various feedstock, steam, and oxidant sources, and of system operating temperature and pressure. Table 35 illustrates the alkali release concentrations that result at the 1300 K, 15 atm gasifier condition. A greater release of background sodium than potassium is expected to result at equilibrium when feldspar complexes form as stable solid phases at process conditions. The stability of the feldspar complex is also shown to be enhanced in the presence of oxygen, minimizing the concentration of alkali released. Alternatively, feedstock sources that do not promote the formation of the feldspar--for example, reduction of the aluminum concentration in the original feedstock mineral content--enhance release of the alkali as a volatile phase.

Throughout these calculations nepheline was not projected to form in the gasification of either Illinois No. 6 or Pittsburgh seam coal. For Wyoming subbituminous, however, nepheline appeared as an alkali phase transition complex that resulted between 300 and 1300 K operating temperatures. As a major ash constituent after gasification, however, feldspar or the water glass phase is projected as the principal solid formed during the gasification of these feedstock materials.

Table 36 summarizes the alkali concentrations released at appropriate operating temperatures and pressures for each process system. Comparison of Tables 35 and 36 permits a ranking of the process systems on the basis of Illinois No. 6 coal gasification. In ascending order of the

Table 34

ESTIMATED VOLATILE ALKALI MOLE FRACTIONS RELEASED DURING THE WINKLER GASIFICATION OF EASTERN KENTUCKY COAL AS A FUNCTION OF TEMPERATURE AND PRESSURE

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 15 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.1152-32	0.1582-33	-	-	-	-
500	0.9295-17	0.2799-17	0.1855-33	0.6712-34	-	-
700	0.4815-10	0.1958-10	0.2987-22	0.1312-22	-	-
900	0.2221-6	0.1035-6	0.5445-16	0.2580-16	-	-
1100	0.5789-5	0.2887-5	0.6709-13	0.3272-13	-	-
1300	0.4202-4	0.2170-4	0.4999-10	0.2458-10	0.4749-34	0.9328-34
1500	0.2608-4	0.1312-3	0.1766-6	0.8286-6	0.2289-25	0.2634-23
1700	0.1535-4	0.1279-3	0.6352-6	0.4859-5	0.1978-24	0.4345-22

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 0.5 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.3456-31	0.4745-32	-	-	-	-
500	0.2789-15	0.8396-16	0.2378-32	0.8604-33	-	-
700	0.1444-8	0.5873-9	0.3829-21	0.1681-21	-	-
900	0.6664-5	0.3106-5	0.4349-15	0.2061-15	-	-
1100	0.3171-4	0.1581-4	0.3675-12	0.1792-12	-	-
1300	0.1311-3	0.6771-4	0.6749-9	0.3317-9	0.2591-31	0.5090-31
1500	0.5984-4	0.1266-3	0.3816-6	0.7527-6	0.3158-26	0.6424-25
1700	0.1648-4	0.1130-3	0.6372-6	0.4014-5	0.3935-29	0.5859-27

Table 34 (Continued)

System: Winkler

Gasifier Type: Fluidized Bed

Pressure: 2.1 atm

Alkali Phase Temp., K	NaCl(g)	KCl(g)	NaOH(g)	KOH(g)	Na ₂ SO ₄ (g)	K ₂ SO ₄ (g)
300	0.8229-32	0.1129-32	-	-	-	-
500	0.6639-16	0.1999-16	0.8105-33	0.2933-33	-	-
700	0.3439-9	0.1398-9	0.1305-21	0.5731-22	-	-
900	0.1587-5	0.7394-6	0.2122-15	0.1005-15	-	-
1100	0.1547-4	0.7715-5	0.1793-12	0.8744-13	-	-
1300	0.1322-3	0.1009-3	0.1563-8	0.1135-8	0.1349-31	0.5785-31
1500	0.6239-4	0.1309-3	0.2069-6	0.4053-6	0.7356-27	0.1474-25
1700	0.1676-4	0.1149-3	0.2436-5	0.1535-4	0.4888-24	0.7277-22

Table 35

ALKALI RELEASE AT 1300 K, 15 atm

Feedstock	% Background Sodium Release	ppm Na as NaCl	% Background Potassium Release	ppm K as KCl	Solid Complexes
Illinois #6 - oxygen -	9.79	19	1.08	4.3	KAlSi_3O_8 (KCl, K_2SO_4)* $\text{NaAlSi}_3\text{O}_8$ (NaCl)
Illinois #6 - air -	18.65	23	4.82	12	KAlSi_3O_8 (KCl) $\text{NaAlSi}_3\text{O}_8$ (NaCl)
Pittsburgh Seam - oxygen -	2.65	7.8	2.92	4	KAlSi_3O_8 $\text{NaAlSi}_3\text{O}_8$ (NaCl, Na_2SO_4)
Pittsburgh Seam - air -	5.89	10.6	6.51	5.5	KAlSi_3O_8 $\text{NaAlSi}_3\text{O}_8$ (Na_2SO_4 , NaCl)
Wyoming Subbituminous - oxygen -	40.5	44(NaCl) 7(NaOH)	100	28(KCl) 4(KOH)	(KAlSi_3O_8 , KCl) Na_2SiO_3 ($\text{NaAlSi}_3\text{O}_8$, NaAlSiO_4 , Na_2CO_3 , NaCl, Na_2SO_4)
Wyoming Subbituminous - air -	42.94	29.5(NaCl) 4.5(NaOH)	100	17.6(KCl) 2.5(KOH)	(KAlSi_3O_8 , KCl) Na_2SiO_3 ($\text{NaAlSi}_3\text{O}_8$, NaAlSiO_4 , Na_2CO_3 , Na_2SO_4 , NaCl)

* Phases projected at temperature less than 1300 K are indicated in parentheses.

Table 36

ESTIMATED ALKALI CONCENTRATION RELEASED IN THE
VARIOUS PROCESS SYSTEMS

Process System \ Alkali (ppm)	Na	K
LURGI 20.4 atm	<0.035	<0.016
30.6 atm	<0.028	<0.013
SHELL KOPPERS 20.4 atm	~45.60	~983.40
30.6 atm	~37.23	~983.40
TEXACO 40.8 atm	~12.31	~6.36
81.6 atm	~ 8.70	~4.49
WINKLER 0.5 atm	~31.71 - 131.10	~15.81 - 67.71
2.1 atm	~15.47 - 132.20	~ 7.72 - 100.9

concentration of released alkali in the effluent at each gasifier outlet, the following is projected for both sodium and potassium: Lurgi < Texaco & Westinghouse < Shell Koppers. Gasification of the eastern Kentucky coal in the Winkler or the Wyoming subbituminous in the Westinghouse fluidized bed does not emit the levels observed for potassium in the Shell Koppers process but borders on, if not exceeds, those for sodium. If each process were operated at 1300 K and 15 atm similarly to the Westinghouse single-stage gasifier, the concentration of the alkali released into the gasifier effluent from minimum to maximum levels would be as follows: Lurgi < Shell Koppers < Texaco < Winkler, with the Westinghouse estimates both lower than the Lurgi and higher than the Winkler, depending on the feedstock and oxidant source utilized.

The preceding discussion has emphasized gasifier reactions at equilibrium conditions. The validity of using the thermodynamic model is borne out in analytical results of samples collected during actual gasifier operations. Often thermodynamic evaluations are based on generalized coal compositions, which may not reflect the actual composition of the feedstock used during a particular test run. Thus, not only proximate and/or ultimate analyses of the major constituents should be obtained, but also data supporting the trace and minor substituent content, when the thermodynamic approach is to be rigorously applied to a particular system.

The thermodynamic model has the ability to define minute concentrations of stable equilibrium phases, all of which may be far below analytical detection limits. Often, phases that are projected as the major constituent in the equilibrium model will, indeed, be detected analytically. The amorphous phase, however, undefinable by analytical techniques, baffles the sophisticated complex mixture projected by the thermodynamic model.

3.1.3 Development of Alkali/Aluminosilicate Phase Diagrams

3.1.3.1 Feedstock Stability

Having estimated the gasifier raw gas and solid composition, we will now estimate the phase stability of these solid products and potential getter materials in the various system environments. The equilibrium

estimates of the projected oxygen (O_2) and sulfur (S_2) partial pressures in the 15 atm gasification systems described in Sections 3.1.2.1 to 3.1.2.3 are summarized in Tables 37 through 42. Figures 3 through 6 illustrate the compositional changes likely to occur within the solids formed at the single-stage gasifier outlet using Illinois No. 6 coal under oxygen-blown conditions at 1300 K and 15 atm total pressure as a function of system oxygen and sulfur partial pressures. As shown in Figure 6, carbides and sulfides are the major constituents of the ash matrix formed at extremely low system oxygen partial pressures, while oxides and sulfates predominate at high system oxygen partial pressures. The stability of the resulting solid or condensed phases is typically governed by the maximum temperature that the compounds experience. Figure 7 projects the complex chemistry of the stable solid phases that form at various temperatures when Illinois No. 6 coal is gasified under oxygen-blown conditions.

3.1.3.2 Getter Stability

The ultimate reactivity of the alkali released during gasification depends not only on the partial pressures of oxygen and sulfur and on system operating temperature and pressure, but also on possible interactions with entrained ash fines or gettering materials. Getters ultimately will be selected on the basis of hot alkali removal efficiencies. Equilibrium estimates of the potential getter material reactions provide a first-level approximation of their performance. Prior to presenting the equilibrium reactions of the aluminosilicate getter kaolin, we will review the phase stability of released Illinois No. 6 feedstock sodium as a function of pO_2 , pS_2 , and temperature for gasification processes maintained at 15 atm total pressure.

As the feedstock sodium experiences a temperature drop from 1300 to 600 K various phases result, depending on the local pO_2 and pS_2 environment, as shown in Figure 8. Initially, at 1300 K gasifier temperatures, ~100 percent of the Illinois No. 6 feedstock sodium content is

Table 37

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
 THE GASIFICATION OF ILLINOIS NO. 6 COAL AS
 A FUNCTION OF TEMPERATURE (OXYGEN BLOWN, 15 atm)

Temperature K(°F)	P _{O₂} , atm	P _{S₂} , atm
300 (81)	--	1.29-14
400 (261)	--	2.27-15
500 (441)	--	4.38-13
600 (621)	1.64-34	2.82-11
700 (801)	1.39-29	8.25-10
800 (981)	6.78-26	5.59-9
900 (1161)	4.68-23	2.64-8
1000 (1340)	7.35-21	9.62-8
1100 (1520)	3.33-19	2.59-7
1200 (1700)	5.22-18	7.69-7
1300 (1881)	1.20-16	2.44-6

Table 38

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
THE GASIFICATION OF ILLINOIS NO. 6 COAL AS
A FUNCTION OF TEMPERATURE (AIR BLOWN, 15 atm)

Temp, K (°F)	P _{O₂} , atm	P _{S₂} , atm
300 (81)	--	0.1291-13
400 (261)	--	0.1724-14
500 (441)	--	0.3138-12
600 (621)	0.6761-34	0.1878-10
700 (801)	0.5759-29	0.5914-9
800 (981)	0.2835-25	0.4329-8
900 (1161)	0.1962-22	0.2311-7
1000 (1340)	0.2991-20	0.8775-7
1200 (1700)	0.1760-17	0.1117-5
1300 (1881)	0.1249-16	0.3757-5

Table 39

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
THE GASIFICATION OF PITTSBURGH SEAM COAL
AS A FUNCTION OF TEMPERATURE (OXYGEN BLOWN,
15 atm).

Temp., K	P _{O₂} (atm)	P _{S₂} (atm)
300	--	0.1292-13
400	--	0.2399-14
500	--	0.4504-12
600	0.1678-33	0.4023-10
700	0.1421-28	0.5141-9
800	0.6912-25	0.3607-8
900	0.4762-22	0.1716-7
1000	0.7481-20	0.6260-7
1100	0.3386-18	0.1861-6
1200	0.5317-17	0.5529-6
1300	0.8768-16	0.1681-5

Table 40

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
THE GASIFICATION OF PITTSBURGH SEAM COAL
AS A FUNCTION OF TEMPERATURE (AIR BLOWN
15 atm)

Temp., K	P_{O_2} (atm)	P_{S_2} (atm)
300	--	0.1216-13
400	--	0.1778-14
500	--	0.3142-12
600	0.6950-34	0.2766-10
700	0.5877-29	0.3609-9
800	0.2884-25	0.2710-8
900	0.1992-22	0.1449-7
1000	0.3028-20	0.6184-7
1200	0.1779-17	0.5302-6
1300	0.1261-16	0.1787-5

Table 41

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
THE GASIFICATION OF WYOMING SUBBITUMINOUS
COAL AS A FUNCTION OF TEMPERATURE
(OXYGEN BLOWN, 15 atm)

Temp., K	P_{O_2} (atm)	P_{S_2} (atm)
300	--	0.7402-12
400	--	0.1971-15
500	--	0.3609-13
600	0.1812-33	0.1802-11
700	0.1527-28	0.2286-10
800	0.7404-25	0.1596-9
900	0.5096-22	0.6263-9
1000	0.9697-20	0.2737-8
1100	0.1152-17	0.1022-7
1200	0.1022-15	0.4647-7
1300	0.5543-14	0.1968-6

Table 42

PARTIAL PRESSURE OF OXYGEN AND SULFUR FROM
THE GASIFICATION OF WYOMING SUBBITUMINOUS
COAL AS A FUNCTION OF TEMPERATURE
(AIR BLOWN, 15 atm)

Temp., K	P_{O_2} (atm)	P_{S_2} (atm)
300	--	0.2175-14
400	--	0.1597-15
500	--	0.2816-13
600	0.8788-34	0.1391-11
700	0.7416-29	0.1797-10
800	0.3629-25	0.1096-9
900	0.2512-22	0.5693-9
1000	0.3471-20	0.2831-8
1100	0.5071-18	0.1199-7
1200	0.5179-16	0.5908-7
1300	0.2941-14	0.2529-6

Figure 3 - Feedstock iron stability diagram for complexes formed in a single-stage Westinghouse gasifier using Illinois No. 6 coal under oxygen-blown conditions at 1300 K and 15 atm total pressure

Figure 4 - Feedstock potassium stability diagram for complexes formed in a single-stage Westinghouse gasifier using Illinois No. 6 coal under oxygen-blown conditions at 1300 K and 15 atm total pressure

Figure 5 - Feedstock sodium stability diagram for complexes formed in a single-stage Westinghouse gasifier using Illinois No. 6 coal under oxygen-blown conditions at 1300 K and 15 atm total pressure

Figure 6 - Interaction of feedstock aluminum, silicon, calcium, magnesium, iron and titanium in a single-stage Westinghouse gasifier unit using Illinois No. 6 coal under oxygen-blown conditions at 1300 K and 15 atm total pressure

Figure 7 - Stability of gasifier solids as a function of temperature

projected to exist as the volatile chloride when the system pO_2 is less than 3.16×10^{-13} atm. The presence of sulfur in the fuel gas does not promote reactions with the gaseous NaCl phase in the reducing conditions. As the pO_2 increases, sodium is projected to condense and undergo a series of phase transitions from a solid sulfide (Na_2S_3) to a solid carbonate (Na_2CO_3) and finally to a liquid sulfate (Na_2SO_4). Each phase defines a particular regime on the stability diagram in relation to the localized environment. Progression to lower reaction temperatures introduces the formation of solid chloride and nitrate ($NaNO_3$) and condensed* cyanide (NaCN) complexes of sodium and potential mixed alkali phases, where the feedstock alkali becomes partitioned between one or more resulting equilibrium species. The stability of these phases is shown to increase as the system pO_2 , pS_2 , and temperature decrease. The complexity of the simple sodium reaction with the major fuel gas constituents (C, H, N, O, S, and Cl) is seen in the phase diagram projected at the lower operating temperatures.

Utilizing the composition of the Illinois No. 6 coal, as shown in Table 3, the 1300 K gasification temperature enhances ~100 percent volatilization of the background alkali content when local oxygen partial pressures are below 3.16×10^{-17} atm in the fuel gas (Figure 9). As the partial pressure of oxygen increases, the feldspar complex ($NaAlSi_3O_8$) is projected to exist as the principal alkali solid. The feldspar is converted into the liquid sulfate phase in the oxidizing environments, which contain relatively high partial pressures of sulfur. Under these conditions, the aluminosilicate ash structure exists as mullite.

The stability of the feldspar complex increases as the local oxygen partial pressures are reduced for 1200 K operations. Similarly,

* Condensed implies either solid and/or liquid phase.

Figure 8 - Sodium phase stability

Figure 8 (Cont'd)

Figure 8 (Cont'd)

Figure 8 (Cont'd)

Figure 9 - Phase stability of ash complexes

Figure 9 (Cont'd)

- (A) $Si_3N_4(s)$, $NaCN(s)$, $Al(s)$
- (B) $SiO_2(s)$, $NaCN(s)$, $Al(s)$

Figure 9 (Cont'd)

Figure 9 (Cont'd)

the liquid regime of sodium sulfate is expanded. Equilibrium no longer projects mullite as the principal aluminosilicate complex at temperatures of 1200 K but favors the formation of the andalusite structure (Al_2SiO_5). Andalusite has a structure similar to that of the kaolin mineral group, which includes kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), nacrite, dickite, allophane, dehydrated halloysite or metahalloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), hydrated halloysite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$), and anauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).

At gasifier temperatures of 900 or 800 K, the sodium feldspar complex is no longer projected to result. Here sulfates, sulfides, chlorides, and cyanides are candidate equilibrium species, depending on the composition of the local environment. Once again $\text{NaAlSi}_3\text{O}_8$ is projected as a stable equilibrium species at temperatures of 700 K but is not projected to form when the ash experiences 600 K temperatures.

The final series of stability diagrams that are presented involves the reactions of gaseous sodium chloride with kaolinite (20.9% Al, 21.76% Si). We assumed in these calculations that the NaCl concentration on a weight percent basis is twice that of the available aluminum/silicon content of the kaolinite material--representing a long-term equilibrium exposure of the getter to fuel gases. As Figure 10 shows, the $\text{NaAlSi}_3\text{O}_8$ complex initially forms as a stable alkali solid in the reducing environment containing a pO_2 of less than 10^{-15} atm. Approximately a 2:1 ratio of NaAlSiO_4 to $\text{NaAlSi}_3\text{O}_8$ results as the pO_2 increases. Select regimes are identified in which an equivalent partitioning of sodium results in the $\text{NaAlSi}_3\text{O}_8$ and liquid Na_2SO_4 species. As seen in the ash reactions of Figure 9, sodium, even though kaolin is present, forms sulfate under oxidizing conditions.

The complex stability of the sodium-kaolinite phases is observed as the system temperature decreases. At 900 K the experimentally observed NaAlSiO_4 structure is no longer projected as an equilibrium phase, but the water glass silicate ($\text{Na}_2\text{Si}_2\text{O}_5$) is projected to form until temperatures of 700 K are attained. Stability regimes of the $\text{NaAlSi}_3\text{O}_8$ structure are limited to specific operating pS_2 and pO_2 as temperatures approach 600 K.

Figure 10 - Phase stability of kaolin

- (A) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$ (E) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2(\text{SO}_4)_3(\text{s})$, $\text{SiO}_2(\text{s})$
 (B) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$ (F) $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$, $\text{Na}_2\text{S}_4(\text{s})$
 (C) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$ (G) $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{SiO}_2(\text{s})$, $\text{NaCN}(\text{l})$
 (D) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{SiO}_2(\text{s})$

- (A) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$ (E) $\text{Na}_2\text{S}_4(\text{s})$, $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$
 (B) $\text{Na}_2\text{SO}_4(\text{s})$, $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$ (F) $\text{Na}_2\text{S}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$
 (C) $\text{Si}_3\text{N}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaCN}(\text{l})$ (G) $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$, $\text{NaCN}(\text{l})$
 (D) $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$, $\text{NaCN}(\text{l})$ (E) $\text{Na}_2\text{S}_4(\text{s})$, $\text{Al}_2\text{SiO}_5(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$
 (F) $\text{Na}_2\text{S}_4(\text{s})$, $\text{Al}_2\text{O}_3(\text{s})$, $\text{NaAlSi}_3\text{O}_8(\text{s})$

Figure 10 (Cont'd)

Figure 10 (Cont'd)

Figure 10 (Cont'd)

This completes the data that have been generated using the thermodynamic equilibrium models for Task 1. Table 43 summarizes the conclusions which have resulted from the development of the alkali aluminosilicate phase stability diagrams. Continued effort in this area is recommended, identifying possible reactions of sodium with alternative candidate getter materials.

Table 43
ALKALI ALUMINOSILICATE PHASE DIAGRAMS

- Phase stability of feedstock sodium in the absence of aluminum and silicon as a function of pO_2 , pS_2 , and decreasing temperature at 15 atm pressure for the gasification of Illinois No. 6 coal under oxygen-blown conditions indicates the condensation of volatile sodium.

Volatiles $\rightarrow$ NaCl (s)

- Phase stability of feedstock sodium in the presence of ash constituents in Illinois No. 6 coal (1.2% Al, 2.4% Si) during gasification under oxygen-blown conditions at 15 atm as a function of decreasing temperature indicates the formation of the solid alkali feldspar phase.

Volatiles $\rightarrow$ NaAlSi₃O₈ (s)

- Chemical reaction of feedstock released NaCl (g) with kaolinite (20.9% Al, 21.76% Si) as a function of decreasing temperature indicates the formation of the nepheline and feldspar solids.

Volatiles $\rightarrow$ NaAlSiO₄ (s) and NaAlSi₃O₈ (s)

3.2 TASK 2: GETTER SELECTION AND QUALIFICATION

The objectives of Task 2 were to select and characterize potential getter material for use in the simultaneous removal of alkali and particulates in pressurized gasification systems and to determine their activity as a function of operating parameters in a high-temperature, pressurized, bench-scale reactor and TGA system. The subtasks include bench-scale tests and TGA studies. This section summarizes our efforts with respect to getter selection (Section 3.2.1), bench-scale evaluation of getter performance (Section 3.2.2), TGA studies (Section 3.2.3), and gettering reactions and mechanisms in aluminosilicate materials (Section 3.2.4). Section 3.2.1 details the getter selection process in terms of three subtasks: Getter Selection Basis (3.2.1.1), Selected Alternative Getter Materials (3.2.1.2), and Alternative Getter Performance (3.2.1.3). The bench-scale evaluation work is described in terms of five subtasks: Activated Bauxite Sodium Gettering (3.2.2.1), PFBC Ash Sodium Gettering (3.2.2.2), Activated Bauxite Potassium Gettering (3.2.2.3), Sodium Gettering in the Presence of Water Vapor by Activated Bauxite (3.2.2.4), and Sodium Gettering in Inert and Simulated Fuel Gases by Emathlite (3.2.2.5). Our TGA studies are described in terms of seven subtasks. The first of these (3.2.3.1) summarizes the problems encountered in initial system operation. Section 3.2.3.2 summarizes our preliminary gettering tests along with the evolution of our operating procedure. Sections 3.2.3.3 through 3.2.3.6 are devoted to summarizing all remaining TGA tests, including those with activated bauxite, alternative getter materials, and the leading candidate getter, emathlite. Section 3.2.3.7 describes work completed on the physical and chemical characterization of gettered TGA emathlite pellets. A final discussion (Section 3.2.4) is presented that illustrates gettering reactions and mechanisms in the aluminosilicate materials, based on both the bench-scale and analytical data. Its three subtasks include a literature review (Section 3.2.4.1), proposed alkali complexes and aluminosilicate reactions (Section 3.2.4.2), and the gettering mechanism in emathlite (Section 3.2.4.3).

3.2.1 Getter Selection

3.2.1.1 Getter Selection Basis

Alternative alkali-gettering materials for use in hot gas cleanup systems were assessed on the basis of potential alkali reactions with minerals and commercial products and on the stability of the resulting complexes at temperatures of 1073 and 1273 K. Initially, chemical phase diagrams and thermodynamic equilibrium calculations were reviewed, and complexes containing either sodium and/or potassium were identified. These complexes included: Si, Al, Si-Al, Ca-Si, Ca-Si-Al, Ca-Al, P, Ca-P, Si-P, Fe, Fe-Si, Mn-Si, B, B-Si, Pb-Si, Cr, Ge, Ti, Ti-Si, Mo, W, Zr, Zr-Si, and V. Possible gas-solid and/or solid solution reactions were then proposed for each gettered phase. As shown in Table 44, several reactions can be written that lead to the formation of a single product phase, depending on the composition of the initial gettering material and the concentration of alkali within the reactant gas.

The change in the free energy of formation (ΔG kcal/mole) for the Al, Si, and Ca reactions with sodium (as NaCl) at 1000 K were calculated from either reported or estimated thermodynamic data. The negative free energy of the reaction indicates that the reaction path, as written, favors the equilibrium formation of the reaction product. Generally, reactions of sodium with Si, Al-Si, or Ca-Al-Si are preferred to reaction with Ca-Si materials. Limited thermodynamic data are reported for the Na-P, -Fe, -Mn, -B, -Pb, -Cr, -Ge, -Ti, -Mo, -W, -Zr, -F, -Be, -I, -Se, and -Te complexes, and, therefore, the $\Delta G_{1000\text{ K}}$ for these reactions were not calculated. With the exception of Na-Mo, -W, and -B, the melt temperatures of the resulting products exceed 1073 K.

Gettering of the alkali has been considered to occur at various reaction sites within the clay lattice or between adjoining crystalline layers. The exact location and mechanism by which the alkali is captured is unknown. Candidate minerals and commercial products listed in Table 45 illustrate the gamut of materials that may be used as getter sorbents. The sorbents can be categorized as either high-alumina or high-silica getters and either alumina-silicate compounds or compounds

Table 44

POSSIBLE GAS-SOLID OR SOLID SOLUTION REACTIONS

	MELT TEMP, (C)	ΔG 727C (KCAL/ MOLE)
2NaCl (G) + H ₂ O (G) + SiO ₂ (S) ----> Na ₂ O.SiO ₂ (S) + 2HCl (G)	1089.	-15.462
4NaCl (G) + 2H ₂ O (G) + SiO ₂ (S) ----> 2Na ₂ O.SiO ₂ (S) + 4HCl (G)	1018	-671.205
2NaCl (G) + H ₂ O (G) + 2SiO ₂ (S) ----> Na ₂ O.2SiO ₂ (S) + 2HCl (G)	874	-32.779
2NaCl (G) + H ₂ O (G) + 3SiO ₂ (S) ----> Na ₂ O.3SiO ₂ (S) + 2HCl (G)		39.282
2NaCl (G) + H ₂ O (G) + Al ₂ O ₃ .2SiO ₂ (S) ----> Na ₂ O.AL ₂ O ₃ .2SiO ₂ (S) + 2HCl (G)	1626	25.18
2NaCl (G) + H ₂ O (G) + Al ₂ O ₃ .2SiO ₂ (S) + 2SiO ₂ (S) ----> Na ₂ O.AL ₂ O ₃ .4SiO ₂ (S) + HCl (G)	1000-	-25.176
2NaCl (G) + H ₂ O (G) + Al ₂ O ₃ .2SiO ₂ (S) + 4SiO ₂ (S) ----> Na ₂ O.AL ₂ O ₃ .6SiO ₂ (S) + 2HCl (G)	1040	
2NaCl (G) + H ₂ O (G) + Al ₂ O ₃ .2SiO ₂ (S) + 4SiO ₂ (S) ----> Na ₂ O.AL ₂ O ₃ .6SiO ₂ (S) + 2HCl (G)	1100	-25.176
2NaCl (G) + H ₂ O (G) + Al ₂ O ₃ (S) ----> Na ₂ O.AL ₂ O ₃ (S) + 2HCl (G)	1800	-5.189
4NaCl (G) + 2H ₂ O (G) + Al ₂ O ₃ (S) ----> 2Na ₂ O.AL ₂ O ₃ (S) + 4HCl (G)		78.558
Na ₂ O.SiO ₂ (S) + 2 CaO.SiO ₂ (S) ----> Na ₂ O.2CaO.3SiO ₂ (S)		73.418
OR		
2CaO.3SiO ₂ .5/2H ₂ O (S) ----> 2CaO.3SiO ₂ (S) + 5/2H ₂ O (G)		
2NaCl (G) + H ₂ O (G) + 2CaO.3SiO ₂ (S) ----> Na ₂ O.2CaO.3SiO ₂ (S)		-4.672
2 Na ₂ O.SiO ₂ (S) + CaO.SiO ₂ (S) ----> 2Na ₂ O.CaO.3SiO ₂ (S)		118.825
OR		
4NaCl (G) + 2H ₂ O (G) + CaO.SiO ₂ (S) + 2SiO ₂ (S) ----> 2Na ₂ O.CaO.3SiO ₂ (S) + 4HCl (G)		186.905
Na ₂ O.3SiO ₂ (S) + 3 CaO.SiO ₂ (S) ----> Na ₂ O.3CaO.6SiO ₂ (S)		28.01
OR		
2NaCl (G) + H ₂ O (G) + 3 CaO.SiO ₂ (S) + 3SiO ₂ (S) ----> Na ₂ O.3CaO.6SiO ₂ (S) + 2HCl (G)		116.798
CaO.2SiO ₂ .2H ₂ O (S) ----> CaO.2SiO ₂ (S) + 2H ₂ O (G)		
2NaCl (G) + H ₂ O (G) + 3 CaO.2SiO ₂ (S) ----> Na ₂ O.3CaO.6SiO ₂ (S) + 2HCl (G)		-57.32
Na ₂ O.3SiO ₂ (S) + CaO.SiO ₂ (S) + 2SiO ₂ (S) ----> Na ₂ O.CaO.6SiO ₂ (S)		-9.337
OR		
2NaCl (G) + H ₂ O (G) + CaO.SiO ₂ (S) + 5SiO ₂ (S) ----> Na ₂ O.CaO.6SiO ₂ (S) + HCl (G)		98.121
2NaCl (G) + H ₂ O (G) + 2CaO.AL ₂ O ₃ .SiO ₂ (S) + 3SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S) + 2HCl (G)		68.784
OR		
CaO.2SiO ₂ .2H ₂ O (S) ----> CaO.2SiO ₂ (S) + 2H ₂ O (G)		
Na ₂ O.AL ₂ O ₃ (S) + 2 CaO.2SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S)		-52.937
OR		
Na ₂ O.3SiO ₂ (S) + CaO.AL ₂ O ₃ (S) + CaO.SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S)		17.884
Na ₂ O.2SiO ₂ (S) + CaO.AL ₂ O ₃ (S) + CaO.2SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S)		31.886
Na ₂ O.SiO ₂ (S) + CaO.AL ₂ O ₃ (S) + CaO.SiO ₂ (S) + 2SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S)		-396.492
Na ₂ O.SiO ₂ (S) + CaO.AL ₂ O ₃ (S) + CaO.2SiO ₂ (S) + SiO ₂ (S) ----> Na ₂ O.2CaO.AL ₂ O ₃ .4SiO ₂ (S)		14.569
4CaO.AL ₂ O ₃ .13H ₂ O (S) ----> 4CaO.AL ₂ O ₃ (S) + 13 H ₂ O (G)		
Na ₂ O.AL ₂ O ₃ (S) + 2 4CaO.AL ₂ O ₃ (S) ----> Na ₂ O.8CaO.3AL ₂ O ₃ (S)		44.467
2NaCl (G) + H ₂ O (G) + GeO ₂ (S) ----> Na ₂ O.GeO ₂ (S) + HCl (G)	1063	
2NaCl (G) + H ₂ O (G) + 2GeO ₂ (S) ----> Na ₂ O.2GeO ₂ (S) + 2HCl (G)		
2NaCl (G) + H ₂ O (G) + 4GeO ₂ (S) ----> Na ₂ O.4GeO ₂ (S) + 2HCl (G)		
2NaCl (G) + H ₂ O (G) + TiO ₂ (S) ----> Na ₂ O.TiO ₂ (S) + 2HCl (G)	1128	
2NaCl (G) + H ₂ O (G) + TiO ₂ (S) ----> Na ₂ O.TiO ₂ (S) + 2HCl (G)		
2NaCl (G) + H ₂ O (G) + TiO ₂ (S) + SiO ₂ (S) ----> Na ₂ O.TiO ₂ .SiO ₂ (S) + 2HCl (G)		
2NaCl (G) + H ₂ O (G) + 2H ₂ O (S) ----> Na ₂ O.2H ₂ O (S) + 2HCl (G)	612	

Table 44 (Cont'd)

2NACL (G) + H2O (G) + MOO3 (S) ----> NA2O.MOO3 (S) + 2HCL (G)	687
2NACL (G) + H2O (G) + MOO3 (S) ----> NA2O.MOO3 (S) + 2HCL (G)	696
2NACL (G) + H2O (G) + ZRO2 (S) ----> NA2O.ZRO2 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + ZRO2.S102 (S) ----> NA2O.ZRO2.S102 (S) + 2HCL (G)	
6NACL (G) + 3H2O (G) + V2O5 (S) ----> 3NA2O.V2O5 (S) + 6HCL (G)	850- 866
2NACL (G) + H2O (G) + P2O5 (S) ----> NA2O.P2O5 (S) + 2HCL (G)	
4NACL (G) + 2H2O (G) + P2O5 (S) ----> 2NA2O.P2O5 (S) + 4HCL (G)	880
6NACL (G) + 3H2O (G) + P2O5 (S) ----> 3NA2O.P2O5 (S) + 6HCL (G)	
4NACL (G) + CAO (S) + 3P2O5 (S) ----> 2NA2O.CAO.3P2O5 (S) + 4HCL (G)	
30NACL (G) + 15H2O (G) + 5P2O5 (S) + 6S102 (S) ----> 15NA2O.5P2O5.6S102 (S) + 30HCL (G)	
18NACL (G) + 9H2O (G) + 2P2O5 (S) + 6S102 (S) ----> 9NA2O.2P2O5.6S102 (S) + 18HCL (G)	
10NACL (G) + 5H2O (G) + P2O5 (S) + 4S102 (S) ----> 5NA2O.P2O5.4S102 (S) + 10HCL (G)	
2NACL (G) + H2O (G) + FE2O3 (S) ----> NA2O.FE2O3 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + FE2O3.S102 (S) ----> NA2O.FE2O3.S102 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + FE2O3 (S) + 4S102 (S) ----> NA2O.FE2O3.4S102 (S) + 2HCL (G)	
4NACL (G) + 2H2O (G) + FE2O3 (S) + S102 (S) ----> 2NA2O.FE2O3.S102 (S) + 4HCL (G)	
10NACL (G) + 5H2O (G) + FE2O3 (S) + 8S102 (S) ----> 5NA2O.FE2O3.8S102 (S) + 10HCL (G)	
12NACL (G) + 6H2O (G) + 4FE2O3 (S) + 5S102 (S) ----> 6NA2O.4FE2O3.5S102 (S) + 12HCL (G)	
2NACL (G) + H2O (G) + MNO.S102 (S) + S102 (S) ----> NA2O.MNO.2S102 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + B2O3 (S) ----> NA2O.B2O3 (S) + 2HCL (G)	966
2NACL (G) + H2O (G) + 2B2O3 (S) ----> NA2O.2B2O3 (S) + 2HCL (G)	743
2NACL (G) + H2O (G) + 4B2O3 (S) ----> NA2O.4B2O3 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + B2O3 (S) + 2S102 (S) ----> NA2O.B2O3.2S102 (S) + HCL (G)	
2NACL (G) + H2O (G) + 2 PBO.S102 (S) + 2S102 (S) ----> NA2O.2PBO.4S102 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + 3 PBO.S102 (S) + 3S102 (S) ----> NA2O.3PBO.6S102 (S) + 2HCL (G)	
2NACL (G) + H2O (G) + 3 PBO.S102 (S) + 4S102 (S) ----> NA2O.3PBO.7S102 (S) + 2HCL (G)	
6NACL (G) + 3H2O (G) + 3 PBO.S102 (S) + 8S102 (S) ----> 3NA2O.3PBO.11S102 (S) + 6HCL (G)	
2NACL (G) + H2O (G) + 3/2O2 (G) + CR2O3 (S) ----> NA2CR2O7 (S) + 2HCL (G)	
4NACL (G) + 2H2O (G) + 3/2O2 (G) + CR2O3 (S) ----> 2 NA2CR04 (S) + 4HCL (G)	
OR	
2NACL (G) + H2O (G) + CR03 (S) ----> NA2CR04 (S) + 2HCL (G)	

containing a high iron content suitable for combined sulfur and alkali removal. The thermodynamic assessment has indicated that the high-alumina, high-silica, and alumina-silicate compounds selected in earlier work reported by ANL and Westinghouse are leading candidate materials. Table 46 lists the various potential sorbent materials that have been tested previously and summarizes such relevant factors as their performance, costs, and physical properties. Table 47 summarizes the same type of data for the potential getter materials that have not been evaluated experimentally. In order to obtain a wider perspective on potential getters, a number of these materials were subjected to a screening test in the bench-scale unit. Data obtained in this test are presented in Section 3.2.1.3.

3.2.1.2 Selected Alternative Getter Materials

The selection of materials for screening tests in the bench-scale reactor was coordinated with concurrent Westinghouse programs^{7,8} and previous materials tested by Westinghouse^{2,9} and ANL.^{10,11} The 14 materials selected for the preliminary screening test include bauxite (as a reference material and as the leading candidate getter identified by ANL), olivine (SiO_4 with Mg and Fe as Fe_2SiO_4 , Mg_2SiO_4 , CaSiO_4 and/or MnSiO_4), Vansil[®] (calcium silicate), Novacite[®] (silica), Ebony Novacite[®] (silica), two talc materials ($\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$), alumina (Al_2O_3), iron ore (Fe_3O_4), activated alumina, three zeolite materials ($(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Ba}) (\text{Al}, \text{Si})\text{O}_2)_n \cdot x\text{H}_2\text{O}$), diatomaceous earth ($\text{SiO}_2, \text{Al}_2\text{O}_3$), and emathlite (Ca, Mg, Al silicate-fuller's earth). A brief description of each material follows:

- Activated Bauxite: Engelhard, Edison, New Jersey
 - High Alumina Porocel
 - Typical chemical composition: 88.3% Al_2O_3 , 1.2% Fe_2O_3 , 3.0% TiO_2 , 7.0% SiO_2 , 1.0% insoluble on a volatile free basis
 - Typical surface area: 6% volatile material, 220 m^2/g
 - Typical volume weight: 6% volatile material, 880 kg/m^3 .

