Correlations between rotational viscosimeter and pilot plant data in CWS pipeline system design

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1. Introduction

Coal can be transported most economically over great distances using a pipeline. Notwithstanding the good technical results achieved by CWS technologies, technical areas, which deserve further development work, still exist.

Design data for pipeline systems are usually obtained using pilot plants. The aim of this work is to investigate the correlations between data achieved using a rotational viscosimeter and data from a pilot plant. The high correlations obtained between the two types of data suggests that it is possible to use a simple rotational viscometer instead of a specially designed pilot plant in the design of pipelines.

2. System components

2.1. Slurry storage tank

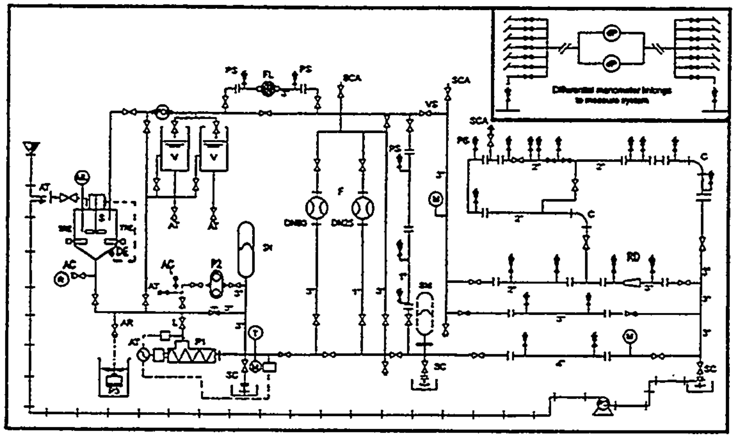
The slurry from the two barrels (about 5 cubic meter each) is pumped into a slurry storage tank of about 4 cubic meter for storage and remixing. The tank is equipped with an agitator designed to provide low shear mixing, avoiding any local settling of the particles. Although it is expected to receive a slurry which have good stability characteristics, periodical agitations will prevent any settling of coal particles.

2.2. Pump

It is very important to have a pump that is suitable for various operating apparent viscosities, flow rates and pressures, so we have used a variable speed, positive displacement screw pump. The maximum values of flow rate and of pressure are rispectively 37.5 m^3/h and 6 bar. The pump is provided with connections for water flushing so that the pump parts are flushed before and after use.

2.3. Piping System

A schematic of the pipe loop system used is shown in figure 1. The pipeline consists of commercial flanged pipes of various diameters (1", 2", 3", 4"), bends, orifices contractions and expansions. The plant is equipped with a data acquisition system which consists of a microcomputer with data acquisition interfaces, Rosemount® differential pressure trasducers, thermocouples and two magnetic flowmeter of different diameters (1" e 2") for the different ranges of flow.



Notation:

AT = tanker connection
AR = water hose connection
AC = compressed air connection
SC = convex unloading
R = CWS collecting tap
PR = pressure gauge
SCA = open air vent-hole
DE = densimeter

dP = differential manometer
V = decanting and clearing tan
S = main tank
L = tank gauge
ML = level gauge
P1 = screw pump
P2 = substitutive pump
TRE = thermoresistance and thermostat

M = manometer
F = flow-meter
SM = pulsation damper
FQJ = volumetric meter
P3 = diaphragm pump
FL = test filter
PS = diaphragm separators
C = ANSI b16-9-90RL DNP 2" bend

Fig. 1 - Pilot plant

2.4. CWS characteristics

Tests were made using a slurry consisting of approx. 60 % weight of South African coal and 40% weight of water. The maximun particle size of the coal in the suspension is approx. 70 μm and its initial viscosity at 100 s^{-1} is about 300 mPas.

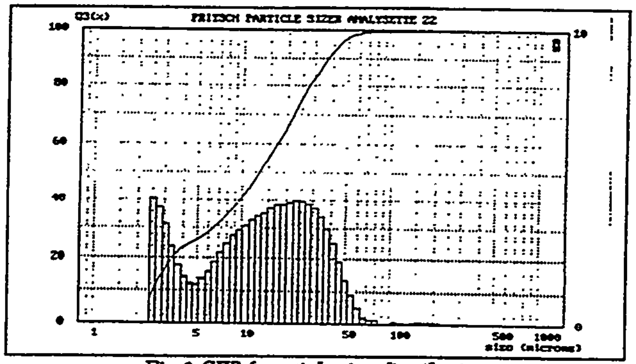


Fig.2 CWM particle size distribution

3. Flow Model

Concentrated fine particle suspensions usually behave as non Newtonian fluids. There are numerous non Newtonian fluid models for a non linear relationship between the shear stress and the rate of shear. Part of them belongs to the class of Pseudoplastic Fluids, which are fluids whose behavior is time independent, for which an infinitesimal shear stress will initiate motion and for which the rate of increase in shear stress with velocity gradient decreases with increasing velocity gradient. Widely used in engineering calculations is the so called Power Law model:

$$\tau = K \cdot \left(\frac{du}{dr}\right)^n \qquad (1)$$

where K is the consistency index or power law coefficient, and n is the flow behavior index or power low exponent (n<1 for pseudoplastics).

On the other hand the equilibrium of forces in the flow direction for a cylindrical element of radius r and length dL yields:

$$\tau = -\frac{r}{2} \cdot \frac{dP}{dL} \qquad (2)$$

where τ denites the shear stress at radial distance r, and ΔP is the pressure drop along the element. Solving the above equation and substituting into (1), solving for the velocity gradient du/dr and subsequently integrating with the no slip condition of u=0 at r=R, the following expression is obtained for the mean velocity V:

$$V = \left(\frac{dP}{2K \cdot dL}\right)^{1/n} \cdot \left(\frac{n}{1+3n}\right) \cdot R^{(1+n)/n} \qquad (3)$$

and finally:

$$\frac{\Delta P}{\Delta L} = \frac{4V^n K}{D^{1+n}} \cdot \left(\frac{2+6n}{n}\right)^n \qquad (4)$$

Hence, the energy E_T required for transporting the suspencion in a pipe of lenght L can be calculated by substituting the pressure gradient obtained from eq. (4) into the following equation:

$$E_T = Q \cdot \left(\frac{\Delta P}{\Delta L}\right) \cdot L \qquad (5)$$

The preceding procedure is valid for laminar flows of power-law fluids, only. The flow regime for power-law fluids is designated through the *generalized Reynolds number* defined as follows:

$$\mathrm{Re}_p = \frac{8D^n V^{2-n} \rho_m}{K} \cdot \left(\frac{n}{2+6n}\right)^n \qquad (6)$$

where ρ_m is the suspencion density. The critical value of Re_p for the transition from laminar to turbolent flow is given by:

$$\mathrm{Re}_{p,c} = \frac{6464n}{(1+3n)^2 \cdot (2+n)^{-(2+n)/(1+n)}} \qquad (7)$$

Hence, when $\mathrm{Re}_p > \mathrm{Re}_{p,c}$, the flow becomes turbolent and the previous relationships based the constitutive relation of eq. (1) may not be used. In this study we will refer to laminar flow only because it is quite rare to achieve turbolent flow conditions using commercial transportation rates.

4. Experimental procedures

4.1. Rheological measurements

Laboratory rheological data were obtained at Pisa Enel CRTN using a Haake Rotovisco viscometer equipped with an M150 measuring/drive head and the MV1P sensor system.

Typical data for MV1P sensor are displayed in fig.3; these data show some noise and an apparent thixotropic behavior. Subsequent experiment at constant shear stress showed no change in shear rate as a function of time for up to 15 minutes. The vertical offset of the *up* curve, the curve corresponding to increasing applied stresses, was approximately 8 Pa above the *down* curve at the middle value of applied stress.

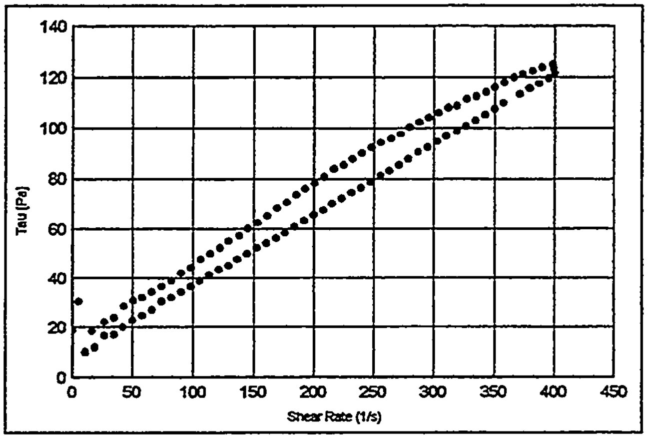


Fig. 3 - Rheological data (sample taken at the end of first day, 25 °C)

Being interested in evaluating the apparent thixotropic behavior of the slurry, experiments on pilot plant were made over two days with the mixture resting for the night between. Samples for viscometer were taken at the beginning and at the end of each day (four samples).

The same offset between *up* and *down* curves was seen in all the rheograms, which seems to imply a mechanical hysteresis rather than a rheological thixotropic behavior. As a matter of fact data from the viscometer show different values for slurry parameters (*K*, *n* see table 1) among samples taken on first and second day, which makes hard to reject the above hypothesis of thixotropic behavior.

The hypothesis of thixotropic behavior has been taken into account using data from the viscometer samples concerning the end of each day. As a matter of fact, sample taken at the beginning of the first day seems to have low significativity because the slurry itself came from a long undesired rest in two barrels during transportation to our pilot plant; for the same reason (rest at night) we decide to discard the sample referring to the beginning of the second day.

For each of the two left samples we used the *up* curve, because the experiments on pilot plant were made using the screw pump running at revolution rates ranging from 70 rpm to 370 rpm in ascending order (0.5 m/s to 2.5 m/s depending on pipe sizes).

The noise observed in all samples, due to start-up, suggested to discard data whose shear rate is below 50 rad/sec.

Sample	k	n
Beginning of first day	1.562	.6578
End of first day	1.595	.7327
Beginning of second day	1.320	.7160
End of second day	1.135	.7826

Table 1 - Slurry parameters

4.2. Analysis of results

Experiments were hold with increasing flow rates, as said above; for each flow rate steady-state pressure drop readings were taken over the three different section pipes of the flow loop.

Figure 4 show experimental data, collected in the first day, against predicted values obtained using viscometer parameters *K* and *n*. The predicted values fit very well the observed ones for all the different pipe sizes. We achieved the best fitting for the largest pipe, and it get worst for the smaller ones. Nevertheless the relative error (see Figure 5), given by:

$$err = \frac{\left(\Delta p_{obs} - \Delta p_{pred}\right)}{\Delta p_{obs}} \tag{8}$$

is quite constant, and always within 10%. Figures 6 and 7 display experimental data collected in the second day, after mixture rest at night; and corresponding relative errors. In all the cases the power law model overpredicts pressure losses for low values of velocity and underpredicts pressure losses for high velocities. There is a good agreement between observed and predicted values at mid range speed, which best represents conditions usually met in CWS industrial transportation.

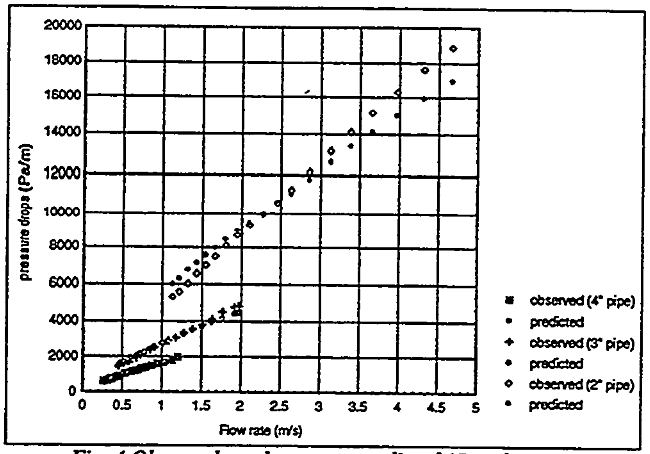


Fig. 4 Observed results versus predicted (first day test)

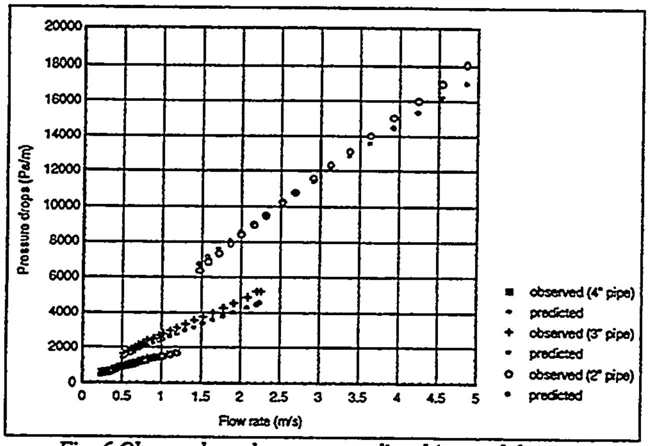


Fig. 6 Observed results versus predicted (second day test)

