PROCEEDINGS OF THE FOURTEENTH BIENNIAL LIGNITE SYMPOSIUM ON THE TECHNOLOGY AND UTILIZATION OF LOW-RANK COALS

INTRODUCTION

The Biennial Lignite Symposia have grown from the original North Dakota Lignite Forum held in 1958 to the present international symposium. These meetings have expanded beyond lignite to include subbituminous coal, brown coal, low-grade (not necessarily low-rank) coals, and peat. Marketing and regulatory policy topics have been included, first, as plenary session topics and, in the current symposium, as a complete stream of concurrent sessions. Based on previews of the many presentations and the strong interest indicated by the number of registrations, the Biennial Lignite Symposia clearly continue to meet a growing need for information exchange through the formal presentations and informal discussions.

The addition of exhibits of products and services provides a major new dimension to the Symposium, and we are very grateful to the companies who are exhibiting and making this new venture a success. These exhibits will expand even further and include more companies at the next symposium.

The poster presentations provide the opportunity for innovative communication of technical results. During the two-hour lunch breaks on Tuesday and Wednesday of the Symposium, authors will exhibit their poster displays and be available for discussion of their results and ideas. This communication medium can greatly facilitate the transfer of technical information, and we expect poster sessions to be featured at future symposia.

This was also the first time that short courses have been presented in conjunction with the Symposium, and we would also like to acknowledge the contributions of these presenters:

> Coal Science: A Practical Approach to Addressing Technological Problems, presented by Dr. Robert B. Finkelman of the U.S.Geological Survey, Dr. Fredrick Rich of the South Dakota School of Mines, Dr. Steven Benson of the UND Energy Research Center, and Dr. John Breyer of Texas Christian University.
>
> Fluidized Bed Combustion Technology, presented by Cabot Thunem of Valhalla Enterprises and Michael D. Mann of the UND Energy Research Center.
>
> Baghouses: Applications to Low-Rank Coal Fired Combustion Sources, presented by John D. McKenna, Gary P. Greiner, and John C. Mycock of Environmental Testing Services, Inc., and Stanley J. Miller of the UND Energy Research Center.

An important reason for having this year's Symposium in Dallas was to provide the opportunity for attendees to visit the region's lignite mines and power plants. The book on **Gulf Coast Lignite Geology** was prepared especially for this Symposium by R. B. Finkelman and D. J. Casagrande through the contributions of many authors with extensive experience and expertise. The book includes papers on lignite geochemistry, mineralogy of surface-mined

lands, engineering applications for Gulf Coast lignite development, recent/current research on lignites, and many related topics. This is a major contribution to the literature and we appreciate the effort of the authors and editors.

Gulf Coast Lignite Geology also provides a detailed guide to the mines which are included in the two tours planned for the final day of the Symposium:

> Big Brown Mine and Generating Station. This tour is hosted by Texas Utilities Mining Company, and we would like to acknowledge the planning and coordination provided by S. E. (Gene) Rand.
>
> Jewett Mine and the Limestone Generating Station. Ted Mayo and Mark Palmquist of Northwestern Resources Company have been extremely helpful in developing and coordinating the mine tour. Charles Weiss of Utility Fuels, Inc., kindly facilitated the tour of Houston Lighting & Power's generating station; he also made the extra effort of chairing a technical session of the Symposium.

As these Lignite Symposia evolve, it is imperative that world-wide representatives from the various industries involved with low-rank coals provide input to shape the planning for upcoming symposia. For this purpose, the newly instituted Lignite Symposium Advisory Council, together with Lignite Symposium session chairmen, will be meeting at the Symposium to review the current Symposium and to assist in the development of plans for the next Biennial Symposium. In addition, the University of North Dakota Energy Research Center welcomes comments and suggestions from all the attendees and readers of these Proceedings. These may be sent to the Director of the Lignite Symposium, UNDERC, Box 8213, University Station, Grand Forks, ND 58202. We are already looking forward to utilizing all these suggestions to make the next Symposium even better and more useful to all the attendees.

The Energy Research Center would also like to express its appreciation for the co-sponsorship of the Lignite Symposia by the U. S. Department of Energy. This support was highlighted by DOE's Assistant Secretary for Fossil Energy, J. Allen Wampler, in his plenary session discussion of "America's Clean Coal Commitment." In addition, there was a great deal of behind-the-scenes assistance, particularly from the Grand Forks Project Office, and session chairmen and speakers from DOE/PETC and DOE/METC made vital contributions to a successful symposium.

As these Symposium Proceedings go to press to be ready for distribution at the start of the Symposium, we would like to dedicate these Proceedings to all the authors who made the necessary extra efforts to be certain that their manuscripts were received in time to be included. For those papers which are not included in these Proceedings, every effort will be made to have copies available at the time of presentation or at the registration desks.

David M. Watt
Director
Fourteenth Biennial Lignite Symposium

Research and Development

Stream Chairman: C. A . Wentz

UND Energy Research Center

DESULFURIZATION OF LOW RANK TURKISH COALS BY FLOTATION

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ABSTRACT

In recent years more emphasis has been given to utilize low rank coals, especially in the countries like Turkey which has large reserves of lignites. These coals have as much as 6% sulfur of which about 80% is pyritic sulfur. The unstable oil prices made low rank coals an alternative energy source. However, many countries have stringent environmental regulations which can only be met with the use of low sulfur coals. In order to clean and desulfurize the low rank Turkish coals down to the acceptable sulfur content, reverse flotation method was used which removed about 70% of total sulfur in the coal.

Channel samples were taken from Beypazari upper and lower coal seams, and representative laboratory samples were prepared in accordance with ASTM standard procedures. Preliminary tests on high sulfur coals indicated the possibility of reducing the pyritic sulfur by flotation. The gravity separation gave unsatisfactory sulfur removal due to very fine pyrite liberation size.

Pyrite is finely disseminated and intergrown with various forms of vitrinite. In coals under study, the pyrite fills cell lumens in vitrinite particles in some cases, and in most of the other cases it is randomly distributed. The size distribution of pyrite was determined by using image analysis technique which made it possible to observe three groups of pyrite as follows:

1. Completely liberated pyrite
2. More than 50% liberated pyrite
3. Pyrite enclosed in organics with organics comprising more than 50% of the particle.

Microscopic analysis indicated that the mean diameter of pyrite in different samples ranged from 2.1 micron to 46.3 micron and the maximum particle size was less than 100 micron. The pyritic sulfur in raw coal, clean coal and tailings were determined in accordance with ASTM standard D2492 and the total sulfurs were determined by LECO acid-base titration method.

The laboratory samples were ground separately to -35/+200 mesh and -200/0 mesh sizes, and the -200 mesh fraction from the first batch of samples were screened out and discarded. The preliminary flotation tests were conducted on each sample to determine the optimum quantity of collector, frother, pyrite depressant, agitator speed, residence time and pulp density for maximum sulfur reduction. The initial tests showed that -35/+200 mesh sample did not give satisfactory sulfur and mineral matter reduction due to low liberation size of the pyrite. The flotation of -200 / 0 mesh size sample consumed excessive reagents. So it was decided to apply two stage flotation as applied successfully by previous workers to -35/0 samples.

During the two-stage flotation, the samples were ground to -35/0 mesh size and in the first stage, kerosene and MIBC used to obtain a preliminary froth. The froth of the first stage was then wet ground to -200/0 mesh to further liberate the finer pyrite. In the second stage of flotation, the reground froth was further cleaned and about 80 percent of pyritic sulfur was removed with an overall recovery of more than 60 percent.

The tests showed that Beypazari upper and lower coal seams can be desulfurized to an acceptable level of sulfur and ash content by applying two stage reverse flotation procedure.

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ABSTRACT

The unstable oil prices made low rank coals an alternative energy source. However, high sulfur coals need to be desulfurized before they can be used because they cause air pollution. In this research, the preliminary tests were conducted on coal samples obtained from the Beypazari Mines in Turkey. These mines contain two seams, designated as upper and lower coal seams. The tests on these coals indicated the possibility of reducing the pyritic sulfur by two stage flotation process. Microscopic studies showed that the pyrite is finely disseminated in these coals and it could only be liberated in fine size range. The conventional flotation process was conducted on each sample utilizing kerosene and MIBC. In order to further liberate the pyrite, the froth concentrate was then wet ground to -200/0 mesh size. Then a second stage reverse flotation was applied by depressing the coal and floating the pyrite. By using the above process, the pyritic sulfur content was reduced from 3.81% to 1.03% for upper coal seam and from 3.21% to 0.96% for lower coal seam with 60.5% coal recovery. From this study second stage reverse flotation appears to give promising results.

INTRODUCTION

In recent years more emphasis has been given to utilize low rank coals. The unstable oil prices made low rank coals an alternative energy source. However, many countries have stringent environmental regulations on the use of high sulfur coals.

Gravity separation on coarse coal is possible due to the density difference between coal and pyrite. However, difficulties occured when attempts were made to separate fine size pyrite from coal. Presently, flotation is the most successful physical separation process(1). As shown in previous studies(2), the floatability of the coal-pyrite system is more

complex than an ore-pyrite system. Brown coal and lignites have strongly hydrophilic character and high inherent moisture unlike the bituminous coal(3). Also, the lignite-pyrite system has low native floatability and the reagent consumption during flotation is greater than that for bituminous coal.

Most coals contain sulfur in three basic forms, namely sulfate sulfur, pyritic sulfur and organic sulfur. Since organic sulfur is an integral part of coal matrix, physical cleaning processes cannot remove it. Pyritic sulfur is in the form of mineral pyrite and normally occurs as discrete microscopic particles. The percentage of sulfate sulfur is usually negligible. Fine grinding and flotation process will generally reduce the pyrite content of most coals. K. J. Miller(4) in his recently published work found that fine grinding of coal increases pyrite liberation. Miller first ground the coal to -28/0 mesh size and applied flotation, then wet ground the froth from the first stage flotation and utilized multi-stage flotation to reduce the pyritic sulfur content. After wet grinding for 30 minutes, liberated pyrite particles were increased from 23% in the -28/0 mesh size coal to over 62% in the -400/0 mesh size coal. Miller also showed that wet grinding resulted in better pyrite liberation than dry grinding. Miller and Deurbrouck(5) published a usefull review about the results of wet grinding.

Two-stage reverse flotation has proved to be more successful in separating pyrite from coal than two-stage coal flotation. In this process, conventional flotation was utilized in the first stage, then froth from the first stage was either used directly, or further ground and repulped to the appropriate pulp density. A suitable coal depressant was added and pyrite was floated with the use of a pyrite collector. HCl was used to adjust the pH to a value near 7(6, 7, 8). Microscopic studies of the clean coals and tailings showed that the tailings contained mostly liberated pyrite particles, whereas clean coals contained only non-liberated pyrite particles.

Aplan(9) suggested that the pyrite in coal is best removed under gentle operating conditions with starvation quantities of frother, low air rate, low impeller speed and short retention time in the cell. He named this procedure as "grab and run" technique.

Carlton(10) studied the relation between pyrite grain-size distribution and pyritic sulfur reduction. The study showed that better prediction of sulfur reduction can be made for a specific coal if pyrite grains are counted under microscope.

Hucko(11) found that a non-ionic polyacrylamide with inorganic dispersant (sodium hexametaphosphate) exhibited selective flocculation towards coal. Attia(12) used xanthate containing polymeric dispersant to disperse and remove ultrafine pyrite during selective flocculation of Kentucky NO.9 coal seam.

Three years ago in Ankara, Turkey, the Mining Engineering Department of the Hacettepe University began a research program concerning low rank Turkish coals. The main objective was to find a mean of reducing the pyritic sulfur of Turkish low rank coals. The initial tests were conducted on coal samples obtained from the Beypazari Mines in Turkey. These mines contained two seams, designated as upper and lower seams. This work includes the results of pyrite liberation and flotation tests on Beypazari upper and lower coal seams. The preliminary experiments were initiated at Hacettepe University in Ankara, Turkey, and completed at the University of Missouri-Rolla, Department of Mining Engineering, Rolla, Mo.

EXPERIMENTAL PROCEDURE

Sample Preparation

For these experiments, channel samples were taken from the Beypazari upper and lower coal seams. The faces were cleaned of dirt and loose coal in a width of about 6 feet, and loose pieces on the roof were also taken down to prevent them from falling into the samples. A channel of 2 inches deep and about 3 feet wide was cut from the roof to the floor in order to remove any altered or mixed coal. The floor was cleaned and sampling cloth was spread. From the coal bed a channel sample was cut 10 inches deep and 25 inches wide. The cut was made perpendicular to the coal bed producing about a 400 pound coal sample. This sampling procedure was applied to both seams. The samples included all the impurities and coal occurring in the channel. Samples were loaded into air tight containers, returned to the laboratory, and prepared using standard laboratory procedures. The sample preparation procedure is outlined in Figure 1. The main sample was first crushed to -1 1/2-inch top size, then blended, coned and divided into two halves. One of the halves was further crushed to -3/8 inch top size by a jaw crusher, and was then coned and quartered. Opposite quarters were mixed together. Then using a hammer mill, alternate quarter mixes were crushed down to -14 mesh top size and riffled. One of the -14/0 mesh size portion was used to prepare laboratory samples for flotation tests. The other -14/0 mesh

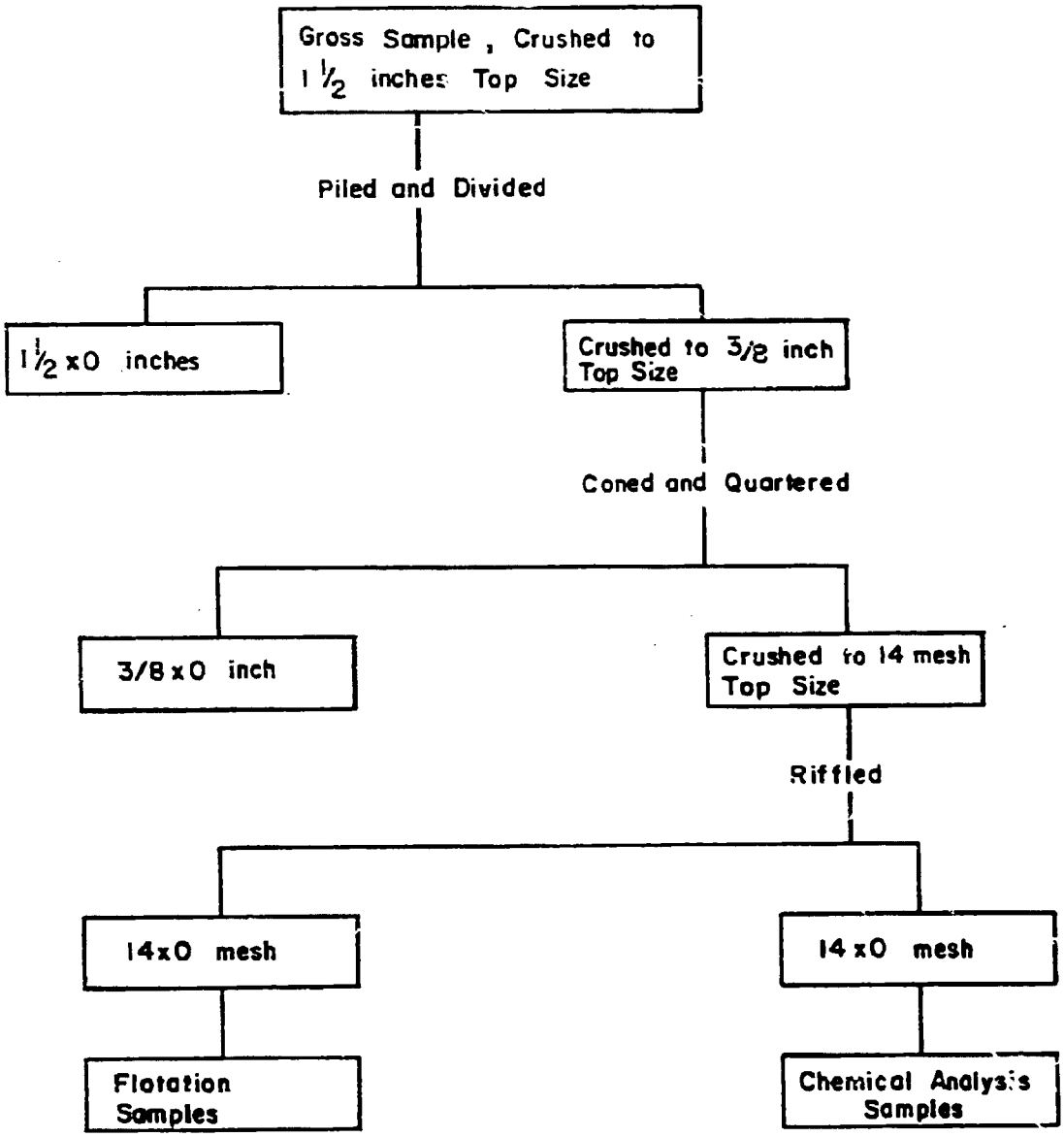

Figure 1. Sample Preparation Procedure

size portion was used to prepare laboratory samples for microscopic, proximate and sulfur analysis. The test samples were prepared by dry grinding separately two batches from -14/0 mesh coal to -35/0 mesh and -200/0 mesh sizes. The -200 mesh size fraction from the first batch of samples was screened out to obtain -35/+200 mesh size sample for the initial tests.

The moisture, ash, and volatile matter of raw coal as well as treated fractions were determined in accordance with ASTM standard procedures. Pyritic sulfurs in raw coal, clean coal and tailings were determined in accordance with ASTM standard D2492, and the total sulfur contents were determined by LECO acid-base titration method. The chemical compositions of Beypazari upper and lower coal seams are summarized in Table 1. Typical size analysis of -35/0 mesh test samples is shown in Table 2.

Pyrite Occurrence and Liberation

To determine the pyrite distribution, representative raw coal samples and samples from each phase of the flotation process were formed into cylindrical briquettes using epoxy resin. Then, using standard procedures, each briquette was sawed at both ends and the surfaces were polished with diamond slurry. Two briquettes were made from each sample, and after sawing four surfaces were examined. Image analysis was used to determine the size distribution of pyrite in all the samples. The size distribution of pyrite in the raw coal is shown in Fig 2. At least 1000 particles were measured per sample. Poor sorting of pyrite was found in both samples. Table 3 summarizes the size distribution of pyrite in raw coal samples taken from upper and lower coal seams. The table also shows that in different samples, the mean diameter of pyrite ranged from 2.1 micron to 46.3 micron with the maximum particle size less than 100 micron. Some of the sub-samples have distinct bimodal distribution with coarse and fine mode, and others are unimodal but are skewed towards the coarser end.

