ANL/CEN/FE-79-17

DR. 1059

ANL/CEN/FE-79-17

458 cps
4/17/80

SCREENING OF GRANULAR SORBENTS FOR THE REMOVAL OF GASEOUS ALKALI METAL COMPOUNDS FROM HOT FLUE GAS

by

MASTER

Sheldon H. D. Lee, William M. Swift,
and Irving Johnson

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
The University of Iowa
Iowa State University
The University of Kansas
Kansas State University
Loyola University of Chicago
Marquette University
The University of Michigan
Michigan State University
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

Distribution Category:
Coal Conversion and Utilization--
Direct Combustion of Coal
(UC-90e)

ANL/CEN/FE-79-17

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

SCREENING OF GRANULAR SORBENTS FOR THE REMOVAL OF GASEOUS ALKALI METAL COMPOUNDS FROM HOT FLUE GAS

by

Sheldon H. D. Lee, William M. Swift,
and Irving Johnson

Chemical Engineering Division

November 1979

Prepared for the

U. S. Department of Energy
under Contract W-31-109-Eng-38

and the

U. S. Environmental Protection Agency
under Agreement IAG-05-E681

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SCREENING OF GRANULAR SORBENTS FOR THE REMOVAL OF GASEOUS ALKALI METAL COMPOUNDS FROM HOT FLUE GAS

by

Sheldon H. D. Lee, William M. Swift,
and Irving Johnson

ABSTRACT

Six commercially available sorbent materials have been tested as granular sorbents to be used in granular-bed filters for the removal of gaseous alkali metal compounds from the hot (800-880°C) flue gas of pressurized fluidized-bed combustors (PFBC) for proposed combined-cycle power generation. Tests were performed by passing simulated relatively dry flue gas of PFBC through granular-bed filters in either a laboratory-scale, fixed-bed combustor or a high temperature sorption test rig. The experimental results of screening tests are presented. Diatomaceous earth and activated bauxite were found to be the two most promising sorbents. Possible sorption mechanisms and applications of the sorbents are discussed.

I. INTRODUCTION

Pressurized fluidized-bed combustion (PFBC) in combined-cycle power generation systems provides a direct coal combustion process having the potential for improved thermal conversion efficiency, reduced costs, and acceptable environmental impacts.[1] In such systems, the pressurized hot flue gas will be expanded through a gas turbine to recover energy and make the system economic. Past experience obtained when operating gas turbines with hot flue gas from (1) the combustion of liquid fuels[2] and (2) the direct combustion of pulverized coal[3] has indicated that particulates of unburned coal and ash and alkali metal compounds (such as chlorides and sulfates of sodium and potassium) in the flue gas cause catastrophic erosion, corrosion, and fouling of gas turbine hardware. Of these corrosive agents, alkali metal compounds in the flue gas are thought to cause hot corrosion of turbine hardware.[4,5] Therefore, for the successful operation of combined-cycle power plants, cleanup of the hot flue gas to remove particulates and alkali metal compounds is imperative.

Sodium and potassium compounds exist in coal in similar chemical forms. Sodium chloride and potassium chloride are present in saline groundwater that permeates the rock and fills the pores and cracks in the coal bed. Both sodium and potassium are also constituents of clay minerals in coal, such as illite and montmorillonite. Sodium chloride is a principal form of sodium in coal; in contrast, potassium in coal occurs largely as nonvolatile aluminosilicates. However, potassium can be released from silicates as potassium chloride by exchange reactions with sodium chloride vapor.[6-8] Since both sodium chloride and potassium chloride have appreciable vapor pressures (0.4 and 0.7 kPa, respectively, at 900°C) at the fluidized-bed combustion temperature range, their vapors are expected to be in the flue gas of PFBC. Thermodynamic calculations indicate that gaseous sodium chloride and potassium chloride are the major sodium and potassium carriers, respectively, in the flue gas of fluidized-bed combustion of coal.[9] Alkali metal sulfates can be formed by the reactions of alkali chlorides with gaseous sulfur compounds.

A way to eliminate the hot corrosion of gas turbine hardware is to reduce the concentration of alkali metal compounds in hot flue gas to a level tolerable for turbine blades. A way to accomplish this is to use a hot granular-bed filter to remove the alkali metal compounds from the hot flue gas before it is expanded into a turbine. Granular-bed filters are among the many devices being actively developed for high-temperature, high-pressure particulate cleanup of flue gas.[10-12] They hold great promise based on their potential advantages over other devices for particulate removal.[13] With a suitable bed material, a granular-bed filter will simultaneously remove particulates and alkali metal compounds.

Several materials have been found to react effectively with alkali metal compounds to form nonvolatile products. For example, Combustion Power Company has demonstrated that the addition of an aluminum silicate clay to the combustion zone of PFBCs effectively reduces the emission of alkali vapors.[14] The chemical reactions pertaining to the fixation of alkali chlorides by an aluminum silicate clay have been well established.[15] The authors have also found that clay minerals, silica gel, and bauxite additives effectively tie up alkalis during the combustion of NaCl-impregnated activated coconut charcoal.[16]

Research has been under way at Argonne National Laboratory to develop effective granular sorbents that can be used as bed material in granular-bed filters for the removal of alkali metal compounds from the hot flue gas of PFBCs. Presented in this report are experimental results obtained on the screening of six commercial products. In these experiments, NaCl, KCl, and K_2SO_4 vapors were each transported in relatively dry gas simulating flue gas of PFBC to test the products for their alkali-vapor sorption capabilities. Possible sorption mechanisms and applications for the two most promising substances are discussed.

II. EXPERIMENTAL

A. Sorbent Material

Six commercial products were first screened as sorbents for the removal of NaCl vapor from a simulated hot NaCl-vapor-bearing flue gas having the composition expected from PFBC combustion. The two most promising substances were then tested for the removal of gaseous KCl and K_2SO_4. Table 1 gives the sources and major constituents of six products screened in this study.

With the exception of Burgess No. 10 pigment, the materials tested were -8 +10 mesh particles obtained by sieving. The sieved sorbents were preheated in a flowing air stream at 900°C to remove volatile alkali metal compounds. In the preparation of Burgess No. 10 pigment (a fine powder), it was formed into cylinders (2.5-cm dia by 3-cm long) using a hydraulic press, heat-treated, and then crushed; -8 +10 mesh particles obtained by sieving were used in the tests.