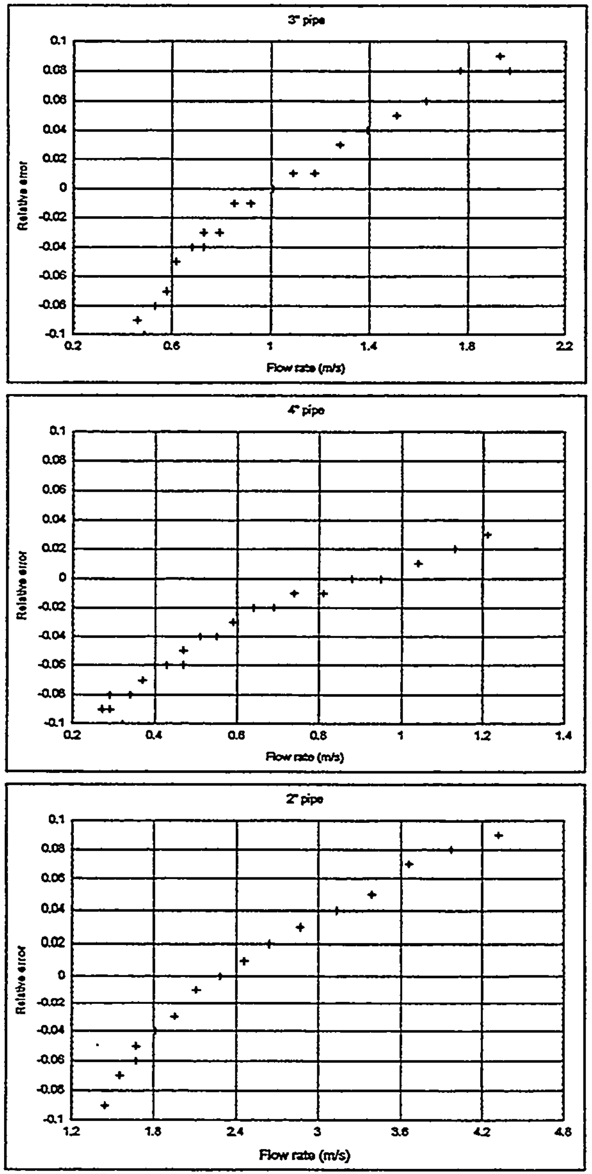


Fig. 5 Relative error for different pipe sizes

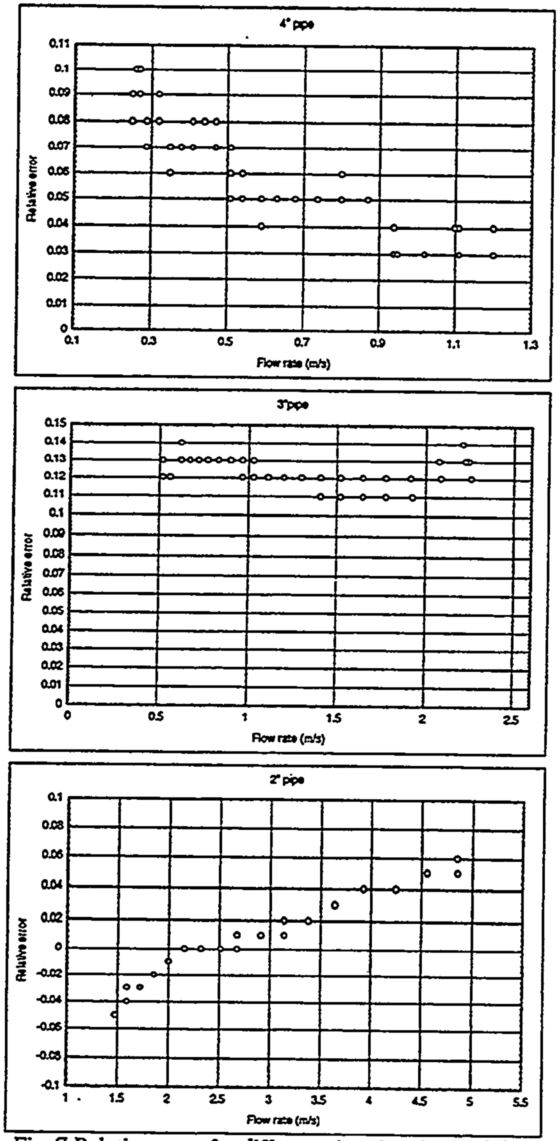


Fig. 7 Relative error for different pipe sizes (second day)

5. Conclusions

In this paper has been shown that it is possible to use data achieved from a simple rotational viscometer instead of a specially designed pilot plant in the design of pipelines. The most peculiar results of the experiments from this study are:

- Power Law model is generally suitable to describe the rheological behavior in loop test;
- time dependence (thixotropy) is generally remarkable both in viscosimetry measurements (hysteresis loop at variable shear testing) and in loop measurements;
- viscosimeter data generally underpredict pressure drops in pipes; mainly at intermediate shear rates, but the deviation from experimental data always remains below 10%;

6. Nomenclature

D	diameter of pipe
E_t	energy required to transport suspencion in a pipe of length L
K	constant in the power low equation (consistency index)
L	length of pipe
dL	length of an element of pipe
ΔL	end to end spacing in a pipe
n	exponent in the power low equation (flow behavior index)
P	pressure
dP	pressure drop
ΔP	pressure drop over a length L
Q	volume rate of flow
r	radial distance
u	local axial velocity
R	radious of pipe
Re_p	generalized Reynolds number

$Re_{p,c}$	critical Reynolds number
V	cross sectional average velocity
ρ_m	suspencion density
τ	shear stress

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Blending High Sulfur Coal with Refuse Derived Fuel to Make SO_2 Compliant Slurry Fuels

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INTRODUCTION

The need for a better method of disposing of the international community's garbage hardly needs emphasizing. In 1993, the United States alone generated approximately 207 million ton per year of Municipal Solid Waste (MSW), with 62% landfilled, 22% recycled, and 16% combusted for energy recovery.[1] Despite strenuous efforts to make these disposal methods meet present needs, the cost of disposal is rising dramatically. In addition to the cost and environmental problems of MSW disposal is the often overlooked fact that landfilling fails to utilize the energy content of this low sulfur, renewable energy resource.

Concurrently, the Clean Air Act Amendments (CAAA) of 1990 have severely restricted the SO_2 emissions from coal fired boilers. Medium and high sulfur coals will not comply with the Phase II CAAA regulation limit of 1.2 lb SO_2/MM Btu, without advanced coal cleaning technologies or flue gas desulfurization, including the majority of the North Dakota lignite reserves.

Utility power plants have attempted to burn refuse derived fuel (RDF), a heterogeneous solid fuel produced from MSW, with coal in utility scale boilers (generally referred to as co-firing). Co-firing of RDF with coal has been attempted in sixteen different boilers, five commercially. While lower SO_2 emissions provided the impetus, co-firing RDF with coal suffered from several disadvantages including increased solids handling,

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[1] Characterization of Municipal Solid Waste in the United States, 1994 Update," U.S. Environmental Protection Agency, Office of Solid Waste, EPA530-R-94-042, November 15, 1994.

increased excess air requirements, higher HCl, CO, NO_x and chlorinated organic emissions, increased slag formation in the boiler, and higher fly ash resistivity. Currently, only two of the sixteen boilers are still regularly used to co-fire RDF.[2]

The overall objective of this research program was to assess the feasibility of blending RDF with lignite coal to form SO_2 compliant slurry fuels using EnerTech's SlurryCarb™ process. In particular, the objective was to overcome the difficulties of conventional co-firing. Blended slurry fuels were produced with the Energy & Environmental Research Center's (EERC) bench-scale autoclave and were combusted in a pressurized fluidized-bed reactor (PFBR).

THE SlurryCarb™ PROCESS

Bituminous and higher rank coals can generally be slurried to pumpable fuels of satisfactory solids loading, and hence heating value. However, low rank solid fuels, like lignite and RDF, slurry less well. Supported by the U.S. DOE and U.S. EPA, EnerTech has developed a process called SlurryCarb™, which greatly improves the solids loading and uniformity of low rank slurry fuels.

With EnerTech's SlurryCarb™ process, a pumpable slurry of low rank fuel is continuously pressurized with a pump to approximately 1200 to 2000 psia (depending on the maximum SlurryCarb™ temperature). The feed slurry is pressurized above the saturated steam curve of the slurry, in order to maintain a liquid state when heated above its boiling point. From the pump, the pressurized slurry will be heated by indirect heat exchange to approximately 480 to 660°F, and its pressure and temperature maintained for less than 30 minutes.

At this temperature and pressure, oxygen functional groups in structures of the low rank fuel will be split off as carbon dioxide gas. This removed carbon dioxide gas will comprise a significant weight percentage of the feed solids, but only a minimal percentage of the heating value. While the mass of total solids will be reduced approximately 20-70%, the carbonized product will still contain approximately 95-98% of the energy content of the feed solids. The carbonized solids are dramatically reduced in size and can be

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[2] Ege, H.D., and Joehsen, Al, "RDF Co-firing with Coal in Utility Boilers - An Update," Burns & McDonnell Engineering Company and Iowa State University, March 1994.

concentrated to a solids loading, and hence heating value, comparable to bituminous coal slurry fuels.

RESEARCH PERFORMED

Bench-scale SlurryCarb™ experiments were performed with EERC's 7.6 liter autoclave system (please see Figure 1). The results from this batch autoclave are comparable to a continuous unit. The bolted closure reactor is externally heated and is equipped with an automatic temperature controller and a variable-speed magnetically driven stirrer. It is instrumented to continuously measure and record pressure plus slurry and vapor temperatures. The stainless steel autoclave is rated to 5500 psia at 660°F.

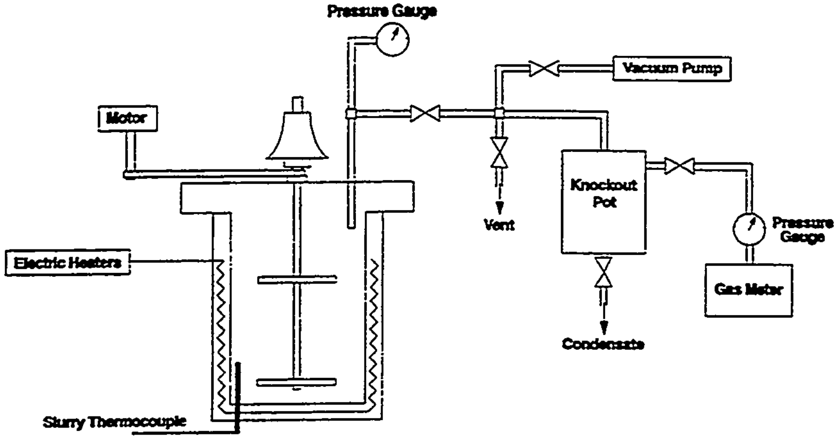


Figure 1 - Simplified Schematic of EERC's 7.6 Liter Batch Autoclave System.

For each autoclave experiment, a standard operating procedure was utilized. Approximately nine pounds of the feed slurry were charged to the autoclave where after the autoclave was sealed and evacuated of residual air. The external heaters were activated and the temperature controller programmed to the desired temperature. Heating up to this temperature took approximately 2.5 to 3 hours. The slurry temperature and pressure were maintained for a nominal period, where after the heaters were shut off. The reactor and contents were allowed to cool down overnight prior to subsequent products collection. The slurry was continually stirred throughout the heat-up, temperature stabilization, and cool-down. After cool-down, carbonization gas was vented via a diaphragm meter to quantify production of noncondensible products and a sample was taken for analysis. The dilute carbonized slurry was collected and separated into a damp carbonized cake and a water stream via Buchner filtration and samples analyzed. Also, samples of the carbonized cake were reconstituted with water and their rheology determined.

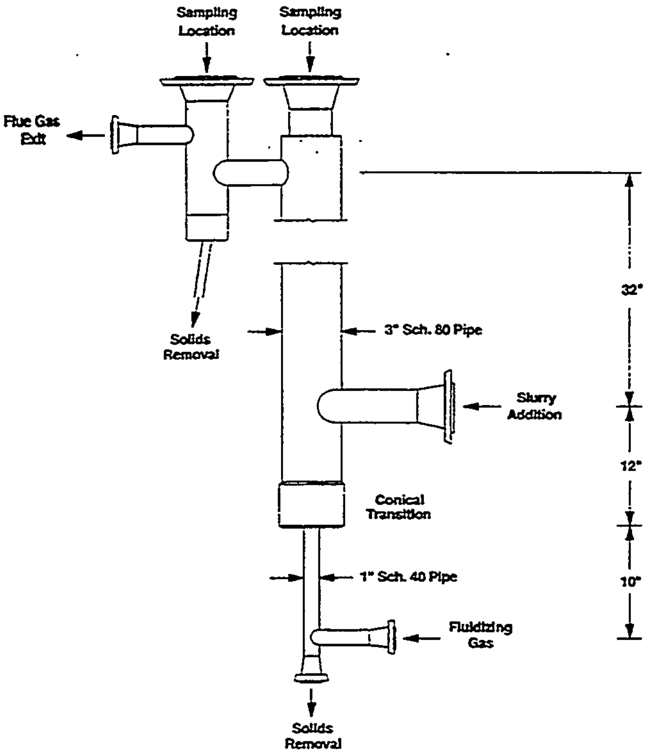


Figure 2 - Simplified Schematic of EERC's Pressurized Fluidized-bed Reactor (PFBR).

