Distribution Category:
Fluidized Bed Combustion
(UC-103)

ANL/FE-94-01

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, IL 60439

MEASUREMENT OF ALKALI VAPORS IN PFBC EXHAUST

FINAL REPORT

by

S. H. D. Lee and W. M. Swift

Chemical Technology Division

January 1994

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ep

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
1.0 INTRODUCTION	5
2.0 CONCEPT OF REGENERABLE ACTIVATED-BAUXITE SORBER ALKALI MONITOR (RABSAM)	5
3.0 LABORATORY-SCALE DEVELOPMENT OF RABSAM	7
3.1 NaCl-Powder Mixing with Activated Bauxite	7
3.1.1 Surface Color Change	8
3.1.2 Soxhlet Extraction	8
3.1.3 HNO ₃ Leaching	8
3.1.4 Alkali Analysis in RABA	9
3.2 NaCl-Solution Impregnation with Activated Bauxite	10
3.2.1 Initial Tests	11
3.2.2 Effects of Heat-Treatment Temperature and Duration	12
3.2.3 Parametric Study of Leaching and Extraction	13
3.2.4 Stability of Residual Sodium Compounds in RABA	15
3.2.5 Removal of Residual Sodium Compounds from NaCl-Deactivated RABA	16
3.3 LiCl-Solution Impregnation with Activated Bauxite	18
3.3.1 Preliminary Study of LiCl Solution-Impregnation	19
3.3.2 Ultrapure LiCl Solution-Impregnation	21
3.3.3 6 M LiCl Solution-Impregnation Technique	24
3.3.4 Removal of Residual Alkalis from 6 M LiCl-Deactivated RABA	27
3.3.5 Effect of High-Temperature Conditioning on Removal of Alkalis	29
3.4 High-Temperature High-Pressure Testing of RABA	30
3.4.1 Pressurized Alkali-Vapor Sorption Test Unit	30
3.4.2 Preparation of RABA by 6 M LiCl-Impregnation Technique	31
3.4.3 Preconditioning Test of RABA	32
3.4.4 NaCl-Vapor Sorption Test of RABA	34
4.0 CONCLUSION	37

TABLE OF CONTENTS (contd)

	<u>Page</u>
5.0 RECOMMENDATIONS	37
6.0 ACKNOWLEDGEMENTS	38
7.0 REFERENCES	39

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Schematic of Regenerable Activated-Bauxite Sorber Alkali Monitor	6
2.	Plots of Captured Alkalis as a Function of Bed Length in Sectioned Beds of Activated-Bauxite Sorber Bed	7
3.	Procedures of Generating RABA by NaCl-Solution Impregnation	18
4.	Distribution of Lithium in RABA as a Function of Heat-Treatment Duration after Treatment with LiCl	27
5.	Procedures for Generating RABA by 6 <u>M</u> LiCl-Impregnation Technique	28
6.	Pressurized Alkali-Vapor Sorption Test Unit	31
7.	Experimental Procedures for the High-Temperature/High-Pressure Testing of RABA	35

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Soxhlet Extraction of NaCl Powder-Treated Activated-Bauxite Adsorbent	8
2.	HNO ₃ Leaching of NaCl Powder-Treated Activated-Bauxite Adsorbent	9
3.	Soxhlet Extraction of HNO ₃ -Leached Activated-Bauxite Adsorbent	10
4.	Alkali Content in Fresh Activated Bauxite and Regenerable Activated-Bauxite Adsorbent	10
5.	Effects of Molarity and Heat-Treatment Duration on Deactivation of Clay Impurities in AB	11
6.	Effects of Heat-Treatment Temperature and Duration on Deactivation of Clay Impurities in AB	12
7.	Water Leaching of NaCl Solution-Impregnated Activated-Bauxite Adsorbent	13
8.	Acid Leaching of Water-Leached Activated-Bauxite Adsorbent	14
9.	Soxhlet Extraction of Acid-Leached Activated-Bauxite Adsorbent	14
10.	Sodium and Chloride Concentrations in Leachates and Extract	15
11.	Sodium Analysis of the Soxhlet Extract from Cyclic Treatment of RABA	16
12.	Material Balance of Sodium	17
13.	Sodium Analysis of the Acid Leachate and Soxhlet Extract from Cyclic Treatment of RABA	19
14.	Ions Extracted from LiCl Solution-Impregnated AB by Water Leaching, Acid Leaching, and Soxhlet Extraction	20
15.	Material Balances for Lithium, Sodium, and Potassium in AB	20
16.	Water Leaching of LiCl Solution-Impregnated AB	21
17.	Removal of Na and K from Water-Leached RABA	22

LIST OF TABLES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
18.	Soxhlet Extraction of PFBC Preconditioned RABA	23
19.	Material Balances for Sodium and Potassium in RABA	24
20.	Lithium Distribution in Water Extract and Extracted RABA as a Function of Heat-Treatment Duration	26
21.	Analyses of Sodium and Potassium in Leachates and Extracts of 6 <u>M</u> LiCl-Impregnated Activated Bauxite	29
22.	Analyses of Sodium and Potassium in Soxhlet Extracts	30
23.	Porosity and Surface Area Measurement for Fresh AB and RABA	32
24.	Chemical Analysis of Water Leachate from Fresh AB and Water Extract from RABA	33
25.	Distribution of NaCl-Vapor Capture for the Test of RABA	35
26.	Chemical Analysis of Water Solution from Water-Leached or Extracted from Various Activated-Bauxite Samples	36

MEASUREMENT OF ALKALI VAPOR IN PFBC EXHAUST

Final Report

by

S. H. D. Lee and W. M. Swift

ABSTRACT

Under the auspices of the U. S. Department of Energy through Morgantown Energy Technology Center, laboratory-scale studies were conducted to develop a regenerable activated-bauxite adsorbent (RABA) for use in an *in situ* regenerable activated-bauxite sorber alkali monitor (RABSAM). The RABSAM is a sampling probe that does not require a high-temperature/high-pressure sampling line for reliable measurement of alkali vapor in the exhaust of pressurized fluidized-bed combustor (PFBC). The RABA can be generated from the commercial grade activated bauxite by deactivating (or reacting) clay impurities in activated bauxite with NaCl or LiCl vapor. Under the atmospheric deactivation process, however, only a partial deactivation of clay impurities is achieved, probably due to limited access of NaCl or LiCl vapor into micropores of activated bauxite. Because LiCl vapor chemically reacts with alumina substrate of activated bauxite, resulting in pore enlargement, loss of pore surface area, and a decrease in the subsequent NaCl-vapor sorption capacity of the RABA, NaCl is a more suitable deactivation agent than LiCl vapor. In a simulated PFBC exhaust environment, the RABA behaves similarly to fresh activated bauxite in capturing NaCl vapor from the simulated PFBC exhaust. Based on results of this work, we recommend generating chemically and thermally stable RABA by deactivating clay impurities of commercial grade activated bauxite with NaCl or KCl vapor under simulated PFBC exhaust environment, that is, high-temperature, high-pressure, and high concentrations of NaCl or KCl vapor in simulated PFBC exhaust compositions.

SUMMARY

Alkali vapor present in the pressurized fluidized-bed combustor (PFBC) exhaust can react with particulate filter medium, causing it to weaken and fail. It can also cause hot corrosion of the gas turbine hardware when it is expanded through a gas turbine. Reliable quantification of alkali-vapor concentration in PFBC exhaust is needed to evaluate the corrosivity of the exhaust and the efficiency of the alkali-vapor control device. Our objective is to develop a reliable *in situ* regenerable activated-bauxite sorber alkali monitor (RABSAM) that requires no high temperature/high pressure sampling line.

The RABSAM is a sampling probe that can be inserted directly into the PFBC exhaust duct through a side arm containing a shut-off valve. The probe contains a bed of regenerable activated-bauxite adsorbent (RABA) that can physically adsorb alkali vapor from the PFBC exhaust and be easily regenerated by simple water leaching. The key to the development of this monitor is to derive RABA from commercially available activated-bauxite (AB) sorbent. Commercial grade AB contains some clay impurities that can react with alkali vapor and, therefore, need to be either removed or deactivated.

We studied three methods to deactivate clay impurities in commercial grade AB: NaCl powder mixed with AB, NaCl-solution impregnation with AB, and LiCl-solution impregnation with AB. Since clay impurities react with alkali vapor, NaCl vapor is a logical choice to deactivate these clay impurities. One simple method to achieve this is to mix activated bauxite with NaCl powder and then heat the mixture to about 700°C to generate sufficient NaCl vapor to react with the clay impurities. After treatment, the mixture is subjected to a series of water washing, HNO₃ leaching, and Soxhlet extraction with deionized water to remove the residual NaCl and water-soluble alkali compounds. Results of this NaCl-powder mixing study show that the HNO₃ leaching is much more effective than water leaching in removing residual water-soluble sodium in the NaCl powder-treated AB adsorbent. Soxhlet extraction is needed as a final refining step to achieve complete removal of the residual water-soluble sodium in the RABA.

We next explored a NaCl solution-impregnation method because it has several potential advantages over the NaCl-powder mixing method. First, NaCl solution enters internal pores of AB during impregnation, providing NaCl at the immediate vicinity of clay impurities; thus, the deactivation of clay impurities during heat-treatment can be accomplished more effectively than the treatment with NaCl powder. In the NaCl-powder treatment, NaCl vapor needs to diffuse into the internal pores before reacting with clay impurities. Second, due to this effectiveness, less NaCl and a shorter heat-treatment duration are required. Third, removing residual NaCl from the treated AB is expected to be easier because less of it was used to begin with. A series of laboratory tests has been conducted to study (1) the effects of heat-treatment temperature, heat-treatment duration, and quantity of NaCl-solution impregnation on the deactivation of clay impurities, (2) the effectiveness of water and acid leaching and Soxhlet extraction steps for removing residual NaCl and water-soluble alkali compounds from RABA, and (3) the stability of RABA.

Results of studies show that sodium in RABA produced by the NaCl-solution impregnation method is present as residual NaCl and non-chloride compounds, such as silicates. The water leaching step effectively removes residual NaCl, while the subsequent acid leaching removes non-chloride sodium compounds. Soxhlet extraction serves as a final cleanup step for both residual NaCl and non-chloride sodium compounds.

The stability of residual water- and acid-insoluble sodium compounds in RABA remains a concern when it is exposed to actual PFBC exhaust. Heat-treating the RABA in a simulated PFBC exhaust at 900°C showed that the residual sodium compounds can be subsequently released in water-soluble forms, indicating the necessity for their complete removal. Cyclic preconditioning of the RABA in a simulated PFBC exhaust, followed by

acid leaching with 2 N H_2SO_4 or Soxhlet extraction with deionized water, has been employed to remove the sodium compounds, but further improvement in the rate of sodium removal from RABA is still needed.

LiCl has chemical properties similar to NaCl but it is more reactive. It was tested as a replacement for NaCl for deactivating clay impurities in fresh AB. One of the immediate advantages for using LiCl over NaCl is that the amount of non-chloride sodium compounds, products of the deactivation in RABA, that need to be removed would be significantly reduced; therefore, the removal of these sodium compounds could be expected to be easier. Also, the presence of lithium compounds in RABA, whether they are water-soluble or not, is not expected to affect the adsorption property of RABA for sodium and potassium vapors.

Tests were made to optimize techniques for LiCl-vapor impregnation and removal of residual alkali compounds in RABA, to study how LiCl deactivation effects the physical and chemical properties of RABA, and finally, to test RABA for its NaCl-vapor sorption in a simulated PFBC environment. Results of experimental tests show that like NaCl vapor, LiCl vapor can deactivate clay impurities in fresh AB; however, only a partial deactivation is achieved by reacting LiCl vapor with clay impurities under atmospheric condition, probably due to the limited access of LiCl vapor to micropores of AB. In addition to deactivating clay impurities, LiCl vapor also chemically reacts with Al_2O_3 , which is the major component of AB, to form water-soluble aluminum compound(s), probably lithium meta-aluminate, LiAlO_2 . Therefore, the treatment of AB with LiCl vapor opens up inherent small pores present in fresh AB and results in a decrease in pore area of RABA.

A batch of LiCl vapor-deactivated RABA was tested for its NaCl-vapor sorption at a bed temperature of 895-900°C and a system pressure of 10 atm absolute in a simulated PFBC exhaust containing 3% O_2 , 16% CO_2 , 6% H_2O vapor, ~1000 ppmV SO_2 , 5-9 ppmW NaCl vapor, and the remainder N_2 . Two cycles of the RABA test were completed. The NaCl-vapor capture efficiency of the RABA was somewhat lower than that of fresh AB tested under the similar test conditions (94.5 and 96.7% for RABA, compared to >99% for fresh AB). The reason is that the RABA has less surface area than the fresh AB and less chemically active clay impurities that are known to effectively capture NaCl vapor; however, an improved capture efficiency can be achieved by RABA by increasing the length of the RABA sorption bed.