Table 1. Sources and Major Constituents of Materials Tested

Sorbent	Source	Major Constituents
Alundum	Norton Company, Massachusetts	α-Al_2O_3 (99.5%)
Celatom MP-91 Diatomaceous Earth	Eagle-Picher Industries, Inc., Ohio	SiO_2 (92.0%); Al_2O_3 (5.0%)
Silica Gel	Fischer Scientific Company, N. J.	SiO_2
Burgess No. 10 Pigment	Burgess Pigment Company, Georgia	SiO_2 (44.8-45.3%) Al_2O_3 (37.5-39.7%)
Attapulgus Clay	Engelhard Minerals and Chemicals Corp., N. J.	SiO_2 (68.0%) Al_2O_3 (12.0%) MgO (10.5%)
Activated Bauxite	Engelhard Minerals and Chemicals Corp., N. J.	SiO_2 (10.0%) Al_2O_3 (81.5%)

B. Equipment

A laboratory-scale, batch-type, fixed-bed combustor system was used to test sorbents for the removal of gaseous sodium chloride and potassium chloride. Figure 1 is a schematic diagram of the combustor system. A detailed description of the system is presented elsewhere.[17]

The combustor is a 8.9-cm-ID 1.8-m-long horizontal stainless steel pipe and consists of four sections: preheating, combustion, filtration, and cold-trap sections. The sorbent is placed between two perforated steel plates in a stainless steel tube, which is fastened upstream from a cold trap tube into which a cold finger is inserted; thus, the sorbent is in the filtration section of the combustor. A weighed quantity of pure alkali metal compound in a platinum sample pan is heated (by induction heating) in the combustion section of the combustor and is vaporized. The vapor is carried by preheated flowing gas downstream through the sorbent bed, and any remaining vapor is condensed on the cold trap tube, the cold finger, and the backup filter (<u>i.e.</u>, the glass-wool filter).

Because alkali metal sulfates have substantially lower vapor pressures than their chlorides, and because the allowable maximum operating temperature of the laboratory-scale, fixed-bed combustor vessel is limited to 900°C, a small-scale sorption test rig (Fig. 2) that can be operated up to

1250°C was used for tests to determine the sorption of gaseous potassium sulfate. In this test rig, a known amount of potassium sulfate contained in a platinum sample pan is vaporized inside a pure Al_2O_3 tube that is heated by a tubular furnace. The preheated simulated PFBC flue gas then carries the alkali metal sulfate vapor downstream through the bed of sorbent to be tested and through a condenser, and finally the gas is vented to an exhaust. The sorbent bed is supported by a platinum gauze and quartz tubing inserted concentrically inside the Al_2O_3 tube. The Al_2O_3 tube is capped on both ends with lava end caps. A ceramic fiber gasket is used as the seal between the Al_2O_3 tube and the end cap.