A sufficient quantity of three carbonized slurry fuels (a RDF, lignite, and 50/50 RDF/lignite blend) were prepared with EERC's autoclave and then combusted in EERC's bench-scale pressurized fluidized-bed reactor (PFBR). The 55 inch tall reactor (please see Figure 2) is constructed of 3 inch Schedule 80 pipe and is externally heated with three electric heaters. The reactor is rated to 150 psig at 1700°F or 550 psig at 1400°F.

For each pressurized combustion test, the reactor was charged with approximately 1400 grams of #10 silica sand. A preheated mixture of air and nitrogen was supplied to the bottom of the reactor to fluidize the sand and preheat the reactor to between 1400 and 1550°F. Approximately 11 SCFM of nitrogen and 11 SCFM of air were utilized to achieve a flue gas velocity of about 3 ft/s in the reactor. The fluidizing gas entered the main section of the reactor through a conical section. This conical section was designed without a distributor plate to allow quick removal and quench of the bed material after the completion of the test. A hot cyclone collected the ash and bed material that was carried out of the reactor into an ash pot. At the end of the combustion experiment, the ash pot, bed ash, and fly ash were weighed and sampled for analysis. From the hot cyclone, the flue gases passed through a water cooled heat exchanger and are analyzed, on-line, for O_2, N_2, CO_2, CO, NO_x, N_2O, SO_2, and hydrocarbons.

Temperatures in the reactor were measured with eleven Type K thermocouples. These were located at 0.25, 1.75, 3.50, 5, 7, 9, 11, 15, 23, 31, and 43.25 inches above the start of the conical transition section. Thermocouples were also located at the gas inlet, cyclone exit, and pressure letdown valve exit. The carbonized slurry fuels were injected into the reactor, from a continuously stirred tank, with a variable speed progressive cavity pump. The feed rates of the slurry fuels were approximately 6 to 8 lb/hr.

RESEARCH RESULTS

Rheology of the raw and carbonized RDF, lignite, and blended slurry fuels were determined with a Haake RV-100 viscometer at several total weight percentage solids. As can be seen in Figure 3, solids loading of the RDF slurry fuel was improved, with EnerTech's SlurryCarb™ process, over 380%, from 9.1 to 43.7 wt.%, at a comparable viscosity of 500 cP (100 Hz, decreasing). The rheology of the 50/50 raw RDF/lignite blend (dry basis) also was dramatically improved approximately 149% to 56.1 wt.% solids at 500 cP. The synergy of the RDF/lignite blend can be explained by a lower average particle size and a bimodal particle size distribution in the carbonized product.

Table 1 summarizes average fuel properties of the carbonized RDF, lignite, and blend slurry fuels produced from EERC's autoclave. On a dry basis, raw RDF had a high weight percentage of oxygen, approximately 38 wt.%, and a low heating value. High quality solid fuels, like bituminous coal, have less oxygen and a much higher heating value, due to the predominance of carbon-carbon and carbon-hydrogen bonds. With EnerTech's

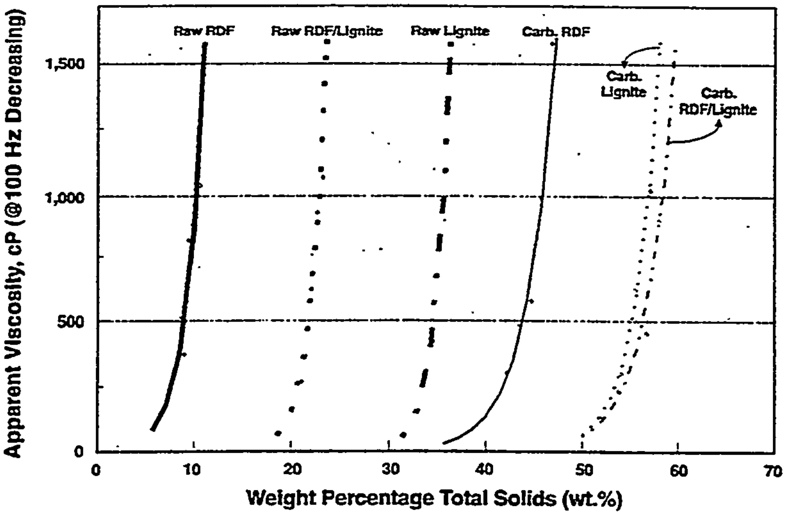


Figure 3 - Rheology of Raw and Carbonized RDF and Lignite Slurry Fuels.

SlurryCarb™ process, the objective is to remove these oxygen functional groups from the low rank fuel particles, so that the heating value of the remaining carbonized particles (now mostly carbon-carbon and carbon-hydrogen bonds) will be higher. As can be seen in Table 1, weight percentage of oxygen in the RDF was reduced approximately 66% (dry basis), while its higher heating value was improved 64% (dry basis). For lignite, wt.% of oxygen was reduced approximately 20% and heating value improved 7%.

The SlurryCarb™ process also extracts a significant portion of the chlorine from the feed slurry fuels. RDF has an appreciable chlorine content due to the presence of PVC plastic. During the SlurryCarb™ process, PVC decomposes to form soluble hydrochloric acid. As can be seen from Table 1, chlorine content of the carbonized RDF was reduced approximately 95% to 0.17 mg/dry gram. Also, chlorine content of the RDF/lignite blend was reduced over 96%, due to the presence of alkali salts in the lignite ash.

Table 2 summarizes the average operating conditions and flue gas emissions from PFBR combustion tests of the carbonized RDF, lignite, and blended slurry fuels. As can be seen from Table 2, combustion performance of each fuel was excellent, with carbon burnouts exceeding 98%, with less than 26% excess air. Also, the SO_2 emissions from all

	Raw RDF	Raw Lignite	Carb. RDF	Carb. Lignite	50/50 RDF/Lig
Ultimate, dry, wt.%					
Carbon	47.6	61.9	68.0	66.0	67.4
Hydrogen	6.6	4.5	7.2	4.6	5.8
Nitrogen	0.2	0.9	0.5	0.9	0.8
Sulfur	0.2	1.8	0.1	1.5	1.1
Oxygen	38.7	20.8	13.1	16.7	15.0
Ash	6.7	9.4	11.1	10.3	9.9
Chlorine, mg/g	4.00	ND	0.17	ND	0.15
Rheology					
Wt.% Solids	9.4	35.9	44.4	55.2	56.4
Viscosity, cP	816	495	250	825	815
Higher Heating Value					
dry, Btu/lb	8,650	10,940	14,200	11,690	12,670
slurry, Btu/lb	813	3,927	6,305	6,453	7,146

Table 1 - Fuel Properties of Raw and Carbonized RDF, Lignite, and Blend Slurry Fuels.

three combustion tests were well below the Phase II CAAA regulation of 1.2 lb SO_2/MM Btu. As expected, carbonized RDF slurry fuel was lowest at 0.10 lb/MM Btu, with the 50/50 blend fuel next at 0.22 lb/MM Btu. Sulfur emissions from the carbonized lignite slurry fuel were 0.62 lb SO_2/MM Btu. No sorbents were added to the PFBR during the combustion test. Ash components of each carbonized slurry fuel were responsible for the manifested sulfur capture.

Nitrogen oxide emissions from the RDF based fuels were lower than those from carbonized lignite slurry fuel owing to the lower fuel bound nitrogen content of carbonized RDF. These levels are below the current federal standards for NO_x. Also, carbon monoxide and hydrocarbon emissions for the RDF based fuels were higher than for the lignite slurry fuel. This trend suggests that the greater amount of volatile matter in the carbonized RDF and blended RDF/lignite slurry fuels resulted in more burning in the freeboard section of the PFBR.

	Carb. RDF	Carb. Lignite	Carb. RDF/Lig
Reactor Pressure, psig	149.8	153.2	146.3
Avg. Reactor Temp, °F	1594	1554	1624
Avg. Slurry Feed Rate, lb/hr	7.0	5.9	6.4
Excess Air, %	22.2	23.3	25.9
Avg. Carbon Burnout, %	99.0	98.5	99.5
Avg. Gas Emissions, ppmv*			
CO_2	12.4	14.0	13.1
CO	8.6	1.6	9.0
SO_2	49.0	407.0	111.0
NO_x	117.0	156.0	113.0
N_2O	8.6	81.6	28.9
Hydrocarbons	8.8	3.6	4.4
HCl	3.8	ND	5.6
Avg. Sulfur Retention, %	35	69	85

*Average Gas Emissions are corrected to 3% O_2, dry, without dilution N_2

Table 2 - Average Operating Conditions from each PFBR Combustion Test.

FUTURE DEVELOPMENT

Since SO_2 emissions from all three combustion tests were well below Phase II CAAA limits, future SlurryCarb™ and combustion experiments will focus on lower weight percentage RDF blends, and higher sulfur lignite and bituminous coals. Since NO_x and CO emissions were exceptionally good from the PFBR, combustion tests also will be attempted with an atmospheric pulverized coal simulator.

Currently, EnerTech and EERC are demonstrating SlurryCarb™ with a continuous 625 lb/hour (wet basis) process development unit at the EERC. Initial demonstrations and analysis with RDF and lignite have been completed. Additional pilot plant runs with RDF are planned for April through July 1995 and preliminary runs with RDF/lignite blends are planned for September 1995. Also, initial atmospheric combustion tests have been completed in a 650,000 Btu/hr pc-boiler simulator, with additional atmospheric and pressurized combustion tests planned for May through December 1995.

SlurryCarb™ research and process development also continues with additional feed stocks including: plastic wastes, municipal and industrial sewage sludge, forest and pulp/paper industry wastes and byproducts, agricultural wastes and other cellulose materials.

CO-FIRING COAL AND BIOMASS WASTE IN AN FB BOILER

BY:- BC NORTH, CSIR, SOUTH AFRICA

INTRODUCTION

The CSIR has been involved in the field of FBC since 1976, when a small 0.25m^2 test facility was erected. Work really began in earnest in 1984, when the National Fluidised Bed Combustion (NFBC) boiler was commissioned. This facility, situated at the CSIR's pilot plant terrain in Pretoria West, was designed to produce 12 tph steam while utilising "waste" coal fuels. South Africa is heavily dependant on coal with some 88 % of its energy being derived from coal. The countries coal reserves are large, accounting for some 11 % of the worlds reserves. Unfortunately the quality of the coal is comparatively poor, and beneficiation is required in order to produce an acceptable fuel for the local and international markets. This leads to a large production of "waste" coal. More detail is given in Table 1.

It was concern about this waste that prompted the Department of Mineral and Energy Affairs (DMEA) to fund the construction of the NFBC boiler, the purpose of which was to prove the ability of FBC technology to utilize the low quality discard coal. The running costs of the unit were at first provided by the DMEA, and later by the National Energy Council (NEC). The NEC also played an active role in the formulation of test campaigns on the boiler. Management of the NFBC was undertaken by the division of Energy Technology (Enertek) at the CSIR in Pretoria, and it was sited at the CSIR's pilot plant facility in Pretoria West.

The boiler has been running since 1984 and many thousands of tonnes of low-grade coal have been burnt in it.

During the course of the test campaign on the NFBC the CSIR developed a great deal of experience in the field of FBC, and in particular use of low grade fuels in FBC equipment. The following paper describes the highlights of this test work and details the commercial plant which have since been built using CSIR technology.

SOUTH AFRICAN COAL AND WASTE COAL PRODUCTION

There are three major waste products from the coal, namely "discard" coal (coarse, high ash), "duff" coal (high fines, low ash) and slurry or slimes. The most recent estimation of coal and waste coal production is given in Table 1 below. These products are considered to be waste because they are unsuitable for use with conventional combustion equipment, e.g. chain grate stokers. The discard has too low a calorific value (CV), the duff is too fine and the slurry is too fine and too wet. (Although duff and dried slurry may at first appear to be suitable fuels for a pulverized fuel-fired boiler, a "captive colliery" policy prevents this).

Table 1: SOUTH AFRICAN COAL AND WASTE COAL PRODUCTION

Coal production:	
Bituminous	*223 Mt/a*
Anthractic	*8 Mt/a*
	231 Mt/a

Coal Waste Production

DESCRIPTION	*ANNUAL PRO-DUCTION RATE*	*AVERAGE CV*	*COMMENTS*
Bitum. coarse. "Discards"	*33Mt/a*	*15 MJkg^{-1}*	*High ash, size 0-150 mm*
Bitum. fine. "Duff"	*6.7Mt/a*	*26 MJkg^{-1}*	*Topsize 6mm*
Slurry (or slimes)	*3.7 Mt/a (dry)*	*24 MJkg^{-1} (dry)*	*Nominally -250 micron* *Produced at ± 50 % H_2O.* *dumped in dams*

EXISTING COAL WASTE DUMPS

Description	*Amount already dumped (in 1986)*
Discard	*254 Mt*
Duff	*8 Mt*
Slurries	*11 Mt*
	283 Mt

It should be noted that the slurry is a discard product, and has been neither beneficiated nor milled. The tests on slurry firing described later were not aimed at investigating the combustion of typical coal-water-mixture (CWM) fuels in a fluidized bed, but rather at the combustion of a naturally arising waste material. The slurry for the trials was made up by rewetting filter cake recovered from a slimes dam, typically to a water content of 35 %.