Adams(13) in his work showed that the error in estimating the percentage of pyrite is proportional to the standard deviation of the grain size distribution. Thus, lower standard deviation should give less error in estimation of pyrite percentile in the sample. Pyrite is predominantly associated with various forms of vitrinite and is usually randomly distributed. Point count analysis was used to determine the liberation degree of pyrite. By using petrographic technique(13), at least 300 pyrite particles per sample were counted. It is possible to consider the pyrite liberation in three groups as follows:

TABLE 1

Chemical Composition of Beypazari Coals

Proximate Analysis	Sample	
Percent	Upper Seam	Lower Seam
Moisture (Residual)	13.55	14.00
Volatile Matter (dry)	26.50	26.10
Ash (dry)	38.60	34.10
Carbon (dry)	34.90	39.80
Pyritic Sulfur (dry)	3.81	3.21
Sulfate Sulfur (dry)	0.10	0.09
Organic Sulfur (dry)	1.07	0.80
Total Sulfur (dry)	4.98	4.10

TABLE 2

Size Analysis of -35/0 Mesh Sized Beypazari Coal

Size, Mesh	Weight % Direct	Weight % Cumulative
35-45	10.2	10.2
45-60	23.4	33.6
60-100	19.6	53.2
100-140	12.9	66.1
140-200	22.6	88.7
200-0	11.3	100.0

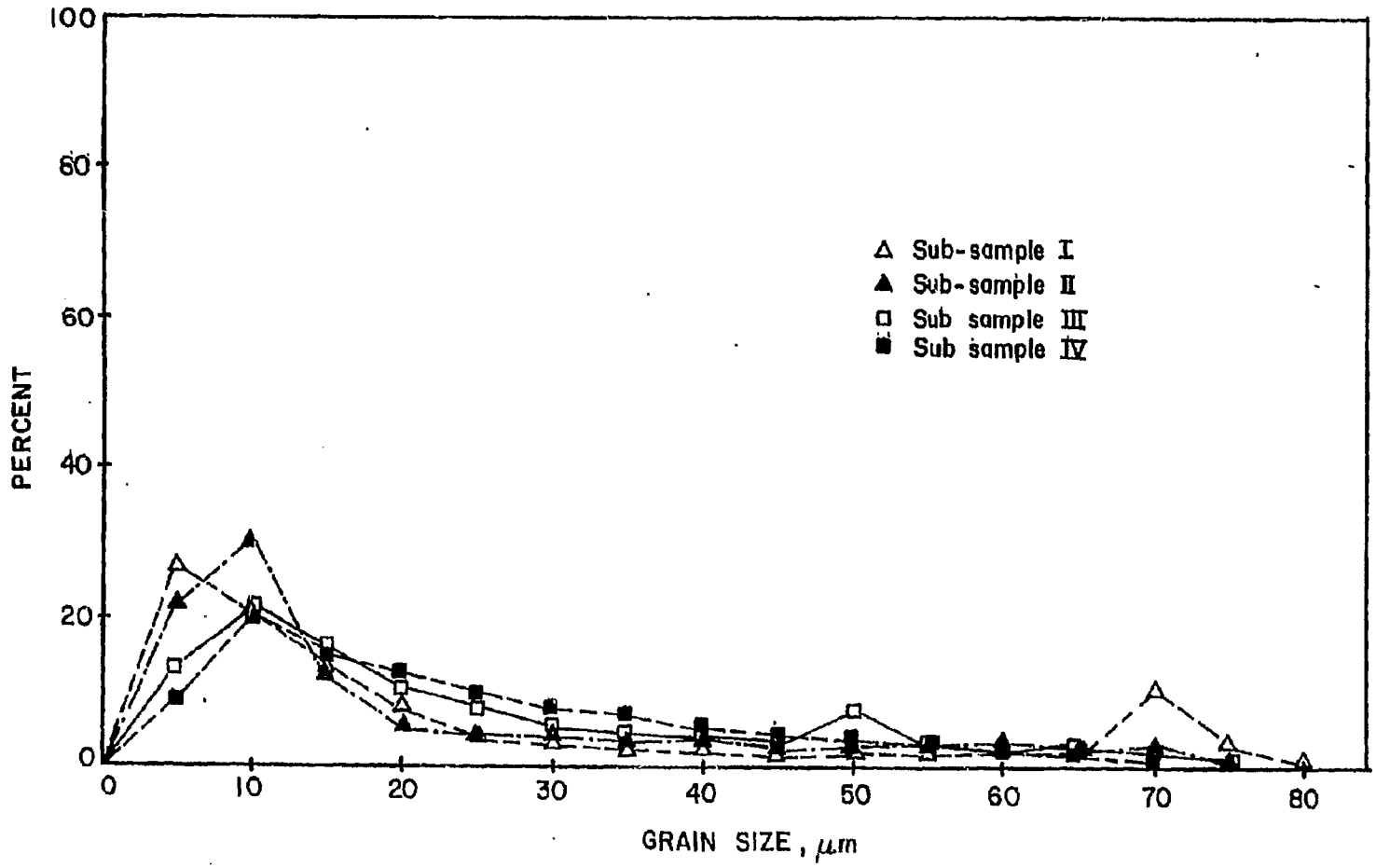

Figure 2. Pyrite Grain Size Distribution in Four Mixtures of Upper and Lower Coal Seams.

TABLE 3

Pyrite Particle Size in Raw Coal

No	Sample	Particle Size, um		
		Mean	Standard Deviation	Range
1	U. Seam	2.1	1.72	0-12
2	U. Seam	6.3	3.42	0-23
3	U. Seam	46.3	12.38	0-83
4	U. Seam	12.6	6.42	0-46
5	L. Seam	4.2	2.18	0-18
6	L. Seam	9.7	4.14	0-37
7	L. Seam	7.3	6.82	0-28
8	L. Seam	3.1	1.19	0-10

TABLE 4

The degree of Pyrite Liberation of -35/+200 Mesh and -200/0 Mesh Sized Coal Samples

No	Sample	Degre of Liberation, %		
		Completely Liberated	More then 50% Liberated	Less than 50% Liberated
1	-35/+200 Mesh	41	22	37
2	-35/+200 Mesh	38	26	36
3	-35/+200 Mesh	39	27	34
4	-200/0 Mesh	76	21	3
5	-200/0 Mesh	78	18	4
6	-200/0 Mesh	74	21	5

1. Completely liberated pyrite
2. More than 50% liberated pyrite
3. Less than 50% liberated due to pyrite being enclosed in the organics which comprises greater than 50% of the particles.

Microscopic studies on samples ground to -35/+200 mesh size and -200/0 mesh size showed that particle size has a marked effect on the degree of pyrite liberation. Testing showed coarse pyrite particles liberate more readily than fine pyrite particles. Further grinding to less than 53 micron showed no additional pyrite liberation. The degree of pyrite liberation of -35/+200 mesh size and -200/0 mesh size coal samples is summarized in Table 4.

Flotation Tests

Flotation experiments were carried out in a Denver Sub-A type laboratory flotation machine with a 3-liter cell. In all the flotation tests, the initial pulp density was taken as 5% (150 grams of coal in 3 liters of water). A series of regular flotation tests were conducted on -35/+200 mesh and -200/0 size coal samples prepared from Beypazari upper and lower coal seams. The preparation of flotation test samples was described in the previous section. Our aim was to determine the optimum values of the process variables for maximum pyritic sulfur reduction. The initial tests on -35/+200 mesh and -200/0 mesh samples did not show satisfactory sulfur reductions. In the first case, the pyrite liberation was not sufficient, and the froth contained high pyrite. In the case of -200/0 mesh samples, the slime fraction absorbed too much reagent, and the entrapment of fine pyrite particles in the froth was high.

Due to the complications mentioned above, the alternative method of two-stage flotation was then conducted on -35/0 mesh samples. In applying the two-stage flotation method to Beypazari coal seams, first we have used the regular flotation of the -35/0 samples to liberate and to remove the coarse pyrite particles. For each test, 150 grams of -35/0 mesh size sample was mixed in the cell and conditioned for 10 minutes. After conditioning, pH value of the pulp was measured and adjusted to between weakly acidic and neutral value. Then the frother(MIBC) and collector (kerosene) were added. After 1 minute, air was applied at a rate of 0.40 cubic feet per minute (cfm) and the froth was collected for 1 minute. Optimum values of flotation parameters for the first stage flotation were determined by these tests and are given in Table 5.

TABLE 5
Optimum Flotation Parameters for -35/0 Mesh Samples.

Parameters	Values
Frother,MIBC	0.3 lb/ton
Collector, Kerosene	0.7 lb/ton
Agitator Speed	900 rpm
pH	6.5-7.0
Air Rate	0.4 cfm

The second stage consisted of using the froth from the first stage and wet grinding the froth to -200/0 mesh to further liberate the locked or partially locked pyrite particles. Wet grinding was preferred to dry grinding because previous experimentors(5) showed that wet grinding was more successful in liberating the pyrite. In second-stage flotation, both the direct coal flotation and reverse flotation (pyrite flotation) were tried, and it was found that pyrite flotation gave better coal recovery and pyritic sulfur reduction. Therefore, pyrite flotation was taken as standard test for second-stage flotation. For pyrite flotation, froth from the first stage flotation was wet ground to -200/0 mesh size and repulped with fresh water for the second-stage flotation. The Aero Depressant 633 was added to depress the coal while the Potassium amyl xanthate was added to collect the pyrite, with 0.1 lb/ton MIBC as the frother. The optimum quantity of Aero Depressant 633 was determined to be 0.5 lb/ton, while agitation speed and air rate were kept at 900 rpm and 0.4 cfm, respectively. The quantity of Potassium amyl xanthate was taken as a variable. After addition of the reagents the froth was conditioned for 1 minute, then air was applied, and the pyrite froth was collected for 1 minute.

Results and Discussion

The results of tests with different amounts of Potassium amyl xanthate are shown in Tables 6 and 7 for upper and lower coal seams. For the upper seam, as seen in Table 6, the coal recovery, ash reduction and pyritic sulfur reduction increased with increasing amount of Potassium amyl xanthate from 0.4 lb/ton to 0.6 lb/ton. A final clean coal with 1.03 percent pyritic sulfur, 15.31 percent ash and 60.52 percent coal recovery was achieved with 0.6 lb/ton Potassium amyl xanthate. Clean coal contained 24.01 percent of ash, 16.36 percent of pyritic sulfur and 29.40 percent of total sulfur present in the feed. The concentrate from the first stage flotation froth contained minimum 2.33 percent pyritic sulfur which is 44.22 percent of the pyritic sulfur present in the feed.

TABLE 6

Reverse Flotation Results of Beypazari Upper Coal Seam
With Various Amounts of Potassium Amyl Xanthate
in the Second-Stage

No	Product	Weight Percent	Analysis, percent			Distribution, Percent		
			Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur
35	C.C.(2)	55.82	19.14	1.16	2.69	27.68	17.00	30.20
	R.(2)	17.04	56.16	8.95	9.36	24.79	40.05	32.03
	C.C.(1)	72.86	27.80	2.98	4.25	52.47	57.05	62.23
	R.(1)	27.14	67.60	6.03	6.93	47.53	42.95	37.77
	FEED	100.00	38.60	3.81	4.98	100.00	100.00	100.00
38	C.C.(2)	59.83	15.79	1.09	2.60	24.48	17.12	31.23
	R.(2)	13.59	75.27	8.55	10.32	26.50	30.49	28.16
	C.C.(1)	73.42	26.80	2.47	4.03	50.98	47.61	59.39
	R.(1)	26.58	71.19	7.51	7.61	49.02	52.39	40.61
	FEED	100.00	38.60	3.81	4.98	100.00	100.00	100.00
41	C.C.(2)	60.52	15.31	1.03	2.42	24.01	16.36	29.40
	R.(2)	11.64	83.27	9.12	11.92	25.11	27.86	27.28
	C.C.(1)	72.16	26.27	2.33	3.91	49.12	44.22	56.68
	R.(1)	27.84	70.54	7.63	7.75	50.88	55.78	43.32
	FEED	100.00	38.6	3.81	4.98	100.00	100.00	100.00

35 0.4 lb/ton Potassium amyl xanthate;
38 0.5 lb/ton Potasium amyl xanthate;
41 o.6 lb/ton Potassium amyl xanthate;
Abbr: C.C.(2): Final clean coal;
R.(2): Final reject;
C.C.(1): First-Stage froth conc.;
R.(1): First-stage reject;
Initial Sample Size: -35/0 mesh;
Froth from first stage ground to -200/0 mesh size
and used for pyrite flotation.

TABLE 7

Reverse Flotation Results of Beypazari Lower Coal Seam With Various Amounts of Potassium Amyl Xanthate in the Second-Stage.

No	Product	Weight Percent	Analysis, percent			Distribution, percent		
			Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur
47	C.C.(2)	58.18	16.81	1.15	2.47	28.68	20.68	35.02
	R.(2)	11.96	62.13	8.68	9.34	21.79	32.35	27.25
	C.C.(1)	70.14	24.54	2.44	3.64	50.47	53.21	62.27
	R.(1)	29.86	56.56	5.03	5.18	49.53	46.79	37.73
	FEED	100.00	34.10	3.21	4.10	100.00	100.00	100.00
50	C.C.(2)	60.12	15.23	0.98	2.14	26.85	18.35	31.43
	R.(2)	11.11	74.22	10.07	10.59	24.18	34.87	28.71
	C.C.(1)	71.23	24.43	2.40	3.46	51.03	53.22	60.13
	R.(1)	28.77	58.04	5.22	5.68	48.97	46.78	39.86
	FEED	100.00	34.10	3.21	4.10	100.00	100.00	100.0
53	C.C.(2)	60.49	14.45	0.96	2.07	25.63	18.09	30.58
	R.(2)	11.36	75.79	9.82	10.61	25.25	34.87	29.41
	C.C.(1)	71.85	24.15	2.36	3.42	50.88	52.85	59.99
	R.(1)	28.15	59.50	5.38	5.83	49.12	47.15	40.01
	FEED	100.00	34.10	3.21	4.10	100.00	100.00	100.00

47: 0.4 lb/ton Potassium amyl xanthate;
50: 0.5 lb/ton Potassium amyl xanthate;
53: 0.6 lb/ton Potassium amyl xanthate;
Abbr: C.C.(2): Final clean coal;
R.(2): Final reject;
C.C.(1): First-stage froth conc.;
R.(1): First-stage reject;
Initial Sample Size: -35/0 mesh;
Froth from first stage ground to -200/0 mesh and used for pyrite flotation.

For the lower seam, Table 7 shows a somewhat different distribution of ash and pyritic sulfur. Even though the lower coal seam has less ash and sulfur than upper coal seam, the pyrite is more finely distributed in this seam. For this reason, the first stage flotation froth had 52.88 percent of the pyritic sulfur that was present in the feed. This is higher than the pyrite percentage found in the first stage froth for the upper seam. Final clean coal contained 0.96 percent pyritic sulfur, 14.45 percent ash and the coal recovery was 60.49 percent. Only 18.09 percent of pyritic sulfur present in the feed reported to final clean coal.

CONCLUSIONS

Microscopic analysis of Beypazari upper and lower coal seams indicated fine dissemination of pyrite in the coal. Regular flotation experiments carried out by using kerosene and MIBC on -35/+200 mesh and -200/0 mesh sized coals did not give satisfactory pyritic sulfur removal due to non-liberated pyrite and entrapment of pyrite particles in the froth concentrate. Then the experiments were carried out with the use of -35/0 mesh samples and two stage flotation was applied. In applying the two stage flotation, first a froth, free from coarse pyrite was obtained. Then the froth from the first-stage was wet ground to -200/0 mesh size to further liberate the pyrite. This froth was used for coal or pyrite flotation. The coal flotation results in the second-stage were again not satisfactory. However, in the case of pyrite(reverse) flotation with potassium amyl xanthate and Aero depressant 633, successful results were obtained. Microscopic analysis of the pyrite flotation products revealed that the clean coal contained only non-liberated pyrite while tailings included mostly liberated pyrite. The analysis also showed that good selectivity was possible.

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HISTORY OF TEXAS LIGNITE UTILIZATION FROM A SOLID WASTE MANAGEMENT PERSPECTIVE

By Donald F. Weber

ABSTRACT:

Texas lignite utilization generates an operating solid waste environment that relies heavily on the use of surface impoundments and landfill disposal. Surface impoundments and landfills have traditionally been designed to support lignite power generation in terms of on-site water management practices and solid waste disposal, respectively. The need for power plant operations to be located near large bodies of water for makeup and cooling water purposes frequently results in locating essential operating ponds and land disposal facilities within distinct hydrogeological locations capable of potentially impacting ground and surface water resources.

Solid Waste Management practices have evolved and currently reflect site selection and corrective action considerations based on environmental assessments, changes in design and operating standards, economics, and changes in social and regulatory climates. A once pure geotechnical/civil engineering approach to solid waste management has now given way to a more interdisciplinary concept which integrates engineering with hydrogeology, geophysics, soil, water and leachate chemistry, computer modeling; and regulatory affairs. As solid waste management regulations continue to focus on the potential impacts of solute transport on valued ground- and surface-water resources, it is increasingly important to expand our understanding of the complexities of lignite combustion waste leachate chemistry and the dynamics of leachate migration, in addition to pursuing markets for the recycling of these combustion wastes.

INTRODUCTION:

Landfills and surface impoundments have traditionally been designed to support lignite power generation in terms of solid waste disposal and on-site water management practices, respectively. The need for power plant operations to be located near large bodies of water for makeup and cooling water purposes frequently results in locating essential operating ponds and land disposal facilities within distinct hydrogeological locations capable of potentially impacting ground and surface water resources.

Past practices for site evaluation and construction of both landfills and impoundments were directed primarily towards satisfying various geotechnical standards and criteria that pertained to dike stability and liner material permeability. The basic geotechnical testing and drilling procedures that are used for soil foundation investigations were also thought to be more than adequate to address site investigation requirements

for selecting, designing and eventually constructing these waste management facilities. Additionally, the same subsurface information developed during such an evaluation was incorporated into the design and installation of associated leachate collection and detection systems, the latter being inclusive of monitoring wells. Therefore, the final site selection, design and construction of these types of facilities were not necessarily considerate nor complimentary inherent site related of potential environmental impacts.

What the Texas lignite community has recognized, through hindsight and experience, is that there is a complexity of underlying considerations that must be addressed when evaluating a site in terms of possible corrective action or its prospects as a suitable candidate for waste management purposes. Among those items for consideration are the surrounding subsurface lithology and stratigraphy; ash and scrubber sludge leachate chemistry; soil, ground- and surface-water chemistry; various attenuation and solute transport mechanisms; and alternatives in primary and secondary containment for controlling and monitoring leachate migration. Subsequently, disciplines have been expanded from geotechnical and civil engineering to include the sciences of geology, hydrology, geophysics, soil and water chemistry, computer modeling and environmental engineering.

ENVIRONMENTAL ASSESSMENTS:

Geophysical and Cultural

Site investigative programs, preliminary and problem solving in nature, require an understanding of the subsurface materials and stratigraphy associated within the area of interest. In the past, a comprehensive drilling and coring program would be developed to ascertain needed information on subsurface conditions. Such a program would typically consist of drilling pilot holes at select intervals while monitoring the cuttings in the drilling fluids from each hole every five to ten feet. Usually one or more continuous cores would also be collected which, along with the cuttings data, would be used to develop cross-sections of the subsurface environment. Experience has shown that supplementing such a program to provide better definition of near-subsurface conditions is essential in the analysis and/or prevention of contamination to the surrounding environment.

Two geophysical analytical tools for enhancing interpretive skills include terrain conductivity and down-hole geophysical logging. Terrain conductivity is based on the applied principle of induced magnetic currents to measure apparent conductivity of shallow subsurface conditions. An electromagnetic field is induced by a primary coil which is transmitted to and received by a secondary coil. A conductivity meter then measures the variations in apparent conductivity from which stratigraphic and possible groundwater quality assessments can be made. By alternating the orientation and spacing of the coils, conductivity data can be obtained

which represents successively deeper components of the subsurface matrix being investigated (Figure 1.) After analyzing the conductivity data developed, a stratigraphic boring program can be designed to provide more accurate information on subsurface conditions. Additionally, if interpreted correctly, such information will offer insight to potential avenues for and/or areas impacted by leachate migration.

As mentioned above, stratigraphic borings are essential to furthering an understanding of true subsurface conditions. However, even if accompanied by continuous cores from select locations, the intricacies of some depositional environments can often be overlooked or misinterpreted thus leading to erroneous conclusions of significant importance. Down-hole geophysical logging, a technique widely applied in the oil and gas exploration industry, can provide details on subsurface stratigraphy via a suite of analytical logs such a natural gamma, self potential, compensated density/porosity, caliper, and medium and deep induction/resistivity (Figure 2.) Natural gamma and compensated density and induction logs are very useful in providing interpretive assistance.