Table 45

MINERALS AND COMMERCIAL PRODUCTS
CONSIDERED AS ALTERNATIVE GETTER MATERIALS

Alundum (99.5% α - Al_2O_3)
 Gibbsite ($\text{Al}(\text{OH})_3$)
 Diaspore (α - $\text{AlO}(\text{OH})$)
 Corundum (Al_2O_3)
 Boehmite (γ - $\text{AlO}(\text{OH})$)
 Activated bauxite (10% SiO_2 , 81.5% Al_2O_3)
 Activated alumina (93.6% Al_2O_3)
 Silica (SiO_2)
 Silica gels
 Sillimanite, andalusite, kyanite (Al_2SiO_5)
 Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)
 Halloysite ($\text{AlSi}_4\text{O}_{10}(\text{OH})_8$)
 Diatomaceous earth (92.0% SiO_2 , 5% Al_2O_3)
 Burgess No. 10 pigment (45% SiO_2 , 38% Al_2O_3)
 Attapulugus clay (68% SiO_2 , 12% Al_2O_3 , 10.5% MgO)
 Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_7(\text{OH})_4$)
 Illite ($(\text{K}_{1-1.5}\text{Al}_4(\text{Si}_{7-6.5}\text{Al}_{1-1.5}\text{O}_{20})(\text{OH})_4)$)
 Montmorillonite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$)
 Illite-sericite ($(\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2)$)
 Cordierite ($\text{NaAl}(\text{Si}_2\text{O}_6)$)
 Zeolites ($(\text{Na}_2, \text{K}_2, \text{Ca}, \text{B})[(\text{Al}, \text{SiO}_2)_n \cdot x\text{H}_2\text{O}]$)
 Gehlenite ($\text{Ca}_2(\text{Al}_2\text{SiO}_7)$)
 Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
 Anhydrite (CaSO_4)
 Limestone or dolomite ($\text{CaCO}_3, \text{Mg}(\text{CO}_3)_2$)
 Wollastonite ($\text{Ca}(\text{SiO}_3)$)
 Vermiculite ($(\text{Mg}, \text{Ca})_{0.7}(\text{Mg}, \text{Fe}^{+3}, \text{Al})_{6.0}[(\text{Al}, \text{Si}_8\text{O}_{20})(\text{OH})_4 \cdot 8\text{H}_2\text{O}]$)
 Chlorite ($\text{Mg}_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$)
 Talc ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_2$)
 Olivine ($(\text{Mg}, \text{Fe})_2(\text{SiO}_4)$)
 Brucite ($\text{Mg}(\text{OH})_2$)
 Goethite ($\text{FeO}(\text{OH})$)
 Hematite (Fe_2O_3)
 Lepidocrocite (γ - $\text{FeO} \cdot \text{OH}$)
 Limonite ($\text{FeO} \cdot \text{OH} \cdot n\text{H}_2\text{O}$)

Table 46
PREVIOUSLY SCREENED GETTERED MATERIALS

Material	Reaction Mechanisms	Comment	Costs
Kaolin ($\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$)	Surface adsorption; chemical reaction.*	Georgia and South Carolina accounted for 88% of the total U.S. kaolin production in 1979. Kaolin is a claylike material approximating the mineral kaolinite in composition. It has a specific gravity of 2.6 and a fusion point of 1785°C. The kaolin mineral group includes kaolinite, halloysite and dickite. Extensively screened at Westinghouse, kaolin demonstrated both physical adsorption and chemical reaction with alkali from hot gases.	Average unit value for all grades of kaolin in 1979 was \$59.57 per ton.
Attapulgitic		Attapulgitic, a fuller's earth-type clay, is widely used in the absorbent and thickening industries. The principal mineral is composed of a crystalline hydrated magnesium aluminum silicate with a colloidal and sorptive unique chain structure. The gettering capacities of Attapulgitic Clay, Alundum, Diatomaceous Earth, Silica Gel, Burgess No. 10 Pigment and Activated Bauxite have been screened at ANL.	Value per ton for attapulgitic reported by producers ranged from \$28.88 to \$63.20.
Montmorillonite [(1/2 Ca, Na) _{0.7} (Al, Mg, Fe) ₄ · [(Si, Al) ₈ O ₂₀](OH) ₄ · mH ₂ O]		Both montmorillonite and illite ($\text{K}_{1-1.5}\text{Al}_4(\text{Si}_{7-6.5}\text{Al}_{1-1.5}\text{O}_{20})(\text{OH})_4$) have demonstrated considerable gettering capacities. The investigations at Westinghouse have also shown the effectiveness of using PDU chars and ashes as suitable getter materials.	Value per ton for montmorillonite ranged from \$29 to \$55.
Activated Bauxite	Physical Adsorption*	Natural minerals widely used as sulfur recovery catalysts, catalyst bed supports, desiccants, decolorizers, adsorbents for acid alkylations, percolation filters, and catalyst carriers. Activated bauxite was identified by ANL to be the leading candidate getter.	
Silica Gel		An amorphous, flocculated, phase material tested at ANL, silica gel was shown to demonstrate gettering capabilities; however, it did not exceed those of activated bauxite or diatomaceous earth.	Less than dollar/lb.
Diatomaceous Earth	Chemical Reaction in which gaseous alkali form water insoluble alkali metal silicates.*	An amorphous, opaline phase material tested at ANL, diatomaceous earth was shown to be an effective gettering material.	\$0.05-0.10 per lb.

*experimental data.

- Comment: Bauxites are generally composed of an aluminum hydrate mineral with a suggested formula of $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, originating from the accepted combination of the monohydrates and trihydrates, particularly boehmite and gibbsite.

The fundamental cell unit of gibbsite is a structural layer of aluminum ions sandwiched between two sheets of closely packed hydroxyl ions. Only two out of the three octahedrally coordinated sites between the oxygen layers are occupied by cations (Na, K). The layers can be regarded as being built of octahedra that have been linked laterally by sharing adjacent edges. The network can be described by an orthogonal (pseudo-hexagonal) cell. In the ideal structure oxygens at the bottom of one layer lie directly above oxygens at the top of the layer below. The ideal structure is distorted, resulting in a monoclinic cell.

Gibbsite contains Fe_2O_3 and minor quantities of additional oxides. It is likely that some Fe^{3+} and small quantities of other ions substitute for Al in the structure. When heated, gibbsite produces γ -alumina, with boehmite as an intermediate structure. The structural transitions that occur within the gibbsite lattice as a result of heating are shown in the following sequence:

Low Temperature

High Temperature (+723 K)

Gibbsite	→	Boehmite	→	Diaspore	→	Corundum
$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$		$\gamma\text{-AlO(OH)}$		$\alpha\text{-AlO(OH)}$		$\alpha\text{-Al}_2\text{O}_3$

Boehmite consists of double sheets of octahedra with aluminum ions at their centers. The sheets are composed of chains of octahedra, with a cubic spinel structure. As shown in the above sequence, gibbsite is converted to boehmite at reaction temperatures between 505 and 616 K,

Table 47

POTENTIAL GETTER MATERIALS

Material	Proposed Getter Reaction Mechanisms	Comment	Costs
Activated Alumina (Al_2O_3)	Surface adsorption; chemical reaction	Principal uses include dehydration of liquids and gases; as a scavenger of organic and free fluoride in an alkylate stream; and in chemical processing. Due to the high surface area along the activated alumina particle, a high gettering capacity is expected. Data obtained from an aluminum complex will demonstrate whether the gettering reaction occurs within the crystalline Al lattice, or at other locations within complex clay structures. Data will support regenerability of the material.	\$0.44 per lb for 300-1900 lb.
Novacite [®] (SiO_2) (Malvern Minerals Co)	Surface adsorption; chemical reaction	Novacite is an extender pigment consisting of a highly pure microform of quartz with platey-disc-shaped particles. The platey shape of the particles, much like kaolin, minimizes wear on equipment. As SiO_2 , data from alkali exposure of a Novacite-like material will detail the alkali-gettering location. Thermodynamically, water glass phases have been projected to result in these reactions.	\$0.20 per pound (50-499 lbs).
Zeolite [®] (Na_2 , K_2 , Ca, B) [(Al, Si) O_2] $_n$ · x H_2O)	Surface adsorption; chemical reaction.	Natural zeolites are commonly used in the "methane from landfill" (MFL) programs, while synthetic zeolites have been used as fluidized cracking catalysts. As a hydrated-aluminosilicate, zeolites are expected to provide cavities for gettering of alkalis during dehydration in the filter chamber. Using a zeolite will provide data which supports the chemical reaction mechanism at either Al or Si.	
Wollastonite ($Ca(SiO_3)$)	Surface adsorption; chemical reaction.	Natural wollastonite, or calcium metasilicate is commonly used in ceramic mixes for floor and wall tile, as pigment and extenders for paints, and as fillers for plastics, rubber and asphalt products. Alkalis reacting at the Si crystalline lattice, may also substitute at locations where Ca has been displaced through rearrangement of the lattice that occurs during heating. The presence of calcium may act simultaneously to remove sulfur from the hot gas stream.	\$86 per ton - fine paint grade, bagged, in car load lots, f.o.b., \$70 per ton - medium paint grade. \$92 per ton - 400-mesh, bagged, car load lots, f.o.b., \$76 per ton - 325-mesh, NYCO/R. T. Vanderbilt Co. Inc. \$98 per ton - acicular, car load lot., f.o.b. \$92 per ton - 400-mesh car load lot, f.o.b. \$76 per ton - 325-mesh, car load lot f.o.b. \$320 per ton-10 micron, car load lot, f.o.b.

Table 47 (Cont'd)

Material	Proposed Getter Reaction Mechanisms	Comment	Costs
Talc ($\text{Mg}_3(\text{Si}_2\text{O}_7)(\text{OH})_4$)	Surface adsorption; chemical reaction.	<p>Talc has been produced at 37 mines in 12 states in 1978, and 36 in the same states in 1979, with California leading all states in the value of talc produced. States producing the highest tonnage were Vermont, Montana, Texas and New York. Talc is generally used in ceramics, paints, plastics, paper, cosmetics, rubber, roofing, insecticides and refractories.</p> <p>Alkalis reacting with the Si crystalline lattice, may also substitute at locations where Mg has been displaced through rearrangement of the lattice that occurs during heating. The presence of Mg may act simultaneously to remove sulfur from the hot gas stream.</p>	Depending on quality and degree, and method of producing, talc prices vary over a wide range. December 1979 quoted prices for domestic talc, ground in car load lots, f.o.b. mine or mill, container included per short ton ranged from \$24 to \$190.
Olivine (Mg, Fe) $_2(\text{SiO}_3)_2$	Surface adsorption; chemical reaction.	Data from olivine exposures to hot alkali gases will support reaction at Si, and will demonstrate the effect of iron in the magnesium-silicate structure during the gettering reaction.	\$43 per ton - #10 Olivine Sand \$55 per ton - #90 Olivine Sand
Sand (SiO_2)	Surface adsorption; chemical reaction.	Thermodynamically, alkali silicates or water glasses are projected to result when SiO_2 reacts with hot alkali-containing gases. Data will provide information required in delineating the gettering mechanism of the alkali as either a chemical reaction with Si, or simply a surface adsorption phenomena. Although similar in composition to the high-purity Novacite material, data will demonstrate the gettering capability of a raw, commercial product as opposed to a specialty product.	
Magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$)	Surface adsorption	The reaction of a high-grade magnetite which is typically used in coal cleaning, is expected to getter alkali from hot gases through a physical adsorption process.	\$100-125 per ton.
Hematite (Fe_2O_3)	Surface adsorption	As a raw material, hematite is expected to act as a nucleation site for gettering condensed alkali at the particle surface. Chemical reaction of iron with the alkali is not proposed.	Natural Ore 51.5% Fe at \$28.50-28.75/long ton Pellets at \$46.3/long ton.
Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)	Surface adsorption	As a sulfur sorbent, dolomite may act as an alkali gettering material. Data from the exposures will determine whether the presence of Al or Si is essential in the gettering reactions.	\$10-25/ton.
Limestone (CaCO_3)	Surface adsorption	As a sulfur sorbent, limestone may act as an alkali gettering material. Data from these exposures will determine whether the presence of Al or Si is essential in the gettering reactions.	\$10-25/ton.

decreasing the true volume of the alumina lattice. At the expense of the true volume, both the pore volume and void volume are known to increase, suggesting that the rapid evolution of water vapor disarranges the structure so that the structural units are less compactly fitted together. At temperatures of 811 to 866 K boehmite is converted to $\gamma\text{-Al}_2\text{O}_3$ in a reaction similar to the decomposition of kaolinite.

- Olivine: International Mineral and Chemical Corporation, Des Plaines, Illinois
 - Olivine Flour
 - Typical chemical composition: 45-59% MgO, 39-43% SiO_2 , 6-8% FeO, 0.6-0.8% Cr_2O_3 , 0.2-0.3% Ni, 0.2-0.8% Al_2O_3 , 0.5% trace elements
 - Mineralogical analysis: 92-93% olivine, 5% enstatite, 1-2% serpentines, 1% chromite
 - Specific gravity: 3.2-3.6
 - Hardness: 6.5-7.0 (Moh scale)
 - Dry bulk density: 100-125
 - Thermal expansion coefficient: 0.0083 in/in
 - Grain shape: angular
 - Fusion point: 1181-2033 K
 - Comment: olivine is a natural mineral, olive-green in color, consisting either of magnesium orthosilicate or fosterite (Mg_2SiO_4) and iron orthosilicate or fayalite (Fe_2SiO_4) or an intermediate, isomorphous olivine mixture of (Mg,Fe) SiO_4 (dunite). Fosterite, like fayalite, is rarely found alone. Dunite consists essentially of evenly grained crystalline olivine, with minor quantities of chromite dispersed through the mass, as well as occasional grains of pyroxene.
- Vansil: R. T. Vanderbilt Company, Inc. Norwalk, Connecticut
 - Vansil® Wollastonite W-50
 - Typical chemical composition: 46.1% CaO, 50.2% SiO_2 ,

- 0.21% Al_2O_3 , 1.86% MgO , 0.15% Fe_2O_3 , 0.22% Na_2O , 0.94% L.O.I.
- Mineralogy: major - wollastonite, minor - calcite, trace - diopside
 - Chemical formula: CaSiO_3
 - Crystalline shape: Acicular
 - Density: 2.9 g/cm^3
 - Hardness: 4.5 (Moh scale)
 - Coefficient of expansion: $6.5 \times 10 \text{ mm/K}$
 - Transition point to pseudo-wollastonite: 1473K
 - Melting point: 1813 K
 - Comment: Vansil W is an important component of ceramic products. It contains naturally low concentrations of iron ore deposits.
- Novacite: Malvern Mineral Company, Hot Springs, Arkansas
 - Novacite® (Lot 207A)
 - Typical chemical composition: 99.12% SiO_2 , 0.04% Fe_2O_3 , 0.15% TiO_2 , 0.61% Al_2O_3 , 0.0% CaO , 0.0% MgO , 0.20% L.O.I.
 - Thermal conductivity: $0.18 - 0.28 \text{ Btu/in/hr/ft}^2/\text{°F}$
 - Coefficient of thermal expansion: $15.5 \text{ to } 41 \times 10^{-6} \text{ in/in/°F}$
 - True specific gravity at 330 K: 2.650
 - Hardness: 7.0 (Moh scale)
 - True density: 2.64 kg/l
 - Bulk density: 847.5 kg/m^3 (loosely packed), 1324 kg/m^3 (densely packed)
 - Surface: highly polar
 - Acidity: 6.0 - 6.3 pH in distilled water
 - Thermal stability: stable from 273 to 846 K
 - Melting point: 1773 to 1973 K
 - Specific heat: Mean value between 273 and 473 K is 0.192 cal/g/°C
 - Comment: Novacite® 207A is composed of SiO_4 tetrahedra terminated at fractures or crystal faces with SiOH or strained siloxane bridges. The particle description is a pseudocubic structure, with parting planes at $85^\circ 46''$. At low magnification, well-rounded crystalline discs are observed. while at 2000X magnification the agglomerates

appear as all shapes in which the finely divided quartz contains many minute cracks and fissures. On the average Novacite® contains 2.8×10^{10} particles/gram, with a surface area of $2 \text{ m}^2/\text{g}$ BET method.

● Ebony Novacite: Malvern Minerals Company, Hot Springs, Arkansas

- 550 Ebony Novacite®
- Typical chemical composition: 63.15% SiO_2 , 3.24% C, 0.13% S, 19.16% Al_2O_3 , 2.29% Fe_2O_3 , 1.80% TiO_2 , 0.25% CaO, 0.15% MgO, 10.25%, L.O.I.
- Appearance: dry-soft black; wet-vivid black
- Apparent bulk density: 561 kg/m^3
- True density: 2.58 kg/l
- Moisture loss (2 hr @ 383 K): 0.21%
- L.O.I. (30 min. @ 2023 K): 8.31%
- Specific gravity: 2.60 (calculated)
- Fischer porosity: 65
- Fischer average particle size: $1.72 \text{ }\mu\text{m}$
 - % finer than $44 \text{ }\mu\text{m}$: 90.74
 - % finer than $20 \text{ }\mu\text{m}$: 94.1
- Comment: 550 Ebony Novacite® is classified as a unique black silica pigment. While this product is typically 60% SiO_2 (novaculitic), the 3.5% carbon seems to encapsulate the silica particles, enhancing effective pigmentation. Novacite®, however, is a naturally occurring, mined product (SiO_2) that is mechanically processed only for particle size distribution. Minor percentage variations in other constituents and trace elements occur.

● Emtal: Engelhard, Edison, New Jersey

- Emtal 599 Platy Talcs
- Typical chemical composition: 30.7% MgO, 58.2% SiO_2 , 0.3% CaO, 3.4% Fe_2O_3 , 0.4% Al_2O_3 , 2.0% CO_2 , 6.9% L.O.I.
- Particle shape: platy
- Average particle size: $2.7 \text{ }\mu\text{m}$
- pH: 9.3 - 9.8

- Specific gravity: 2.8
 - Bulking value: 2.79 kg/l
 - Bulk density: 224 kg/m³ (loosely packed), 336 kg/m³ (packed)
 - Free moisture: 0.5% maximum
 - Comment: Emtal Talcs are naturally occurring hydrous magnesium silicates, occurring as nonmetallic minerals exhibiting high brightness and low abrasion. These talcs are platy in character, with no trace of any fibrous, tremolitic talc, or other asbestiform minerals.
- Zeolite: Engelhard, Edison, New Jersey
 - Zeolite X-6002
 - Typical chemical composition: 55% Al₂O₃, 35% SiO₂, 4.0% Na₂O, 0.5% Fe₂O₃
 - Particle size distribution: 1% 0-20 μm, 12% 0-40 μm, 38% 0-60 μm, 59% 0-80 μm
 - Average particle size: 70 μm
 - Comment: X-6002 Zeolite contains microspheres, promoted with rare earths.
- Talc: R. T. Vanderbilt Company, Inc. Norwalk, Connecticut
 - Nytal® 400
 - Typical chemical composition: magnesium silicate pigment
 - Density: 2.85 g/cm³
 - One kg bulk: 0.350 l
 - pH: 9.5 by ASTM D 1208-65 (4a)
 - Plus 325 mesh: trace %
 - Comment: Nytal is a New York State talc. This magnesium silicate pigment is mined and especially processed by the Gouverneur Talc Company to ensure thorough blending and continuous uniformity. Nytal® 400 is a superfine magnesium silicate pigment. This grade consists of an average particle size of about 3 μm.
- Iron Ore: Pea Ridge Iron Ore Co., Missouri
 - Iron Ore - 96 Grade Heavy Media
 - Typical chemical composition: 70.7% Fe_T, 1.45% SiO₂, 0.52% P

- Activated Alumina: Kaiser Chemicals, Oakland, California
 - A-300 activated alumina (powder)
 - A-201 activated alumina (spheres)
 - Typical chemical composition: A-300 - 93.93% Al_2O_3 , 0.02% SiO_2 , 0.45% Na_2O , 5.6% L.O.I.; A-201 - 93.60% Al_2O_3 , 0.35% Na_2O , 0.02% SiO_2 , 0.02% Fe_2O_3 , 0.002% TiO_2 , 6.00% L.O.I.
 - Bulk density: A-300: 640-672 kg/m^3 ; A-201: 460-480 kg/m^3
 - Form: A-300: powder; A-201: spheres
 - Surface area: A-300: 260 m^2/g ; A-201: 325 m^2/g
 - Particle Size: A-300: 25% + 325 mesh, 5% + 325 mesh
 - Pore volume: A-201: 0.51 cm^3/g
 - Comment: A-300 is a fine active alumina powder having high surface area and reactivity. Principally used as a raw material, A-300 can be used to manufacture catalyst supports that can be tabulated or formed by other means into hard granules. A-201 activated alumina is produced by carefully controlled calcination of alumina trihydrate. Its spherical shape provides better abrasion resistance, fewer fines, and lower pressure drop. The unique crystalline phase increases cyclic stability. A-201 is used as a catalyst carrier and to remove contaminants, trace fluorides, chlorides, H_2S , and alcohols in various solutions.

- Zeolite: Davison
 - Molecular sieve M522 Type 5A (Grade 522)
 - Particle Shape: 3.2 mm spheres
 - Pore size: 5A
 - Comment: Alumina-silicate substrate with attached cations of calcium.

- Diatomaceous Earth: Johns Manville
 - Chromosorb P
 - Size: 30/60 mesh
 - Color: orange
- Emathlite: Mid Florida Mining Co., Emathla, Florida
 - Emathlite VMP
 - Typical chemical composition: 70.12% SiO_2 ,
13.29% Al_2O_3 , 4.84% CaO , 3.20% Fe_2O_3 , 2.47% MgO ,
1.13% K_2O , 0.10% Na_2O , 0.360% TiO_2 , 4.49% L.O.I.
at 1493 K
 - pH: 4.4 - 4.9
 - Color: cream
 - Free moisture: 4-6%
 - Specific gravity: 2.40
 - Bulking value: 20.02 lb/gal
 - Cation exchange: 45 me/100g
 - Surface area: 700 m^2/g
 - Liquid limit: 132%
 - Plastic limit: 54%
 - Water of plasticity: 70%
 - Drying shrinkage: 10%
 - Fusion point: 1616 K
 - Comment: A sorptive, high-surface-area material, light
in color. Composed principally of calcium-magnesium-
aluminosilicates as a type of fuller's earth. Emathlite
is processed from selected quality microcellular mineral
reserves located near Emathla, in central Florida.
- Zeolite: Coast Engineering Lab, Gardena, California
 - Molecular Sieve: 60/80 mesh

3.2.1.3 Alternative Getter Material Performance

Previous gettering studies conducted at Westinghouse demonstrated the potential of kaolin, PDU char ash, and gasifier ash to react with gaseous NaCl at 1123 K. These data indicated that gettering after 5 hours of reaction favored the formation of an acid insoluble alkali-aluminosilicate complex. Both char and gasifier ash were eliminated as candidate getter materials because of their high background potassium concentrations and the significant loss of potassium from the sorbent during gettering. Subsequently, at the conclusion of our initial study, kaolin was considered the most promising sorbent material screened for hot gas cleaning.

In search of a better getter, alternative materials were selected on the basis of information obtained by reviewing the literature and from thermodynamic criteria. Pellets* of 20 alternative getter materials were exposed at 1123 K to 80 ppmv NaCl in argon for 5 hours at 11 atm pressure in the bench-scale unit illustrated in Figure 11. Atomic absorption data on the gettered sodium concentration within the water soluble and acid soluble-insoluble fractions for these alternative getter materials are summarized in Table 48. The addition of the water soluble alkali data in this study has provided information that represents the concentration of condensed alkali, as opposed to the concentration of chemically reacted alkali. This partitioning was not conducted in our initial study, however, and discretion should be used when comparing both sets of data.

Although we did not rescreen kaolin in this study, the gettering data presented in Table 48 indicate that as chemically similar getter materials, activated bauxite, diatomaceous earth, and activated alumina outperform kaolin. Both activated bauxite and diatomaceous earth have a significantly higher sodium gettering ability in the acid insoluble complexes. For any alternative material to be considered an effective getter, chemical reactions must occur to remove sodium from the vapor phase and must retain sodium at a higher gettered concentration within either the acid soluble or the insoluble complexes. This conclusion is

*1/8 in. diameter by 1/8-1/4 in. cylinders.

Orig. 1705813

Figure 11 - High-temperature, high-pressure bench-scale unit

based on the assumption that desorption of the water soluble alkali could occur if higher reaction temperatures and reduced alkali concentrations in the fuel gas were experienced. Vansil,[®] Ebony Novacite,[®] zeolite (Davison and Coast Engineering Lab), emathlite, and calcined diatomite diatomaceous earth meet these criteria. Comparable to the activated bauxite gettering in the acid soluble and insoluble fraction are talc (Emtal Platy and New York State), Novacite,[®] calcined diatomite, and Microcell synthetic calcium silicate diatomaceous earth. Although the Coast Engineering zeolite contains 1.7 wt% background sodium, the acid soluble and insoluble gettering activity exceeds that in activated bauxite. At the same time, the 2.6 wt% background sodium in the Davison zeolite effectively lowers the gettering activity to that observed in activated bauxite.

Background potassium concentrations must also be monitored during the course of sodium gettering because of possible release of background potassium during either an ionic exchange reaction with sodium or possible direct volatilization reactions. Ebony Novacite,[®] zeolite (Davison and Coast Engineering Lab), emathlite, the diatomaceous earths, and the 7.28 percent Fe_2O_3 activated bauxite are shown in Table 48 to exceed 0.1 wt% background potassium and to release 91.8, 66.7, 80.0, 83.1, 72.6, and 25.0 percent of the background potassium content, respectively, during the 6 hour sodium exposure. Table 48 also indicates a possible increase of potassium over background concentrations for many of the remaining getter materials. The increase in potassium is considered to be within the experimental detection limits and represents a marginal change of the initial potassium content during the course of the sodium gettering reaction, possibly through the adsorption of released potassium from adjacent pellets.

Activated bauxite, which has been used throughout the course of this study as a reference material, contains 1.2 wt% Fe_2O_3 . Variation of the trace contaminant concentrations has often been considered to contribute to activating sodium gettering. The 1.2 wt% Fe_2O_3 activated bauxite demonstrates an enhanced sodium gettering in both the water soluble and acid soluble-insoluble phases. Increasing the Fe_2O_3

Table 48

ATOMIC ABSORPTION ANALYSES OF BACKGROUND AND GETTERED ALKALI CONCENTRATION
IN ALTERNATIVE GETTER MATERIALS

Dwg. 5599C78

Alternate Getter Material	Company	Background Total Alkali		Pellet Weight, mg	Sodium Chloride Reacted Getter Analysis								
		Na, Wt%	K, Wt%		Water Soluble Na, Wt%	Acid Soluble-Insoluble Na, Wt%	Total Gettered Na, Wt%	ΔNa Acid Soluble-Insoluble Over Background, Wt%	ΔNa Total Over Background, Wt%	Water Soluble K, Wt%	Acid Soluble-Insoluble K, Wt%	Total K Wt%	K Release*, Wt%
Activated Bauxite	Englehard	0.015	0.016	39.1 38.7 27.0	0.95 1.25 0.76	1.6 2.4 1.0	2.55 3.65 1.76	1.585 2.385 0.985	2.535 3.635 1.745	< 0.01 < 0.06 < 0.01	< 0.2 < 0.05 < 0.2	< 0.21 < 0.11 < 0.21	(0.194) (0.094) (0.194)
Olivine	IMC Olivine	< 0.01	< 0.01	31.1	0.13	0.74	0.87	0.73	0.86	< 0.06	< 0.04	< 0.10	(0.09)
Vansil	Vanderbilt Co. Inc.	0.24	0.028	26.9	1.06	7.5	8.56	7.26	8.32	< 0.09	< 0.04	< 0.13	(0.102)
Novacite	Malvern Co.	< 0.01	0.044	11.2	8.93	1.1	10.03	1.09	10.02	< 0.09	0.09	< 0.18	(0.136)
Ebony Novacite	Malvern Co.	0.057	2.2	12.7	0.51	5.83	6.34	5.773	6.283	< 0.1	0.08	< 0.18	2.02
Emtal Platy Talc	Englehard	< 0.01	< 0.01	25.5	4.02	2.20	6.22	2.19	6.21	< 0.06	< 0.04	< 0.10	(0.09)
Zeolite	Englehard	0.30	< 0.01	35.9	0.11	0.31	0.42	0.01	0.12	< 0.06	< 0.03	< 0.09	(0.08)
New York State Talc	Vanderbilt Co.	0.15	0.085	37.2	0.17	1.2	1.37	1.05	1.22	< 0.03	< 0.03	< 0.06	0.025
Iron Ore	Pea Ridge Iron Ore	< 0.01	0.06	36.9	0.16	0.27	0.43	0.26	0.42	< 0.03	< 0.06	< 0.09	(0.03)
Activated Alumina (pellets)	Kaiser Chem. Co.	0.18	< 0.01	34.5	1.65	0.41	2.06	0.23	1.88	< 0.03	< 0.03	< 0.06	(0.05)
Activated Alumina (spheres)	Kaiser Chem. Co.	0.22	< 0.01	36.3	15.29	0.14	15.43	-0.08	15.21	0.11	< 0.03	< 0.14	(0.13)
Zeolite	Davison Co.	2.6	0.30	9.8	0.31	4.4	4.71	1.8	2.11	< 0.1	< 0.10	< 0.20	0.10
Diatomaceous Earth**	Johns-Manville Co.	0.55	0.68	1.7	37.1	< 0.6	< 37.7	< 0.05	< 37.15	0.88	< 0.6	< 1.48	(0.80)
Emathlite	Mid Florida Mining Co.	0.09	0.83	35.5	0.06	3.5	3.56	3.41	3.47	< 0.03	0.11	< 0.14	0.69
Zeolite	Coast Engineering Lab.	1.7	0.40	29.7	0.57	6.4	6.97	4.7	5.27	< 0.03	0.05	< 0.08	0.32
Diatomaceous Earth - Flux Calcined Diatomite	Johns-Manville	2.40	0.30	7.7	0.19	2.60	2.79	0.20	0.39	< 0.13	< 0.26	< 0.39	(0.09)
Diatomaceous Earth - Celite Diatomite	Johns-Manville	0.46	0.62	17.6	14.5	1.70	16.20	1.24	15.74	0.06	0.11	0.17	0.45
Diatomaceous Earth - Microcell Synthetic Calcium Silicate	Johns-Manville	0.38	0.35	8.8	3.64	2.16	5.80	1.78	5.42	0.11	< 0.23	< 0.34	0.01
Activated Bauxite (1.38% Fe ₂ O ₃)	Englehard	< 0.06	< 0.06	30.7	0.68	0.94	1.62	0.88	1.56	< 0.03	< 0.06	< 0.09	(0.03)
Activated Bauxite (2.66% Fe ₂ O ₃)	Englehard	< 0.06	0.06	33.6	0.58	1.25	1.83	1.19	1.77	< 0.03	< 0.06	< 0.09	(0.03)
Activated Bauxite (7.28% Fe ₂ O ₃)	Englehard	0.09	0.12	32.5	0.52	1.66	2.18	1.57	2.09	< 0.03	< 0.06	< 0.09	0.03

*() Indicates Increased Potassium Over Background Material Due to Lower Detection Level Limits

** Insufficient Gettered Sample Weight for Meaningful Atomic Absorption Results

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concentration to 1.38, 2.66, and 7.28 wt% in activated bauxite tends to reduce water soluble sodium gettering while increasing sodium in the gettered acid soluble-insoluble fraction. The total gettered sodium content in these materials, however, did not exceed that obtained in the 1.2 wt% Fe_2O_3 activated bauxite.

Table 48 demonstrates also the gettering of iron as Fe_3O_4 . As a gettering material, Fe_3O_4 has one of the lowest sodium gettering capacities, with 62 percent of the reacted alkali resulting within an acid insoluble fraction. On the basis of these results, a direct correlation may exist between the increased gettered acid soluble-insoluble sodium and higher iron content in activated bauxite..

3.2.2 Bench-Scale Evaluation of Candidate Getters

Bench-scale evaluation of the alternative getter materials and other considerations provided direction for continued study for gaining insight into the possible alkali reactions and mechanisms occurring in aluminosilicate materials, and in the definition of the optimal getter sorbent. As a result, five test series were conducted in the bench-scale unit. The final test matrix included: screening of activated bauxite at 1123 and 1153 K with 80 ppmv NaCl in Ar at 11 atm for 1, 3, and 6 hours; screening of PFBC ash at 1123 and 1153 K with 80 ppmv NaCl in Ar at 11 atm for 1, 3, and 6 hours; screening of activated bauxite with 80 ppmv KCl in Ar at 11 atm for 1, 3, and 6 hours; gettering of sodium by activated bauxite in the presence of water vapor; and evaluation of the sodium gettering capacity of emathlite in an inert gas containing alkali; and in a simulated fuel gas. The initial activated bauxite work was based on ANL's identification of activated bauxite^{10,11} as the leading candidate getter. The addition of PFBC ash in this phase of the program resulted from consideration of an alternative process material for use as a gettering sorbent. However, its high background potassium content (Table 49), as discussed in Section 3.2.2, eliminated it from consideration as a potential getter. The final emathlite series resulted from data concurrently generated by the TGA that indicated an enhanced gettering performance relative to all alternative getter materials tested. Analytical data obtained in each of these series are presented in the following sections.

3.2.2.1 Activated Bauxite Sodium Gettering

Activated bauxite initially contains a higher background level of sodium than of potassium, principally within the insoluble clay fraction (Table 49). When exposed to gaseous NaCl at temperatures of 1123 and 1153 K and 11 atm total pressure, gettering results within water soluble, acid soluble, and acid insoluble phases. The concentration of sodium in the water soluble phase is consistently maintained at an average of 0.07 to 0.08 wt% in the 1123 K activated bauxite pellets during the 1 to 6 hour gaseous NaCl exposures. Sodium concentration in the water soluble phase varies, however, in the pellets exposed to temperatures of 1153 K.

The concentration of sodium in the acid soluble and insoluble phases of 1123 K activated bauxite pellets continuously increases with exposure time (Figure 12). Approximately 73 percent of the total gettered sodium content is partitioned within the acid insoluble lattice after 1 hour and is maintained at this level throughout the remainder of the gettering reaction. Although activated bauxite has the capacity to getter 0.72 wt% sodium after 6 hours at 1123 K, the data indicate that the principal gettering reaction of sodium is within the insoluble, activated bauxite lattice and that secondary reactions of the alkali with the acid soluble phases have not achieved saturation concentrations.

Within the first 3 hours of gaseous NaCl exposure at 1153 K, the concentration of sodium in all three phases of activated bauxite increases to concentrations higher than those obtained in the 1123 K reaction. Atomic absorption data indicate that the principal gettering reaction at 1153 K is once again through reaction of the alkali with the insoluble lattice (Figure 13). A maximum of 0.05 wt% insoluble sodium is established within the pellet after 1 hour of reaction at 1153 K, comparable to the concentration detected within the 1123 K insoluble activated bauxite phase after 6 hours of alkali exposure. This level is maintained after 3 hours of alkali exposure, tentatively indicating that maximum saturation of available active sites for sodium within the insoluble activated bauxite lattice has been achieved. Once the insoluble sites

Table 49

SODIUM GETTERING DATA FOR ACTIVATED BAUXITE AND PFBC ASH

Dwg. 5596C63

TEST PARAMETERS									ATOMIC ABSORPTION, WT %							
TEST NO.	MATERIAL	GAS COMPOSITION	GAS FLOW RATE (scfm)	PRESSURE (ATM)	PARTICLE SIZE (INCHES)	GETTER TEMP. (K)	NaCl TEMP. (K)	EXPOSURE TIME (HRS)	WATER SOLUBLE NA	WATER SOLUBLE K	ACID SOLUBLE NA	ACID SOLUBLE K	INSOLUBLE NA	INSOLUBLE K	TOTAL NA	TOTAL K
BACKGROUND DATA																
	BAUXITE	-	-	-	-	-	-	-	< 0.02	< 0.01	< 0.05	< 0.05	0.06	< 0.05	0.06	< 0.05
		-	-	-	-	-	-	-	< 0.02	< 0.01	< 0.05	< 0.05	0.09	< 0.05	0.09	< 0.05
		-	-	-	-	-	-	-	< 0.02	< 0.01	< 0.05	< 0.05	0.07	< 0.05	0.07	< 0.05
	PFBC ASH	-	-	-	-	-	-	-	< 0.02	0.02	0.32	0.56	0.37	1.15	0.69	1.73
		-	-	-	-	-	-	-	< 0.02	0.01	0.27	0.50	0.42	1.29	0.69	1.80
		-	-	-	-	-	-	-	< 0.02	0.02	0.28	0.50	0.38	1.17	0.66	1.69
PRELIMINARY SCREENING DATA - TEMPERATURE DEPENDENCE																
1A	BAUXITE (29 MG)	AR	0.5	11	1/8	1123	1088	1	0.09	< 0.03	0.04	< 0.02	0.31	< 0.03	0.44	< 0.03
1B	BAUXITE (30 MG)	AR	0.5	11	1/8	1123	1088	1	0.07	< 0.03	0.02	< 0.02	0.28	< 0.03	0.37	< 0.03
1C	BAUXITE (28.6 MG)	AR	0.5	11	1/8	1123	1088	1	0.07	< 0.03	0.02	< 0.02	0.23	< 0.03	0.32	< 0.03
2A	BAUXITE (30 MG)	AR	0.5	11	1/8	1123	1088	3	0.06	< 0.03	0.04	< 0.02	0.37	< 0.03	0.47	< 0.03
2B	BAUXITE (28.4 MG)	AR	0.5	11	1/8	1123	1088	3	0.09	< 0.03	0.10	< 0.02	0.44	< 0.03	0.63	< 0.03
2C	BAUXITE (29.4 MG)	AR	0.5	11	1/8	1123	1088	3	0.07	< 0.03	0.05	< 0.02	0.37	< 0.03	0.49	< 0.03
3A	BAUXITE (32.6 MG)	AR	0.5	11	1/8	1123	1088	6	0.09	< 0.03	0.13	< 0.02	0.52	< 0.03	0.74	< 0.03
3B	BAUXITE (30 MG)	AR	0.5	11	1/8	1123	1088	6	0.07	< 0.03	0.07	< 0.02	0.52	< 0.03	0.66	< 0.03
3C	BAUXITE (30 MG)	AR	0.5	11	1/8	1123	1088	6	0.08	< 0.03	0.12	< 0.02	0.56	< 0.03	0.76	< 0.03
4A	BAUXITE (28.2 MG)	AR	0.5	11	1/8	1153	1103	1	0.06	< 0.03	0.12	< 0.02	0.50	< 0.03	0.68	< 0.03
4B	BAUXITE (24.2 MG)	AR	0.5	11	1/8	1153	1103	1	0.18	< 0.03	0.15	< 0.02	0.45	< 0.03	0.78	< 0.03
4C	BAUXITE (24.6 MG)	AR	0.5	11	1/8	1153	1103	1	0.05	< 0.03	0.13	< 0.02	0.48	< 0.03	0.66	< 0.03
5A	BAUXITE (33 MG)	AR	0.5	11	1/8	1153	1103	3	2.04	< 0.03	0.23	< 0.02	0.48	< 0.03	2.75	< 0.03
5B	BAUXITE (28 MG)	AR	0.5	11	1/8	1153	1103	3	0.13	< 0.03	0.29	< 0.02	0.44	< 0.03	0.86	< 0.03
5C	BAUXITE (31.6 MG)	AR	0.5	11	1/8	1153	1103	3	0.05	< 0.03	0.11	< 0.02	0.56	< 0.03	0.72	< 0.03
6A	BAUXITE (26.6 MG)	AR	0.5	11	1/8	1153	1103	6	0.23	< 0.03	0.04	< 0.02	0.35	< 0.03	0.62	< 0.03
6B	BAUXITE (28.4 MG)	AR	0.5	11	1/8	1153	1103	6	< 0.01	< 0.03	< 0.02	< 0.02	0.13	< 0.03	0.13	< 0.03
6C	BAUXITE (30.3 MG)	AR	0.5	11	1/8	1153	1103	6	< 0.01	< 0.03	< 0.02	< 0.02	0.07	< 0.03	0.07	< 0.03
6D	BAUXITE (29.2 MG)	AR	0.5	11	1/8	1153	1103	6	0.02	< 0.2	< 0.02	< 0.2	0.08	< 0.2	0.10	< 0.2
6E	BAUXITE (31.0 MG)	AR	0.5	11	1/8	1153	1103	6	0.13	< 0.2	< 0.02	< 0.2	0.11	< 0.2	0.24	< 0.2

Table 49 (Cont'd)

Reg. 5596C62

TEST PARAMETERS									ATOMIC ABSORPTION, WT %							
TEST NO.	MATERIAL	GAS COMPOSITION	GAS FLOW RATE (scfm)	PRESSURE (ATM)	PARTICLE SIZE (INCHES)	GETTER TEMP. (K)	NACL TEMP. (K)	EXPOSURE TIME (HRS)	WATER SOLUBLE NA	WATER SOLUBLE K	ACID SOLUBLE NA	ACID SOLUBLE K	INSOLUBLE NA	INSOLUBLE K	TOTAL NA	TOTAL K
7A	ASH (16.6 MG)	AR	0.5	11	1/8	1123	1088	1	0.12	< 0.01	1.70	0.12	0.81	0.09	2.63	0.21
7B	ASH (15.8 MG)	AR	0.5	11	1/8	1123	1088	1	0.89	0.03	1.28	0.06	1.67	0.05	3.84	0.14
7C	ASH (18.8 MG)	AR	0.5	11	1/8	1123	1088	1	0.08	< 0.01	1.13	0.29	0.74	0.29	1.95	0.58
8A	ASH (24.2 MG)	AR	0.5	11	1/8	1123	1088	3	0.08	< 0.01	1.36	< 0.01	1.02	< 0.01	2.46	< 0.01
8B	ASH (22.8 MG)	AR	0.5	11	1/8	1123	1088	3	0.07	< 0.01	0.98	< 0.01	1.59	< 0.01	2.64	< 0.01
8C	ASH (17.2 MG)	AR	0.5	11	1/8	1123	1088	3	0.09	< 0.01	1.68	0.03	1.17	< 0.01	2.94	0.03
9A	ASH (29.0 MG)	AR	0.5	11	1/8	1123	1088	6	15.36	0.03	4.31	0.03	0.39	0.02	20.06	0.08
9B	ASH (43.0 MG)	AR	0.5	11	1/8	1123	1088	6	16.28	0.03	4.62	0.02	0.40	< 0.01	21.30	0.05
9C	ASH (35.4 MG)	AR	0.5	11	1/8	1123	1088	6	14.78	0.04	4.66	0.03	0.42	< 0.01	19.86	0.07
10A	ASH (21.0 MG)	AR	0.5	11	1/8	1153	1103	1	0.52	< 0.01	1.04	0.07	1.41	0.13	2.97	0.20
10B	ASH (23.2 MG)	AR	0.5	11	1/8	1153	1103	1	0.09	< 0.01	0.97	0.19	0.88	0.52	1.94	0.71
10C	ASH (18.0 MG)	AR	0.5	11	1/8	1153	1103	1	0.11	< 0.01	1.53	0.33	0.74	0.26	2.38	0.59
11A	ASH (19.0 MG)	AR	0.5	11	1/8	1153	1103	3	0.32	< 0.01	4.03	< 0.01	1.13	< 0.01	5.48	< 0.01
11B	ASH (27.6 MG)	AR	0.5	11	1/8	1153	1103	3	0.82	< 0.01	1.92	< 0.01	1.60	< 0.01	4.94	< 0.01
11C	ASH (35.4 MG)	AR	0.5	11	1/8	1153	1103	3	13.56	0.04	3.59	0.04	0.70	< 0.01	17.85	0.08
12A	ASH (31.1 MG)	AR	0.5	11	1/8	1153	1103	6	12.54	0.02	1.26	0.02	0.86	< 0.01	14.66	0.04
12B	ASH (29.8 MG)	AR	0.5	11	1/8	1153	1103	6	12.25	< 0.01	1.38	0.02	0.87	< 0.01	14.50	0.02
12C	ASH (25.2 MG)	AR	0.5	11	1/8	1153	1103	6	12.10	< 0.01	3.83	0.02	1.71	< 0.01	17.64	0.02

Figure 12 - Partitioning of gettered sodium at 1123 K in activated bauxite and PFBC ash

Figure 13 - Partitioning of gettered sodium at 1153 K in activated bauxite and PFBC ash

have been saturated, gettering continues within the acid soluble fraction of the getter material. The sodium concentration in the soluble phase is enhanced at 1153 K, possibly as a result of saturation of the insoluble active sites at the higher temperature.