The regenerability of RABA can be simply measured by the extractability of the captured sodium from the NaCl-sorbed RABA. It was found that for the first cycle test, only 52.1% of the total NaCl vapor captured by the RABA was extractable by three consecutive Soxhlet extractions with deionized water. Thus, clay impurities in AB may not be totally deactivated by LiCl vapor under atmospheric condition; that is, the RABA may still contain some residual clay impurities. However, these residual clay impurities were further deactivated by NaCl vapor in the first cycle test, thereby resulting in a significant increase in the amount of water-extractable sodium to 74.5% for the second cycle test. All these results suggest that NaCl (or KCl) should be used to generate RABA at high pressure to achieve the complete deactivation of clay impurities in fresh AB.

Chemical analyses of Soxhlet extracts from both cycles of the test were conducted to study the possible sorption mechanism of NaCl vapor by RABA. Results of chemical analyses show that NaCl vapor present in the simulated PFBC exhaust containing SO₂ was captured by RABA essentially as sodium sulfate, as well as NaCl, but to a lesser extent. Therefore, it is concluded that RABA behaves similarly to fresh AB in terms of capture mechanisms of NaCl vapor from simulated PFBC exhaust.

1.0 INTRODUCTION

Several demonstration and commercial plants¹⁻⁴ are operating or are under construction to use the pressurized fluidized-bed combustion/gas-turbine combined-cycle system (PFBC/GTCCS) for power generation. In this PFBC/GTCCS system, the high-temperature/high-pressure (HTHP) PFBC exhaust needs to expand through a gas turbine to recover energy for improved overall cycle efficiency. Vapor-phase alkalis, such as chlorides and sulfates of sodium and potassium, are present in PFBC exhaust and can cause the turbine blades to corrode. The current industrial gas-turbine specification limit for total alkalis in the combustion gas entering a turbine is equivalent to 0.024 ppm.⁵ Many institutions have attempted to quantify the alkali vapor in PFBC exhaust. A conventional batch-type extraction of the exhaust followed by the analysis of the condensate resulted in a measured alkali-vapor concentration on the order of 0.1 to 10 ppm,⁶⁻⁹ well above the specification limit.

Under the support of the U.S. Department of Energy, an on-line, real-time alkali analyzer has been developed and is widely used in the field.¹⁰⁻¹³ Studies by Lee and Myles¹² have shown that the alkali-vapor measurements by an on-line real-time alkali analyzer were distorted, at least partially due to capture of the alkali vapor by the HTHP stainless steel sampling line. Recently, we demonstrated that a time-averaged alkali-vapor concentration in the PFBC exhaust can be reliably obtained by an analytical activated-bauxite sorber bed technique.¹⁴ The objective this work is, based on this technique, to develop a regenerable activated-bauxite sorber alkali monitor (RABSAM) that requires no HTHP sampling line for reliable measurement of alkali vapors in PFBC exhaust.

2.0 CONCEPT OF REGENERABLE ACTIVATED-BAUXITE SORBER ALKALI MONITOR (RABSAM)

Figure 1 is a schematic of the RABSAM. Basically, it is a stainless steel sampling probe with a regenerable activated-bauxite (AB) cartridge at the tip. The other end of the probe is connected to the gas-stream conditioning and measuring devices. It can be inserted directly into the PFBC exhaust duct through a side arm containing a shut-off valve. The activated-bauxite cartridge will be designed and operated in such a condition that alkali vapors will be totally adsorbed by the AB bed. At the end of the sampling period (about 1-2 h), the AB adsorbent is collected and leached with water; the leachate is analyzed for alkalis by a commercially available atomic absorption (AA). With the known total gas flow passing through the probe (measured from the wet-test meter recording) and the total alkalis from the AA analysis, the time-average alkali-vapor concentration in the PFBC exhaust can be calculated.

In a PFBC/GTCCS, the HTHP PFBC exhaust needs to be cleaned of fly ash particulates, probably by one stage of cyclone followed by a second-stage high-efficiency cyclone or advanced particulate filters (e.g., SiC candle filters, granular-bed filters, or cross-flow membrane filters) before it is expanded through a gas turbine. These cyclone and advanced particulate filters are not absolute devices in that they are not expected to achieve 100% particulate removal efficiency. The PFBC exhaust could contain 10-20 ppm of particulates

Fig. 1.

Schematic of Regenerable Activated-Bauxite Sorber Alkali Monitor

after passing through a second-stage advanced particulate filter device that is assumed to have 99% particulate removal efficiency; therefore, it is reasonable to anticipate the presence of both particulates and alkali vapors in the PFBC exhaust that enters the gas turbine. It is well-known that fly ash particulates contain a significant amount of alkalis in the form of sulfates and silicates. In the analysis of alkali-vapor concentrations in PFBC exhaust, it has been a challenging task to separate the vapor-phase alkalis and the particulate alkalis (that are contributed by fly ash particulates).

The RABSAM is an *in situ* technique (as shown in Fig. 1). In other words, no sampling line is required, eliminating the problems of alkali-vapor condensation on the sampling line and of reactions between alkalis in the exhaust and the sampling line. The stainless steel sampling line at HTHP was demonstrated to capture alkalis.¹² In RABSAM, the PFBC exhaust containing both alkali vapors and fly ash particulates flows directly through a column of regenerable activated-bauxite adsorbent. The fly ash particulates are captured by the first layer of the adsorbent, while alkali vapors are physically adsorbed by the adsorbent as they flow through the column. By using sectioned beds for the RABSAM adsorbent column,^{14,15} the amount of vapor-phase alkalis captured by the first section of the adsorbent column can be derived by (1) plotting the amount of alkali-vapor capture in each section as a function of the bed length, and (2) extrapolating the least-square-fit curve to intercept the coordinate, as shown in Fig. 2. The intercept value is considered to be a reasonable amount of vapor-phase alkalis being captured by the first section. By adding all vapor-phase alkalis captured by the entire bed, a time-averaged, alkali-vapor concentration in the PFBC exhaust can be calculated. Based on experience obtained from several tests of the analytical activated-bauxite sorber bed,^{14,15} the RABSAM concept offers the following two advantages over the other analytical techniques.

1. The RABSAM requires no sampling line, eliminating the potential problems of alkali-vapor condensation on the sampling line and of reactions between the alkalis and the sampling line.

Fig. 2.

Plots of Captured Alkalis as a Function of Bed Length in Sectioned Beds of Activated-Bauxite Sorber Bed (Ref. 15)

2. By using sectioned beds in adsorbent column, the RABSAM can effectively differentiate particulate alkalis (that were present in fly ash) from vapor-phase alkalis.

3.0 LABORATORY-SCALE DEVELOPMENT OF RABSAM

Developing the RABSAM requires developing a regenerable activated-bauxite adsorbent (RABA) to capture the alkali vapors in PFBC exhaust purely through physical adsorption. This work was to develop the RABA from a commercially available activated-bauxite (AB) sorbent. Commercial grade AB contains some clay impurities that can react with alkali vapors, and thus need to be either removed or deactivated. Three methods to deactivate these impurities were studied and are described below.

3.1 NaCl-Powder Mixing with Activated Bauxite

Since clay impurities in AB react with alkali vapors, NaCl vapor is an obvious choice to deactivate them. One simple method is to mix the AB with NaCl powder and heat the mixture at a high temperature so that sufficient NaCl vapor will be generated to react with the clay impurities. A batch of fresh AB in sizes ranging from 1.68 to 2.38 mm (-8 + 10 mesh Tyler Equivalent Designation) was mixed well with NaCl powder (ACS reagent) and heated in a muffle furnace at 700°C for 85 h. After the treatment, the mixture was washed with tap water to remove excess NaCl powder. The washed AB sorbent was then leached three times with deionized water at a gentle boil to remove any residual salt. After drying, it was heated again in the muffle furnace at 850°C for 5 h.

3.1.1 Surface Color Change

Commercial grade AB is light pink. Our earlier study showed that it becomes milky white after it captures alkali vapor.¹⁶ The prepared batch of AB indeed became milky white and, despite of some loss of AB fines during the washing and leaching, gained 0.23% in weight. All these observations show that NaCl vapor was captured and that it reacted with clay impurities in AB during the NaCl treatment.

3.1.2 Soxhlet Extraction

The prepared AB adsorbent underwent a series of Soxhlet extractions with deionized water to evaluate the effectiveness of the water extraction on removing residual water-soluble sodium from the adsorbent. Thirty-gram samples of the AB adsorbent were Soxhlet-extracted with 250 mL deionized water as a function of time. Table 1 summarizes the results of this extraction study.

As shown in Table 1, a significant amount of sodium was still being extracted from the AB adsorbent over time, although the extracted amount decreased with the extraction duration. Even after 100 h, water-extractable sodium remained in the AB adsorbent; thus, water extraction is not very effective in removing the residual water-soluble sodium from the adsorbent.

Table 1. Soxhlet Extraction of NaCl Powder-Treated Activated-Bauxite Adsorbent

Sample No.	Cumulative Extraction Duration, h	Cumulative Amount of Na Extracted, mg	Cumulative Unit Amount of Na Extracted, mg Na/g AB
1	4	38.64	1.29
	8	56.40	1.88
2	4	38.64	1.29
	28	63.64	2.12
	52	75.74	2.52
	100	81.74	2.73

3.1.3 HNO₃ Leaching

Twenty-gram samples of the adsorbent were leached with 1:1 HNO₃ solution in a beaker at a gentle boil to study the effectiveness of HNO₃-leaching in removing the residual water-soluble sodium. The leachate was collected, filtered through a HNO₃-treated filter paper to remove adsorbent fines that were produced during the leaching, and analyzed for sodium by AA. Table 2 summarizes the results of this study.

Table 2. HNO₃ Leaching of NaCl Powder-Treated Activated-Bauxite Adsorbent

Sample No.	Vol. of Leaching Solution, mL	Leaching Duration, h	Wt. of Leached AB Adsorbent, ^a g	Amount of Na Leached, mg	Unit Amount of Na Leached, mg Na/g AB
1	80	0.5	19.08	64.25	3.21
2	160	0.5	19.01	69.25	3.46
3	80	1	18.67	64.00	3.20

^aRepresents particle sizes ranging from 1.68 to 2.38 mm (-8 + 10 mesh). Adsorbent fines produced during leaching were discarded.

Table 2 shows that the adsorbent fines plus the extracted sodium represent <5 wt% for 0.5-h leaching and about 7 wt% for 1-h leaching. This procedure leached out much more sodium from the adsorbent than the water extraction (shown in Table 1), especially in a much shorter time. The amount of leached sodium increased directly with the volume of the leaching solution, but the extension of the leaching time did not appear to affect the amount of sodium leached from the adsorbent.

After leaching, the sample was extracted in a Soxhlet apparatus with deionized water as a function of extraction duration. As the results in Table 3 show, some water-soluble sodium was extracted (last column in Table 3); however, as we expected, the extracted amount was much less (an order of magnitude less) than that extracted from the adsorbent without being leached first with HNO₃ (last column in Table 1). Also, the extracted amount decreased quickly with the extraction time. After 12 h, the amount of sodium extracted in an additional 4 h was <0.05 mg, or <3 µg Na/g AB, which is negligible compared to the maximum adsorption capacity of 370 µg Na/g AB. These results show the nearly complete removal of the residual water-soluble sodium in the AB adsorbent.

Results of this HNO₃-leaching study show that simple leaching by HNO₃ effectively removes residual water-soluble sodium in the NaCl powder-treated AB adsorbent. The Soxhlet extraction after the HNO₃ leaching serves as a final refining step to completely remove the residual water-soluble sodium.

3.1.4 Alkali Analysis in RABA

Fresh AB and the RABA (treated AB that had been leached and extracted) were analyzed for their alkali contents. As shown in Table 4, the RABA contains about nine times as much sodium as the fresh AB, indicating that the clay impurities captured sodium during the NaCl-powder treatment. Table 4 also shows a significant decrease in potassium content, which is believed to be due to the exchange reactions of potassium silicates in AB with NaCl vapor. Potassium can be released from silicates as KCl through exchange reactions with NaCl vapor.¹⁷⁻¹⁹

Table 3. Soxhlet Extraction of HNO₃-Leached Activated-Bauxite Adsorbent

Sample No.	Cumulative Extraction Duration, h	Cumulative Amount of Na Extracted, mg	Cumulative Unit Amount of Na Extracted, ^a mg Na/g AB
1	4	3.43	0.17
	8	4.06	0.20
	12	4.15	0.21
	16	4.18	0.21
2	4	2.39	0.12
	8	2.94	0.15
	12	3.00	0.15
	16	3.03	0.15
3	4	2.23	0.11
	8	2.67	0.13
	12	2.72	0.14
	16	2.77	0.14

^a20 g HNO₃-leached AB adsorbent was Soxhlet-extracted with deionized water.

Table 4. Alkali Content in Fresh Activated Bauxite and Regenerable Activated-Bauxite Adsorbent

Type of Sample	Alkali Content, wt %	
	Na	K
Fresh AB ^a	0.003	0.004
RABA ^b	0.026	0.001

^aThe AB was washed with deionized water to remove fines.

^bThe RABA was prepared by treating with NaCl powder in a muffle furnace at 700°C for 85 h, followed by 1:1 HNO₃ leaching for 0.5 h and a subsequent Soxhlet extraction with deionized water for a total of 20 h.