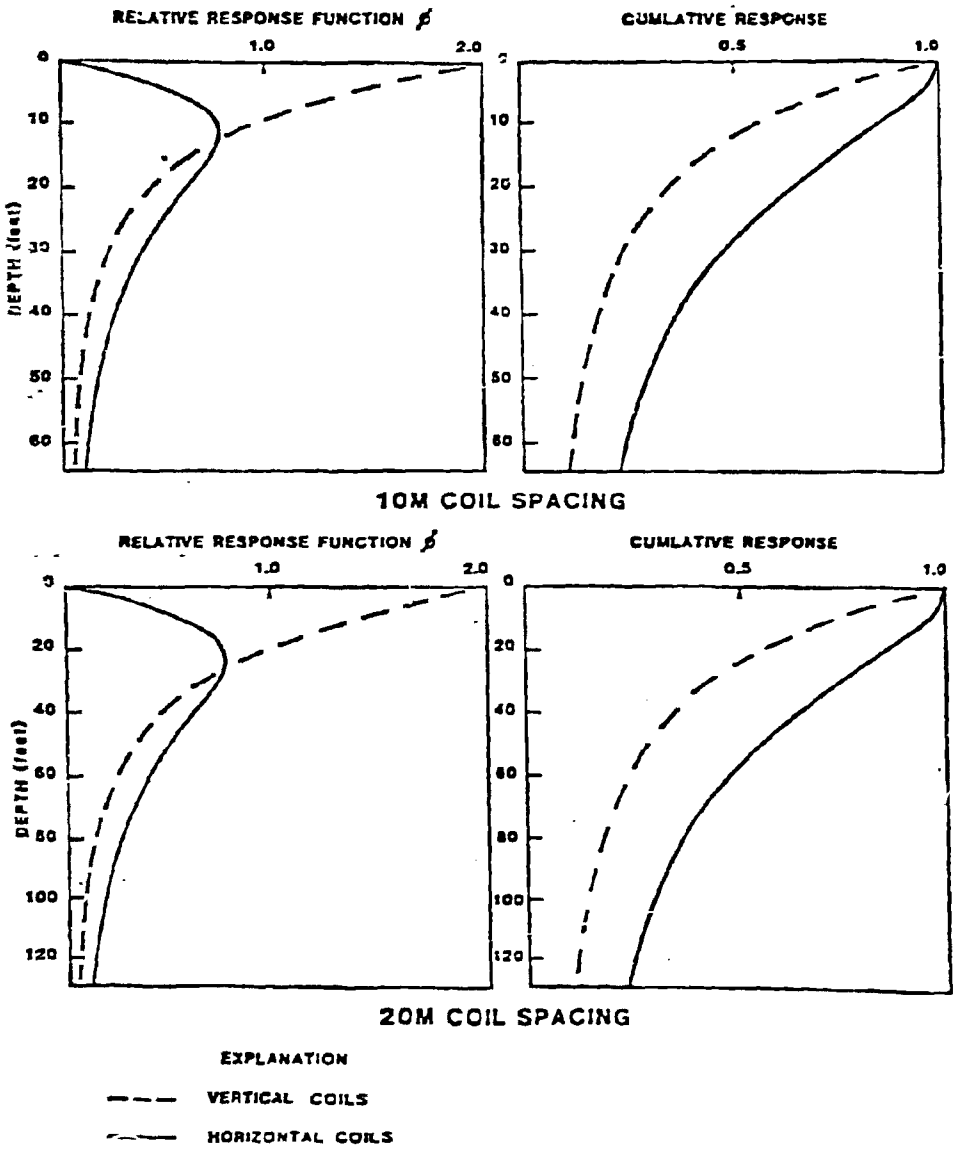
Natural gamma has a direct relationship to the permeability of the subsurface strata from which delineations of significant sand and clay lenses can be made. Apparent resistivity of pore water (Rwa) can be calculated from compensated density and induction data by developing Rwa relationships between surrounding wells of known water quality and Rwa values with the observed Rwa values from borings without monitoring wells. Major cation and anion composition can then be extrapolated from such a relationship.

Additional information that should not be overlooked are the precultural and current activities associated with the site under investigation. Land use, precipitation and evapotranspiration data, both past and present, are essential in helping to develop seasonal and other cyclic fluctuation information. Past practice in routine site investigations, whether it had been for pre-site development purposes or in response to corrective action, rarely took such information into account. Site investigations are anything but routine, and any additional history on site activities that can be obtained from company and public information files at the state are considered a valuable resource.

Leachate and Water Chemistry

Major components of ash and scrubber sludge leachate chemistry consist of calcium, magnesium, sodium, potassium, sulfates, chlorides, boron, selenium, arsenic, aluminum, silicates and a variety of other trace constituents. Additionally, many of these components are normally found in dissolved form in natural ground- and surface-water environments. Traditionally, analytical assessments of leachate and water chemistry had been limited to evaluating the data obtained in terms of waste characteristics as related to RCRA and chemical equilibrium as determined by cation-anion balance of the major constituents in solution. The next generation of analytical tools used for assessment of data added visual

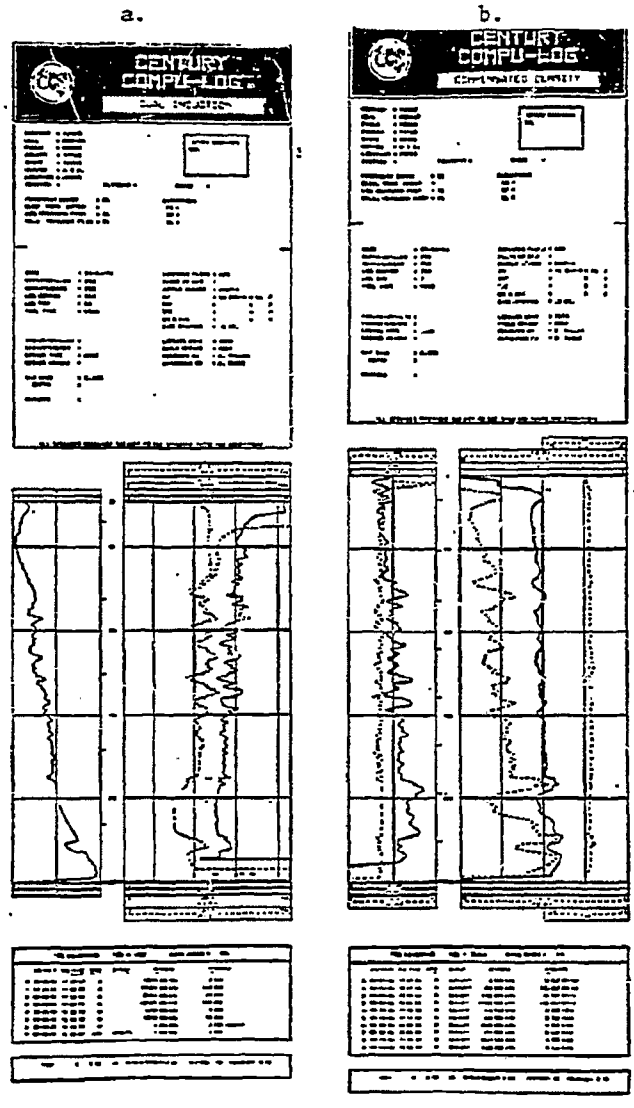
FIGURE 1



EM response vs. depth

Source: Geonics (1980)

FIGURE 2



Examples of geophysical logs. a. Dual Induction and
b. Compensated Density

Source: Century Geophysical (1986)

aids such as trilinear and Stiff diagrams (Figures 3. and 4., respectively). More recent laboratory and field investigations have identified numerous physical and chemical transport and attenuation mechanisms that exist which dramatically affect the characteristics of the leachate and ground- and surface-water chemistry involved.

Several of the more important relationships to be considered include: sulfate-selenate competition, chemical speciation-adsorption/ co-precipitation of trace metals, cyclic fluctuations due to intermittent releases of solutes from water soluble salts on land surfaces and/or in unsaturated soils,pE (redox)-pH status and the effects this relationships has on determining chemical speciation, and exergonic microbiological mediated oxidation and reduction reactions (Figures 5.-7. and Table 1. illustrate examples of the referenced relationships, respectively). The relative importance of understanding these relationships is manifested by the microbiologic catalysis of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron by such microorganisms as Thiobacillus ferroxidan and Ferrobacillus ferroxidan. Under controlled conditions, these organisms are able to accelerate the oxidation of Fe^{2+} to Fe^{3+} by a factor close to 10^6 times over that rate of oxidation via oxygen only.

High volume combustion waste leachate and associated water quality chemistry is now a multi-faceted science that has significantly improved and enhanced the analytical resources available for evaluating leachate and water quality related issues.

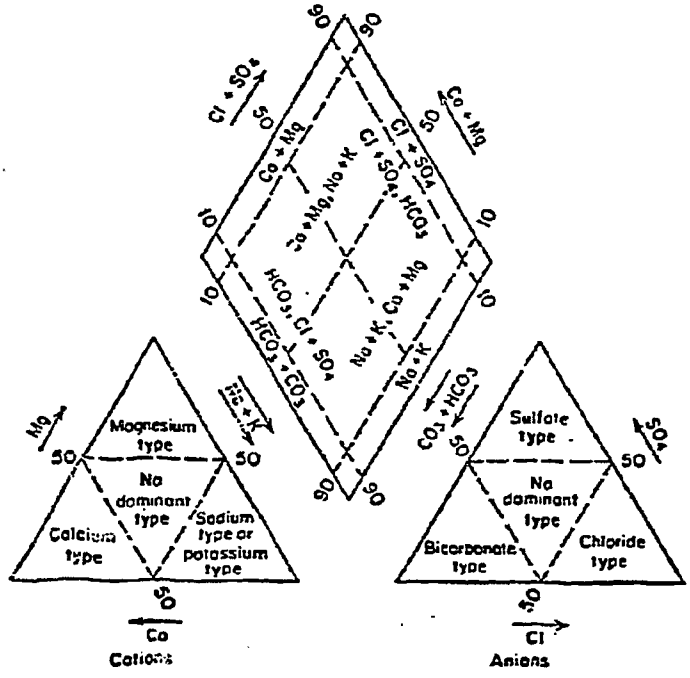
Computer Modeling

The topic of computer modeling is so broad that any serious discussion could not be adequately covered in this paper. Suffice it to say, computers have greatly enhanced our abilities to evaluate and predict ground water flow and chemistry scenarios. There is nothing novel about lignite combustion waste management in terms of applying the variety of models available (e.g., chemical equilibrium models; 1,2,3-dimensional flow models; iterative numerical models; solute transport models; etc.) to ascertain reasonable estimates of ground water flow directions, rates of movement and changes in both ground- and surface-water chemistry, potential impacts of same and assessments of corrective action alternatives -- active and passive. However, what is significant to our industry is that with an increased understanding of lignite combustion waste chemistry and hydrogeologic environment associated with solid waste management activities, employment of such modeling efforts is becoming more proactive in nature with an emphasis being placed on predictive assessments for future waste management sites and facility design and operating standards equivalency demonstrations.

Design and Operating Standards

Changes in design and operating standards regarding lignite combustion waste management are a direct consequence of changes in three extremely critical areas. The first relates to water budgets and its management,

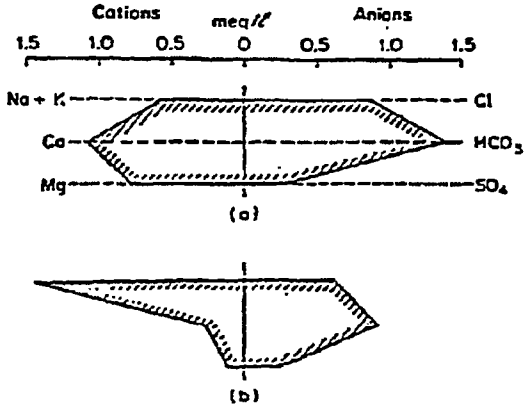
FIGURE 3



Trilinear diagrams provide visual aid to water type and mixing zones.

Source: Reference 3

FIGURE 4

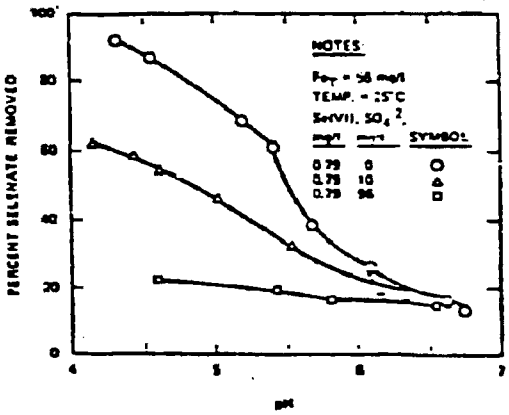


Stiff diagrams provide geometric references of water type.

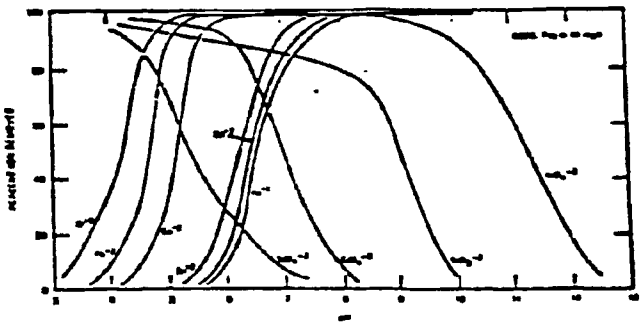
Source: Reference 3

FIGURE 5

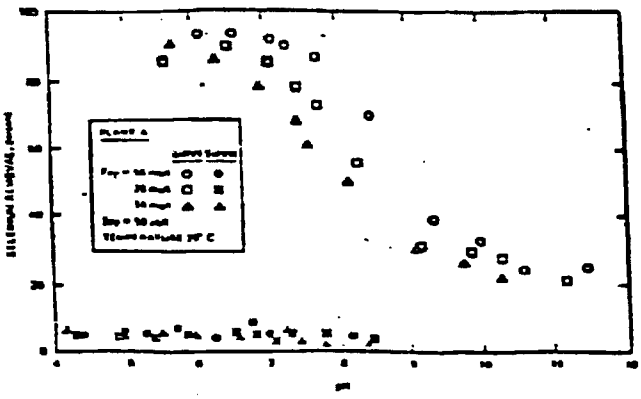
a.



b.



c.



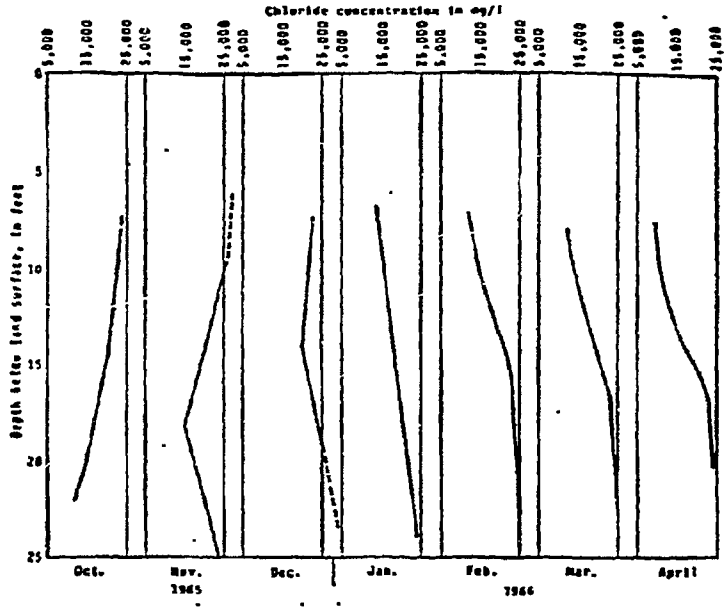
a. Effect of sulfate-selenate competition for adsorption sites on iron oxyhydroxide.

b. Approximate trace element removal vs. pH in ligand-free single cation and single anion systems.

c. Selenium removal vs. pH for coprecipitation with iron oxyhydroxide in lignite ash pond effluent.

Source: Reference 7

FIGURE 6

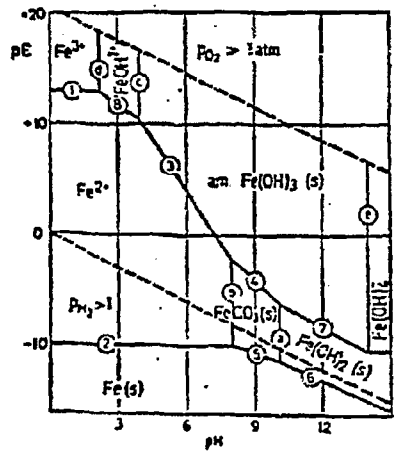


Vertical distribution in soil of chlorides from post oil production contamination showing seasonal cyclic fluctuations vs. depth.

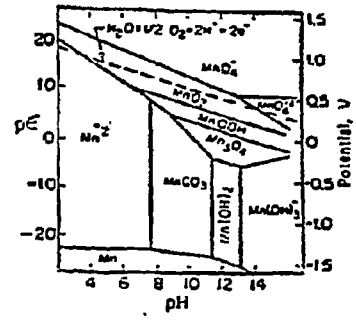
Source: Ground Water Monitoring Review (1982)

FIGURE 7

a.



b.



pE - pH diagrams for a) Fe, CO_2, H_2O and
b) Mn - CO_2 systems

Source: Reference 9

TABLE 1. REDUCTION AND OXIDATION REACTIONS THAT MAY BE COMBINED TO RESULT IN BIOLOGICALLY MEDIATED EXERGONIC PROCESSES (pH = 7)

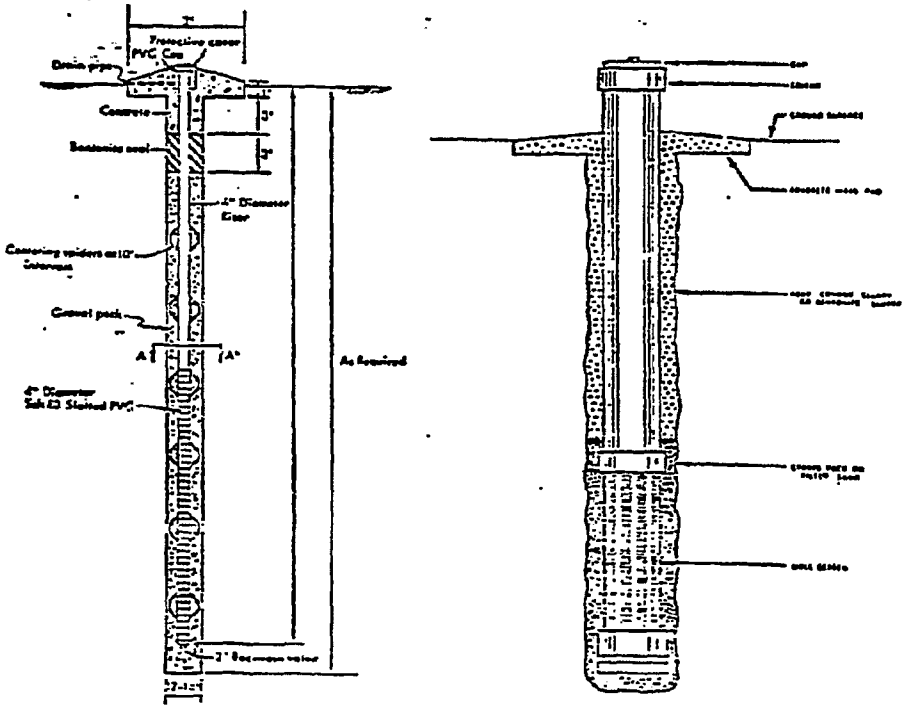
Reduction	$pe^{\circ}(W) = \log K(W)$	Oxidation	$pe^{\circ}(W) = -\log K(W)$
(A) $\frac{1}{4}O_2(g) + H^+(W) + e = \frac{1}{2}H_2O$	+13.75	(L) $\frac{1}{8}CH_2O + \frac{1}{8}H_2O = \frac{1}{8}CO_2(g) + H^+(W) + e$	−8.20
(B) $\frac{1}{5}NO_3^- + \frac{6}{5}H^+(W) + e = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+12.65	(L-1) $\frac{1}{8}HCOO^- = \frac{1}{8}CO_2(g) + \frac{1}{8}H^+(W) + e$	−8.33
(C) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-(10^{-3}) + \frac{3}{2}H^+(W) + e = \frac{1}{2}MnCO_3(s) + H_2O$	+8.9	(L-2) $\frac{1}{8}CH_2O + \frac{1}{8}H_2O = \frac{1}{8}HCOO^- + \frac{1}{8}H^+(W) + e$	−7.83
(D) $\frac{1}{8}NO_3^- + \frac{5}{4}H^+(W) + e = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+6.15	(L-3) $\frac{1}{6}CH_3OH = \frac{1}{6}CH_2O + H^+(W) + e$	−1.03
(E) $FeOOH(s) + HCO_3^-(10^{-3}) + 2H^+(W) + e = FeCO_3(s) + 2H_2O$	−0.8	(L-4) $\frac{1}{6}CH_4(g) + \frac{1}{6}H_2O = \frac{1}{6}CH_3OH + H^+(W) + e$	+2.88
(F) $\frac{1}{6}CH_2O + H^+(W) + e = \frac{1}{6}CH_3OH$	−3.01	(M) $\frac{1}{8}HS^- + \frac{1}{8}H_2O = \frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+(W) + e$	−2.75
(G) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+(W) + e = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	−3.75	(N) $FeCO_3(s) + 2H_2O = FeOOH(s) + HCO_3^-(10^{-3}) + 2H^+(W) + e$	−0.8
(H) $\frac{1}{8}CO_2(g) + H^+(W) + e = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	−4.13	(O) $\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O = \frac{1}{8}NO_3^- + \frac{9}{8}H^+(W) + e$	−6.16
(I) $\frac{1}{2}N_2 + \frac{5}{2}H^+(W) + e = \frac{1}{2}NH_4^+$	−4.68	(P) $\frac{1}{2}MnCO_3(s) + H_2O = \frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-(10^{-3}) + \frac{1}{2}H^+(W) + e$	8.9

Source: Reference 9

the second issue is the growing community and regulatory concerns on ground water protection, and the third aspect is limited space for disposal of ash and sludge, especially when dealing with the state regulatory agency (i.e., Texas Water Commission) guidelines of a 2-5% slope on the final cap for closure purposes.