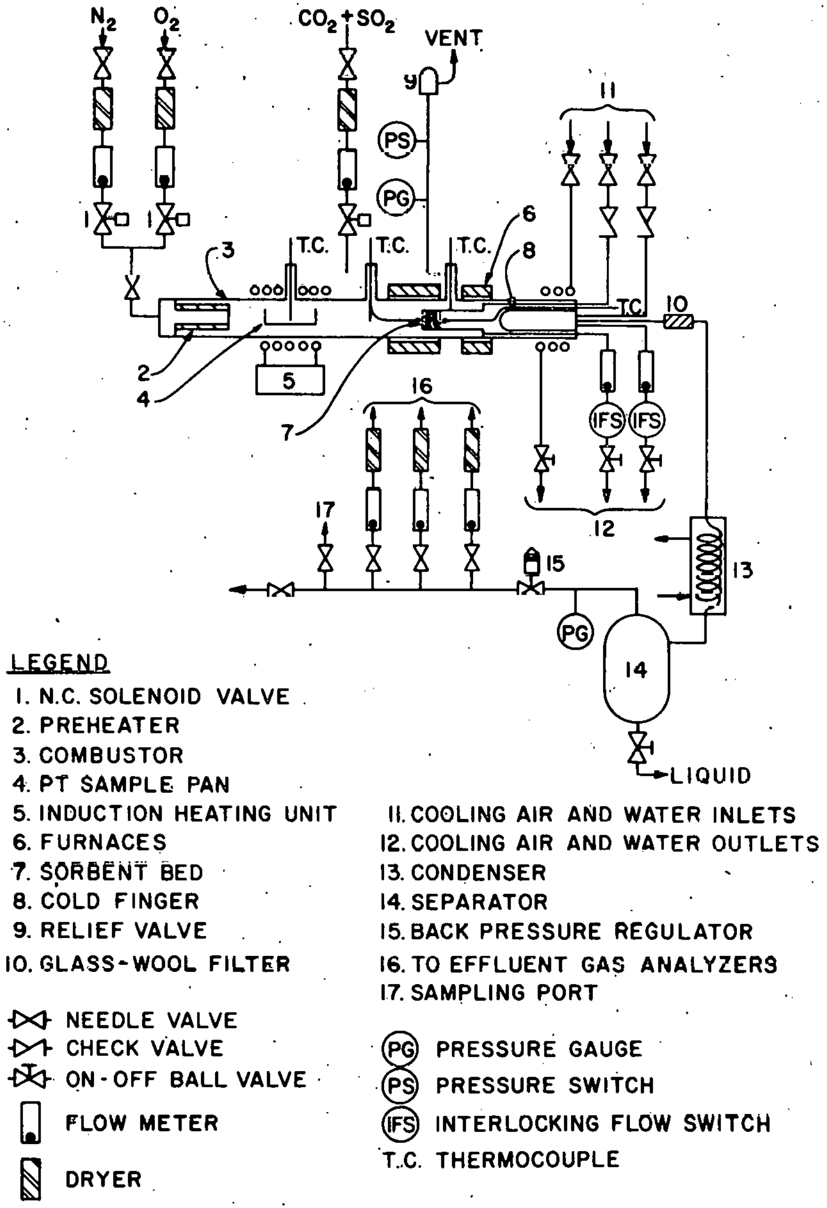

Fig. 1. Batch-Type Fixed-Bed Combustor System

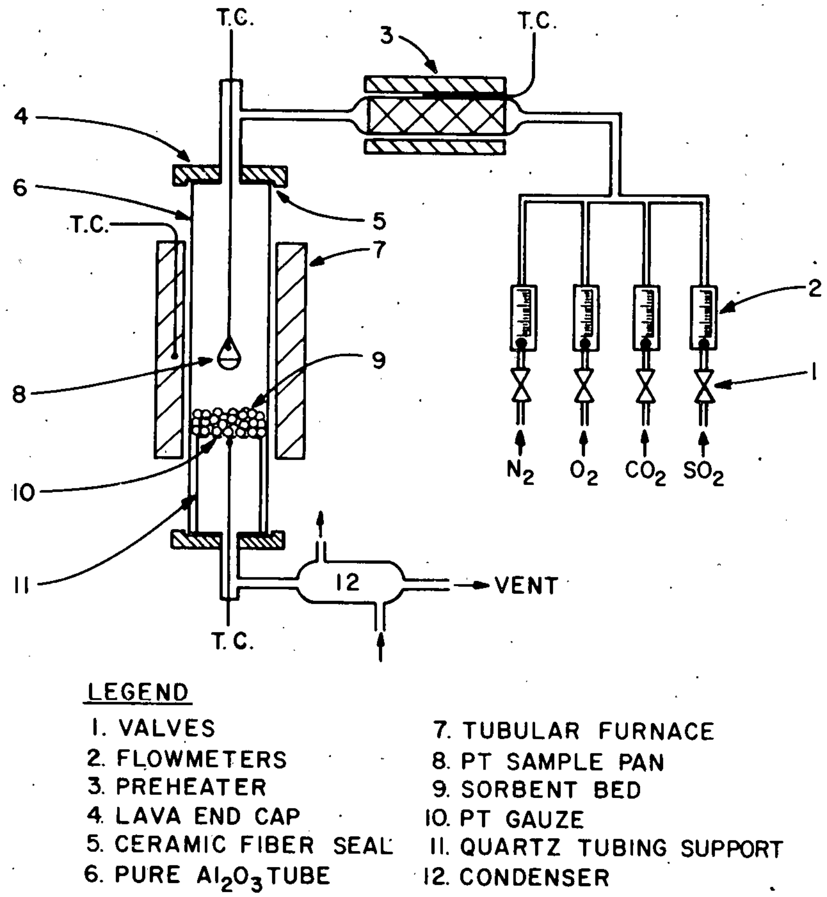

Fig. 2. K_2SO_4-Vapor Sorption Test Apparatus

C. Procedures

1. Sorption Tests

All tests conducted in this study were performed at atmospheric pressure. Except in screening tests for gaseous NaCl in which air was used as the carrier gas, sorbents were tested using simulated relatively dry flue gas of PFBC. For tests with NaCl and KCl vapors, the sample temperature was controlled at 900°C, which was greater than the sorbent bed temperature of about 875°C. Because of the substantial dilution of the alkali metal chloride vapor by the hot carrying gas, the alkali metal chloride present in the carrying gas should be in the gas phase. This was supported by vapor pressure calculations showing that the alkali metal chloride vapor pressure in the carrying gas was significantly lower than its saturation vapor pressure at the sorbent bed temperature. The amount of alkali metal chloride vaporized for a test was controlled by varying the size of the sample pan. For these tests, the volumetric composition of the simulated flue gas was 3% O_2, 16% CO_2, ∿180 ppm H_2O, ∿300 ppm SO_2, alkali metal chloride vapor ranging from 56 to 103 ppm, and the balance N_2. The trace amount of the moisture was the moisture present in O_2, CO_2, and N_2 cylinders. Although the estimated alkali concentration in the flue gas of PFBC is in the order of 10 ppm, a fairly high alkali concentration in the flue gas was used in this work so that a detectable amount of alkali vapor could be obtained within a reasonable experimental period. For the tests with K_2SO_4 vapor, the sample was heated at 1250°C. The volumetric composition of the simulated flue gas was 2.3% O_2, 13% CO_2, $\sim$120 ppm H_2O, $\sim$110 ppm SO_2, $\sim$3 ppm K_2SO_4 vapor and the balance N_2.

At the end of each experiment, the weight loss of alkali metal compound in the sample pan was measured; the condensates were collected by washing with distilled water and were analyzed for the alkali metal of interest. The amount of alkali metal chloride vapor captured by a sorbent was obtained by subtracting from the total alkali metal chloride vaporized the sum of (1) the amounts of alkali metal chloride condensed on the cold traps and the backup filter and (2) the amount of alkali metal chloride lost to the combustor (due to reactions with the hot combustor pipe) before it reached the sorbent bed. The latter value was obtained from averaging the amounts of alkali metal chloride vapor loss obtained from several blank runs in which the sorbent had been directly analyzed for the amount of alkali-vapor capture. The sorption capability of a sorbent was evaluated by its effectiveness in removing alkali vapor from flue gas.

2. Sorbent Leaching

For the purpose of obtaining insight into the reactions between alkali metal compound vapors and the sorbents, either distilled water-leaching alone or distilled water-leaching followed by leaching with 5% HCl solution were performed on (1) fresh sorbents and (2) sorbents after sorption tests. Both water leaching and acid leaching were conducted in a beaker at gentle boiling temperature (95°C) for a specified period of time. The leachates were then analyzed for elemental concentrations of the elements of interest.

D. Analytical Methods

Sodium concentrations in either water or acid solutions were determined by flame emission spectrometry, and potassium concentrations by atomic absorption spectrometry. An Instrumental Laboratory Model 153 spectrometer was used for the analyses. For the analysis of chloride ion in solution, an argentometric method was used[18]—a method of titration in which AgCl precipitates.

III. RESULTS AND DISCUSSION

A. Screening Tests

Six commercial products (Table 1) were first screened by measuring their effectiveness for removing NaCl vapor from hot NaCl vapor-bearing flowing air. The two most promising substances were then tested as sorbents for KCl and K_2SO_4 vapors, using a simulated flue gas of PFBC. Results of these screening tests are given and discussed below.

1. NaCl-Vapor Tests

Two sets of tests (HGC series), the first at 870°C in air flow and the second at 880°C in simulated flue gas, were completed. For these two sets of tests, the superficial gas velocities and the gas hourly space velocities (GHSV) of the flowing gas passing through the bed were 8 cm/s and 3,500 h^{-1}, and 25 cm/s and 12,000 h^{-1}, respectively. GHSV is defined as the volumetric flow rate of the gas in units of sorbent volume per hour.

Table 2 shows the material balances of NaCl from testing the six commercial products for NaCl vapor capture. As can be seen in this table, the alundum behaved inertly. This is in good agreement with the way it behaved in the combustion of a mixture of alundum and activated coconut charcoal impregnated with 0.5% by wt NaCl. In that combustion study also, alundum was observed to fail to capture NaCl vapor.[16,17]

Inert alundum was used in these screening tests to test the experimental system. The good material balance obtained from experiment HGC-3 demonstrated that there was no purely physical condensation of NaCl vapor on the sorbent under the experimental conditions. The output of NaCl was slightly greater than the input because sodium was released from alundum itself during the test, as is confirmed by the data shown in Table 5.

In comparison to alundum, Celatom MP-91 diatomaceous earth was much more effective in removing NaCl vapor; it captured 74% of the NaCl vapor passing through it. In the combustion of activated coconut charcoal to which silica gel had been added,[16,17] silica gel demonstrated its effectiveness for tying up sodium in the ash bed. Also, Nelson and Lisle[19] reported that silica gel, with its large internal structures, was the most effective of all silicates tested as corrosion-inhibiting additives to prevent high-temperature liquid-phase corrosion in coal-fired boilers. However, when silica gel was used as a sorbent in the tests reported here, it showed only moderate effectiveness in tying up NaCl vapor. This was due to loss of porosity of the silica gel caused by the preheat-treatment of the sample, as is seen in Fig. 3.