These fuels were all successfully utilised in the NFBC boiler. This boiler is described in more detail below.

THE NFBC FACILITY

The NFBC boiler has been in operation since October 1984, and has successfully burned both duff and discard coals with high efficiencies. Several papers have been written on various aspects of the work carried out on the NFBC. A brief description of the plant is given below.

The NFBC is a fluidized-bed boiler, designed to produce 12 t/h of steam from discard and duff coal. A sectional side view is given in Figure 1, a flow chart in Figure 2 and design parameters in Table 2.

The furnace is of membrane wall construction, with heat transfer also being effected by a bi-drum convection bank and inbed tubes. The fluidized bed itself is nominally 800 mm deep with an area of 9.3 m^2.

Coal or slurry can be fed either overbed or inbed. Limestone may also be fed overbed to reduce sulphur dioxide emissions. Elutriated solids are returned to the bed via an internal trickle valve and, optionally, from the primary cyclone.

Gas clean-up is effected by two cyclones in series and a baghouse.

The bed is sectioned into five zones, two of which enclose the superheater, to assist with bed temperature control and turn-down.

Figure 1: Section side elevation of NFBC Boiler

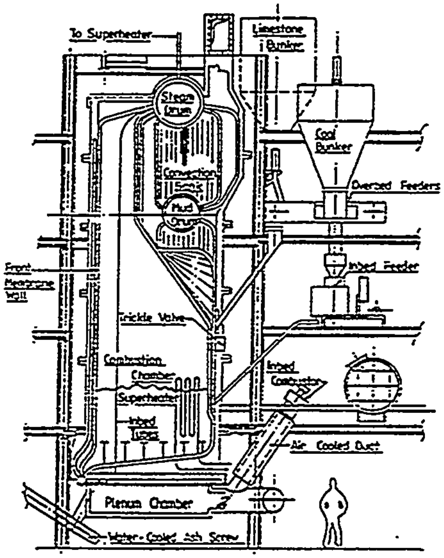


Figure 2: NFBC Boiler - Flowchart

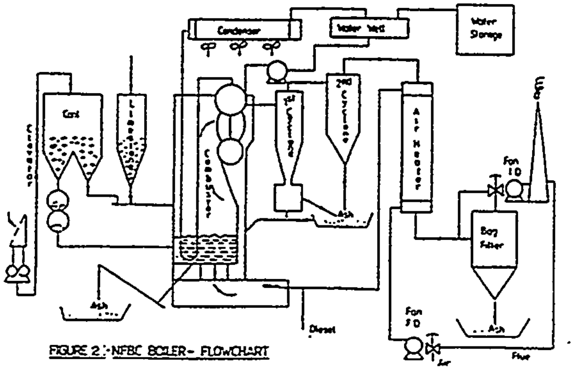


Table 2: NFBC BOILER OPERATING PARAMETERS (BASIS: DUFF COAL)

STEAM FLOW	*KG/H*	*12000*
Steam conditions: *Pressure* *Temperature*	 *MPa* °C	 *1,5* *255*
Feedwater temperature	°C	*95*
Bed temperature	°C	*780 to 900*
Bed dimensions	*m*	*3.05 x 3,05*
Freeboard height	*m*	*8*
Superheater area	m^2	*2,35*
Suphur capture	%	*80*
Boiler turndown	-	*3:1*
Boiler efficiency	%	*80*
Max. freeboard velocity	*m/s*	*1.9*
Exit flue gas temperature	°C	*170*

RESULTS OF TEST CAMPAIGN ON THE NFBC

DUFF AND DISCARD COAL

The results of the testwork on duff and discard coal have been published extensively previously, and will not be discussed in detail here. Suffice it to state that thermal efficiencies of about 81 % and 84 % were achieved when firing discards and duff respectively (both with employing primary cyclone grit refiring). In addition, up to 90 % of the SO_2 production from the discard coal was captured by employing limestone injection into the bed.

COAL SLURRIES

The results of the testwork on coal slurries has also been published previously, however, as the experience gained during this work is relevant to the biomass incineration to be covered later, it is discussed in some detail.

COMBUSTION OF SLURRIES

The slurry chosen for the testwork was from Goedehoop Colliery. A full analysis is given in Table 3. The size distribution is shown graphically in Figure 3.

Table 3: ANALYSIS OF GOEDEHOOP SLURRY

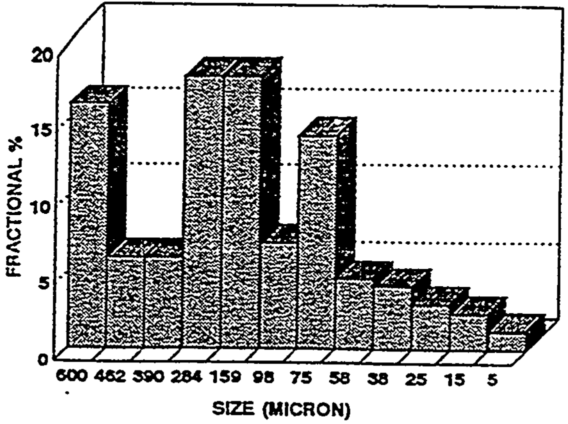
Proximate		*Ultimate*	
H_2O (%)	*2.6*	*C (%)*	*60.24*
Ash (%)	*20.7*	*H (%)*	*3.64*
Volatiles (%)	*26.2*	*N (%)*	*1.52*
Fixed Carbon (%)	*50.5*	*S (%)*	*1.00*
CV (MJ/kg)	*24.6*	*O (%)*	*10.30*

Ash Fusion Temperature		*Moisture*	
DT	*1380°C*	*SUP*	*6.3%*
HT	*+1400°C*	*INH*	*4.4%*
FT	*+1400°C*	*TOT*	*10.4%*

Table 3: (cont) ANALYSIS OF GOEDEHOOP SLURRY

Size (microns)	*Fractional %*	*Cumulative %*
+500	*16*	*100.0*
-500+425	*6*	*84.0*
-425+355	*6*	*78.0*
-355+212	*18*	*72.0*
-212+106	*18*	*54.0*
-106+90	*7*	*36.0*
-90+60	*13.9*	*29.0*
-60+45	*4.6*	*15.1*
-45+30	*4.1*	*10.5*
-30+20	*2.9*	*6.4*
-20+10	*2.3*	*3.5*
-10	*1.2*	*1.2*

Figure 3: Size Distribution of Goedehoop Slurry



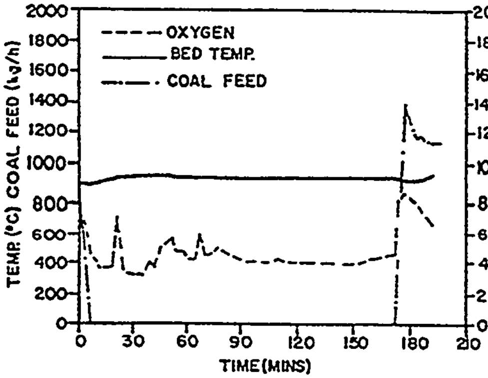
This slurry was first subjected to laboratory viscosity trials. These trials indicated that the pressure drop through the delivery line could be as high as 9.5 bar per meter for a 65 % solids slurry. It was decided to proceed with further trials, hoping that the results were not a true reflection of actual pipeline pressure drops. (As noted by other researchers, slurry pipeline pressure drops are difficult to predict from laboratory trials). This proved to be the case, and pressure drops in the region of 5 kPa per meter were recorded while pumping the slurry.

Tramp material which originally caused many problems with pump and line blockages, was easily removed by fitting a 5 mm mesh sieve over the inlet to the suction side of the slurry line. The material was removed from the stirred tank through a large diaphragm valve, in a similar fashion to a boiler blowdown.

Before any proper combustion tests could be performed, a series of familiarization runs were carried out. This entailed firing the slurry overbed and inbed for a period of approximately two weeks, with factors such as bed temperature excess air and boiler controllability being monitored.

Figure 4 shows the trend of some of the important plant parameters during one of these "familiarization" trials. The trend starts at zero time, just as the slurry feed was started. It can be seen that the coal feed dropped off rapidly to zero as combustion of slurry was now generating sufficient heat to satisfy the steam demand. The bed temperature stayed fairly stable at approximately 900 to 930°C. The oxygen in the flue gas fell from 8% (60 % excess air) to about 4 % (24 % excess air).

Figure 4: Steady State Operation with Slurry Firing



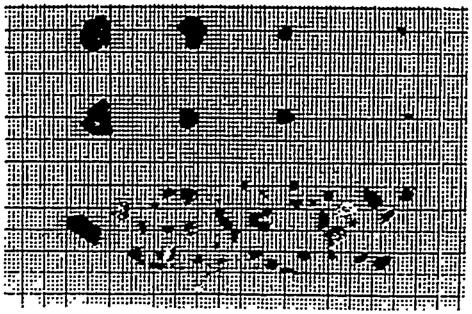
It was also attempted to start up the boiler on slurry alone after an overnight slump (generally it is started on coal, and slurry is fired once the boiler is stable). The bed temperature was initially indicated at 400°C when slumped. Upon fluidization, hot material was mixed throughout the bed and a more accurate average bed temperature of 640°C was indicated. this was brought up to 800°C over 40 minutes on slurry firing alone, after which the slurry pumping rate was cut back slightly. The bed temperature was then slowly increased to the normal operating temperature.

It is clear that the slurry can be combusted while maintaining an acceptable excess air level and bed temperature. This is theoretically impossible, as the residence time in the bed of particles of less than 212 micron has been estimated as one second, equating to a 1 % burn-out. There must be some mechanism, therefore, that causes the carbon to be present in the bed in particles significantly larger than the parent coal particles.

Two mechanisms which have been proposed are char-sand agglomerates and char-flecked sand. The agglomerates consist of relatively large (up to 1 cm) clusters of devolatized coal and sand. These agglomerates are formed while the individual slurry droplets are drying and devolatizing. In this respect the concept of the combustion of coal-water slurries in a fluidized bed differs from the concept of the combustion of commercial coal-water mixture (CWM) fuels in a burner. In the former case, large droplets are desirable, while in the latter case fine atomization is essential.

A sample of the bed material was taken after an extended period of slurry firing. This was found to contain 3-4% carbon, which was present in the form of char sand agglomerates. Figure 5 shows some of these agglomerates which have been placed on a standard metric grid in order to indicate size. Also shown below the agglomerates is some of the bed material. It consists mostly of the ash residue of discard and duff coal which has been fired in the boiler over a period of several months. During extended slurry combustion trials, the nature of this bed material would almost certainly change, and in all probability would consist of the burnt-out shells of the agglomerates in various stages of degradation. This places a restriction on the size of the agglomerates. The size of the agglomerates is generally increased by reducing the amount of atomizing air. This is beneficial from a combustion efficiency viewpoint but, if the agglomerates become too large, there is a danger of bed defluidization.

Figure 5: Char-Sand Agglomerates



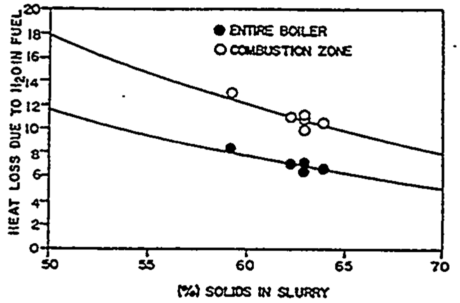
Once it had been proved that the slurry could be burnt autothermally, a series of combustion tests were carried out.

Firstly, slurries with a solid concentration ranging from 59 % to 64 % were fired under similar operating conditions. Data were collected in the normal fashion and the results processed to give a breakdown of the heat losses from the system (i.e. losses due to unburnt carbon, water in fuel, etc.) and the thermal and combustion efficiencies.

Figure 6 shows the effect of solids concentration on heat loss due to water in the fuel. Presented on the same graph is the heat lost from the entire system and the heat lost from the bed (assuming all the water is driven off in the bed). The former has a direct influence on the thermal efficiency of the system, while the latter would have an influence on the allowable inbed heat transfer surface area if a fluidized bed was to be purpose-designed to burn slurries. It can be seen that when a 60 % solids slurry is combusted, a 7 % penalty in thermal efficiency is incurred (i.e. 8 % lost, compared with a normal heat loss of 1% when firing ordinary coal). When the slurry concentration is increased to 67 % this penalty falls to 5 %. This relatively high heat loss due to water is an unavoidable fact when burning slurries.

Roberts et al. investigated the combustion of coal-water mixtures in a pressurized fluidized-bed combustor (PFBC) and concluded that the heat loss due to water was "not prohibitive". This is due in large part to the fact that the PFBC was part of a combined cycle power-generation system in which approximately half the heat lost is recovered due to increased gas flow through the turbine.

Figure 6: Effect of Solid Concentration on Heat Loss Due to H_2O



COMMERCIALISATION OF CSIR FBC TECHNOLOGY

In line with the CSIR's mission to assist South African Industry, our FBC technology has been effectively applied in industry to utilise low grade "fuels". Two of these applications are discussed briefly below. A third, the biomass sludge incineration boiler, is discussed in detail.