Design features have changed from the use of three feet of 10^{-7} cm/sec clay for liner material in both landfills and surface impoundments to conducting site feasibility studies for implementing end-of-pit disposal practices and the use of dual liner-leachate detection/collection systems for surface impoundment applications. Additionally, this industry has seen changes in the use and construction of monitoring wells precipitated by the variability in subsurface stratigraphy and water chemistry. Whereas monitoring wells in the past were actually nothing more than vertical leachate detection systems, and in some cases served as potential conduits for cross communication between distinct hydrological units, current monitoring wells are designed to differentiate these unique hydrological units and provide water quality data from each of these distinct zones of interest (Figure 8.). Finally, because of the physical consistency of ash and scrubber sludge in solution and the relatively high conductivity exhibited by such solutions, state of the art electropotential leak detection methods for evaluating flexible geomembrane integrity (eg. Figures 9. and 10.) are now being incorporated into equivalency demonstrations for surface impoundment construction in an effort to provide rapid, more accurate leak detection systems and a cost effective alternative to current construction standards.

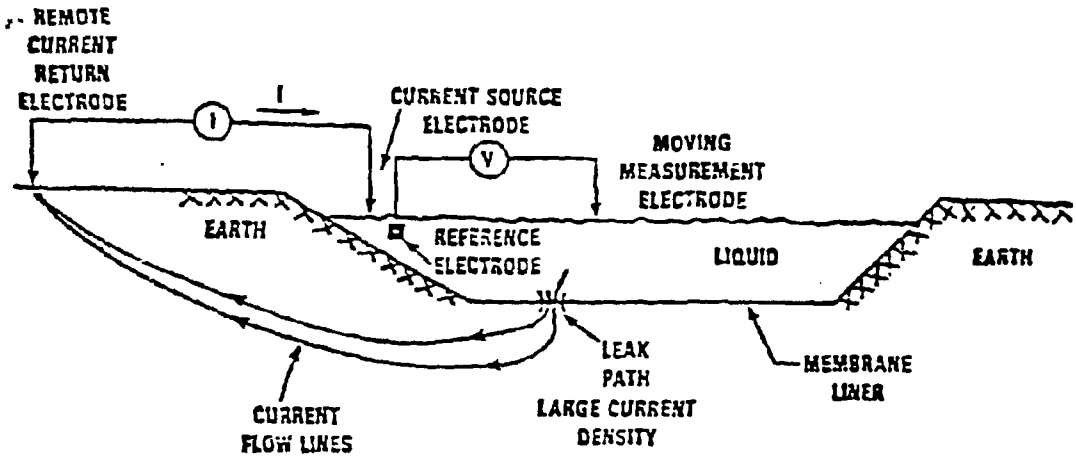
FIGURE 8



Monitoring Well Installations a) Full verticle monitoring vs.
b) Selective hydrologic unit monitoring.

Sources: NFS (1979), Reference 4

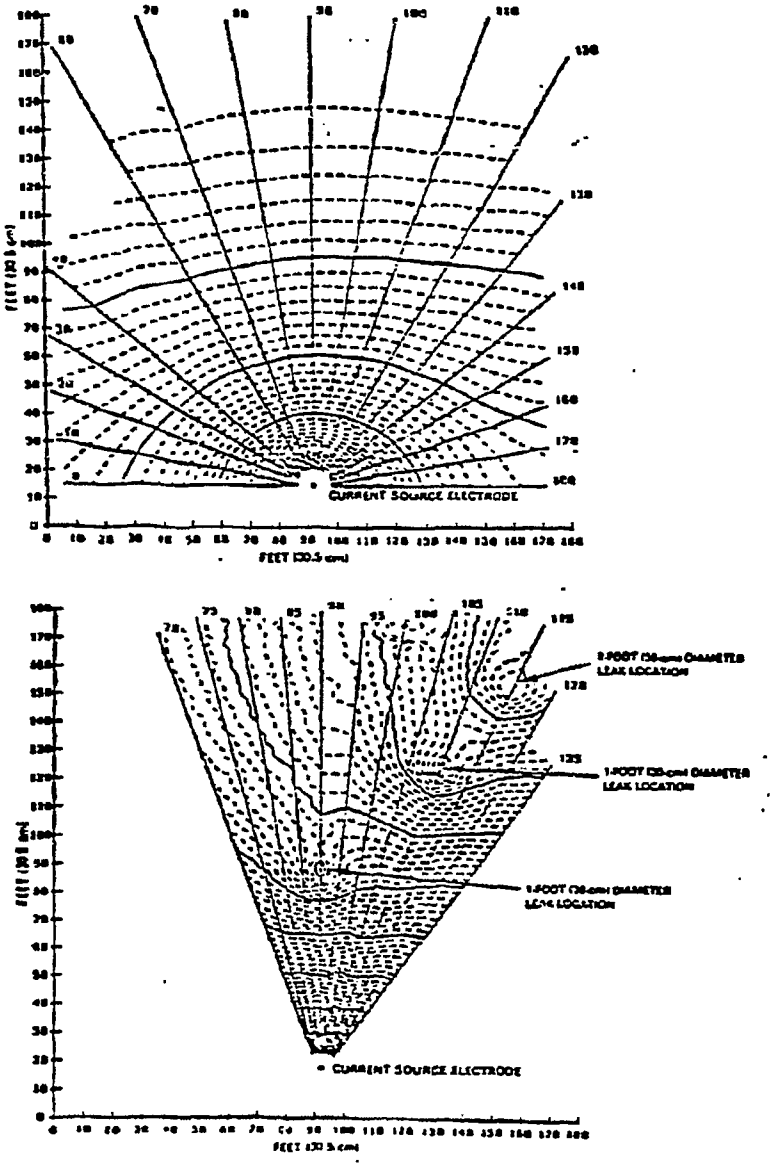
FIGURE 9



Conceptual electrical resistivity testing technique applied to detect and locate leaks on geomembrane liner systems.

Source: Reference 8

FIGURE 10



Examples of a) an equipotential contour plot of non-leak measurements vs.

b) equipotential contour plot showing distortions caused by leaks in liner system.

Source: Reference 8

Operating changes have come about due to space economics coupled with increased regulatory and neighboring community scrutiny and the realization that in some cases what should have been a water consuming feature (e.g., scrubbers) is operationally just the opposite. With lignite operations in Texas experiencing normal annual precipitation of 38" to 46", deliberate decisions are being made to reduce the water and space demands that accompany waste handling and disposal activities. Conversion from wet sluicing and decant operations to dry disposal/recycling systems via clarifiers, dewatering bins, forced oxidation and/or vacuum filtration is taking place at many facilities, if not already in place. In an effort to minimize the disposal of lignite combustion waste, markets for these wastes are actively being utilized and pursued. (See Table 2.)

Finally, regarding regulatory considerations, with the TWC promoting groundwater conservation districts, federal drinking water regulations concentrating on well head protection legislation, and RCRA Subtitle D proposed rule changes for solid waste management facility requirements to be based on matching facility performance standards with (1) the potential for harmful waste constituents to migrate from the facility, and (2) the

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Markets For

Lignite Combustion Waste

Waste Type	Use
FGD Gypsum	1. Wall Board
	2. Portland Cement for Controlling Set Time
	3. Cement Stabilization
Fly Ash	1. Additive for Ready Mix Concrete
	2. Additive for Type 1-P Cement
	3. Soil Stabilization by Texas Highway Department
Bottom Ash	1. In Hot Asphaltic Concrete for Stability and Skid Value
	2. Deicing Medium by Texas Highway Department
	3. Oil Well and Plant Service Roads for Traction and Stability
	4. Manufacturing of Clay Brick

TABLE 2

Source: TU Electric (1987)

value of the resources that may subsequently be affected by such releases, the commitment to controlling and minimizing environmental releases from lignite utility landfills and operating surface impoundments is obvious from an environmental and political standpoint.

CONCLUSION:

Environmental concerns, economic and social considerations and increasing regulatory impacts are the predominant factors that have affected the attitudes, philosophies, perspectives and ultimately the changes that have occurred in solid waste management activities at lignite utilities in the state of Texas. Once an activity governed by pure geotechnical and civil engineering disciplines, such solid waste practices now incorporate an interdisciplinary approach with a conscious effort to integrate engineering with hydrogeology, geophysics, soil, water and leachate chemistry, computer modeling, social climates, and regulatory affairs. As solid waste management at these facilities continues to focus on the potential impacts to valued ground- and surface-water resources, it is increasingly important to expand our understanding of the complexities of lignite combustion waste leachate chemistry and the dynamics of leachate migration, in addition to pursuing markets for recycling these combustion wastes in an effort to minimize, to the extent possible, the amount of waste to be disposed.

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PHYSICAL-CHEMICAL COMPOSITION OF LIGNITE COAL ASH: A REVIEW

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ABSTRACT

The combustion of Texas and North Dakota lignite coal results in an ash consisting of essentially inorganic glassy, spherical particles. (The organic content is <<0.1%.) Physical properties, species solubility, and elemental and mineral composition are documented. The ash contains numerous minerals, quartz being the dominant mineral. The flue ash particles are 5 to 100 μm in diameter, relatively richer in gallium, lead, selenium, and zinc compared to the 100 to 10,000 μm bottom ash particles. The solubility of inorganic constituents in the lignite ashes is a measure of the leaching potential. The extractor species greatly influences the elemental concentrations in the extracts. For example, ash elemental concentrations in nitric acid extracts are typically a few orders of magnitude higher than in hot water extracts. Sulfate and calcium are the most abundant species observed in hot water and nitric acid extracts, respectively. A comparison of the toxicity characteristic leaching procedure (TCLP) versus the existing extraction procedure (EP) shows notable differences only for iron extract concentrations.

INTRODUCTION

Lignite coal is burned in utility boilers to generate electricity. Power plants (approximately 30 units of 20 to 1,000 MW size generation capacity) that burn lignite coal as their principle fuel are located in four states (Minnesota, North Dakota, South Dakota, and Texas). Their total generating capacity is 11,000 MW. The lignite coal as mined contains 35-40% water and 6-9% "mineral" matter (ash) (1). Lignite coal has a relatively lower heat value (i.e., 22,000 to 24,000 Btu/kg on a dry-weight basis) (1). As a result of lignite coal-combustion in

electric utility boilers, lignite ash is generated. At some power plants removal of sulfur (scrubbing) from flue gas produces flue-gas desulfurization (FGD) sludges. This paper summarizes the physical-chemical composition of lignite ash based on the literature and recent data from continuing EPRI research under the Solid Waste Environmental Studies project (EPRI Research Project 2485) (2).

Increased interest in the lignite ash comes from issues raised by solid-waste disposal management requirements under the Resource Conservation and Recovery Act (RCRA). Regulators under RCRA are examining the release, migration, and changes in groundwater quality owing to land disposal of solid wastes. Most of the lignite ash at electric power plants is disposed of in landfills, ponds, or as backfill in mines. To address the release and migration of chemicals to groundwater from these disposal units, it is necessary to know the physical-chemical composition of the lignite ashes.

PHYSICAL PROPERTIES:

Coal combustion ash has been categorized into two groups: (1) "fly ash" which accounts for the majority of the ash generated and consists of smaller size particles of unburned mineral matter less than 1% of which is emitted into the atmosphere as fly ash with the remainder generally collected as flue ash by a baghouse or an electrostatic precipitator (ESP), and (2) bottom ash which is collected at the bottom of the furnace, consisting of much larger size particles. This paper will not cover the fly ash emitted into the atmosphere. The term "flue ash" will be used when referring to the ash collected by a baghouse and ESP although "fly ash" has also been used in the literature to mean this type of ash. Most ash particles are glassy and spherical, indicative of their prior molten state in the boiler. Some particles are solid, some are hollow, having an average density of 2.5 g cm^{-3}.

Some particles are magnetic owing to dendritic iron oxide, and the ash is a good electrical insulator ($\sim 10^9$ ohm cm^{-1}). Coal ash may possess pozzolanic and cementitious characteristics if its siliceous--aluminous content is mostly noncrystalline (glassy). An important physical characteristic of coal ash is its particle size. Available data indicate that bottom ash particles have diameters 100 to 10,000 μm. Most flue ash particles have diameters 5 to 100 μm whereas fly ash particles are typically 0.05 to -5 μm aerodynamic diameter (3-5). Figures 1 and 2 are scanning electron micrographs (SEM) showing morphology of flue ash from the P1 plant. Figures 3 and 4 are the corresponding SEM for bottom ash from the P1 plant.

Another physical characteristic of the lignite ash is its permeability which is important in estimating water movement potential through the ash. Most bottom ashes have a permeability of 10^{-3} to 10^{-1} cm/s. Permeability of lignite flue ash appears to be around 10^{-6} to 10^{-7} cm/s. Through compaction and various fixation treatments the permeability of ashes can be further reduced.

ELEMENTAL COMPOSITION:

Total elemental concentrations are the most commonly measured composition descriptions. Both the lignite flue ash and the bottom ash contain aluminum, calcium, iron, silicon, magnesium, potassium, sodium and sulfur, each at >0.3% concentration. These elements generally occur in oxide forms and including oxygen, account for over 90% the mass. Table 1 shows the data on composition of flue ash and bottom ash from Texas and North Dakota lignite coals. The samples were analyzed by X-ray fluorescence (XRF). Generally, the lignite flue ash has higher amounts of K and Na, whereas the bottom ash is generally higher in Fe and Mg content. Aluminum, Si, and Ca concentrations are approximately the same in flue ash and bottom ash from lignite coals.

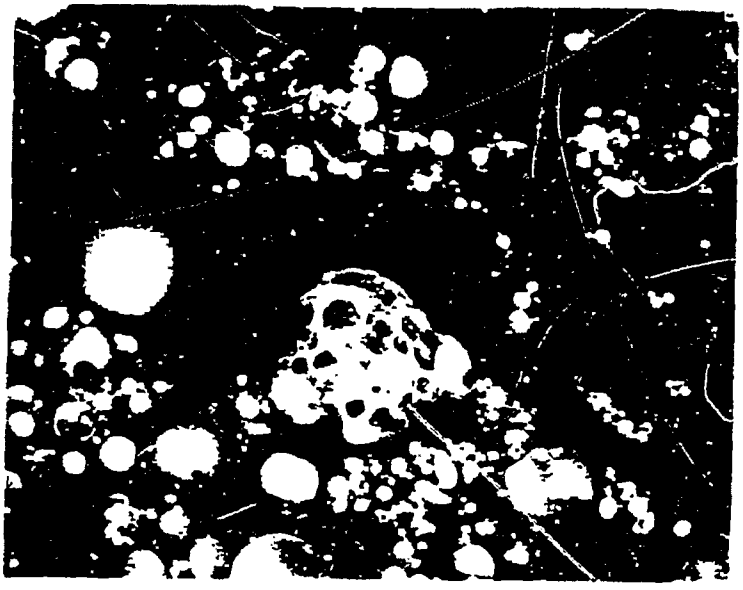

Figure 1: Microphotograph showing morphology of a flue ash sample from the P1 plant. (26.6 µm)

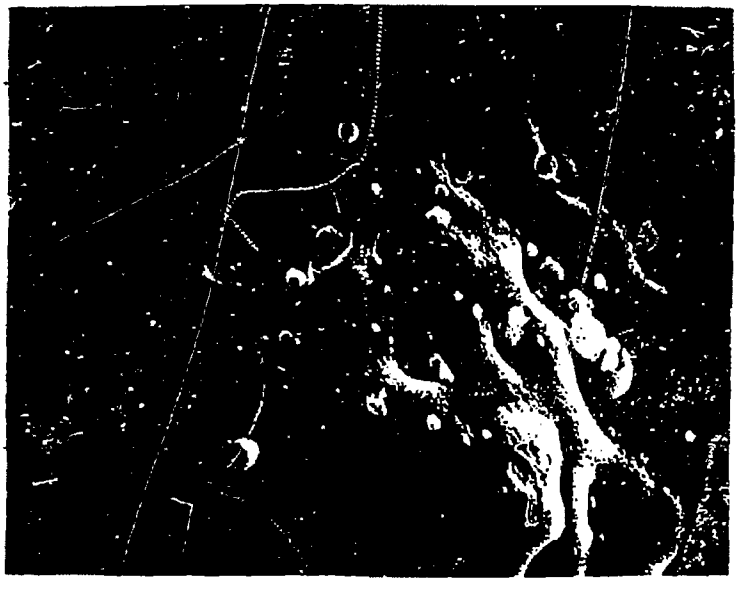

Figure 2: Micro photograph showing a typical flue ash particles morphology from the P1 plant. (6.6 µm)

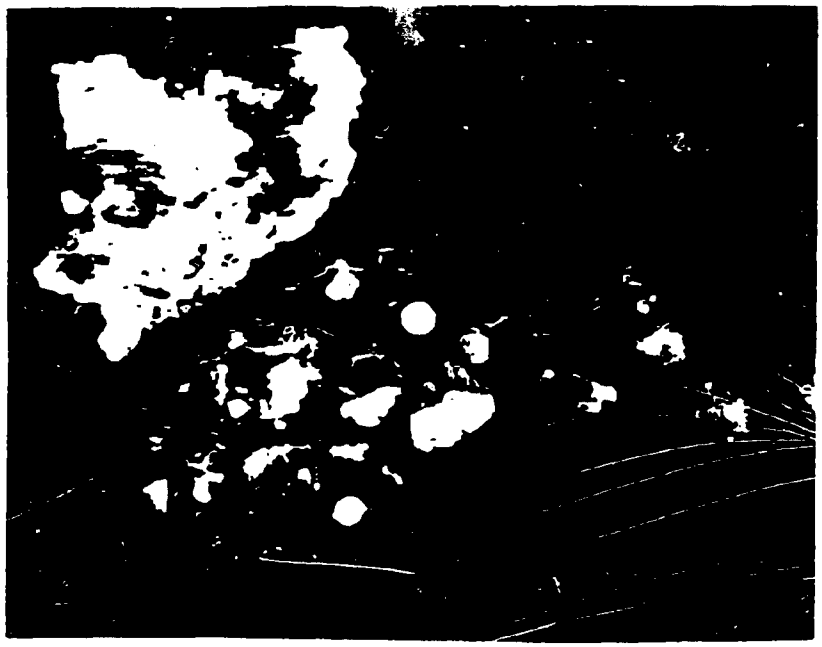

Figure 3: Microphotograph showing morphology of a bottom ash sample from the P1 plant. (20 μm)

Figure 4: Microphotograph showing a typical bottom ash particles morphology from the P1 plant. (6.6 μm)

Elements present in trace concentrations (by XRF) in these ash samples are illustrated in Table 2. The following differences in abundance of these elements in flue ash and bottom ash are observed:

- As, Ga, Pb, Se, and Zn concentrations are higher in flue ash than in bottom ash.