3.2 NaCl-Solution Impregnation with Activated Bauxite

This method was explored because it has several potential advantages over the NaCl-powder method studied earlier. First, the NaCl solution enters the internal pores of AB during impregnation, providing NaCl at the immediate vicinity of the clay impurities, which should be deactivated more effectively during heat-treatment. In the NaCl-powder treatment, NaCl vapor must diffuse into the internal pores before it can react with the clay impurities. Second, less NaCl and a shorter heat-treatment duration are required. Third, the removal of residual NaCl from the after-treated AB is easier because less NaCl is used to begin with.

3.2.1 Initial Tests

Several batches of RABA were prepared to investigate the effect of molarity of NaCl solution and the length of heat-treatment duration on the deactivation of clay impurities in AB. The RABA was prepared by (1) wetting the fresh AB with a known amount of NaCl solution, (2) heat-treating the NaCl solution-impregnated AB in a muffle furnace at 730°C for a specific duration, (3) leaching the heat-treated AB with 1:1 HNO₃ solution for 30 min, and (4) finally, Soxhlet-extracting the HNO₃-leached AB with deionized water for 24 h. The resulting RABA was then further Soxhlet-extracted with deionized water for an additional 4 h to determine the amount of water-soluble sodium and analyzed for sodium content in the RABA. Results of these analyses are summarized in Table 5. For comparison, the sodium contents of fresh AB and the RABA prepared by the NaCl-powder technique are also included in the table. The extent of deactivation of clay impurities in AB is represented by the amount of sodium captured or the sodium content in the RABA, as shown in the last column in Table 5.

Table 5. Effects of Molarity and Heat-Treatment Duration on Deactivation of Clay Impurities in AB

Sample No.	Molarity of NaCl Solution	Duration of Heat-Treatment, h	Water-Extractable Na, ^a mg	Na Content in RABA, %
RAB-1M/1H	1	1	0.084	0.12
RAB-2.5M/1H	2.5	1	0.244	0.26
RAB-5.0M/1H	5.0	1	0.130	0.27
RAB-5.0M/2.5H	5.0	2.5	0.196	0.28
RAB-5.0M/5H	5.0	5	0.204	0.30
RAB-5.0M/8H	5.0	8	0.129	0.29
Fresh AB				0.003
RAB-14-2&3 ^b				0.02

^aAmount of Na extracted in 4-h Soxhlet extraction with deionized water after the sample has been Soxhlet-extracted with deionized water for 24 h.

^bThe RABA was prepared by treating with NaCl powder in a muffle furnace at 700°C for 85 h, followed by 1:1 HNO₃ leaching for 0.5 h and a subsequent Soxhlet extraction with deionized water for a total of 20 h.

Table 5 shows that the extractable amount of sodium is still somewhat higher than expected, indicating that extended Soxhlet extraction is needed to completely remove the water-soluble sodium from these RABA. Table 5 also shows that the increase in molarity of NaCl solution used in the impregnation increases the sodium capture; however, with the molarity of greater than 2.5, the sodium capture appears to be constant, despite the heat treatment duration. With 5 M NaCl, the complete deactivation of clay impurities in AB was

achieved within 5 h. Extending the heat-treatment to 8 h did not appear to increase the sodium content. The maximum sodium content of 0.30 wt% is more than an order of magnitude greater than that obtained from the NaCl-powder technique with an 85-h heat-treatment, indicating the effectiveness of this impregnation technique.

3.2.2 Effects of Heat-Treatment Temperature and Duration

Four batches of RABA were prepared to look into the effects of (1) heat-treatment temperature (780 and 820°C) and (2) heat-treatment duration (2 and 5 h) on the deactivation of clay impurities by the NaCl-impregnation technique.

Fresh AB in sizes ranging from 1.41 to 1.68 mm (-10 + 12 mesh) was first impregnated with 1 M NaCl solution and then dried in an oven at 100°C for overnight. The resulting AB sample contains about 11.5 mg Na/g AB. The well-mixed NaCl-impregnated AB was divided into four equal fractions for the subsequent treatments. Heat-treatment was conducted at 780°C, which is below the melting temperature (801°C) of the NaCl, and at 820°C for heat-treatment durations of 2 and 5 h. After heat-treatment, each sample was screened through a 1.41-mm opening (12-mesh) screen to remove any fines. The samples were then subjected to (1) three consecutive water leachings to remove residual NaCl, (2) three consecutive acid leachings with 2 N H₂SO₄, and (3) Soxhlet extraction with deionized water for a total of 12 h. Table 6 shows the sodium analysis results for all leachates and extracts.

During heat-treatment, the NaCl vaporizes and reacts with the clay impurities in AB. Some NaCl also diffuses out of the sample into the furnace open space and is lost. Table 6 shows the expected trend of increasing the amount of deactivation of clay impurities as a result of increasing the heat-treatment temperature and duration. This trend is supported by the amount of sodium leached out by acid leaching. Sample 1M/5H-820 deviates from this trend, probably due to the exceptionally high NaCl-vapor loss during heat-treatment, which is evidenced by the significantly lower NaCl recovery from water-leaching.

Table 6. Effects of Heat-Treatment Temperature and Duration on Deactivation of Clay Impurities in AB

Sample No.	Heat-Treatment Temp., °C	Duration of Heat-Treatment, h	Amount of Sodium, mg Na/g AB			
			Water Leaching	Acid Leaching	Soxhlet Extraction	Sum
1M/2H-780	780	2	7.56	2.77	0.07	10.40
1M/2H-820	820	2	7.26	3.39	0.07	10.72
1M/5H-780	780	5	7.27	2.97	0.06	10.30
1M/5H-820	820	5	6.50	2.88	0.07	9.45

3.2.3 Parametric Study of Leaching and Extraction

More experimental work was conducted to quantitatively examine the effectiveness of each water-leaching, acid-leaching, and Soxhlet-extraction steps for the removal of residual NaCl from the heat-treated, NaCl-impregnated AB adsorbent. A batch of NaCl-impregnated AB was prepared by impregnating the fresh AB with 5 M NaCl solution, then heat-treating the AB in a muffle furnace at 730°C for 1 h. The batch was then subjected to the following series of treatments.

Water Leaching. The batch of the NaCl solution-impregnated AB was first divided into three equal portions, each of which was leached with deionized water three times. Water leaching was carried out in a beaker at a gentle boil for two minutes. Table 7 shows the amount of leached sodium for each water-leaching step. As expected, the residual sodium in the NaCl-impregnated AB was largely leached out by the first water leaching, and the amount of leached sodium was sharply decreased in the second and third leaching steps.

Table 7. Water Leaching of NaCl Solution-Impregnated Activated-Bauxite Adsorbent

Sample No. ^a	Wt. of Sorbent Leached, g	Amount of Sodium Leached, mg Na/g AB			
		First Leaching	Second Leaching	Third Leaching	Sum
RAB-5M/1H-1	27.00	29.21	6.42	1.28	36.91
-2	27.00	29.47	6.08	1.10	36.65
-3	27.00	30.42	6.21	1.14	37.77
				Avg.	37.11

^aAB was leached with deionized water with gentle boiling for 2 min.

Acid Leaching. The three batches of the water-leached AB were thoroughly mixed and then divided into four equal portions for leaching by nitric and sulfuric acids as a function of two acidic strengths of 2 N and 5 N. Acid leaching was performed in a beaker with gentle boiling for ten minutes. At the end of leaching, the leachate was collected, and the AB was rinsed with boiling water three times. The acidic leachate and the water rinse were combined as one batch of solution for the analysis of sodium by atomic absorption spectrometry. Results of the acid leaching are given in Table 8. Within the limit of experimental and analytical errors, the effectiveness of both nitric acid and sulfuric acid in removing the residual sodium from the water-leached AB is the same. Also, these 2 N and 5 N acidities for both acids showed the similar effectiveness.

Soxhlet Extraction. Each batch of the acid-leached AB was Soxhlet-extracted stepwise as a function of time. After each extraction, the extract was collected for sodium analysis. The sorbent was then further extracted with a new batch of deionized water for an additional length of time. The adsorbent was first extracted for 24 h and then extracted for

Table 8. Acid Leaching of Water-Leached Activated-Bauxite Adsorbent

Sample No. ^a	Acidic Type and Strength	Wt. of AB Leached, g	Amount of Na Leached, mg Na/g AB
RAB-5M/1H-2NNA	2 <u>N</u> HNO ₃	18.00	3.51
-5NNA	5 <u>N</u> HNO ₃	18.00	3.41
-2NSA	2 <u>N</u> H ₂ SO ₄	18.00	3.45
-5NSA	5 <u>N</u> H ₂ SO ₄	18.00	3.47

^aAB was leached at a gentle boiling temperature for ten minutes.

additional durations of 4, 4, 4, 12, and 4 h. Table 9 summarizes the amount of sodium extracted in micrograms of sodium per gram of activated bauxite. These results show that after a total of 48 h of extraction, the extractable amount of sodium in an additional 4 h (last column of Table 9) was <5 µg Na/g AB, which, when compared with the maximum adsorption capacity of 370 µg Na/g AB, is negligible; therefore, the nearly complete removal of the residual water-soluble sodium in the regenerable AB is considered to have been achieved.

Table 9. Soxhlet Extraction of Acid-Leached Activated-Bauxite Adsorbent

Sample No. ^a	Wt. of AB Extracted, ^b g	Amount of Na Extracted, µg Na/g AB					
		First 24-h Extraction	Additional Extraction Duration, h				
			4	4	4	12	4
RAB-5M/1H-2NNA	16.23	223	9.1	9.6	7.3	41.8	2.9
-5NNA	15.87	195	10.8	8.9	6.9	62.6	4.7
-2NSA	16.24	232	9.6	11.6	10.0	51.7	2.8
-5NSA	15.99	203	9.9	8.3	7.3	62.7	4.4

^aSee Table 8 for sample identification.

^bAB was Soxhlet-extracted with deionized water.

Chemical Form(s) of Leached Sodium. In order to obtain information about chemical form(s) of the leached sodium in each of the water-leaching, acid-leaching, and Soxhlet extraction steps, the leachate and extract were also analyzed for chloride concentration by ion chromatography. Table 10 shows the comparison of sodium and chloride concentrations. Table 10 clearly shows that in the water leachate, sodium is mostly present as a form of NaCl, indicating that the residual NaCl in the NaCl-impregnated AB was leached out by water in this water-leaching step. A small fraction of the leached sodium (averaging 13% of the total) is present as non-chlorides, possibly as water-soluble sodium silicates formed during heat-treatment of the NaCl-impregnated AB through chemical reactions of the clay impurities with NaCl vapor. In contrast, acid leaching leached out mostly the non-

chloride sodium. About 19% of the total acid-leached sodium is present as NaCl, representing the residual NaCl left in the water-leached AB. After water leaching of most of the residual NaCl and acid leaching of most of the water-soluble non-chloride sodium (such as sodium silicates), Soxhlet extraction serves as a final cleanup step of both forms. Table 10 shows that the extracted sodium is present approximately equally as chloride and non-chloride forms.

Table 10. Sodium and Chloride Concentrations in Leachates and Extract

Type of Sample	Concentration, $\mu\text{mol/mL}$		
	Na	Cl	Na/Cl Mole Ratio
Water Leachate ^a			
First Leachate	161.7	140.0	1.2
Second Leachate	49.6	44.9	1.1
Third Leachate	9.8	8.2	1.2
Acid Leachate ^b			
RAB-5M/1H-2NNA	11.0	2.0	5.5
-2NSA	10.0	1.9	5.3
Soxhlet Extract ^c			
RAB-5M/1H-2NNA-24	1.0	0.4	2.5
-2NSA-24	1.1	0.5	2.2

^aSamples of RAB-5M/1H-1 of Table 7.

^bSee Table 8 for sample identification.

^cFirst 24-h extract in Table 9.

3.2.4 Stability of Residual Sodium Compounds in RABA

In a practical application, the RABA will be used in the PFBC environment. One concern is the stability of the residual sodium compounds in the RABA when the RABA is exposed in the PFBC exhaust environment. To study this, a laboratory-scale setup was constructed to further heat-treat the RABA in a simulated PFBC exhaust environment.

The RABA was packed inside a 2.54-cm-dia Al_2O_3 tube and heat-treated at 850°C and atmospheric pressure for 4 h. A simulated PFBC exhaust (containing 3.0% O_2 , 14.2% CO_2 , 1.7% H_2O , and 550 ppmV SO_2 , with the remainder N_2) flowed through the bed during the entire 4-h period. After heat-treatment, the RABA was subjected to Soxhlet extraction with deionized water to determine the amount of water-extractable sodium and its possible form(s).

The sodium extracted from the RABA in 4 h was shown to be less than $5 \mu\text{g/g-AB}$ (Table 9). After the first heat-treatment in a simulated PFBC exhaust environment, the amount of water-extractable sodium sharply increased to greater than

1000 µg/g-RABA for the first 4-h extraction period and then gradually decreased in subsequent extraction steps. The concentration eventually decreased to an average of less than 5 µg/g-AB in the fourth 4-h extraction. The water-extractable sodium is largely present as non-chlorides. As expected, the RABA captured SO₂ from the simulated PFBC exhaust, and the captured SO₂ was released as SO₄²⁻ in water solution. Results of these heat-treatment studies clearly indicate that the residual sodium compounds in RABA can be further released as water-soluble sodium compounds after the RABA is exposed in the PFBC exhaust; therefore, this heat-treatment with a simulated PFBC exhaust becomes a necessary step to produce the RABA that contains no water-soluble sodium compounds.