1 MW FB CARBON AND WOOD-CHIP INCINERATOR

This contract was undertaken by the CSIR in 1988. The client wished to recover minerals from a wide range of carbon-bearing materials, ranging from high-purity carbon to wood, and even plastic. His prime concern was to reduce carbon levels as much as possible in order to optimise further processing. The fluidised bed supplied to him was able to burn out all of the above materials to very low carbon levels, and was able to cope with swings in feed quality and water content. An air-distribution system consisting of horizontal sparges being fed from a plenum running the length of the unit ensured that oversize material could be continually removed. A conventional "flat plate" design would not have permitted this, and de-fluidisation with subsequent bed clinkering would have happened frequently. The plant has been in continuous operation since installation. Recently, a further 3 MW of FB capacity has been installed as the client is expanding his operation.

10MW FB HOT GAS GENERATOR

In 1988 the client operated conventional hot-gas generators fired by chaingrate stokers. These supplied hot gas to a dryer, in which he dried slag. He was unhappy with the performance of these hot-gas generators as they had a high maintenance cost and, more importantly, required a high-quality, high-cost, graded coal. Duff coal was available locally at a low price, but chain grates cannot use duff coal.

The solution was to install a purpose-designed FBC hot-gas generator. Some specific points which were required by the client, and which were addressed by the CSIR's design, were:

Extremely high carbon burn-out. All of the fly ash was carried over into the slag. Contamination in excess of 0.1 % carbon in the slag would cause noticeable discoloration.

The plant was designed with a relatively low fluidising velocity (maximum 1.7 ms^{-1}) and a large freeboard area (4m high). With these features, the fine carbon being elutriated from the bed was fully combusted before it left the furnace. Of further assistance was the fact that an FBC hot-gas generator operates at a high excess air level (about 150 %), thereby supplying oxygen for this final burn-out. The carbon efficiency achieved was about 99 %, which caused a carbon contamination of less than half of the allowable limit. This was despite the fuel containing, in some instances, about 40 % of particles with a size of less than 1mm.

Removal of tramp material. The duff coal was cheap, but it was of low quality. The ash content was inherently high, and the coal also contained some discrete stone particles of up to 25mm. These would cause defluidisation unless they could be removed from the bed.

An air-distribution system similar to that in the wood chip incinerator design was used. It again consisted of horizontal sparges, but for this unit the sparges were fed from a central plenum under the furnace. This allowed the large stones to be removed by draining bed material from the static bed region under the distributor. Another consideration was the fact that a flat plate-type of distributor would have been impractical in a bed of this size (26 m^2). Thermal expansion would cause excessive warping. The horizontal sparge system allows expansion and shrinkage as it goes through thermal cycling without affecting the integrity of the distributor.

Extended slump periods. The unit had to be capable of being slumped, or "banked" to use a term from chain-grate stokers, for periods of up to 30 hours, and restarted without the need to fire the start-up burner.

A deep bed was employed. In fact, the bed may be run as deep as 1m if required. However, it is generally run at about 500 mm, and this gives the required heat retention. The start-up burner is only required about once every year, after an extended stoppage, for example after the Christmas break.

In 1990 the team of CSIR technologists was awarded the SA Institute of mechanical Engineers Project and Systems Award for this contract. The criteria for this award included technological innovation, local content and complying to specification.

26 T/H FBC BOILER COFFEE GROUNDS SLUDGE INCINERATOR

General

The CSIR was approached by one of it's licensees, International Combustion (Africa) Ltd (ICAL), to design the fluidised bed combustion zone for a 26 t/h boiler. This boiler had been requested by a multi-national food company based in Estcourt, Natal, South Africa.

Two design requirements emerged from the clients needs: Additional plant steam and disposal of 12 t/h of coffee grounds sludge containing up to 87 % water. No conventional combustion technology could burn the coffee grounds in this form, hence pre-drying would be necessary. However, this would entail installing additional plant. The CSIR investigated the possibility of firing the coffee grounds as a sludge, with no pre-drying, in a fluidised bed.

The dual purpose of the FB posed a considerable challenge. Coffee sludge, although combustible, contains insufficient energy to evaporate its own water and maintain the bed at operating temperature (900°C). Coal therefore had to be co-fired as a support fuel. Further, additional fuel was required in order to produce the full rated capacity of 26 t/h steam. Duff coal could have been used, but site logistics and a high transport cost led to a decision to use pea sized coal.

Heat balance consideration

Neither the steaming rate nor the coffee grounds feed was constant. the steaming rate varied with plant demand, and the coffee grounds sludge rate varied with plant production. These were not necessarily linked.

The fluidising air had to be controlled such that:

- At all times the bed was fluidised;
- Sufficient excess air was present to ensure complete combustion;
- The forced draught (FD) fans were kept to a minimum physical size and power requirement.

The sludge injection system had to ensure good distribution across the bed, and also ensure adequate residence time above the bed to promote some flash drying. This flash drying is required to counteract the occurrence of over-bed combustion of the volatile matter fraction of the grounds which distorts the theoretical heat balance over the bed.

It is important to realise that the coffee grounds sludge cannot really be considered as a fuel. If a heat balance is carried out over the bed, upon combustion the coffee grounds release less than half the energy required to maintain the bed at its operating temperature of 900°C. The heat losses out of this system are principally the sensible heat in the gases, and the latent and sensible heat in the superheated steam arising from the water content of the sludge.

A great deal of theoretical calculations were carried out to determine how much coal should be co-fired in order to obtain a heat balance over the bed while operating at an acceptable excess air level. (The excess air level is directly related to the heat removed from the bed by the gases). The goal was to minimise the coal requirements and, conversely, maximise the amount of coffee grounds which could be incinerated. Table 4 shows a theoretical heat and mass balance for operation at full load while incinerating the full suply of coffee grounds.

Table 4: COMPOSITE FUEL TABLE

Component	Coal	Coffee	Other	Total (Mass)	Composite Fuel
CV MJ/kg	26.60	3.77	0.00		7.56
Rate kg/h	2385.00	12000.00	0.00	14385.00	14385.00
C %	67.70	10.53		2878.42	20.01
H %	3.40	0.71		166.59	1.16
O %	7.00	3.64		603.15	4.19
N %	1.60	0.01		39.41	0.27
S %	0.00	0.03		3.74	0.03
Ash%	14.60	0.08	25.00	357.76	2.49
H_2O%	5.70	85.00	75.00	10335.95	71.85
Total Heat	MJ/h:	108751			
Thermal	Efficiency:	54%	Steam	Produced:	26000 kg/h

The amount of coffee grounds which could be incinerated is related to the steam production rate. This is a consequence of a heat balance over the entire boiler. The logic is explained in more detail below.

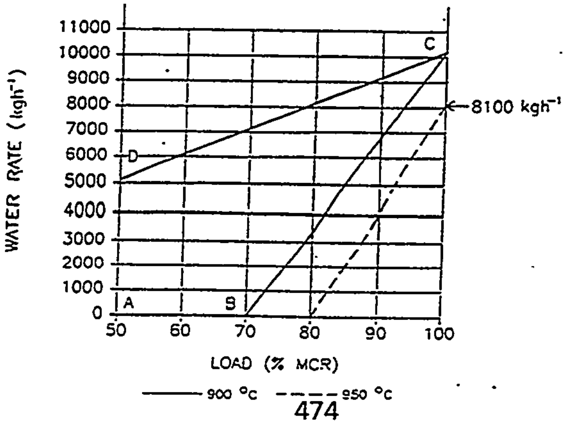
As the steaming rate is reduced at constant sludge injection rate, the coal feed is automatically cut back to reduce the energy input. However, the bed cooling remains the same, as the sludge injection rate has not changed. This would tend to cause the bed temperature to fall.

To maintain the bed temperature at set point, the forced draught (FD) fan damper is closed to reduce the fluidising air and therefore reduce air cooling of the bed. Essentially the excess air level will have been reduced. However, there is a limit to this procedure since sufficient excess air is required to ensure good combustion and stable operation.

This constraint led to the development of an "operability map" (Figure 7). It can be seen that the maximum allowable sludge injection rate is dependent on steam production (upper line). An additional point of interest on Figure 7 is the lower line. The FD fans are specified to deliver sufficient air to operate the boiler at full load when burning coffee grounds. The boiler cannot be operated at full load without sludge injection (to do so would have meant unnecessarily oversizing of the FD fans). Therefore, to increase the steaming rate above about 70 % maximum continuous rating (MCR) in the absence of coffee grounds, water may be injected as a substitute. The operability map has been programmed into the control system. It automatically limits the sludge-injection rate as the load falls, and also detects if there is a sludge deficiency as the load increases upon which an appropriate amount of water is injected.

It is only by staying within the bounds of this operability map that the boiler will be able to fire the coffee grounds as a wet sludge.

Figure 7: "Operability" Map



Practical implications of heat balance constraints

There is a further factor inherent in the above logic. In order to maximise the coffee grounds incineration, all other sources of bed cooling must be eliminated. For this reason a fully refractory-lined combustion chamber was employed as opposed to a more conventional water cooled wall panel. Even the roof of the combustor was refractory, as cooling surfaces in the freeboard area would lead to bed cooling by radiative losses.

Extensive trials in CSIR's test facilities showed that the problem was even more complicated than the theoretical case. In the theoretical studies it was assumed that all of the coffee grounds would dry and burn in the bed. However, due to the fact that the solids content of the sludge was actually 80% volatile matter, a significant portion of the heat was released in the freeboard area. The injection points were therefore positioned at a height where the flight time before entering the bed caused sufficient flash drying to counteract this effect. The flight time can also be varied within limits by increasing or decreasing the degree of air assisted dispersion.

Coffee grounds sludge injection

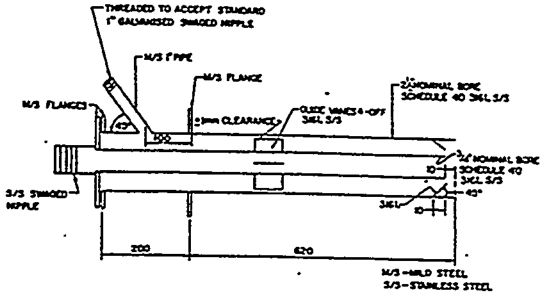
To this point, it has been assumed that the sludge was simply fed into the furnace. However, in reality this was no simple matter. Although the grounds contain 87 % water, they are still highly 'unpumpable'. Early trials in which the sludge was screw-fed onto the bed proved that this technique caused excessive localised cooling with subsequent bed de-fluidisation. With the client's experience of the material, a reliable sludge handling system was designed. The pumps chosen were wide-throat, auger-fed mono pumps. All valves in the lines were pinch valves with pneumatic activators. All bends were given as large a radius as possible.

The design of the injection nozzles also required careful consideration and experimentation. To achieve good dispersion and "throw" across the bed, the grounds must enter at a sufficiently high velocity. However, this high velocity cannot be achieved by forcing it through a small nozzle which would simply block. The inherent problems of handling the thick sludge are further complicated by the presence of relatively large (up to 15mm) lumps of chicory in the sludge. The final injector design chosen was a modification of those used to inject pyrite slurries into FB roasters. Figure 8 shows this concept. The principle features of it are as follows:

- The sludge is pumped through the inner pipe. Not shown on the diagram is direct air injection into the sludge. This artificially boosts the velocity of the sludge, facilitating good distribution across the bed even with a large fan-tail type nozzle at the tip of the injector. As a further refinement, the compressed air has been replaced by steam injection which reduces the compressor load. Increasing or decreasing this air/steam injection varies the distribution across the bed, and therefore the degree of flash drying as discussed above.
- Air from the FD fans is fed into the annulus around the central pipe. This is mainly to avoid the sludge heating and drying in the pipe, which would cause a blockage. It also provides some dispersion at the tip.
- The injector is fully removable, even while the bed is in operation to enable maintenance or replacement.
- Linked to the above, the pumps and nozzles were sized such that the full 12 t/h of grounds may be injected through any three of the four injectors.

The boiler was successfully commissioned in January 1994 and the actual thermal performance has matched predicted performance exactly.

Figure 8: Slurry Injector



In summary, the main innovative features of the Biomass and coal fired FBC boiler are as follows:

The entire concept is novel since conventionally coffee grounds are pre-dried to produce a self sustainable fuel. Injecting the grounds as a sludge has removed the necessity of presses and/or evaporation plant, saving capital and running costs.

The furnace is completely refractory lined in order to limit heat removal from the bed. If conventional water cooled walls had been employed only about half of the coffee grounds could have been incinerated. Even the roof is refractory as radiative heat transfer to cool surfaces above the bed can cause significant heat "losses" from the bed. All steam raising occurs in a bi-drum boiler bank to which the hot gases are ducted from the furnace.

In the unusual event of no coffee grounds being available, full load can be achieved by injecting water onto the bed. This is contrary to expection since instinctively one would assume that spraying water onto the bed would decrease steam production. However, it does work both in theory and in practice. This allowed a reduction in the size of the FD fans. This was critical, as the fans are already large and consume large amounts of power. Larger fans may not have physically fitted into the space available and may also have had to be imported rather than manufactured locally.