- Zr concentration is somewhat lower in flue ash than in bottom ash.

- The botton ash from one power plant had much higher concentration of Cr and Ni than that of the other four power plants sampled.

For elements that were not observed, their concentration values are listed as less than a detection limit. The detection limit is determined by standard addition and varies owing to matrix effects. The X-ray fluorescence technique used could not detect elements having atomic number <11.

CRYSTALLINE PHASES

Coal ash consists of crystalline and noncrystalline (amorphous) phases. The crystalline phase composition is often referred to as the "mineralogy" of the ash analogous to the naturally occurring minerals [although some "mineralloids" are not crystalline; e.g., opal and chalcedony, $SiO_2(H_2O)_x$] (6, 7). The crystalline phase composition of lignite coal ash is illustrated in Table 3 (8, 9).

CHEMICAL COMPOSITION OF AQUEOUS EXTRACT:

It is a common practice to examine the solubility of inorganic constituents in the lignite ashes to assess leaching potential of wastes. Many approaches have been used to obtain solution concentrations from solids extracted with a variety of liquids.

The lignite ash samples used in the XRF analyses summarized in Tables 1 and 2 were subjected to four different extraction tests in the laboratory. All extractions were made for a period of 18 to 24 hours. Table 4 shows a summary of the test methods. Tables 5 and 6 give the results on extract concentrations for selected elements.

These data clearly show that depending on the extraction medium, one can get very different elemental concentrations for the extracts. Nitric acid is the strongest extractor of the group yet, even nitric acid did not always dissolve the entire solid phase. The hot water extract concentrations should be interpreted as the release amounts which are most likely to occur over several decades of a landfill operation where lignite flue ash or bottom ash may be deposited. The U.S. EPA prescribed procedures yield solution concentrations which are generally lower than the nitric acid extraction medium and are comparable to the hot water extraction medium. The following are general conclusions on the leachability of inorganic constituents from lignite coal ashes:

- When compared to Texas coal bottom ash (TCBA), the North Dakota coal bottom ash (NDCBA) is relatively higher in leachable Na and SO_4^{2-}. Considering only hot H_2O extractor, the NDCBA is relatively higher in leachable Al, B, and K, but is relatively lower in leachable Mg. Considering only HNO_3 extractor, the NDCBA is relatively higher in leachable As and Cr.

- Considering only hot H_2O extractor, the TCBA has relatively higher leachable Fe than the Texas coal flue ash (TCFA). The opposite is true for B.

- Solutions from hot H_2O extraction of Texas and North Dakota lignite ash have low concentrations of Fe, Ti, As, Ba, Cd, Co, Cu, Pb, Mn, Ni, and Zn.

- Solutions from HNO_3 extraction of Texas and North Dakota lignite ash have low concentrations of Cd and Pb.

- Sulfate is the most abundant species observed in hot H_2O extracts from both the Texas and North Dakota lignite ash.

- HNO_3 dissolves essentially all the Ca from Texas and North Dakota lignite ash. Ca is the most abundant species observed in HNO_3 extracts.

- A comparison of TCLP versus EP shows notable differences only for Fe extract concentrations.

SUMMARY AND CONCLUSIONS

This paper has reviewed the physical, chemical, and leaching characteristics of inorganic constituents from lignite coal ash produced at electric power plants. The lignite ash is essentially an inorganic earth-like material (organic content <<0.1%) conisting of glassy spherical particles containing numerous minerals. Quartz is the dominant mineral. The flue ash consists of 5 to 100 µm particles relatively richer in Ga, Pb, Se, and Zn compared to the 100 to 10,000 µm bottom ash particles. Sulfate and Ca are the most abundant species observed in hot H_2O and HNO_3 extracts, respectively. A comparison of TCLP versus EP shows notable differences only for Fe extract concentrations.

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Table 1: Total Elemental Composition (%) for Dominant Constituents in Lignite Flue Ash and Bottom Ash Samples

Element	Texas Lignite						North Dakota Lignite			
	Flue Ash			Bottom Ash			Flue Ash		Bottom Ash	
	P1*	P2	P3	P1	P2	P3	P4	P5	P4	P5
Aluminum	9.32	10.47	11.59	5.88	7.34	8.94	7.22	6.7	7.22	6.29
Silicon	21.5	24.9	27.5	28.4	25.4	32.9	10.26	15.8	9.73	20.8
Calcium	11.47	8.19	7.41	7.13	5.93	5.01	18.69	14.9	17.67	16.1
Iron	10.27	4.79	2.52	13.37	5.95	1.96	5.43	3.21	8.96	8.25
Magnesium	2.25	1.97	1.36	1.55	1.5	1.08	3.98	4.18	3.35	4.55
Potassium	1.00	1.43	0.76	0.80	1.03	0.78	0.72	0.92	0.55	0.48
Sodium	0.78	0.82	0.57	0.49	0.52	0.31	6.25	4.75	4.13	2.11
Sulfur	0.59	0.28	0.13	0.06	0.97	0.05	6.23	4.66	4.4	<0.04
Phosphorus	<0.11	<0.10	<0.10	<0.09	<0.09	<0.08	0.55	0.36	0.46	<0.13
Titanium	0.69	0.71	0.95	0.54	0.62	0.75	0.65	0.60	0.59	0.69

Measurements made by X-ray fluorescence.
Mg and Na were measured by acid digestion followed by Atomic Absorption Spectroscopy.
*P1 = Plant 1, P2 = Plant 2, P3 = Plant 3, P4 = Plant 4, P5 = Plant 5.

Table 2: Total Elemental Composition (mg/kg) for Additional Elements in Lignite Flue Ash and Bottom Ash Samples

Element	Texas Lignite						North Dakota Lignite			
	Flue Ash			Bottom Ash			Flue Ash		Bottom Ash	
	P1	P2	P3	P1	P2	P3	P4	P5	P4	P5
Arsenic	55	48	20.7	9.7	10	2.2	95.7	52.4	36.5	2.8
Barium	2610	2230	1260	2850	1730	816	10850	4770	9360	7700
Cadmium	<6.7	<7	<6	<8.1	<6.4	<7.7	<7.6	<6.3	<6.6	<6.6
Cerium	94	69	76	71	57	71	62	81	55	55
Chromium	651	90	113	95	105	122	<46	<36	<48	4710
Copper	214	138	132.4	115.4	69.6	69.7	63.5	110.6	47.7	82.4
Gallium	29.8	33.9	44.9	9.3	11.9	16.5	26.9	40.9	11.4	12.3
Lanthanum	52	66	69	40	42	36	61	58	48	69
Lead	58.3	43.2	63.8	12.9	10	16.1	39.1	76.4	9.5	<4.2
Manganese	365	801	573	154	681	479	960	1332	908	1684
Molybdenum	16.6	12.4	14	4.3	5	6.3	7.7	19.7	<2.8	45.5

Table 2: Total Elemental Composition (mg/kg) for Additional Elements in Lignite Flue Ash and Bottom Ash Samples

--Continued--

Element	Texas Lignite						North Dakota Lignite			
	Flue Ash			Bottom Ash			Flue Ash		Bottom Ash	
	P1	P2	P3	P1	P2	P3	P4	P5	P4	P5
Nickel	309	72.2	44.5	106	86.9	68.8	44	33.8	43	1267
Niobium	16.8	19	33	14.4	18.8	30.8	17	17.4	18.1	21.2
Rubidium	39.7	65.3	37.8	30.5	46.1	38.1	<6.3	30.2	<5.7	9.3
Selenium	46.9	21.6	9.5	<1.6	9.0	<1.4	10.7	14.2	2.1	<1.8
Silver	<6.4	<6.4	<5.5	<8	<6	<7.3	6.9	<5.9	<6.9	7.1
Strontium	2910	2520	1400	1898	1812	840	6820	4720	6440	4600
Vanadium	182	178	268	<67	151	263	<110	<87	<100	<100
Yttrium	97.2	50.4	56	79.4	38.4	50.2	43.6	41.7	41.2	44.4
Zinc	127.2	82	57.5	38.5	28.8	18.6	32.2	24.8	14.6	3.8
Zirconium	249	258	331	330	333	411	117.5	207	149	323

Measurements made using X-ray fluorescence.

Table 3: Crystalline Phase Composition of Lignite Coal Ash in Order of Decreasing Concentration

Phase	Chemical Formula
Quartz	SiO_2
Periclase	MgO
Tricalcium aluminate	$Ca_3Al_2O_6$
Merwinite	$Ca_3Mg(SiO_4)_2$
Ferrite spinel	$(Mg,Fe)(Fe,Al)_2O_4$
Anhydrite	$CaSO_4$
Lime	CaO
Dicalcium silicate	Ca_2SiO_4
Melilite	$(Ca,Na,)_2(Mg,Fe^{3+},Fe^{2+},Al,Si)_3O_7$

Note: Quartz and ferrite spinel are common to all coal ashes. Mullite, $Al_6Si_2O_{13}$, is characteristic of bituminous and some sub-bituminous coal ashes. Melilite is essentially a solid solution of gehlenite, $Ca_2Al_2SiO_7$, and åkermanite, $Ca_2MgSi_2O_7$, including minor constituents such as Fe, K, Ti, Mn, and H_2O.

Table 4: Summary of Extraction Methods Used

	HNO_3 Extraction	Hot H_2O Extraction	EP	TCLP
Extraction Solution Used	Concentrated Nitric Acid	Deionized Distilled Water	Deionized Distilled Water	0.1N sodium acetate buffer solution for nonalkaline wastes and 0.1N acetic acid solution for alkaline wastes. Solution based on an alkalinity test.
Extraction Medium pH	<0.5	7	pH adjusted to 5.0 if initial waste-extract mixture >5.0	5 for the buffer solution 2.9 for the actic acid solution
Solid/Liquid Ratio	1/20	120	1/20	1/20
pH Adjustment During Extraction	Not adjusted	Not adjusted	Adjusted at 5.0±0.2 with 0.5N acetic acid at an interval of 15-45 min. pH adjustment made until a maximum of 400 mL of acid has been used up	Not adjusted
Equipment Used	Teflon Paar autoclave	Teflon Paar autoclave	Rotary mixer ≥40 rev./min or blade stirrer	Rotary mixer (end-over-end), 30±2 rev./min.
Time Used	18h	6h	24h	18h
Filtering at the end of Extraction	0.22-μm membrane	0.22-μm membrane	0.45-μm membrane filter	0.6 to 0.8-μm prerinsed glass fiber filter
Physical Preparation of Samples for Extraction	Crushed and screened to pass through 0.044-mm mesh	Crushed and screened to pass through 0.149-mm mesh	Crushed and through 9-mm mesh	Crush and Screen to pass through 9-mm mesh
Extraction Temperature	105°±2°C	105°±2°C	20°-40°C	22°±3°C

Table 5: Major Species Concentrations Range (mg/kg) in Extracts Obtained With Different Methods

Chemical "Species"	Texas Lignite				North Dakota Lignite			
	Flue Ash		Bottom Ash		Flue Ash		Bottom Ash	
	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract
Aluminum	54.8-514	38000-53500	14-75	24000-38750	296.8-440	57200-65000	61-852	58000-64200
Silicon	25.8-176.2	20-658	264-596	265-408	38.2-54	458-1590	29-250	146-856
Calcium	1536-4380	47750-86500	432-3640	21600-58500	4600-7200	127000-131600	434-3536	127400-150800
Iron	0.1-0.22	11525-61000	0.2-36.8	5360-56750	.32-.4	21600-39800	<.1-0.3	54800-55400
Magnesium	.66-1.28	8250-18175	1-434	3200-12725	<1	35800-36800	<1	29000-42200
Potassium	42-85	512.5-2880	20-74	426-1175	1472-1664	3220-3420	16-624	1980-2460
Sodium	117.8-334	1085-2440	52-110	614-2130	16920-40160	37800-65800	170-17240	19480-42400
Sulfate	2800-5840	N/A	300-9180	N/A	39100-71620	N/A	316-37140	N/A
Titanium	0.02-0.08	1928-2252.5	<.02-.20	796-1832.5	<.02-0.08	1720-1770	<.02	1560-1950

N/A = Not Available

Table 6: Additional Species Concentrations (mg/kg) and pH Range in Extracts Obtained With Different Methods

Chemical "Species"	Texas Lignite				North Dakota Lignite			
	Fly Ash		Bottom Ash		Fly Ash		Bottom Ash	
	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract
Arsenic	<2-3.98	N/A	<2-3	N/A	2.6-7.0	N/A	<2-6	N/A
Barium	1.9-14.2	722.5-1695	.9-11.68	266-1922.5	4.3-4.6	3880-4880	2.3-6.3	2520-5880
Boron	135.2-364	660-1980	9.7-49.2	102-758	543.2-1648	1780-3740	14-543.2	1132-1356
Cadmium	<0.04-.06	2.25-6.25	<0.04-0.06	<.4-1.75	<.04	5.2-9	<.04	5.2-8.2
Chromium	2.4-19.2	71-92	<.2-92	19-61	11-47.8	44-49	<.2	54-1034
Cobalt	<.08-.14	11.25-37	<.08-.60	3.6-15.75	<.08-.32	10.8-15.4	<.08	12.8-24
Copper	<.08-.2	51-113	<.08-.10	17.6-68.75	<.08-.4	41-52	<.08	36.8-51.2
Fluoride	5.6-26.6	N/A	2-3	N/A	14.-18.4	N/A	1-2	N/A
Lead	<1.2	<12	<1.2	<12	<1.2	<12	<1.2	<12-200
Lithium	3.22-4.26	38-66	.50-2.76	24-50	16.4-16.5	102-114	.78-6.48	88.8-127.8
Manganese	0.02-4.04	255-500	.04-22.8	167-206	<.02-.08	758-914	<.02-.04	686-1160

Table 6: Additional Species Concentrations (mg/kg) and pH Range in Extracts Obtained With Different Methods

--Continued--

Chemical "Species"	Texas Lignite				North Dakota Lignite			
	Flue Ash		Bottom Ash		Flue Ash		Bottom Ash	
	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract	Hot H_2O Extract	HNO_3 Extract
Molybdenum	3.68-5.12	11-19	<.2-1.0	<2-11	6.7-15.3	16-23	<.2-3.7	14-34
Nickel	<.2	18-79	<.2-1.9	5-61	<.2	30-39	<.2	37-490
Strontium	28.8-174.8	920-2380	3.9-53.2	360-1598	262.4-432	4120-5460	13.9-146	4000-4660
Zinc	<.2	7-85	<.2-.7	7-41	<.2	24-37	<.2	23-24
pH	10.8-11.6	N/A	4.33-10.5	N/A	11.8-12.1	N/A	10.7-11.7	N/A

Table 7: Elemental Concentrations (mg/L) Obtained Through EP & TCLP Extractions of Texas Lignite Coal Ashes

Element	Flue Ash				Bottom Ash			
	EP		TCLP		EP		TCLP	
	P2	P3	P2	P3	P2	P3	P2	P3
As	<0.08	<.08	<.08	<.08	<.08	<.08	<.08	<.08
B	38.3	13.5	35.3	13.4	1.2	0.3	1.0	0.35
Ba	0.55	0.6	0.49	1.17	0.09	0.11	0.19	0.24
Ca	695	302	610	323	101	34	78	39
Co	<.01	<.01	<.01	<.01	<.01	<.01	<.01	0.62
Cr	<.02	0.25	0.22	04	<.02	<.02	<.02	<.02
Cu	<.004	0.10	<.004	0.21	<.004	<.004	<.004	<.004
Fe	0.72	0.15	0.05	3.16	2.15	<.005	0.49	0.26
Mg	92.8	34	69	38	16.6	2.3	14	3.11
Mn	1.47	0.65	0.99	0.87	0.79	0.32	0.59	0.50
Ni	<.02	<.02	<.02	<.02	<.02	<.02	<.02	<.02
Pb	<.06	<.06	<.06	<.06	<.06	<.06	<.06	<.06
Sb	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Si	48.4	31.5	23	57	3.6	2.9	1.8	4.24
Sr	18.6	4.9	16.7	5.42	1.7	0.26	1.56	0.32
V	<.01	<.01	<.01	0.11	<.01	<.01	<.01	<.01
Zn	<.02	<.02	<.02	0.23	<.02	<.02	<.02	<.02

USE OF LIGNITE COKE FOR REDUCTION OF NOx AFTER FLUE GAS DESULPHURIZATION

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of Stadtwerke Düsseldorf AG, Düsseldorf,

A B S T R A C T

To meet the government regulations with their stringent limits for the SOx, NOx, HCl, HF, CO, CH flue gas emissions, but also the cancerogenous substances including heavy metals as particles and in their vapour state an effective, simple handling and efficient system for mainly medium and small sized power plants, district heating plants, refuse incinerators etc. up to 300 MW electric output could be developed. For the 80 to 90 % decrease of the acidic components in the flue gas the "Spray Drying System Düsseldorf" has be applicated in the meantime for more than 25 units of different sizes and a total of more than 3 million cubicmetres of flue gas. Especially in case of retrofitting this system is an optimal approach for the small space available in most of the elder existing plants. The usual denitrification by oxygen reduction, overfire air etc. decreases the content of NOx for coalfired boilers at least to 50 %. Further, socalled secondary methods are necessary.

An optimal solution instead of a SCR NOx reduction seems to be the combination of a lignite coke filter and catalyst. This type of a multistage filter coupled with the spray drying system, filters the rest of solids, adsorbes (the rest of) the acidic components, the vaporous heavy metals, the carbon hydrates etc.

After adding ammonia to the flue gas the coke coal then works as a catalyst for the NOx-reduction at temperatures of about 80 to 100 deg. C, that means without any expensive reheating, as known from the metal typ SCR-catalysts. The lignite coke is an uncomplicated, unexpensive material, which will be burned as fuel after use. The coke consumption only depends on the amount of the acidic components in the flue gas (i.e. efficiency of the scrubber). The results measured up to now have shown that with lignite coke

1) the flue gas from a coalfired boiler can be completely desulphurized, whereby SO2 loadings of the coke of 10 - 15 % are to be achieved,

2) and a flue gas remaining for a period of 15 - 20 seconds it is possible to achieve NOx reductions of 80 - 90 %,

3) the NOx content in the clean gas varies between 150 and 250 mg/m^3n.

1. Introduction

After desulphurization of the flue gases in their power stations the next step to be taken by Stadtwerke Düsseldorf in the chemical cleaning of the flue gases is the reduction of the nitrous oxides.

The municipal utility of Düsseldorf is operating different test units for NOx-reduction, SO2 and heavy metals (especially mercury) removal by means of coke coal. The experiments were carried out with activated coke coal manufactered by Bergbauforschung, Essen and lignite coke coal manufactered by Rheinbraun, Köln.