3.2.2.2 PFBC Ash Sodium Gettering

Reaction of the PFBC ash pellets to gaseous 80 ppmv NaCl at 1123 K and 11 atm total pressure begins through the interaction of sodium and both the acid soluble and insoluble lattice (Figure 12). The available insoluble sites within the PFBC ash appear to become saturated after 3 or 4 hours under these conditions, prior to what appears to be the release of gettered alkali from the acid insoluble phase into the acid soluble fraction. Saturation of the acid soluble phase also appears to result within the first few hours of the reaction.

The gettering of 15 wt% sodium is observed within the water soluble phase after 6 hours of reaction. Although this represents 75 percent of the total gettered sodium within the PFBC material at 1123 K, saturation of the 1/8 in. pellets is not established. As the water soluble alkali concentration increases, both acid soluble and insoluble reactions are suppressed.

Atomic absorption analysis of PFBC ash pellets exposed to 80 ppmv NaCl at 1153 K indicates a gettering reaction pattern similar to that of the 1123 K reaction (Figure 13). Although gettering begins in the acid soluble and insoluble phase, after extended exposure periods the predominate reaction results within the water soluble phase. Saturation appears to be achieved within the insoluble ash lattice after 1 to 3 hours of alkali exposure. Similarly, saturation of the acid soluble fraction appears to occur after 3 hours of reaction. As both the insoluble and acid soluble sites attain saturation, additional sodium is gettered predominantly through the water soluble fraction. After 6 hours of exposure to the alkali-laden gas at 1153 K, 75 percent of the total gettered sodium content within the 1/8 in. PFBC ash pellet is within the water soluble fraction.

Table 50 indicates the percent of background potassium released from the PFBC ash material during sodium gettering as a function of reaction temperature and time. Release is predominantly from potassium bound within the acid insoluble phases and, secondarily, from the potassium acid soluble phases. Both reaction temperatures indicate virtually 100 percent release of the background potassium content after 6 hours of exposure to the sodium environment.

Evolution of potassium from the PFBC insoluble phase in the presence of sodium is considered to occur as an ionic exchange mechanism. The ratio of sodium gettered to potassium released from the acid insoluble lattice indicates that for every potassium ion released, one sodium ion is repositioned within the PFBC ash lattice (Table 51). The simple ionic exchange between the alkalis is not evident in the water or acid soluble phases.

3.2.2.3 Activated Bauxite Potassium Gettering

Exposure of activated bauxite to 80 ppmv KCl in Ar at 1123 and 1153 K and 11 atm total pressure for 1, 3, and 6 hours demonstrates an enhanced gettering capacity for potassium relative to sodium within the water and acid soluble phases (Table 52 and Figure 14). In the initial 1123 K gettering reaction potassium is also driven into the insoluble lattice, but a reduction in the insoluble getter phase capacity takes place as the reaction exposure is extended to 6 hours.

As shown in Table 52, when potassium is gettered by activated bauxite, sodium is released simultaneously, principally from the acid insoluble lattice. The release of background sodium during potassium gettering occurs within the first hour of reaction.

A marked increase in the water soluble potassium content is observed after 6 hours of exposure to the 80 ppmv KCl environment at 1153 K (Figure 15). At these temperatures secondary reactions within the acid soluble fraction are suppressed to a greater extent than at 1123 K. Potassium gettering, however, continues to increase within the acid insoluble fraction as a function of time, as opposed to what had appeared to be saturation within the insoluble phase of activated bauxite after 3 hours of reaction at 1123 K.

Table 50

POTASSIUM RELEASE FROM PFBC ASH

REACTION CONDITIONS		Percent K Released	wt% K
Temp, K	Time, hr		
1123	1	82	1.43
1123	3	99	1.72
1123	6	96	1.67
1153	1	71	1.24
1153	3	98	1.71
1153	6	98	1.71

Table 51

RATIO OF INSOLUBLE SODIUM GETTERED TO INSOLUBLE POTASSIUM
RELEASED IN PFBC ASH

REACTION CONDITIONS		Percent Insoluble Na Gained	Percent Insoluble K Released	$\frac{Na}{K}$
Temp, K	Temp, hr			
1123	1	0.68	1.06	0.64
1123	3	0.87	1.20	0.72
1153	1	0.62	0.90	0.68
1153	3	0.75	1.20	0.62
1153	6	0.75	1.20	0.63
radius of Na^+ : 0.97 Å radius of K^+ : 1.33 Å $Na^+/K^+ = 0.73$				

Table 52

SUMMARY OF BENCH-SCALE POTASSIUM GETTERING DATA FOR ACTIVATED BAUXITE

Dwg. 6598C11

TEST PARAMETERS									ATOMIC ABSORPTION, WT %							
TEST NO.	MATERIAL	GAS COMPOSITION	GAS FLOW RATE (scfm)	PRESSURE (ATM)	PARTICLE SIZE (INCHES)	GETTER TEMP. (°K)	KCL TEMP. (°K)	EXPOSURE TIME (HRS)	WATER SOLUBLE NA	WATER SOLUBLE K	ACID SOLUBLE NA	ACID SOLUBLE K	INSOLUBLE NA	INSOLUBLE K	TOTAL NA	TOTAL K
13A	BAUXITE (44.7 MG)	AR	0.5	11	1/8	1123	1073	1	0.03	0.97	< 0.02	0.74	< 0.02	0.15	0.03	1.86
13B	BAUXITE (36.9 MG)	AR	0.5	11	1/8	1123	1073	1	< 0.02	0.68	< 0.02	0.49	< 0.02	0.19	< 0.02	1.36
13C	BAUXITE (35.3 MG)	AR	0.5	11	1/8	1123	1073	1	0.02	0.81	< 0.02	0.57	< 0.02	0.21	0.02	1.59
14A	BAUXITE (33.7 MG)	AR	0.5	11	1/8	1123	1073	3	< 0.02	0.91	< 0.02	0.80	< 0.02	0.45	< 0.02	2.16
14B	BAUXITE (35.3 MG)	AR	0.5	11	1/8	1123	1073	3	< 0.02	0.93	< 0.02	0.86	0.04	0.42	0.04	2.21
14C	BAUXITE (30.0 MG)	AR	0.5	11	1/8	1123	1073	3	0.05	8.83	< 0.02	0.73	< 0.02	0.42	0.05	9.98
15A	BAUXITE (32.5 MG)	AR	0.5	11	1/8	1123	1073	6	< 0.02	8.09	< 0.02	1.43	< 0.02	0.28	< 0.02	2.80
15B	BAUXITE (37.3 MG)	AR	0.5	11	1/8	1123	1073	6	< 0.02	3.10	< 0.02	1.40	< 0.02	0.27	< 0.02	2.77
15C	BAUXITE (44.5 MG)	AR	0.5	11	1/8	1123	1073	6	0.06	15.7	0.02	1.04	< 0.02	0.17	0.08	16.91
16A	BAUXITE (43.0 MG)	AR	0.5	11	1/8	1153	1073	1	< 0.02	0.66	< 0.02	0.27	< 0.02	0.34	< 0.02	1.27
16B	BAUXITE (36.2 MG)	AR	0.5	11	1/8	1153	1073	1	< 0.02	0.73	< 0.02	0.29	< 0.02	0.35	< 0.02	1.37
16C	BAUXITE (36.6 MG)	AR	0.5	11	1/8	1153	1073	1	< 0.02	6.61	< 0.02	0.19	< 0.02	0.30	< 0.02	1.10
17A	BAUXITE (37.1 MG)	AR	0.5	11	1/8	1153	1073	3	< 0.02	0.71	< 0.02	0.54	< 0.02	0.61	< 0.02	1.86
17B	BAUXITE (41.3 MG)	AR	0.5	11	1/8	1153	1073	3	< 0.02	0.71	< 0.02	0.48	< 0.02	0.63	< 0.02	1.82
17C	BAUXITE (39.1 MG)	AR	0.5	11	1/8	1153	1073	3	< 0.02	0.74	< 0.02	0.43	< 0.02	0.63	< 0.02	1.80
18A	BAUXITE (40.9 MG)	AR	0.5	11	1/8	1153	1073	6	0.04	6.23	< 0.02	0.99	< 0.02	0.76	0.04	7.98
18B	BAUXITE (44.6 MG)	AR	0.5	11	1/8	1153	1073	6	0.11	17.3	0.04	0.64	< 0.02	0.66	0.15	18.60
18C	BAUXITE (35.5 MG)	AR	0.5	11	1/8	1153	1073	6	< 0.02	0.79	< 0.02	0.80	< 0.02	1.03	< 0.02	2.62

Figure 14 - Partitioning of gettered potassium at 1123 K in activated bauxite

Figure 15 - Partitioning of gettered potassium at 1153 K in activated bauxite

Although the data indicate wide gettering scatter bands in the various pellets sampled for a given test, two reaction mechanisms seem to be occurring within the temperature range investigated. The minimal potassium gettering within the water soluble fraction of activated bauxite and the enhanced gettering within both the acid soluble and insoluble phases indicate that for effective hot gas cleaning of potassium-laden gases, the reaction temperature should approach 1153 K.

At 1123 K reaction of sodium and potassium with activated bauxite at 11 atm follows two independent mechanisms. Sodium enters the acid insoluble clay lattice principally from the initiation of the gettering reaction (Figure 16). For potassium, however, that phase is the least favored reaction site. The data indicate that gettering in the water soluble fraction of activated bauxite remains constant over the 6 hours of reaction with sodium, averaging approximately 0.076 wt% sodium. Conversely, gettering of potassium within the water soluble fraction increases as a function of time, attaining an average potassium concentration of 5.96 wt% after 6 hours of reaction. The acid soluble fraction of the 1123 K activated bauxite pellet increased in both the sodium and potassium content as a function of time, with an enhanced gettering affinity for potassium. Comparison of the final gettered acid soluble alkalis indicates that potassium is gettered at approximately 10 to 12 times the concentration of sodium after 6 hours (average 0.107 wt% Na vs 1.29 wt% K). The acid insoluble fraction of the activated bauxite pellet after one hour of reaction getters a higher concentration of sodium. A comparable affinity for both alkalis in the acid insoluble phase occurs after 3 hours of reaction, while a higher affinity for sodium exists after 6 hours of exposure. On the basis of the total gettered concentration, the affinity of potassium for the activated bauxite lattice is much greater than that of sodium when the alkalis are present as discrete volatile chlorides at reaction temperatures of 1123 K.

The basic differences in the gettering reactions of sodium and potassium are as follows:

Getter Temperature: 1123K
 Gas Composition: 80 ppmv NaCl or KCl/Ar
 Gas Velocity: 0.5 scfm (1039 m/hr)
 Pressure: 11 atm

Figure 16 - Comparison of sodium and potassium gettering at 1123 K in activated bauxite

- Potassium appears to be released from the insoluble lattice as a function of time, while sodium remains chemically bound within this fraction.
- Potassium is possibly released from the insoluble activated bauxite lattice and recaptured within the acid soluble fraction, while sodium does not appear to be involved in either a release or recapture mechanism.
- The gettering reactivity within the nepheline or feldspar fractions of the acid soluble phase has a higher affinity for potassium than for sodium.
- The water soluble gettering reaction favors the capture of potassium over sodium, possibly through physical adsorption or condensation.

At 1153 K the water soluble fraction of activated bauxite rapidly getters potassium after 1 hour of alkali exposure (Figure 17). Extended exposure time enhances the gettering of potassium within the activated bauxite water soluble fraction, while depletion of water soluble gettered sodium as a function of time is observed. Within the acid soluble fraction, potassium is gettered at approximately twice the concentration of sodium after 1 and 3 hours of reaction. Potassium continues to getter within the acid soluble fraction after 6 hours, while sodium appears to be released from this matrix. Reactions within the acid insoluble fraction initially favor the sodium reaction over the potassium, with a saturation of sodium achieved after 3 hours followed by its depletion or release from the lattice. Saturation of potassium within the acid insoluble lattice is not achieved after 6 hours of exposure. If we disregard the 6 hour, 1153 K sodium data, the total average gettering of both alkalis appears to increase as a function of time, with comparable gettering affinity.

Throughout the gettering reactions we have observed that the capture of alkali has led to the equivalent displacement of background alkali from various phases within the activated bauxite lattice. Similar

Curve 731149-8

Temperature: 1153K.
Gas Composition: 80 ppmv NaCl or KCl/Ar
Gas Velocity: 0.5 scfm (1067 m/hr)
Pressure: 11 atm

Figure 17 - Comparison of sodium and potassium gettering at 1153 K in activated bauxite

reactions should apply to gaseous potassium displacing background sodium, provided sufficient area is available for the larger potassium ion to enter the original, smaller, sodium ion position.* From the data in Table 52, the initial total background sodium averaged 0.073 wt%. Approximately two-thirds of the reacted activated bauxite pellets contained 0.02 wt% total sodium at the completion of each potassium gettering reaction. Approximately 72.7 wt% of the background sodium content has been lost during potassium gettering, predominantly from the acid insoluble complex. The sensitivity of the background potassium data does not permit us to make a similar comparison.

3.2.2.4 Sodium Gettering in the Presence of Water Vapor by Activated Bauxite

An enhanced gettering capacity in activated bauxite was demonstrated after 6 hours of reaction at 1183 K and 11 atm when the 80 ppmv NaCl gas contained 4.6% H₂O. As shown in Table 53, sodium gettering increases by a factor of 2.8 in the water soluble phase and by 1.7 in the acid soluble-insoluble fraction in the presence of water vapor.

Preliminary chloride analysis of the water soluble fraction of these gettered pellets indicates that 2.5, 0.12, and 0.15 wt% chlorine is present in the 3.3, 2.5, and 2.5 wt% water soluble fraction of activated bauxite. These percentages clearly indicate that NaCl is not the principal resulting sodium gettered phase in the water soluble fraction of activated bauxite. Further detailed analysis is required to define the resulting sodium species.

* Ionic radii: Na⁺ 0.97Å; K⁺ 1.33Å; Cl⁻ 1.81Å; Cl⁵⁺ 0.34Å; Cl⁷⁺ 0.27Å.

Table 53

EFFECT OF WATER VAPOR ON SODIUM GETTERING IN ACTIVATED BAUXITE

80 ppmv NaCl/Ar

Pellet Weight, mg	Sodium Water Soluble, wt%	Sodium Acid Soluble-Insoluble, wt%	Sodium Total, wt%
39.1	0.95	1.6	2.55
38.7	1.25	2.4	3.65
27.0	0.76	1.0	1.76
Average:	0.99	1.67	2.66

80 ppmv NaCl/H₂O/Ar

Pellet Weight, mg	Sodium Water Soluble, wt%	Sodium Acid Soluble, wt%	Sodium Acid Insoluble, wt%	Sodium Total wt%
40.9	3.3	2.3	0.49	6.09
39.8	2.5	2.41	0.52	5.43
39.9	2.5	2.28	0.50	5.28
Average:	2.77	2.33	0.50	5.60

3.2.2.5 Sodium Gettering in Inert and Simulated Fuel Gases by Emathlite

The improved gettering activity of emathlite relative to activated bauxite, as demonstrated in the bench-scale and TGA units (Tables 48 and 60, respectively) has warranted further study of the emathlite gettering capacity in various reactant gases. The data obtained in the bench-scale test matrix provide information on the general gettering reaction mechanism in aluminosilicate materials and identification of alkali-getter-promoting phases.

A series of seven tests were conducted in the bench-scale unit using a plug of ten 1/8 in. diameter by 1/8 to 1/4 in. long cylindrical emathlite pellets. The pellets were exposed at 1123 K and 11 atm total pressure for up to 24 hours to reactant gases consisting of an inert gas containing 4.6% H₂O; an inert gas containing 4.6% H₂O and 80 ppmv NaCl; and a simulated fuel gas (7.49% CO₂, 23.03% CO, 13.90% H₂, 4.6% H₂O, 0.2725% H₂S, 0.0025% HCl, 50.705% N₂, 80 ppmv NaCl). The resulting 4.6% H₂O pellets were greyish tan and did not form a surface glass coating (Figure 18). The 4.6% H₂O, 80 ppmv NaCl pellets appeared greenish black, with localized areas of glass formed at the surface of the pellet. A glass-encased, black agglomerate of pellets resulted in the simulated fuel gas environment.

Atomic absorption analyses of the sodium concentration in the reacted emathlite pellets are presented in Table 54. The increased alkali concentration in emathlite over background in the absence of gaseous alkali may have resulted from the reaction of sodium leached from the bench-scale unit's inner alumina tube in the presence of water vapor.

Four sets of data are presented in Table 54 for the reaction of emathlite with 80 ppmv NaCl and 4.6% H₂O. The initial test conducted in the bench-scale unit at 1123 K and 11 atm for 24 hours demonstrates that a maximum of 5.04 wt% sodium can be gettered by 1/8 in. emathlite pellets. Eighty-eight percent of the total gettered alkali has been driven into the acid insoluble phase. The second set of test data, however, indicates that an average of 13.5 wt% total sodium is gettered by emathlite after 6 hours of exposure. Since the predominant gettered phase in the 6 hour test is

4.6% H₂O/N₂

80 ppm NaCl, 4.6% H₂O/N₂

**Simulated Fuel Gas:
80 ppm NaCl, 7.49% CO₂,
23.03% CO, 13.90% H₂,
0.2725% H₂S, 0.0025% HCl,
4.6% H₂O, 50.705% N₂**

Figure 18 - Surface morphology of emathlite after 6 hours of exposure in various reactant gases at 1123 K and 11 atm total pressure in the bench-scale test unit

Table 54

SUMMARY OF ATOMIC ABSORPTION ANALYSES OF
GETTERED EMATHLITE PELLETS IN THE BENCH-SCALE UNIT

Orig. 55-08001

Bench-Scale Test Conditions					Atomic Absorption Analyses, Wt. %							
Test No.	Gas Composition	Temp., K	Pressure, atm	Exposure Time, Hrs	Water Soluble		Acid Soluble		Acid Insoluble		Total	
					Na	K	Na	K	Na	K	Na	K
Background	—	—	—	—	—	—	—	—	—	—	0.09	0.83
Blank	4.6% H ₂ O	1123	11	6	NA*	NA	NA	NA	NA	NA	0.31	NA
1	80 ppmv NaCl, 4.6% H ₂ O	1123	11	24	0.32	<0.011	0.28	0.025	4.44	0.39	5.04	0.43
2	80 ppmv NaCl, 4.6% H ₂ O	1123	11	6	NA	NA	NA	NA	NA	NA	15.1	NA
					NA	NA	NA	NA	NA	NA	11.9	NA
					NA	NA	NA	NA	NA	NA	14.0	NA
					9.38	NA	0.65	NA	3.49	NA	13.52	NA
					9.32	NA	0.53	NA	3.22	NA	13.07	NA
3	80 ppmv NaCl, 4.6% H ₂ O	1123	11	6	8.51	NA	1.36	NA	3.52	NA	13.39	NA
					NA	NA	NA	NA	NA	NA	18.3	NA
					NA	NA	NA	NA	NA	NA	18.3	NA
4	80 ppmv NaCl, 4.6% H ₂ O	1123	11	6	6.54	NA	2.23	NA	5.24	NA	14.01	NA
					5.11	NA	2.59	NA	5.55	NA	13.25	NA
					4.61	NA	2.37	NA	6.40	NA	13.38	NA
5	Simulated Fuel Gas **	1123	11	6	NA	NA	NA	NA	NA	NA	8.06	NA
					NA	NA	NA	NA	NA	NA	10.2	NA
					NA	NA	NA	NA	NA	NA	5.67	NA
					0.23	NA	0.62	NA	4.38	NA	5.23	NA
					5.14	NA	1.61	NA	5.63	NA	12.38	NA
6	Simulated Fuel Gas	1123	11	2	0.71	NA	0.73	NA	5.52	NA	6.96	NA
					NA	NA	NA	NA	NA	NA	4.17	NA
					NA	NA	NA	NA	NA	NA	4.15	NA
7	Simulated Fuel Gas	1123	11	6	NA	NA	NA	NA	NA	NA	3.38	NA
					10.3	NA	0.76	NA	3.81	NA	14.87	NA
					11.1	NA	0.72	NA	4.04	NA	15.86	NA
7	Simulated Fuel Gas	1123	11	6	8.70	NA	0.95	NA	4.08	NA	13.73	NA

* NA: Not Analyzed

** Simulated Fuel Gas: 80 ppmv NaCl, 7.49% CO₂, 23.03% CO, 13.90% H₂O, 0.275% H₂S, 0.0025% HCl, 4.6% H₂O, 50.705% N₂

a water soluble sodium complex, condensation of NaCl must be considered. Repeating the bench-scale experiment under similar test conditions again reproduces the 13.5 to 18.3 wt% total gettered sodium concentration, with 40 percent of the total gettered alkali present as a water soluble complex. Although condensation of NaCl appears to be solely responsible for the high total gettered sodium concentrations, the fuel gas data indicate that after 6 hours of reaction, 4.57 wt% sodium exists as an acid insoluble complex. This result compares favorably with the 4.44 wt% acid insoluble sodium concentration observed after 24 hours of exposure, implying that saturation of the insoluble active sites may have resulted. In the presence of condensed alkali at the pellet surface, an increase in the acid soluble and insoluble sodium concentration results. We believe that this is a direct reaction of NaCl and the substrate initially forming an acid soluble complex with subsequent conversion into an insoluble complex. The exact mechanism of these reactions remains to be determined.

Numerous white areas were observed along the emathlite pellet surface after 6 hours of exposure to gases containing 80 ppmv NaCl and 4.6% H₂O at 1123 K at 11 atm (Figure 19). These areas were identified by BSE/SXM (back scattering electron/scanning electron microscopy) as crystals of sodium chloride along the aluminosilicate (Al, Si, O) pellet surface (Figure 20). Regions along the surface of the pellet that did not contain visible salt deposits, however, did contain localized high concentrations of both sodium and chlorine in what may have been the inclusion of a gettered phase embedded between an external glass layer and the pellet surface (Figure 21).

When the 80 ppmv NaCl, 4.6% H₂O emathlite pellet was cross sectioned at a salt deposit and examined by BSE/SXM, a somewhat darker outer zone at the periphery of the pellet was observed (Figure 22). The arrow on the photograph defines the location of the salt formation at the pellet surface. The external surface is rich in sodium and associated with chlorine only at the edge of the alumina-rich, silica-containing particle. The concentration of silicon and aluminum appears to vary throughout the gettered sodium layer, while the oxygen concentration appears to be

20x

50x

Figure 19 - Surface morphology of an emathlite pellet after exposure of 6 hours to 80 ppmv NaCl and 4.6 mol% water vapor at 1123 K and 11 atm in the bench-scale unit

Na 300 sec	Si 300 sec
Cl 100 sec	Al 300 sec
K 300 sec	O 300 sec

Figure 20 - Microprobe analysis of a gettered emathlite pellet surface after exposure of 6 hours to 80 ppmv NaCl and 4.6% H₂O at 1123 K and 11 atm total pressure in the bench-scale unit (Area 1)

Na	300 sec	Si	300 sec
Cl	300 sec	Al	300 sec
K	300 sec	O	300 sec

Figure 21 - Microprobe analysis of a gettered enathlite pellet surface after exposure of 6 hours to EC p_{env} NaCl and 4.6% H₂O at 1123 K and 11 atm total pressure in the bench-scale unit (Area 2)

Na	300 sec	Si	300 sec
Cl	300 sec	Al	300 sec
K	300 sec	O	300 sec

Figure 22 - Cross-sectional microprobe analysis of gettered emathlite pellet at surface salt deposit formation

constantly distributed. Within the alumina particle, localized regions of chlorine are observed. Because the prepared sample was polished prior to analysis, the crystals observed in Figure 20 are not apparent in this micrograph. Surface spikes that indicate considerable sodium and chlorine concentrations are possibly remnants of salt crystals.

Moving along the periphery of the gettered pellet to area 1 (Figure 23), we once again observed sodium in the smooth, external, getter surface. At this location chlorine is not associated with sodium. As previously indicated, sodium outlines the periphery of the alumina-rich, silica-containing particle. Localized chlorine pockets are detected within the silica-rich regions but are not found within the sodium-rich zone. An interesting feature of Figure 23 is the high affinity of sodium for the calcium particle at the periphery of the pellet.

One final set of BSE/SXM analyses were conducted along the edge of the gettered pellet (Figure 24). Again, a sodium-rich band extends to approximately 60 μm from the edge of the pellet. The region is observed to be rich in oxygen but deficient in chlorine. Aluminum within this region is somewhat lower than within the interior of the pellet, while no observable gradient in the concentration of silicon is indicated. Although these analyses demonstrate the nonhomogeneity of the gettered pellet composition, an enriched sodium layer always exists at the pellet surface.

Further polishing, which removes a thin layer of the cross-sectioned pellet, followed by reexamination of the area directly below the salt deposit, indicates the presence of reasonably high sodium concentrations from the pellet edge to 300 μm into the pellet interior (Figure 25). Chlorine is also observed at relatively high concentrations at this location, but the gradient slopes inwardly at 80 to 100 μm from the pellet edge. The sodium-rich layer contains high silica concentrations in addition to dispersed alumina particles. The presence of the high sodium chloride region below the Na-Si-O-Al zone represents the inclusion of salt embedded between the external glass layer and pellet substrate.

Ca	300 sec	Si	300 sec
Na	300 sec	Al	300 sec
Cl	300 sec	O	300 sec
K	300 sec		

Figure 23 - Cross-sectional microprobe analysis of gettered emathlite pellet (Area 1)

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Ca	300 sec	Si	300 sec
Na	300 sec	Al	300 sec
Cl	300 sec	O	300 sec
K	300 sec		

Figure 24 - Cross-sectional microprobe analysis of gettered emathlite pellet (Area 2)

Na	300 sec	Si	300 sec
Cl	300 sec	Al	300 sec
K	300 sec	O	300 sec

Figure 25 - Cross-sectional microprobe analysis of replaned gettered emathlite pellet

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Figure 26 - Panoramic micrograph of gettered emathlite pellet surface

A final panoramic view of the getter emathlite pellet surface is shown Figure 26. The smooth continuous layer lying above the mottled internal layers is probably the gettered glass phase. Note the high porosity of the resulting material in this zone.

Exposure of emathlite to simulated fuel gases containing alkali results in the formation of a substantially thicker glass coating, encapsulating and agglomerating blackened pellets. After 6 hours of exposure to the simulated fuel gas, an average 4.57 wt% sodium concentration results within the acid insoluble phase. This is equivalent to the acid insoluble content that results when emathlite is exposed for 6 hours to 80 ppmv NaCl, 4.6% H₂O in inert gas. The gettered acid soluble phase resulting in the simulated fuel gas exposure is approximately one-half the acid soluble concentration gettered in the 80 ppmv NaCl, 4.6% H₂O exposure. The blackened pellet surface observed on the simulated fuel gas pellets most likely resulted from the deposition of a thin layer of carbon at the glass-pellet interface through the Boudouard reaction of the simulated fuel gas constituents. The presence of 0.13 wt% carbon and 0.12 wt% sulfur in the resulting simulated fuel gas gettered pellets does not directly influence the sodium gettering activity of emathlite relative to the activity demonstrated in alkali-laden inert gas environments.

3.2.3 TGA Studies

A double-balance, high-temperature TGA apparatus was developed in a prior DOE program.^{2,9} This unit allows us to obtain kinetic and capacity data on gettering by various materials at relatively low gas-phase salt concentrations that are of interest in gasification systems and with carefully controlled and accurately measured conditions.

In the TGA system (Figure 27) a cup of molten salt such as NaCl or KCl is suspended from a microbalance and maintained at a desired temperature in the lower region of a furnace. The cup is suspended by two hangdown wires attached to opposite points on the cup rim. A stream of carrier gas, such as nitrogen, or simulated fuel gas, can be made to flow upward through a 2.54 cm id furnace tube, past the cup, mixing with vaporized salt as it does so. The concentration of salt in the carrier gas can be controlled by adjusting either the carrier gas flow rate or

Figure 27 - Two-balance TGA system for kinetic studies of gettering process

the salt bath temperature, which affects the vapor pressure of the salt and, hence, the rate at which its vapor is made available. The gas-phase salt concentration can be accurately calculated as a function of time, given the continuously recorded weight loss of the salt bath and the carrier gas flow rate. The concentration is always maintained well below the equilibrium vapor pressure at the lowest temperature in the furnace to prevent condensation.

The salt-laden carrier gas flows upward through the furnace tube, eventually past a pellet of sorbent material suspended from a second microbalance to permit continuous recording of the weight change of the sorbent. The suspension assembly for the pellet is a thermocouple, the juncture of which is inserted into the pellet to permit accurate and continuous recording of temperature. The suspension/thermocouple wire passes from balance to pellet via the center of the suspension channel so as not to interfere with the two salt cup suspension wires. The pellet temperature can be maintained independently of the salt bath temperature because of the four vertically arranged and independently controlled furnace heating elements.

The furnace is connected to the balance housing by a narrow neck through which pass the suspension wires for the salt pan and pellet. Between the wires and the wall of the neck is a tube, called the shroud, which can be remotely actuated to move up or down. A purge stream of an inert gas is introduced into the balance housing and flows out through the shroud and into the furnace. The purposes of the purge gas stream are to carry away any heat that may be conducted from the furnace zone to the balance housing and also to prevent the penetration of salt-laden gas into the balance environment. When the shroud is fully lowered it shields the getter pellet from the salt carrier gas and exposes it only to inert purge gas. When the shroud is raised, the pellet is exposed to the carrier gas, and the purge gas is diverted upward before it reaches the pellet because its momentum is much lower than that of the carrier gas. An additional small purge stream is provided between the shroud and the neck to prevent migration of salt

into this area. The carrier gas and purge gas streams mix above the pellet, leave the furnace, and are cooled to condense salt.

Most testing (except as noted) was done at atmospheric pressure, although we are able to test at 10 atm pressure with the TGA system. We tested primarily at low pressure for several reasons:

- Noise levels are proportional to pressure.
- Lower salt partial pressures can be achieved, permitting examination of the critical question of whether there is a lower equilibrium gas-phase concentration limit to gettering.
- The pressure level slowly drifts during pressurized operation because of an accumulation of impurities in the back-pressure regulator, causing a corresponding buoyant drift in weight readings.
- The equipment can be run unattended for extended overnight tests if in an unpressurized state.
- There is a reasonable basis for predicting the effect of operation at higher pressure, given data at atmospheric pressure.

3.2.3.1 TGA System Shakedown

The object of these initial tests was to assess the performance of the new TGA system in nonreactive operation so as to identify and solve any problems. Consequently, nitrogen was used as both the reaction gas inside the furnace tube and as the purge gas for the balance housing. Substantial noise levels in the balance weight readings were observed. As a result, the initial tests were basically attempts to understand and solve this problem.

The first test was made at 10 atm pressure with 5 l/min reaction gas and purge flows. During heatup to 1123 K, sample balance noise gradually increased to about 2 mg (peak to peak). Alkali balance noise increased rapidly to ~2 mg and leveled off. While the sample was being held at 1123 K for 7 min, the sample balance noise continued to rise to 3 to 4 mg. Various reaction gas and purge flows (from 0 to 5 l/min) had no noticeable effect on noise level. This pattern was

repeatable in subsequent runs. Two tests at 1 atm pressure showed the same qualitative behavior but much lower noise levels (0.6 mg) for both balances.

During the last low-pressure run we discovered that blowing air across the top flange of the furnace vessel caused a gradual reduction in sample balance noise. This effect was confirmed at pressure, where this noise level was reduced from 4 mg to less than 1 mg after cooling for 160 min. We postulated that cold purge gas passing down inside the shroud would be heated by the shroud, which was in contact with the hot reaction zone. Such heating would result in turbulent eddies that would collide with the hangdown assembly and cause noise. Noto and Matsumoto¹² showed analytically the turbulent vortex resulting from opposing laminar-flow-forced convection and free convection. We presumed that cooling the throat area of the system caused cooling of the shroud by convection and radiation (the shroud is not in contact with the metal surfaces except at a few ball bearings) and thereby repressed eddy formation.

Consequently, a water-cooled jacket was installed around the neck containing the shroud to cool the shroud more effectively. A test at 10 atm pressure showed that sample weight noise was only slightly reduced (from 4 to 3 mg) when this cooling was used. Blowing air across the flange, however, again caused a drop of noise to 0.6 mg. Alkali pan noise did not respond to either modification. A run was then made without the shroud, since apparently it was important to cool the purge gas stream by cooling the intervening air pocket and shroud between the flange and purge stream. Noise was only slightly less than previously observed but response to blowing air across the flange more rapid.

Since the presence of the shroud was unimportant, we next postulated that turbulence generation occurred at the hangdown assembly. Such turbulence could occur if the assembly were overheated by direct radiation from the furnace walls. To test this possibility we

lowered the shroud so as to shield the sample pan from radiation during the next run. Again, no effect on noise levels was discernible.

The next hypothesis to be tested was that the noise was caused by turbulent buoyant flow upward through the hangdown channel from the hot zone to the balance housing (and a forced countercurrent cold flow). At 5 l/min purge flow the value of Gr/Re^2 , a measure of the ratio of buoyant-to-inertial forces, is 16, indicating the importance of buoyancy. Cox et al.¹³ examined a vacuum microbalance in which buoyant flow caused by a vertical temperature gradient completely overwhelmed the cocurrent imposed flow by a factor of several hundred. Our system is somewhat different since the buoyant gas enters an enclosed space requiring circulation, but the magnitude of the recirculating flow should be enough to cause a transition from laminar flow to turbulence. Cox et al. found that baffling the hangdown tube to restrict upward flow or filling the balance housing with helium was an effective technique for eliminating the noise problem. Baffling would be difficult with our system because of possible interference with the three hangdown wires. On this basis we concluded that the use of a helium gas purge should be considered in the next test series.

In order to find out if a turbulent buoyant flux of nitrogen from the furnace to the balance housing was responsible for the noise levels observed, we attempted to quantify the problem. We calculated the quantity of gas that could be expected to pass upward through a narrow channel from a hot zone to a nonenclosed cold zone at the same pressure because of buoyancy effects. For turbulent flow the rate is:

$$Q = A \sqrt{\frac{Dg}{2f} \cdot \frac{\rho_c - \rho_h}{\rho_a}}, \quad (4)$$

where Q = the volumetric flow rate (at ρ_a)

D = the hydraulic diameter

g = gravitational acceleration

ρ_c = the cold gas density

ρ_h = the hot gas density

ρ_a = the mean gas density

A = the tube cross-sectional area

f = the friction factor for pipe flow.

For typical conditions equation (4) gives about 240 l/min (STP), compared to a purge flow of 1 to 5 l/min (STP). The Reynolds number for the calculated buoyant flow is about 8000, so the flow is turbulent. In reality the receiving cold zone is enclosed, so equation (4) will not be strictly valid, but there would probably be simultaneous upward and downward flows with a shear layer or alternating (in time) upward and downward flow that would, in any case, result in turbulence.

At this point we modified the TGA system to provide helium for the purge gas. Since cold helium is always lighter than hot nitrogen, it should have been possible to suppress the buoyant flow. A test run was made with no sample hangdown tube assembly except the thermocouple-balance wire connector in the balance chamber. Flow rates were 5 l/min N_2 forward flow and 1.25 l/min He purge flow (both STP) at 10 atm pressure. No sample balance noise was noticeable until the system temperature had reached 923 K. At this point the balance noise began but rose to only about 0.4 mg (peak to peak) at 1128 K. Alkali balance noise reached only about 0.3 mg. These were order-of-magnitude improvements from the previous nitrogen purge cases. Cooling the upper flange with air then caused further reductions in noise levels to 0.2 mg (alkali) and 0.1 mg (sample).