The injector and nozzle design are a customised adaption of existing pyrite injector applications. The nozzle orifice had to be sufficiently large to avoid blockage, particularly by chicory lumps. However, the sludge had to be injected at a relatively high velocity in order that it travels about 2m before entering the bed. This is necessary to ensure both good dispersion and the in-flight drying required to counteract over-bed combustion. This was achieved by direct air injection (later converted to steam injection) into the sludge. An annulus around the sludge-carrying pipe was cooled by air from the FD fans in order to prevent drying of the sludge and to provide some dispersion at the tip.

COMBUSTION AND INORGANIC EMISSIONS OF GROUND WASTE TIRES

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Abstract

An experimental study was undertaken to assess the combustion characteristics and emissions of SO_2, NO_x and CO_2 gases from ground waste tires. Results were contrasted with those obtained from burning pulverized coal. Laboratory bench-scale experiments were conducted in a drop-tube, laminar-flow furnace, in air at fuel-lean conditions, at gas temperatures ranging from 1300 K to 1600 K. Two particle size cuts were burned from both materials, 75-90 μm and 180-212 μm. Blends of coal and tire particles, at equal weight ratios, were also burned. Pyrometric and cinematographic observations revealed that the coal particles exhibited distinct volatile and char combustion phases, while tire particles exhibited a distinct primary volatile phase followed by a char combustion phase, which was accompanied by burning of secondary pyrolysis products. The total recorded combustion times were considerably shorter for tire particles because of their lower density. At a gas temperature of 1500 K, primary volatile flame temperatures for both coal and tire were in the neighborhood of 2200-2400 K, while char temperatures were 2000-2100 K for the tire and 1850-2000 K for the coal particles.

SO_2 emissions of burning ground tires increased from 160 to 500 ppm (corresponding to 30 to 90 wt% of their sulfur content) as the temperature increased from 1300 K to 1600 K. Combustion of coal produced SO_2 emissions in the neighborhood of 200-300 ppm (corresponding to 40 to 60 wt% of its sulfur content) independent of the gas temperature. The blend of coal and tire particles (equal mass ratios) exhibited SO_2 values which fell in between the above.

NO_x emissions were constant at approximately 175 ppm for tire crumb (corresponding to approximately 45 wt% of its fuel nitrogen content) and 625 ppm for coal (corresponding to 55 wt% of its fuel nitrogen content) in the temperature range studied. Smaller coal particles released more NO_x than the larger size particles. The coal-tire particle blends had emissions of 400 ppm.

CO_2 emissions from tire were 8-9 molar %, while for coal particles they were 5-7 molar %; the upper limits corresponded to approximately 100% combustion efficiency.

As a means to reduce the SO_x emissions, pulverized coal and tire crumb were fluidized together with particles of a calcium bearing sorbent - calcium magnesium acetate (CMA). CMA has been identified as an effective SO_x scrubbing agent in previous studies. Addition of CMA, indeed, reduced the SO_2 emissions for both materials. NO_x and CO_2 emissions remained unaffected.

INTRODUCTION

Of the several different routes available to solve the disposal problem of waste tires, energy recovery is considered one of the most promising. Waste tires can be burnt as whole tires (eg. cement kilns) or after shredding (eg. fluidized bed combustion) to smaller sizes. Shredded and ground tires can be co-fired with coal in existing coal power plants with little or no modifications. Tires contain sulfur, which is added to rubber during the vulcanization process. Tires also contain organically bound nitrogen. The sulfur contents of coal and tires are generally comparable, but the nitrogen content of tires is usually lower.

Unlike the scarce literature on the combustion of tires, the literature on the combustion of coal is voluminous. Release of sulfur bearing gases, such as SO_2, H_2S, etc., from coal combustion and ways of controlling them has been the subject of a multitude of investigations (see, for example, Chs. 3 and 8 of [1], for a synopsis). The source of such emissions is the sulfur in the coal which is oxidized during combustion to SO_2.[1] Sulfur removal, either from the fuel or from the combustion products, is required for emission control. SO_2 emissions are controlled at the effluent by wet or dry "flue gas desulfurizarion" involving compounds of calcium such as limestone and lime.

Nitrogen oxides (predominantly NO) are formed either by oxidation of organically bound fuel nitrogen to NO (fuel NO_x) or by oxidation of atmospheric nitrogen at the high temperature regions of flames (thermal NO_x). For fuels containing nitrogen, most of the released NO is due to the fuel nitrogen. This was demonstrated in experiments by Pershing and Wendt [2, 3] burning coal, where 80% of the released NO was produced from fuel nitrogen. However, even if fuel nitrogen was the major source of the produced NO, only 20-30% of fuel nitrogen conversion (oxidation) was observed in those experiments. To minimize the emissions of fuel nitrogen - derived NO, the gases in a combustor should be maintained fuel-rich long enough for the N_2 reactions to proceed [1]. Existing NO_x reduction technologies concentrate on either minimizing the NO_x formation in the combustion process (staged combustion, flue gas recirculation, low NO_x burners, etc.) or on removing already generated NO_x by chemical reaction with suitable reagents. The latter approaches include selective catalytic or non-catalytic techniques (using ammonia, urea, isocyanuric acid, etc.) [4, 5, 6, 7, 8]. Another very promising technique for in-furnace NO_x reduction employs additional fuel as the reducing agent (non-selective) and has been termed "reburning" [9]. Finally, to achieve combined SO_2-NO_x control carboxylic acid salts of calcium and magnesium, such as calcium magnesium acetate (CMA), calcium acetate (CA), calcium propionate (CP), calcium formate (CF) and calcium benzoate (CB) can be dry- or wet- sprayed in the post combustion region of furnaces [10, 11, 12, 13, 14]. While extensive literature exists on the SO_2 and NO_x emissions from the combustion of coal and on the methods for their control, limited work has addressed such emissions from the combustion of tires. For instance, SO_2-NO_x emissions from co-firing whole tires with pulverized coal in a modified 42 MW wet-bottom Ohio Edison boiler were monitored by Horvath [15]. Tires were introduced to the boiler at varying feed rates and, thus, the mass fraction of tires as a fuel varied from 0 to 1. It was reported that co-firing whole tires with coal reduced stack emissions of SO_2, NO_x and particulates.[2] Tire burn tests and associated SO_2-NO_x emissions were also mentioned by Pope [16], and in two issues of *Power* magazine [17, 18]. However, due to the complexity of the tests in utility furnaces, little fundamental understanding has been gained. This work is a fundamental experimental study aiming at monitoring the emissions from burning tires under controlled conditions so that inputs and outputs can be correlated. To put the emissions of tires into perspective, a comparison was conducted with the emissions

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[1] H_2S may also survive in fuel-rich flames.

[2] Neither the chemical composition of coal and tires used nor the firing conditions were given in that report.

of pulverized coal (which have been widely studied) burning under the same conditions. To facilitate such comparison, and also to accommodate the constraints of the small bench scale apparatus that was used in this work, ground tires were burned. Two particle size cuts were used for tires and coal: 75-90 μm and 180-212 μm. While pulverizing tire rubber to such small size is currently economically questionable, it may become viable in the future if appropriate economic incentives are established. Current estimates [19, 20] show that the cost of tire crumb from cryogenically grinding of tires can be as much as 3-5 times the cost of pulverized coal. However, increased tipping fees for tires in the future may offset most of this difference.

In this work, experiments were performed to determine the inorganic emissions (primarily SO_x and NO_x) of pulverized waste tire particles, see Figure 1. The particles were fluidized at steady-state steady-flow conditions in an electrically heated drop-tube furnace, at different gas temperatures (1300 K-1600 K). Their emissions were contrasted with those from pulverized coal particles of the same size burning under similar conditions. The SO_x and NO_x emissions were coupled with observations on their combustion behavior obtained with three-color optical pyrometer and high speed cinematography, see Ref. [21].

EXPERIMENTAL APPARATUS AND PROCEDURE

Electric Furnaces. Two similarly-configured, externally-heated, laminar-flow, drop-tube furnaces of similar construction were used in this work. Water-cooled injectors were used to introduce particles to the top of an 25 cm long and 3.5 cm in diameter isothermal zone sections. One furnace was sealed [10] and the effluent from the combustion of dilute clouds of particles in controlled atmospheres was monitored. The other furnace [22] incorporated long slotted windows at two sides to facilitate cinematographic observations and was coupled to a three-color optical pyrometer [23, 22] through an optical fiber. In this furnace, single particles were burned in air and their combustion intensity was monitored by the pyrometer along the vertical path of their flight, in the manner of Timothy and Sarofim [24], and Levendis and Flagan [25]. A simplified schematic of the furnaces is shown in Figure 2. Gas was introduced in both furnaces through the furnace injectors and also through concentric flow straighteners, positioned in the annular space between the injectors and the alumina tubes. The main air-flow through the flow straighteners was preheated (to about 1250 K for a T_w of 1500 K) before it entered the radiation cavities. The gas temperature along the centerline of each furnace was measured to be $\approx$50 K lower than the wall temperatures of 1350 and 1650 K of the current experiments. The flow rate for the combustion experiments was kept at 0.2-0.3 lpm through the flow straightener and 3 lpm through the furnace injector. The gas temperature profile along the centerline of the furnace was essentially isothermal, see Ref. [26]. Furnace wall temperatures were continuously monitored by type S thermocouples attached to the wall. Gas temperatures inside the furnace were measured at various axial and radial positions by an aspirated thermocouple [27, 13].

Pyrometer and Data Acquisition. A three-color near-infrared pyrometer was used to obtain the time-temperature histories of burning particles. The details of the pyrometer are described in Ref. [23]. The interference filters used had working wavelengths of 0.64, 0.81 and 0.998 μm. Silicon photodetectors were used for recording the radiation in all three channels. The current output was converted to voltage and was then amplified by pre-amplifiers ($\times 10^9$).

TABLE I: Composition of the Fuels

Composition on a mass basis	Ground Tire (SBR)	Bituminous Coal (PSOC -1451)
Fixed Carbon (%)	26.3	51.9
Volatiles (%)	65.0	34.4
Ash (%)	8.7	13.7
Carbon (%)	78.16	70.05
Hydrogen (%)	5.89	4.55
Sulfur (%)	1.7	1.4
Nitrogen (%)	< 0.5	1.4
Oxygen (%)	5.05	6.81

The time constant of the circuit was less than 1 ms. The signals were converted by a *Data Translation* (*DT2828*, 12 bit resolution) A/D high speed board and were recorded on a *IBM-AT* (8 MHz, 2.64 MB RAM) personal computer using the *Asyst* software.

SO_2 and NO_x Monitoring. Emissions from the combustion of dilute clouds of ground tires and pulverized coal were measured in the sealed furnace. The powders were pneumatically introduced with the aid of a particle feeding system [10, 26] through the furnace injector. All experiments were conducted in air and a background SO_2 concentration of 50 ppm (which was introduced to offset the absorbing tendencies of the alumina tube of the furnace [26]). When saturation was reached and the effluent concentration did not change any longer, the fuel particles were introduced and dispersed in the furnace.

Upon removing moisture with a *Permapure* dryer, the furnace effluent was monitored for SO_2 using a *Rosemount Analytical 590* UV SO_2 analyzer and for NO_x using a *Beckman 951A* chemilluminescent NO/NO_x analyzer. The analyzer signals were recorded using an *Omega* analog-to-digital converter interfaced with an *IBM AT-286* personal computer running *Omega* data acquisition software and *Lotus 123*.

The injection rate of the powders was 0.15 g/min +/- 7% and the mass flowrate of air was 3.6 g/min, hence, fuel-lean conditions were experienced. The calculated bulk equivalence ratios, ϕ, were 0.42 for coal and 0.48 for ground tires.

The signals from the analyzers were recorded for the duration of the tire/coal injection and later converted to concentration. Each experiment lasted between 10 and 15 minutes. The gas flowrate that was introduced to the furnace was constant (at STP) thus, the gas residence time varied from 1.1 to .89 seconds as the furnace gas temperature increased from 1300 K to 1600 K.

EXPERIMENTAL RESULTS AND DISCUSSION

The composition of the ground tire and coal samples used in this study is given in the following table.

A scanning electron micrograph of a tire particle of about 160μm in diameter is shown in Figure 1 a, and a close up detail of its surface is shown in Figure 1 b. A similar particle, after being pyrolyzed at T_g = 1450 K for a fraction of a second in the vertical furnace, is shown in

TABLE II: Combustion Emissions

Material	T_g (K) ↪ Size (μm) ↓	SO_2 (ppm)		NO_x (ppm)		CO_2 (%)	
		1300	1500	1300	1500	1300	1500
Coal	80μm	150	325	650	825	6.5	8.5
	200μm	220	150	550	625	5.5	6.25
Tire	80μm	200	250	80	125	7.0	6.5
	200μm	200	400	150	175	7.25	9.3
Coal + CMA	200μm	0	25	500	475	5.5	4.5
Tire + CMA	200μm	0	250	175	200	8.75	7.5
Coal + Tire	80μm	200	220	400	350	6.0	5.0
	200μm	200	260	350	425	5.75	6.5

Figure 1 c. A detail of its surface is shown in Figure 1 d. Big blowholes and a rough surface are apparent in the last SEM micrograph.