3.2.5 Removal of Residual Sodium Compounds from NaCl-Deactivated RABA

In the RABSAM, alkali vapors in the PFBC exhaust are expected to be captured purely through physical adsorption, and the adsorbed alkalis are totally recovered by a simple water leaching. To prevent the contamination of the water leachate, the RABA used in the RABSAM should not contain water-soluble compounds. Previous studies (Sect. 3.2.4) showed that the residual non-chloride sodium in the RABA continues to be released as water-soluble compounds after it is treated in the PFBC environment, suggesting their complete removal necessary.

PFBC Preconditioning/Soxhlet-Extraction Cyclic Treatment. To study the effect of the PFBC exhaust preconditioning of the RABA on the sodium release, the Soxhlet-extracted samples prepared from Sect. 3.2.2 were subjected to six cycles of preconditioning with simulated PFBC exhaust and Soxhlet extraction with deionized water. The sample was heat-treated at 900°C for 4 h in the simulated PFBC exhaust, which contained 3% O₂, 14.2% CO₂, 550 ppmV SO₂, and 1.7% H₂O, with the remainder N₂. The sodium analysis of the extract from this cyclic treatment is given in Table 11. Earlier studies showed that the sodium in the extract exists essentially as non-chloride compounds (presumably as silicates); therefore, the extracted sodium represents the removal of the residual non-chloride sodium that has been formed by deactivation of clay impurities and left from previous acid leaching. Table 11 shows that, as observed earlier, the amount of sodium extracted decreases gradually with the cycle, indicating the gradual depletion of the extractable sodium in the RABA. In order to determine the extent of removal of the residual non-chloride sodium, each sample (after six cycles of the cyclic treatment) was finally analyzed for its sodium content. All four

Table 11. Sodium Analysis of the Soxhlet Extract from Cyclic Treatment of RABA

Sample No.	Heat-Treatment Temp., °C	Heat-Treatment Duration, h	Amount of Sodium Extracted in Each Cycle, mg Na/g AB						Sum, mg Na/g AB
			1	2	3	4	5	6	
1M/2H-780	780	2	0.67	0.18	0.19	0.10	0.04	0.03	1.21
1M/2H-820	820	2	0.72	0.23	0.20	0.09	0.06	0.04	1.34
1M/5H-780	780	5	0.86	0.22	0.08	0.04	0.05	0.03	1.28
1M/5H-820	820	5	0.87	0.26	0.07	0.03	0.04	0.03	1.30

samples had 0.07 mg Na/g AB as compared to the 0.03 mg Na/g AB for fresh AB. Based on the rate of sodium removal as shown in Table 11, the residual non-chloride sodium in RABA could probably be totally removed with a few more cycles of the cyclic treatment.

Based on the data presented above, sodium material balances were determined and are given in Table 12. The input sodium includes the original sodium content in fresh AB (0.03 mg Na/g AB) and the sodium added by the 1 M NaCl-solution impregnation. As mentioned previously, some NaCl loss is expected during heat-treatment; however, except for the 1M/5H-820 sample, this loss is believed to be small because the sample crucible was covered with a lid during heat-treatment. Despite this loss, Table 12 shows reasonably good sodium material balances.

Table 12. Material Balance of Sodium

Sample No.	Input Amount, ^a mg Na/g AB	Output Amount, mg Na/g AB			
		A ^b	B ^c	C ^d	Sum (A+B+C)
1M/2H-780	11.53	10.40	1.21	0.07	11.68
1M/2H-820	11.53	10.72	1.34	0.07	12.13
1M/5H-780	11.53	10.30	1.28	0.07	11.65
1M/5H-820	11.53	9.45	1.30	0.07	10.82

^aIncludes sodium content (0.03 mg Na/g AB) in fresh AB and the sodium added by 1 M NaCl-solution impregnation.

^bSodium removed by water leaching, acid leaching, and Soxhlet extraction.

^cSodium extracted from cyclic treatment, as shown in Table 11.

^dSodium content in after-treated RABA.

The results of these studies show that the residual non-chloride sodium compounds (such as silicates), products of the deactivation of clay impurities, may be totally removed by the cyclic treatment of preconditioning the sample with simulated PFBC exhaust followed by Soxhlet extraction with deionized water.

PFBC Preconditioning/Acid-Leaching Cyclic Treatment. The residual non-chloride sodium compounds are gradually removed by the cyclic treatment of preconditioning the sample with simulated PFBC exhaust, followed by Soxhlet extraction with deionized water. However, total removal of these residual non-chloride sodium compounds requires many tedious cyclic steps (may be up to 10 cycles). In order to see if the removal process can be speeded up by using acid leaching instead of Soxhlet extraction, a batch of RABA was prepared according to procedures shown in Fig. 3.

In this study, the acid-leached sample was divided into two equal fractions. Each fraction was then subjected to six cycles of preconditioning the sample with simulated PFBC exhaust, followed by the acid leaching with 2 N H₂SO₄ for four cycles (referred to as "PFBC preconditioning/acid-leaching cyclic treatment"). The PFBC preconditioning

Fig. 3.

Procedures of Generating RABA by NaCl-Solution Impregnation

^aConducted at 780°C.

^bConducted in a beaker at gentle boiling temperature for 2 minutes. Three consecutive leachings were carried out.

^cConducted in a beaker with 2 N H₂SO₄ gentle boiling temperature for ten minutes. Three consecutive leachings were carried out.

^dTreated for 4 h at either 900°C or 950°C in a simulated PFBC exhaust containing 3% O₂, 14.2% CO₂, 550 ppmV SO₂, 1.7% H₂O, and the remainder N₂.

^eExtracted with deionized water for 4 h.

temperature was 900°C for one fraction of the sample (Sample 2) and 950°C for another fraction of the sample (Sample 3). Both acid leachate and water extract were analyzed for sodium to evaluate the effectiveness of removing sodium compounds for each cyclic step. Results of the sodium analysis are given in Table 13. For comparison, Table 13 also includes results (presented in Table 11) obtained from six cycles of the PFBC preconditioning/Soxhlet-extraction cyclic treatment, in which a similar sample (Sample 1) was preconditioned with simulated PFBC exhaust at 900°C, followed by Soxhlet extraction with deionized water for all six cycles.

Results of Table 13 show that the removal of non-chloride sodium compounds from RABA is slightly improved over extraction by acid leaching. Increasing the PFBC preconditioning temperature further improved this removal process. However, these results still show that total removal of the sodium compounds from RABA requires more than six cycles of the PFBC preconditioning/acid-leaching cyclic treatment. Further improvements in the rate of sodium removal from RABA is needed.

3.3 LiCl-Solution Impregnation with Activated Bauxite

LiCl is chemically similar to but more reactive than NaCl. It was tested as a replacement for NaCl for the deactivation of clay impurities in fresh AB because it has advantages over NaCl. One advantage is that the amount of non-chloride sodium compounds, products of the deactivation of clay impurities, in RABA that need to be removed would be significantly reduced; therefore, their removal should be much easier. Also, the presence of lithium compounds in the RABA, whether they are water-soluble or water-insoluble, is not expected to affect the adsorption property of the RABA for sodium and potassium vapors.

Table 13. Sodium Analysis of the Acid Leachate and Soxhlet Extract from Cyclic Treatment of RABA

Sample No.	PFBC Preconditioning Temp., °C	Amount of Sodium Removal in Each Cycle, mg Na/g AB						Sum, mg Na/g AB
		1	2	3	4	5	6	
1 ^a	900	0.67	0.18	0.19	0.10	0.04	0.03	1.21
2 ^b	900	0.78	0.21	0.13	0.15	0.07	0.03	1.37
3 ^c	950	0.93	0.22	0.06	0.11	0.07	0.02	1.41

^aSample was subjected to the treatment of preconditioning the sample with simulated PFBC exhaust, followed by Soxhlet extraction with deionized water. Results were obtained from Table 11.

^bSample was subjected to the treatment of preconditioning the sample with simulated PFBC exhaust, followed by acid leaching with 2N H₂SO₄. For cycles 3 and 6, the preconditioned sample was subjected to Soxhlet extraction with deionized water.

3.3.1 Preliminary Study of LiCl Solution-Impregnation

A batch of the RABA was prepared with 1 M LiCl using the same procedures as the NaCl (shown in Fig. 3). The water leachate, acid leachate, and Soxhlet extract were analyzed by atomic absorption spectrometry (AA) for ion concentrations of Li, Na, K, and Cl.

Ion Extraction. Table 14 shows the amounts of ions extracted by each step of the treatment. As shown in Table 14, most of the lithium was removed from the RABA by the water and acid leachings. Residual lithium was further extracted when the water- and acid-leached RABA sample was subjected to a cyclic treatment of preconditioning the sample in a simulated PFBC exhaust, followed by Soxhlet extraction with deionized water (referred to as the PFBC conditioning/Soxhlet extraction treatment).

Table 14 shows that the water-leachable lithium is largely present as residual LiCl that was impregnated in AB as a deactivation agent for clay impurities in AB. In contrast, the lithium that was leached out by 2 N H₂SO₄ and the PFBC conditioning/Soxhlet extraction treatment is essentially from non-chloride compounds, such as silicates. As expected because of their similar chemical properties, all the observations described are very similar to those when NaCl was used as the deactivation agent.

Alkali Material Balance. Based on the data presented above, material balances for lithium, sodium, and potassium were made and are given in Table 15. When the LiCl solution-impregnated AB is heat-treated, some LiCl loss is expected due to vaporization; therefore, Table 15 shows a reasonably good material balance for lithium. For sodium and potassium material balances, the output amounts are noticed to be much greater than the input amounts, which may be due to contamination of the LiCl solution-impregnated AB during heat-treatment. The contamination was attributed to the use of the old ceramic crucible that had been used for the heat-treatment of NaCl solution-impregnated AB. It is highly possible that this old ceramic crucible contains some residual NaCl as a result of the heat-treatment of the NaCl solution-impregnated AB. The source of potassium may be due to the ion-exchange

Table 14. Ions Extracted from LiCl Solution-Impregnated AB by Water Leaching, Acid Leaching, and Soxhlet Extraction

Samples	Amount of Ion, $\mu\text{g/g-AB}$			Ion Conc., $\mu\text{mol/mL}$			
	Li ⁺	Na ⁺	K ⁺	Li ⁺	Na ⁺	K ⁺	Cl ⁻
I. Water Leaching							
1st Leachate	553	120	96	19.60	1.28	0.60	18.53
2nd Leachate	183	20	33	5.62	0.18	0.18	4.03
3rd Leachate	60	4	12	1.80	0.04	0.06	0.76
Sum	796	144	141				
II. Acid Leaching							
1st Leachate	417	114	55	6.28	0.52	0.15	<0.15
2nd Leachate	169	38	6	1.08	0.17	0.02	<0.15
Sum	586	152	61				
III. 1st PFBC Conditioning/ Soxhlet Extraction							
1st Extract	291	10	2	7.35	0.07	0.01	0.05
2nd Extract	40	1	0	0.85	0.01	0	0.01
IV. 2nd PFBC Conditioning/ Soxhlet Extraction							
1st Extract	153	6	1				
V. 3rd PFBC Conditioning/ Soxhlet Extraction							
1st Extract	147	7	1				
Sum	631	24	4				

Table 15. Material Balances for Lithium, Sodium, and Potassium in AB

Element	Input Amount ^a $\mu\text{g/g-AB}$	Output Amount, $\mu\text{g/g-AB}$				
		A ^b	B ^c	C ^d	D ^e	Sum (A+B+C+D)
Li	3470	796	586	631	1040	3053
Na	72	144	152	24	18	338
K	42	141	61	4	0	206

^a Li content in fresh AB was not analyzed and therefore is not included in this input amount. For Na and K, this input amount includes (1) 0.20% Na and 0.01 % K impurities in the LiCl used as a deactivation agent and (2) Na and K contents in fresh AB.

^b Ion amount recovered by water leaching (Table 14).

^c Ion amount recovered by acid leaching (Table 14).

^d Ion amount recovered by cycling PFBC conditioning/Soxhlet extraction treatment (Table 14).

^e Ion content in the final RABA.

reactions of LiCl vapor and the potassium silicate compounds contained in the ceramic crucible. These ion-exchange reactions would release potassium as KCl.

3.3.2 Ultrapure LiCl Solution-Impregnation

Results of the preliminary study presented in the preceding section suggest that LiCl is a better deactivation agent than NaCl for clay impurities in fresh AB. Further studies were conducted (1) to use ultrapure LiCl (+99.99% purity) to reduce the sodium and potassium inputs during LiCl-solution impregnation and (2) to use a Pt crucible for heat-treatment to eliminate sodium and potassium contamination of the RABA.

The ultrapure LiCl reagent used in this study contains only 2 ppm Na and 5 ppm K impurities. One batch of RABA was prepared by impregnating the fresh AB with 1 M LiCl solution and another batch with 2 M LiCl solution. Both batches of the LiCl-impregnated AB were placed in Pt crucibles and heat-treated in a muffle furnace at 700°C for 5 h.