Burgess No. 10 pigment, which is primarily a kaolin clay, has been shown by Combustion Power Company, Inc.,[14] to be a very effective "getter" for alkali metals. Similarly, it effectively captured 78% of the NaCl vapor in this test system. Attapulgus clay is essentially a magnesium aluminum silicate. It was fairly effective in removing NaCl vapor; however, this clay, following the test, became fragile. For practical application of a candidate sorbent, fragility is not an acceptable property because the fine particles produced would increase the load on downstream particulate-removal facilities.

The activated bauxite tested in these screening tests is thermally treated high-alumina-content natural bauxite ore. Of the six sorbents screened in this series, activated bauxite was the most active in removing NaCl vapor, as is shown in the bottom row of Table 2.

Table 2 also shows that in the second set of tests, in which the simulated flue gas was used, the efficiencies of NaCl vapor capture of diatomaceous earth, activated bauxite, and Burgess No. 10 pigment were significantly increased--to 96, 98, and 85% capture, respectively. This increase resulted from the combined effects of (1) shorter experiment duration, (2) higher NaCl-vapor concentration in the flue gas, and (3) higher superficial velocity of the flue gas, which increased mass transfer of NaCl vapor from the bulk of flue gas to the surface of the sorbent, thereby increasing sorption of NaCl vapor by the sorbent.

Table 2. Material Balances for NaCl from Testing Sorbents for NaCl-Vapor Capture

Experiment No., HGC-	3	4	5	6	7	8	11	11R	12R	13
Sorbent	Alundum	Diatomaceous Earth	Silica Gel	Burgess No. 10 Pigment	Attapulgus Clay	Activated Bauxite	Diatomaceous Earth	Diatomaceous Earth	Activated Bauxite	Burgess No. 10 Pigment
Flowing Gas	Air[a]	Air	Air	Air	Air	Air	S.F.G.[b]	S.F.G.	S.F.G.	S.F.G.
Experiment Duration, min	180	180	180	180	180	180	100	100	100	100
NaCl-Vapor Concentration in Flowing Gas, ppmv	56	56	56	56	58	58	82	103	83	85
	Total NaCl, mg									
Input										
(1) NaCl Transported[c]	92	91	91	92	95	96	242	303	245	252
Output										
(2) NaCl Collected by										
(a) Cold Traps	71	18	40	15	25	6	6	8	3	26
(b) Glass-wool Filter	24	6	15	5	9	2	4	4	5	13
(3) Total	95	24	55	20	34	8	10	12	8	39
(4) NaCl Capture by Sorbent, 100 x [(1) - (3)]/(1)	-3%	74%	40%	78%	64%	92%	96%	96%	98%	85%

---

[a] At 870°C. Superficial gas velocity, 8 cm/s. Gas hourly space velocity, 3500 h^{-1}.

[b] Simulated relatively dry flue gas. At 880°C. Superficial gas velocity, 25 cm/s. Gas hourly space velocity, 12,000 h^{-1}.

[c] Amount of NaCl vapor transported to the sorbent bed.

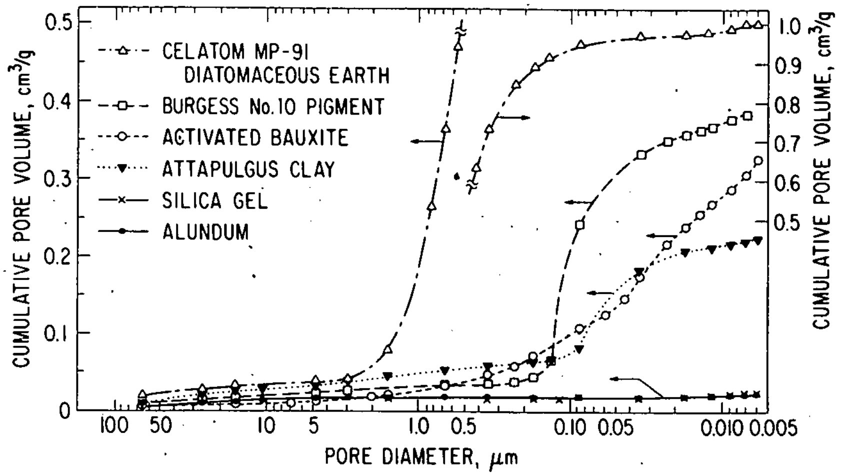

Fig. 3. Cumulative Pore Volume as a Function of Pore Diameter for Six Sorbents

It is concluded from this set of tests that among the six sorbents screened, diatomaceous earth, activated bauxite, and Burgess No. 10 pigment are the most effective sorbents in capturing NaCl vapor from flue gas, and therefore, they were further tested for KCl-vapor capture.

2. Relationship of NaCl-Vapor Sorption Capability to Sorbent Porosity

In a gas-solid sorption reaction, one parameter that has an important effect on the reaction rate is the internal surface area (in large enough pores) of a sorbent; therefore, the porosity of each type of sorbent was measured. Figure 3 shows plots of the cumulative pore volume vs. pore diameter. It may be observed in this figure that diatomaceous earth has the greatest total pore volume; its pore volume is essentially contributed by large pores. The pore volume of Burgess No. 10 pigment is second largest, mainly contributed by smaller pores. In contrast to these two sorbents, the pore volume of activated bauxite is evenly contributed by a wide range of small pores. Silica gel and alundum have about the same total pore volumes and are very nonporous. Since the internal surface area is primarily contributed by small pores, the effectiveness of a sorbent for capturing NaCl vapor (as shown in Table 2) is generally related to its internal surface area (Fig. 3).

3. KCl-Vapor Tests

Except for Western low-rank coals, the potassium content of typical U.S. coals is higher than the sodium content--approximately two moles of potassium for each mole of sodium.[20] Potassium chloride is present in saline groundwater permeating the rock and filling the pores and cracks in the coal bed, and can also be released from silicates by exchange reactions with NaCl vapor. Because potassium chloride has an appreciably high vapor pressure at the fluidized-bed combustion temperature range (0.7 kPa at 900°C), its vapor is expected to be in the flue gas of PFBC. Therefore, the three most effective sorbents screened using NaCl vapor--diatomaceous earth, activated bauxite, and Burgess No. 10 pigment--were further tested for their sorption capability for KCl vapor. The results for these tests are shown in Table 3.

Table 3. Material Balances for KCl from Testing Sorbents for KCl-Vapor Capture[a]

Experiment No. HGC-	16	17	18
Sorbent	Diatomaceous Earth	Activated Bauxite	Burgess No. 10 Pigment
	Total KCl, mg		
Input			
(1) KCl Transported[b]	321	271	263
Output			
(2) KCl Collected by			
(a) Cold Traps	3	10	45
(b) Glass-wool Filter	1	4	22
(3) Total	4	14	67
(4) KCl Captured by Sorbent, 100 x [(1) - (3)]/(1)	98%	95%	74%

[a] Conditions: 880°C for 100 min. Superficial gas velocity, 25 cm/s. Gas hourly space velocity, 12,000 h^{-1}.

