DOE/PC/90365--T12-

D-1
2

Contract No. DE-AC22-91PC-90365

**FUNDAMENTAL MECHANISMS
IN FLUE GAS CONDITIONING**

QUARTERLY REPORT

July 1993 - September 1993

Prepared for

U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

DISCLAIMER

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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ps

BK

81

FUNDAMENTAL MECHANISMS IN FLUE GAS CONDITIONING

QUARTERLY REPORT
July 1993 - September 1993

SRI-ENV-93-854-7375-Q9

Contract No. DE-AC22-91PC90365

October 26, 1993

Todd R. Snyder

SOUTHERN RESEARCH INSTITUTE
2000 NINTH AVENUE SOUTH
P.O. Box 55305
BIRMINGHAM, ALABAMA 35255-5305

Prepared for

Felixa Eskey, Project Manager
UNITED STATES DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
Post Office Box 10940, MS 922-206
Pittsburgh, Pennsylvania 15236-0940

TABLE OF CONTENTS

	<u>PAGE</u>
INTRODUCTION.....	1
SUMMARY	1
TASK 3: ANALYSES OF ASHES AND POWDERS	4
E 3.2 Characterization of Water Adsorption by Powders and Fly Ashes	4
E 3.3 Characterization of Water-Conditioned Powders and Fly Ashes.....	6
E 3.5 Determination of the Effects of the Deposition of Chemical Compounds on Particle Surfaces	10
PLANS FOR THE UPCOMING QUARTER.....	10

INTRODUCTION

This project is divided into four tasks. We developed our Management Plan in Task 1. Task 2, Evaluation of Mechanisms in FGD Sorbent and Ash Interactions, focuses on characteristics of binary mixtures of these distinct powders. Task 3, Evaluation of Mechanisms in Conditioning Agents and Ash, is designed to examine effects of various conditioning agents on fine ash particles to determine mechanisms by which these agents alter physical properties of ash. We began Tasks 2 and 3 with an extensive literature search and assembly of existing theories. We completed this phase of the project with publication of two special Topical Reports. During the past several quarters we performed our analyses of the samples in our database. Pilot-scale evaluations are scheduled to occur during the next two quarters. We will include the results of laboratory and pilot-scale work performed under Tasks 2 and 3 in a Flue Gas Conditioning Model that we will issue under Task 4. The Final Report for the project will also be prepared under Task 4.

Task 2 and Task 3 each include several groups of experiments. Each experiment has a title and a corresponding number. We described all these experiments and tests that are included under each experiment (except Experiment 3.5, which is discussed in our last quarterly report) in our fourth Quarterly Report (April - June 1992). In our literature reviews reported in Topical Reports 1 and 2, we emphasized the roles adsorbed water can have in controlling bulk properties of powders. The experiments we have been performing are primarily designed to define the extent to which water affects key properties of ashes, powders, and mixtures of sorbents and ashes. We have included selected data from prior quarterly reports in this report for the sake of completeness, and for comparisons with newly-acquired data. In several places in this report samples are referred to by their identification (SID) numbers. Table 1 provides a brief description of all the samples we have used in this project along with their SID numbers.

SUMMARY

As suggested by our literature review, our data indicate that water adsorption depends on particle morphology and surface chemistry. Our recent laboratory efforts were directed primarily toward the determination of the effects of adsorbed water on the tensile and cohesive strengths of powders, and the conditioning of powders and ashes with SO_3 and organosiloxane. Details of these conditioning methods are discussed under section 3.5.

Table 1
Identification of Samples

	SID	Description of Sample
sorbents and base line ashes	2870	Muskingum base line ESP hopper ash
	2871	DITF dry $\text{Ca}(\text{OH})_2$ injection
	2872	DITF $\text{Ca}(\text{OH})_2$ slurry injection
	2873	DITF $\text{Ca}(\text{OH})_2$ slurry injection with CaCl_2 addition
	2884	Kintigh base line ESP hopper ash
	2885	spray dryer ash (High Sulfur Test Center)
	2883	Edgewater furnace $\text{Ca}(\text{OH})_2$ injection
	2890	ADVACATE injection
	2907	Yorktown furnace injection of lignosulfonate-modified lime
dust cake ashes	2101	Scholz dust cake ash
	2029	Monticello dust cake ash
	2515	Harrington dust cake ash
	1994	AFBC dust cake ash
powders	3063	silicon dioxide (Cabosil L-90)
	3064	silicon dioxide (Cabosil M-5)
	3065	silicon dioxide (Cabosil EH-5)
	1856	glass beads
	3238	aluminosilicate (Neutralite)
	2769	silicon dioxide (Kenite 900)
	2874	alumina powder
leached dust cake ashes	2101-W	leached Scholz dust cake ash (first set)
	2029-W	leached Monticello dust cake ash (first set)
	2515-W	leached Harrington dust cake ash (first set)
	1994-W	leached AFBC dust cake ash (first set)
	2101-L	leached Scholz dust cake ash (second set)
	2029-L	leached Monticello dust cake ash (second set)
	2515-L	leached Harrington dust cake ash (second set)
	1994-L	leached AFBC dust cake ash (second set)