Water-Leaching. The heat-treated sample was leached three times with deionized water at a gentle boil for two minutes. The three leachates were then analyzed by AA for both Na and K to determine the total amount of water-leachable alkalis. Table 16 summarizes the results. As expected, the total leachable amounts of Na and K are very small (<10 µg/g AB) because ultrapure LiCl is as the deactivation agent. For comparison, this leachable amount of Na was a thousand times greater when 1 M NaCl solution was the deactivation agent.

Table 16. Water Leaching of LiCl Solution-Impregnated AB

Sample No.	Amount of Ion Leached, µg/g-AB							
	1st Leachate		2nd Leachate		3rd Leachate		Sum	
	Na	K	Na	K	Na	K	Na	K
1 <u>M</u> /Li ^a	0.9	4.4	0.2	1.1	0.1	0.4	1.2	5.9
2 <u>M</u> /Li ^b	0.2	3.2	0.1	0.6	0.1	0.2	0.4	4.0

^aSample impregnated with 1 M LiCl solution.

^bSample impregnated with 2 M LiCl solution.

When 1 M LiCl is used, the input amounts of Na and K present in the LiCl solution as impurities are calculated to be 0.05 µg Na⁺/g AB and 0.13 µg K⁺/g AB. For 2 M LiCl, this input amount is double. Table 16 shows that the total leachable amounts are much greater than these impurity levels. Apparently, some of the inherent alkalis present in fresh AB, namely, 30 µg Na⁺/g AB and 40 µg K⁺/g AB, were also leached out.

After water-leaching, each sample was dried, mixed well, and divided in half. One half was subjected to Soxhlet extraction with deionized water; the other was acid leached.

Soxhlet Extraction and Acid Leaching. One half each water-leached sample underwent two consecutive 4-h Soxhlet extractions with deionized water. The extracts were then analyzed for Na and K by AA. The results of this analysis are given in Table 17. Soxhlet extraction serves as a refining step to remove residual water-soluble sodium and potassium from RABA. As shown in Table 17, the second extract contains only negligible amounts of Na and K, indicating the complete removal of the water-soluble Na and K by this Soxhlet extraction step. One interesting observation shown in Table 17 is that more sodium was extracted than potassium by this Soxhlet extraction step. In contrast, more potassium than sodium was leached out by water leaching (Table 16). These results suggest that water-soluble potassium is present in one or more chemical forms that are more water soluble than water-soluble sodium compound(s) in RABA; therefore, potassium is more readily soluble in boiling water in a 2-min water-leaching step than in a 4-h Soxhlet extraction. In 100°C water, NaCl and KCl have solubilities of 391 and 567 mg/mL, respectively. Besides that, the level of potassium impurities is higher than that of sodium in the RABA. Therefore, it is reasonable to conclude that both water-soluble sodium and potassium impurities in RABA are present as chlorides.

Table 17. Removal of Na and K from Water-Leached RABA

Sample No.	Amount of Ion Extracted, $\mu\text{g/g-AB}$					
	1st Extract		2nd Extract		Sum	
	Na	K	Na	K	Na	K
Soxhlet Extraction:						
1M/LI-2 ^a	5.0	0.1	1.0	0.1	6.0	0.2
2M/LI-2 ^b	3.0	0.2	1.0	0.1	4.0	0.3
Acid Leaching:						
1M/LI-2 ^a	23.2	18.4	3.9	2.8	27.1	21.2
2M/LI-2 ^b	23.6	25.3	2.8	2.1	26.4	27.4

^aSample impregnated with 1 M LiCl solution.

^bSample impregnated with 2 M LiCl solution.

Based on the amounts of leached and extracted sodium and potassium, we can easily see that the sodium and potassium impurities in LiCl reagent used (2 ppm Na or 0.05 $\mu\text{g Na}^+/\text{g AB}$, and 5 ppm K, or 0.13 $\mu\text{g K}^+/\text{g AB}$) are not the only source of these chlorides. We believe that when the LiCl-impregnated AB is heated, LiCl vapor reacts with sodium and potassium silicates in fresh AB to form sodium and potassium chlorides. This type of ion exchange reaction has been reported.¹⁷⁻¹⁹

The other set of each of the water-leached samples was acid leached twice with 2 N H_2SO_4 in a beaker at a gentle boil for 10 min. The results of the AA analysis of the leachate are also given in Table 17. Significantly more sodium and potassium were leached out by acid than by water. (See Table 16.) As reported earlier, acid is effective in leaching

alkalis from silicates; therefore, these acid-leaching results indicate that the residual sodium and potassium impurities left in the water-leached RABA are mostly present as silicates.

PFBC Preconditioning/Soxhlet Extraction. To study the stability of the residual alkali compounds left in the RABA, the samples that had been Soxhlet-extracted or acid-leached were further heat-treated in a simulated PFBC exhaust environment containing 3.0% O₂, 14.2% CO₂, 1.7% H₂O, 550 ppmV SO₂, with the remainder N₂. The samples were heat-treated at 900°C. After the PFBC preconditioning, they were subjected to two consecutive Soxhlet extractions with deionized water for 4 h and the amount of sodium and potassium extracted was determined by AA. Table 18 summarizes the results. Only very small amounts of sodium and negligible amounts of potassium were leached. Table 18 also shows that the amounts of sodium and potassium released are essentially independent of whether the sample was acid leached or Soxhlet extracted.

Table 18. Soxhlet Extraction of PFBC Preconditioned RABA

Sample No.	Amount of Ion Extracted, $\mu\text{g/g-AB}$					
	1st Extract		2nd Extract		Sum	
	Na	K	Na	K	Na	K
1M/LI-1 ^a	3.2	0.4	1.6	0.1	4.8	0.5
1M/LI-1 ^b	4.7	0.6	1.4	0.2	6.1	0.8
2M/LI-1 ^c	3.8	0.3	1.7	0.2	5.5	0.5
2M/LI-1 ^d	3.8	0.9	1.6	0.4	5.4	1.3

^a Sample impregnated with 1 M LiCl solution and then acid-leached with 2 N H₂SO₄. (See Table 17.)

^b Sample impregnated with 1 M LiCl solution and then Soxhlet-extracted with deionized water. (See Table 17.)

^c Sample impregnated with 2 M LiCl solution and then acid-leached with 2 N H₂SO₄. (See Table 17.)

^d Sample impregnated with 2 M LiCl solution and then Soxhlet-extracted with deionized water. (See Table 17.)

Alkali Material Balance. Based on the data presented in all previous sections, material balances for sodium and potassium can be made and are shown in Table 19. For the samples that had been subjected to water leaching, acid leaching, and PFBC preconditioning/Soxhlet extraction steps, Table 19 shows that 100% of the sodium and about 70% of the potassium were removed. Because of the negligible amount of potassium being leached out in the PFBC preconditioning/Soxhlet extraction step, the residual 30% potassium in RABA is expected to be stable for subsequent application in the actual PFBC environment. For the samples that had been subjected to water leaching, Soxhlet extraction, and PFBC preconditioning/Soxhlet extraction steps, only 33-44% Na and 14-17% K were removed from RABA. However, the residual sodium and potassium also appear to be quite stable.

Table 19. Material Balances for Sodium and Potassium in RABA

Sample No.	Output Amount, µg/g-AB											
	Input Amount ^a µg/g-AB		Water Leaching		Soxhlet Extraction		Acid Leaching		PFBC/Soxhlet Extraction		Sum	
	Na	K	Na	K	Na	K	Na	K	Na	K	Na	K
1M/LI-1	30.1	40.1	1.2	5.9	Na ^b	Na	27.1	21.2	4.8	0.5	33.1	27.6
1M/LI-2	30.1	40.1	1.2	5.9	6.0	0.2	NA	NA	6.1	0.8	13.3	6.9
2M/LI-1	30.1	40.3	0.4	4.0	NA	NA	26.4	27.4	5.5	0.5	32.3	31.9
2M/LI-2	30.1	40.3	0.4	4.0	4.0	0.3	NA	NA	5.4	1.3	9.8	5.6

^aInput amount includes (1) alkalis present in fresh AB, which are 30 µg Na/g AB and 40 µg K/g AB and (2) alkali impurities in LiCl reagent used, which are 0.05 µg Na/g AB and 0.13 µg K/g AB for 1 M LiCl-impregnated sample and 0.10 µg Na/g AB and 0.26 µg K/g AB for 2 M LiCl-impregnated sample.

^bNA - Not applicable.

Results of this study indicate that RABA can be produced by using ultrapure LiCl (+99.99% purity) for impregnating the commercial grade AB, followed by heat treatment, water leaching, acid leaching, and PFBC preconditioning/Soxhlet extraction steps. The resulting RABA contains no sodium and only trace potassium impurities that appear to be stable in the simulated PFBC environment.

3.3.3 6 M LiCl Solution-Impregnation Technique

Results of the study so far obtained indicate that RABA can be produced by using 1 M ultrapure (+99.99% purity) LiCl-solution impregnation of the commercial grade AB, followed by heat treatment, water leaching, acid leaching, and PFBC preconditioning/Soxhlet extraction steps. The resulting RABA contains no sodium and only trace potassium impurities that appear to be stable in the simulated PFBC environment. However, it was unclear if all clay minerals in AB had been completely deactivated. To answer this question, the amount of LiCl needed to completely deactivate the clay minerals in fresh AB was estimated, and experimental studies were conducted to see if it is achievable.

Estimate of LiCl for Complete Deactivation. Fresh AB contains about 82% Al₂O₃, 10% SiO₂, and other impurities. The SiO₂ can also exist as aluminosilicates (Al₂O₃·X SiO₂) in many chemical forms, such as Kaolin clay (Al₂O₃·2SiO₂). Both SiO₂ and aluminosilicates can be deactivated with LiCl vapor as shown by the following:

The maximum amount of LiCl needed for the complete deactivation of SiO_2 can be estimated by assuming that $x = 1$. Based on this assumption, we calculated that the maximum Li content in the completely deactivated AB should be 2.30 wt%. To achieve this percentage requires using a 6 M LiCl solution and impregnating the AB at the ratio of 3 mL of LiCl solution to 5 g of AB. By doing so, the resulting LiCl-impregnated AB would have 2.49 wt%, which has about 8% more than 2.30% needed for achieving the complete deactivation of SiO_2 and would be enough to account for the possible loss of LiCl during preparation and the subsequent heat-treatment of the LiCl-impregnated AB.

6 M LiCl Solution-Impregnation. We prepared several batches of RABA by impregnating 6 M LiCl to both raw (fresh) AB and the pre-heat-treated (at 900°C for 5 h) AB. The LiCl-impregnated AB was heat-treated at 700°C as a function of heat-treating duration to generate the RABA. At 700°C , LiCl melts and generates LiCl vapor to deactivate the clay minerals. After the heat-treatment, the RABA was subjected to Soxhlet extraction with deionized water for 72 h to remove any remaining LiCl. Finally, the Soxhlet-extracted RABA was analyzed for its Li content. This Li content would represent the amount of LiCl that reacted with the SiO_2 and clay minerals and reflect the extent of deactivation of the SiO_2 and clay minerals. Table 20 summarizes the results of lithium analysis in the water extract and the extracted RABA. The results are further plotted in Fig. 4.

If 6 M LiCl is used, the LiCl-impregnated AB would contain 25.0 mg Li^+/g AB. As shown in the last column of Table 20, the sum of the lithium recovered from the Soxhlet extraction and the lithium retained in the extracted RABA is less than the input lithium amount of 25.0 mg Li^+/g AB. This difference is expected because of the unavoidable loss of lithium chloride during the preparation of the LiCl-impregnated AB and the loss of RABA fines generated during the handling and Soxhlet extraction. This sum also decreases with heat-treatment duration, indicating the expected loss of LiCl vapor during the heat-treatment of the LiCl-impregnated AB.

Table 20 and Fig. 4 clearly show that the amount of water-extracted lithium decreases with the heat-treatment duration. At the same time, the lithium content in the extracted RABA increases with the heat-treatment duration, strongly indicating that an increasing amount of LiCl reacts with clay minerals in AB. Thus, the extent of deactivation of the clay minerals by LiCl vapor during heat-treatment increases. For the pre-heat-treated AB used, the extent to which clay minerals are deactivated increases almost linearly up to 25 h and appears to reach the maximum lithium content of 15.6 mg Li^+/g RABA at 100 h. Table 20 and Fig. 4 also clearly show that the extent of deactivation occurs at a much faster rate for the raw AB than the pre-heat-treated AB. Within limits of experimental and analytical errors, the lithium content of the RABA prepared from raw AB reaches the maximum of about 19 mg Li^+/g RABA after 50 h. Extending the heat-treatment to 100 h did not increase the lithium content of the RABA, indicating that the SiO_2 and clay minerals in the raw AB had been completely deactivated by LiCl vapor after 50 h.