Examples of the combustion behavior of single particles of tires and coal are shown in Figures 2 and 3. A more detailed investigation is included in Ref. [21]. Time sequences of high speed cinematography photographs (500 and 250 frames/s) are shown in Figure 2 for two single burning particles, 180-212 μm in diameter, of tire and coal, respectively. Combustion took place in air at a gas temperature of 1450 K. Two distinct phases of primary volatile combustion and char combustion can be distinguished in both types of particles. Close examination has shown that the tire particles also exhibited a secondary devolatilization phase that occurred simultaneously with their char combustion phase. This is why the flames appeared large and bright during both phases of the combustion of the tire particles; for more details see Ref. [21]. The overall combustion times of tire particles were generally half those of coal particles of similar size, mainly because of the lower density of the tire particles. These results, from a different perspective, are shown in the pyrometrically-recorded profiles of Figure 3. The radiation intensity profiles, shown in the top row of Figure 3, depict the two distinct phases of volatile and char combustion. The profiles at the bottom row depict the derived flame/particle temperature profiles using Planck's theory for three two-wavelength combinations [23, 22, 21] and assuming that the emissivity ratios were unity for both flame and char combustion periods. Primary devolatilization flame temperatures in the range of 2200-2300 K and char temperatures of 1900-2000 K were recorded. Combustion durations were in agreement with high speed photography, and were in the range of 100 to 200 ms for coal and tire particles, respectively. It is encouraging to note that tires can burn faster than coal, when pulverized, despite the fact that approximately half their mass is carbon black, which is hard (slow) to burn. This was attributed to the aid of the secondary devolatilization during the char combustion phase of the tire particles.

The SO_2, NO_x and CO_2 emissions results are included in Figure 4 and Table II. Two different sizes of coal and rubber particles, 75-90 and 180-212 μm, and blends thereof were experimented with.

The SO_2 emissions from tire crumb increased with increasing gas temperature, see Figure 4 and Table 2. The emissions of SO_2 from coal stayed between 200-300 ppm for all temperature

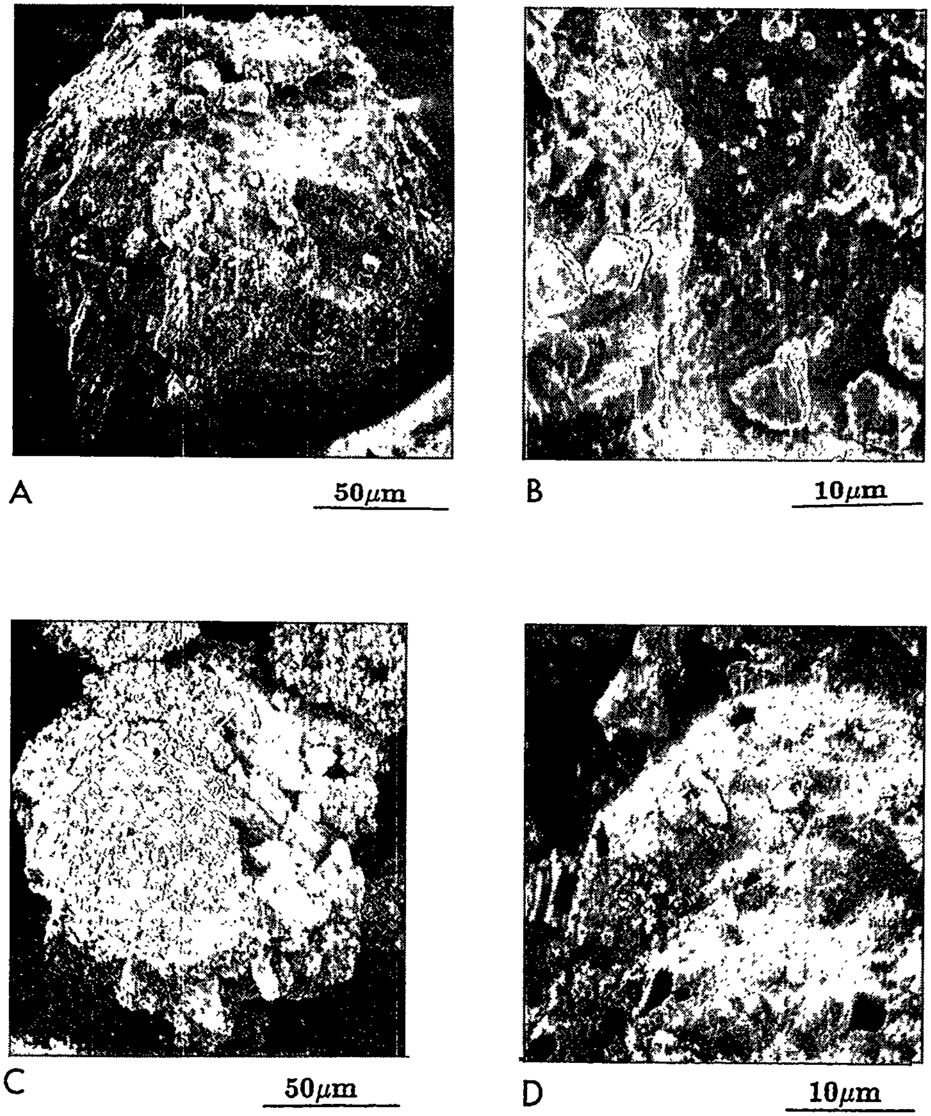

Figure 1: SEM photographs of tire particles. a) after cryogenic crushing; b) crushed particle surface detail; c) after pyrolysis at $T_g = 1450$ K in nitrogen for a fraction of a sec.; d) detail of this surface.

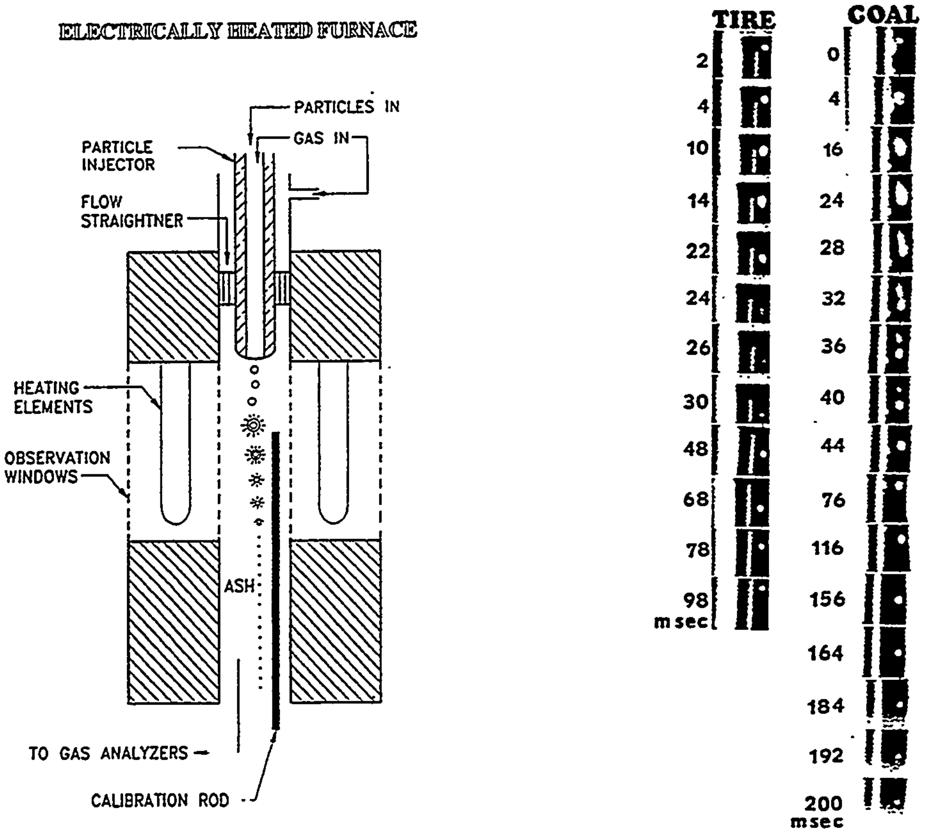

Figure 2: Experimental apparatus and high-speed cinematography photographs of burning (a) tire and (b) coal particles. The cylindrical rod that can be seen next to the burning particles is a size calibration device that was inserted in the furnace, its diameter is 1.23 mm.

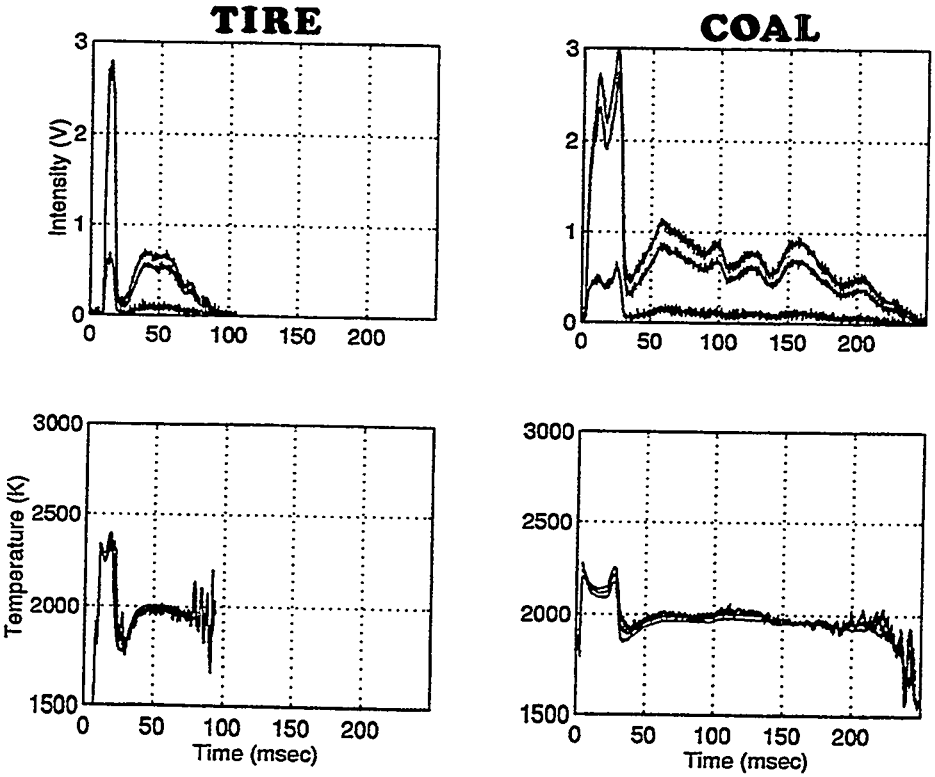

Figure 3: Combustion behavior of tire and coal particles. Pyrometric traces for single coal particles showing a) the radiation intensity vs. time, and b) the flame/particle temperature vs. time. In the temperature calculations, the emissivity was assumed to be independent of wavelength.

and particle sizes. This is about 50% of the calculated expected SO_2 emissions (530 ppm) if all the sulfur in the coal, listed in Table I, was converted to SO_2 at the calculated ϕ of 0.42. The rest either becomes encapsulated by the ash (primarily by the aluminosilicate components [28, 29]) or remains in any unburned carbon, that exited the furnace. Evidence of unburned carbon was detected by examining the ash under an oprical microscope, and gravimetric analysis revealed that unburned carbon amounted to only 1% of the original weight of coal.

For tires, theoretical calculations revealed an expected 580 ppm of SO_2 at the conditions of these experiments, $\phi = 0.48$. The fact that the ground tire SO_2 emissions increased with gas temperature from 200 to 500 ppm (i.e from 30 to 90 % of fuel S was converted to SO_2) was attributed to more effective combustion, as attested by higher emissions of CO_2 and less visible carbon in the ash. The fact that the SO_2 emissions from the tire crumb approached those theoretically calculated at high temperatures may be an indication that ash encapsulation of sulfur may not be as an important mechanism in tire particle combustion. A comparison of the results with the larger particles with those from a limited number of experiments with the smaller size particles, did not reveal any obvious dependencies of the SO_2 emissions with the particle size (Table II). Finally, the emissions from 50-50 blends of coal and tire particles fell in between those of their constituents (Table II).

NO_x emissions from the combustion of these particles are shown in Figure 4 b. If based on previous findings [1], we assume that most of the NO measured was formed from fuel N, then about 45 to 55% of fuel N was converted to NO for the tire and coal, respectively. Small, 75-90μm, coal particles released more NO_x, up to 850 ppm (see Table 2) than large particles. The contributions of the volatile combustion and char combustion phases will be investigated in future work. While the contribution of the "thermal NO_x" was not quantified in these experiments, it was not expected to have played an important role at the observed char combustion temperatures (Figure 3), but it might have contributed some during volatile flame combustion.

CO_2 emissions from both coal and tire particles increased with increasing temperature (Figure 4 c). CO_2 emissions per heating value (BTU or kJ) are roughly equal for tire and coal [15]. Greater CO_2 emissions from tire particles were measured since both tire and coal particles were burned at the same mass flow rate and the heat content per unit mass of tire is greater than that of coal [15].

Experiments were also conducted to investigate the addition of pulverized calcium magnesium acetate (CMA), 50μm size particles, to the ground tire and coal samples. CMA was simply mixed with the tire and coal particles at a weight fraction *ca.* 0.13 to provide a Ca/S ratio of 1 in the mix. Results are shown in Table 2. CMA remarkably reduced the concentration of the emitted SO_2 (by over 90%) both for coal and rubber. CMA did not appreciably affect the NO_x emissions from either ground tire or pulverized coal.