Table 1 (continued)

	SID	Description of Sample
ashes and powders conditioned with organo- siloxane	2101-L-S	leached Scholz dust cake ash, conditioned with organosiloxane
	2029-L-S	leached Monticello dust cake ash, conditioned with organosiloxane
	2515-L-S	leached Harrington dust cake ash, conditioned with organosiloxane
	1994-L-S	leached AFBC dust cake ash, conditioned with organosiloxane
	1856-S	glass beads, conditioned with organosiloxane
	2769-S	aluminosilicate (Neutralite), conditioned with organosiloxane
	2874-S	silicon dioxide (Kenite 900), conditioned with organosiloxane
	3238-S	alumina powder, conditioned with organosiloxane
ashes and powders conditioned with SO ₃	2101-A	Scholz dust cake ash, conditioned with SO ₃
	2029-A	Monticello dust cake ash, conditioned with SO ₃
	2515-A	Harrington dust cake ash, conditioned with SO ₃
	1994-A	AFBC dust cake ash, conditioned with SO ₃
	1856-A	glass beads, conditioned with SO ₃
	2769-A	aluminosilicate (Neutralite), conditioned with SO ₃
	2874-A	silicon dioxide (Kenite 900), conditioned with SO ₃
	3238-A	alumina powder, conditioned with SO ₃
	2101-L-A	leached Scholz dust cake ash, conditioned with SO ₃
	2029-L-A	leached Monticello dust cake ash, conditioned with SO ₃
	2515-L-A	leached Harrington dust cake ash, conditioned with SO ₃
	1994-L-A	leached AFBC dust cake ash, conditioned with SO ₃

TASK 3: ANALYSES OF ASHES AND POWDERS

Measurements made under Task 3 during the past quarter included selected bulk porosity and tensile strength measurements, and determinations of water content. The conditioning and testing of samples generated under Experiment 3.5 consumed the majority of effort under Task 3 during the past quarter.

E 3.2 Characterization of Water Adsorption by Powders and Fly Ashes

Conditioning with organosiloxane had the greatest effect on alumina powder, increasing water content by 2 to 3 times. (The effect of this adsorbed water is discussed later in this report.) Conditioning with SO_3 had the greatest effect on Harrington ash, increasing water content by 7 to 8 times. Apparently the high calcium content of the Harrington ash does not alter the hydrophilic nature of the SO_3 adsorbed on the surfaces of the ash particles. Although the Monticello ash might be expected to react to SO_3 conditioning in much the same way as the Harrington ash, no significant increase in water content was measured for this ash. Possibly high silica content, or the way the calcium is bound within the Monticello ash particles may explain this difference. For the AFBC ash, either its high calcium content, and/or its particle morphology prevented adsorbed SO_3 from increasing overall water content significantly.

Water content data that we measured for the Scholz ash showed that the unconditioned ash retained somewhat more water than the ash conditioned with SO_3 . We cannot offer an explanation for this data at this time. Although we successfully removed sulfuric acid and sulfate salts from the surfaces of the Scholz ash during leaching and consequently lowered the affinity of this ash for water, SO_3 conditioning of the leached Scholz ash could not restore the affinity of this ash to its unleached condition. Possibly insufficient amounts of SO_3 were deposited to reestablish this affinity for water. Another explanation may be that for this affinity for water to be reestablished, the particles need the sulfate salts to be redeposited on their surfaces.

Because the Harrington and AFBC ashes tend to pick up relatively large amounts of water by hydration during exposure to excess water, the process we used for organosiloxane conditioning (which involved suspending the ash sample in a water/organosiloxane slurry) may obscure data on water contents taken for these two samples.