Table 20. Lithium Distribution in Water Extract and Extracted RABA as a Function of Heat-Treatment Duration

Sample No.	Type of AB Used	Heat-Treatment Duration, h	Li Content in Water Extract, ^a mg Li ⁺ /g RABA	Li Content in Extracted RABA, ^b mg Li ⁺ /g RABA	Sum, mg Li ⁺ /g RABA
6M/LI-5H	Pre-HT ^c	5	13.9 ± 0.7	8.1 ± 0.4	22.0 ± 1.1
-15H(1)	Pre-HT	15	11.8 ± 0.6	9.5 ± 0.5	21.3 ± 1.1
-15H(2)	Pre-HT	15	12.4 ± 0.6	9.8 ± 0.5	22.2 ± 1.1
-25H	Pre-HT	25	8.8 ± 0.4	11.2 ± 0.6	19.9 ± 1.0
-50H	Pre-HT	50	5.8 ± 0.3	13.9 ± 0.7	19.7 ± 1.0
-100H	Pre-HT	100	2.9 ± 0.2	15.6 ± 0.8	18.6 ± 0.9
6M/LI-5H(R)	Raw ^d	5	N.D. ^e	10.2 ± 0.5	
-15H	Raw	15	5.0 ± 0.3	16.9 ± 0.9	21.9 ± 1.2
-25H(1)(R)	Raw	25	4.8 ± 0.2	17.3 ± 0.9	22.1 ± 1.1
-25H(2)(R)	Raw	25	4.5 ± 0.2	16.5 ± 0.8	21.00 ± 1.0
-50H(1)(R)	Raw	50	3.5 ± 0.2	18.7 ± 0.9	22.2 ± 1.1
-50H(2)(R)	Raw	50	3.2 ± 0.2	19.0 ± 1.0	22.2 ± 1.2
-100H(R)	Raw	100	2.9 ± 0.2	18.8 ± 0.9	21.7 ± 1.1

^aSoxhlet extracted with deionized water for 72 h.

^bThe extracted RABA was fused with NH₄HF₂ and then dissolved in an acidified (HCl) solution.

^cRaw AB material was thoroughly washed with deionized water to remove fines, dried in an oven and finally heat-treated in a muffle furnace at 900°C for 5 h.

^dRaw AB material was thoroughly washed with deionized water to remove fines and then dried in an oven.

^eN.D. - Not determined due to loss of solution during handling.

To optimize the amount of LiCl needed to completely deactivate the SiO₂ and clay minerals in the raw AB, a batch of RABA was prepared by impregnating the raw AB with 5 M LiCl at the same ratio used in the previous 6 M LiCl tests, i.e., 3 mL per 5 g of AB. This batch contained 20.8 mg Li⁺/g AB, slightly more than the 19 mg Li⁺/g RABA needed to completely deactivate the SiO₂ and clay minerals in the raw AB.

The 5 M LiCl-impregnated AB was then heat-treated at 700°C for 50 h. Like 6 M LiCl-impregnated RABA, the sample was Soxhlet-extracted with deionized water to remove residual LiCl, and the extracted sample was finally analyzed to contain 16.3 mg Li⁺/g RABA. This value is significantly lower than the maximum lithium content of 19 mg Li⁺/g RABA needed to completely deactivate the SiO₂ and clay minerals in the raw AB.

Apparently, some losses of LiCl occurred during the impregnation and heat-treatment (LiCl vaporization) steps and caused the shortage of LiCl needed for complete deactivation. Results of these studies can be summarized as follows:

1. The deactivation of SiO_2 and clay minerals in AB with LiCl vapors occurs at a much faster rate for the raw AB than the pre-heat-treated (at 900°C for 5 h) AB.
2. A minimum of 6 M LiCl solution is needed to impregnate the raw AB to completely deactivate SiO_2 and minerals in the raw AB.
3. The complete deactivation of SiO_2 and clay minerals in the raw AB is achieved by impregnating the raw AB with 6 M LiCl at the impregnation ratio of 3 mL solution per 5 g AB, followed by the heat-treatment at 700°C for >50 h.

Fig. 4.

Distribution of Lithium in RABA as a Function of Heat-Treatment Duration after Treatment with LiCl

3.3.4 Removal of Residual Alkalis from 6 M LiCl-Deactivated RABA

In the RABSAM, alkali vapors in PFBC exhaust are expected to be captured purely through physical adsorption, and the adsorbed alkalis are totally recovered by a simple water leaching. To prevent the water leachate from being contaminated for alkali analysis, the residual water-soluble alkali (Na and K) compounds in the RABA must be completely removed. Our earlier studies (Sect. 2.3.2) indicated that most of the residual alkalis in the LiCl-treated AB sample can be removed by a series of water-leaching, acid-leaching, and Soxhlet extraction; however, to produce a thermally stable RABA, the cyclic treatment of the

sample with high-temperature (900°C) conditioning, followed by the subsequent Soxhlet extraction with deionized water (referred to as cyclic high-temperature conditioning/Soxhlet extraction) is needed to further remove the last portion of the residual water-soluble alkalis in the sample.

More experimental work has been conducted to study the extent of the cyclic treatment of high-temperature conditioning/Soxhlet extraction needed to completely remove the residual water-soluble sodium and potassium in the 6 M LiCl-deactivated RABA. In this study, a batch of 6 M LiCl-treated AB sample was subjected to a series of water leaching, acid leaching, Soxhlet extraction, and the cyclic treatment of the high-temperature conditioning/Soxhlet extraction, as shown in Fig. 5. The leachates and extracts were analyzed by AA for both sodium and potassium to evaluate the effectiveness of each treatment step for the removal of residual alkalis in the sample. Table 21 summarizes the results of these analyses.

Fig. 5.

Procedures for Generating RABA by 6 M LiCl-Impregnation Technique

- ^a Conducted at 700°C for 50 h.
- ^b Conducted in a beaker at gentle boil for two minutes. Three leachings were made.
- ^c Conducted in a beaker at gentle boil for ten minutes. Three leachings were made.
- ^d Extracted with deionized water for 48 h.
- ^e Heated in a muffle furnace at 900°C for 12 h.
- ^f Extracted with deionized water for 4 h.
- ^g Five cycles.

As expected, the total water-leachable amounts of Na and K are small because of the ultrapure LiCl used as the deactivation reagent. For comparison, this water-leachable amount of Na was several thousand times greater when 1 M NaCl solution was used as the deactivation reagent (Table 6). Table 21 shows that significantly more Na and K were leached out by acid than water. Acid solution is effective in leaching alkalis from silicates; therefore, the residual Na and K impurities left in the water-leached RABA are mostly present as silicates.

Soxhlet extraction with deionized water serves as a refining step to further remove the water-soluble alkalis from RABA. Like earlier observations (Table 17), Table 21 shows that more sodium was extracted than potassium by this Soxhlet extraction step. In

Table 21. Analyses of Sodium and Potassium in Leachates and Extracts of 6 M LiCl-Impregnated Activated Bauxite

Samples	Amount of Ion, $\mu\text{g/g-AB}$	
	Na	K
I. Water Leaching	1.0 ± 0.4	17.6 ± 0.8
II. Acid Leaching		
1st Leaching	31.2 ± 0.8	36.4 ± 2.0
2nd Leaching	6.2 ± 0.1	5.2 ± 0.1
3rd Leaching	2.2 ± 0.1	1.5 ± 0.1
III. Soxhlet Extraction	11.0 ± 0.2	4.3 ± 0.2
IV. High-Temperature Conditioning/ Soxhlet Extraction		
1st Cycle	3.7 ± 0.1	0.4 ± 0.1
2nd Cycle	2.1 ± 0.2	$<0.2 \pm 0.2$
3rd Cycle	1.1 ± 0.1	0.1 ± 0.1
4th Cycle	0.8 ± 0.1	<0.1
5th Cycle	0.8 ± 0.1	<0.1

contrast, more potassium than sodium was leached out by water. A possible explanation was given in Sect. 3.3.2.

Based on the amounts of leached and extracted sodium and potassium, we can easily see that the sodium and potassium impurities in the LiCl reagent used, 2 ppm Na or $0.3 \mu\text{g Na}^+/\text{g AB}$ and 5 ppm K or $0.8 \mu\text{g K}^+/\text{g AB}$, are not the only source of these chlorides. We believe that during heat treatment, LiCl vapor reacts with sodium and potassium silicates in raw AB to form sodium and potassium chlorides. This type of ion-exchange reaction has been reported.¹⁷⁻¹⁹

As shown in Fig. 5, the Soxhlet-extracted sample was finally subjected to the cyclic high-temperature conditioning/Soxhlet extraction treatment. In the high-temperature conditioning, the sample was heat-treated in a muffle furnace at 900°C for 12 h. After that, the sample was Soxhlet-extracted with deionized water for 4 h. Table 21 shows that after the third cycle, the water-extractable amounts of sodium and potassium are <1.0 and $<0.1 \mu\text{g/g-AB}$, respectively, which, compared with the maximum adsorption capacity of 370 mg Na/g AB , are negligible. These results indicate that complete removal of the residual water-soluble sodium and potassium in the RABA is achievable by a series of water leaching, acid leaching, Soxhlet extraction, and the cyclic high-temperature conditioning/Soxhlet extraction treatment.

3.3.5 Effect of High-Temperature Conditioning on Removal of Alkalis

The cyclic treatment is a critical step to produce a thermally and chemically stable RABA by stabilizing the RABA structure with high-temperature conditioning at the

PFBC exhaust temperature (900°C) and by removing trace residual water-soluble alkalis in RABA with Soxhlet extraction. To optimize this cyclic treatment step, the effect of the high-temperature conditioning duration on the rate of removal of residual water-soluble alkalis was studied. A batch of RABA that had been subjected to a series of water leaching, acid leaching, and Soxhlet extraction to remove most of the water-soluble alkalis was divided into two equal portions. One half was conditioned at 900°C for 24 h and another half for 6 h. The conditioned samples were then Soxhlet-extracted with deionized water for 4 h. The extract was finally analyzed by AA to evaluate the removal rate of both sodium and potassium. Table 22 shows the results of these studies. For comparison, similar results obtained from earlier studies (Table 21) were also included in the table.

Table 22. Analyses of Sodium and Potassium in Soxhlet Extracts

Samples	Amount of Ion, $\mu\text{g/g-RABA}$					
	Na			K		
	24h	12h ^a	6h	24h	12h ^a	6h
1st Cycle Extract	9.1 ± 0.2	3.7 ± 0.1	2.8 ± 0.2	1.3 ± 0.2	0.4 ± 0.1	1.3 ± 0.2
2nd Cycle Extract	2.0 ± 0.2	2.1 ± 0.2	0.9 ± 0.1	$<0.2 \pm 0.2$	$<0.2 \pm 0.2$	$<0.2 \pm 0.2$
3rd Cycle Extract	1.5 ± 0.1	1.1 ± 0.1	1.2 ± 0.1	N.A. ^b	0.1 ± 0.1	N.A.
4th Cycle Extract	0.8 ± 0.1^c	0.8 ± 0.1	1.4 ± 0.1^c	N.A.	<0.1	N.A.
5th Cycle Extract	0.8 ± 0.1^c	0.8 ± 0.1	0.9 ± 0.1^c	N.A.	<0.1	N.A.

^aResults obtained from different batch of RABA (than those of 24 h and 6 h). These results were reported in Table 21.

^bN.A. - Not analyzed.

^cSample was conditioned at 900°C for 48 h.

As observed earlier, the complete removal of water-soluble potassium can be easily achieved by one cycle of the high-temperature conditioning/Soxhlet extraction step. However, the removal of water-soluble sodium from the RABA requires at least 3 cycles of the >12-h high-temperature conditioning step to achieve $<1.0 \mu\text{g Na}^+/\text{g RABA}$ in the extract.

3.4 High-Temperature High-Pressure Testing of RABA

The RABA is expected to capture alkali vapors purely through physical adsorption and be regenerated by releasing the adsorbed alkali vapors in water solution by simple water leaching or water extraction. To evaluate these characteristics, a batch of RABA prepared by the 6 M LiCl-impregnation technique was tested for its NaCl-vapor sorption in a pressurized alkali-vapor sorption test unit under a simulated PFBC environment.

3.4.1 Pressurized Alkali-Vapor Sorption Test Unit

Figure 6 shows the schematic of the pressurized alkali-vapor sorption test unit. Sectioned RABA beds (each 2.54-cm long and separated by Pt gauges) are packed inside a

Fig. 6. Pressurized Alkali-Vapor Sorption Test Unit

1.6-cm-ID high-purity (99.8%) Al_2O_3 tube. A section of NaCl bed is packed in a separate tube and situated on the top of the RABA beds. Both the NaCl-bed and the RABA-bed tubes are contained inside a 2.54-cm (1-in.) ID high-purity Al_2O_3 tube that serves as a pressure shell. A three-zone tubular furnace is used to control the bed temperature of the NaCl and RABA beds. A controlled amount of the simulated PFBC exhaust containing O_2 , CO_2 , H_2O , SO_2 , and N_2 , is preheated and flows into the sorption tube. The NaCl bed is controlled at a specific temperature to generate a controlled amount of NaCl vapor. The vapor is carried by the simulated PFBC exhaust downward through the RABA beds. Three water bubblers are installed in the downstream of the RABA beds to capture any NaCl vapor that breaks through the RABA beds. The system pressure is controlled by a back-pressure regulator and monitored by a pressure gauge. Before being vented, a small fraction of the exhaust is diverted to a series of gas analyzers for the verification of the controlled gas composition of the simulated PFBC exhaust.