The first result of these investigations was, that the Denox-process with activated coke coal is expensive, because sulfur, fly ash and heavy metals in vapour state are removed from the gas by the coke coal as a secondary effect causing a drop of denitration activity. Therefore a regeneration of the activated coke coal is necessary.

The disadvantage of the regeneration is the high cost for the regeneration process, the chemical loss of carbon and the mechanical loss of coke coal (abrasion). To reduce the costs for the flue gas cleaning low cost lignite coke coal with costs of 10 % of the activated coke coal was tested.

2. Concept for cleaning the flue gases at the Lausward and Flingern power stations

When taking account of all flue gas cleaning processes the use of the lignite coke technique results in a 5-stage flue gas system for the slag tap firing used by Stadtwerke Düsseldorf (Figure 1):

Stage 1: Electrofilter for fly ash precipitation

Stage 2: Flue gas desulphurization

Stage 3: Electrofilter for precipitation of desulphurization products

Stage 4: Residual desulphurization by lignite coke

Stage 5: Denitrification with NH3 and lignite coke as catalyst

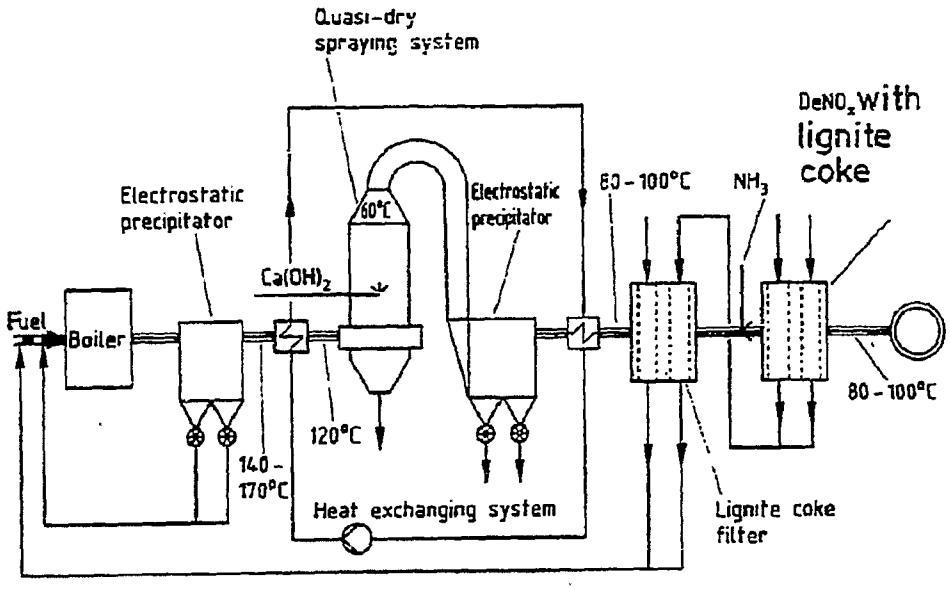


Fig.1 : Flue gas cleaning process

As shown in Figure 1, the fly ash is firstly precipitated in an electrofilter and then fed back to the furnace and completely retained in the molten clinker. This return of the fly ash also ensures the utilization of the 20-30 % proportion of unburnt carbon that remains in the fly ash. Furthermore, this system dispenses with the problem of fly ash disposal.

The second stage consists of desulphurization of the flue gas. The principle of the quasi-dry process is that a suspension of hydrated lime is sprayed into the flue gas stream within a reaction section. The reaction of the SO2 with the hydrated lime primarily produces calcium sulphite and calcium sulphate which are then precipitated in a downstream electrofilter. The degree of desulphurization is between 85 and 90 % so that the SO2 content in the flue gas varies between 200 and 400 mg/m^{3}n.

The desulphurized flue gas then passes to the socalled Denox plant, which is made up of two stages. The residual SO2 contents (200-400 mg/m^{3}n) and dust (approximately 50 mg/m^{3}n) are completely adsorbed in the first stage. This adsorbation process is necessary because the residual SO2 content and dust so heavily load the activated coke in the catalyst stage that very soon it functions no longer as a catalyst. In the second Denox stage, after addition of ammonia the gas is passed through lignite coke, whereby, depending on the entering concentration of NOx

and the dwell time, it is sought to achieve 80 to 90 % denitrification in order to maintain the extreme NOx value of 200 mg/m³n.

3. Denox - reactor

The Denox-reactor, produced by firm Krantz, consists of a number of filter beds arranged one above another (Figure 2).

The flue gas firstly passes through the bottom filter bed, then enters a reversing chamber and passes through the next bed.

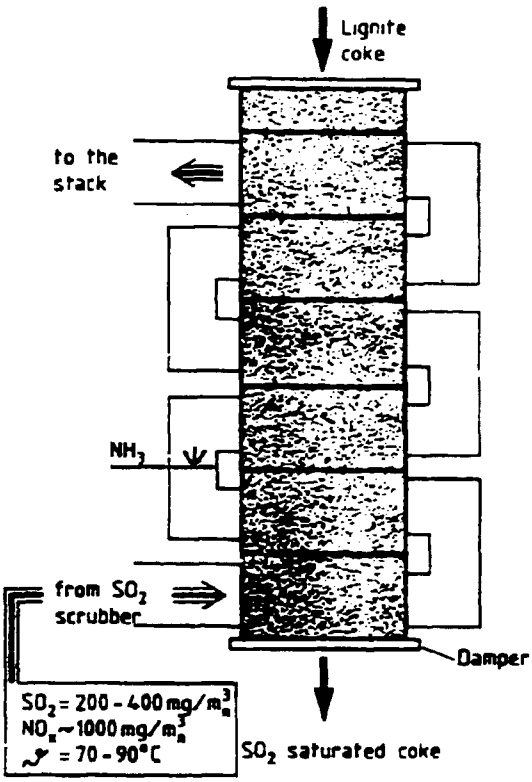


Fig 2: $DeNO_x$ Krantz system

The 200-400 mg/m³n concentrations of SO2 entering the reactor are removed from the flue gas in the 2 lower filter beds through adsorption by the coke. After complete removal of the SO2, gaseous ammonia (NH3) is added to the gas in the 2nd reversing chamber so that the nitrous oxides are catalytically reduced in the four upper filter beds.

3.1 Test plant in the Lausward power station

Figure 3 shows a schematic layout of this test plant, which is built up in accordance with the Krantz system. This plant was installed downstream of a slag tap furnace in order to investigate the Denox characteristics of lignite coke with high concentration of NOx in the entering gas.

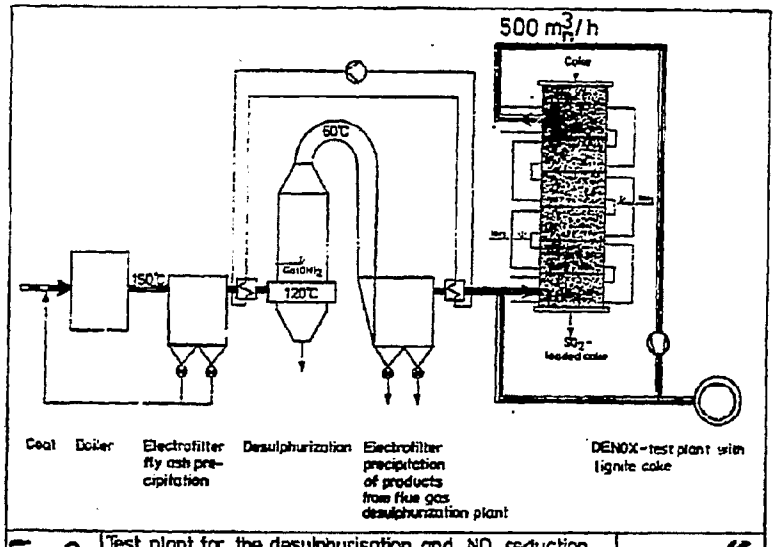


Fig. 3 Test plant for the desulphurisation and NO_x reduction of flue gases with lignite coke

The 6-stage Denox reactor operates on the cross counterflow principle, with the residual desulphurization of the flue gas taking place in the lower filter beds. After the addition of ammonia in the 2nd reversing chamber the nitrogen is extracted in the upper four beds. The control parameter for the movement of coke through the reactor from top to bottom is the SO2 content after the second stage.

As soon as SO2 is measured at this point, coke is discharged at the lower end of the reactor so that SO2-free material settles into the 2 lower filter beds.

4. Lignite coke for flue gas cleaning

Lignite coke is produced in the Federal Republik of Germany from Rhineland brown coal by the so-called hearth furnace process. The current production capacity is 230.000 t/year. The fine-grained lignite coke basically differs from activated char coal not only with respect to the production process but also in its properties. The special properties of Rhineland brown coal, namely, high reactivity, low sulphur content and a basic ash, are also characteristic features of the lignite coke.

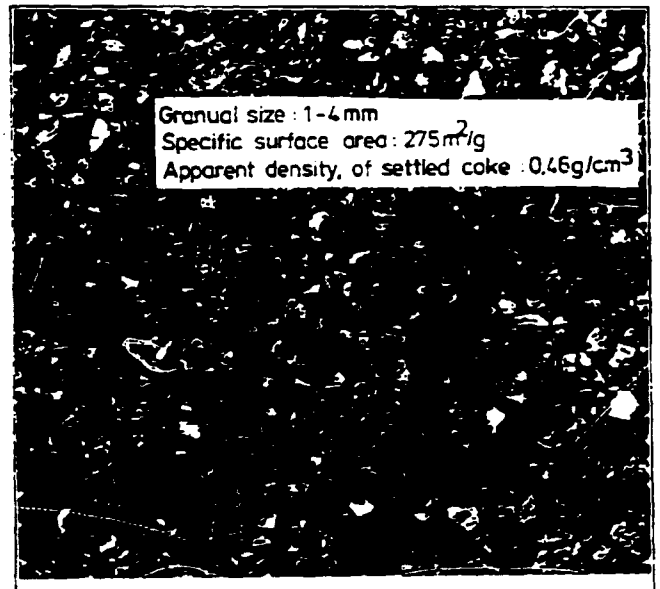


Fig. 4 Lignite coke for flue gas cleaning

Figure 4 shows the grain fraction of lignite coke that can be used for flue gas cleaning. It can be seen from this figure that

the lignite coke is produced without any preceding shaping process. The irregulary shaped grain produced by the coking of dry brown coal is used in the flue gas cleaning without any further treatment. The surface area of 275 m^2/g denotes the high surface activity of the product.

Figure 5 shows additional physical and chemical characteristic data for the material. In addition to the very low water content of 0,5 % wt. and the 3,5 % wt. of volatiles that essentially consist of CO2, special attention is to be drawn to the basic ash.

Flash analysis		
	Water content	0,5 % wt.
	Ash content	9,0 % wt.
	Volatiles	3,5 % wt.
	Calorific value	29 800 kJ/kg
Elemental analysis		
	C	87 %wt.
	H	0,7 %wt.
	O	2,1 %wt.
	N	0,6 %wt.
	S	0,45 %wt.
Oxide analysis of the ash		
	SiO_2	9,5 %wt.
	Fe_2O_3	15,0 %wt.
	Al_2O_3	5,0 %wt.
	SO_3	13,5 %wt.
	CaO	41,0 %wt.
	MgO	14,0 %wt.
	Na_2O+K_2O	2,0 %wt.

Fig.5 Analytical reference values for lignite coke

Up to now, lignite coke has mainly been used for the sintering of dolomite, various metallurgical processes, lime burning and waste water purification. Its use for flue gas cleaning opens up new and wide field of application.

5. Results

5.1 SO2 adsorption of lignite coke

Lignite coke adsorbs SO2 from the flue gas and catalytically oxides it to sulphuric oxid which is not only retained in the coke through adsorption but partically through chemical combination (Figure 6).

$$SO_{2(Gas)} \longrightarrow SO_{2(ad)}$$

$$2SO_{2ad} + O_2 + 2H_2O \longrightarrow 2H_2SO_{4ad}$$

Partially

$$H_2SO_{4ad} + CaO_{(Ash)} \longrightarrow CaSO_4 + H_2O$$

Fig. 6	Loading capacity of lignite coke 15 - 20% wt. H_2SO_4 ≙ 10 - 15% wt. SO_2	

Slightly dependent on the SO2 content in the flue gas, the maximum loading capacity of lignite (coke) determined under laboratory conditions amounts to approximately 25 % wt. sulphuric acid, which corresponds with over 16 % wt. SO2. Nevertheless, the prerequisite for this high loading is a very long life of the coke bed, which is not possible to achieve in practical use. The practicably realizable dwell times of 6-10 s with approach flow rates of 0,1-0,15 m/s result in lower SO2 loadings. The following operating conditions in the plant at the Lausward power station produced 10 to 12 % SO2 concentrations in the coke:

SO2 concentration on entry	approx. 400	mg/m³n
SO2 concentration on exit	0	mg/m³n
Flue gas temperature	90	°C
Depth of bed in coke reactor for residual desulphurization	0,6 - 1	m

5.2 NOx reduction with lignite coke

In these tests the residual desulphurization of the flue gas took place in the bottom or the 2 lower filter beds. NH3 was then added to the SO2-free gas in the first or second reversing

chamber so that the nitrous oxides were broken down into N2 and H2O in the upper filter beds:

$$6\ NO + 4\ NH_3 \longrightarrow 5\ N_2 + 6\ H_2O$$
$$2\ NO_2 + 2\ C \longrightarrow 2\ CO_2 + N_2$$

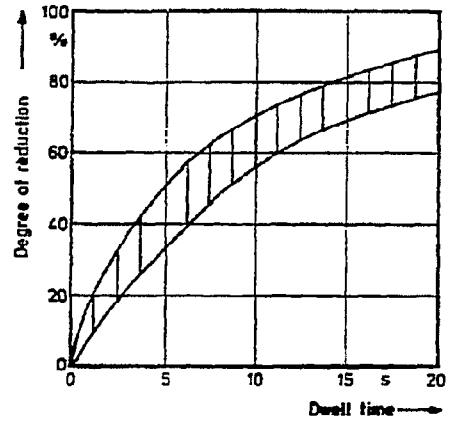


Fig. 7 Degree of NO_x reduction for lignite coke in relationship to the dwell time with initial NO_x concentrations between 800 and 1200 mg/m³

Figure 7 clearly shows that in order to achieve high degrees of NOx precipitation with lignite coke it is necessary to have long dwell times. In order to achieve 80-90 % precipitations with this catalyst material it is necessary that the flue gas remains in the coke filter for approximately 20 seconds. This results in the fact that, with flue gas flow rates of approximately 0,13 m/s, lignite coke catalysts must have filter bed depth of approximately 2,5 m.

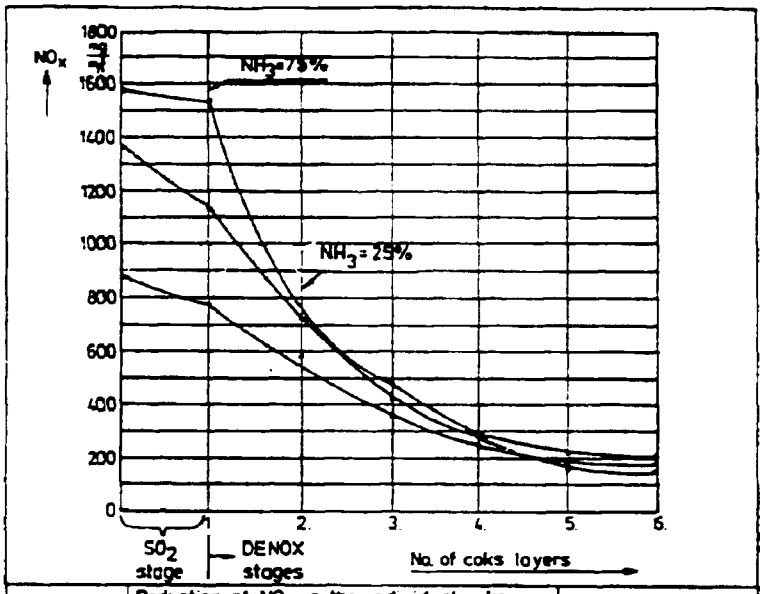


Fig. 8 Reduction of NO_x in the individual coke layers in the DENOX reactor

Figure 8 shows the curve of the NOx concentration in relationship to the bed depth and the number of coke layers in the 6-stage Denox plant at the Lausward power station.

In this case the bottom coke bed operated as the residual desulphurization stage and the 5 upper beds as denitrogenization, whereby the NH3 was added in the first reversing chamber. The first interesting fact to emerge from the test results is that, even without the addition of NH3, there is already a distinct reduction of NOx of 100 to 200 mg/m³n in the residual desulphurization stage. After the addition of NH3 the catalytic breakdown of NOx into N2 and H2O then follows in the upper five filter beds. The tests conducted up to now have resulted in NOx concentrations in the clean gas of around 200 mg/m³n with NH3 slip values of between 5 and 30 mg/m³n. Furthermore, it could be established that the NOx content in the clean gas is no affected by its content in the gas entering the system. Both with low NOx contents of approximately 800 mg/m³n and also with values of 1600 mg/m³n the NOx content on the exit side varied between 150 and 250 mg/m³n (Figure 9). Contrary to this, the figure shows that the degree of reduction of NOx is strongly dependent on the NOx concentration on entry. Whilst high initial NOx concentrations show a degree of precipitation of around 90 %, with low initial concentrations this figure drops to below 80 %.

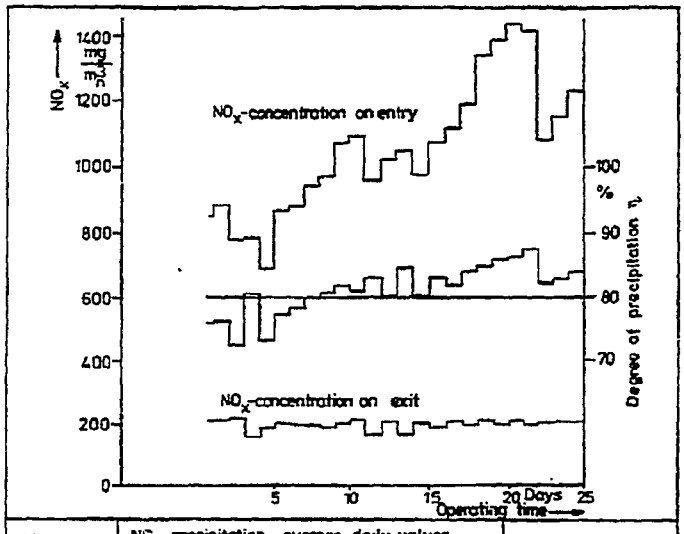
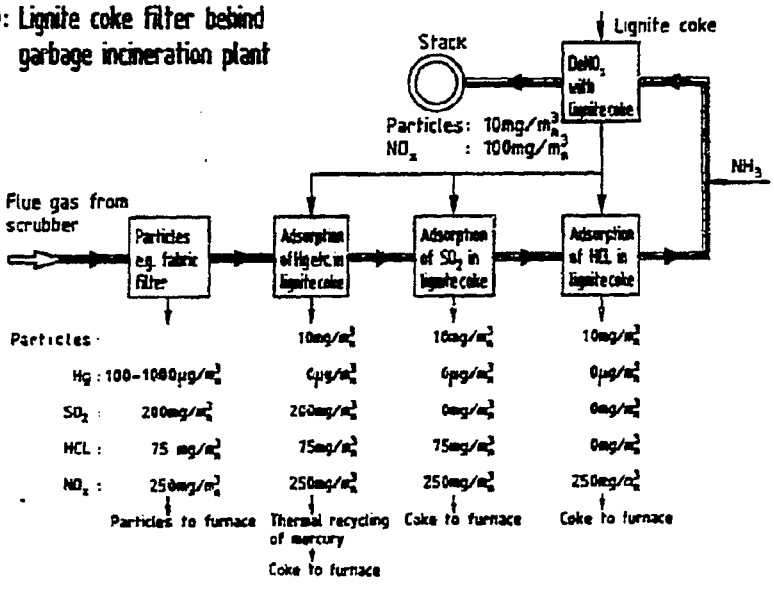


Fig. 9 | NO_x-precipitation - average daily values

5.3 More extensive flue gas cleaning with activated carbon

In addition to the reduction of NOx and the complete removal of SO2 the first tests with lignite coke established that this material also adsorbs other pollutants. A test plant in the Flingern refuse incineration plant proved that lignite coke simultaneously and almost completely removes gaseous and particulate heavy metals (e.g. Hg), halogen compounds (e.g. HCl), sulphur dioxide, ammonia and high molecular weight organic compounds (e.g. dioxines) from the flue gas (Figure 10).