[b] Amount of KCl vapor transported to the sorbent bed.

In each of this set of tests, the sorbent was tested at an average bed temperature of 880°C for 100 min in a simulated flue gas at a superficial gas velocity of 25 cm/s and a GHSV of 12,000 h^{-1}. The KCl-vapor concentration in flue gas was 76 ppm by volume on the average. Table 3 indicates that diatomaceous earth and activated bauxite effectively captured 98 and 95%, respectively, of the KCl vapor (as effectively as they captured NaCl vapor). Burgess No. 10 pigment was less effective (74% of the KCl vapor captured). Burgess No. 10 pigment was similarly less effective in capturing NaCl vapor, as shown in Table 2. The similar sorption activity of these sorbents toward NaCl and KCl vapors is not surprising because the chemical properties of NaCl and KCl are similar.

4. K_2SO_4-Vapor Tests

In the flue gas from coal combustion, sodium and potassium may be present not only as chlorides but also as sulfates produced by the reactions of alkali chlorides with gaseous sulfur compounds. Sodium sulfate and potassium sulfate in liquid form are generally believed to be the precursors for metal sulfidation, the most common form of hot corrosion occurring in gas turbines;[4] therefore, candidate sorbents have to demonstrate the capability of retaining alkali metal sulfates.

Two tests (KSO-4 and -5) were conducted using the small-scale sorption test rig (Fig. 2). Diatomaceous earth and activated bauxite were tested as sorbents at ~900°C for 24 h at a superficial gas velocity of 27 cm/s and a GHSV of 62,000 h^{-1}. The material balances of K_2SO_4 are given in Table 4, which shows that 93 and 72% of the total K_2SO_4 vapor was captured by activated bauxite and diatomaceous earth, respectively. Since the sorbent was tested at a fairly high gas hourly space velocity or a contact time of only 0.05 s, a better capture efficiency can be expected if the contact time of the flue gas with the sorbent is increased. The capabilities of these sorbents for retaining K_2SO_4 vapor from hot flue gas appear to be comparable to their capabilities for retaining alkali metal chloride vapors (discussed above). On the basis of the similar chemical properties of K_2SO_4 and Na_2SO_4, it is reasonable to expect that the capabilities of these sorbents for retaining Na_2SO_4 vapor also are similar.

Table 4. Material Balances for K_2SO_4 from Tests of K_2SO_4-Vapor Capture by Diatomaceous Earth and Activated Bauxite[a]

Experiment No., KSO-	4	5
Sorbent	Activated Bauxite	Diatomaceous Earth
	Total K_2SO_4, mg	
Input		
(1) K_2SO_4 Vaporized	346	264
Output		
(2) K_2SO_4 Collected from		
(a) Combustion Tube	8	23
(b) Downstream Line & Condenser	2	3
(3) K_2SO_4 Captured by Sorbent[b]	322	191
Total	332	217
(4) K_2SO_4 Loss	14	47
(5) K_2SO_4 Capture, [100 x (3)/(1)]	93.1%	72.3%

[a] Conditions: 900°C for 24 h. Superficial gas velocity, 27 cm/s. Gas hourly space velocity, 62,000 h^{-1}.

[b] Potassium contents of the sorbents were obtained by dissolving two representative samples of activted bauxite in NH_4HF_2 and two representative samples of diatomaceous earth in a mixture of H_2SO_4, HF, and HNO_3. Then the resulting solutions were analyzed by atomic absorption.

B. Sorption Mechanisms

To obtain an insight into the mechanism of NaCl capture by these sorbents, a water-leaching study has been carried out on fresh sorbents and on sorbents with NaCl sorbed. The sorbents from the first set of NaCl-vapor tests (870°C in air flow, Table 2) were leached for 30 min. Sorbent from the second set of tests (880°C in simulated flue gas, Table 2) was first ground to -200 mesh powder, and then 10 g of the powder was leached with distilled water for 1 h. The filter cake was then leached with 5% HCl solution for another hour. During both leachings of sorbents from the second set of tests, magnetic stirring was used. Table 5 shows the sodium and chloride ion concentrations in leachates from the first set of tests (water leaching), and Table 6 shows the sodium distributions in the NaCl-vapor-absorbed sorbents from the second set of tests.

Table 5. Comparison of Sodium and Chloride Ion Concentrations in Water Leachates from Fresh and NaCl-Absorbed Sorbents

Experiment No. HGC-	Sorbent	Concentration, mole x 10^6/g Sorbent: Fresh Sorbent Na^+	Fresh Sorbent Cl^-	NaCl-Absorbed Sorbent Na^+	NaCl-Absorbed Sorbent Cl^-
3	Alundum	2.21	N.A.[a]	1.52	N.A.
4	Celatom MP-91 Diatomaceous Earth	0.91	0.11	1.20	0.15
5	Silica Gel	0.47	0.03	1.78	1.39
6	Burgess No. 10 Pigment	0.04	N.A.	0.09	N.A.
7	Attapulgus Clay	0.04	N.A.	0.11	N.A.
8	Activated Bauxite	0.05	N.A.	2.76	2.83

[a] N.A., not analyzed

As shown in Table 5, the Na^+ concentrations in the leachates from NaCl-absorbed diatomaceous earth, Burgess No. 10 pigment, and Attapulgus clay were only slightly higher than in the leachate from fresh sorbents. This indicates that NaCl vapor was primarily tied up by these sorbents in chemical forms that are not soluble in water. Results in Table 6 further support these observations.

Table 6. Distribution of Sodium Ion in the NaCl-Vapor-Absorbed Sorbents

Experiment No., HGC-	11R	12R	13
Sorbent	Diatomaceous Earth	Activated Bauxite	Burgess No. 10 Pigment
	Na^+, μg/g sorbent[a]		
Water-Soluble	50 (3%)	400 (69%)	5 (1%)
Acid-Soluble	570 (73%)	180 (31%)	430 (86%)
Acid-Insoluble[b]	910 (60%)	0 (0%)	65 (13%)
	1530	580	535

[a] For example, "50" in the first column represents the μg of water-soluble Na^+ from 1 g diatomaceous earth after sorption minus the μg of water-soluble Na^+ from 1 g of fresh diatomaceous earth.

[b] The final filter cake was dissolved in a mixture of HCl, HNO_3, and HF. This solution was then analyzed for sodium.

Next considered are the reactions of clay minerals. Clay minerals are known to be effective "getters" for alkali metal compounds.[2,14,16,19] Burgess No. 10 pigment is essentially a kaolin clay; therefore, it is concluded that NaCl vapor was retained by Burgess No. 10 pigment and Attapulgus clay by chemical reactions that formed water-insoluble products such as sodium aluminum silicates.