3.4.2 Preparation of RABA by 6 M LiCl-Impregnation Technique

A batch of RABA was prepared from fresh AB according to the 6 M LiCl-impregnation technique (Fig. 5). To examine the change, if any, of the pore structure of the

RABA as compared to fresh AB, a representative sample of the RABA was sent for pore structure analysis by mercury porosimetry. Table 23 summarizes the results of this analysis, along with results of fresh AB for comparison.

Table 23. Porosity and Surface Area Measurement for Fresh AB and RABA

	Fresh AB ^a	RABA ^b
Porosity Measurement		
Total Porosity, %	56.61	50.56
Avg. Pore Diameter, μm	0.0362	0.0499
Median Pore Diameter (Volume Basis), μm	0.0759	0.0833
Median Pore Diameter (Area Basis), μm	0.0154	0.0368
Total Pore Area, m^2/g	48.40	31.87
Surface Area Measurement		
N_2 BET Specific Surface Area, m^2/g	41.01	23.57

^aFresh AB (1.41-1.68 mm or -10 +12 mesh) was thoroughly washed with deionized water to remove fines and then heat-treated in a muffle furnace at 900°C for 5 h.

^bPrepared from the same batch of fresh AB by a 6 M LiCl-impregnation technique (Fig. 5).

As shown in Table 23, the treatment of AB with 6 M LiCl at 700°C, followed by the subsequent water-leaching, acid-leaching, and five cycles of PFBC preconditioning/ Soxhlet extraction to completely remove the water-soluble alkali compounds in RABA, results in some loss of total porosity. Since the average pore diameter and the median pore diameter were both increased in the RABA, the treatment apparently opened up the inherently small pores present in the untreated AB. As a result of the pore enlargement, the pore area of the RABA shows about 35% decrease as compared to that of the fresh AB.

The alkali-vapor sorption capacity of RABA is related to the surface area; therefore, the decrease in pore area of the RABA would mean the decrease in the alkali-vapor sorption capacity of the RABA. This decrease, in turn, indicates that a longer bed may be needed for the RABA to achieve the same alkali-vapor sorption performance as the fresh AB.

3.4.3 Preconditioning Test of RABA

The batch of RABA was subjected to preconditioning at 895-900°C and 10 atm absolute for 3.5 h with the simulated PFBC exhaust containing no NaCl vapor. The purpose of this preconditioning test was to stabilize the chemical and physical properties of the RABA

in the PFBC environment. After the preconditioning test, a portion of the preconditioned RABA (about 20 g) was Soxhlet-extracted with deionized water for 4 h, and the extract was analyzed for Na^+ , Li^+ , Al^{3+} , Si^{4+} , Cl^- , and SO_4^{2-} . The remaining portion of the preconditioned RABA (about 25 g) was used for the subsequent NaCl-vapor sorption test.

Table 24 shows results of the chemical analysis for the Soxhlet extraction obtained from the preconditioned RABA. For comparison, similar results for the fresh AB are included in the table. In addition to the change in the pore structure of the RABA as a result of LiCl treatment on AB (as described in Sect. 3.4.2), the LiCl treatment also appears to cause a significant increase in the water solubility of the aluminum ion of the RABA, which is the major component of AB (81.5% Al_2O_3). The LiCl treatment was conducted to deactivate the clay impurities (such as silicates and aluminum silicates) in AB. Apparently, LiCl also chemically reacts with Al_2O_3 to form water-soluble aluminum compounds. One possible chemical reaction is the formation of water-soluble lithium meta-aluminate as follows:

The lithium ion concentration in the Soxhlet extract of the RABA has the same order of magnitude on a mole basis as the aluminum ion, which supports the above reaction.

Table 24. Chemical Analysis of Water Leachate from Fresh AB and Water Extract from RABA

Sample No.	Ion Concentration, $\mu\text{mol/g-AB}$ (or RABA)					
	Na^+	Li^+	Cl^-	SO_3^{2-}	Al^{3+}	Si^{4+}
AB/ SO_2^a	0.6	N.A. ^c	0.1	4.0	1.2	14.6
RABA/ SO_2^b	0.8	19.0	0.2	0.8	17.2	9.3

^aFresh AB was heat-treated in a simulated PFBC exhaust (containing 3% O_2 , 16.1% CO_2 , 4.5% H_2O vapor, ~400 ppmV SO_2 , and the remainder N_2) at 800°C and 10 atm absolute for 8 h. The tested AB was leached with deionized water in a beaker at 90°C for 1 h. Data was obtained from Table 3 of Reference 20.

^bRegenerable activated bauxite adsorbent (RABA), which was prepared by a 6 M LiCl-impregnation technique, was heat-treated in a simulated PFBC exhaust (containing 3% O_2 , 16% CO_2 , 6% H_2O vapor, and ~1000 ppmV SO_2 , with the remainder N_2 at 895-900°C and 10 atm absolute for 3.5 h. The tested RABA was Soxhlet-extracted with deionized water for 4 h.

When the fresh AB was preconditioned in the simulated PFBC exhaust containing ~400 ppmV SO_2 , a fair amount of SO_2 was adsorbed by AB and was released as SO_4^{2-} in the leachate, as shown in Table 24. Al_2O_3 , which is the major composition of the AB, has been demonstrated to readily adsorb SO_2 in the presence of O_2 and to oxidize the SO_2 to SO_3 .²¹ The SO_3 adsorbed on the Al_2O_3 does not desorb at temperatures lower than 800°C.²² The RABA has been shown to have less adsorptive capacity for SO_2 than the fresh

AB, even though the RABA was preconditioned in the simulated PFBC exhaust that contained much higher SO_2 (~1000 ppmV) than that used in the preconditioning of fresh AB.

Table 24 also shows the decreased silicon ion concentration in the Soxhlet extract of the RABA. This decrease is expected because of the combined results of the fixation of clay impurities by LiCl and the removal of silicates by water- and acid-leaching and Soxhlet extraction conducted during the generation of the RABA by the 6 M LiCl-impregnation technique.

3.4.4 NaCl-Vapor Sorption Test of RABA

A portion of the preconditioned RABA (about 25 g) was tested for NaCl-vapor sorption under the experimental procedures shown in Fig. 7. A 12.7-cm-long (5-in.-long) RABA bed was tested with a bed temperature of 895-900°C, a system pressure of 10 atm absolute, and a superficial gas velocity of 30.5 cm/s (1 ft/s) passing through the bed at the test temperature and pressure. The simulated PFBC exhaust contained 3% O_2 , 16% CO_2 , 6% H_2O vapor, 1000 ppmV SO_2 , and 5~9 ppmW NaCl vapor, with the remainder N_2 . The post-test RABA was subjected to Soxhlet extraction with deionized water. The extract was analyzed for ion concentrations of Na^+ , Li^+ , Al^{3+} , Si^{4+} , Cl^- , and SO_4^{2-} . Three consecutive extractions of 4, 4, and 12 h duration, respectively, were conducted to extract as much water-soluble sodium from the RABA as possible. A small portion of the extracted RABA (about 3 grams) was weighed, pulverized, and totally dissolved in acidic solution using a NH_4HF_2 fusion technique. The solution was then analyzed by AA for sodium. The remaining extracted RABA was recycled for the second cycle's high-temperature/high-pressure (HT/HP) test, as shown in Fig. 7.

Two cycles of the HT/HP NaCl-vapor testing were completed for the batch of the preconditioned RABA. The test lasted 10 h. The first test was coded RABA-10H(1)/ SO_2 and the second test was RABA-10H(2)/ SO_2 .

NaCl-Vapor Capture. Table 25 summarizes the distribution of NaCl-vapor capture for both tests. NaCl-vapor capture efficiency of 94.5% was achieved by the 12.7-cm-long (5-in.-long) RABA bed for the first cycle test; this efficiency increased to 96.7% for the 11.4-cm-long (4.5-in.-long) RABA bed for the second. Under the similar test conditions, the fresh AB achieved >99% NaCl-vapor capture efficiency.²³ The lower capture efficiency for the RABA is not surprising because the RABA has a smaller surface area than the fresh AB (as shown in Table 23) and has less chemically active clay minerals that are known to effectively capture NaCl vapor by chemical fixation. However, the capture efficiency by RABA can be improved by increasing the length of the RABA sorption bed.

Table 25 shows that for the first cycle test, only 52.1% of the total NaCl vapor captured by the RABA was extractable by three consecutive Soxhlet extractions with deionized water, clearly indicating that a significant amount of NaCl vapor captured by the RABA is still not readily extractable by water. This finding suggests that clay minerals in AB were not totally deactivated by a 6 M LiCl-impregnation technique, namely, the RABA

Fig. 7.

Experimental Procedures for the High-Temperature/High-Pressure Testing of RABA

^aConducted with a bed temperature of 895-900°C, a system pressure of 10 atm absolute, and a superficial gas velocity of 30.5 cm/s (1 ft/s) at the test conditions. The simulated PFBC exhaust contained 3% O₂, 16% CO₂, 6% H₂O, 1000 ppmV SO₂, 5-9 ppmW NaCl vapor, with the remainder N₂. The test duration was 10 h.

^bExtracted with deionized water for three consecutive extractions for 4, 4, and 12 h, respectively.

^cAnalyzed ion concentrations for Na⁺, Li⁺, Al³⁺, Si⁴⁺, Cl⁻, and SO₄²⁻.

Table 25. Distribution of NaCl-Vapor Capture for the Test of RABA

Test No.	RABA-10H(1)/SO ₂	RABA-10H(2)/SO ₂
I. Amount of Sodium Captured by the RABA Bed		
Water-Extractable Fraction, µg		
First Extraction (4 h)	4,450 ± 130	15,100 ± 300
Second Extraction (4 h)	1,480 ± 20	1,800 ± 30
Third Extraction (12 h)	1,570 ± 40	3,070 ± 80
	7,500 ± 190	19,970 ± 410
Water-Unextractable Fraction, ^a µg	6,900 ± 1,700	6,820 ± 3,250
II. Amount of Sodium Breaking Through the RABA Bed,^b µg	840 ± 40	910 ± 40
III. Sum [I + II], µg	15,240 ± 1,930	27,700 ± 3,700
IV. Avg. NaCl-Vapor Conc. in the Simulated PFBC Exhaust,^c ppmW	5.2 ± 0.7	9.4 ± 1.3
V. NaCl-Vapor Capture Efficiency,^d %	94.5	96.7

^aThe water-extracted RABA was fused with NH₄HF₂ and dissolved in acidic solution for sodium analysis by AA.

^bSodium captured by the downstream gas transport line and three water bubbles.

^cObtaining by dividing the total NaCl captured (III x 58.45/23) by the amount of PFBC exhaust passing through the RABA bed.

^dObtained by (I/III) x 100%.

may still contain some residual clay minerals. These clay minerals were shown to be further deactivated by NaCl vapor in the first cycle test, resulting in a significant increase in the amount of water-extractable sodium to 74.5% of the total NaCl vapor captured by the RABA for the second cycle test. Likewise, the amount of water-extractable sodium (4,450 μg in the table) for the first Soxhlet extraction (4 h) of the first cycle test represents only 59.3% of the total water-extractable sodium, and this percentage increases to 75.6% for the first Soxhlet extract of the second cycle test. These results suggest that it may be necessary to generate RABA by using NaCl vapor (or KCl vapor) at high pressure to achieve complete deactivation of the clay minerals in fresh AB.

Chemical Analysis of Water Extract. Table 26 shows results of chemical analysis for Soxhlet extract of the NaCl-vapor sorbed RABA with deionized water. For comparison, Table 26 includes also similar results obtained with fresh AB bed and RABA

Table 26. Chemical Analysis of Water Solution from Water-Leached or Extracted from Various Activated-Bauxite Samples

Sample No.	Ion Concentration, $\mu\text{mol/g}$ AB (or RABA)					
	Na ⁺	Li ⁺	Cl ⁻	SO ₄ ²⁻	Al ³⁺	Si ⁴⁺
AB/SO ₂ ^a	0.6	N.A.	0.1	4.0	1.2	14.6
AB10800-8 ^b	52.7	N.A.	3.4	28.1	0.6	17.5
AB10800-15 ^b	740.4	N.A.	40.1	377.8	0.4	11.6
RABA/SO ₂ ^c	0.8	19.0	0.2	0.8	17.2	9.3
RABA-10H(1)/SO ₂ ^d	8.1	37.6	0.5	16.6	11.2	7.0
RABA-10H(2)/SO ₂ ^d	27.9	26.5	3.6	14.3	16.1	6.8

^aFresh AB was heat-treated in a simulated PFBC exhaust (containing 3% O₂, 16.1% CO₂, 4.5% H₂O vapor, ~400 ppmV SO₂, and the remainder N₂) at 800°C and 10 atm absolute for 8 h. The tested AB was leached with deionized water in a beaker at 90°C for 1 h. Data was obtained from Table 3 of Reference 20.

^bSame batch of fresh AB as above was tested for NaCl-vapor sorption at 800°C and 10 atm absolute for 8 h (AB10800-8) and 15 h (AB10800-15). The simulated PFBC exhaust contained 3% O₂, 16.1% CO₂, 4.5% H₂O vapor, ~400 ppmV SO₂, 12 and 4 ppmV NaCl vapor for AB10800-8 and AB10800-15, respectively, and the remainder N₂. Data was obtained from Table 2 of Reference 20.