Fig 10: Lignite coke filter behind garbage incineration plant



5.4 Operational experience, safety considerations

During the work with lignite coke a high measure of importance was accorded to technical safety aspects. No critical conditions have yet been experienced on the different plants during the approximately 3000 hours of operation. The feeding and removal operations were always carried out without any problems. Even operating conditions with very low throughputs of flue gas did not in any case lead to unusual temperature increases.

At the start, a low nitrate loading on the lignite coke in the denitrogenization section was looked on as being critical because it was feared that continous nitrate enrichment would occur here. A small part of the NOx contained in the flue gas is oxidized to nitrate, which is then combined in the lignite coke as calcium nitrate. Figure 11 shows a loading profile of SO2 and NO3 in the Krantz plant coke bed.

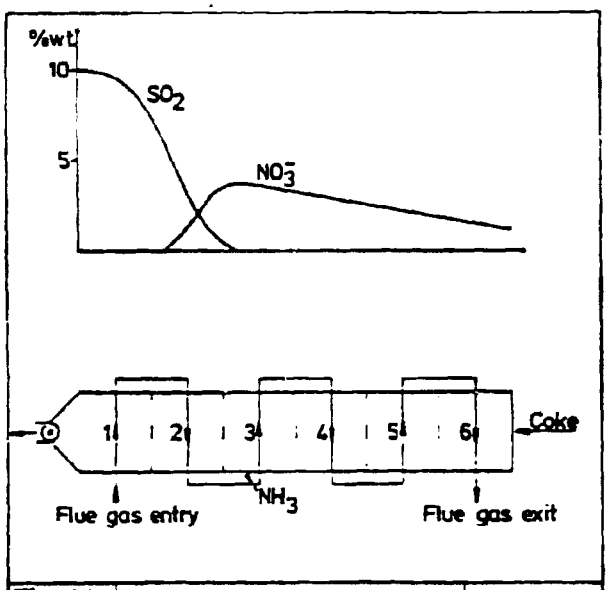


Fig.11 SO_2/NO_3^- loading profile

Continous tests over a number of months resulted in a max. of 2-3 % wt. concentration of NO3 in the first denitrogenization section is broken down by the sulphuric acid that is formed when the coke settles in the desulphurization section, so that nitrate-free coke is discharged from the plant.

Thermal tests in order to determine the self-ignition temperature showed that coke samples from the filter beds are substan-

tially less reactive than fresh coke. Whilst the self-ignition temperature of fresh coke in air is 200-220 °C, the measured temperature of the samples from the filter beds (also on samples with 3 % wt. NO3) was 250-300 °C (in air!). The self-ignition temperature of the coke in the flue gas atmosphere is considerably higher than 300 °C.

Combustion tests in the meantime carried with SO2 loaded lignite coke in the boiler plants in question have shown that there are no difficulties to be expected with the planned disposal of the material. According to these tests the lignite coke can be burnt not only in slag tap but also in travelling grate furnaces without any further grinding.

5.5 Dust measurements

The determination of the dust concentrations with the static bed operation after the coke reactors shows that the dust content in the clean gas varies from 0,5 to 10 mg/m³n, whereby the majority of measurements are below 5 mg/m³n. During the starting up of a coke reactor and during the discharge or movement of the packed coke bed there is a short term considerable increase in the dust contents in the flue gas. Because a large plant incorporates numerous coke reactors operating in parallel, these operating conditions are not expected to exceed the dust limits if only one reactor at a time is in the start up or coke discharge phase.

6. Operation costs

The data available up to now has been used to estimate the operating costs for a lignite coke catalyst for the denitrification of the coal fired boilers in a 4 x 150 MWe-power station, where an amount of around 900 000 t/a of black coal and around 75 000 t/a of lignite powder is fired. The lignite coke from the catalyst will substitute 30 000 t/a of low cost lignite powder. The operating cost calculation has been based on the data shown in Fig. 12.

1) Flue gas	2 mill. m_n^3/h
2) Operating time on maximum demand	5000 h/a
3) Flue gas behind scrubber	300 mg SO_2/m^3
4) Loss of pressure by catalyst	1300 Pa/m
5) Cost of ammonia	600 DM/t
6) Cost of lignite coke (catalyst)	226 DM/t; 30,200 kJ
7) Cost of lignite powder (fuel)	127 DM/t; 21,500 kJ
8) Difference of costs [(6) minus 7)]	30 DM/t
9) Consumption of lignite coke	30,000 t/a

a) Cost of lignite coke (for catalyst)	approx. 900,000 DM/a
b) Independent needs for flue gas ventilator	approx. 2,114,000 DM/a
c) Consumption of ammonia (= 800 mg NO_x/m^3)	approx. 1,778,000 DM/a
d) Maintenance and repairs	approx. 700,000 DM/a
Total	5,493,000 DM/a
Specific costs	0.21 pfennigs/KWh

e) Investment costs for 4 units each 500,000 m^3/h flue gas
200 DM/KW = approx. 120 mill. DM
= 0.7 pfennigs/KWh

Specific costs in total	approx. 0.91 pfennigs/KWh

Fig. 12: Operating cost calculation

When taking both the operating and capital investment costs together this then produces an additional power generation cost of around 0,9 Pfennings/kWh for this Denox process. By comparison with other Denox processes this cost calculation shows that lignite coke catalysts can be expected to involve by far the lowest increases in the costs for power generation.

7. Further proceedings

On the basis of the positive results of the measurements on the activated carbon Denox system it is planned to carry out trials in two demonstration plants. One at the Garath heating and power station for the full flue gas volume of 120.000 m^3n/h and the

other on one module at the Lausward power station with a flue gas volume of 7500 m^3n/h. The Lausward plant is planned for commissioning in May 1987 and that at Garath in October 1987.

The denitrogenization stages in both these demonstration plants will not only provide for the use of lignite coke but also activates carbon from Bergbauforschung Essen (BF). This is being considered on the basis of a combination of 80 % lignite coke and 20 % BF activated carbon. Initial tests in the technical study plant at the Lausward power station confirmed that the replacement of the lignite coke in the 6th packed bed of the Denox stage by Bergbauforschung D52/4 activated carbon reduced the NOx content in the clean gas from about 200 to 100 mg/m^3n.

MODIFIED COMBUSTION EMISSION CONTROL SYSTEM WITH SORBENT INJECTION DEMONSTRATION PLANT FOR NO_x/SO_2 REDUCTION FOR LIGNITE COAL

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Abstract

Since 1982, Saskatchewan Power Corporation and C-E Canada Power Systems have jointly conducted research to reduce NO_x and SO_2 emissions from steam generators firing lignite coal. This paper summarizes the previous results of this joint research effort and presents the results of a recent program to demonstrate a relatively low cost technology to control both NO_x and SO_2 emissions for low rank fuels on a full scale 150 MW lignite coal fired steam generator. Design considerations for Saskatchewan lignite coals are reviewed. The Modified Combustion Emission Control System with Sorbent Injection demonstration plant is described. The test program carried out with the demonstration plant using two Saskatchewan lignite coals, Boundary Dam and Shand, and two sorbents, limestone and pressure hydrated lime, is outlined. Test results are presented for NO_x and SO_2 emissions reduction and the effects of the demonstration plant on steam generator operation. The impact of these results on new lignite coal fired steam generator design is discussed.

MODIFIED COMBUSTION EMISSION CONTROL SYSTEM WITH SORBENT INJECTION DEMONSTRATION PLANT FOR NOx/SO2 REDUCTION FOR LIGNITE COAL

Introduction

Since 1982, Saskatchewan Power Corporation and C-E Canada Power Systems have jointly conducted research to reduce NO_x and SO_2 emissions from steam generators firing lignite coal. Results from research conducted in 1983 indicated that staged combustion could significantly lower NO_x emission levels from what is achieved with conventional tangential firing systems and that staged combustion could increase the utilization of alkali material inherent in the coal for SO_2 reduction (1). These results made it appear possible to combine staged combustion with furnace dry sorbent injection technology to create a system that would have the potential to reduce the NO_x emission of conventional tangential firing systems without overfire air by up to 75% and reduce the SO_2 emission by over 50% for steam generators firing low sulfur lignite coals.

In parallel with this effort the University of North Dakota was contracted by Saskatchewan Power to perform a series of pilot scale tests to ascertain the effectiveness of dry sorbent injection of various sorbents on several Saskatchewan lignite coals.

The results of this testing encouraged Saskatchewan Power Corporation and C-E Canada Power Systems to carry out a program to design, manufacture, install and test a demonstration plant to evaluate and optimize a "Modified Combustion Emission Control System with Sorbent Injection" for simultaneous NO_x and SO_2 emissions reduction.

This paper presents the results of the research performed at the demonstration plant and discusses the significance of these results on the design of new lignite coal-fired steam generators.

Previous NO_x/SO_x Reduction Research for Lignite Coals

From 1982 to 1984, research was conducted on Saskatchewan Power Corporation's Boundary Dam Generating Station Unit #6 to determine the effect of the C-E Concentric Firing System on NO_x emission, SO_2 capture by sorbents inherent to the coal ash, and the slagging behaviour of this furnace. As well, the effect of direct furnace injection of sorbent on SO_2 capture was also investigated.

The results of this research showed that the most influential parameters affecting NO_x reduction were primary air to fuel ratio, excess air, and firing techniques, i.e. the use of the Concentric Firing System and overfire air. SO_2 capture was influenced by the concentration of SO_2,

heat input to the furnace, and both the inherent and injected Ca/S ratios. The results showed that staged combustion could significantly lower NO_x emission levels from the low levels already achieved with conventional tangential firing systems, and that staged combustion could increase the utilization of alkali material inherent in the coal for SO_2 reduction.

These results encouraged Saskatchewan Power and C-E Canada Power Systems to initiate a research program to develop and install a full scale NO_x/SO_2 reduction demonstration plant on a lignite coal fired steam generator.

Objectives of the Present Research

The objectives of this demonstration project were as follows (2):

1. To demonstrate at full scale on a 150 MW lignite coal fired steam generator a low cost technology to control both NO_x and SO_2 emissions.

2. To demonstrate that NO_x emission reductions of up to 75% are achievable with the new technology compared to conventional tangential firing methods.

3. To demonstrate that SO_2 emission reductions of over 50% are achievable for fuels with sulfur contents between 0.5 and 1% at calcium to sulfur ratios of 2:1 (inherent or added).

4. To demonstrate that the technology reduces NO_x and SO_2 emissions without any significant detrimental effects on steam generator operation, availability, maintenance, or efficiency.

Boiler Design Considerations for Saskatchewan Lignite Coals

At the present time Saskatchewan has four coal fired power plants. The largest one is the Boundary Dam Generating Station located near Estevan, with an installed capacity of 875 MW, of which C-E Canada Power Systems has supplied steam generators totaling 809 MW. The next largest is the 2 unit - 592 MW Poplar River station located near Coronach. One of the Poplar River units was supplied by C-E Canada Power Systems and has been in operation since 1983.

Fuel Characteristics

Saskatchewan coals are classified as Lignite-A, and possess the following unique characteristics:

- High Moisture Content
- High Volatile Matter, usually High Oxygen Content
- Low Heating Value
- Low Sulfur Content, and
- Highly Variable and Alkaline Ash.

These coals vary from mine to mine, and frequently the coal specification indicates a range of values for boiler design.

Pulverizer Selection

Saskatchewan lignites are non-agglomerating and highly reactive by nature, properties which are ideal for pulverized fuel firing systems. These easy to burn lignites achieve good combustion efficiency in liberally sized furnaces with a pulverized fuel product of 65% through 200 mesh U.S. sieve size (75μm). The carbon in flyash is controlled at less than 0.5 percent as a necessary prerequisite for marketing this by-product.

Since the 1960's, when the Saskatchewan Power Corporation began specifying unit sizes of 150 MW with 12 400 KPa turbine cycles, all pulverizers have been of the pressurized type. The overwhelming reason for this is the power savings associated with the primary air fans handling only cold, clean air. Pressurized milling systems have also improved availability, because this type of air handling equipment is not subject to erosion.

The variable nature of Saskatchewan lignite properties leads to some difficulty in specifying the hardness of the coal for pulverizer selections. This is compounded by the fact that the hardness of the coal, as specified by the Hardgrove Index (HGI), varies with fuel moisture content - even as the fuel is dried and pulverized within the mill. Figure 1 illustrates this important effect.

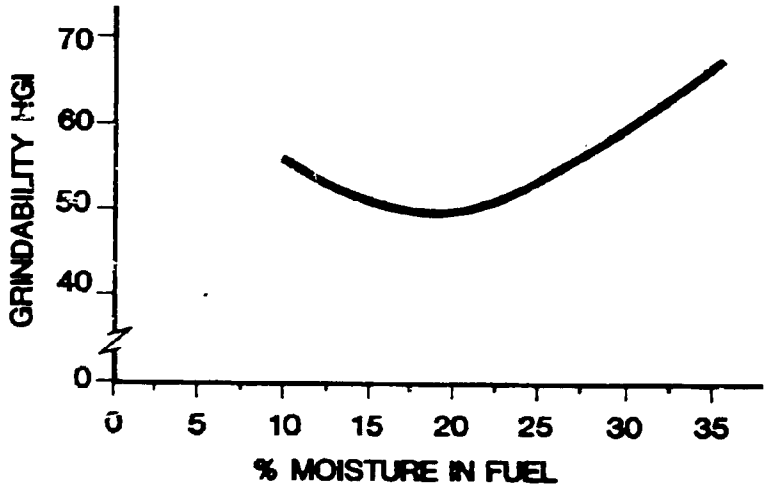

Figure 1 Grindability vs. Moisture, Typical Lignite Coal

Slagging and Fouling

The various indices C-E uses to characterize slagging and fouling potential have been reported previously (3,4,5). Saskatchewan lignite coals are characterized by base/acid ratios in the range of 0.4 - 0.5 which indicates a high slagging potential. See Table 1.

Experience has shown that ash with a sodium oxide content in excess of 3% is subject to fouling at a rate that increases as the sodium concentration increases. Saskatchewan lignite coals have been fired with up to 10% alkali in ash, leading to high fouling potentials.

Table 2 summarizes the major unit design parameters.

Generally, one can say that all liquid and most sticky ash deposits are confined to areas within the platenized superheater and reheater surfaces, where they can be effectively controlled by normal sootblowing procedures.

All of the units mentioned in Table 2 use the C-E tangential firing method. The resulting single flame envelope created within the furnace promotes more uniform heat flux profiles along the furnace walls. This minimizes build-up on the furnace walls due to local hot spots.

Superheater outlet steam temperatures are maintained over the required control ranges by interstage spraying, and fuel and air admission assembly tilt is used for reheat steam temperature control.

Demonstration Plant Steam Generator Description

The Saskatchewan Power Corporation made available their Boundary Dam Generating Station Unit 4 for the demonstration plant installation. The Unit 4 Steam Generator is a Combustion Engineering natural circulation, Radiant Reheat, tangentially fired steam generator rated at 476,190 kilograms per hour of superheated steam at 541°C and 131 bar and 419,500 kilograms per hour of reheated steam at 541°C. Lignite coal, with 37.5% moisture, at a rate of 111,340 kilograms per hour is dried and pulverized by six 743 RP Combustion Engineering Bowl Mills and transported to the furnace where the coal is fired through 6 elevations of tilting tangential fuel admission assemblies. Combustion air is supplied by two forced draft fans and preheated by two secondary Ljungstrom air preheaters. Flue gas is drawn by two induced draft fans from the furnace over radiant superheater and convective superheater and reheater surfaces in the front pass and an economizer in the backpass, through the two Ljungstrom secondary airheaters for preheating secondary air for combustion, and through a mechanical dust collector, and discharged from the I.D. fan to the stack. A portion of the flue gas leaving the front pass bypasses the economizer and is diverted to two tubular primary airheaters used to preheat primary air for drying and transport of pulverized coal and returns to the backpass upstream of the secondary airheaters.

Table 1

COAL ANALYSES

			Boundary Dam (Unit #6) February 1979	Poplar River February 1979	Shand February 1985
Proximate Analysis					
Moisture		%	34.3	36.0	34.8
Volatile Matter		%	28.8	25.1	25.7
Fixed Carbon		%	29.1	29.9	30.3
Ash		%	9.7	9.0	9.5
Heating Value		kJ/kg	15,570	15,876	16,040
		Btu/lb	6,684	6,825	6,896
Classification			.....Lignite "A".....		
Ultimate Analysis					
Hydrogen		%	2.80	2.60	2.63
Carbon		%	39.20	38.10	42.16
Sulfur		%	0.20	0.30	0.36
Nitrogen		%	0.70	0.60	0.72
Oxygen		%	13.10	12.60	9.87
Flammability		°C	482	482	-
Hardgrove Grindability Index			54	52	-
Ash Analysis					
Silica	SiO_2	%	39.1	42.9	41.4
Alumina	Al_2O_3	%	22.3	22.4	18.8
Ferric Oxide	Fe_2O_3	%	5.0	5.6	4.8
Lime	CaO	%	8.8	8.6	13.1
Magnesia	MgO	%	2.3	2.9	2.8
Sodium Oxide	Na_2O	%	6.5	6.5	7.2
Potassium Oxide	K_2O	%	0.6	0.9	0.6
Titanium	TiO_2	%	0.9	1.0	0.8
			86.0	90.8	89.5
Ash Indices					
Ash in Coal		%	9.70	9.00	9.3
Delta "T" (Fluid - I.D.)		°C	105	150	60
Base/Acid Ratio			0.38	0.39	0.47
Fe_2O_3/CaO Ratio			0.57	0.65	0.37
SiO_2/Al_2O_3 Ratio			1.75	1.92	2.20
Ash Fusibility Temperature					
Initial Deformation		°C	1116	1093	1154
Softening		°C	1127	1116	1166
Fluid		°C	1221	1243	1214

Table 2

UNIT DESIGN PARAMETERS

Unit	Year Type	Ash I.D. (°C)	Furnace Leaving Temp. (°C)	Gas Temp To Convection Section (°C)	Combustion Rate (kW/m³)	Heat Release Rate (kW/m²)
BOUNDARY DAM #3,4,5	1966 RR	1116	1204	1100	150.4	197.3
BOUNDARY DAM #6	1973 RRD	1116	1170	1025	140.5	175.5
POPLAR RIVER #1	1978 RR	1093	1200	1020	105.9	196.4

Figure 2 is a side elevation of the Boundary Dam Unit 4 Steam Generator.