Since the combination of helium purge and cooling proved very effective, the purge arrangement was made permanent and a water cooling jacket was built on the upper furnace flange. With this arrangement we reinstalled the sample hangdown assembly with a 42 mg kaolin pellet in place. The salt pan was filled with about 2.5 g of alumina chips and a 10 atm run was conducted. This test confirmed that acceptable noise levels of less than 0.4 mg could be achieved but that balance readings are very sensitive to slight flow adjustments, such as occur when the

back-pressure regulator is adjusted, indicating that such adjustments should be avoided by regular maintenance. In this run the alkali balance showed a continuous weight increase (over 27 mg). We repeated this run at 1.07 atm pressure. Noise levels were one-tenth those in the high-pressure case. The sample balance showed a continuous weight loss (~3 mg) during this test. Various explanations, including chemical reaction with trace gas species, spalling, and gas adsorption were postulated to explain the behavior of the alkali balance readings, but no conclusive explanation had yet been confirmed. In the next test the alumina chips were removed and replaced by salt (NaCl). Under these conditions the alkali balance performance was as expected, and the previous weight gain problem was attributed to the presence of the alumina chips on the alkali pan.

The salt had previously been melted in its boat in a furnace. The kaolin pellet used in the previous tests remained in the reactor when the salt pan was replaced. At 10 atm pressure, forward flow (N₂) and purge (He) flow of 5.0 and 1.25 l/min (STP), respectively, were set. With the shroud down (pellet covered), protecting the pellet from salt, both balances showed irregular weight increases during heatup (12.5 mg alkali and 4 mg sample). Both leveled off at temperature (1093 K alkali, 1171 K sample), with low noise levels (0.4 mg sample, 0.3 mg alkali). Alkali concentration as NaCl in the gas was calculated to be 2.2 ppm (volume). We discerned no gettering by the kaolin sample pellet over the 2-to-3 hr exposure time.

This run was repeated with the same mass flow rates at 1.07 atm pressure. At 1093 K salt mole fractions of 1.8 to 2.6 ppm were calculated from the salt pan balance weight change data. At these conditions no gettering was indicated. At 1133 and 1163 K, mole fractions of 3.1 to 3.9 and 6.5 ppm were determined. Again, at these conditions no gettering of the kaolin pellet was indicated.

These and subsequent tests have shown that the salt feed control and measurement system operates reliably, that test data are

reproducible, and that the level of salt concentration can be quickly calculated. As shown below, theoretical considerations can be used to predict the result of a change in conditions. Balance reading noise levels are low, and salt can be fed at concentrations in the 0.5 to 20 ppmv range for extended time periods. Over this range the reproducibility of the salt feed system is estimated at ± 15 percent. Later in the test program lower levels of salt concentration were tried.

The mole fraction of salt in the gas stream was found to be inversely proportional to gas flow, as would be expected when the rate-controlling step is diffusion through stagnant gas in the salt pan above the molten salt. Since diffusivities are inversely proportional to pressure, mole fraction will be inversely proportional to pressure at a constant carrier gas mass flow rate, but partial pressure or concentration of salt will be relatively unaffected by pressure levels. For diffusion control the mole fraction is given by:

$$Y = \frac{\frac{P_o}{RT}}{\frac{P}{RT} + \frac{Qx}{DA}}, \quad (5)$$

where Y = mole fraction of salt in gas

P_o = equilibrium vapor pressure of salt (function of T)

P = system absolute pressure

T = system absolute temperature

Q = carrier gas molar flow rate

x = distance from top of molten salt in pan to pan opening

A = average open cross-sectional area in pan above salt

D = diffusivity of salt in carrier gas.

The first term in the denominator of equation (5) is trivial compared to the second for conditions in this test program, because x must be kept significantly larger than zero to avoid spilling molten salt.

3.2.3.2 Preliminary Gettering Tests and Operating Procedure Optimization

3.2.3.2.1 Initial exploratory tests. There were six phases of TGA testing in the program. The first phase was a system shakedown in which operating conditions were modified to combat unacceptable noise levels in the balance readings. In the second phase preliminary getting data were taken for a number of materials, but occasional operating problems were encountered that had to be solved. The third phase was a detailed look at getting by a single material, activated bauxite, the effects of temperature and gas-phase salt concentration on the sorption, and an evaluation of getting reversibility. In the fourth phase various candidate getters identified with the batch reactor screening tests were tested on the TGA in an attempt to find a getter material of higher capacity. The fifth set of tests was a brief examination of the effect of water vapor on bauxite getting. Finally, a detailed examination of the leading identified getter, emathlite, was performed. Details of these phases of TGA operation are described chronologically below.

Three materials were tested briefly during the shakedown and alkali-feed portions of the program on the double TGA. The first, as reported above, was kaolin, which showed no getting ability at any set of conditions. This lack may have been the result of poor porosity, small pellet size (3 mm), or inherently low reactivity.

A second material, a PFBC ash pellet (6 mm), was fabricated from Exxon PFBC miniplant third-stage cyclone catch and used in one test. Despite the fact that the pellet had been ashed in an oven to expel volatile matter, it continually lost weight during the TGA test run, even with a 9 ppmv salt level in the gas stream. This material and other ashes obtained from coal gasifiers have shown excellent NaCl sorption in batch reactor tests. They contain a significant quantity of potassium, however, which has been shown to be completely displaced into the gas stream by the adsorbed sodium.

Subsequent preliminary TGA tests were made with the leading candidate getter, bauxite (identified by ANL), conventional boiler ash, gasifier ash, and char ash. These are summarized in Table 55 and described here. Additional tests run specifically to deal with operating problems we encountered are also discussed. All available AA analyses for the TGA runs are summarized in Table 64.

The first four tests were made with bauxite as the getter material and were essentially exploratory in nature. In each run getter weight gradually leveled off, indicating an approach to the saturation gettering capacity of the pellet. In the first run a 0.36 g bauxite pellet gained 0.86 mg when exposed to 6.3 ppm salt at 1169 K. This is several times the pickup rate one would calculate from ANL^{10,11} data for activated bauxite, if one assumed a first-order dependence on salt concentration.

In the second run the same pellet was tested under five different sets of conditions, including one at 10 atm pressure to permit a higher gas-phase salt concentration. We could maintain gettering activity in succeeding test segments on this pellet only by increasing the alkali concentration from segment to segment. This is an indication that gettering capacity is proportional to gas-phase salt concentration, meaning that if nearly complete cleaning of a gas stream is desired the getter system configuration must be carefully selected to avoid a requirement of large quantities of sorbent.

Run 3 was made with a new bauxite pellet and only one set of operating conditions so that the pellet could be submitted for AA analysis. The bauxite performance was similar to that in the previous tests, and the corrected AA data¹⁴ showed a sodium weight gain of 0.82 mg, as compared to a recorded weight gain of 1.49 mg.

Preliminary analysis of the bauxite data indicated that the capacity of the bauxite was 0.4 wt% Na or less. These results were somewhat lower than those measured in the batch reactor tests conducted

Table 55
SUMMARY OF PRELIMINARY TGA RUNS^a

Test No.	Material, original wt, mg	Pressure, atm	Getter Temperature, K	Run Duration, hr	NaCl Concentration, ppmv	Getter Weight Gain, mg
1	Bauxite (360)	1	1169	2.0	6.3	0.86
2 A ^b	Bauxite (390)	1	1171	1.75	7.2	0.74
B		1	1170	1.75	11.5	0.75
C		1	1173	1.87	14.5	0.58
D		1	1214	2.7	17.3	0.80
E		10	1215	2.0	4.5	0.27
3	Bauxite (405)	1	1175	4.0	10.5	1.49
4	Bauxite (434)	1	1175	93	0.65	1.42
5	Shattered Bauxite (198)	1	1175	15	5.1	1.33
6	Boiler ash (180)	1	1175	27	5	1.57
7	Gasifier ash (210)	1	1175	16.5	10.1	0.5
8	Gasifier ash	1	1176	42+	8.7	>8 ^c
9 A	Char ash (225)	1	1175	140	9.5	>7 ^{d,e}
B		1	1173	180	0	-3.2
10 A	Bauxite (208)	1	1124	71	21	0.05 ^f
B		1	1128	18	8	~2.5 ^e
11	Bauxite (213)	1	1123	18	4	4.2

- Notes: a. Normal flows: 5 lpm N₂ carrier gas, 1.25 lpm He purge gas. (STP)
 b. Test numbers with alphabetic designations indicate continued exposure of the same pellet.
 c. Run conducted at low (0.12 lpm) STP purge helium flow, salt found on hangdown wires after run.
 d. Salt found on hangdown wires after run.
 e. Resume normal flows.
 f. Run made with 3 lpm N₂, 5 lpm He (STP).

on the same material but at much higher gas-phase salt concentrations. Porosimetry measurements on bauxite pellets preheated to 1173 K for 3 hours showed a porosity of 54% and a surface area of 98 m²/g. At this point in the program, gettering performance of the bauxite was disappointing, considering its excellent physical characteristics.

A TGA test (No. 4) was also conducted to determine whether bauxite was capable of gettering alkali present at low concentrations (1 ppmv at 1 atm, equivalent to 0.1 ppmv at 10 atm on a mol/cc basis). In this test the TGA was operated continuously (24 hr/day basis) without difficulty. A 93 hr run was completed in which a 372 mg (after devolatilization) sample of activated bauxite was exposed to an NaCl concentration of 0.6 to 0.7 ppmv (fluctuating) at 1175 K. The sample weight's curve trace showed the gradually decreasing slope characteristic of previous runs. Overall, a weight gain of 1.4 mg was observed, corresponding to 0.15 wt% Na if NaCl is absorbed without release of any substances. An extrapolation of the data suggested a maximum capacity of about 1.8 mg (0.19 wt% Na).

After test 4 an examination of the base-line sample weight trace (made during the period before the protective shroud was raised to expose the sample to salt) showed an unaccountable negative drift in the pellet weight reading of about 0.01 mg/hr. The observed rate of gettering had varied from 0.034 to 0.005 mg/hr during the run itself, so the background drift was an unacceptable source of error. The estimated capacity of the 93 hr bauxite pellet, corrected for the observed drift, would be 0.3 wt% Na. Atomic absorption analysis of the 93 hr test pellet indicated a 1.12 mg Na weight gain, which compared reasonably well to the corrected TGA balance weight data (0.94 mg Na). Results from this 93 hr test showed, therefore, that sodium gettering activity is present at relatively low salt concentrations, but the capacity and rate are low for the untreated activated bauxite material.

3.2.3.2.2 Drift tests. At this point we needed a series of tests to identify the source of the pellet weight drift. In these tests no getter sample was used and the sample pan was held at 1173 K, with salt.

concentrations of 6 to 8 ppm. Various start-up/shutdown and operational procedures were investigated.

In the first test the system was heated up over several hours with the shroud lowered. Then the system was held at 1173 K for about 20 hours, during which a weight loss of about 0.005 mg/hr occurred. Next, the shroud was raised, exposing the empty sample pan and the lower part of the alumina thermocouple support tube that holds the sample pan. A sudden apparent weight loss of 1.2 mg occurred. This effect had often been observed in the past and is attributable to changes in aerodynamic condition (drag, buoyancy) as the environment of the sample pan changes from downward-flowing helium to upward-flowing nitrogen. Then, during the next 34 hours, there was a drift indicating a weight loss of 0.04 mg/hr. At this point the salt concentration was reduced to less than 0.5 ppmv, and for the next 18 hours the average rate of loss was about 0.02 mg/hr and appeared to be decreasing. The sample temperature was raised to 1216 K for 30 hours, during which weight was relatively constant. It was unclear whether this represented simply a continuation of the 1173 K curve or a temperature effect.

In the second run heatup was again conducted with the shroud down. Then the sample pan was held at 1175 K, salt at about 6 ppmv. For 21 hours the average loss was 0.05 mg/hr and again seemed to be decreasing near the end of this period. The temperature was then raised to 1216 K and the weight held steady for 42 hours. No weight change could be detected when the temperature was reduced to 1174 K for another 5 hours. At this point the shroud was raised and the weight suddenly increased by 1.2 mg. This was directly contrary to the result when the shroud was raised in the first run and in our prior experience. Something other than hydrodynamics was clearly the cause. There then followed a 21 hour period in which weight was lost at 0.02 mg/hr before the run was terminated.

Various explanations for balance behavior during these two exploratory runs were examined. The one that seems to fit the results

best is that the drift is due to the degassing of adsorbed nitrogen gas by the alumina thermocouple support tube, which is the sample pan hangdown assembly. The lower part of the tube desorbs nitrogen slowly when exposed to hot helium with the protective shroud down (pellet covered) and adsorbs nitrogen very quickly when exposed to nitrogen with the shroud up (testing position). The upper part of the tube desorbs nitrogen slowly when exposed to hot helium with the shroud up. It never readsorbs nitrogen during a normal test run because when the shroud is lowered this section meets only cool helium. This theory also holds that the observed drift is independent of salt concentration, and, accordingly, there will be a one-time slow rate loss the first time the shroud is raised from the upper section and a slow weight loss each time it is lowered. There will also be a sudden weight gain each time the shroud is raised if it had been down long enough to complete desorption from the lower section. These are all in addition to the sudden aerodynamic effects occurring when the shroud is raised or lowered.

This theory was supported by a third exploratory test made without exposing the assembly to either air or nitrogen since the end of the previous test. With the shroud up, the weight held constant for about 20 hours. Then the shroud was lowered and a sudden (aerodynamic) gain of 1.2 mg was observed. During the next 40 hours the balance showed a weight gain of over 1.2 mg, which appeared nearly complete at the end of this period. Then the shroud was raised and the sudden (nonaerodynamic) weight increase of 0.4 mg occurred. Apparently enough time had been allowed to cook off the bottom section before this event. An hour later the shroud was again lowered and an additional 0.4 mg aerodynamic weight increase occurred. During the next 3 hours a gradual weight loss of 0.2 mg occurred, and this was obviously not complete. Still, the shroud was raised and a 0.2 mg weight loss occurred - desorption had not advanced far in the previous step, so aerodynamics predominated. Again the shroud was lowered, giving a 0.8 mg weight increase followed by the beginning of slow desorption before the run was terminated. This result was confirmed in another test with

salt off in which the protective shroud was repeatedly raised and lowered, with predictable results.

The operating procedure was consequently modified. The shroud is kept up during heatup, during which time the weight of the hangdown assembly becomes constant. During heatup the temperature of the salt is kept well below the level necessary to vaporize any significant amount of salt. The actual run is then started by raising the salt reservoir to the desired temperature level as quickly as possible. It takes about half an hour to reach the desired temperature (because of conduction within the liquid salt mass) and partial pressure, but the gettering rate is so low that the error introduced by this procedure is insignificant.

3.2.3.2.3 Additional exploratory tests. Using the new testing procedures, two additional materials were tested in the double balance TGA. The first was activated bauxite that had been pretreated in a shatter box for 15 minutes. This was an attempt to increase the adsorptive capacity of the bauxite by causing lattice dislocations in its structure that might create additional stable adsorption sites. The results are shown as run 4 in Figure 28. A 198 mg pellet gained 1.35 mg in 15 hours exposed to 5 ppmv NaCl in nitrogen. This corresponds to a capacity of about 0.3 wt% Na if gettering is by capture of NaCl with no release of material - the same capacity as previously observed for the untreated activated bauxite. The rate at which this capacity was reached was also about the same. Apparently, shatter box treatment of the bauxite powder did not significantly improve its gettering capability.

The second material tested was a 180 mg of boiler fly ash (run 6) that was exposed to 5 ppmv NaCl and reached a weight gain of 1.3 mg in 25 hr. This corresponds to a capacity of about 0.35 wt% Na adsorbed as NaCl. Because this fly ash material is similar to the gasifier ash materials that had performed well on the batch reactor, the TGA results are somewhat discouraging if potassium losses¹⁴ are not considered.

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Figure 28 - TGA alkali gettering data

This supposed similarity, and its wider availability, were the reasons for selecting this fly ash for testing. Surface area loss for this material was also significant, as discussed below.

Results of the first six TGA tests conducted are summarized in Figure 28. The first two runs were again exploratory and covered a consisted of exposing a bauxite pellet to a variety of salt concentrations, temperatures, and pressures. The data, however, are quite consistent if plotted in the form of weight gain versus salt broad range of test conditions. The second run, in particular, exposure (partial pressure of NaCl x time) as shown in Figure 28. This behavior is consistent with a rate expression of the form:

$$\frac{dx}{dt} = k P_{\text{NaCl}} [x_e - x], \quad (6)$$

where x is the weight fraction of Na (or NaCl)

x_e is the maximum weight fraction of Na (the gettering capacity)

k is a rate constant

and P_{NaCl} is the partial pressure of NaCl.

The results of the bauxite tests fall fairly close together. The curve for run 4 is probably low, relative to the other bauxite curves, because of the drift error discussed above. The boiler ash material seems to approach a higher capacity than does bauxite, but not nearly as high as had been anticipated if potassium loss¹⁴ is not taken into account.

A gasifier ash pellet was tested at 1173 K and 10 ppm NaCl at 1 atm (run 7). This material showed a weight gain of only 0.5 mg (corresponding to 0.1 wt% Na if no species are released upon capture of NaCl) in 16.5 hr of exposure. This gain was about one-third that of gettering observed for other materials - bauxite and boiler ash - after similar exposure. This test run may have been terminated prematurely, since the observed rate of weight gain had not yet begun to decline. Once again, however, potassium loss must be taken into consideration.¹⁴ Run 8 was made with a gasifier ash pellet, but with one-tenth the helium

purge rate. Its primary purpose was to investigate the possibility that the helium purge might be blowing past the pellet and diluting the NaCl concentration near the pellet. At the end of this run, salt was found to have condensed on the hangdown wire within the shroud, negating interpretation of the test results but indicating that helium flow through the shroud must be maintained at its prior, relatively high level.

3.2.3.2.4 Interaction of carrier gas and purge gas. At this point we calculated the flow momenta in the vicinity of the shroud exit. The results for our normal operating conditions of 5 l/min of N₂ and 1.25 l/min of helium showed that nitrogen had twenty times the momentum of the helium, suggesting that penetration of the helium into the vicinity of the pellet would be unlikely. This analysis was supported in a test at ambient conditions in which a laser beam shadow graph was used to visually distinguish the interface (by density difference) of nitrogen and helium at their characteristic flows. We found that the helium was swept upward within a very short distance (~0.5 cm) of the shroud exit. On the basis of analysis and tests, we conclude that helium penetration, therefore, is not a problem and that the weight gain of the gasifier ash in run 7 was real. This conclusion again suggests the possibility that the reaction is based upon a proportionality between the salt concentration in the gas and absorbed phases (adsorption equilibria). This possibility has important implications for a getter system in which the gas phase alkali concentration would have to be reduced to a very low level.

Long-duration, continuous test runs had now been made on several candidate getter materials at relatively low salt concentrations, 10 ppm and less (equivalent to 1 ppm and less at 11 atm). Testing had encompassed activated bauxite, boiler ash, PFBC ash, gasifier ash, and gasifier char ash. Each of these materials had been screened previously in the 11 atm batch reactor apparatus and showed relatively high capacities, at least at the high (80 ppm) salt concentrations, and indicated relatively fast reaction rates. Results,

in general, from the double balance TGA tests, however, showed significantly lower performance levels on all these materials. The low adsorption rates on the TGA tend to support rate and/or capacity dependence on gas phase salt concentration.

This observation was partially supported by results from test 9 on a char ash pellet in which some desorption from the pellet of the salt may have been indicated when the bulk gas salt was turned off and the pellet continued to be exposed to hot, salt-free gas. In this test a 225 mg char ash pellet was exposed to 9.5 ppm NaCl at 1175 K. This material had shown good gettering capacity (~10% Na by weight) in batch reactor tests at 1173 K, 11 atm, and 80 ppm NaCl. A rate expression developed from these batch reactor data predicted that the TGA-tested pellet should have gained about 9 mg in 75 hours, but we actually measured a gain of only 1 mg in the first 75 hours of the TGA test. The rate of weight gain accelerated during this period, in contrast to previous experience with both reactors. In the next 65 hours the pellet gained about 6 mg and acceleration was continuing. At this point the salt supply became insufficient to continue the salt-exposure of the char ash pellet, so, to avoid a slowly declining salt concentration, the salt was turned off completely.

The reversible mechanism would mean that desorption of salt should occur if the pellet were kept hot and exposed to salt-free gas. Consequently, with the salt off we exposed the pellet to flowing nitrogen at 1173 K for 180 hours before terminating the run. Desorption of 3.2 mg occurred.

The TGA reactor was then opened, and a thin layer of salt was found to have accumulated within the shroud, evidently across its entire cross section and in contact with the hangdown wires. Salt was apparently able to diffuse upward through the slowly moving helium purge gas. We hypothesized that this most likely occurs in the boundary layer near the wall of the shroud, since the diffusion velocity is orders of magnitude less than the mean helium velocity in the tube, and that salt

condenses first on the shroud at the point where the temperature is low, gradually expanding across the cross section until it contacts the pellet hangdown assembly. This process is very slow, and no salt had been seen within the shroud in any of the previous, shorter runs, except for the gasifier ash test in which a small fraction of the usual helium purge was used.

In order to evaluate this phenomenon independently of gettering by the pellet, we made a blank run (no pellet) at conditions identical to the char ash test just finished. No weight gain was observed for the first 80 hours, but then a sharp weight gain began, ~5 mg in the next 40 hours. This result indicated that it takes about 3 days at this salt concentration and these flow rates for salt diffusion up along the inside of the shroud to influence balance readings. The early portion of the char ash run, therefore, might be valid. Whether or not it is so, we tentatively concluded that the char ash, like the gasifier ash, was a poor getter, especially considering potassium loss. Further testing of both materials was abandoned.

In order to try to extend run times beyond the apparent 80 hour limit, another blank run (no pellet) was made at the same conditions, except that the nitrogen carrier gas flow was reduced from 5 to 3 l/min and the helium shroud purge flow was increased from 1.25 to 5 l/min. These numbers were chosen so that the helium momentum at the shroud exit would now exceed the nitrogen momentum by a factor of two and possibly preclude salt penetration of the shroud and condensation on the wires. This run lasted over 180 hours. No weight gain was detected and no salt was found inside the shroud after the test. This result suggested that long runs could, indeed, be made.

In the next TGA run (test 10), activated bauxite was run at ~1123 K using the new helium and nitrogen flows at a salt concentration of 21 ppm. No significant gettering occurred in 70 hours. Then the flows were changed back to the old values of 5 l/min (N_2) and 1.25 l/min (He). The pellet gained 2.5 mg in 18 hours. This result presumably

meant that the higher helium flow used to protect the hangdown wires from salt also formed a jet into the reaction zone that prevented salt from reaching the pellet. On the other hand, the rapid gettering at the lower helium flow suggests that this operating flow could be used, since long runs might not be necessary with bauxite.

An analytical investigation was performed for the TGA unit to predict the interaction between the salt-bearing nitrogen reactant gas (5 ℓ/min) and the helium purge gas used to protect the balance and hangdown assembly from salt contamination. This study has confirmed previous experimental findings in that operating the TGA with a 1.25 ℓ/min helium gas does not result in the purge gas interfering with the pellet reaction. At 5.0 ℓ/min helium flow the purge gas does sweep down over the reacting pellet, possibly resulting in the dilution of the local salt concentration or preventing salt from entering the pellet reaction zone (see appendix). We decided to make subsequent runs with 1.25 ℓ/min helium purge gas and 5 ℓ/min nitrogen carrier gas.

3.2.3.2.5 Salt accumulation. A subsequent test on a bauxite pellet (test 11) at the 1.25 ℓ/min helium flow condition and 1123 K showed a 4.2 mg pellet weight gain in 18 hours, with 2.5 mg of that effect occurring in only about 1 hour. This high initial rate was too fast to be accounted for by vaporization of the available salt from the boat. We suspected that some salt had accumulated in the packed bed at the bottom of the reactor used to heat the nitrogen carrier gas. This salt would have fallen there from the condensation zone on the outside of the shroud during cool down and reactor disassembly. Consequently, the reactor was opened up, vacuumed, and restarted with a fresh sample of bauxite but with no salt in the boat. Again, a rapid weight gain occurred. Then the reactor was opened and washed out with water until the conductivity of the filtrate was similar to that of the feed deionized water. A similar test followed in which no gettering occurred, indicating that the salt had been purged from the reactor. Washing the reactor between runs was added to the operating procedure.

Although extra salt may have been available in early portions of previous runs, within a few hours the true gaseous salt concentration should have been as measured by the salt balance. On this basis, the capacities estimated from the previous tests should be valid.

As discussed above, a number of operating problems, including noise, drift, purge gas effects on the getter, and salt accumulation between runs, were encountered and solved. The system was now operating smoothly and routinely with the revised operating procedure. Following a brief note on pellet surface areas, we will describe extensive data taken after this optimization of the operating procedure.

3.2.3.2.6 Surface area measurements. The low performance levels of all the different getter materials tested on the TGA up to this point relative to results of tests in the batch reactor apparatus have led us to speculate that other mechanisms may be present. One possible explanation was that the TGA pellets may be sintering during the TGA start-up procedure, when the pellet is first exposed to the hot gas (1173 K) for about 24 hours prior to beginning the salt feed and for many hours during the actual test. This environment and operating procedure would be similar to that expected in an actual plant. In the batch reactor apparatus, cold getter pellets are introduced directly into the hot, salt-laden gas, and exposure times are significantly shorter (6 hours or less).

To examine this possibility, surface area measurements were made of dried (573 K) samples of each candidate getter tested so far, as well as samples heated for 48 hours at 1173 K. The results (Table 56) showed that surface area loss does occur, but apparently not to the extent needed to explain the reactivity decline in the ash materials, except for the conventional boiler ash. Bauxite showed about the same surface area, indicating better surface stability.

Table 56
SURFACE AREAS OF HEATED GETTER MATERIALS, m^2/g

<u>Material</u>	<u>573 K, 3 hr</u>	<u>1173 K, 48 hr</u>
Char Ash	1.1	0.39
Gasifier Ash	9.8	5.4
Boiler Ash	12	0.33
Bauxite	39	44
Shattered Bauxite	26	11
Kaolin	0.42	0.10

3.2.3.3 Activated Bauxite Characterization

Eight successful runs were subsequently made to test bauxite as a getter material. These are summarized in Table 57. All were made at 1 atm total pressure. The first six runs were adsorption tests, and, in Figures 29 to 31, both weight gain and gas-phase salt concentration are given as a function of time. Notice that capacity is higher at 1123 K than at 1173 K at each gas phase concentration level, and capacity is greater at higher gas-phase salt concentrations at each temperature. These results are consistent with a reversible adsorption mechanism.

For a first-order reaction, weight gain should depend on the duration of exposure to NaCl at a given concentration. The product of the partial pressure of NaCl and time, therefore, is a useful index of the accumulated exposure of a pellet. Figure 32 compares the results of Tests 12 to 18 on this basis. Note that this is similar to Figure 28.

Two tests were run to see if the adsorption is completely or only partially reversible and to quantify the rate at which desorption occurs. These tests also are shown in Table 57. Each test consisted of an adsorption portion in which a pellet was exposed to a relatively high salt concentration until virtually saturated and a desorption portion in which the temperature of the salt vaporization section of the TGA

Figure 29 - Results of TGA bauxite tests (high salt concentration)

Figure 30 - Results of TGA bauxite tests (medium salt concentration)

Figure 31 - Results of TGA bauxite tests (low salt concentration)

Figure 32 - Summary of TGA bauxite tests

Table 57

SUMMARY OF DRY GAS ACTIVATED BAUXITE CHARACTERIZATION TESTS ON THE TGA*SYSTEM

Test No.	Original Wt, mg	Getter Temperature, K	Run Duration, hr	Mean NaCl Concentration, ppmv	Getter Weight Gain, mg
12	208	1123	19	11.5	4.0
13	203	1174	22	9.4	2.7
14	201.7	1123	44	3.3	3.2
15	212.4	1173	46	3.4	2.2
16	205.8	1123	96	0.79	1.8
17	217.8	1173	92	0.78	1.4
18	201.7	1123	43 ^a	12	4.4
			30 ^d	0	-1.1
19	197	1173	48 ^a	11	3.4
			70 ^d	0	-0.3

* All runs with 5 l/min(STP) N₂ carrier gas.^a Adsorption test^d Desorption test

tubular reactor was suddenly lowered to such a point that virtually no salt was transferred to the gas stream passing the pellet. The weight gain and salt concentration histories of these two runs are shown in Figures 33 and 34.

The adsorption results agree well with the previous bauxite runs if allowance is made for the greater time of exposure, as shown in Figure 32, where tests 12 and 18 are compared. The results also confirm the hypothesized effects of temperature and gas-phase salt concentration on capacity in a reversible mechanism.

The desorption results mean that the adsorption is not completely reversible. Transfer of salt from the gaseous state to the adsorbed reversible and irreversible states may be by competing parallel or consecutive mechanisms. If we assign a lesser value to reversibly adsorbing salt than to irreversibly adsorbing salt, the capacity advantages of operating at lower temperatures are apparently reduced.

Several additional bauxite runs were made later in conjunction with system testing during emathlite evaluation. See Section 3.2.3.6.

3.2.3.4 TGA Evaluation of Alternative Getters

On the basis of the batch reactor screening results, six of the leading candidates, i.e., those with a gettering capacity significantly better than that of activated bauxite, were selected for testing on the TGA system. Table 58 summarizes our results for the six candidate getters evaluated. In two tests at 1073 K and 1173 K, Vansil® performed much worse than in batch reactor tests. The cause of this difference is unknown, but we suspect it to be the loss of reactivity (perhaps surface area or active sites) during the long, hot, TGA start-up period.

Two tests were also run with Ebony Novacite.® In the first of these, the raw pellet was placed in the reactor, and it continuously lost weight through oxidation of carbon residue. This loss was still

Figure 33 - Results of TGA bauxite desorption test at 1123 K

Figure 34 - Results of TGA bauxite desorption test at 1173 K

occurring when the actual salt exposure was begun. The results of run 22 are therefore invalid, except to show that significant gettering did occur. The test was repeated using a pellet that had been baked in air for several days to remove carbon before the run. This pellet showed a 4.7% weight gain in 267 hours. In run 23, the highest weight gain obtained

Table 58
ALTERNATIVE GETTER TGA DATA SUMMARY*

Run	Material	Salt Concentration, ppmv	Temp. K	Run Length, h	Weight Gain, mg	AA Na ^c Wt Gain, mg	Original Pellet Wt, mg
20	Vansil®	13.4	1173	26	0.3	0.13	207.3
21	Vansil®	12	1073	24	0.3	0.19	187.9
22	Ebony Novacite® ^a	13.9-5.7	1123	165	2.3	9.66	276.0
23	Ebony Novacite® ^b	12.1-3.1	1123	267	14.5	17.11	308.0
24	Zeolite	12.0-9.6	1123	50	0.8	3.10	172.1
25	Emathlite	11.0-3.7	1123	284	10.8	10.57	197.1
26	Diatomaceous earth	9.7-4.2	1123	300	6.5	5.85	139.1
27	Novacite®	11.2-5.0	1123	283	4.9	4.22	196.5

* All runs with 5 l/min(STP) N₂ carrier gas.

^aEffect masked by carbon oxidation.

^bPrebaked to remove volatiles.

^cIncludes adjustment for background sodium.

with any material on the TGA up to that point. The results are plotted in Figure 35. The length of the run was limited by the salt supply.

Zeolite failed to absorb much salt in its TGA test; the weight gain was only 0.5% and had leveled off.

Emathlite was the fourth candidate getter to be tested. It performed very well, gaining 5.5 wt% in a 280 hr test. As with the

Ebony Novacite,[®] saturation had not yet occurred when the run had to be ended, as shown in Figure 36.

The last two getters to be tested on the basis of the batch reactor screening results were diatomaceous earth and Novacite.[®] Both materials demonstrated a substantial increase in capacity over that of activated bauxite, but both materials absorbed salt at much lower rates than those previously obtained with activated bauxite. On a weight percentage basis, the diatomaceous earth at 4.7 wt% gain showed a particularly high capacity. Along with emathlite and Ebony Novacite,[®] it was the most promising candidate emerging from the bench-scale and TGA systems. These results were confirmed further by AA analyses, as shown in Table 58. Diatomaceous earth and Novacite[®] TGA curves are shown in Figures 37 and 38.

At this point, we decided to eliminate Ebony Novacite[®] from further consideration. First, its high background potassium content is detrimental, because it is displaced by sodium during the initial gettering period. Second, the need to pretreat the material for residual carbon would add to its processing costs. Third, its initial cost was higher than that of the other two candidates. This narrowed our choices to diatomaceous earth and emathlite. The selection of emathlite was due to its lower initial cost and better performance in the TGA tests. Another factor involved was the availability of Lee and Johnson's data,^{10,11} if necessary, to aid in choosing between the two candidates.

3.2.3.5 Effect of Water Vapor on Bauxite Gettering

Lee et al.¹¹ have found evidence to indicate that absorption of alkali by bauxite is greatly enhanced by the presence of water vapor in the carrier gas. Consequently, after run 27, the TGA system was modified to permit the addition of several parts of water vapor to the carrier gas stream. Upon completion of system modifications, two tests (runs 28 and 29) were made to investigate system performance with

Figure 35 - Results of TGA testing of Ebony Novacite®

Figure 36 - Results of TGA testing of emathlite

Figure 37 -- Results of TGA testing of diatomaceous earth

Figure 38 -- Results of TGA testing of Novacite®

activated bauxite in the presence of water vapor. Both the weight gain and gas-phase salt concentration for these two runs are shown as a function of time in Figure 39.

In each of these tests (summarized in Table 59), a 204.5 mg activated bauxite pellet was held at 1123 K and exposed to salt concentrations on the order of 10 ppmv. During run 28, the pellet gained 5 wt% in the first 110 hours of operation. In this same period, the salt concentration decreased from an initial value of 20 ppmv to 7.5 ppmv. An additional 2.8 wt% gain was obtained in the next 147 hours of operation, in which time the concentration decreased to 6.6 ppmv. At the conclusion of the test, the reactor was opened, and salt was found to have accumulated inside the shroud. As on other similar occasions, we concluded that the run had been allowed to proceed for too long a period of time.

Figure 39 -- TGA results for activated bauxite in the presence of water vapor

Table 59
TGA DATA SUMMARY - ACTIVATED BAUXITE, WATER VAPOR

Run	Material	Concentration, ppmv	Temperature, K	Length, hr	Wt Gain, mg	Original Wt, mg
28	Activated bauxite	22.0-6.6	1123	257	16.1	204.5
29	Activated bauxite	24.0-8.1	1123	113	12.5	204.5

Carrier gas: 5 l/m (STP) with 4 mol% H₂O, balance: N₂.

On the basis of the above observation, we decided to repeat the previous test conditions but to discontinue TGA operations prior to the initiation of salt accumulation within the shroud. Consequently, run 29 was made, in which the activated bauxite pellet gained 6.0 wt% in 113 hours of operation. During this period the salt concentration decreased from an initial value of 24 ppmv to 8.1 ppmv. The observed weight gain was consistent with that observed in run 28, since the salt concentration was somewhat higher. No salt was found in the shroud at the conclusion of the run. The capacity observed in the presence of water vapor was found to be a factor of two to three times greater than was observed for activated bauxite without moisture present in the system, verifying the finding of Lee et al.¹¹

3.2.3.6 Emathlite Characterization

The last phase of TGA testing was an examination of emathlite as a getter (Table 60). Most of these runs were made with 4 mol % water vapor in the carrier gas stream. Salt was occasionally found to have accumulated on the hangdown wire of the pellet holder after a run. The point at which this accumulation began could easily be discerned by

Table 60

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EMATHLITE TGA DATA SUMMARY

Run ^a	Salt Concentration, ppmv	Temperature, K	Run Length, h	Weight Gain, mg	AA Na Wt Gain, mg	Original Pellet Wt, mg
30	17 to 7	1123	117	20.8	— ^b	218.6
31	19 to 7	1123	143	23.4	18.6	216.5
33	8.2	1173	135	18.7	15.9	207.6
34 ^c	3 to 2.2	1123	193	17.2	9.6	207.5
			(60) ^d	(2.9) ^d		
35 ^c	3 to 2.4	1123	255	6.2	6.3	177
			(195) ^d	(3.0) ^d		
36	~ 3.9 ^e	1123	97	3.4	3.6	236.3
37	5.8 to 4.0	1175	95	3.3	3.7	220.4
38 ^f A	4.3 to 3.5	1123	117	3.2		210.9
D	0	1123	20	0.1	3.7	
39 ^c	~ 15.1 ^e	1123	121	19.4	11.5	263.3
			(38) ^d	(4.3) ^d		
40 ^c	20 to 16	1123	95	10.5	9.1	206.2
			(58) ^d	(5.5) ^d		
41	8	1123	28	1.	1.9	180.8
42 ^g	43 to 49	1123	18	3.7	3.8	192.5
44 ⁱ	11 to 9	1123	70	3.3	4.1	208.0
45	~ 13 ^e	1123	66	5.5	5.3	191.4
46 ^c	12 to 9.5	1123	98	5.7	6.6	201.9
			(85)	(4.2)		
47 ^{c, j}	43 to 32	1123	77	12.9	10.6	218.7
			(36) ^d	(5.2) ^d		
48 ^j	55 to 38	1123	146	20.3	15.5	229.5

^a All runs 5L/min carrier gas with 4 mol % H₂O, balance N₂ except as noted^b Not available^c Salt found on hangdown assembly inside shroud after test.^d Approximate time and weight gain at which salt accumulation on hangdown assembly began.^e Mean salt concentration based on salt weights before and after runs.^f Run consisted of adsorption and desorption portions.^g Carrier gas flow 1.25 lpm nitrogen.^h Not yet available.ⁱ 1% H₂O^j Carrier gas flow, 1 L/min nitrogen

looking at the curve of weight gain vs time. Atomic absorption sodium weight gains are also shown in Table 60, and these closely follow the TGA observed weight gains, except in those runs in which earlier hangdown-wire salt accumulation had begun. In those cases the AA number is between the weight gain at the breakthrough point and the final, high, weight gain.

In run 30, the emathlite pellet gained 9.5 wt% in less than 120 hours. In the previous emathlite run (No. 25), made with a water concentration of only several parts per million, the pellet gained only 5.5 wt% in 280 hours of operation, and this had been the best performance of any getter tested to date without the presence of any substantial amount of water vapor. The further improvement of run 30, as well as the results presented earlier on activated bauxite, suggest that gettering occurs to a much greater extent in the presence of water vapor.

Run 30 was terminated before saturation to avoid salt migration onto the hangdown assembly. With respect to run 30, we found upon opening the system that the pellet was encased in a hard, glassy material. Subsequent analysis by electron spectroscopy for chemical analysis (ESCA) showed the surface of the pellet to be composed of Na_2SiO_5 . No chlorine was present, indicating that the amount of sodium gettered must have been rather large, since in previous runs a portion of the weight gain had been attributed to chlorine.

Run 31 was made at the same conditions as run 30 in an attempt to verify the significant results obtained in that run. Confirmation was achieved since the weight gain versus time curves for both runs were essentially identical, and, furthermore, the same hard, glassy material was found on the pellet of run 31. Figure 40 shows the results of runs 30 and 31.