Table 2
Water Contents of Task 3 Samples Titrated in the Karl Fischer Device
after Baking at 300°C, %

SID	Relative Humidity used to Condition Samples, %						
	1	11	33	50	75	82	93
2101	1.9	2.3		2.0	3.1		
2029	0.15	0.16		0.18	0.25		0.36
2515	0.25	0.18		0.22	0.27		
1994	1.5	1.9		2.6	2.7		
3063	0.20	0.27	0.35	0.63	1.4		
3064	0.28	0.36	0.54	2.2	1.7		
3065	0.60	1.4	1.9	5.0	2.6		
1856	0.064	0.15		0.20	0.22	0.51	0.58
3238	2.2	2.0		2.7	2.0		2.2
2769	0.040	0.16		0.20	0.41		
2874	0.048	0.051		0.10	0.16		
2101-W	0.62	0.79		1.1	1.3		1.7
2029-W	0.12	0.17		0.26	0.33		1.2
2515-W	2.9	3.3		3.6	3.9		7.0
1994-W	1.3	2.8		3.5	4.2		
2101-L-S	0.66		0.88		0.99		
2029-L-S	0.17	0.17			0.35		0.64
2515-L-S	3.9				6.3		8.1
1994-L-S	4.1	4.5			6.5		8.4
1856-S	0.052	0.14	0.11		0.35		0.41
2769-S	0.063				0.54		
2874-S	0.11	0.15			0.29		0.29
3238-S	1.0				2.3		2.2
2101-A	1.0				1.6		1.7
2029-A	0.12				0.26		
2515-A	1.7				2.4		
1994-A	1.0				2.8		
1856-A	0.093				0.26		
2769-A	0.075				0.20		
2874-A	0.031				0.12		0.17
3238-A	0.89		0.44		2.3		
2101-L-A	0.28		1.2		1.5		1.8
2029-L-A	0.13		0.27		0.33		0.63
2515-L-A	2.6				6.4		
1994-L-A	0.85				4.6		

E 3.3 Characterization of Water-Conditioned Powders and Fly Ashes

Table 3 summarizes all uncompacted bulk porosity data that have been measured for Task 3 samples. Conditioning with organosiloxane had the greatest effect on Harrington ash, glass beads, and alumina powder. Cohesive strength was increased for the Harrington ash and the glass beads, presumably because adsorbed water was readily available at the interparticle contact points. This type of conditioning *decreased* the tensile strength of the alumina powder. Possibly the particle morphology of the alumina powder accounts for this behavior. The alumina particles (mean size 45 μm) appear to be agglomerates of smaller (approximately 1 μm) particles. (See Quarterly Report #5 for SEM photographs of this sample.) The many contact points between these smaller particles may occupy the adsorbed water in the interior of the overall 45 μm particle, leaving little water available for the interparticle bonding of the larger particles.

Conditioning the alumina powder with SO_3 may also have been affected by the morphology of these particles. This type of conditioning would be expected to cause the particles to adsorb more water, making liquid bridges between particles more likely. However, the cohesivity of the alumina powder dropped after SO_3 conditioning. Since the 45 μm particles are quite porous, it is probable that the surfaces of the smaller particles adsorbed SO_3 , even though these surfaces may be well within the interior of the larger particle. If so, the contact points between these smaller particles may occupy adsorbed water in the same way as with organosiloxane conditioning.

Table 3
Uncompacted Bulk Porosities of Conditioned Ashes and Powders

SID	Relative Humidity used to Condition and Test Samples, %						
	7	13	27	53	75	83	93
2101	77		76	78	82	84	87
2029	64		67	68	69	70	80
2515	74		76	75	76		78
1994	90		88	90	89		91
1856	44		45	57	70	73*	77*
2769	91						92
2874	77				79		81
3238	94						95
2101-W	73		72	72	72	73	80
2029-W	65		63	64	64		80
2515-W	77		74	76	76		80
1994-W	90		89	91	90		91
2101-L			72				79
2029-L			64				73
2515-L			79				80
2101-L-S		70	68		72		76
2029-L-S		65	65		68		76
2515-L-S		85	84		87		83
1994-L-S		87	86		88		
1856-S		73	73		74		
2769-S		90	90		91		91
2874-S		65	64		65		66
3238-S		94	95		95		96
2101-A		71			79		87
2029-A		66			70		83*
2515-A		75			70		77
3238-A							95
2769-A							93
2874-A		65			68		72
2101-L-A		72			74		81
2029-L-A		62			65		75
2515-L-A		79			81		82

* powder got quite moist, forcing it through screen created "gummy spindles"

Table 4 summarizes all tensile strength data that have been measured for Task 3 samples. Measurements made during the past quarter indicated that conditioning with organosiloxane or SO_3 tended to increase tensile strength in several of the samples. The most pronounced increases were measured for Harrington ashes. SO_3 conditioning significantly increased the tensile strength of leached Harrington ash. To a lesser degree, the tensile strengths of leached Monticello and Scholz ashes were also increased, as was the case with the unleached Monticello ash. Increased affinity for water is the most probable explanation for these data.