The reaction mechanism of diatomaceous earth, a sedimentary rock of marine or lacustrine deposition, is related to its compositions, primarily of silicon dioxide and various amounts of impurities such as clay, carbonaceous matter, iron oxide, and sand. As shown in Table 1, the Celatom MP-91 diatomaceous earth contains 92% SiO_2, 5% Al_2O_3, and other impurities. The reaction

$$2\ NaCl(g) + H_2O(g) + n\ SiO_2(s) = Na_2O\cdot n\ SiO_2(s) + 2\ HCl(g)$$

$$\Delta H_{800°C} = -5.71\ \text{kcal mol}^{-1}\ \text{for}\ n = 1$$

is well known and has been studied.[21,22] In the present work, the NaCl vapor is believed to react primarily with diatomaceous earth according to the above reaction, forming sodium silicates that are not readily soluble in water. The solubility of an alkali metal silicate depends on the ratio of silica to alkali metal oxide and is also controlled by the quantity of impurity present.[23] Part of the NaCl vapor may also react with clays present as impurities in diatomaceous earth. In an investigation of the kinetics of the above reaction, Chirkov[21,24] reported that between 840 and 940°C, the rate of the above reaction increases with the temperature according to the Arrhenius equation. In other work,[25] the rate of reaction of NaCl vapor with diatomaceous earth in the present system was also noted to increase with temperature.

In contrast to these three sorbents, the NaCl captured by silica gel and activated bauxite was readily leached out by water, as shown in Tables 5 and 6. Within the limits of experimental and analytical errors, the mole ratio of sodium to chloride in the leachates from these two sorbents is close to unity. These results appear to indicate that capture of NaCl vapor by these two sorbents was primarily due to a physical action--an adsorption process. A similar observation was made by Nelson and Lisle,[19] who attributed the capability of silica gel for inhibiting high-temperature alkali sulfate liquid phase corrosion in coal-fired boilers to a physical adsorption mechanism. Bauxite is a principal ore of aluminum; it consists mainly of aluminum oxide and other impurities including SiO_2 and clay minerals. Activated bauxite used for this study contains more than 10% SiO_2 and clay minerals (Table 1). Chemical reactions of these impurities with NaCl vapor may play a role in NaCl vapor capture.

The amount of NaCl vapor adsorbed at equilibrium on activated bauxite at 900°C and atmospheric pressure has been measured using the sorption test apparatus (Fig. 2). It was found to approach 25 mg NaCl per gram of activated bauxite.[25] The adsorption of NaCl vapor on activated bauxite was also found to approach the equilibrium amount at the end of 6 h, and the equilibrium amount of NaCl vapor captured was noted to decrease with increasing temperature.[25] Since an adsorption process is always exothermic, the amount of adsorbate adsorbed at equilibrium must always decrease with increasing temperature according to the principle of Le Chatelier; consequently, the present observation clearly substantiates the argument made previously that NaCl-vapor is primarily captured by activated bauxite by an adsorption process.

To gain an understanding of the reactions of K_2SO_4 vapor with both activated bauxite and diatomaceous earth, the K_2SO_4 vapor-adsorbed sorbents from K_2SO_4-vapor-capture tests (Table 4) were leached with distilled water for 1 h, using magnetic stirring. Table 7 shows the distributions of water-soluble and water-insoluble potassium species in the two sorbents.

Table 7. Distribution of Potassium Ion in the K_2SO_4-Vapor-Absorbed Sorbents

	K^+, g-mol	
	Activated Bauxite	Diatomaceous Earth
Water-Soluble	0.61 (16.5%)	0.06 (2.7%)
Water-Insoluble[a]	3.09 (83.5%)	2.14 (97.3%)
Total[b]	3.70	2.20

[a] The difference between total potassium and water-soluble potassium.

[b] Obtained by analysis of K^+ in the sorbent.

Table 7 indicates that, in contrast to NaCl vapor which is primarily adsorbed on activated bauxite, K_2SO_4 vapor is essentially captured by reactions with activated bauxite that form water-insoluble compounds.

The products of the K_2SO_4-vapor reactions with diatomaceous earth are essentially water-insoluble. At the end of the experiment, significant quantities of diatomaceous earth particles were observed to be coated with a layer of transparent, vitreous material, which had not been observed on the activated bauxite sorbent. X-ray diffraction analysis of the vitreous material showed that it was an amorphous substance, not melted K_2SO_4. This indicates that during the experiments, K_2SO_4 vapor reacted with diatomaceous earth to form glassy potassium silicates. The silicates so formed may be in chemical forms that dissolve very slowly in water, or they may further combine with impurities such as oxides of aluminum, iron, calcium, and magnesium to form water-insoluble products.

C. Sorbent Applications

Experimental results presented above demonstrate the effectiveness of diatomaceous earth and activated bauxite as granular sorbents for the capture of alkali metal compounds from hot flue gas. Both diatomaceous earth and activated bauxite have inherent properties of stability at high temperatures and resistance to attrition. With these specific characteristics, these two sorbents hold great promise as filter media in granular-bed filters for removing particulate and alkali corrodents simultaneously from hot flue gas of PFBC.

Another possible application of diatomaceous earth and activated bauxite is in a low-Btu gasification combined-cycle system, which has been identified as an alternative to the PFBC combined cycle for efficient power generation.[26,27] Because of the effective alkali removal capability, high-temperature stability, and attrition resistance of diatomaceous earth and activated bauxite, a granular-bed filter containing either sorbent may also be applicable for high-temperature, high-pressure removal of particulates and alkali corrodents from the hot flue gas of a low-Btu gasification combined-cycle system. The potential gas turbine hardware problems for the latter system are similar to those for the PFBC combined cycle. These two sorbents should be tested for this application.

IV. SUMMARY

In the prospective application of pressurized fluidized-bed combustion (PFBC) of coal for power generation, corrosion of turbine blades due to attack by alkali metal compounds in the hot flue gas is a potential problem. Six commercial products--alundum (pure Al_2O_3), Celatom MP-91 diatomaceous earth, silica gel, Burgess No. 10 pigment, Attapulgus Clay, and activated bauxite have been screened. Their use as sorbents in granular-bed filters to remove gaseous alkali metal compounds from the hot (800-900°C) flue gas of PFBCs in proposed combined cycle power generation is being evaluated. Tests were performed using a simulated relatively dry flue gas of PFBC in a laboratory-scale, fixed-bed combustor and a high-temperature sorption test rig.

Experimental results from this work show that both diatomaceous earth and activated bauxite are very effective granular sorbents for the removal of all gaseous NaCl, KCl, and K_2SO_4 from hot (800-880°C) simulated flue gas of PFBC. The retention of gaseous alkali metal compounds by diatomaceous earth is attributed to chemical reactions of diatomaceous earth with alkali metal compounds to form water-insoluble or difficultly soluble alkali metal silicates. K_2SO_4 vapor reacts with activated bauxite to form water-insoluble compounds; however, capture of gaseous alkali metal chlorides by activated bauxite is primarily by an adsorption mechanism.