We modified the TGA system by installing an additional salt vaporization boat on the hangdown assembly, positioned in tandem with the existing crucible and approximately 2 cm below it. The addition of

Figure 40 — TGA results for emathlite at 1123 K (high salt concentration)

Figure 41 — Results of bauxite test after addition of second salt vaporization boat

the new assembly doubles both the surface area for salt vaporization and the salt capacity. With this arrangement it was now possible to achieve the same concentration of salt in the gas as in previous tests, but at a reduced salt reservoir temperature. In the past we found that the concentration would decline during the course of a test as the depth of molten salt in the crucible was reduced because the vaporized salt had to diffuse a greater distance through the stagnant gas in the crucible to the flowing carrier gas. With the new arrangement the salt level declines at only half the rate for a given concentration in the bulk gas, and salt concentrations should, therefore, be steadier over the reaction periods under study (100-200 hours).

A trial run (TGA 32) was made with bauxite and was intended as a demonstration of the operability of the new salt vaporization system. It was allowed to proceed for only 25 hours, as opposed to the 100 to 250 hours in previous bauxite/water vapor runs. Results (Figure 41) were consistent with those of previous tests. In addition, salt concentration was found to be steadier than in similar data from previous runs using only one vaporization boat.

In run 33 our test matrix for emathlite was resumed with a test at 1173 K and 8.2 ppmv salt (Figure 42). Again, the salt concentration in the bulk gas stream remained very steady. The weight gain history for run 33 at 1173 K was very similar to those of the duplicate 1123 K runs 30 and 31 plotted in Figure 43 as weight gain vs cumulative salt exposure (NaCl partial pressure times time). This means that the temperature effect on the gettering rate is minimal. The small temperature effect and the fact that rate declines slightly with increased temperature suggest that the rate-controlling step may be physical absorption (or diffusion), although there is apparently a subsequent, relatively fast, chemical step involved in the sequence, as concluded from the analytical chemistry results discussed below.

After run 33 the TGA sample shroud was replaced because of the severe corrosion it had suffered over the course of the program. At

Figure 42 -- TGA results for emathlite at 1173 K

Figure 43 -- Summary of early TGA results for emathlite

this time, also, the platinum hangdown wires were replaced and the pellet suspension system was changed. Up to this point the pellet had been supported on a platinum mesh that was attached to the hangdown alumina thermocouple tube with wires. It had been difficult to remove the pellet from this arrangement because the molten glass formed during the gettering reaction attached the pellet to the mesh. In the new arrangement a platinum wire would be wrapped several times around the pellet and attached to wires holding it to the hangdown assembly. After a run the pellet would now be removed with its platinum wrap and sent to Analytical Chemistry, where the platinum would be recovered during analysis.

A run (No. 34) was then made in which an emathlite getter pellet was exposed to about 2.5 ppmv NaCl in nitrogen at 1123 K, 1 atm, for 193 hours. The pellet gained weight corresponding to 8.3% of its original weight of 207.5 mg. Noise in the weight signal, however, was severe in the latter part of the run. After the run, salt was found to have condensed up inside the shroud on the hangdown wires. Figure 44 shows the weight gain history of run 34. The rapid and essentially linear increase in weight gain subsequent to approximately 80 hours appears due in part to salt pickup by the hangdown assembly. Examination of the system following the run showed that a substantial leak had developed in the seal between the shroud and the reactor vessel neck. This leak permitted helium to bypass the shroud in transit from the balance housing to the reaction zone. In turn, we attributed the apparent early salt accumulation observed in TGA 34 to the absence of a sufficient helium purge flow through the shroud. At this point the TGA system was disassembled and a new seal installed.

Subsequent to reassembly of the TGA system, TGA 35 was run in an attempt to duplicate the test conditions used in TGA 34. An emathlite pellet was exposed at 1123 K and atmospheric pressure to approximately 2.6 ppmv salt for 255 hours. The pellet weight was initially 177 mg. During the 255-hour exposure period, an overall weight gain of 6.2 mg was observed, with only about 3.1 mg of this gain achieved in the first 200 hours of the run, as shown in Figure 45. The

Figure 44 — TGA results for emathlite run 34

Figure 45 — TGA results for emathlite run 35

200 hour point is especially relevant because a sharp increase in pellet weight was observed for the remaining 55 hours. In addition, the sample weight had essentially leveled off prior to the final weight gain excursion. We attributed most of the additional 3.1 mg weight gain to salt accumulation on the hangdown assembly during the final 55 hours of the run. Salt accumulation was indeed observed on the pellet hangdown assembly in a postrun inspection. By comparing Figures 44 and 45, we can see that repair of the seal appeared to extend the "salt-free" period of exposure by a factor of about two.

Although the salt accumulation problem had been addressed, two other concerns arose during runs 34 and 35. The first of these was the increase in noise level on both balances relative to previous runs. The sample noise increased from an average value of ± 0.05 mg to ± 0.2 mg, while the salt balance level increased from ± 0.1 mg to ± 0.4 mg. Secondly, weight gains before salt accumulation began were much less than expected, based on a first-order extrapolation of the data previously obtained at higher bulk gas phase salt concentrations and that assumed the emathlite capacity to be invariant. At this point we attempted to pinpoint any problem sources by examination and recalibration, if necessary, of the balance and associated electronics, flow control systems (helium and nitrogen), water injection system, and all other hardware involved, such as seals, regulators, and fittings. The only problem uncovered was a leaky seal in the nitrogen carrier gas circuit. A leak in this seal permitted carrier gas to short-circuit the reactor tube and flow in the annular area between the outside of the reactor tube and the inside of the pressure vessel wall. The seal was replaced. Subsequent to replacing the seal, we conducted a flow test using a laser light shadow graph, which indicated that the helium and nitrogen flows were behaving as expected. We decided to continue testing, using the same conditions as in TGA runs 34 and 35.

In a further attempt to resolve the discrepancy between the expected and the achieved weight gain at the lower concentrations, microscopic examination and AA analyses were made of the two pellets

from runs TGA 34 and 35. Under the microscope both pellets exhibited the characteristic glass coating observed in previous runs with emathlite. More sodium had apparently been gettered than is indicated by extrapolating the "salt-free" portion of the weight gain curve to the conclusion of the run. On a dry basis extrapolated values were 2.1 and 1.9 wt% gain for runs 34 and 35, respectively. On the same dry basis the overall weight gain obtained in TGA runs 34 and 35 was 8.68 and 3.67 wt%. The AA analyses tend to confirm the above observation. Total sodium values of 4.95 and 3.80 wt% were obtained for TGA runs 34 and 35, respectively. After correction for weight loss during heat-up (4.49%) and background sodium (0.09 wt%) and potassium (0.83 wt%), the above AA values give expected weight gains of 4.07 and 2.92 wt%, respectively. Postreaction values for potassium used in the above calculations were based on AA analyses for this element. The results of all completed AA analyses are presented in Table 64. Although we cannot be certain about the quantity involved, gettering seemed to occur during the final segment of both runs.

We proceeded with the emathlite test matrix as summarized in Table 60. Run 36 was a repeat of the test conditions used in runs 34 and 35, in which salt accumulation on the hangdown assembly had made the results questionable. Run 36 was not allowed to proceed for a long enough time to permit the occurrence of salt breakthrough to the hangdown assembly. The observed weight gain for this run (see Figure 46) approximated that of runs 34 and 35 before salt accumulated on the hangdown assembly. A salt concentration curve is not presented for run 36 because of excessive noise in the salt balance, which made it impossible to measure concentration over a short period. We were able, however, to calculate an average concentration of 3.9 ppmv, based on the initial and final weights.

Run 37, summarized in Figure 47, was at test conditions similar to those of run 36, except for reaction temperature. A temperature of 1175 K was used rather than the 1123 K used in run 36. The observed weight gain was very similar but slightly lower than that

Figure 46 — TGA results for emathlite run 36

Figure 47 — TGA results for emathlite run 37

Figure 48 — TGA results for emathlite run 38

obtained at 1123 K, indicating that chemical reaction itself is not rate limiting. Possible explanations include diffusion effects (gas through solid or solid state) or an adsorption-type process.

Run 38, summarized in Figure 48, consisted of two periods of testing. The first was essentially a duplicate of run 36. For this period, the two runs were similar. The second period was with the same pellet, except that we terminated the salt flux by switching off the vaporization zone furnace. The objective of this portion of the test was to find out if a gettered emathlite pellet desorbs. This was not the case, however, because of the insoluble nature of the NaCl/emathlite reaction observed in previous AA analyses.

Run 39, Figure 49, was an attempt at a high salt concentration test to confirm earlier (runs 30, 31, and 33) TGA results, which showed excellent gettering performance by emathlite. Unfortunately, problems were encountered with the salt balance. The highest salt balance noise levels to date were obtained during the course of TGA 39. This made it impossible to determine actual salt flux while the test was in progress. Thus, the average value of 15.1 ppmv reported in Table 60 is

Figure 49 -- TGA results for emathlite run 39

based on actual salt boat weights made before and after the run. Subsequent to the run we determined that the noise was generated by contact of the lower salt boat with the thermocouple located in the carrier gas preheat zone. This problem was resolved by reducing the length of the boat suspension wires by about 1/2 in. The problem did not occur in the subsequent test, TGA 40. Examination of the sample weight time curve for run 39 showed that breakthrough of salt to the hangdown assembly occurred about 40 hours into the run, at which point the pellet had gained 1.52 wt% or 4 mg, as compared to 7.37 wt% or 19.4 mg over the entire 121 hour reaction period. The 19.4 mg weight gain includes any salt that accumulated on the pellet hangdown assembly.

Because of the problems encountered in run 39, we attempted to repeat this test in run 40. In TGA 40 a 206.2 mg emathlite pellet was exposed to approximately 19 ppmv NaCl in the nitrogen carrier gas at 1123 K. The pellet gained 5.24 wt% in the 95 hour run, but salt was found inside the shroud on the hangdown wires after the test. The sample weight time curve (Figure 50) revealed that breakthrough of salt to the hangdown assembly had begun to occur at about 58 hours into the

Figure 50 — TGA results for emathlite run 40

run, at which point the pellet had gained 2.3 wt%. We believe that the run was valid to this point, on which basis this high concentration run showed much less gettering activity than had been observed in the earlier 10 ppmv emathlite runs mentioned above.

Several hypotheses for the explanation of this phenomena were investigated in the next several runs. The first hypothesis was that in earlier runs the platinum mesh used to support the sample pellet had acted as a substrate for molten glass migration from the pellet. In turn, this would reduce the degree of saturation of the sample at any point and, hence, allow a greater weight gain versus time to occur. In the more recent runs (subsequent to TGA 33), the pellet had been supported by a few wraps of a single platinum wire. We tested this hypothesis in TGA 41 by attaching a platinum mesh to the emathlite pellet. The gettering activity observed in this test was again relatively low, thus substantially disproving this hypothesis. The curve for run 41 is shown in Figure 51.

The second hypothesis tested was that the helium purge gas for the balance housing was diluting the salt concentration in the vicinity of the pellet in the more recent tests. We thought this had not

Figure 51 -- TGA results for emathlite run 41

occurred in the earlier tests because a leaky seal (replaced between runs TGA 34 and 35) was operative. This seal between the shroud and the annular neck joining the balance housing and reactor vessel provided an alternate means of escape for this purge gas. We tested this theory during the latter part of TGA 41 by reducing the helium purge from the normal value of 1.25 l/m to 0.5 l/m at 21.5 hr into the run. No change in gettering activity occurred. We had expected this, since earlier in the program we had demonstrated with shadow graphs and analytically that the purge gas at 1.25 l/m was unlikely to influence the environment of the pellet. These analyses and shadow graph data were based on a nitrogen carrier gas flow of 5 l/m.

The third hypothesis was that during the earlier test a portion of the nitrogen carrier gas was escaping through a leaky seal (replaced after TGA 35) at the bottom of the reactor. On this basis the pellet would then be exposed to a considerably higher salt concentration than that based on normal flows and salt boat weight loss measurements. We decided to make a test (TGA 42 in Table 60) at a low carrier gas flow and high salt concentration. We would thus be able to discern

Figure 52 — TGA results for emathlite run 42

what magnitude of leak would have been necessary to explain the discrepancy. A flow meter had been installed prior to TGA 42 to ascertain if carrier gas was bypassing the reactor. No leakage was observed.

When the weight gain in TGA 42 (see Figure 52) is plotted against cumulative exposure ($\mu\text{atm-hr}$), the curve closely coincides with curves of the more recent runs (TGA 36, etc.). On this basis, a leak rate of about 80 to 90% would have had to occur in the earlier runs for the curves to coincide.

Another conceivable explanation was that the character of the emathlite had changed, but this conflicts with the fact that all pellets were made from the same batch of emathlite.

Run 43 was an attempt to determine whether the discrepancy was the result of a change in the TGA system or of a change in the emathlite. Therefore, bauxite was tested in a water-vapor-laden carrier gas in an attempt to duplicate bauxite runs 28, 29, and 32. The TGA curve for run 43 is shown in Figure 53. The results showed that the apparent activity of bauxite, too, was reduced in TGA 43 relative to the earlier

Figure 53 -- TGA results for activated bauxite, run 43

Figure 54 -- TGA results for emathlite run 44

runs. After exposure to 500 $\mu\text{atm}\cdot\text{hr}$ NaCl, the bauxite gained ~ 3.6 wt% in runs 28, 29, and 32 but only about 1.3 wt% in TGA 43. This decline is similar to that observed for emathlite and indicates that the difference was system related and not a function of the particular getter used.

While considering tests to identify system-related changes in apparent activity, we made run TGA 44 to test the effect of water vapor content on the gettering activity of emathlite. In TGA 44 the water vapor content of the carrier gas was maintained at 1 mol % as compared to the 4 mol % utilized in other runs. Apparent activity was slightly less in TGA 44 than in the other emathlite runs subsequent to TGA 35. The results are shown in Figure 54.

At this point we resumed investigation of system-related effects. We postulated that perhaps there were flow streamlines in the pellet vicinity that affect the salt concentration there. These streamlines would arise as a result of the expected buoyancy of hot nitrogen carrier gas from the reactor tube to the reactor outlet plenum. In turn, this would be accompanied by a downward flow of salt-free gas in a different area of the tube. The old shroud, which had been replaced after run TGA 33, was warped, and as a result its outlet cross section expanded, thereby restricting the supposed recirculation flow. On the other hand, the new shroud still retained its original, elliptical cross section. To test this hypothesis, run TGA 45 was made, in which a baffle was attached to the shroud to essentially eliminate the recirculating flow. The results obtained (see Figure 55) showed a small improvement in activity relative to recent baffle-free tests.

As a further test, we reinstalled the old warped shroud and tested to see if the old emathlite performance was thus recovered. The results are shown as run TGA 46 in Figure 56. Salt eventually began to accumulate inside the shroud at 85 hr into the run, but until this point the weight gain versus exposure ($\mu\text{atm}\cdot\text{hr}$) curve fell within those of the later runs, thus disproving the shroud geometry hypothesis.

Figure 55 — TGA results for emathlite run 45

Figure 56 — TGA results for emathlite run 46

We had thus explored several possible explanations for the discrepancy in gettering rates between TGA runs 30, 31, and 33, on the one hand, and later runs (TGA 36 on), on the other. We concluded that the major difference was the leaking carrier gas seal that had been fixed after run TGA 35. The weight gains observed in the earlier runs had been real, as verified by AA results, but the salt concentration was much higher than had been thought. To verify the high gettering capacity demonstrated for the emathlite in the earlier tests, we made several more runs at high salt concentration.

The results of TGA 47 are shown in Figure 57. Significant salt capture occurred, but salt was found on the hangdown wire after the test, accounting for the high weight gain rate observed near the end of the run. Inspection of the equipment after the run showed that the top seal was again leaking and the shroud purge gas was short-circuiting through the leak, allowing salt to enter the shroud. The system was modified to eliminate the rubber seal and to attach the shroud rigidly to the reactor neck, precluding further leaks.

Run TGA 48 (Figure 58) was a repeat of the previous run. A long successful run was obtained. The emathlite gained almost 9 wt% in 146 hr at high salt concentration. This was an important verification of emathlite's high gettering capacity, which, as will be shown, is essential for a getter reactor to be of reasonable size.

To summarize, TGA runs 30, 31, and 33 showed exceptionally good gettering behavior for the emathlite. Later TGA runs (TGA 36 on) had lower gettering rates. The early runs are consistent with one another when plotted as weight gain vs cumulative exposure, defined as the product of salt concentration and time. Similarly, the later runs are mutually consistent. A corresponding decline in bauxite performance between TGA runs 32 and 43 and the fact that all the emathlite pellets had been made from the same batch of emathlite powder demonstrate that the emathlite had not changed. We believe that the difference is the result of several system mechanical problems that created an

Figure 57 -- TGA results for emathlite, run 47

Figure 58 -- TGA results for emathlite, run 48

artificially high salt concentration near the pellets in the earlier tests, principally because the carrier gas bypassed the reactor tube. These problems were eliminated between runs 33 and 36.

Rate data from only the later runs has been used to evaluate emathlite system performance in Section 3.3.

3.2.3.7 Physical and Chemical Characterization of Gettered TGA Emathlite Pellets

In an attempt to gain insight into the alkali gettering reaction mechanism in emathlite, TGA 30 was subjected to extensive physical and chemical analyses. Using ESCA, we analyzed the pellet's outer glass surface and identified it as Na_2SiO_5 . The sodium-to-silicon ratios vary within 100 Å from the pellet surface, as shown in Table 61. At a magnification of 12.6X, the glasslike Na_2SiO_5 phase is observed to contain bubbles and fractures and appears to be raised from the underlying pellet surface (Figure 59).

Table 61
ESCA ANALYSIS OF GETTERED EMATHLITE (TGA 30), wt%

Location	Na	Si	O	Ca	K	Cl	P	Al
Surface	0.26	0.12	0.62	ND*	ND	ND	ND	ND
100 Å depth	0.11	0.20	0.59	0.02	0.008	0.01	0.02	0.04

*ND = not detected

The TGA 30 glass phase was carefully separated from the emathlite substrate material. Both the glass and substrate were subjected to emission spectroscopy characterization. The emission data presented in Table 62 indicate that a significant increase in the sodium concentration results in the glass phase formation. Silicon also, is, detected in the glass phase, while aluminum and calcium tend to segregate specifically within the pellet substrate. An almost

12.6X

12.6X

Figure 59 -- Gettered emathlite pellet (TGA 30)

Table 62
EMISSION SPECTROSCOPY DATA OF GETTERED EMATHLITE
(TGA 30), wt%

Element	Unreacted Material	Exterior Glass Phase	Interior Black Phase	Interior Tan Phase
Al	2	2	7	3
B	<0.07	<0.07	<0.05	<0.07
Be	<0.07	<0.07	<0.05	<0.07
Bi	<0.07	<0.07	<0.05	<0.07
Ca	1	0.3	0.5	1
Cd	<0.07	<0.07	<0.05	<0.07
Co	<0.07	<0.07	<0.05	<0.07
Cr	0.05	0.09	0.09	0.05
Cu	<0.07	<0.07	<0.05	<0.07
Fe	3	2	2	2
Ga	<0.07	<0.07	<0.05	<0.07
Ge	<0.07	<0.07	<0.05	<0.07
Mg	0.7	0.9	1	0.7
Mn	<0.07	<0.07	<0.05	<0.07
Mo	<0.07	<0.07	<0.05	<0.07
Na	<0.07	13	2	2
Nb	<3	<2	<2	<3
Ni	<0.07	<0.07	<0.05	<0.07
P	0.7	0.5	0.7	1
Pb	<0.07	<0.07	<0.05	<0.07
Sb	<0.07	<0.07	<0.05	<0.07
Si	15	18	16	14
Sn	<0.3	<0.2	<0.2	<0.3
Sr	<0.07	<0.07	<0.05	<0.07
Ti	0.3	0.2	0.7	0.3
V	<0.07	<0.07	<0.05	<0.07
Zn	<0.3	<0.2	<0.2	<0.3
Zr	<0.07	<0.07	0.2	<0.1

equivalent magnesium concentration is observed in both the glass and pellet material.

The partitioned and total alkali concentrations in TGA 30 were determined quantitatively by means of AA analysis. Table 63 indicates that a final concentration of 10.66 wt% sodium results after gettering, while less than 0.2 wt% of the background potassium is retained. In the pellet interior only 3.81 wt% sodium is detected. The ratio of sodium in the glass phase to that in the interior of the pellet is approximately equivalent in both the water soluble and acid soluble fractions. Seventy-six percent of the total gettered sodium concentration in the glass phase is detected in the acid insoluble fraction, while 85 percent of the total sodium content is detected within the acid insoluble pellet substrate material. During sodium gettering in emathlite, 76 percent of the 0.83 wt% total background potassium concentration is estimated to have been released.

Table 63
ATOMIC ABSORPTION ANALYSIS OF GETTERED EMATHLITE (TGA 30), wt%

<u>Atomic Absorption</u>								
Phase	<u>Water Soluble</u>		<u>Acid Soluble</u>		<u>Acid Insoluble</u>		<u>Total</u>	
	Na	K	Na	K	Na	K	Na	K
Glass	0.69	<0.06	1.86	<0.06	8.11	<0.06	10.66	<0.2
Interior	0.16	<0.06	0.42	<0.06	3.23	<0.06	3.81	<0.2

Microprobe analysis of the interior pellet substrate indicates that two types of material result during gettering (Figures 60-62). Smooth regions are rich in either sodium or silicon but deficient in aluminum, relative to the surrounding areas, or are silicon and aluminum rich but sodium deficient. Chlorine, calcium, and magnesium are not detected within these high-oxygen-containing regions. We suggest that these regions most likely were part of the original gettered glass phase. Coexisting with the smooth areas are porous mottled regions that

Figure 60 -- Microprobe analysis of TGA 30 emathlite

Figure 61 -- Microprobe analysis of TGA 30 emathlite

Figure 62 -- Microprobe analysis of TGA 30 emathlite

contain a lower sodium concentration. Chlorine, again, is not detected in these areas, but localized regions of magnesium and calcium are. The silicon content varies, while aluminum appears to be present in concentrations either equal to or lower than those detected in the smooth region. This region is considered to represent the pellet interior, which has gettered sodium but has not formed the glass structure.

Repeating the TGA 30 test successfully produced getter pellet TGA 31 with a similar glass encased surface. Cross-section SEM analysis of TGA 31 revealed the formation of three concentric zones within the pellet: a 250-to-550- μm thick exterior glass phase; a 1100-to-1600- μm darkened region, and an interior light region (Figure 63).

Because of the high porosity at the surface of the gettered emathlite pellet, only a semiquantitative elemental scan line profile could be generated. Figure 64 shows that a sodium gradient within the pellet has appeared during gettering and that it is not limited to within the glass phase formation. The oxygen and silicon scans indicate a possible increase in concentration within the pellet interior.

Secondary BSE of Area 1 in Figure 63 indicates an enhanced concentration of silicon at the periphery of the glass phase, with a somewhat depleted sodium concentration relative to that observed within 100 to 150 μm of the pellet edge (Figure 65). As the concentration of both silicon and sodium decreases at distances greater than 150 μm from the pellet edge, aluminum tends to increase. In the glass phase the oxygen concentration tends to be constant, while carbon is detected in isolated regions. Although the initial gettering reaction had been conducted with gaseous sodium chloride, chlorine is not observed within the resulting glass phase. Similarly, magnesium, calcium, and iron, which are present in the original getter material, do not partake in the formation of the surface glass.

In Area 2 of Figure 63, the BSE/SXM data indicate a lowered sodium concentration relative to the external glass phase, while both silicon and aluminum coexist as principal and secondary elemental constituents (Figure 66). Oxygen is present in this phase at

10 X

Figure 63 -- Cross-sectional view of sodium gettered emathlite in water vapor (TGA 31)

Figure 64 -- Semiquantitative Na, Si, and O concentration profile through gettered emathlite pellet TGA 31

Figure 65 — Microprobe analysis of sodium gettered emathlite in water vapor - area 1 (TGA 31)

Figure 66 -- Microprobe analysis of sodium gettered emathlite in water vapor - area 2 (TGA 31)

concentrations equivalent to the external surface concentration, while localized concentrations of magnesium, calcium, and carbon are observed in the absence of chlorine and iron.

The BSE/SXM micrographs of Area 3 in Figure 63 indicate the sodium-free, high-silica, secondary alumina getter pellet center (Figure 67). From these data we conclude that after extended exposure in the alkali-laden environment, gettering proceeds inwardly from the exterior pellet surface but does not completely saturate all available reaction sites within the emathlite matrix after 143 hours.

Prior to analytical characterization of the gettered sodium concentration, several of the TGA pellet surfaces were photographed. As shown in Figure 68, the surface of TGA 36 is glassier at a position located directly in the gas flow path and, along the pellet sides. Bubbles are observed in localized areas, and, in the region where the platinum wire is in contact with the pellet, the glass has flowed around the wire. The reaction time and gettered alkali concentration for this TGA exposure has not permitted the wire to become entirely encased with the glass. Figure 69 clearly demonstrates the variation in glass coverage at the pellet surface as a dependence of alkali concentration for TGA pellets 37 and 39.

Prior to gettering, there had been gaps between the platinum wire and the TGA 40 pellet surface. After gettering in several areas, the gaps had been filled by the glass, which extended to the bottom and along the platinum wire (Figure 70). Numerous bubbles were also observed in the resulting glass phase. These micrographs do not clearly dismiss the possibility that platinum catalyzes sodium gettering in emathlite, but they do demonstrate that platinum serves as an additional substrate for glass flow.

3.2.4 Gettering Reactions and Mechanisms in Aluminosilicate Materials

Numerous chemical and physical reactions have been considered to occur during gettering of sodium by aluminosilicate materials. This

3-211

Figure 67 -- Microprobe analysis of sodium gettered emathlite in water vapor - area 3 (TGA 31)

32x

32x

32x

Figure 68 -- Surface morphology of TGA 36

TGA 37

Temperature: 850°C

Pressure: 1 Atm

Gas Composition: 4 ppm NaCl, 4% H₂O/N₂

Time: 140 Hours

TGA 39

850°C

1 Atm

10-15 ppm NaCl, 4% H₂O/N₂

120 Hours

Figure 69 -- Surface morphology of TGA 37 and TGA 39

Figure 70 — Surface morphology of TGA 40

section reviews the literature, siting phase transitions and chemical reactions in aluminosilicate complexes that have been previously investigated. A discussion is also presented that attempts to define the composition of the phases that result in the water soluble, acid soluble, and acid insoluble fractions of the getter materials. Finally, a preliminary gettering reaction mechanism is proposed, emphasizing the alkali reactions in emathlite.

3.2.4.1 Literature Review

Two principal chemical phases have been identified during the course of the Westinghouse studies. By x-ray diffraction analysis nepheline (NaAlSiO_4) was detected in the gettered kaolin material, while using ESCA, the surface of gettered emathlite that had been exposed to alkali in the presence of water vapor was identified as a Na_2SiO_5 glass phase.

Kaolin consists of a hexagonal network of silicon-oxygen tetrahedra with a superimposed layer of aluminum-oxygen/hydroxide octahedra that share oxygen at the tetrahedra apex. The repeating Si-O/Al-O-OH unit typifies the $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ kaolinite structural unit. Charges within the unit cell are balanced, since very little substitution occurs within the lattice. Dickite and nacrite contain structural units similar to kaolinite, only differing in the manner in which the silicate units are stacked one above the other. Halloysite or hydrated kaolin consists of the kaolinite unit layer separated from adjacent unit layers by molecular water.

During heating kaolin undergoes a series of dehydration reactions and lattice rearrangements. These include:

- Shrinkage and loss of pore water from the lattice at 373 to 423 K.
- Volatilization of residual organic material inclusions at 200 to 573 K.
- Volatilization of pyritic sulfur at 673 to 773 K.
- Loss of hydroxyl water at 773 to 1173 K.

These reactions are capable of altering, but not completely destroying, the lattice cell structure. When kaolin is heated, phase transitions concurrently result within the structural lattice. As a function of temperature these transitions can schematically be written as:

As demonstrated in this study, activated bauxite outperforms the sodium gettering activity of kaolin. Activated bauxite is composed of 81.5% Al_2O_3 and 10% SiO_2 , with trace concentrations of additional elements as iron within the gibbsite or boehmite lattice. The functional unit structure of gibbsite $[\text{Al}(\text{OH})_3]$ consists of a layer of Al ions sandwiched between two closely packed hydroxyl ions. In gibbsite two of the three octahedrally coordinated sites are occupied. In the ideal gibbsite structure, oxygen lies at the bottom of one layer, directly above the oxygen at the top of the underlying layer. The true gibbsite structure is somewhat distorted, resulting in a monoclinic cell. Heating gibbsite produces γ -alumina, usually through the metastable formation of boehmite $[\text{AlO}(\text{OH})]$. Although gibbsite is stable at low temperature, a transition to diasporite $[\alpha\text{-AlO}(\text{OH})]$ can occur at elevated temperature. This is followed by a conversion of the alumina lattice into corundum ($\alpha\text{-Al}_2\text{O}_3$) at temperatures greater than 723 K. The

phase transitions during the thermal heating of activated bauxite can schematically be written as:

Although kaolin and activated bauxite demonstrated effective sodium gettering capacities, emathlite outperformed both materials. As a fuller's earth, emathlite (70.12% SiO₂, 13.29% Al₂O₃, 4.84% CaO, 3.20% Fe₂O₃, 2.47% MgO, 1.13% K₂O, 0.10% Na₂O, 0.36% TiO₂, and L.O.I. 4.49%) belongs to the smectite group [(1/2 Ca, Na)_{0.7}(Al, Mg, Fe)₄ [(Si, Al)₈O₂₀](OH)₄ · xH₂O]. The quantity of interlayer water adsorbed varies according to the type of smectite and the nature of the interlayer cations. Calcium smectites usually take up two layers of water molecules, while sodium smectites have a greater swelling capacity, and the quantity of water continuously varies. The interlayer water can be regarded as a hydration molecule that surrounds replaceable cations as sodium and calcium. In the di-octahedral smectites, magnesium ions that occupy interlayer sites are considered to contribute to the cation exchange capacity. This capacity ranges between 80 and 150 meg/100 g but varies with particle size and the nature of the cation. Usually, the exchange capacity is greater for calcium than for sodium. The principal cause of cation exchange in smectites is the imbalance of charge in the fundamental layer, and not the presence of unsatisfied surface valence sites.

The typical mineral structure of smectites consists of separated layers, each of which contains a plane of Al ions sandwiched between two inwardly pointing sheets of linked SiO₄ tetrahedra. The central structure can be considered as a layer of gibbsite in which two out of every three OH ions are replaced by apical oxygens in a Si₄O₁₀ pseudo-hexagonal network. The charge

balance in smectites results from the substitution in both the octahedral and tetrahedral sites of interlayer cations, usually sodium or calcium. Upon heating, the interlayer water of smectite is lost between 373 and 523 K. Residual bound water remains within the smectite lattice to about 573 K, at which time a slow loss of the constitutional OH water begins. Rapid loss of this water occurs at 773 K and is nearly complete at 1023 K.

Differential thermal analysis (DTA) curves of smectite vary, displaying generally one endothermic peak at low temperature, corresponding to loss of interlayer water, and another at a maximum of 973 K, corresponding to loss of OH water.

The chemical reactivity of aluminosilicate materials as kaolin or activated bauxite results from reaction at the Al^{3+} ions. In nature, minerals with the Al^{3+} ions that have coordination numbers of 4, 5, and 6 include the nepheline series. Carnegieite, NaAlSiO_4 , defined as the reaction product of kaolin and gaseous NaCl , belongs to the nepheline series. Carnegieite forms a tetrahedral network of SiO_4 and AlO_4 with Na^+ ions occupying cavities in the lattice framework.

Smith¹⁵ indicated that NaAlSiO_4 has four polymorphic structures. High carnegieite (cubic) is stable from the liquidus temperature down to 1523 K, where it is transformed into the high nepheline (orthorhombic). At 1173 K an inversion occurs, forming low-nepheline (hexagonal), which is stable to room temperature. If high carnegieite is rapidly quenched to 963 K, a displacive inversion results, forming the low carnegieite structure.

Structurally similar potassium complexes of KAlSiO_4 are known to form. Five polymorphs of KAlSiO_4 have been identified and include kalsilite (hexagonal), which is stable below 1123 K, and synthetic kaliophilite (hexagonal), which forms near 1273 K. More commonly, the orthorhombic KAlSiO_4 structure is stable from 1173 K to the liquidus temperature.

The structure of high carnegieite is based on the cristobalite framework, and the presence of the high-low inversion suggests that the structure of the low carnegieite that forms has resulted from a collapse of the cristobalite-type framework. In the nepheline unit half the Si ions can be replaced by Al, with the charge balanced by the dispersion of Na or K ions into the cavities of the structure.

As previously shown in the kaolin and activated bauxite phase transitions that occur at elevated temperatures, γ -alumina and/or solid solutions with silica as cristobalite result. These glasslike structures, depending on their position within the aluminosilicate matrix, influence the adsorption and chemisorption reactions of the alkali that occur. Belousov and Kruchinin¹⁶ demonstrated that as the alkali content within the glass increases, the melting temperature and upper crystallization limit is lowered by 323 to 353 K. The anomalous dependence of the properties of the glass on the $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ ratio (the alumina effect) is due to a change in the structural role of the Al^{3+} ion. Decreasing the coordination number of aluminum results in a looser packing of the ions, with a simultaneous decrease in the density, hardness, and chemical stability of the glassy and crystalline silicates.

In the molecular dynamic studies by Soules,¹⁷ the silicon atoms in sodium silicate glasses were shown to be tetrahedrally coordinated by oxygen atoms, with the tetrahedra linked at the corners to form random, interconnected rings. Sodium atoms were shown to be clustered around nonbridging atoms. These features produced by the molecular dynamics calculations demonstrated that the resulting structure was independent of direction and/or covalent bonding. Soules concluded that the basic structure of the glass, including tetrahedral coordination of the Si atoms, Si group linkage, and the location of Na^+ , depends only on the relative size of the ions and the short-range repulsive forces and is not sensitive to the use of different attractive potentials. He also demonstrated that the average number of sodium atoms within 3Å of a nonbridging oxygen atom goes from 2 to 3 as the

concentration of the alkali increases from 9 to 30 percent. The sodium ion bonding to nonbridging oxygen atoms is relatively weak, while the distribution of sodium ions around bridging oxygen atoms for the random distribution calculation indicates no preferential bonding. Potassium and calcium ion clusters around nonbridging oxygen atoms in a random network of silicon tetrahedra were proposed in a similar manner to that of the sodium ion. A coordination of six Na ions, however, was projected around the free oxide ions.

The free oxide ions may result on the alkali silicate glass surface from the cleavage of Si-O- and Na-O- bonds within the lattice, forming a "new" glass surface possessing adsorption and chemisorption characteristics different from the original glass material. Weyl¹⁸ proposed that the surface chemistry of the solid must obey the Pauling electrostatic valence rule. That is, electroneutrality must be observed even in the smallest unit, resulting in a screening formation by an electron cloud or anions around a positively charged nucleus. On the "newly" formed glass, ions present on or coming to the glass surface are electrically polarized so that a maximum screening of the surface ions results. Screening may be improved by a structural rearrangement of the surface whereby less polarizable ions remain at the initial location or tend to sink into deeper layers of the surface, while more polarizable ions protrude from the surface. This mechanism can bring about an electrostatic charge on the "new" surface, or, if strongly deformed surface anions completely screen the less polarizable cations in the deeper layers, a negative supercharge may form. Charles¹⁹ demonstrated that polarization and diffusion in a silicate glass was the result of alkali ions self-diffusing, ultimately eliminating surface defects.

The ion adsorption properties of glass surface first observed by Gunther²⁰ were those of bivalent metal ions into glass. The bonds were shown to be weakened by heating, while bonds between the glass surface and monovalent cations were unaffected. Solutions containing Sn^{2+} , Bi^{3+} , Fe^{3+} , and Ti^{4+} ions in contact with the glass surface cause

an adsorption of the metal ion to the glass in a frequently accompanied ion exchange process. This adsorption proceeds in the form of a zeolite-type exchange of a heavy metal ion by an alkali ion.

Weyl²¹ states that alkalis can be exchanged only by movement ions (Li^+ , Tl^+ , Ag^+) below the relaxation temperature of the glass and that an ion exchange of this type does not modify the lattice. In the relaxation interval, valency does not influence the ion exchange any longer, and the alkalis are readily exchanged, probably through an ion rearrangement.

The mobility of alkali ions in silicate glasses is rather high. When the glass is heated, the most mobile alkali ions are expected to be the first to evaporate from the surface, while alkali ions inside the glass material begin to migrate toward the surface by diffusion. Having reached the surface, the alkali ions have the potential to leave, thus influencing the properties of the resulting glass. The dealkalinization mechanism of alkali-bearing silicate glasses or the reduction of the alkali (i.e., oxide) concentration within the surface layer is

- Affected by diffusion or by an electric field in which the alkalis migrate from the glass to the surface, or is
- Affected by the alkali ions leaving the surface through evaporation, by chemical processes with the surroundings, or by an ion exchange process.

Rexer's data²² supported the first phase of the dealkalinization process. The glass plates used in Rexer's studies were heated to 873 to 923 K for 24 to 36 hours, and an increase of 14 to 18 percent alkali resulted on the surface. Keppeler and Hechter's data^{23,24} on glass containing a total of 18.5 percent alkali oxide when exposed to 723 to 848 K temperatures for 7 hours indicated that, up to 823 K, the alkali concentration on the surface continually increased, while at higher temperatures this rate of increase was lowered, suggesting evaporation of the surface alkali.

Williams and Weyl²⁵ experimentally demonstrated that, in aqueous solutions, an ion-exchange process occurred in the glass whereby H^+ ions replaced surface Na^+ ions. This reaction was related to the

square root of time. The dependence of the reaction on temperature showed that the reaction rate was primarily controlled by the diffusion velocity of Na^+ ions to the surface. King²⁶ demonstrated that alkali can be removed from the surface of lime alkali silicate glasses by electrodialysis. When in contact with the glass surface, melted or fused salts precipitate in an ion exchange reaction. Kraus and Darby²⁷ demonstrated that when the glass surface is in contact with the melt, Na^+ may be exchanged by Li, K, Cu, Pb, Zn, and Ag ions. They proposed that during the exchange only the sodium ions within the glass structure were replaced by metals of adequate radius.

Jones and Homer²⁸ investigated the hydrolytic processes that occur on the surface gel layer of silicate glasses. They found that acid did not affect the Si-O-Si bonds within the glass structure but disrupted the Si-O-Na bonds. The alkali forms a soluble salt with the anion of the acid and leaves the system to be replaced by hydrolyzed Si-OH or Si-OH₃ groups, conceptually the reverse of the alkali-gettering process. Boggs and Mosher²⁹ showed that gaseous HCl dissolves in the gel surface layer of the alkali lime silicate glasses, and the H^+ ions that migrate into the gel surface are ultimately replaced by Na^+ ions.

Budd and Frackiewicz^{30,31} proposed that electrophilic and/or nucleophilic attack on the silicate structures was possible. The simple silicate glasses were generally agreed to consist of a continuous network containing Si-O bonds with certain discontinuities. The discontinuities in the network take the form of singly bonded oxygen atoms, each bearing a negative charge.