Although organosiloxane should make the particle surfaces more hydrophobic, it also increased the tensile strength of selected samples. The most notable increase was for leached Harrington ash, which showed about an order of magnitude increase in tensile strength. As we have speculated based on uncompacted bulk porosity data taken for glass beads, water adsorbed on hydrophobic surfaces is easily drawn to contact points between particles, strengthening interparticle bonds.

Table 4
Tensile Strengths of Conditioned Ashes and Powders, N/m²

SID	Relative Humidity used to Condition and Test Samples, %							
	1	11	22	34	50	75	83	93
2101	11	4.7		1.5	5.1	5.4	28	
2029	> 32	19		4.1	8.2	8.5	8.5	12
2515		> 32	> 32	19	15	> 26	30	
1994				> 13	> 7.7			
1856	7.9	3.6		0.6	0.8	> 27	32	
2769				> 6.6	> 4.4			
2874	3.3	1.5		0.8	0.8		1.2	2.1
3238	> 30	4.9		2.0	1.4		1.9	3.4
2101-W	15	6.3		1.8	2.8		3.9	3.1
2029-W	> 30	15		3.1	3.2	3.6	3.8	6.1
2515-W	> 32	8.8		2.0	1.6	2.5	3.4	3.8
1994-W				> 14	> 9.5			
2101-L-S				6.1		3.8		
2029-L-S				5.3		9.0		11
2515-L-S				24	13	19		
1856-S				> 32				
2874-S				1.3				1.8
2029-A				10		10		> 32
2515-A						> 20		
3238-A				2.5				
2101-L-A				6.3		6.3		
2029-L-A				7.7		6.1		
2515-L-A				> 23		18		

E 3.5 Determination of the Effects of the Deposition of Chemical Compounds on Particle Surfaces

Experiment 3.5 was designed to determine if the characteristics of ashes or powders could be significantly altered by the surface deposition of soluble salts, silanes, or SO_3 . Due to problems with the methods we tried for the spray drying of ash and powder slurries, we abandoned our attempts to condition with soluble salts. We have conditioned selected ashes and powders with organosiloxane and SO_3 .

Under Experiment 3.5, we conditioned twelve samples with SO_3 . Our conditioning system generated SO_3 vapor by the passage of metered, dry N_2 over a container of heated fuming sulfuric acid. Several trials were made to establish a concentration of SO_3 between 10 and 30 ppm. We settled on a final concentration of 24 ppm SO_3 in our conditioning gas stream. Our conditioning system consisted of a flowing stream of SO_3 vapor passing through a porous bed of the powder or ash and then on through a water bath to absorb excess SO_3 .

Selected characteristics of these conditioned materials have been measured. Potential effects of these compounds include changes in appearance, surface area, affinity for adsorption of water, and tensile strength. The results of these analyses have been compared with analyses performed on unconditioned samples under Experiments 3.1, 3.2, 3.3, and 3.4.

PLANS FOR THE UPCOMING QUARTER

In the early part of the next quarter, we will be preparing for pilot-scale evaluation of water conditioning. Preliminary preparations for these tests are already under way. Detailed plans for our pilot-scale tests will be established after further consultations with our Contracting Officer's Representative. Scheduling of these pilot-scale tests will depend on when SRI's 6 million Btu/hr combustor will be in operation, the type of testing planned, and the type of coal being burned.

FUNDAMENTAL MECHANISMS IN FLUE GAS CONDITIONING

QUARTERLY REPORT
July 1993 - September 1993

SRI-ENV-93-854-7375-Q9

Contract No. DE-AC22-91PC90365

October 26, 1993

Approved by

A handwritten signature in dark ink, appearing to read "P. Vann Bush", is written over a horizontal line.

P. Vann Bush Head, Particulate Science and Engineering Division

END

DATE

FILMED

3/3/94