V. CONCLUSIONS AND RECOMMENDATIONS

Activated bauxite and diatomaceous earth are very promising granular sorbents for removing gaseous alkali metal compounds from hot flue gas of PFBCs.

Further studies of these two sorbents are recommended to obtain the technical data base needed for applications, i.e., to determine effects of operating variables on the sorption behavior of the sorbent.

From the results of water-leaching of activated bauxite, it was concluded that an adsorption mechanism primarily controls the retention of alkali metal chlorides by activated bauxite. An adsorption process is known to be a reversible process; therefore, investigation of water-leaching as a means for regenerating activated bauxite for reuse is recommended.

ACKNOWLEDGMENTS

The authors express their appreciation to R. W. Bane for flame emission and atomic-spectrometry analyses and to A. A. Jonke for helpful discussions.

REFERENCES

1. Comparative Evaluation of Phase I Results from the Energy Conversion Alternatives Study (ECAS), NASA Report TM-X-71855 (1976).

2. W. T. Reid, Ed., External Corrosion and Deposits--Boilers and Gas Turbines, 1st Ed., American Elsevier Publishing Co., Inc., New York (1971).

3. Interdepartmental Gas Turbine Steering Committee, The Coal Burning Gas Turbine Project, Department of Minerals and Energy, Department of Supply, Australia, Australian Government Publishing Service (Canberra) (1973).
4. H. H. Lunt, Hot Corrosion in Gas Turbine, ASME Paper 77-WA/FU-3, the AMSE Winter Annual Meeting, Atlanta, Georgia, November 27-December 2, 1977.

5. A. M. Beltran and D. A. Shores, Hot Corrosion, Superalloys, C. T. Sims and W. C. Hagel, Eds., Wiley, Chapter II (1972).

6. P. J. Jackson and J. M. Ward, Operational Studes of the Relationship between Coal Constituents and Boiler Fouling, J. Inst. Fuel 29, 154-164 (1956); Discussion, p. 441.

7. P. J. Jackson and H. C. Duffin, Laboratory Studies of the Deposition of Alkali-Metal Salts from Flue Gas, Proceedings of the International Conference on the Mechanism of Corrosion by Fuel Impurities, Central Electricity Generating Board, Marchwood, England, pp. 427-442 (1963).

8. E. Raask, The Behavior of Potassium-Containing Silicate Minerals in Pulverized-Coal-Fired Boilers, Mitt. Ver. Grosskesselbetr 48, 348 (1968).

9. An Investigation of Hot Corrosion and Erosion Occurring in a Fluid Bed Combustion-Gas Turbine Cycle Using Coal as Fuel, Prepared for ERDA, FE/1536-2 (May 1977).

10. J. P. Meyer and M. S. Edwards, Survey of Industrial Coal Conversion Equipment Capabilities: High-Temperature, High-Pressure Gas Purification, Oak Ridge National Laboratory Report ORNL/TM-6072 (June 1968).

11. Particulate Control for Pressurized Fluidized Bed Combustion, Prepared by Gilbert/commonwealth for U.S. Department of Energy, HCP/T220-16 (May 1978).

12. H. Wigton and G. Wade, Granular Bed Filter Development Program - Theoretical Analysis of Granular Bed Filtration Principles and Performance Prediction, Combustion Power Company, Menlo Park, California, FE-2579-18 (January 1978).

13. F. A. Zenz and H. Krockta, The Evolution of Granular Beds for Gas Filtration and Adsorption, Brit. Chem. Eng. Process Technol. 17 (3), 224-227 (1972).

14. Energy Conversion From Coal Utilizing CPU-400 Technology, Final Report, Combustion Power Company, Inc. (California), Report FE/1536-1, Vol. I (March 1977).

15. C. J. Wall, J. T. Graves, and J. E. Robert, How to Burn Salty Sludges, Chem. Eng. (N.Y.), 77 (April 14, 1975).

16. S. H. D. Lee and I. Johnson, Alkali Emission and Fixation during Combustion of Coals at the Normal Temperature Range of PFBCs, Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, Vol. I., pp. 942-948, American Chemical Society, Washington, D.C. (August 1979).

17. S. H. D. Lee, I. Johnson, and J. Fischer, Alkali Emission during Combustion of Coals at the Normal Temperature Range of PFBCs, Argonne National Laboratory Report ANL/CEN/FE-79-10 (June 1979).

18. Standard Methods for the Examination of Water and Wastewater, prepared and published jointly by American Public Health Assoc., American Water Works Assoc., and Water Pollution Control Federation, 13th Ed. (1971).

19. W. Nelson and E. S. Lisle, High-Temperature External Corrosion on Coal-Fired Boilers: Siliceous Inhibitors, J. Inst. Fuel 38, 179-186 (1965).

20. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, Occurrence and Distribution of Potentially Volatile Trace Elements in Coal, Final Report, Illinois State Geological Survey, No. 72 (August 1974).

21. James G. Vail, Ed., Soluble Silicates--Their Properties and Uses, 1st Ed., Reinhold Publishing Corporation, New York (1952).

22. R. K. Iler and E. J. Tauch, Sodium Silicate and Hydrochloric Acid from Sand, Salt and Steam, Trans. Am. Inst. Chem. Eng. 37, 853-877 (1941).

23. Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Vol. 18, Interscience Publishers, New York, p. 134 (1963).

24. S. K. Chirkov, The Preparation of Water Glass without the Use of Alkalies, J. Chem. Ind. (Moscow) 13, 469-474 (1936).

25. S. H. D. Lee, W. Swift, and I. Johnson, Activated Bauxite and Diatomaceous Earth Used as Granular Sorbents for the Removal of Sodium Chloride Vapor from Simulated Atmospheric Hot Flue Gas, Argonne National Laboratory Report, to be published.

26. F. L. Robson and A. J. Giramonti, The Use of Combined-Cycle Power Systems in Nonpolluting Central Stations, J. Air Pollution Control Asso. 22 (3), 177-180 (1972).

27. J. Agosta, H. F. Illian, R. M. Lundberg, and O. G. Tranby, Low B.t.u. Gas for Power Station Emission Control, Chem. Eng. Prog. 69(3), 65-66 (1973).