In order to achieve electrical neutrality, positive metal ions as Na^+ or Ca^{2+} are located adjacent to the discontinuity. Because of positive charge, the M^+ ions could then be subject to nucleophilic attack (i.e., OH^- , O^{2-}). With the monovalent and divalent ions, nucleophilic attack is unlikely because of extreme stability of these ions. If present, the trivalent Al^{3+} ion could possibly be attacked, resulting in a tetravalent Al^- ion. The positive ions are generally disregarded as centers for chemical attack, and any movement of these ions into the attacking reagent is assumed to result from diffusion induced by localized electrical forces.

The negatively charged, nonbridging oxygen atoms could be subject to electrophilic attack (i.e., H^+ , Na^+). In considering the Si-O network, the silicon atom will be more subject to nucleophilic attack, while the oxygen will undergo electrophilic attack. The actual mechanism of attack will depend on the type of reagent and on the position of the attack within the network. The electrophilic attack on nonbridging atoms can schematically be written as

In the gettering reaction H is characteristic of Na or K, while X represents Cl. In this reaction the negative charge on the oxygen atom is transferred to the X-leaving group, simultaneously releasing M. The resulting structure now contains the entering cation at the exposed Si-O site.

Small quantities of oxygen, the high-temperature fuel gas, or metal oxides (i.e., Na_2O , K_2O) dissolved within the glass structure may also react with the Si-O network. These reactions are generally classified as a nucleophilic attack on the silicon atom.

O^{2-}

Initial State

Transition State

Final State

In this case the charge on the oxide ion is transferred to the glass. In order to maintain electroneutrality, metal cations must enter the glass structure, providing gettering sites for the gaseous alkali to enter the silicate lattice.

Similarly, a simultaneous nucleophilic and electrophilic attack may occur at the bridging oxygens within the network. In order to disrupt this bond, a strong nucleophile is required. This reaction, depending on the degree of association between the alkali and the chloride, can be written as two possible reaction sequences. These are:

or

Some agents have an inhibiting influence on the alkaline dissolution of glass surfaces. Gieffcken³² demonstrated that $\text{Al}(\text{OH})_3$ offers the most effective protection against decomposition because of the insolubility of the aluminum hydrosilicates. Weyl¹⁸ stated that an ion, if present in the glass lattice, will hamper the decomposition, influencing the alkali adsorption, since it forms a composition that is difficult to dissolve in the surrounding gaseous or lattice alkali. Williams and Weyl²⁵ also investigated the ion exchange process that occurs in the metakaolin lattice. They concluded that the sodium glass phase, when reacted with hydrogen-clay material, produced hydrogen glass and a sodium clay by means of the base exchange of the glass surface and metakaolin, as shown in the following reaction:

The alkali appears to be exchanged from the acid soluble fraction. This phenomenon of the acid insoluble lattice and vice versa has frequently been observed during the gettering reaction.

Differences in the orientation of the structural layers within the aluminosilicate as well as in the degree of structural order should influence the positions of the -OH groups that coordinate with Al, Si, or Fe in the mineral structure. These, in turn, are expected to influence the symmetry of the crystal field formed by ligands, in particular, surrounding the Fe^{3+} sites in the lattice. Since the crystal field symmetry is known to affect the electron paramagnetic resonance (EPR) signal of Fe^{3+} , the EPR technique may be suitable in determining the form of iron in clay, the position of iron in the lattice, and the degree of order within these structures. Complementing the EPR data, Mossbauer spectroscopy is theoretically capable of identifying the oxidation state and position of the iron substitution in the kaolinite structure. Komusinski³³ demonstrated that amorphous forms of kaolin contain poorly crystallized hematite and goethite structures. The Fe^{3+} associated within the lattice may exist as substitutions in the

octahedral or tetrahedral sheets supporting the multiple resonance features that were observed, since the lattice Fe^{3+} could occupy two different sites. Alternatively, the Fe^{3+} may exist as discrete particles within the kaolin lattice in association with surface oxides and hydroxide groups. In all the minerals contained in kaolin, with the exception of nacrite, iron exists only as the ferric state. Nacrite contains iron in both the ferric and ferrous states, with the Fe^{3+} for Al^{3+} in the octahedral structure. The ionic substitution of Fe^{3+} for Al^{3+} in the octahedral sheets may catalytically affect the gettering of the alkali in the silicate or aluminosilicate material. The enhancement of the gettering capacity after 6 hours was observed in the process development unit (PDU) chars and ash materials, which contained more than 1.0 wt% iron, as compared with the gettering capabilities of either kaolin or activated bauxite, which contained 0.05 and 0.5 wt% iron, respectively. The presence of iron in either the silicate or the aluminosilicate network may promote the formation of low melting temperature silicate phases ($\text{FeSiO}_4 = 1419 \text{ K}$; $\text{SiO}_2 = 1883 \text{ K}$ (quartz); $\alpha\text{-Al}_2\text{O}_3 = 2288 \text{ K}$; $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 = 1818 \text{ K}$).³⁴

Differential thermal analysis conducted on the as-received gasifier PDU ash and Minnehaha PDU char (Figures 71 and 72) indicates a simultaneous exothermic decomposition of the pyrite structure and crystalline transitions in both materials at temperatures between 873 and 1273 K. The slow, low-temperature devolatilization procedure performed prior to pellet fabrication yields structures that undergo no further structural changes when reheated, as shown in the lower DTA plots in Figures 71 and 72. The tailing of the Minnehaha PDU char ash DTA resulted from a depletion of sample material within the sample chamber and should not be interpreted as a structural change or chemical reaction. As the scanning electron micrographs in Figures 71 and 72 indicate, the exposure of the ash pellet material to temperatures of 1473 to 1673 K was apparently sufficient to melt the external surface of each material. Large voids remain within the melted gasifier lattice, however, and the PDU char ash material appears to have melted completely,

Gasifier PDU Ash

Curve 725640-A

Figure 71 -- SEM/DTA of gasifier PDU ash getter material

Minnehaha PDU Ash

Figure 72 -- SEM/DTA of Minnehaha PDU char ash getter material

encapsulating the charge. This melting and/or sintering may aid in the initial gettering mechanism of the aluminosilicate structure, but once the surface has been scaled, further gettering may be diminished.

Both the literature and the information generated in this study indicate the complexity of the alkali aluminosilicate reaction mechanisms. Simply by altering the chemical composition or physical properties of the aluminosilicates, variations in the reaction mechanism and overall gettering capabilities are most likely to occur. Continued effort in this area is required in order to delineate a generic alkali aluminosilicate reaction mechanism and to define an optimal sorbent material.

3.2.4.2 Proposed Alkali Complexes and Aluminosilicate Reactions

Typical analyses conducted throughout the Westinghouse experimental program have quantitatively determined the concentration of alkali partitioned within various phases. In this study, unreacted material or getter pellets were first pulverized and then leached in distilled water at 368 K for one hour. The water leach is removed and analyzed for the total sodium and potassium water soluble content using AA techniques. The solid residue is then treated on a 1:1 volumetric basis with HCl and heated for one hour. The resulting filtrate contains the acid soluble alkali, while the solid material contains the acid insoluble alkali. Hydrogen fluoride is added to the crucible, which is then heated for one hour. Perchloric acid is added to the entire sample and taken to fuming. The concentrations of the insoluble alkali present in the hydrogen fluoride and perchloric acid solution and the acid soluble alkali present in the HCl filtrate were determined using AA techniques.

Each fraction (water soluble, acid soluble, and acid insoluble) contains a specific alkali constituent that either deposited or condensed along the pellet surface or reacted chemically within the aluminosilicate matrix. The proposed partitioned alkali constituent composition and the possible gettering reactions are presented below.

- Water soluble alkali phases: These include gettering through either physical adsorption of the alkali chloride along the pellet surface or through the attraction of the alkali chloride or ion to the alumina or aluminosilicate lattice that results from polarization of the attacking molecule or ion with the substrate. Typical water soluble alkali reactions can be written as:

Similar reactions can also be written for potassium.

- Acid soluble alkali phases: These reactions are proposed to result from the substitution of sodium or potassium between the hexagonal network of the silicon-oxygen tetrahedra and/or the aluminum-oxygen/hydroxide octrahedra where water had initially been positioned. Displacement reactions may occur similarly within this fraction. For example, the sodium or potassium cation may replace hydrogen in exposed hydroxyl groups while simultaneously substituting the chloride anion at an adjacent hydroxyl site. These reactions can be written in the following manner:

Similar reactions can also be written for potassium.

- Acid insoluble alkali phases: These reactions are proposed to result through the formation of a strong alumina or aluminosilicate bond within the amorphous lattice or through a mechanism that collapses the lattice, entrapping the alkali into a nonreleasable, cage-like structure. These reactions can be written as:

Again, similar reactions can be written for potassium.

3.2.4.3 Gettering Mechanism in Emathlite

Throughout this study the TGA has provided data concerning the apparent weight gain of the aluminosilicate materials when they are exposed to various NaCl gas environments. Water vapor has been included in the latter half of the study to illustrate the potential influence on the gettering capacity in a somewhat more realistic simulation of an actual fuel gas environment. As identified by the bench-scale studies, the controversy between the possible variation in the gettering reaction capacity in the inert alkali, water gas environment vs a simulated fuel gas containing CO, CO₂, H₂, H₂S, HCl, H₂O, and N₂, has been resolved, since the gettered insoluble sodium concentrations under both test conditions are equivalent. For this reason, the TGA gettering data represent the reactions and capacities comparable to the gettering reactions that would result in either a simulated fuel gas or an actual process stream. Carbon or alternative species deposited may minimize the overall effectiveness of the getter material when the deposits form at the getter surface, blocking reaction sites. Particulate fines included in the alkali-laden gas stream can become attached to the glassy outer surface of the getter material but can also serve as an additional getter material. They can also be viewed as an additional getter source because of the aluminosilicate composition of the fines. If these fines contain low levels of alkali and experience a lower temperature during gettering than during gasification, thus preventing release of the background alkali, problems resulting from low gas stream solids loading are not likely to result.

As discussed in Section 3.2.3, the TGA study initiated a series of activated bauxite and several ash exposures to 815 to 1173 K and 0 to 21 ppm total NaCl in the absence of water vapor for various exposure durations. Following this sequence, a series of alternative getter materials were screened under a standard set of conditions, and emathlite was selected as the candidate getter sorbent for hot gas cleaning. Because of the enhanced sodium gettering capacity of emathlite in the presence of water vapor, a final series of emathlite testing in a mixed NaCl-H₂O-N₂ environment was conducted. Data on the possible alkali gettering reaction mechanism were obtained using both the TGA weight gain and AA analysis while a major portion of the TGA was refurbished. Since the details of each test have been presented in previous sections, Table 64 presents only a summary of the materials, test alkali concentrations, exposure temperatures, pressures and durations, and the AA data. Because of the lack of water vapor in the early tests and demonstration of the enhanced gettering capacity of emathlite in the presence of water vapor, only TGA tests 31 through 48 have been used to define the preliminary gettering reaction mechanism of alkali in aluminosilicate materials. TGA 30 has been eliminated from these analyses, since the gettered pellet had been split into two fractions, and a total final gettered alkali concentration could not be determined.

The unreacted pellet weight on a dry basis and the gettered pellet weight varied throughout this test series, as shown in Table 65. With the exception of TGA 40, 47, and 48, the dry unreacted pellet weights always exceed the gettered pellet weights. The total potassium removed from the unreacted pellet weight, in addition to the 4.49% moisture lost during gettering, approaches the reported final pellet weight. This implies that an additional species or phase is released during gettering at the high reaction temperature.

The relation of the reported AA data for the gettered TGA pellets and the test $\mu\text{atm}\cdot\text{hr}$ is shown in Figure 73. Although scatter in the test data is observed, the data indicate that emathlite in the

Table 64
SUMMARY OF TGA ATOMIC ABSORPTION DATA

Dwg. 5608C19

Test No.	Material	Gas Composition, gm/v NaCl	Temp., K	Pressure, atm	Total Exposure Time, Hrs	Atomic Absorption Analyses, Wt %							
						Water Soluble		Acid Soluble		Acid Insoluble		Total	
						Na	K	Na	K	Na	K	Na	K
1	Activated Bauxite	6.3	1169	1	2	0.0064	<0.005	<0.005	<0.005	0.014	0.011	0.020	0.011
2	Activated Bauxite	4.5 - 17.3	1173-1215	1-10	14.3	0.0074	<0.005	<0.005	<0.005	0.014	0.011	0.021	0.011
3	Activated Bauxite	10.5	1175	1	4	NA	NA	NA	NA	NA	NA	NA	NA
4	Activated Bauxite	0.65	1175	1	93	NA	NA	NA	NA	NA	NA	NA	NA
5	Activated Bauxite	5.1	1175	1	15	0.19	<0.006	0.15	<0.006	0.14	<0.01	0.48	<0.01
6	Boiler Ash	5	1175	1	27	0.0076	<0.007	0.24	0.016	1.11	0.27	1.36	0.29
7	Gasifier Ash	10.1	1175	1	16.5	0.017	<0.006	0.081	0.014	1.25	0.78	1.35	0.79
8	Gasifier Ash	8.7	1176	1	42*	0.025	<0.006	0.23	0.011	2.77	0.16	3.03	0.17
9	Char Ash	0 - 9.5	900-902	1	180	0.021	<0.006	0.42	<0.006	3.24	0.036	3.68	0.036
10	Activated Bauxite	8 - 21	851-855	1	89	NA	NA	NA	NA	NA	NA	NA	NA
11	Activated Bauxite	4	1123	1	18	NA	NA	NA	NA	NA	NA	NA	NA
12	Activated Bauxite	11.5	1123	1	19	NA	NA	NA	NA	NA	NA	1.25	<0.05
13	Activated Bauxite	9.4	1174	1	22	NA	NA	NA	NA	NA	NA	1.06	<0.05
14	Activated Bauxite	3.3	1123	1	44	NA	NA	NA	NA	NA	NA	1.18	<0.05
15	Activated Bauxite	3.4	1173	1	46	NA	NA	NA	NA	NA	NA	0.96	<0.05
16	Activated Bauxite	0.79	1123	1	96	NA	NA	NA	NA	NA	NA	0.78	<0.05
17	Activated Bauxite	0.78	1173	1	92	NA	NA	NA	NA	NA	NA	0.68	<0.05
18	Activated Bauxite	12	1123	1	43	NA	NA	NA	NA	NA	NA	1.43	<0.05
19	Activated Bauxite	0 - 11	1173	1	70	NA	NA	NA	NA	NA	NA	1.47	<0.05
20	Vansil	13.4	1173	1	26	NA	NA	NA	NA	NA	NA	0.36	<0.05
21	Vansil	12	1073	1	24	NA	NA	NA	NA	NA	NA	0.34	<0.05
22	Ebony Novacite	13.9 - 5.7	1123	1	165	0.047	<0.01	NA	NA	3.51*	<0.02*	3.56	<0.03
23	Ebony Novacite	12.1 - 3.1	1123	1	267	0.026	<0.01	NA	NA	5.58*	<0.02*	5.61	<0.03
24	Zeolite	12.0 - 9.6	1123	1	50	0.010	<0.01	NA	NA	2.91*	0.18*	2.92	0.18
25	Emathlite	11.0 - 3.7	1123	1	284	0.058	<0.01	NA	NA	5.39*	<0.02*	5.45	<0.03
26	Diatomaceous Earth	9.7 - 4.2	1123	1	300	0.095	<0.01	NA	NA	4.49*	<0.02*	4.59	<0.03
27	Novacite	11.2 - 5	1123	1	283	0.22	<0.01	NA	NA	1.93*	<0.02*	2.15	<0.03
28	Activated Bauxite	22 - 6.6	1123	1	257	3.10	<0.05	2.82	<0.05	0.69	<0.05	6.61	<0.15
29	Activated Bauxite	24 - 8.1	1123	1	113	1.64	<0.05	3.25	<0.05	0.37	<0.05	5.26	<0.15
30	Emathlite	17 - 7	1123	1	117	0.69**	<0.06	1.86	<0.06	8.11	<0.06	10.66	<0.2
						0.16***	<0.06	0.42	<0.06	3.23	<0.06	3.81	<0.2
31	Emathlite	19 - 7	1123	1	143	0.34	<0.01	0.91	<0.01	7.83	0.047	9.08	0.047
32	Activated Bauxite	10	1123	1	25	0.69	<0.01	1.43	<0.01	0.24	<0.02	2.36	<0.02
33	Emathlite	8.2	1173	1	135	0.19	<0.01	0.41	<0.01	7.49	0.033	8.09	0.033
34	Emathlite	3 - 2.2	1123	1	193	NA	NA	NA	NA	NA	NA	4.95	NA
35	Emathlite	3 - 2.4	1123	1	255	NA	NA	NA	NA	NA	NA	3.80	NA
36	Emathlite	- 3.9	1123	1	97	NA	NA	NA	NA	NA	NA	1.71	NA
												1.68	
37	Emathlite	4.5	1173	1	95	NA	NA	NA	NA	NA	NA	1.84	NA
38	Emathlite	4	1123	1	136	NA	NA	NA	NA	NA	NA	1.92	NA
39	Emathlite	15.1	1123	1	121	NA	NA	NA	NA	NA	NA	4.67	NA
40	Emathlite	19	1123	1	95	NA	NA	NA	NA	NA	NA	4.69	NA
41	Emathlite	6	1123	1	28	NA	NA	NA	NA	NA	NA	1.21	NA
42	Emathlite	45	1123	1	18	NA	NA	NA	NA	NA	NA	2.13	NA
43	Activated Bauxite	9 - 7	1123	1	70	NA	NA	NA	NA	NA	NA	1.43	NA
44	Emathlite	11 - 9	1123	1	70.5	NA	NA	NA	NA	NA	NA	2.14	NA
45	Emathlite	- 13	1123	1	65.5	NA	NA	NA	NA	NA	NA	2.97	NA
46	Emathlite	12 - 9.5	1123	1	98	NA	NA	NA	NA	NA	NA	3.50	NA
47	Emathlite	43 - 31	1123	1	94	NA	NA	NA	NA	NA	NA	5.17	NA
48	Emathlite	55 - 38	1123	1	146	0.25	NA	0.60	NA	6.30	NA	7.15	NA

NA = Not Analyzed
* Combined Acid Soluble and Insoluble Concentrations
** Glass Phase
*** Pellet Interior

Figure 73 — Relation of gettered sodium concentration in emathlite as determined by atomic absorption to total $\mu\text{atm}\cdot\text{hr}$.

presence of water vapor has not achieved a maximum sodium saturation capacity. The open circles in Figure 73 represent test data where salt had accumulated along the sample hangdown wire during the course of the reaction. The half-filled circles in Figure 73 project an alkali- $\mu\text{atm}\cdot\text{hr}$ relation for TGA 31 and 33 if 80 ppm NaCl had been present in the reactant gases.

Table 66 summarizes the TGA data and corrects the gettered sodium concentration relative to the reported TGA weight gain and the total loss of background moisture and potassium content. From this table an appreciable weight gain of an additional species labeled "X" is observed to result during sodium gettering. The number of moles of sodium gettered can be calculated directly, in addition to the number of moles of "X" assumed to be water (Table 67). The ratio of the moles of sodium to moles of water plotted as a function of the reaction $\mu\text{atm}\cdot\text{hr}$ is shown in Figure 74. The maximum mole ratio resulting after extended

Table 65

SUMMARY OF ATOMIC ABSORPTION ANALYSES AND PELLET
WEIGHTS OF GETTERED EMATHLITE IN THE TGA

Dwg. 4262871

TGA	Gettered Wt % Na	Initial Pellet Wt , mg Wet (Dry) *	Gettered Pellet Wt , mg	Percent Dry Weight Change During Gettering
31	9.08	216.5 (206.77)	NR	—
33	8.09	207.6 (198.28)	NR	—
34	4.95	207.5 (198.18)	195.297	1.45
35	3.80	177.0 (169.05)	164.358	2.78
36	1.69	236.3 (225.69)	216.357	4.14
37	1.84	220.4 (210.50)	202.201	3.94
38	1.92	210.9 (201.43)	195.492	2.95
39	4.67	263.3 (251.48)	250.743	0.29
40	4.69	206.2 (196.94)	198.13	(0.60) **
41	1.21	180.8 (172.682)	163.85	5.12
42	2.13	192.5 (183.856)	173.74	5.50
44	2.14	208.0 (198.661)	191.904	3.40
45	2.97	191.4 (182.806)	178.664	2.27
46	3.50	201.9 (192.835)	190.094	1.42
47	5.17	218.7 (208.880)	209.043	(0.08)
48	7.15	229.5 (219.195)	224.015	(2.20)

* Dry Basis of LOI: 4.49%

NR: Not Reported

** () Indicate Gettered Pellet Weight Gain Over Initial Dry Weight

Table 66

Dwg. 5608C18

EMATHLITE GETTERING REACTION MATERIAL BALANCE

Test No.	Temp., K	Length, hr	ppm NaCl	Dry Weight of Pellet, mg	Potassium, mg			Sodium, mg			Observed Wt Gain, mg	Corrected Wt Gain, mg	Weight of X Gained, mg
					Initial	Final	Lost	Initial	Final	Gained			
31	1123	143	19 to 7	206.71	1.716	0.097	1.619	0.186	18.775	18.589	23.4	25.019	6.430
33	1173	135	8.2	198.28	1.646	0.065	1.581	0.178	16.041	15.863	18.7	20.281	4.418
34	1123	193	3 to 2.2	198.18	1.645	0.079	1.566	0.178	9.810	9.632	17.2	18.766	9.134
35	1123	255	3 to 2.4	149.05	1.403	0.068	1.335	0.152	6.424	6.272	6.2	7.535	1.263
36	1123	97	~3.9	225.64	1.873	0.090	1.783	0.203	3.837	3.634	3.4	5.183	1.549
37	1173	95	4.5	210.50	1.747	0.084	1.663	0.189	3.873	3.684	3.27	4.933	1.060
38	1123	138	4	201.43	1.672	0.081	1.591	0.181	3.867	3.686	3.35	4.941	1.074
39	1123	121	15.1*	251.48	2.087	0.101	1.986	0.226	11.744	11.518	19.4	21.386	9.642
40	1123	95	19	196.94	1.634	0.079	1.555	0.177	9.236	9.059	10.5	12.055	2.819
41	1123	28	8	172.682	1.433	0.069	1.364	0.155	2.089	1.934	1.8	3.164	1.075
42	1123	18	45	183.856	1.526	0.074	1.453	0.166	3.916	3.751	3.7	5.152	1.236
44	1123	70.5	11-9	198.661	1.649	0.079	1.570	0.179	4.251	4.072	3.3	4.869	0.618
45	1123	65.5	~13	182.806	1.517	0.073	1.444	0.165	5.429	5.264	5.6	7.044	1.615
46	1123	98	12-9.5	192.835	1.601	0.077	1.523	0.174	6.749	6.575	5.3	6.823	0.074
47	1123	94	43-31	208.880	1.734	0.084	1.650	0.188	10.799	10.611	13.0**	14.650	3.851
48	1123	146	55-38	219.195	1.819	0.088	1.731	0.197	15.672	15.475	20.3	22.032	6.359

Assumptions

Background Na: 0.09 wt %, K: 1.83 wt %, LOI: 1.49 %

No Loss of the Background Na Content During Gettering

Average K Concentration in Pellet after Gettering = 0.04 wt % for TGA 31, 34, and 36

Corrected Wt Gain = Observed Wt Gain + Wt K Lost

Weight of X Gained = Corrected Wt Gain - Wt Na Gain

- * Average Concentration Based on Salt Boat Weights Before and After Run
- ** Maximum Weight Gain after 81 Hours

Table 67

RATIO OF MOLES Na/MOLES X GAINED DURING GETTERING

Dwg. 4263B 27

TGA	μ atm-hr	Na Gained, mg	Moles Na Gained	X Gained, mg	Moles H ₂ O Gained	$\frac{\text{Moles Na}}{\text{Moles H}_2\text{O}}$
36	378	3.634	1.581×10^{-4}	1.549	8.598×10^{-5}	1.839
37	428	3.684	1.602×10^{-4}	1.060	5.884×10^{-5}	2.723
38	552	3.686	1.603×10^{-4}	1.074	5.962×10^{-5}	2.689
41	224	1.934	8.412×10^{-5}	1.075	5.967×10^{-5}	1.409
42	810	3.751	1.632×10^{-4}	1.236	6.861×10^{-5}	2.379
45	852	5.264	2.290×10^{-4}	1.615	8.965×10^{-5}	2.554
48	6789*	15.475	6.731×10^{-4}	6.359	3.530×10^{-4}	1.907

Uncertainty in Actual NaCl Concentration During Gettering: TGA 31, 32

Salt Accumulation on the Hang-Down Wire: TGA 34, 35, 39, 40, 46, 47

1% H₂O in Reactant Gas Versus 4.6% H₂O: TGA 44

* Averaged Concentration

Figure 74 -- Ratio of gettered moles Na to moles H₂O in emathlite as a function of μatm-hr.

exposure or high alkali concentrations in the reactant gases approaches 2 moles of sodium gettered for every mole of water gettered. On this basis the following reaction stoichiometry can be written:

Figure 74 implies that initially emathlite getters an equivalent or perhaps a somewhat higher concentration of water. Enrichment of sodium within the gettered phase then continues until a maximum of between 2 and 3 moles of sodium are gettered for every mole of water gettered. A final transition within either the substrate or gettered reaction product may have resulted, so that after extended exposures or after exposure to high levels of alkali in the reactant gas, 1.9 moles of sodium result for every mole of water in the reacted emathlite pellet. The 1.9 as opposed to 2 moles of sodium for every mole of water may, in

part, be due to the sharing of sodium within the polymerizing oxygen atoms that bridge adjacent substrate silica.

Relatively simple surface reactions are proposed for reaction of the high-temperature, unsaturated valence surface oxygen atoms in the silicon tetrahedron with water and NaCl (Figures 75 to 78). In each system, adsorbed water bonds selectively with the surface oxygen atom or establishes an ionic bond between oxygen and sodium, followed by release of either H, HCl, Cl, or Cl₂. Cross linkages of adjacent silicon tetrahedra are also considered to form through the dehydration of the silicon structure at high temperatures, followed by adsorption of two sodium atoms at every cross-linked oxygen atom.

In addition to these reactions, which may be chiefly responsible for the concentration of sodium gettered in the acid insoluble, and perhaps acid soluble phase, the following ionic exchange reaction between the gettered sodium and the background potassium in emathlite is proposed:

Although these data have provided a basis for formulating a preliminary gettering reaction mechanism, further investigation is required to define the influence of reaction gas composition, temperature, pressure, and exposure time on the ultimate sodium gettering capacity in emathlite and related aluminosilicate materials.

3.3 TASK 3: SYSTEM PERFORMANCE PROJECTIONS

3.3.1 Introduction

Throughout this program we have tried to collect, analyze, and use data as they become available to gain insight into the feasibility of various process configurations for alkali gettering. In the previous program⁹ we analyzed Westinghouse batch reactor data for kaolin, char ash, and gasifier ash getters and ANL³⁵ data on diatomaceous earth and

Figure 75 - Proposed reactions of NaCl with silica along the emathlite particle surface

2 Adjacent Na
May be Bulky Depending
on Surface Si Position

Figure 76 - Proposed reactions of NaCl and water vapor along the emathlite particle surface

Figure 77 - Proposed alternative reactions of NaCl and water vapor along the emathlite particle surface

Figure 78 - Proposed polymerization and gettering reactions of NaCl and water vapor along the emathlite particle surface

activated bauxite. The rates corresponding to those tests were then shown not to be limited by external diffusion effects, and preliminary sizing and costing were presented.

Much attention has been given by various investigators to the use of bauxite as a getter material. Consequently, we try below to unify these data and to see what they imply about conceptual gettering reactor engineering. Several types of reactors, including an entrained, very fine particle reactor and a batch packed bed have been proposed. We examine these configurations in light of the bauxite data, assuming that the sorption kinetics are not infinitely fast. We believe the available information indicates that gettering is not a simple, unactivated, physical absorption with infinite intrinsic rate, and we present our reasons.

In the current program we have identified emathlite as an excellent getter of sodium, with high capacity. A definite chemical reaction has been demonstrated to occur. Emathlite is a natural mineral and cannot be generated as a smoke, and it forms a molten, sticky, glass phase upon gettering. For these reasons we do not examine the use of emathlite in an entrained smoke reactor, but we do characterize the basics of packed-bed reactor design for emathlite.

On the basis of the above, this section summarizes our system performance projection efforts with activated bauxite getter reactors (Section 3.3.2) and emathlite getter reactors (Section 3.3.3) and comments on system performance projections (Section 3.3.4). The bauxite getter evaluation work is described in terms of four subtasks: data summary (3.3.2.1), diffusion effects (3.3.2.2), equilibrium consideration (3.3.2.3) and gettering reactors (3.3.2.4). Our emathlite getter reactor work is described in terms of three subtasks. The first of these deals with the kinetic implications of emathlite gettering (3.3.3.1); the preferred packed-bed configuration for this material is described in 3.3.3.2; and the engineering implications to be considered in integrating the emathlite packed bed into a hot-gas cleaning system are addressed in the final subtask (3.3.3.3).

3.3.2 Activated Bauxite Getter Reactors

3.3.2.1 Data Summary

Activated bauxite was chosen for detailed analysis because it has been tested most extensively. Above we have presented data from both our batch reactor and our TGA systems. In addition, ANL^{10,11,35} and GE^{36,37} have compiled useful data on this material, although with quite different systems. Other materials have shown higher gettering capacities. In an earlier program⁹ a gasifier bed ash and a char ash were shown to have high capacity in the batch reactor, as a PFBC ash has been in the present report. The ash materials released much potassium upon sodium pickup and therefore are not considered further. Sizing ash beds for sodium gettering while ignoring the potassium problem was reported.³⁸

A selection of bauxite tests from the various sources is shown in Table 68. A variety of test systems have been used so far. ANL's tests¹⁰ were made with a 1.3 cm deep fixed bed of bauxite particles (not pelleted) screened to a 2000 to 2380 μm particle size distribution. The bed was operated with salt-laden gas blown through batches of getter for a selected time period. Salt sorption rates were determined by flame emission spectrometry on dissolved getter samples. Relatively high concentrations of salt were used. The degree of contact was such that about 90% of the salt in this gas was removed. We therefore estimated the average concentration experienced by the bed to be about half that calculated from the amount of NaCl vaporized, the run length, and the gas flow.

The tests made by GE³⁷ used a TGA-suspended basket of particles (not pelleted) past which the salt-bearing gas flowed. In runs "B" and "E", respectively, 0.25 and 0.62 g of particles were used. The particles were 500 to 700 μm in size. No significant change in bulk gas concentration of NaCl occurred as the gas passed the sample.

Table 68
BAUXITE DATA FROM VARIOUS SOURCES

Run No.	Source											
	ANL ³⁸		GE ³⁷		W-Bench Scale			W-TGA				
	HGC-25	HGC-30	B	E	1	4	12	13	14	15	16	17
Configuration	Packed bed of particles, flow through		Bed of particles, flow past		Bed of pellets, flow through			Single pellet, flow past				
Carrier Gas	Simulated flue gas		Argon		Argon			Nitrogen				
Pressure, atm	1	1	1	1	11	11	1	1	1	1	1	1
Temperature, K	1073	1153	1073	1073	1123	1153	1123	1173	1123	1173	1123	1173
Gas Density, g/l	0.34	0.32	0.45	0.45	4.77	4.64	0.30	0.29	0.30	0.29	0.30	0.29
Viscosity, cp	0.045	0.047	0.058	0.058	0.059	0.060	0.046	0.048	0.046	0.048	0.046	0.048
Diffusivity, cm ² /s	1.1	1.2	1.0	1.0	0.10	0.11	1.2	1.3	1.2	1.3	1.2	1.3
Salt Concentration, ppmv	~50 ^a	~70 ^a	440	26	80	80	11	9	3	3	0.8	0.8
(mol/cm ³) x 10 ¹⁰	6.1	7.4	50	3.0	95	93	1.2	0.94	0.33	0.31	0.087	0.083
Observed Initial Rate (g NaCl/100 g sorb.-hr) (mol NaCl/cm ³ sorb.-hr) x 10 ⁴	0.66	0.91	0.73	0.027	1.50	3.46	0.38	0.32	0.15	0.11	0.031	0.025
Curve Fit (eq. 26)												
A (g NaCl/100 g sorb.)	6.38	2.41	4.44	4.05	1.76	-	2.63	1.63	2.13	1.41	1.32	0.85
B, hr	9.74	2.65	6.07	148	1.17	-	6.86	5.12	14.6	13.4	43.1	33.5

^a Estimate - see text.

The Westinghouse tests, all of which were made with pelleted samples, have been described in earlier sections of this report. The pellets for the bench-scale tests were cylindrical, with length and diameter of 3.2 mm (1/8 in), while both these dimensions of the cylindrical pellets for the TGA tests were 6.4 mm (1/4 in). In the batch reactor, salt-carrying gas flowed through a bed of 10 to 15 pellets, with no significant reduction in gas phase salt concentration occurring. A single pellet was used for each of the TGA tests, again with no decline in concentration in the passing gas. Very high gas-phase salt concentrations, on a volumetric basis, were achieved with the batch reactor, while very low concentrations were achieved with the TGA.

The viscosities of the carrier gases listed in Table 68 were determined from nomographs in Perry's Handbook.³⁹ Table 68 presents binary bulk diffusivities for NaCl in the appropriate carrier gas. These were calculated using the method outlined by Satterfield⁴⁰ whereby the boiling points and liquid densities at the boiling points of the substances are used to predict Lennard-Jones force constants, which are in turn used to calculate diffusivities.

Estimation of particle or pellet physical properties is important to the evaluation of pore diffusion effects. Porosimeter data are available for the Westinghouse-made bauxite pellets. This information shows a surface area of about 40 m²/g in a getter pellet. The pore volume is 0.35 cc/g, the pellet density 1.26 g/cc, and the porosity 0.45. The mean pore radius for the pellets, calculated as⁴¹

$$\frac{2 \times (\text{pore volume})}{(\text{surface area})} \quad (25)$$

is about 180 Å.

We do not have access to any material measurements made by GE or ANL beyond those reported. ANL⁴² reports a bulk density of 0.83 g/cc for a bed of their bauxite. This corresponds to a particle density of about 1.43 g/cc if we assume a typical packed-bed voidage of 0.42. If the

material has the same skeletal density as the Westinghouse material, then the porosity is 0.37 and the specific pore volume is 0.25 cc/g. We assume these numbers also applied to the GE material, both materials having been supplied by Englehard, both being unpelleted, and both having been similarly heat-treated before use (15 hr @ 1173 K for ANL and 20 hr @ 1223 K for GE). GE³⁷ reported a surface area of about 85 m²/g after heat treating. We do not know why this is larger than the value we obtained for both unheated and heated (1173 K, 48 hr) bauxite pellets. Perhaps the 3 to 5 min of shatter box grinding and the subsequent isostatic pressing to form pellets resulted in a loss of area. We assumed that the 85 m²/g figures also applied to the ANL bauxite. Given this specific area and the pore volume of 0.26 cc/g, we estimate the mean pore radius by the above technique to be 62 Å.

For the examination of diffusion effects that we present here, we chose to use the initial observed adsorption rate whenever possible. The initial rates were estimated from the data as follows. The GE tests and the Westinghouse TGA tests each produced a plot of weight gain versus time, in each of which the rate of increase declines with time. Consequently, each such curve could be represented by an expression of the form

$$w = At/(B + t), \quad (26)$$

where w is the weight gain per hundred g sorbent, t is time, and A and B are constants. Equation (26) was rearranged to give w as a linear function of w/t , and the data for each run were fitted by a least-squares analysis to this equation for determination of A and B . The derivative of equation (26) then shows that the initial rate is A/B . Note, also, that this method provides a consistent way of estimating the sorbent capacity, as A . Table 68 gives the initial rates as well as A and B for each test. A similar procedure was used for the ANL tests and Westinghouse batch reactor tests except that the curves were fitted with data taken from additional tests at the same conditions, except for run

duration. This difference was necessary because a continuous plot of weight gain versus time is not produced for these tests. Data for batch reactor test 4 and similar tests at the same condition but different duration were too scattered for determination of A and B. Rather, an initial rate was estimated by examination.

Some assumptions about stoichiometry must be made in order to compare data obtained through different techniques. ANL¹⁰ reports weight gain as weight of NaCl gained, based upon the measured Na content in the sample. We surmise that ANL assumed that a Cl atom is picked up with each Na atom, and we have accepted this assumption in our tabulation of initial rates in terms of weight of NaCl. The Westinghouse batch reactor data presented earlier in this report were in terms of weight of sodium, and we have made the one Cl per Na assumption in presenting the rates of Table 68 for these tests. The TGA data of both GE and Westinghouse give directly simply a weight gain. In the development of the rates in Table 68 we assumed that this is a NaCl weight gain. Evidence presented above on atomic absorption analysis of the Westinghouse TGA data strongly suggests that the stoichiometry is not that simple. We believe that GE's data support this finding (see Section 3.3.2.3). This is equivalent to saying that chemical reaction occurs in some circumstances, and that adsorption is not simply physical. This implies a finite intrinsic rate. Nevertheless, we must still assume a stoichiometric simplification in order to compare the rate data in the present analysis, and this we do with the simple NaCl adsorption model.

3.3.2.2 Diffusion Effects

In adsorption the gaseous NaCl must first be transported by convection or diffusion from the bulk gas stream to the geometric surface of the particle or pellet of getter material (film diffusion), then from this exterior surface through the pores of the material to material-pore interfacial surfaces. Most of the adsorption occurs here because with any porous material of moderate particle size, such as all

those listed in Table 68, interior surface exceeds external surface by orders of magnitude. Thus, several kinetic events influence the actual observed rate of alkali gettering — namely film diffusion, pore diffusion, and the true rate of the adsorption (if we assume that the latter is finite), which depends on the concentration of NaCl deep in the pores of the material. If one of these processes is much slower than the others, it alone will determine the observed rate, within the accuracy of our ability to measure it. Well-developed techniques are available to roughly estimate rates of diffusional steps. We can therefore compare observed rates with hypothetical observed rates to get an idea of which step is most important. This we do in this section, examining the importance of film diffusion, then pore diffusion, and finally the combined effects of both. Implications for true kinetic rates and the feasibility of increasing the achievable observed rate are then presented.

3.3.2.2.1 Film Diffusion. Table 69 summarizes the calculations relative to the effects of film diffusion. The rate of film diffusion is given by:

$$R_{fd} = k_g a (C_o - C_g) , \quad (27)$$

where

R_{fd} is in mol/sec · cm³ getter

k_g is the film mass transfer coefficient, cm/s

a is the specific external geometric surface area of the particle, pellet, or aggregate, cm²/cm³ getter

C_o is the concentration of NaCl in the bulk gas at a distance from the getter, mol/cm³

C_g is the concentration of NaCl at the getter surface, mol/cm³.

The mass transfer coefficient depends primarily on the velocity of gas flow past the sample, whether the sample is a fixed bed through which the gas flows or a single particle or aggregate past which the gas flows, and the diffusivity of the salt molecule in the gas.

For packed beds, such as are used in the ANL tests and in our bench-scale screening reactor tests, Carberry⁴³ gives the following correlation for k_g :

$$\frac{k_g \epsilon}{U_o} = 1.15 \left(\frac{\mu}{\rho_g D_{12}} \right)^{-2/3} \left(\frac{d_p U_o \rho_g}{\mu \epsilon} \right)^{-1/2}, \quad (28)$$

where

ϵ is the packed-bed voidage, volume interparticle space/volume bed

U_o is the superficial gas velocity through the bed, cm/s

μ is the gas viscosity, g/cm · s

ρ_g is the gas density, g/cm³

D_{12} is the diffusivity of NaCl in the gas, cm²/s

d_p is the particle size, cm.