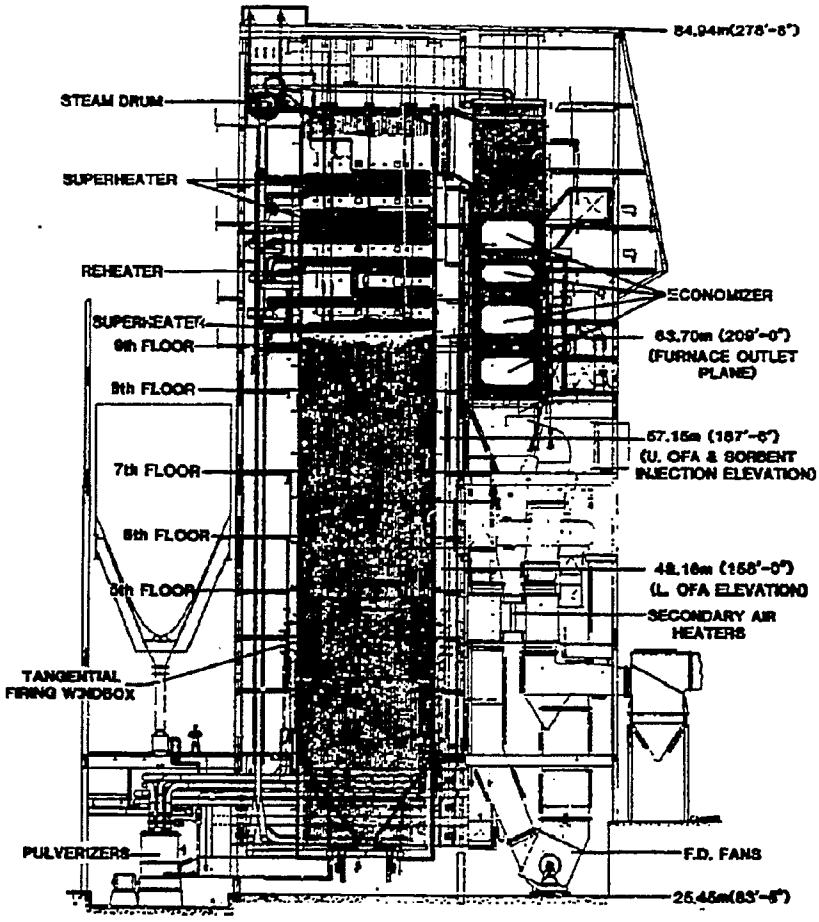

Figure 2 Boundary Dam Unit 4 Steam Generator

Emissions Considerations for Saskatchewan Lignite Coals

NO_x is formed in an around the flame zone by the oxidation of both atmospheric nitrogen (thermal NO_x) and nitrogen contained in the fuel (fuel NO_x).

Thermal NO_x formation is usually modelled via the Zeldovich mechanism where the rate of formation is exponentially dependent on temperature and is proportional to the square root of oxygen concentration. Reducing both the amount of oxygen available to the fuel and the combustion temperature are effective methods of controlling NO_x formation by this mechanism.

Although only a fraction of fuel bound nitrogen is converted to NO_x, fuel NO_x can account for 50% to 75% of the total NO_x emissions when firing high moisture low rank coals. Furthermore, the degree of fuel nitrogen conversion is itself an increasing function of the oxygen to nitrogen ratio within the coal (6). This is particularly important due to the high oxygen content of Saskatchewan lignites.

Fuel NO_x formation can be controlled by reducing the oxygen concentration in the combustion zone, but it is relatively insensitive to temperature effects.

SO_x is formed in the combustion process through the oxidation of sulfur contained within the coal.

The unique character of Saskatchewan lignite is that it contains very little sulfur, typically less than 0.6%, and that up to 25% inherent SO_2 capture is achieved in normal practice due to the previously mentioned high alkali content of the coal ash.

Description of the Modified Combustion Emission Control System with Sorbent Injection

The Modified Combustion Emission Control System with Sorbent Injection installed on Boundary Dam G.S. Unit 4 consisted of the following equipment systems (7):

- Concentric Firing Windbox
- Lower Overfire Air Windbox with Ducting
- Upper Overfire Air Windbox with Sorbent Injection and Ducting
- Sorbent Storage System
- Sorbent Feed System
- Sorbent Transport System

The systems are described below. A diagram of the Modified Combustion Emissions Control System with Sorbent Injection is shown in Figure 3.

Concentric Firing Windbox

The existing windbox was modified such that the top five auxiliary air compartments were converted to concentric nozzles to divert approximately 50% of the secondary air along the furnace walls. See Figure 4. The windbox retained its tilt travel of 30 degrees up or down for reheat steam temperature control.

Lower Overfire Air Windbox with Ducting

Secondary air was taken off the existing windbox connecting duct and introduced into the furnace through overfire air nozzles installed at elevation 48.16 meters at each of the four corners of the furnace.

Each overfire air windbox consisted of an upper and a lower nozzle in the overfire air compartment. The lower nozzle introduces secondary air concentrically along the furnace walls to maintain the oxygen rich layer

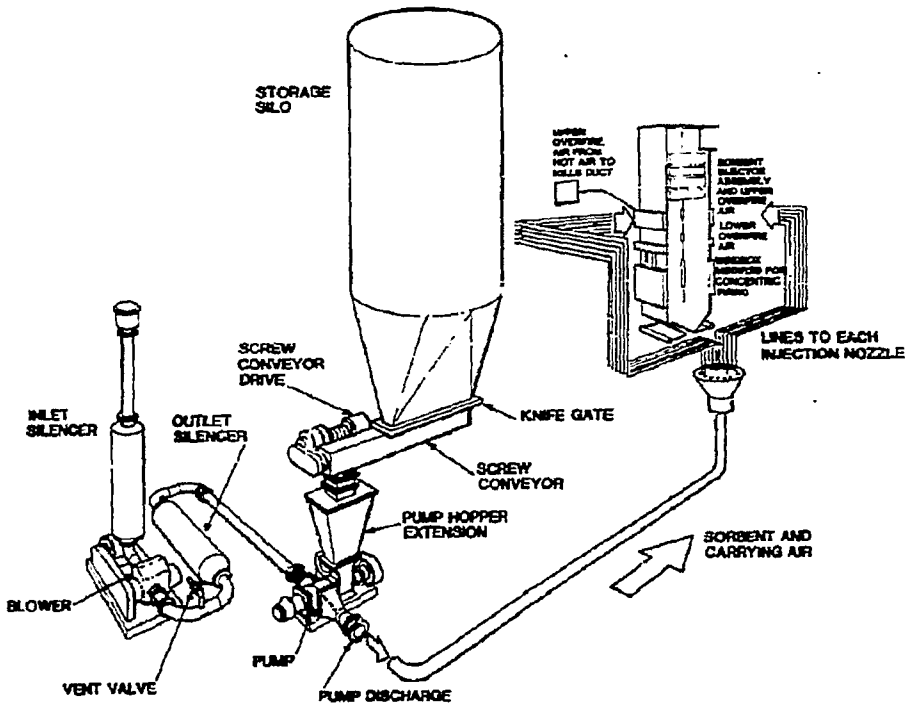

Figure 3 Modified Combustion Emissions Control System with Sorbent Injection

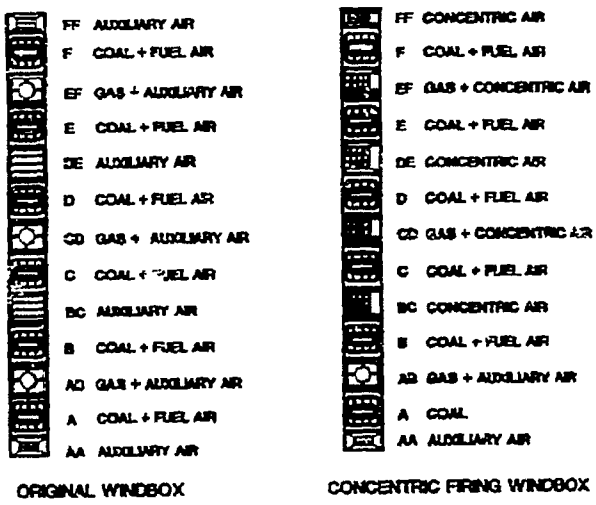

Figure 4 Windbox Modifications

at the furnace walls created by the concentric firing windbox and the upper nozzle introduces secondary air in the normal tangential manner to mix fuel and air for staged combustion.

Upper Overfire Air Windbox with Sorbent Injection and Ducting

The upper overfire air and sorbent were injected at each of the four corners at elevation 57.15 meters. At each corner the upper overfire or injection air and sorbent were injected through nozzles arranged in such a way that the injection air and sorbent were dispersed into the furnace as shown in Figure 5. Injection air was taken from the existing mill hot air duct and was routed to the injectors. The sorbent was transported pneumatically from the storage silo and fed to each of the sorbent injectors. The sorbent injection assembly for one corner is shown in Figure 6.

Sorbent Storage System

The sorbents, limestone and calcium hydroxide, were delivered already pulverized and were unloaded pneumatically from sorbent transport trucks into the sorbent storage silo.

Sorbent Feed System

The sorbents were fed from the discharge of the silo, equipped with 4 air slides, into the inlet hopper of a solids pump using a variable pitch screw conveyor. The sorbent was mixed with the transport air in the solids pump and discharged into the pneumatic transport piping. Transport air was withdrawn from the atmosphere by a 93 KW positive displacement blower and discharged into the solids pump. The sorbent feeding capacity of the system was 4760 kilograms per hour for limestone and 3400 kilograms per hour for hydrated lime.

Sorbent Transport System

From the discharge of the solids pump, the sorbent- transport air mixture travelled in a 150 mm diameter pipe to a 12 way splitter where the flow was split equally into 12 - 50 mm diameter pipes. Four groups of three of these twelve balanced resistance piping lines transported the sorbent - transport air mixture to the four sorbent injector assemblies located at each of four corners at elevation 57.15 metres.

Description of Test Program

A test program was conducted to evaluate the effectiveness of the demonstration plant on the reduction of NO_x and SO_2 emissions and the effect of the demonstration plant on the operation of the steam generator.

A comprehensive test program was carried out over a 10 month period encompassing 4 series of tests during which two Saskatchewan lignite coals, Boundary Dam and Shand, and two sorbents, limestone and hydrated lime, were tested. One series of baseline tests before the

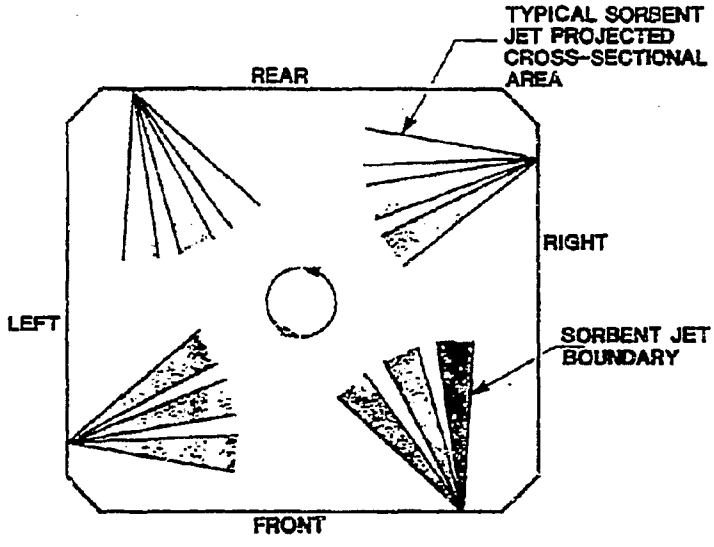

Figure 5 Sorbent Injector Key Plan, Boundary Dam #4

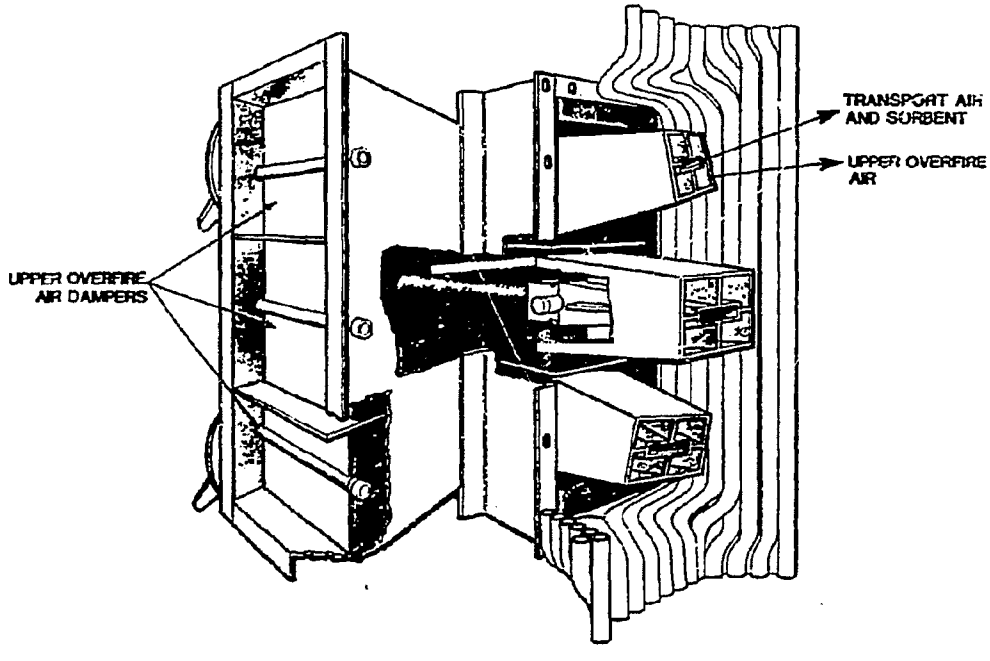

Figure 6 Cutaway View of a Typical Sorbent Injector Assembly

demonstration plant was installed, and three series of tests after the demonstration plant was installed, were carried out.

Properties of the Boundary Dam and Shand lignite coals tested are given in Table 1.

Properties of the two tested sorbents are given in Table 3.

Discussion of Results

NO_x and SO_2 Reduction

Measurements of NO_x, SO_2 and O_2 were taken for various parametric test conditions throughout the entire test program. The results of the test program displayed the following trends (8):

- NO_x emission was decreased by decreasing excess air quantity, increasing overfire air quantity, decreasing upper overfire air tilt, and decreasing load.
- Inherent SO_2 capture was increased by increasing excess air, decreasing overfire air, increasing upper overfire air tilt, decreasing load, and increasing coal % sulfur.
- Injected SO_2 capture was increased by increasing, excess air, decreasing overfire air, increasing upper overfire air tilt, decreasing load, increasing injected Ca/S ratio, and increasing coal % sulfur.

The test data was then used to formulate predictive models which can be used to determine the best NO_x and SO_2 emissions reduction achievable at this demonstration plant.

The results of these predictive models are shown in Table 4.

NO_x emission reduction of about 60% with respect to baseline conditions can be obtained while firing Boundary Dam coal at the operating conditions shown by modifying the firing system configuration as described herein.

While firing Boundary Dam coal at the demonstration plant, a total SO_2 capture of about 34% can be achieved for limestone injection and about 41% for hydrated lime injection for an inherent and injected Ca/S ratio of 2.0 for the operating conditions shown.

For Shand coal firing at the demonstration plant, a total SO_2 capture of about 54% can be achieved for limestone injection and about 65% can be achieved for hydrated lime injection for an inherent and injected Ca/S ratio of 2.0 for the operating conditions shown.

An important result determined by the researchers was that, as Table 4 demonstrates, the optimum conditions for maximum NO_x emission reduction are not the same as those for maximum SO_2 capture.

Table 3

PROPERTIES OF TEST SORBENTS

	Sorbents	
	Alberta Calcium Carbonate - Finely Ground	Wisconsin Calcitic Pressure Hydrated Lime
Chemical Properties		
% Moisture	0.03	0.9
% CaO	53.0	70.08
% H_2O (water of hydration)	—	21.1
% CO_2	41.7	3.4
% MgO	0.72	0.95
% Fe_2O_3	0.14	0.12
% SiO_2	1.68	2.42
% Al_2O_3	0.38	0.09
Surface Property Data		
% < 1 μm	5	10
% < 5 μm	40	70
Median Diameter, μm	6.45	3.60
Surface Area, m^2/g	1.85	14.9
Pore Volume, cm^3/g	0.007	0.066

Table 4

PREDICTED OPTIMUM RESULTS FOR NOx - SO_2 REDUCTION AT 93% MCR

Coal	% N_2	% Excess O_2	L. OFA	Firing System	PPM NOx	% NOx Reduction
B. Dam	0.65	3.2	No	Pre-Mod	285	-
B. Dam	0.65	2.0	Yes	Post-Mod	110	60
Shand	0.65	2.0	Yes	Post-Mod	100	-

Coal	Sorbent	% Sulfur	% Excess O_2	Inherent Ca/S	% Inherent SO_2 Cap.	Injected Ca/S	% Injected SO_2 Cap.	% Total SO_2 Cap.
B. Dam	$CaCO_3$	0.45	5.0	2.0	23	2.0	14	34
B. Dam	$Ca(OH)_2$	0.45	5.0	2.0	23	2.0	24	41
Shand	$CaCO_3$	0.50	5.0	2.0	32	2.0	32	54
Shand	$Ca(OH)_2$	0.50	5.0	2.0	32	2.0	49	65

Effects on Unit Operation

Visual observations of furnace slagging and samples of convective surface deposits were obtained throughout the test series. Furnace slagging was observed to be reduced by 66% from the baseline test series by installing the Modified Combustion Emissions Control System. Sorbent injection did not appear to affect furnace slagging. Convective surface deposits were unaffected by installation of the demonstration plant. Also, the convective surface deposits did not increase during sorbent injection even though at an injected Ca/S of 1.6 the ash loading to the convective surface would effectively be increased by 20%.

Measurements were taken and steam generator efficiency was calculated using the ASME abbreviated heat loss method for selected non-injection and injection tests. It was found that the steam generator efficiency was slightly lower for the sorbent injection tests as compared to the baseline tests due to the net heat loss of the calcination and sulfation reactions and the sensible heat loss for the sorbents.

In situ fly ash resistivity measurements were made of the fly ash and sorbent entrained in the flue gas entering the induced draft fans throughout the test series. It was found that fly ash resistivity increased marginally for the sorbent injection tests as compared to the non-injection tests.

All other facets of steam generator operation were unaffected by the installation of the demonstration plant.

Influence on Design of New Lignite Coal Fired Steam Generators

The application of this abatement technology to new steam generators shows great promise for overall improvements in system performance. Retrofitting such a NO_x/SO_2 emissions control system to an existing furnace compromises certain design variables, such as:

- Location of the sorbent injection point
- Residence time of the injected sorbent within the reaction "window"
- Availability of air used for dispersing the limestone throughout the furnace plan area
- Excess air value used

Whereas the demonstration plant simulated variations in furnace gas temperature by reducing the boiler load, on a new unit, the boiler designer can be given the freedom to design the furnace temperature profiles specifically for optimum injection and retention of the sorbents to be utilized.

Furthermore, on an new unit, the backend heat recovery system can be optimized for the production of the necessary quantities of air used for dispersing the sorbents within the furnace.

Finally, it is practical on a new unit to evaluate the long term economic benefits of using higher excess air levels to achieve improved SO_2 emission reductions and/or greater sorbent utilization while still maintaining acceptable NO_x emission levels.

Because of the experience gained during the demonstration plant testing, reduced levels of furnace wall slagging are anticipated for new units using this modified combustion technique.

New units are not expected to see increased levels of fouling or degraded electrostatic precipitator performance due to this modified combustion emission control system with sorbent injection.

Conclusions

1. A full scale low cost technology to control both NO_x and SO_2 emissions for low rank fuels was demonstrated on a 150 MW lignite coal fired steam generator.

2. NO_x emission reductions of up to 60% are achievable with the new technology compared to conventional tangential firing methods.

3. SO_2 emission reductions ranging from 34 to 65% are achievable for Saskatchewan lignite coals at inherent and injected calcium to sulfur ratios of 2:1 depending on the coal fired and the sorbent injected.

4. The technology reduces NO_x and SO_2 emissions without any significant detrimental effects on steam generator operation, availability, maintenance, or efficiency.

5. New steam generator designs for these lignite coals will be influenced by the results and experience gained through this full scale demonstration plant testing.

Acknowledgements

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