Distribution for ANL/CEN/FE-79-17

Internal:

W. E. Massey
L. Burris
W. L. Buck
F. Cafasso
E. Carls
P. T. Cunningham
J. Fischer
H. Huang
B. R. Hubble
I. Johnson (20)
A. A. Jonke (6)
J. A. Kyger
S. Lawroski
S. H. D. Lee (20)
J. F. Lenc
S. A. Miller
D. C. Fee
W. A. Ellingson
L. Cuba
G. M. Kesser
E. G. Pewitt
A. F. Melton
W. Podolski
J. Royal
S. Siegel
J. W. Simmons
G. W. Smith
K. M. Myles
W. M. Swift (10)
F. G. Teats
S. Vogler
D. S. Moulton
A. A. Siczek
J. E. Helt
R. F. Henry
D. S. Webster
W. I. Wilson
J. E. Young
R. Bane
E. J. Croke
J. D. Gabor
K. Jensen
N. Sather
J. Shearer
E. Smyk
C. B. Turner
A. B. Krisciunas
ANL Contract File
ANL Libraries (5)
TIS Files (6)

External:

DOE-TIC, for distribution per UC-90e (458)
Manager, Chicago Operations and Regional Office, DOE
Chief, Office of Patent Counsel, DOE-CORO
V. H. Hummel, DOE-CORO
M. Jackson, DOE-CORO
President, Argonne Universities Association
Chemical Engineering Division Review Committee:
  C. B. Alcock, U. Toronto
  R. C. Axtmann, Princeton U.
  J. T. Banchero, U. Notre Dame
  T. Cole, Ford Motor Co.
  P. W. Gilles, U. Kansas
  R. I. Newman, Warren, N. J.
  H. Perry, Resources for the Future, Washington
  G. M. Rosenblatt, Pennsylvania State U.
  W. L. Worrell, U. Pennsylvania
D. H. Archer, Westinghouse Research Labs., Pittsburgh
E. C. Bailey, John Dolio and Associates, Chicago
O. L. Bennett, West Virginia U.
R. Bertrand, Exxon Research and Engineering, Linden, N. J. (5)
R. R. Boericke, General Electric Co., Schenectady
M. Boyle, Valley Forge Labs., Devon, Pa.
J. A. Brooks, Amoco Oil Co., Naperville, Ill.
R. D. Brooks, General Electric Co., Schenectady
C. Busch, Spectron Development Laboratory, Inc., Costa Mesa, Calif.
J. Chen, Lehigh U.
D. Cherrington, Exxon Research and Engineering Co., Florham Park, N. J.
J. Clark, Tennessee Valley Authority, Chattanooga
N. Coates, The MITRE Corp., McLean, Va.
R. C. Corey, Office of Fossil Energy Programs, USDOE
R. Covell, Combustion Engineering, Inc.

G. Curran, Conoco Coal Development Co., Library, Pa.
D. DeCoursin, Fluidyne Engineering Co., Minneapolis
J. Dodge, Tetra Tech, Inc., Arlington, Va.
M. Dudukovic, Washington U.
S. Ehrlich, Electric Power Research Inst.
M. Evans, Aerotherm Division of ACUREX Corp., Mountain View, Calif.
M. H. Farmer, Exxon Research and Engineering Co., Linden, N. J.
C. Fisher, U. Tennessee
T. Fitzgerald, Oregon State U.
J. F. Flagg, Universal Oil Products Co., Des Plaines, Ill.
H. B. Forbes, Stone & Webster Engineering Corp., Boston
F. Frable, Bethlehem Mines Corp.
G. Frazier, U. Tennessee
S. Freedman, Office of Fossil Energy Programs, USDOE
R. L. Gamble, Foster Wheeler Energy Corp., Livingston, N. J.
D. E. Garrett, Garrett Energy Research and Engineering, Inc., Ojai, Calif.
L. Gasner, U. Maryland
J. Geffken, Office of Fossil Energy Programs, USDOE (5)
C. Georgakis, Massachusetts Inst. Technology
R. Glenn, Combustion Processes, Inc., New York City
J. S. Gordon, TRW, Inc., McLean, Va.
O. J. Hahn, U. Kentucky
J. Halow, Morgantown Energy Technology Center
W. Hansen, Babcock & Wilcox Co., Barberton, O.
M. J. Hargrove, Combustion Engineering, Inc.
R. D. Harvey, Illinois State Geological Survey, Urbana
R. Helfenstein, Illinois State Geological Survey, Urbana
R. G. Hickman, Lawrence Livermore Lab.
F. Hsing, Pratt & Whitney, East Hartford
D. Huber, Burns and Roe, Inc., Paramus, N. J.
F. D. Hutchinson, Gibbs and Hill, New York City
D. L. Keairns, Westinghouse Research Labs., Pittsburgh
D. Kirchgessner, U. S. Environmental Protection Agency, Research Triangle Park (16)
C. B. Leffert, Wayne State U.
A. M. Leon, Door-Oliver, Inc., Stamford, Conn.
R. M. Lundberg, Commonwealth Edison Co., Chicago
J. J. Markowsky, American Electric Power Service Corp., New York City
M. J. Mayfield, Tennessee Valley Authority, Chattanooga
W. McCurdy, Office of Fossil Energy Programs, USDOE
J. Mesko, Pope, Evans and Robbins, New York City (2)
A. Metcalfe, Solar Turbine International, San Diego
T. A. Milne, Solar Energy Research Inst.
S. Moskowitz, Curtiss-Wright Corp., Wood Ridge, N. J.
W. Norcross, Combustion Engineering, Inc.
T. A. Pearce, Dow Chemical, Freeport, Tex.
W. A. Peters, Massachusetts Inst. of Technology
C. Petty, Michigan State U.
M. I. Rednicki, Aerojet Energy Conversion, Sacramento
R. Reed, Pope, Evans and Robbins, Inc., Alexandria, Va.
A. F. Sarofim, Massachusetts Inst. Technology
S. Saxena, U. Illinois, Chicago
J. Shang, Morgantown Energy Technology Center
A. Sherman, Combustion Power Co., Menlo Park
C. Space, Reynolds, Smith & Hills, Jacksonville, Fla.

W. K. Stair, U. Tennessee
F. Staub, General Electric Corp., Schenectady
M. Steinberg, Brookhaven National Lab.
D. Stewart, Gilbert Associates, Reading, Pa.
L. Strickland, Morgantown Energy Technology Center
W. Strieder, U. Notre Dame
S. E. Tung, Massachusetts Inst. Technology
V. Underkoffler, Gilbert Associates, Inc., Reading, Pa.
W. E. Wallace, Jr., Morgantown Energy Technology Center
F. A. Walton, Combustion Power Co., Menlo Park
A. E. Weller, Battelle Columbus Labs.
G. Weth, Office of Fossil Energy Programs, USDOE
T. D. Wheelock, Iowa State U.
J. S. Wilson, Morgantown Energy Technology Center
K. Yeager, Electric Power Research Inst.
D. Zallen, Energy and Environmental Research Corp., Santa Ana
R. E. Zoellner, Stearns-Roger, Denver
J. F. Davidson, U. Cambridge, England
J. Highley, U. K. National Coal Board, Gloucestershire, England
H. R. Hoy, BCURA Ltd., Leatherhead, England
G. Moss, Esso Research Centre, Abington, England
H. Schreckenberg, Bergbau-Forschung GmbH, Essen, Germany
B. A. Wiechula, Imperial Oil Enterprises, Sarnia, Canada