The values of μ , ρ_g , and D_{12} are given in Table 68. The void fraction ϵ was taken as 0.42 for the ANL tests and 0.5 for the Westinghouse bench reactor tests. The gas velocities and particle or pellet size are listed in Table 69. The values calculated for k_g with equation (28) applied to the ANL and Westinghouse bench-scale tests are also listed there.

Kunii and Levenspiel⁴⁴ give the mass transfer coefficient for single particles in a gas stream as:

$$\frac{k_g d_p}{D_{12}} = 2 + 0.6 \left(\frac{\mu}{\rho_g D_{12}} \right)^{1/3} \left(\frac{d_p U_o \rho_g}{\mu} \right)^{1/2}. \quad (29)$$

Calculated values of k_g and the velocities used are given in Table 69 for the GE and Westinghouse TGA tests. For the Westinghouse tests the particle size corresponds to the pellet size. For the GE tests the particle size used corresponds not to the actual granule size but to the size of the aggregate of particles suspended on the TGA sample pan because little bulk flow of gas could have occurred between the sample's many small particles where resistance to flow is strong and there is virtually no resistance around the sample.

Table 69

FILM AND PORE DIFFUSION EFFECTS
(See text for symbol definitions.)

Run Number	Source											
	ANL ³⁸		GE ³⁷		W-Bench Scale		W-TGA					
	HGC-25	HGC-30	B	E	1	4	12	13	14	15	16	17
Film:												
Voidage	0.42	0.42	-	-	0.5	0.5	-	-	-	-	-	-
Gas Velocity, cm/s	25	27	3.6	3.6	320	320	63	66	63	66	63	66
Aggregate Size, cm	0.22	0.22	0.8	1.1	0.36	0.36	0.72	0.72	0.72	0.72	0.72	0.72
k_g , cm/s	19	20	3.7	2.8	15	15	9.4	10	9.4	10	9.4	10
a , cm ² /cm ³	27	27	7.5	5.5	19	19	9.4	9.4	9.4	9.4	9.4	9.4
ϵ_f	0.14	0.15	0.21	0.23	0.03	0.08	2	2	3	3	2.4	2
Fore:												
D_{eff} , cm ² /s	0.0047	0.0047	0.047	0.060	0.016	0.016	0.17	0.17	0.17	0.17	0.17	0.17
L_{eff} , cm	0.037	0.037	0.13	0.18	0.053	0.053	0.006	0.106	0.106	0.106	0.106	0.106
ϕ_p	190	220	19	9	15	35	110	120	160	130	130	110
r_p	0.05	0.04	0.35	0.56	0.42	0.22	0.08	0.07	0.05	0.07	0.07	0.08
Film and Pore:												
R_o (mol/cm ³ sorb.-hr) x 10 ⁴	1.6	2.2	1.8	0.066	3.2	7.5	0.21	0.17	0.053	0.040	0.014	0.014
C_s (mol/cm ³) x 10 ¹⁰	5.2	6.3	40	2.3	92	86	0.54	0.43	0.16	0.19	0.043	0.043
ϕ	220	260	24	12	15	38	21	23	20	12	19	19
η	0.04	0.03	0.30	0.48	0.42	0.20	0.13	0.13	0.14	0.26	0.15	0.15
Rate Constant:												
k (cm ³ gas/cm ³ sorb.-hr)x10 ⁻⁵	77	87	1.5	0.60	0.83	4.4	58	62	59	19	48	28

The specific interfacial surface of an aggregate, pellet, or particle was calculated from geometry. Values are given in Table 69.

If film diffusion controls the observed rate, then $C_s = 0$ in equation (27). The observed rate may be compared to the film diffusion controlling rate by:

$$\frac{R_o}{k_g a C_o} = \phi_f, \quad (30)$$

where R_o is observed rate, $\text{mol/cm}^3 \text{ getter} \cdot \text{s}$
and ϕ_f is the ratio as defined by equation (30).

When ϕ_f is around 1 we can conclude that film diffusion is important, and when ϕ_f is much less than 1 we can conclude that film diffusion is fast and not controlling the observed rate. Note that whatever controls, the observed rate must equal the rate of film diffusion [i.e., $R_o = k_g a (C_o - C_s)$], so that if ϕ_f is less than 1 the real value of C_s is not near zero. Values of the observed rate R_o are given in Table 68, and corresponding values of ϕ_f are given in Table 69. For the GE data the rate must be expressed per unit volume of bulk sample, which can be done by multiplying the rate per unit volume of particle given in Table 68 by an estimated 0.58 cm^3 particle per cm^3 bulk sample.

The results show that the ANL, GE, and Westinghouse bench-scale reactor data were relatively unaffected by film diffusion limitations. The initial rates of the Westinghouse TGA tests were controlled by film diffusion. Of course, ϕ_f cannot really be more than unity. The high values shown in Table 69 are caused by the method of estimation of initial rates by using equation (26) to fit the data. The derivative of equation (26) mandates an increasing rate with decreasing time. In reality, the rate increases with decreasing time only until $\phi_f = 1$, and at lower times equation (26) does not apply - a straight line w vs. t relation does apply. Examining the derivative of equation (26), we find that only a short initial portion of each run is completely limited by film diffusion and that the rest of each run provides useful

kinetic data. For runs 12 and 13 the transition occurs 2 or 3 hours into the 20 hour duration test. Similarly, for runs 14 and 15 the transition occurs at about 6 hours (of 40) and for runs 16 and 17 at about 15 hours (of 80). Interestingly, the initial rates of our TGA tests were fast enough that, despite favorable mass transfer characteristics (k_g and a) relative to GE's TGA data, film diffusion was much more important a consideration. We shall return to this point later.

3.3.2.2.2. Pore Diffusion. Estimation of pore diffusional effects is much more difficult because of the complicated nature of diffusion within porous particles. Nevertheless, some estimate is necessary in order to understand what is happening and to draw conclusions about the most favorable contacting schemes.

Diffusion in small pores is governed not by bulk diffusion but by Knudsen diffusion, which can be estimated by:

$$D_k = 9700 r_p \frac{T}{M} \quad (31)$$

where

D_k is the Knudsen diffusivity, cm^2/s

r_p is the mean pore radius, cm

T is the temperature, K

M is the molecular weight of the diffusing species (NaCl).

For the ANL tests we have estimated the mean pore radius as 6.2×10^{-7} cm, as noted above. This gives values of D_k of 0.026 and 0.027 for the two ANL tests. The overall diffusivity can then be estimated from:⁴⁵

$$\frac{1}{D_t} = \frac{1}{D_{12}} + \frac{1}{D_k} \quad (32)$$

The diffusivity must still be corrected because much of the particle volume consists of impenetrable solid material and because a gas molecule must travel a twisted path to reach its site of adsorption. These effects are crudely taken into account by assuming:⁴⁶

$$D_{\text{eff}} = D_t \theta / \tau, \quad (33)$$

where

D_{eff} is the effective diffusivity of the gas molecule through the pellet

θ is the porosity

and

τ is the tortuosity.

The greatest difficulty is in estimating τ , and we have selected 2 as its value, based on the discussions of Satterfield,⁴⁶ to whose text the reader is referred. The final values of D_{eff} for the ANL data are given in Table 69.

Analysis of pore diffusion effects for the GE data is further complicated by the fact that the NaCl molecules must first diffuse through the space between particles in the sample bed and then through the pores of the particles themselves. This situation can be analyzed with a resistances in series model:

$$(C_s - C_m) \frac{D_1}{L_1} = (C_m - C_c) \frac{D_2}{L_2} = (C_s - C_c) \frac{D_{\text{eff}}}{L'}, \quad (34)$$

where

C_s is the concentration of salt in the gas at the boundary of the sample

C_m is the concentration of salt in the gas at the boundary of the individual particle

C_c is the concentration of salt in the gas at the final site of adsorption

D_1 is the interparticle diffusivity

D_2 is the intraparticle diffusivity

D_{eff} is the overall diffusivity

L_1 is the length of the average path from the sample boundary

L_2 is the length of the average pore

and

L' is the total path length ($L_1 + L_2$).

By eliminating C_m using the first equality in equation (34) and rearranging, we find that:

$$\frac{L'}{D_{\text{eff}}} = \frac{L_2}{D_2} + \frac{L_1}{D_1}. \quad (35)$$

Since the length of the average pore is much smaller than the sample dimension, $L' \approx L_1$. If the average pore radius is 62 Å, then D_2 is 0.0047 cm²/s, by the procedure leading to equation (33). The average particle size for the GE data was 0.06 cm, and the appropriate length of the intraparticle diffusional path was⁴⁷ the particle volume divided by the particle circumferential area, so L_2 is 0.01 cm. Similarly, L_1 is 0.13 cm and for GE test B and 0.18 cm for test E. The radius of the interparticle path is about 0.01 cm, so the Knudsen diffusivity for the interparticle path is about 400 cm²/s. This is much larger than the binary diffusivity of 1.0 cm²/s (Table 68), indicating that we can accurately represent D_1 by the 1.0 cm²/s figure, corrected for a porosity of 0.42 and a tortuosity of 2, to conclude that $D_1 = 0.21$ cm²/s. From equation (35), we then get effective net diffusivities of 0.047 and 0.060 cm²/s for GE tests B and E.

In the Westinghouse tests we used pellets that have bimodal pore size distributions. The large pores are those between the small grains compacted to form the pellet. The small pores are those in the grains themselves. An effective overall diffusivity, D_{eff} , can be obtained in a manner similar to that applied to the GE data. In this case we assume that the material has a similar microstructure to that assumed for the ANL and GE data, so that again D_2 is about 0.0047

cm²/s. The pellets were made of fine particles of about 14 μm mean size⁹ so that L₂ is about 2.3 x 10⁻⁴ cm. L₁ is the external surface area of the cylinder divided into its volume, or about 0.053 cm for the 3.2 mm (1/8 in.) cylinders in the bench-scale reactor tests and 0.106 cm for the 6.4 mm (1/4 in.) cylinders in the TGA tests. The Knudsen diffusivity in the large pores of approximate radius 2 μm is 9 cm²/s, while the bulk diffusivities are as in Table 68. Consequently, the effective diffusivities, before correction for porosity and tortuosity, are 0.1 for the Westinghouse bench-scale tests and 1.1 for the Westinghouse TGA tests. After correcting for porosity (0.33) and tortuosity, we apply equation (35) to get the effective net diffusivities in Table 69.

The effective diffusion lengths L_{eff} are also given in Table 69. For the ANL data this is the particle volume divided by the particle external surface area. For the GE and Westinghouse data this is L₁, as calculated above.

We can compare the observed rate per unit volume of sample to a hypothetical rate of pore diffusion in a manner similar to that used for film diffusion above. For spherical geometry with no film diffusion resistance, the rate of diffusion per unit volume of sample may be approximately represented by:

$$\frac{D_{eff} C_o}{r} \cdot \frac{Area}{Volume} \sim \frac{D_{eff} C_o}{r^2}, \quad (36)$$

where r is the sample radius. One can thus express the ratio of observed rate to this so-defined diffusion rate as

$$\frac{R_o r^2}{D_{eff} C_o} = \phi_p, \quad (37)$$

where ϕ_p is the observable modulus so defined. Weisz and Hicks⁴⁸ have presented graphical representations of ϕ_p versus an effectiveness factor, η_p , defined as the ratio of the achieved rate to that which would have been had there been no pore diffusion effects. This approach is

extensively utilized and accepted in the field of heterogeneous catalysis. The method is presented in many standard texts. It can be extended to heterogeneous reactions, providing the physical properties of the sorbent are not much modified with extent of reaction. The analysis is for first-order reactions and is presented relative to parameters representing the temperature gradient through the pellet caused by the heat of reaction and the activation energy. Because of the low concentrations and rates involved in alkali gettering, there will be not such internal temperature gradient, in which case the activation energy is of no importance. Therefore, knowledge of heat of reaction and activation energy are not needed for the present analysis.

Table 69 presents values of ϕ_p calculated as in equation (37). Note that:

$$r = 3 L_{\text{eff}} \quad (38)$$

Again, for the GE data, the observed rate of reaction given in Table 69 must be multiplied by about 0.58 to get it in terms of unit volume of bulk sample. The ratio of observed reaction rate to pore diffusion rate must really be one, of course, but the value of ϕ_p as calculated above can be greater than one. In that case we see that the intraparticle concentration gradient occurs near the exterior of the particle and that the reference diffusion rate of equation (36) is invalid.

Values of the effectiveness factor η_p for each data point have been read from the charts of Weisz and Hicks⁴⁸ at the appropriate value of ϕ_p , and are recorded in Table 69. We see that pore diffusion has reduced the rates of adsorption for all data points, but least for the GE and Westinghouse batch reactor data.

3.3.2.2.3. Combined Effects of Film and Pore Diffusion. The pore diffusion analysis to this point has ignored the effect of film diffusion limitation. We can repeat the analysis by first calculating C_s , the concentration of salt at the sample external surface, from the requirement that the observed rate must equal the rate of film diffusion, or:

$$R_o = k_g a (C_o - C_s). \quad (39)$$

Then C_s is used in this modification of equation (37):

$$\frac{R_o r^2}{D_{eff} C_s} = \phi. \quad (40)$$

Application of this technique to the ANL, GE, and Westinghouse batch reactor data is straightforward. We cannot use initial rates for the Westinghouse TGA tests, however, since then $C_s = 0$. Instead, we select the point on each w -vs- t curve where the observed instantaneous rate gives a value of the film diffusion modulus, ϕ_f of 0.5. For run 14, for instance, this occurs at 15 hours into the 40 hour run, at which time the rate, again given by the equation (26) curve-fit is one sixth that listed as the initial rate in Table 68, and one half the real initial rate. The values of C_s calculated at such points of reduced rate for our TGA tests are given in Table 69, as are the values of C_s for the other points' initial rates. Values of ϕ and η , the effectiveness factor in terms of C_s are also given in Table 69.

Since both film and pore diffusion limitations have now been taken into account, we can use this information to estimate the true rate that would have occurred had all diffusion limitations been eliminated. This rate is:

$$R_t = R_o / \eta. \quad (41)$$

If we assume that the adsorption is first order in gas-phase salt concentration, then for the ANL, GE, and Westinghouse batch reactor data we can calculate a rate constant:

$$k = R_t / C_s. \quad (42)$$

If we also assume that the adsorption is first order in the fraction of active sites remaining unoccupied, then for the Westinghouse TGA data we get:

$$k = (R_t / C_s) / (1 - w/w_s), \quad (43)$$

where w_s is the capacity of the sorbent at the appropriate temperature and salt concentration, and w is the weight gain at the point where R_o is measured. The value of w_s is identical to A in Table 68.

The values of k calculated from the various sources of data vary widely, as shown in Table 69. This is not surprising when one considers the many assumptions needed in the analysis. On closer examination, however, we see that calculated rate constants fall into two major groups. The first group, consisting of GE and Westinghouse bench-scale reactor data, showed relatively low rates of adsorption. The second group, consisting of the ANL and Westinghouse TGA data, featured much faster intrinsic kinetics. Each group has one set of flow-through packed-bed tests and one set of TGA tests. Each group also has one set of pellet tests and one set of off-the-shelf particle tests.

About the only factor that the members of a group have in common is the presence of water vapor. The ANL tests were performed using a simulated fuel gas with about 180 ppm H_2O , a concentration of the same order of magnitude as that of the NaCl vapor in those tests. The Westinghouse TGA tests were conducted with a house N_2 carrier gas containing several ppm H_2O , again the same order of magnitude as the salt concentration in those tests. On the other hand, the GE and Westinghouse batch reactor tests were made with argon as a carrier gas. Our argon had

a water content of about 0.03 ppm, very low compared to the concentration of salt. GE had high salt concentrations, and we presume that their argon had a similar moisture content. This information leads us to suspect that the presence of water vapor at a concentration similar to that of NaCl accelerates the rate of adsorption. ANL concluded that alkali gettering by bauxite is better with gas containing a few percent H₂O than with gas containing only 180 ppm H₂O.^{11,42} The fact that water can accelerate the sorption indicates that it is not a simple physical adsorption mechanism. The data we evaluate here suggest that a drier gas will be cleaned even less effectively.

3.3.2.2.4 Implication for Systems Design. This examination of diffusion effects on gettering suggests that some improvement in alkali gettering rates may be achieved by eliminating pore diffusion effects. The possible extent of that improvement, however, is limited.

Film diffusion limitations can be overcome either by increasing the mass transfer coefficient or by increasing the particle external surface to such an extent that mass transfer is fast simply by diffusion. The former approach can easily be implemented by increasing the velocity of gas flow past the getter particle. This is readily accomplished for flow through fixed granular beds where the gas does not support the solid sorbent particles. This is the approach that we advocate. If small particles are used, they will be suspended by any reasonable gas flow, and so the relative gas velocity is limited to the particle terminal velocity. On the other hand, the available area for diffusion per unit sorbent weight will be very large. The entrained dust approach suggested by GE^{36,37} accomplishes the elimination of film diffusion effects on overall rates in this way. Thus, several techniques can be used in the design of systems to avoid film diffusion problems.

Pore diffusion effects are most readily reduced or eliminated by increasing the porosity or decreasing the particle size of the getter material. Activated bauxite is a material whose porosity is already about as high as can be achieved, but "activation" of any other material

that is active as a getter in a similar manner should be considered. Reducing particle size is certainly a reasonable way to eliminate pore diffusion effects, but again, only a limited increase is possible. Unless, contrary to the evidence, it is a purely physical adsorption, the intrinsic rate will still be so low that an entrained dust will adsorb little salt in its limited (seconds) residence time. We will show this below. A deep packed bed, on the other hand, can remain on stream for indefinite periods since the sorbent is not carried away by the hot gas. Of course, relatively large particles must be used, and this will somewhat limit the achieved rate. For such systems, however, using deep beds, the absolute rate is not important in determining the depth of the bed required, but the ultimate capacity of the sorbent (g NaCl/g sorbent) is. We will show this below also. For this reason we prefer the fixed-bed approach. Fixed beds have other practical advantages relating to operation, as will be discussed.

3.3.2.2.5 Comments on Diffusion Analysis. A brief discussion of methods of evaluating pore diffusion effects is necessary at this point. In the above analysis we have analyzed this effect with the use of conventional techniques familiar to those involved in heterogeneous reactor design. While we have had to make a number of difficult assumptions, we have been able to assess the magnitude of the diffusivity of NaCl in getter systems. A diffusivity of about $0.05 \text{ cm}^2/\text{s}$ (a reduction by a factor of 20 from the gas phase value), for instance, has been calculated for the GE data. Based upon these data we conclude that a rate reduction of 50 to 70% due to pore diffusion limitations has occurred.

Available data, including GE's, show that pore diffusion does not preclude salt access to the pellet interior. The external surface area per unit mass of a 600 μm particle size used by GE is $71 \text{ cm}^2/\text{g}$ (compared to an internal area of $8.5 \times 10^5 \text{ cm}^2/\text{g}$). If the entire external area were occupied by salt molecules, a weight gain of 0.0036 mg/g would have been observed. Even one hundred times this amount would have been insignificant. We must conclude that salt has found its way

into the interior of the pellet if we are to explain the 20 to 50 mg/g recorded in only a few days.

Furthermore, GE's data³⁷ show that pore diffusion is not completely controlling. For instance, a run was made at conditions identical to those listed for run E in Table 68 except that the particle size was smaller (~ 250 to $300 \mu\text{m}$) and a smaller sample weight was used (run F³⁷). Under such conditions, the larger particles should have reacted much more slowly than the small particles if pore diffusion were the slow step. In fact, the smaller particles were observed to adsorb more slowly, although at a level that is most likely insignificantly different.

The GE analysis⁴⁹ stated that the applicable rate-determining diffusivity, when physical adsorption equilibrium is assumed at every point in a particle, is the average of the diffusivity of the molecules in the gas phase in the pellet and the diffusivity (zero) of the molecules already adsorbed. The calculated average is 10^{-9} times the binary gas-phase diffusivity. This number gives the impression that since adsorption reduces the diffusivity, it reduces the overall rate of pick-up of salt. There are several problems with this analysis:

1. It has not been demonstrated that a purely physical (i.e., infinitely fast) adsorption is occurring.
2. If the physical adsorption is valid, then probably the adsorbed molecules will have considerable mobility on the surfaces to which they are held by very weak forces, and the assumption of zero diffusivity for this phase will be incorrect. In this case the average diffusivity may easily exceed the gas-phase value.⁵⁰
3. The average diffusivity technique is used to calculate gas-phase concentration as a function of time and position in a particle. A lower average diffusivity means that at any time and position the gas-phase concentration will be much lower than for diffusion without adsorption in the same pellet⁵¹ - i.e., it will take longer for the gas-phase concentration in the pellet pores to reach the ambient gas-phase concentration. The total concentration, however, gas and surface, at any point and time will be greater with adsorption than without it. The total amount of material (NaCl) that has passed into the pellet up to any time

will be much greater with adsorption than without it. This makes physical sense because sorption provides a sink. It also follows from Crank's mathematical treatment,⁵² since although at any time the fraction of ultimate take-up is lower with adsorption, the ultimate take-up is much higher.

Also, the adsorbed molecules do not significantly hinder movement of gas molecules through the pores. GE estimates the area per NaCl molecule as $19 \text{ \AA}^2$, which corresponds to 4.3 wt% NaCl if the bauxite has an area of $85 \text{ m}^2/\text{g}$. Then the volume occupied by the adsorbed NaCl at monolayer coverage is

$$\begin{aligned} & \frac{0.043 \text{ g NaCl}}{\text{g bauxite}} \times \frac{\text{mole}}{58.5 \text{ g NaCl}} \times \frac{6 \times 10^{23} \text{ molecules}}{\text{mole}} \times \frac{19^{1.5} \text{ \AA}^3}{\text{molecule}} \\ & \times \frac{(10^{-8})^3 \text{ cm}^3}{\text{\AA}^3} = 0.037 \frac{\text{cm}^3}{\text{g}} \end{aligned} \quad (44)$$

This represents a 14% reduction in pore volume from the estimated value of $0.26 \text{ cm}^3/\text{g}$ reported earlier and a 7% reduction in mean pore radius. An overall reduction of 14% in the normal diffusion coefficient and 22% in the Knudsen diffusivity would result, hardly significant. This is not a factor of 10^{-9} , and is hardly even significant.

In the GE report⁵³ pore diffusion control and very fast sorption kinetics were assumed, and an effective diffusivity of $0.08 \text{ cm}^2/\text{s}$ was calculated to fit the data. This is similar to the values (0.047 to $0.060 \text{ cm}^2/\text{s}$) we determined on the basis of standard methods of estimation above and is certainly a number in the range expected. GE concluded that this was therefore a diffusion-controlled, physical adsorption process. The issue is not closed, but we believe there is evidence (additionally see Section 3.3.2.3 below) that the adsorption is not completely reversible, not strictly physical, and therefore not extremely fast. The rate is reduced by the slow pore diffusion, but not completely controlled by it. Thus, the assumption of complete diffusion control gives a back-calculated diffusivity in the right magnitude. It is prudent, pending experimental

demonstration of rapid gettering rates, contrary to all available data, to assess system performance based on finite kinetics, as done here.

3.3.2.3 Equilibrium Considerations

3.3.2.3.1 Introduction. Equilibrium considerations include the capacity of the getter at various conditions, the reversibility of the sorption process, the regenerability of the spent sorbent, and the stoichiometry of the process. The importance of these issues and the implications of the data regarding them are examined in the following sections.

3.3.2.3.2 Capacity. Knowledge of capacity is important to the design of a gettering system. For efficient systems, such as the deep fixed bed, that use nearly all the capacity of the getter, the depth of bed required and the annual sorbent consumption will be determined by getter capacity. For other systems in which sorbent is continuously processed and in which therefore the sorbent particles do not reach saturation, the capacity is important in the determination of the achievable rate, and so in determining the size of the contactor.

A further complication is that the capacity of the getter may be proportional to the gas-phase salt concentration, at least for the lower concentrations of interest. This means that when solid and gas are contacted cocurrently the gas-phase concentration will fall and the sorbent-phase concentration will rise, at most only until an equilibrium is established. In countercurrent operation, however, the gas-phase concentration at any point can fall to a value in equilibrium with the solids there. Thus, the gas leaving the reactor can approach zero salt concentration, since the inlet solids salt concentration is zero. Also, the solids can reach a high salt concentration before they are discarded, because exiting solids are in contact with fresh, salt-laden gas. The entrained dust reactor is an example of a cocurrent reactor and must have limited capacity, regardless of kinetics, if sorption capacity depends on gas-phase concentration. The fixed-bed reactor that we advocate is a

countercurrent device, so virtually complete gas cleaning and much reduced getter consumption are possible, even if kinetics are very fast.

3.3.2.3.3 Reversibility. A related question is that of reversibility. If the capacity is proportional to gas-phase concentration, then desorption of salt can occur when the inlet concentration drops, perhaps because of fluctuating operating conditions in the alkali source, the gasifier. In a cocurrent adsorber, equilibrium is approached nearest the adsorber exit. Desorption would therefore occur here first, and penetration would occur. In a countercurrent contactor equilibrium is approached throughout, but desorption occurs first at the input end of the contactor, since gas-phase concentration is already near zero at the other end. The desorbed salt will thus be transferred downstream and, given a well-designed reactor with some extra depth, be picked up by the clean solids there. The net effect is to stretch out the saturated zone of the solids flowing countercurrently to the gas. We believe this is another reason for preferring the packed-bed device.

Reversibility also relates to achievable rates. An adsorption that is only partially reversible when the getter is exposed to salt-free gas must contain relatively strong bonds - i.e., it is a chemisorption with finite activation energy and limited intrinsic rate. This does not preclude the "reversibility" of the reaction (that is, that the salt can be removed from the getter) by some other means that act to break these bonds, such as water solution.

3.3.2.3.4 Experimental Evidence. Available data support the idea that sorbent capacity decreases as gas-phase salt concentration declines. GE³⁷ found convincing evidence that this is so over a wide range of concentrations up to half the vapor pressure of salt at 1073 K. They developed a model adsorption isotherm that is essentially a hybrid of the BET isotherm for multilayer adsorption and the Langmuir isotherm for less than monolayer adsorption.

The Westinghouse TGA data, runs 12 through 17, also show that there is some effect of gas-phase concentration on capacity. This can be

seen by referring to the capacity row (A) in Table 68. Here the apparent capacity declines with decreasing concentration at each of the two temperatures.

Desorption runs were also made by both GE³⁷ and Westinghouse. In GE's desorption tests weight loss occurred when salt concentration was reduced. From examination of their data, it seems that about the same capacities were reached for a given concentration whether the concentration was reached by an increase from a lower concentration or a decrease from a high concentration, but they never turned the salt flow off completely. Instead, the lowest concentration was 0.4 ppmw Na, at which the apparent capacity was about half that at 255 ppmw Na. Both the Langmuir and BET isotherms assume zero capacity at zero concentration. GE assumed that a similar isotherm applied to their data, requiring that the concentration be moderately sensitive to concentrations above 0.4 ppmw Na but extremely sensitive to concentration at lower concentrations. There is nothing wrong with this analysis in light of the GE TGA data, but an alternative analysis in which a substantial part of the adsorbed NaCl is irreversibly bound would also fit the information.

Westinghouse made two TGA desorption runs: runs 18 and 19 reported above. In these runs, made at 1123 and 1173 K respectively, salt concentration was reduced suddenly from about 10 ppmv to about 0.002 ppmv after 40 hour periods of adsorption. Desorption was limited to about 25 and 10% for the two runs. While again there was a trace of salt still present, this is evidence of an irreversible step in the adsorption process.

Lack of reversibility implies that assuming very fast intrinsic kinetics, such as for physical adsorption, may be incorrect.

3.3.2.3.5 Physical Adsorption vs Chemisorption. There has been some question about whether the adsorption process is a simple physical adsorption mechanism or a chemisorption. The question is of some importance because of its implication for system design. GE³⁷ has modeled the adsorption process as a combination of these processes, with the physical mechanism somewhat more important. ANL⁵⁴ concludes that a physical adsorption mechanism permits regeneration of the activated bauxite. In reality, there is no real dividing line between physical and chemisorption. There will be a range of salt-substrate bond strengths ranging from weak to strong. To conclude that only one or the other dominates is not really appropriate. Chemisorption and physical adsorption are generally used as conceptual devices to address the important issues. These issues include:

- Sorbent capacity. If physical adsorption occurs, then presumably a multilayer adsorption is possible and, hence, a much higher degree of getter utilization is achievable. All the available data for bauxite indicate that complete monolayer coverage of the accessible interior surface area is not achieved at salt partial pressures of interest. Thus the issue is moot, except that physical adsorption has not been proved.
- Capacity dependence on partial pressure. A question related to the previous one is how we should model the dependence of capacity on salt partial pressure. Typically, for this purpose a Langmuir isotherm is used for chemisorption, and a BET isotherm is used for physical adsorption. If data are taken over a limited range of concentrations, then the type of model will greatly affect extrapolation to other concentrations. We can easily show that the BET isotherm reduces to the Langmuir form for partial pressures much lower than the equilibrium vapor pressure. Since we are only interested in gases with such salt vapor pressures, we might as well use the simple Langmuir form, regardless of whether physical or chemisorption occurs.
- Regenerability. Physically adsorbed molecules should be easily driven off thermally or washed off in a solvent. Some, but not all, chemically adsorbed molecules can be

removed in a like manner. Regenerability by water washing does not prove physical adsorption. Lack of regenerability, however, proves only that a chemical step is involved somewhere in the overall mechanism. Molecules can be initially removed from the gas phase as physically adsorbed species, and then some of the relatively mobile molecules could gradually migrate to sites where permanent chemical bonding occurs.

- Reversibility. Loss of previously adsorbed salt during in-service periods of low partial pressure can occur with either type of adsorption. Limited reversibility again does not necessarily mean that chemisorption is the initial mechanism of capture, but does show that chemical bonding does indeed occur at some point. Available data, discussed above, support this point. It has not been proved that irreversibility is not associated with the actual adsorption step.
- Kinetics. Finite, slow rates in the absence of strong diffusional limitations must mean an activated sorption which is best represented by chemisorption. The above analysis of diffusional constraints and the extraction of finite, intrinsic rates suggests that the process is best modeled as chemisorption. Assuming very fast intrinsic rates is not justified by the available bauxite data.
- Stoichiometry. Analysis of TGA data and, to some extent, assessing which gas-phase species exit from a getter contacting device depend on a knowledge of stoichiometry. Physical adsorption means that the stoichiometry is simple; gas-phase salt becomes solid phase salt. Chemisorption may also have this stoichiometry, or it can produce gaseous H_2O , HCl , or KCl , among others, but so can a chemical step after initial physical adsorption.

Atomic analysis of Westinghouse TGA and batch reactor sorbent samples, as reported above, showed distinct adsorbed sodium-to-chlorine ratios greater than one, indicating that significant chemical steps are involved, such as the displacement of potassium in the sorbent structure by sodium.

GE's data³⁷ on sodium-to-chlorine ratios also strongly suggest that chemical dissociation of $NaCl$ occurs. Their runs at 15 ppm Na showed Na-to-Cl ratios approaching two. The runs at 255 ppm Na showed Na-to-Cl ratios of around one. We speculate that at 255 ppm physical adsorption or nondissociating chemisorption dominates, while at 15 ppm strongly bonded chemisorption predominates over physically adsorbed salt. Another interpretation is that there was more

time for migration of adsorbed material to reactive sites for subsequent dissociation, since the low concentration runs were longer. Furthermore, of three runs (C, D, B) conducted initially at 255 ppmw Na, only run B was then further exposed to desorption conditions, its exposure to hot conditions thus being significantly longer. This run showed a significantly higher Na-to-Cl ratio than the other two.

- Temperature effect on capacity. All physical adsorption and most chemisorptions are exothermic processes. Thus, one cannot distinguish between them on the basis of a temperature effect unless increased temperature results in increased adsorption. ANL's bauxite data,¹⁰ GE's data,³⁷ and our TGA data show decreasing adsorption with increasing temperature.

In summary, it appears that the adsorption process is a complex one, involving several parallel and sequential steps. Physical, nondissociative chemical, and dissociative chemical steps may all be involved. Based on the data available, however, a simple, single-step adsorption model, treating capacity with a Langmuir isotherm and kinetics as finite, is appropriate.

3.3.2.4 Gettering Reactors

There are two main approaches to the design of hot alkali gettering systems. These are the entrained fine particle reactor suggested by GE^{36,37} and the fixed-bed reactor that we advocate. (In addition ANL⁵⁴ has proposed a staged, fixed-bed reactor with the sorbent being periodically or continuously regenerated.) In this section we examine the sizing of entrained-particle and fixed-bed reactors, as well as sorbent consumption, based on kinetics and equilibria estimated from the data presented above. Finally, we note other important factors, primarily operational, involving these alternative systems. First, however, we present the basic kinetic expressions used in the analysis.

3.3.2.4.1 Rate Expressions. The intrinsic rate of alkali gettering is assumed to be first order in salt concentration and first order in the fraction of possible adsorption sites remaining at any point. We assume that the Langmuir adsorption isotherm adequately represents the dependence of sorbent capacity on gas-phase salt

concentration and temperature. Furthermore, water vapor is present, so the higher intrinsic rate constant from Table 69 applies. In each case the intrinsic rate constant must be multiplied by an effectiveness factor to get an effective rate constant.

The Langmuir adsorption isotherm leads to a rate expression as follows: At any given time the fraction of adsorption sites on a particle that are already occupied by adsorbed molecules is:

$$w/w_m, \quad (45)$$

where

w = concentration of adsorbed Na on getter, gNa/g sorbent

w_m = w if all possible sites are occupied.

The rate of adsorption is proportional to the fraction of sites unoccupied and to the concentration of salt. The desorption rate is proportional to the fraction of sites occupied. The net adsorption rate is:

$$\frac{dw}{dt} = k_1 \left(1 - \frac{w}{w_m}\right) C - \frac{w}{w_m} k_2, \quad (46)$$

where

k_1 = forward rate constant, gNa $\cdot$ m³gas/g sorbent $\cdot$ gmol Na $\cdot$ hr

k_2 = reverse rate constant, gNa/g sorbent $\cdot$ hr

C = salt concentration in gas-phase, gmol Na/m³ gas

t = time, hr.

Eventually an equilibrium is reached at which $\frac{dw}{dt} = 0$. At that time w reaches the sorption capacity, w_s , found by rearranging equation (46):

$$w_s = \frac{w_m}{K + 1}, \quad (47)$$

where

w_s = sorption capacity at C , gNa/g sorbent

$K = k_2/k_1$, gmol Na/m³ gas.

Equation (47) can be combined with equation (46) to give:

$$\frac{dw}{dt} = \frac{k_1 C}{w_s} (w_s - w), \quad (48)$$

where w_s is given by the two-parameter model of equation (47).

From the data of Table 69 we estimate:

$$\begin{aligned} k_1 &= 60 \times 10^5 \frac{\text{cm}^3 \text{ gas}}{\text{cm}^3 \text{ sorbent hr}} \times \frac{23 \text{ g Na}}{\text{gmol Na}} \times \frac{\text{cm}^3 \text{ sorbent}}{1.4 \text{ g sorbent}} \times \frac{\text{m}^3 \text{ gas}}{10^6 \text{ cm}^3 \text{ gas}} \\ &= 100 \text{ gNa} \cdot \text{m}^3 \text{ gas/g sorbent} \cdot \text{gmol Na} \cdot \text{hr}. \end{aligned} \quad (49)$$

The data do not support estimation of a temperature dependence for k_1 .

We are primarily interested in performance at low salt concentrations. We, therefore, derived the constants for equation (47) from the Westinghouse TGA-based capacity estimates, reported as g NaCl/100 g sorbent in Table 68. After conversion to gNa/g sorbent, the 1123 K capacity estimates were used in a least-squares analysis to determine w_m and K for the linearized rearrangement of equation (47):

$$w_s = w_m - K \left(\frac{w_s}{C} \right). \quad (50)$$

The parameter K can be expected to have an Arrhenius-type temperature dependence:

$$K = B e^{H/T}, \quad (51)$$

where:

B = a constant, gmol NaCl/m³ gas

H = the heat of adsorption divided by the ideal gas constant, K

T = Temperature, K.

The six TGA capacity estimates were used to assess the best values of B and H, given the value of w_m determined in the preceding analysis. This was again done by a least-squares analysis of the equation resulting from equations (47) and (51).

$$\ln \left(C \left(\frac{w_m}{w_s} - 1 \right) \right) = \ln B + H \left(\frac{1}{T} \right). \quad (52)$$

The results of this procedure gave:

$$\begin{aligned} w_m &= 0.0111 \text{ g Na/g sorbent} \\ B &= 2.28 \times 10^8 \text{ g mol NaCl/m}^3 \text{ gas} \\ H &= -34500 \text{ K.} \end{aligned}$$

3.3.2.4.2 Entrained-Flow Reactor. In an entrained particle reactor, which would presumably be a length of pipe preceding the GBF vessel or directly preceding a turbine, getter is injected at the beginning of the reactor and is conveyed by the gas stream, stripping alkali as it goes. In the analysis of this system, we have assumed that the particle size is small enough for the slip velocity of the particle relative to the gas to be insignificant relative to the absolute gas velocity through the pipe. We assumed further that the chemical kinetics above control the reaction rate, so particle size is unimportant, and the effectiveness factor is one - i.e., no diffusional limitations.

The mass balance for sodium in the entrained-flow reactor gives the design equation:

$$U \frac{dC}{dx} = -r, \quad (53)$$

where U = gas velocity, m/hr

C = concentration of sodium in gas stream, mol Na/m³

x = distance through reactor, m

r = rate of conversion, mol Na/m³-hr.

The rate r is determined from equation (46):

$$r = \left[k_1 \left(1 - \frac{w}{w_m} \right) C - \frac{w}{w_m} k_2 \right] \frac{G}{M}, \quad (54)$$

where G = getter loading in gas stream, g-sorbent/m³ gas

M = atomic weight of Na, 23 g/mol.

We know that $k_2 = K \cdot k_1$ and, since gas and solid travel cocurrently,

$$w = \frac{M (C_{in} - C)}{G}, \quad (55)$$

where C_{in} = concentration of Na in dirty gas entering reactor, mol/m³.

Combining these relations we obtain:

$$-U w_m \frac{dC}{dx} = k_1 C^2 + \left(\frac{k_1 w_m G}{M} - k_1 C_{in} + k_2 \right) C - C_{in} k_2. \quad (56)$$

Variables (x and C) can be easily separated, and this equation can be solved with the use of a table of integrals. At $x = 0$ we know that $C = C_{in}$, while at $C = C_{out}$, $x = L$,

where C_{out} = concentration of salt in leaving cleaned gas, mol/m³

L = reactor length, m.

Once L has been obtained by solution of equation (56) we can evaluate the percent of sorbent ultimate capacity utilized:

$$Y = \frac{100M (C_{in} - C_{out})}{G w_m} \quad (57)$$

and the residence time required, τ , in hr:

$$\tau = \frac{L}{U}, \quad (58)$$

which is equivalent to the reactor volume requirement in (m^3 vessel)/(m^3 gas/hr).