^cRegenerable activated bauxite adsorbent (RABA), which was prepared by 6 M LiCl-impregnation technique, was heat-treated in a simulated PFBC exhaust (containing 3% O₂, 16.1% CO₂, 6% H₂O vapor, ~1000 ppmV SO₂, and the remainder N₂) at 895–900°C and 10 atm absolute for 3.5 h. The tested RABA was Soxhlet-extracted with deionized water for 4 h.

^dThe batch of heat-treated RABA (from above but not Soxhlet-extracted) was tested for NaCl-vapor sorption at 895–900°C and 10 atm absolute for 10 h. The simulated PFBC exhaust contained 3% O₂, 16% CO₂, 6% H₂O vapor, ~1000 ppmV SO₂, 5.2 and 9.4 ppmW NaCl vapor for RABA-10H(1)/SO₂ and RABA-10H(2)/SO₂, respectively, and the remainder N₂. The tested RABA was Soxhlet-extracted with deionized water for 4 h. The Soxhlet-extracted RABA from RABA-10H(1)/SO₂ was used for the RABA-10H(2)/SO₂ test.

(Table 24) and results obtained from NaCl-vapor sorbed fresh AB (referred to as samples AB10800-8 and AB10800-15) tested earlier²⁰ under similar experimental conditions as that used to test RABA. For AB10800-8 (8-h test) and AB10800-15 (15-h test), a 2.54-cm-dia (1 in.-dia), 12.7-cm-long (5-in.-long) fresh AB was tested for NaCl-vapor capture at 800°C and 10 atm system pressure of the simulated PFBC off-gas containing 3.0% O₂, 16.1% CO₂, 4.5% H₂O vapor, ~400 ppmV SO₂, 12 and 4 ppmV NaCl vapor for AB10800-8 and AB10800-15, respectively, and the remainder N₂. After the test, the NaCl-vapor sorbed AB was leached with deionized water at 90°C in a beaker for 1 h.

It was concluded earlier²³ that NaCl vapor present in PFBC exhaust (containing SO₂) was captured by fresh AB essentially as sodium sulfate because the mole ratio of sodium to sulfate was close to two, as shown in Table 26 for samples AB10800-8 and AB10800-15. Since the amount of chloride ion in the leachate increased with greater amount of sodium present in the leachate, a smaller amount of NaCl vapor was also captured by fresh AB as NaCl through a physical adsorption process. Similarly, results of the tests for RABA also show that NaCl vapor was captured by RABA essentially as sodium sulfate, as well as NaCl, but to a lesser extent. Therefore, it is concluded that RABA behaves similarly to fresh AB in terms of capture mechanisms of NaCl vapor from simulated PFBC exhaust.

4.0 CONCLUSION

Clay impurities in commercial grade AB can be deactivated by NaCl or LiCl vapor to generate the regenerable activated-bauxite adsorbent (RABA) needed for the regenerable activated-bauxite sorber alkali monitor (RABSAM). However, studies of this work conclude that only a partial deactivation is achieved by reacting NaCl or LiCl vapor with clay impurities under atmospheric deactivation condition, probably due to limited access of the vapor into micropores of AB. Since LiCl vapor also chemically reacts with alumina substrate of AB, resulting in pore enlargement, decreased pore surface, and decreased NaCl-vapor sorption capacity of the RABA, NaCl vapor is a more suitable deactivation agent than LiCl vapor. The testing of a batch of RABA for its NaCl-vapor sorption in a simulated PFBC exhaust environment (i.e., a bed temperature of 895-900°C, a system pressure of 10 atm absolute, and a simulated PFBC exhaust containing 3% O₂, 16% CO₂, 6% H₂O vapor, ~1000 ppmV SO₂, 5-9 ppmW NaCl vapor, and the remainder N₂) shows that the RABA behaves similarly to fresh AB in terms of capture mechanisms of NaCl vapor from the simulated PFBC exhaust.

5.0 RECOMMENDATIONS

The RABSAM concept is a technically sound device that can provide reliable on-line alkali-vapor measurement in PFBC exhaust. Based on results obtained from this work, we recommend (1) generating chemically and thermally stable RABA by deactivating clay impurities of fresh, commercial grade activated bauxite with NaCl or KCl vapor under simulated PFBC exhaust environment, namely, high-temperature, high-pressure, and high dose of NaCl or KCl vapor in simulated PFBC exhaust compositions, and (2) continuing the development of RABSAM for field application.

6.0 ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the administrative assistance of K. M. Myles and J. E. Battles, Associate Director and Director of the Chemical Technology Division, ANL. Assistance with chemical analyses were given by I. M. Fox, F. L. Williams, and E. A. Huff of the Analytical Chemistry Laboratory, ANL. Valuable assistance has also been given by C. M. Zeh, V. P. Kothari, and N. T. Holcombe, Program Managers for this project at the U.S. DOE/Morgantown Energy Technology Center.

7.0 REFERENCES

1. D. R. Hafer, M. J. Mudd, and M. E. Zando, "Test Results from the 70 MW Tidd PFBC Demonstration Plant," Proc. 1993 Int. Conf. on Fluidized Bed Combustion, San Diego, CA, May 9-13, 1993, Vol. 2, pp. 921-929 (1993).
2. Anders Dahl, "Operation Experience of the PFBC Plant in Värtan, Stockholm," Proc. 1993 Int. Conf. on Fluidized Bed Combustion, San Diego, CA, May 9-13, 1993, Vol. 2, pp. 931-935 (1993).
3. K. K. Pillai, J. Rubio, and J. Tome, "The Escatron PFBC Project," Proc. 1987 Int. Conf. on Fluidized Bed Combustion, Boston, MA, May 3-7, 1987, Vol. 1, pp. 266-271 (1987).
4. Masao Fujita, "Progress Report on Technical Development of PFBC Combined Cycle Power Plant in Japan, 1993," Proc. 1993 Int. Conf. on Fluidized Bed Combustion, San Diego, CA, May 9-13, 1993, Vol. 2, pp. 907-919 (1993).
5. J. R. Peterson and V. H. Lucke, "Commercial Power Plant Design Development for the Coal Fired Combined Cycle," Combustion, 25(7), pp. 29-36 (1979).
6. R. C. Hoke et al., "Miniplant and Bench Studies of Pressurized Fluidized-Bed Coal Combustion," Final Report, Exxon Research and Engineering Co., EPA-600/7-80-013 (1980).
7. National Research Development Corp., "Pressurized Fluidized-Bed Combustion," R&D Report No. 85. Interim No. 1, prepared for Office of Fuel Research, Department of Interior, Washington, DC (1975).
8. A. G. Roberts et al., "Fluidized-Bed Combustion - 1000 Hour Test Program, Vol. III, Combustion Emission and Hot Gas Cleanup," NCB/Coal Utilization Research Laboratory, DOE/EF/10423-1103 (1981).
9. V. Zakkay et al., "Gas and Alkali Emission from Pressurized Fluidized-Bed Combustion of Lignite," Proc. Eighth Int. Conf. on Fluidized-Bed Combustion, Houston, TX, Vol. 3, pp. 1186-1196 (1985).
10. W. J. Haas, Jr., D. E. Eckels, R. N. Kniseley, and V. A. Fassel, "Development of Alkali and Trace Heavy Metal Monitors," Proc. DOE Contractors' Meeting on High Temperature, High Pressure Particulate and Alkali Control in Coal Combustion Process Streams, Morgantown, WV, pp. 599-620 (1981).
11. J. P. Hensel, D. R. Goff, R. G. Logan, R. Pineault, R. R. Romanosky, Jr., and J. K. Wachter, "On-Line, Real-Time Alkali Monitor for Process Steam Analysis," Rev. Sci. Instrum 58(9), 1647-1659 (1987).

12. S. H. D. Lee and K. M. Myles, "Alkali Measurement in PFBC and Its Control by a Granular Bed of Activated-bauxite," Proc. 1987 Int. Conf. on Fluidized Bed Combustion, May 3-7, 1987, Boston, MA, pp. 793-801 (1987).
13. W. J. Hass, Jr., and D. E. Eckels, "Real Time Monitoring of Sodium and Potassium Concentrations in Flue Gas Producing during July and August 1987 Coal Combustion/Hot Gas Cleanup Studies at the Grimethorpe (England) PFBC Establishment," Ames Laboratory, Iowa State University, IS-4956, UC-90 (1988).
14. S. H. D. Lee and E. L. Carls, "Measurement of Sodium and Potassium Vapors in PFBC of Beulah Lignite," J. Inst. Energy 63(457), 203-210 (1990).
15. S. H. D. Lee, F. G. Teats, W. M. Swift, and D. D. Banerjee, "Alkali-Vapor Emission from PFBC of Illinois Coals," Combust. Sci. Technol. 86, 327-336 (1992).
16. S. H. D. Lee, W. M. Swift, and I. Johnson, "Regeneration of Activated-bauxite used as a Granular Sorbent for Removing Gaseous Alkali Metal Compounds from Hot Flue Gas," Proc. 25th Int. Gas Turbine Conf. and Products Show, March 10-13, 1980, New Orleans, LA, Paper No. 80-GT-165 (1980).
17. P. J. Jackson and J. M. Ward, "Operational Studies of the Relationship between Coal Constituents and Boiler Fouling," J. Inst. Fuel 29, 154-164; discussion, 441 (1956).
18. P. J. Jackson and H. C. Duffin, "Laboratory Studies of the Deposition of Alkali-Metal Salts from Flue Gas," Proc. Int. Conf. on the Mechanism of Corrosion of Fuel Impurities, Central Electricity Generating Board, Marchwood, England, pp. 427-442 (1963).
19. E. Raask, "The Behavior of Potassium-Containing Silicate Minerals in Pulverized-Coal-Fired-Boilers," Mitt-Ver. Grosskesselbetr. 48, 348 (1968).
20. I. Johnson and S. H. D. Lee, "Alkali Metal Vapor Removal from Pressurized Fluidized-Bed Combustion Flue Gas," Annual Report for October 1980 - September 1981, Argonne National Laboratory Report ANL/FE-81-59 (January 1982).
21. J. S. Summers, "Reaction of Sulfur Oxides with Alumina and Platinum/Alumina," Environ. Sci. Technol. 13(3), 321-325 (1979).
22. C. C. Chang, "Infrared Studies of SO₂ on γ -Alumina," J. Catalysis 53, 374-385 (1978).
23. S. H. D. Lee, K. M. Myles, and A. A. Jonke, "Alkali Metal Vapor Removal from Pressurized Fluidized-Bed Combustor Flue Gas," Annual Report for October 1981 - September 1982, Argonne National Laboratory Report ANL/FE-82-24 (March 1983).

Distribution for ANL/FE-94-01Internal:

J. E. Battles	S. A. Miller	W. M. Swift
J. E. Harmon	K. M. Myles	TIS Files
S. H. D. Lee (5)	D. K. Schmalzer	

External:

DOE-OSTI, for distribution per UC-103 (40)

ANL-E Library (2)

ANL-W Library

Manager, Chicago Operations Office, DOE

D. L. Bray, DOE-CH

Chemical Technology Division Review Committee Members:

E. R. Beaver, Monsanto Company, St. Louis, MO

D. L. Douglas, Consultant, Bloomington, MN

R. K. Genung, Oak Ridge National Laboratory, Oak Ridge, TN

J. G. Kay, Drexel University, Philadelphia, PA

G. R. St. Pierre, Ohio State University, Columbus, OH

J. Stringer, Electric Power Research Institute, Palo Alto, CA

J. B. Wagner, Arizona State University, Tempe, AZ

D. D. Banerjee, Illinois Clean Coal Institute, Carterville, IL

R. C. Bedick, USDOE, Morgantown Energy Technology Center, Morgantown, WV

D. Bonk, USDOE, Morgantown Energy Technology Center, Morgantown, WV

D. C. Cicero, USDOE, Morgantown Energy Technology Center, Morgantown, WV

A. S. Clark, Department of the Army, Vicksburg, MS

K. Das, USDOE, Morgantown Energy Technology Center, Morgantown, WV

M. R. Ghate, USDOE, Morgantown Energy Technology Center, Morgantown, WV

N. Holcombe, USDOE, Morgantown Energy Technology Center, Morgantown, WV

F. I. Honea, Illinois Clean Coal Institute, Carterville, IL

D. L. Keairns, Westinghouse Research Laboratories, Pittsburgh, PA

Illinois Institute of Natural Resources, Librarian, Champaign, IL

K. E. Markel, USDOE, Morgantown Energy Technology Center, Morgantown, WV

M. W. Pitt, USDOE, Office of Fossil Energy, Germantown, MD

J. Shang, USDOE, Office of Fossil Energy, Washington, DC

M. Williams, USDOE, Morgantown Energy Technology Center, Morgantown, WV

C. Zeh, USDOE, Morgantown Energy Technology Center, Morgantown, WV

J. F. Zievers, Industrial Filter & Pump Manufacturing Co., Cicero, IL

DATE

FILMED

6 / 2 / 94

END