Table 70 shows some calculated residence times, sorbent utilizations, and sorbent consumption rates for various degrees of cleaning and an inlet concentration of 1.09×10^{-3} mol Na/ m^3 (10 ppmv at 10 atm, 1123 K). Note that the degree of gas cleaning possible at a specific getter dust loading is limited because the exiting getter is in contact with clean gas, and so its saturation capacity will be low [equation (47)]. The only way to achieve a lower outlet gas-phase concentration is to accept lower sorbent utilization, which requires greater sorbent consumption rates.

Also note that the reactor length can be found by multiplying the value of τ in Table 70 by the superficial gas velocity required. The vessel volumes and depths are very large for any reasonable degree of cleaning. For example, if a velocity of 10^4 m/hr (2.8 m/s) is used, then depths of 4500, 1400, 220, and 110 m will be required at respective dust loadings of 5, 10, 50, and 100 g/m^3 . Shorter vessels can be obtained for proportionately more cross-sectional area. Alternatively, smaller vessels can be obtained by going to higher dust loadings. Note that dust loadings are already very high ($100 \text{ g/m}^3 = 44 \text{ gr/ft}^3$) and that at 100 g/m^3 only about 2% of sorbent ultimate capacity is being used.

3.3.2.4.3 Fixed-Bed Reactor. With a fixed-bed reactor, a vessel is filled up with sorbent particles once or twice a year. Alkali-laden gas is passed through the bed until the getter becomes saturated with adsorbed salt. Then the bed material must be changed or alkali will penetrate. A sufficiently deep bed can be specified so that changing the material can be accomplished during regular annual or semiannual plant maintenance shutdowns. No equipment is needed for continuously feeding, transporting, and removing solids. Handling is only occasional, and then with conventional equipment, because the solids are allowed to cool down before the vessel is opened.

Table 70
ENTRAINED PARTICLE REACTOR PERFORMANCE

G	1.0		5.0		10		50		100	
	Y	τ	Y	τ	Y	τ	Y	τ	Y	τ
C_{out}/C_{in}										
0.57	97.2	0.67								
0.50	*	*	22.6	0.037	11.4	0.017	2.26	0.0032	1.14	0.0016
0.10			40.7	0.15	20.4	0.062	4.07	0.011	2.04	0.0054
0.05			42.9	0.21	21.6	0.083	4.29	0.014	2.16	0.0070
0.01			44.7	0.45	22.5	0.14	4.47	0.022	2.25	0.011
0.005			*	*	22.6	0.17	4.49	0.026	2.26	0.013
0.001					*	*	4.51	0.036	2.27	0.017
0.0005							4.51	0.047	2.27	0.019
0.0001							*	*	*	*

Y = percent of ultimate sorbent capacity utilized in exiting dust.

τ = residence time required, hr; or equivalently, volume of reactor required in m^3 per (m^3/hr) of gas cleaned.

G = sorbent loading in gas stream and sorbent consumption, g sorbent/ m^3 gas processed.

C_{in} = inlet stream alkali concentration, 1.09×10^{-3} mol Na/ m^3 gas.

C_{out} = outlet stream alkali concentration.

* = this and lower outlet concentrations are not possible at this G.

A packed bed is a countercurrent contacting device. This permits a greater degree of adsorption (g Na/g sorbent) than a cocurrent device operating to clean a gas stream to an equal extent. If alkali-laden gas were put in at the bottom of a packed bed we would see that at any particular time the lower part of the bed is completely saturated with alkali and that the upper part of the bed contains no alkali. The lower part of the bed is exposed to the highest available salt concentration, the inlet-gas concentration, and so has the highest possible capacity [equation (47)]--which it reaches. As time passes, the boundary between the dirty lower portion of the bed and the clean upper part of the bed rises until it reaches the top of the bed, at which point no further gas cleaning can occur and the bed must be changed. If the bed is deep enough, a long time can pass between changes.

In reality, there is a boundary of finite but narrow thickness that separates the two zones. All the actual gettering occurs in the boundary region, and there the degree of sorbent utilization will vary with position from saturation to zero. If the bed is deep enough to require replacement only once or twice a year, then the width of the boundary zone will be negligible compared to the total bed depth. Thus, nearly complete saturation of the bed material is possible. If replacement on a frequent (several hours to several days) basis is attempted, then the reaction zone thickness becomes important and since in it the getter is unsaturated, mean sorbent utilization will be reduced.

A batch, packed-bed reactor is characterized by both concentration and getter utilization varying with time and distance through the reactor. Do and Weiland⁵⁵ have obtained a solution for the performance of a fixed-bed catalytic reactor in which a first-order conversion of a gas species occurs in parallel with a first-order (with respect to some other gas species) poisoning of a catalyst. Thus, the kinetics are modeled by:

$$r_f = k_f \bar{a} C \quad (59)$$

and

$$\frac{d\bar{a}}{dt} = -k_d \bar{a}, \quad (60)$$

where

r_f = rate of gettering, mol Na/m³ reactor-hr

k_f = gettering rate constant, m³ gas/m³ reactor-hr

$\bar{a}$ = solid activity

k_d = rate constant for deactivation, m³ gas/mol Na-hr.

t = time, hr.

This development can be extended to noncatalytic reactions of first order by defining the activity to be [referring to equation (48)]:

$$\bar{a} = \frac{w_s - w}{w_s}, \quad (61)$$

from which

$$\frac{d\bar{a}}{dt} = \left(\frac{1}{w_s} \right) \left(-\frac{dw}{dt} \right). \quad (62)$$

We see from equations (48), (60), (61), and (62) that:

$$k_d = \eta k_1 / w_s, \quad (63)$$

where η is the effectiveness factor, accounting for diffusional limits.

Furthermore,

$$r_f = \left(\frac{dw}{dt} \right) \frac{\rho_B}{M}, \quad (64)$$

where ρ_B = solids bulk density in the reactor, g/m³,

so

$$k_f = \eta k_1 \frac{\rho_B}{M}. \quad (65)$$

The solution of the mass balance equation for near plug flow of gas through a packed bed with kinetics given by equations (59) and (60) gives the outlet concentration at any time:⁵⁵

$$\frac{C_{out}}{C_{in}} = \frac{1}{e^{-k_d C_{in} t} (e^{k_f L/U} - 1) + 1}, \quad (66)$$

where again U = the superficial fluid velocity, m/hr

L = the depth of the bed, m

C_{in} = the inlet concentration of alkali in the gas, mol/m³

C_{out} = desired outlet concentration of alkali, mol/m³.

Equation (66) can be rearranged, and k_f and k_d eliminated, to give:

$$L = \frac{UM}{\rho_B} \left(\frac{\ln(R-1)}{nk_1} + \frac{C_{in} \tau_s}{w_s} \right), \quad (67)$$

where $R = C_{in}/C_{out}$ at the end of the useful bed life

and τ_s = bed life, hr.

Note that again the required bed depth is proportional to the velocity of gas through it. Also, the depth is given by the sum of two terms, the first of which is the thickness of the reaction zone and the second of which is the depth of the saturated zone at the conclusion of the useful life of the bed. The thickness of the reaction zone depends on the ratio of inlet to outlet concentration and on the effective rate constant. The thickness of the saturated zone is independent of these but depends on the inlet concentration, the life of the bed, and the saturation capacity of the getter. In general, the second term is much more important if a long bed life is required. Therefore, we see the importance of having a getter with a large capacity.

In using equation (67), we use w_s from equation (47) evaluated at C_{in} . For a packed bed the rate constant k_1 must be multiplied by the effectiveness factor. For 0.65 cm particles we estimate that the film mass transfer coefficient, k_g , at 1123 K and 10 atm, is 4 cm/s for flow

through packed beds using Carberry's⁴³ correlation discussed above. The film transfer area, a , is $9.2 \text{ cm}^2/\text{cm}^3$. The initial effectiveness factor for film diffusion is:⁴³

$$\eta_f = \frac{1}{1 + \frac{k}{k_g a}}, \quad (68)$$

where k is $60 \times 10^5 \text{ cm}^3 \text{ gas}/\text{cm}^3 \text{ sorbent} \cdot \text{hour}$, as estimated in Table 69. Thus $\eta_f = 0.02$. From the analysis of Table 69, we estimate the effectiveness factor for pore diffusion as 0.15. The overall effectiveness factor will be the product of these, or 0.003 for fresh sorbent. As alkali is picked up by the sorbent, the intrinsic rate will decline, so the effectiveness factor will increase, eventually reaching 1 as the getter approaches saturation. The development of equations (66) and (67) assumes a constant effectiveness factor, but we know the value of this factor varies. Nevertheless, we can get a conservative estimate of bed depth by assuming the above lower factor applied throughout.

For the batch packed-bed reactor the amount of sorbent consumed per unit of gas processed is:

$$G' = \frac{L \rho_B}{U \tau_s}, \quad (69)$$

where $G' = \text{g sorbent}/\text{m}^3 \text{ gas}$.

Then the percent of sorbent ultimate capacity actually utilized is

$$Y' = \frac{100 M C_{in}}{G' w_m}. \quad (70)$$

Note that equation (70) uses C_{in} , whereas equation (57), for an entrained-particle reactor, uses $(C_{in} - C_{out})$. This is because in a deep-packed-bed reactor $C_{out} = 0$ for nearly the entire life of the bed. The required gas residence time or, equivalently, vessel volume required in $\text{m}^3 \text{ vessel}/(\text{m}^3 \text{ gas}/\text{hr})$ is given by equation (58).

Table 71 illustrates design parameters for a packed-bed getter reactor designed to achieve 4000 hours of use before alkali breaks through at the indicated level. Conditions are the same as those used to develop Table 70. Typical bed depth for a superficial velocity of 1000 m/hr are shown. Sorbent consumption and required volume are low. Longer bed life would require a proportionately deeper bed, but sorbent consumption would be the same. Note that the outlet concentrations in Table 71 are those at the end of 4000 hr. Outlet concentrations are nearly zero for most of the run. For instance, $C_{out}/C_{in} = 10^{-5}$ at 3906 hours for the case labeled $C_{out}/C_{in} = 0.1$ in Table 71. This suggests the possibility that a smaller bed would be required if the mean outlet concentration over the life of the bed, rather than the concentration at the end of this life, were our criterion.

Equation (61) gives the outlet gas concentration as a function of time. We can integrate equation (61) over the period $0 \leq t \leq \tau_s$, divide by τ_s , and obtain the mean outlet concentration over the life of the bed:

$$\frac{C_{out}}{C_{in}} \Big|_{\text{mean}} = \frac{\ln \left(1 + \frac{e^{k_d C_{in} \tau_s - 1}}{e^{k_f L/U}} \right)}{k_d C_{in} \tau_s} \quad (71)$$

Table 72 shows the bed depth required to achieve a desired mean outlet salt concentration over the life of the bed. Only slight reduction in bed depth from the previous case (Table 71) is achieved.

3.3.2.4.4 Comparison of Reactor Types. The entrained-particle reactor can be compared to the fixed-bed reactor using Tables 70 and 71. Consider a case where the maximum allowable salt concentration is 0.01 times the inlet concentration. A packed-bed reactor would consume 2.37 g sorbent/m³ gas processed and would require a reactor volume of 0.011 m³/(m³/hr) of gas processed. With an entrained-particle reactor we have to choose between greater sorbent consumption and greater reactor volume to achieve the same degree of cleaning. At one extreme we can use 5.0 g sorbent/m³ gas with a reactor 40 times the volume of

the packed-bed reactor. At the other extreme we use 100 g sorbent (40 times the consumption rate for the fixed bed) in an equivalent volume. We pointed out that the calculations leading to Table 70 have used the highest justifiable rate constant. Since entrained-reactor performance depends strongly on rate constant, we think that actual entrained particle reactor performance is more likely to be worse than better than predicted here. On the other hand, packed-bed reactor performance calculations used a very low rate constant and the performance is largely unaffected by the rate constant anyway, so the estimations of Tables 71 and 72 should be realistic. Comparing further the packed-bed reactor with an ideal entrained-flow reactor of infinite rate constant is instructive. In that case the gas and solids instantly reach equilibrium, so the reactor can be small, just large enough to ensure uniform dispersal of the smoke in the gas. Sorbent consumption, however, will be greater than for the packed-bed reactor, because of the cocurrent contacting mode. Sorbent consumption in the ideal entrained-flow reactor can be found by using equation (47) to determine sorbent capacity at the outlet concentration of interest. Then the material balance requires that

$$G = \frac{M}{w_s} (C_{in} - C_{out}) . \quad (72)$$

Continuing the example, 4.4 g sorbent /m³ gas processed would be required, compared to 2.37 g/m³ in the packed-bed case. If the maximum allowable outlet concentration were 0.001 times the inlet concentration, the ideal entrained-flow reactor would require 23.8 g/m³, as compared to 2.41 g/m³ for the packed-bed reactor.

Nonetheless, Tables 71 and 72 indicate that rather large reactor volumes are required for hauxite because of its low capacity.

A number of other considerations are relevant in comparing the two reactor types. First, for the entrained-particle reactor we have these issues:

Table 71

BAUXITE PACKED-BED REACTOR PERFORMANCE IN TERMS OF MAXIMUM (FINAL)
OUTLET CONCENTRATION

C_{out}/C_{in}	0.1	0.01	0.001	0.0001
L, m	11.19	11.41	11.62	11.83
G', g sorbent/m ³ gas	2.32	2.37	2.41	2.45
Y', % utilization	98.2	96.2	94.6	93.0
τ , hr	0.011	0.011	0.012	0.012

Bed life = 4000 hr.

$C_{in} = 1.09 \times 10^{-3}$ mol Na/m³ gas.

C_{out} = outlet concentration at 4000 hr.

Bed depth, L, for 1000 m/hr superficial velocity.

Table 72

BAUXITE PACKED-BED REACTOR PERFORMANCE IN TERMS OF MEAN
OUTLET CONCENTRATION

C_{out}/C_{in}	0.1	0.01	0.001	0.0001
L, m	9.97	10.96	11.06	11.07
G', g sorbent/m ³ gas	2.07	2.27	2.29	2.30
Y', % utilization	99.1	99.4	99.4	99.1
τ , hr	0.010	0.011	0.011	0.011

Bed life = 4000 hr.

$C_{in} = 1.09 \times 10^{-3}$ mol Na/m³ gas.

C_{out} = mean outlet concentration over life of bed.

Bed depth, L, for 1000 m/hr superficial velocity.

- Generation of submicron dust. GE^{36,37} suggests the continuous oxidation of metal chlorides to generate the oxide dusts. To our knowledge, the demonstration of this process on this scale has not yet occurred.
- Activity of the dust. There is no evidence that such a dust will adsorb alkali.
- Fate of the chlorine. The chlorine liberated in the dust production step may be damaging to the turbine.
- Dust injection. The generated dust will have to be introduced into the gas stream, which will be at pressure and, for gasification systems, will be a reducing gas. Unless very long, narrow getter reactors are used, special care will have to be taken to ensure that the getter is distributed across the gas stream.
- Removal of the dust from the gas stream. The loading of submicron dust will be much greater than the loading of dust of any size escaping the inertial dust collectors of the process. A huge and difficult filtration problem will have to be solved.

For the fixed-bed reactor these issues remain:

- Pressure drop. A fixed-bed operated at the conditions discussed above will have a pressure drop of about 1 kPa/m (0.045 psi/ft). This means a loss of 11 kPa (1.6 psi) for an 11 m deep bed. The pressure drop can be substantially reduced by using larger particles, a step that will cause the effective rate constant to become even lower. The rate constant, however, has very little effect on reactor performance, as discussed above.
- Dust accumulation. A fixed bed will act as a filter for dust carried by the gas stream. It will probably be necessary to place the getter reactor following the final particulate control device. In addition, care will have to be taken to periodically destroy, or to prevent, cakes formed by surviving dust. It may be possible to prevent cake formation by using large particles, turning the reactor into a deep bed filter, with little consequent increase in pressure drop caused. More attention needs to be given to this area.

3.3.3 Emathlite Getter Reactor

In this section we examine the use of the packed-bed gettering reactor, using the preferred getter material, emathlite. We do not consider other modes for the reasons stated in Section 3.3.1.

3.3.3.1 Kinetics

We observed during TGA and bench-reactor testing of emathlite that the gettering reaction is essentially an irreversible one, resulting in the formation of a product glass layer around the emathlite pellet, and that the interior of the pellet is not converted. Consequently, we modeled the reaction's rate as having been determined by diffusion of Na through the product layer to the reaction zone. In any practical system this glass layer will be narrow when reaction rate has slowed to a near halt, so we used a flat-plate model⁵⁶ to describe mathematically the inward progression of the product layer. Thus,

$$\frac{dm}{dt} = \frac{A^2 F D k_c C_s}{m} = \frac{A^2 k C_s}{2m}, \quad (73)$$

where m = moles Na/pellet

t = time, hr

A = pellet exterior surface area, m^2 /pellet

F = moles Na absorbable per m^3 of pellet at saturation

D = diffusivity of Na through product layer, m^2 /hr

k_c = ratio of concentration of adsorbed Na on the pellet surface to concentration of NaCl in gas phase at pellet surface

C_s = NaCl concentration in gas phase in contact with pellet, mol/m^3

k = lump diffusion rate constant defined as $2FDk_c$, collecting all unknowns that are assumed to be constant for emathlite, $mol/(m \cdot hr)$.

Furthermore, the reaction rate must equal the rate of diffusion through the gas film surrounding the pellet:

$$\frac{dm}{dt} = k_g A (C - C_s), \quad (74)$$

where k_g = film diffusion coefficient, m/hr

C = concentration of NaCl in bulk gas, mol/m³.

Combining equations (73) and (74) to eliminate C_s , we have

$$\frac{dm}{dt} = k_g AC \left[1 / \left(1 + \frac{2 k_m}{Ak} \right) \right] . \quad (75)$$

For purposes of stoichiometry, the following reactions are assumed:

Reactions (76) and (77) are assumed to compete for a brief period at the start of pellet exposure to NaCl-carrying gas, but reaction (77) is complete in a few hours, to the extent that 95 percent of all potassium initially in a pellet is released, as showed by AA test results on the reacted emathlite.

For each TGA run with a well-defined bulk gas salt concentration history, the value of k_g was determined by a standard correlation.⁴⁴ Then the weight-gain-vs-time curve was fitted by an expression of the form of equation (26) for mathematical convenience. Then the value of k was determined for each run from the integrated form of equation (75) between two points on the mathematically approximated curve of weight gain vs time: one point near the end of the useful portion of the run (i.e., prior to accumulation on the hangdown wires, if applicable); the other point early in the run but after the completion of reaction (77). From reaction (76) we established the stoichiometric basis for

conversion of the TGA observed weight gain to moles Na gained in this period when only reaction (76) is occurring (31 g wt gain/mol Na).

The following rate constants were determined:

TGA run	37	38	40	41	42	44	46	47	48
k, mol/(m·hr)	146	140	121	102	92	77	110	83	192

The rate constants represent the combined effects of diffusion through the glass layer, the ultimate capacity of the getter, and assumed equilibria between gas-phase and surface NaCl concentrations at the pellet surface. TGA run 44 had a low water vapor concentration (1 mol% vs 4 mol% in the other runs), which might explain the low constant for that run. TGA 48 gave a relatively high constant, probably an artifact of the method of curve approximation using equation (26): if the early part of run 48 (a long exposure run) is approximated this way, a lower rate constant is eventually obtained. Therefore, we believe the rate constant given for run 48 is more representative of the kinetics for long-duration exposure. At this point, however, we use the average of the TGA rate constants above, 120 mol/(m·hr), in a system modeling, to be conservative.

3.3.3.2 Packed-Bed Reactor

The packed-bed catalytic reactor model of Do and Weiland⁵⁵ was also solved by those authors for the case of first-order conversion of gas accompanied by third-order (in activity) deactivation of the catalyst. In that case equation (59) still applies, but equation (60) is replaced by

$$\frac{d\bar{a}}{dt} = -k_d C \bar{a}^3. \quad (78)$$

Do and Weiland⁵⁵ note that equation (78) is applicable for reactions whose rates are determined by diffusion through the deactivated (or

converted) layer formed from the outer surface of the particle inward, as in the current application.

Equations (75) and (59) are related by

$$r_f = N \frac{dm}{dt}, \quad (79)$$

where

r_f = gettering rate, mol Na/m³ reactor-hr

N = number of getter particles or pellets per m³ of reactor.

Now, let us define the activity as

$$\bar{a} = \left(1 + \frac{2 k_g m}{Ak} \right)^{-1}. \quad (80)$$

Combining equations (75), (79), and (80) we get:

$$r_f = N k_g A \bar{a} C. \quad (81)$$

By comparing equations (59) and (81), we see that

$$k_f = N k_g A \quad (\text{hr}^{-1}). \quad (82)$$

Now, differentiating equation (80) and eliminating dm/dt from equation (75) give:

$$\frac{d\bar{a}}{dt} = - \frac{2 k_g^2}{k} C \bar{a}^{-3}. \quad (83)$$

Comparing equations (78) and (83) shows that

$$k_d = 2 k_g^2 / k \quad (\text{m}^3/\text{mol-hr}). \quad (84)$$

Do and Weiland's analytical solution of equations (59) and (78), in terms of bed depth, is

$$L = \frac{U}{k_f} \left\{ \ln R + \left(1 - \frac{1}{R}\right) \left[(1 + 2 k_d C_{in} \tau_s)^{1/2} - 1 \right] \right\}, \quad (85)$$

where

U = superficial gas velocity through the bed, m/hr

C_{in} = concentration of NaCl in gas entering reactor, mol/m³

C_{out} = concentration of NaCl in gas leaving reactor, mol/m³

$R = C_{in}/C_{out}$

τ_s = bed life, hr.

The first term in equation (85), $(U/k_f) \ln R$, represents the thickness of the reaction zone. The second term represents the thickness of the "saturated" zone. The latter predominates if a long bed life is required, just as for bauxite. Note that even in the long time frame, however, a pellet does not become really saturated, as indicated by the assumed kinetics of equation (75).

The sorbent consumption is

$$G = \frac{LN m_p}{U \tau_s}, \quad (86)$$

where

G = g sorbent/m³ gas

m_p = mass of single pellet, g.

The required gas residence time or, equivalently, the reactor volume requirement in m³ reactor/(m³ gas/hr) is

$$\tau = \frac{L}{U}. \quad (87)$$

The sodium concentration in the bed at τ_s is

$$w = \frac{C_{in} M}{G}, \quad (88)$$

where $M = 23$, sodium atomic weight.

Consider the example conditions of sections 3.3.2.4.2 and 3.3.2.4.3 in which gas at 10 atm and 1123 K, containing 1.09×10^{-3} mol Na/m³ must be cleaned. Use a packed bed of large (1.27 cm diameter) emathlite particles. Then the parameters for use in equations (82) and (84) through (88) are

$$\begin{aligned}k_g &= 2.5 \text{ cm/s} \\N &= 4.66 \times 10^5 \text{ particles/m}^3 \\A &= 5.07 \times 10^{-4} \text{ m}^2/\text{particle} \\k &= 120 \text{ mol/(m}\cdot\text{hr)} \\m_p &= 1.10 \text{ g.}\end{aligned}$$

Table 73 shows bed depth, sorbent consumption, gas residence time required, and sorbent sodium content as functions of degree of cleaning. Compared to bauxite (Section 3.3.2.4.3), the sorbent

Table 73
EMATHLITE PACKED-BED PERFORMANCE IN TERMS OF MAXIMUM
(FINAL) OUTLET CONCENTRATION

C_{out}/C_{in}	0.1	0.01	0.001	0.0001
L, m	1.50	1.75	1.87	1.98
G, g sorbent/m ³ gas	0.192	0.224	0.239	0.253
τ , hr	0.0015	0.0018	0.0019	0.0020
w, g Na/g sorbent	0.131	0.112	0.105	0.099

Bed life = 4000 hr

$C_{in} = 1.09 \times 10^{-3}$ mol Na/m³ gas

C_{out} = outlet concentration at 4000 hr

Bed depth, L, for 1000 m/hr velocity

consumption and reactor volume requirements are much lower, primarily because of greater getter capacity. The results are summarized in Figure 79, which shows required bed depth as a function of both desired bed life and degree of cleaning required for this example.

The large particle size (1.27 cm) used in the calculations leading to Figure 79 was selected to minimize the possibility that the bed would become plugged by very fine particles from the gas stream adhering to the molten glass faces of the particles. We do not know what particle size is actually necessary to prevent this occurrence. A smaller size might be acceptable, in which case a shallower bed would be required. In any case, the getter bed should be placed downstream of the final particulate filter.

3.3.3.3 Engineering Considerations

We have identified a batch packed bed of emathlite pellets as the preferred means of removing alkali from hot gas streams. A packed bed is necessary to achieve countercurrent contacting of gas and solids, thereby ensuring maximum getter capacity, and to provide sufficient exposure time for the solids to capture significant amounts of alkali. While a nonmixed moving bed could also meet these objectives, the added complexity required for feeding and removing solids continuously is undesirable.

In the packed-bed mode a vessel is filled with fabricated getter pellets through which the alkali-contaminated gas will pass. The batch getter bed will periodically have become saturated with captured alkali and will need to be replaced. The quantities of emathlite required are small enough for this operation to be carried out only infrequently - we have assumed after 4000 hr of operation in some of the above calculations.

We have ruled out regeneration of the getter material because much of the alkali has been found in the laboratory tests to be irreversibly bound. The low cost of the raw emathlite (~ 12¢/kg) also reduces any incentive for regeneration.

Figure 79 -- Emathlite bed depth requirements

The packed-bed getter reactor must be placed after the final particulate control device to minimize the chances of its becoming plugged by dust during its long on-line life. Plugging is likely because of the probable stickiness of the emathlite pellets as they develop a molten glass coating during the gettering process. The use of large particles is recommended as further insurance against plugging, since there will always be some surviving dust, even after a final dust removal step. The large particles may allow some of this stray dust to pass through the alkali bed, or at least prevent the formation of a dust cake at the inlet to the getter reactor (perhaps the alkali bed would act as a deep-bed filter rather than a cake-forming filter). The prevention of plugging by these methods is at this point a postulate that should be tested on an appropriate small scale.

Another problem that must be addressed in engineering design is the method of removing the getter bed at the end of its useful life. The sticky particles will probably adhere to each other and to the vessel walls. The resulting mass may be very difficult to remove. A full-vessel-diameter flange and a disposable sleeve, protecting the pressure vessel from the emathlite mass, will probably be necessary.

In the previous sections we outlined methods for finding the volume of the required getter reactor. The height, diameter, and number of parallel getter reactors may be selected so as to give the required volume (or gas residence time) for the degree of alkali cleanup desired. In general, a high gas velocity (and therefore, a large height-to-area ratio) will result in: 1) better gas distribution across the reactor cross section so that all the emathlite meets alkali, and therefore premature alkali breakthrough does not occur; 2) maximum fine dust penetration past the front surface of the bed, where a filter cake might form; 3) a greater gas-to-particle mass transfer coefficient and therefore a slightly smaller total bed volume; and 4) increased pressure loss.

Table 74 shows the velocity trade-off applied in a particular example. Required bed volume is only weakly dependent on gas velocity.

The bed area is of course, the volumetric gas flow divided by the gas velocity, and gives the bed depth when divided into the required volume. At low velocities a shallow bed and a large area are needed. Achieving gas distribution would be very difficult, and fabrication would require multiple beds and be expensive. On the other hand, pressure drop would be very low. At high velocities the depth-to-area ratio becomes more reasonable, but pressure drop becomes rather high. An economic optimization on velocity would have to consider both the mechanical design and the effect of pressure loss on the overall system. Another parameter that would effect the optimization is the time between getter bed replacements (constant at 4000 hr in Table 74). A shorter time would reduce the required vessel volume.

3.3.4 Comments on System Performance Projections

- The packed-bed getter reactor is the most promising means of removing alkali from a hot gas stream.
- Emathlite is an inexpensive mineral with higher gettering capacity, making it a leading candidate for use in the getter reactor.
- Operation of the fixed-bed reactor will require a periodic (annual or semiannual) changing of the bed material by conventional low-temperature techniques. At other times it will require very little, if any, maintenance or attention. The entrained-particle reactor will require continuous operation at severe conditions for equipment designed to generate, feed, and remove sorbent.
- The entrained-particle reactor will permit the alkali gettering rate to approach the intrinsic chemisorption rate. The rate will still be very much too low, however, for good performance. Performance of the fixed-bed getter reactor will depend only slightly on either the intrinsic or effective rate constant.
- Available rate data indicate that the entrained-particle reactor cannot achieve an acceptable degree of gas cleaning without either a huge reactor volume or consumption of very large amounts of getter.

Table 74
EMATHLITE BED DESIGN EXAMPLE^a

Superficial Velocity, m/hr	Film Mass Transfer Coefficient, cm/s	Gas Residence Time, s	Total Bed Volume, m ³	Total Bed Area, m ²	Bed Depth, m	Pressure Loss, kPa	Getter Consumption, g/kg coal
1000	2.7	6.7	125	66.7	1.9	0.4	0.320
2000	3.8	6.5	120	33.4	3.6	3.0	0.308
3000	4.7	6.4	118	22.3	5.3	9.4	0.302
4000	5.4	6.3	116	16.7	7.0	21	0.297
5000	6.0	6.2	116	13.4	8.7	41	0.293

^aBasis: Westinghouse 501-D5 Turbine, Coal Gasifier
Coal feed 5×10^4 kg/hr

Getter Bed Conditions

Pressure: 10 atm

Inlet NaCl concentration: 1.1×10^{-3} mol/m³ (10 ppmv)

Temperature: 1123 K

Outlet NaCl concentration: 1.1×10^{-6} mol/m³

Gas flow: 6.7×10^4 m³/hr

Getter pellet size: 1.27 cm

On-line time between getter bed replacements: 4000 hr

- Countercurrent contacting without backmixing is essential to maximize sorbent capacity and therefore to minimize sorbent consumption.
- Important unresolved concerns in the use of an emathlite packed bed are the possibility of its acting as a particulate filter and the stickiness of the reacted emathlite.
- The technical issues remaining to be solved for the development of the entrained particle reactor seem more numerous and difficult than for the fixed-bed reactor.
- Bauxite is much less active than emathlite as an alkali getter.

3.4 TASK 4: PROGRAM DEFINITION FOR CONCEPT SCALE-UP

On the basis of previous discussions, it is apparent that the primary objective of any future scale-up studies should be directed at examining the performance of the preferred gettering system — a packed bed containing emathlite. Thus, the scale-up studies will be required to show that such a system can be designed and operated successfully under practical conditions. To this end, we have addressed the three key factors involved in such an effort: the equipment requirements, the test plan, and the data utilization. A brief discussion of each of these areas is presented below. Two key considerations figured in the formulation of our approach. First, development costs will be minimized by limiting the size of the packed-bed system to the smallest practical size. Second, test conditions (salt concentration, operating temperature, etc.) should be well controlled to maximize the design data procured. This requirement precludes installation in a pilot plant environment.

We estimate that the minimum practical size for the packed bed would be ~ 15 cm dia. × 15 to 45 cm long. The selected three-to-one variation in the ratio of bed depth to diameter is within the scope of reasonable aspect ratios for packed-bed operation. Other relevant system requirements and process conditions for evaluating a practical bed of this size are:

Pressure	10 atm
Temperature	1073 to 1173 K
Water vapor	0 to 7 mol % at temperature
Dust injection	0 to 0.4 g/min (0 to 200 ppmw)
Gas flow	0 to 1.8 kg/min
NaCl injection	0 to 4 g/hr (0 to 20 ppmv)

As indicated above, this system would also have to provide for injection of alkali and for the hardware to detect alkali penetration of the packed bed. Other requirements would include the ability to inject moisture and dust under HTHP conditions. Furthermore, the system should be designed to permit about 30 days of continuous operation, and the pellet utilized should be produced by industrial fabrication techniques. The suggested dust loading is higher than would be expected after a final particulate removal device but would permit evaluation of the potential plugging problem in the time frame of a single test, rather than a year.

The test sequence envisioned for the above system is outlined in Figure 80. The sequence would entail an initial shakedown test followed by a shallow bed test in which large particles of emathlite would be used. The crucial questions to be answered in this test are: whether the dust in the gas stream and the stickiness of the getter pellets would combine to cause the bed to plug before it becomes saturated and whether this could be avoided by design (such as by using large particles); and whether the time of alkali breakthrough could be adequately predicted, based upon available data. Consequently, for the remainder of the test matrix (tests 2 through 4) the particle size and bed depth would be varied as needed to answer these questions. The effects of dust loading, gas velocity, temperature, and/or pressure would be evaluated in the last three tests as required, on the basis of prior test results.

The primary objective of the data obtained from the above test series would be to generate the correlations required to elucidate packed-bed performance in terms of extended operation (~ 1 year) in a commercial

hot gas cleaning application. This objective would best be realized by analyzing the data in order to: 1) refine current alkali breakthrough predictions; 2) develop plugging-pressure drop correlations; 3) project attrition resistance over extended operating periods, 4) define bed removal and replacement intervals for full-scale systems; and 5) identify potential problems caused by the glass coating produced by emathlite during the alkali gettering process.

Figure 80 — Bench Scale Development Tests

4. CONCLUSIONS

1. The thermodynamic projections indicated that the compositional stability of solids formed during gasification is dependent on the particular process conditions. Specifically, the resulting gasifier alkali ash complexes consist of silicate or aluminosilicate species. In equilibrium with the solid alkali feldspars is the release of a greater proportion of the feedstock sodium chloride than of the potassium chloride. Gasifiers operating under oxygen-blown conditions as opposed to air-blown conditions enhance the stability of the alkali feldspar phases within the ash, thus minimizing the concentration of alkali released into the effluent stream. Systems that utilize a low ash feedstock containing a low aluminum concentration promote volatilization of background alkali.
2. The thermodynamic model provided data on the release of alkali at process conditions for a number of gasification systems. Illinois No. 6 coal was used as a basis for comparison with the following results: Lurgi (0.028-0.035 ppm Na, 0.013-0.016 ppm K), Texaco (8.70-12.3 ppm Na, 4.5-6.4 ppm K), Westinghouse (19-23 ppm Na, 4.3-12 ppm K), and Shell Koppers (37.2-45.6 ppm Na, 983 ppm K). Variation of the feedstock indicated that gasification of eastern Kentucky Coal in the Winkler process (15.5-132.2 ppm Na, 7.7-101 ppm K) or Wyoming subbituminous coal in the Westinghouse fluidized bed (34-51 ppm Na, 20-32 ppm K) is not projected to emit as much potassium as the Shell Koppers process but borders on, if not exceeds, emissions of sodium.
3. The thermodynamic projections indicated that alkali removal tended to increase with reaction temperature (1200 vs 950 K) and with reduced system pressure (1 vs 10 atm).
4. The reaction of volatile alkali with a typical aluminosilicate material (kaolin) is projected to result in a mixed feldspar-nepheline solid complex. The stability of these phases over a wide range of oxygen and sulfur partial pressures implies the effectiveness and utility of aluminosilicate additives in numerous hot gas cleaning applications.
5. The bench-scale and double-balance TGA systems used in this study enabled us to generate the required kinetic data in an expeditious manner. The TGA system in particular allowed us to obtain kinetic and capacity data on gettering by various materials at relatively low gas-phase concentrations that are of interest in gasification systems and

with carefully controlled and accurately measured conditions. These data, in turn, supported evaluation of various getters and system design options.

6. Both TGA and bench-scale tests with the initial leading candidate getter (activated bauxite) showed that the sodium gettering capacity approached a maximum of 1 wt%. Bench-scale tests showed that its gettering activity for potassium is approximately an order of magnitude greater than for sodium. The presence of water vapor was found in both systems to improve the sodium gettering activity by a factor of two. General observations from the TGA tests were that:
 - Capacity is higher at 1123 K than at 1173 K for each gas phase concentration.
 - Capacity is greater at higher gas phase concentrations at each temperature studied.
 - Desorption is not completely reversible at either temperature level studied.
7. Of the twenty alternative getters screened in the bench-scale and TGA units, several candidates that appeared to be more effective than activated bauxite included: Vansil®, Ebony Novacite®, zeolite, emathlite, and diatomaceous earth. The most promising of these was emathlite. Key factors in the selection of alternative getters included their initial cost, capacity, the formation of insoluble reaction product, and background potassium level. The relevance of the latter factor is due to what appears to be an ion exchange reaction during sodium gettering that results in the release of background potassium.
8. Further testing of the leading candidate getter -- emathlite -- in the bench-scale and TGA units resulted in the following observations:
 - In the presence of water vapor, a glass coating formed at the surface of the pellet and was identified as Na_2SiO_5 .
 - The sodium gettering activity of the acid insoluble complex of emathlite was equivalent in inert and simulated fuel gas environments.
 - A continuous sodium gradient is produced in reacted pellets that can be segregated into three distinct reaction zones.
 - Gettering kinetics are proportional to the product of exposure period and bulk gas phase alkali concentration ($\mu\text{-atm}\cdot\text{hr}$).
 - The capacity of emathlite capacity for sodium is in excess of 10 wt%.

9. The gettering reaction mechanism for emathlite has been proposed as the attachment of sodium to bridging oxygens in adjacent lattice silica tetrahedra. On the basis of the calculated number of moles of sodium gettered and the assumed number of moles of water that compensate for the total net weight gain of the pellet during gettering, the following stoichiometry can be written:

During sodium gettering, potassium is simultaneously released from the lattice, possibly through the following ionic exchange reaction:

10. The packed bed is the only practical gas-solids contacting scheme for high-temperature alkali removal on a practical, commercial scale. This conclusion is based on the long solids contacting time required, the preferred countercurrent gas/solids contacting method, and simplicity.
11. The gettering reaction rate for emathlite is too slow for short residence time devices, such as entrained flow reactors, to effectively use available gettering capacity. In addition, the low initial cost of this getter, coupled with the insoluble nature of the reaction product, indicates that regeneration of the sorbent is not a satisfactory approach.
12. A commercial-scale emathlite unit would require a bed height of 2 m or less (based on a 1000 m/h gas velocity) for approximately 4000 h bed replacement intervals on the basis of bed saturation.
13. The effects on a practical getter reactor design have to be addressed with respect to the molten glass phase that forms on reacted emathlite pellets.

5. RECOMMENDATIONS

1. Emathlite should be analyzed quantitatively to determine the chemical composition and concentration of Si, Al, Ca, Mg, Na, K, Fe, and Ti within the water soluble, acid soluble, and acid insoluble fractions. These data should be used to project the stability and alkali reactivity of the getter at equilibrium as a function of reaction temperature, pressure, and gas composition. Phase diagrams should be generated to identify those operating conditions that maximize alkali gettering and retention within the sorbent matrix. The equilibrium calculations should then be correlated with the analytical gettering data.
2. Efforts should be continued to define the emathlite gettering reaction mechanism, stoichiometry, and reaction kinetics using the TGA system and various analytical techniques. These data will provide direction for the selection of suitable alternative getters and will define the sorbent physical and chemical characteristics that maximize gettering. Definition of the reaction kinetics and stoichiometry will provide data for process scale-up.
3. Tests should be performed with a small packed bed of emathlite to verify performance predictions and to evaluate the effect of the glass phase on reactor operation.
4. The ultimate alkali capacity of emathlite should be defined together with predictive methods for its determination.
5. An alternative high-capacity getter, such as diatomaceous earth, should be evaluated if emathlite stickiness proves to be a major obstacle in the development of a commercial-scale unit.
6. Getter pellet fabrication technology should be defined to ascertain its effects on getter performance and process economics.
7. A preliminary system design and cost estimate should be developed to gain a more detailed perspective of the impact of alkali gettering in power generation systems.

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