CONCLUSIONS

1. The sulfur content of ground tires and bituminous coal were comparable and SO_2 emissions were also comparable at 1300 K. However, while SO_2 emissions from 200 μm coal particles were independent of temperature, those from 200 μm coal particles increased with increasing gas temperature.

2. The nitrogen content of tires was lower than that of coal and their NO_x emissions were

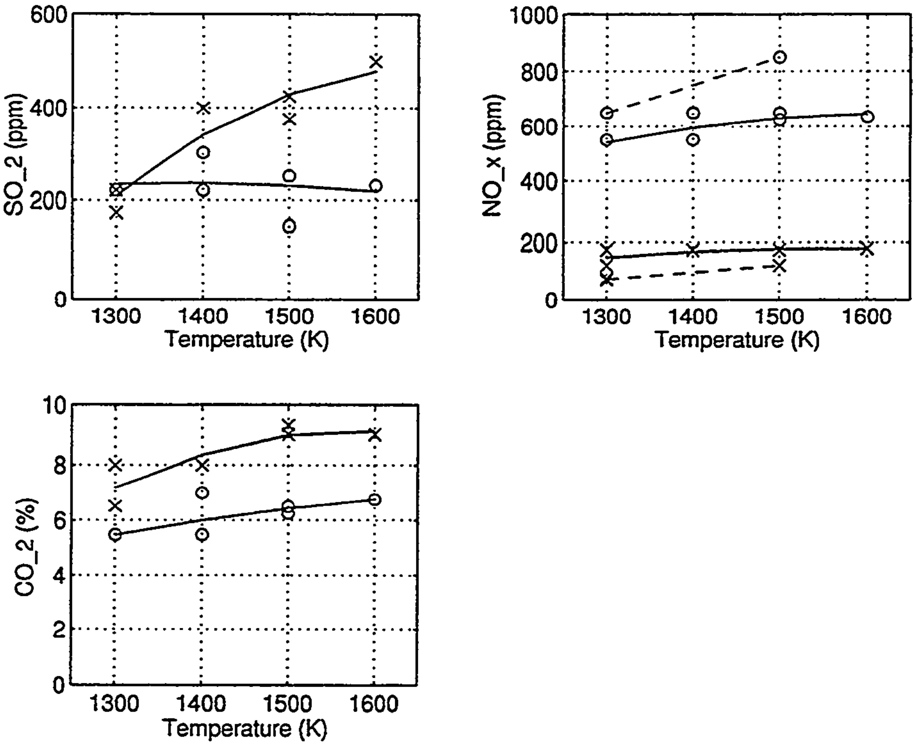

Figure 4: Gaseous emissions from combustion of ≈200 μm coal and tire particles as a function of temperature. a) SO_2 (ppm). o - coal; x - tire. b) NO_x (ppm). o - coal; x - tire. solid line - 200 μ particles; dashed line - 100 μm particles. c) CO_2 (%). o - coal; x - tire.

proportionally lower. NO_x emissions from 200 μm tire and coal particles did not change appreciable with gas temperature.

3. The CO_2 emissions of ground tires were higher than those of coal. CO_2 emissions from 200 μm tire and coal particles increased with increasing gas temperature.
4. The emissions of SO_2, NO_x and CO_2 from the combustion of blends of coal and tire particles were between those from the combustion of tire or coal particles.
5. Addition of pulverized CMA (13% by mass) to the fuel powders drastically reduced the SO_2 emissions by over 90%, while it did not appreciably reduce NO_x.

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AN EXTENSIVE STUDY ON RANEY Cu-Co CATALYSTS FOR THE SYNTHESIS OF HIGHER ALCOHOLS FROM COAL BASED SYNGAS

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ABSTRACT

Raney Cu-Co catalysts of different Cu-Co (atomic ratio = 0.2- 0.3) have been prepared and tested for the synthesis of higher alcohols (at 563 K, 6 MPa, and H_2 / CO=2) and characterized by XRD, XPS, and H_2-TPD. Raney Cu-Co catalysts prepared from Cu-Co-Al alloys are composed of two kinds of Cu-Co solid solution. One is enriched in Cu , while another is enriched in Co . The surface composition of the Raney Cu- Co catalysts is considerablly different from the bulk composition . Enrichment of Cu on the surface is intensive, and can be weakened by the ambient gases of CO,CO_2, and syngas, For CO hydrogenation , the main products on Raney Cu-Co catalysts are C_1– C_6 normal alcohols and C_1– C_6 normal aliphatic hydrocarbons. The distributions of the products follows the Schulz-Florry equation , but the probability of carbon chain growth for alcohols (0.3-0.55) is lower than that for hydrocarbons(0.6-0.75). The stable alcohol yield of the Raney Cu-Co catalysts with Cu/Co =0.3- 1. 5 (atomic ratio) are higher than those of the coprecipitated Cu- Co catalysts. At Cu/Co=0.8 (atomic ratio), the stable alcohol yield of the catalyst reaches 0.57 g/g/h. In the H_2- TPD spectra on Raney Cu- Co catalysts, four peaks (A, B, C, and D) are observed when hydrogen adsorption temperature is high (563->303K), while only three peaks (A,B, and D) are observed when H_2 adsorption temperature is low(298K). Peak C results from the activatedly adsorbed H_2 , and is attributed to low -coordinated Co sites. The area fraction of peak C changes with catalysts in the same order as that of alcohol selectivity. Based on the results obtained , the nature of CO insertion sites has been discussed.

KEY WORDS: higher alcohols, Raney Cu-Co catalysts, XRD, XPS, and H_2-TPD

INTRODUCTION

Among the various routes of syngas conversion, the prioduction of higher alcohols as fuels , octane boosters, and feed stocks of chemical industry remains an attractive goal for the near future, and can be achieved by using a number of catalytic processes. Of the catalysts currently available , Cu-Co coprecipitated catalysts are known as the most selective towards alcohols, and therefore , are considered to be the most promising[1]. In recent years, many researches have been carried out, and Cu-Co solid solutions have been proposed to be the active phase[2]. However, no studies (except ours) have ever been done on Raney Cu-Co catalysts in which Cu-Co solid solutions are most probabily formed. In this work , Raney Cu-Co catalysts of different Cu/Co have been prepared and tested for the synthesis of higher alcohols, and characterized by XRD, XPS, and H_2 -TPD.

EXPERIMENTAL

●Catalyst Preparetion

Cu-Co-Al alloys of different compositions were prepared in an arc furnace under Ar atmosphere. Granulated alloy samples were leached with KOH soluation (6%) at 333 K, washed with distilled water under H_2, dried in H_2 stream, reduced with H_2 at 563K for 3hrs and kept sealed. The bulk compositions of the Raney Cu-Co catalysts prepared are given in table 1.

Table 1 Compositions of alloys and their products Raney Catalysts

No.	Alloy(atom %)			No.	Catalysts (atom %)		
	Cu	Co	Al		Cu	Co	Cu/Co
A1	4.50	27.2	68.3	B1	14.2	85.8	0.17
A2	8.60	22.6	68.8	B2	27.6	72.4	0.38
A3	13.0	16.6	70.4	B3	43.9	56.1	0.78
A4	16.2	13.3	70.5	B4	54.9	45.1	1.22
A5	23.1	1.0	75.9	B5	95.9	4.1	23.1

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[2] Tong, k., Liu, C. J., and Liu, J. Y., J. catal. (Chinese) 7(2), 124 (1986).

●Characterization by XRD

Under N_2, the reduced Raney Cu- Co catalyst samples were granulated to 300 mesh, held on the sample holder, sealed with transperent adhesive tape, and measured immediately by XRD (Rigaku/MAX -II A, Target: Cu K_α).

●Characterization by XPS

Under N_2, reduced and further treated(with CO,CO_2,and syngas at 563K , for 2 hrs) Raney Cu-Co catalyst samples were granulated to 200 mesh, held on the sample holder, put into analysis chamber , and measured immediately by XPS (PHI-5300, Mg K_α). Au $4f_{7/2}$ (= 83. 8eV) was used to calibrate work function. The contaminated carbon (C1s= 284.8 eV) was used to calibrate binding energy.

●CO Hydrogenation

The experiments were carried out in a continuous flow high pressure micro-reactor (Φ10X1) . The temperature of the reactor was controlled by a digital temperature controllor. The temperature fluctuation was less than ±1 K.

Under H_2, leached and washed Raney Cu-Co catalysts were put into the reactor , dried at 383 K for 2hrs , reduced at 563K for 3 hrs , and tested at 563 K, 6MPa, H_2/CO=2(8.5 l/hr), and catalyst 0. 5g. The products as well as the syngas were analysed by two sets of on-line gas chromatograph. Alcohols and hydrocarbons were analysed on a Chromosorb 101 column (3m,353-423K,2K/min.) and detected by a FID. H_2,CO, CO_2,and CH_4 were analysed on a carbon molecular sieve column (2m, 373K) and detected by a TCD. Two sets of data were calibrated to the same basis with methane as a reference, and processed with carbon atom balance .

●Characterization by H_2-TPD

The experiments were carried out on a TPD equitment with a U type squartz reactor (Φ6X1). The temperature of the reactor was controlled by a temperature programed controllor . The catalyst temperature was detected by a EU type thermal couple . The desorbed gases were detected by a TCD . The H_2-TPD spectra were recorded by a two- pen recorder.

☆Low Temperature Adsorption

0.3g catalysts were put ino the reactor , reduced with H_2(>99. 99%) at 563K for 3hrs , treated with Ar(>99.99%) at the same temperature for

0.5 hrs and cooled down in Ar stream to RT(298K). H_2 adsorption took place at RT for 10 min. Then, the catalyst was purged in Ar stream (30ml/min.) at RT for 20 min., and heated linearly from RT to 773K at 18 K/min.

☆High Temperature Adsorption

The same procedure as above was used here except that the catalyst, after reduction , was coolled down in H_2 rather than Ar stream to RT.

RESULTS AND DISCUSSION

●Characteriation by XRD

XRD patterns of Raney Cu–Co catalysts(R_1–R_5)are shown in Fig. 1 . These patterns are much like those of pure Cu and pure FCC Co. With Cu/Co increasing, the XRD peaks of the catalysts approach to those of pure Cu (the strongest peak 2θ=43.3° . While, with Cu/Co decreasing ,

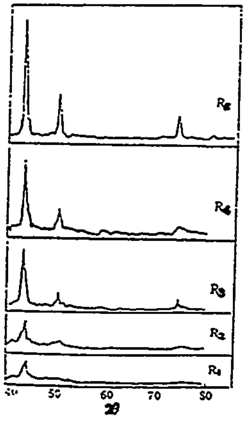

Fig. 1 XRD patterns of Raney Cu – Co catalysts (target: Cu)
Cu/Co (atomic ratio): R_1, 0.17: R_2, 0.38: R_3, 0.78; R_4, 1.22: R_5, 23.1

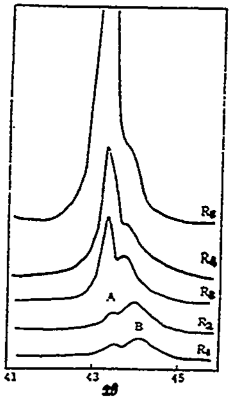

Fig. 2 Comparison of the XRD patterns of the Raney Cu – Co catalysts (target: Cu)
Cu/Co (atomic ratio): R_1, 0.17; R_2, 0.38; R_3, 0.78; R_4, 1.22; R_5, 23.1
peak *A*: Cu – Co solid solution enriched in Cu.
peak *B*: Cu – Co solid solution enriched in Co.

the XRD peaks of the catalysts approach to those of pure FCC Co (the strongest peak $2\theta=44.3^{\circ}$). The results of fine scaning at $2\theta=41-46^{\circ}$ (see Fig.2) indicate that the stongest peaks in Fig. 1 are all composed of two peaks (marked as A and B). Peak A and Peak B are located between the strongest peaks of Pure Cu and Pure FCC Co, and move towards the peak of pure Cu with Cu/Co increasing, but towdrds the peak of pure FCC Co with Cu/Co decreasing. All the above results indicate that Raney Cu-Co catalysts prepared here are all composed of two kinds of Cu-Co solid solution. One is enriched in Cu (A) , the other is enriched in Co(B).

Table 2 Valence state of Cu and Co after treating with different gases at 563 K for 2 hrs (catalyst : R4)

Gases	Surface composition (atom %)[a]				Co° (%)	Cu/Co
	Cu°	Cu^{+1}	Co°	Co^{+2}		surface
none [b]	16.25	trace	0.43	1.20	26.3	9.97
syngas	16.93	trace	0.74	1.71	30.8	6.90
CO	19.06	trace	0.46	2.15	17.6	7.3
CO_2	15.71	trace	0.33	2.06	13.8	6.6

a : Al, K, O, and C not shown in the table
b : measured directly after reduction

●Characterization by XPS

The surface composition and valence state of Raney Cu-Co catalysts reduced and further treated with different gases were determined by XPS. The results are listed in Table 2 . On the surface of the reduced catalyst, not only Cu°and Co°,some Co^{+2}still exists but no Cu^{+1} and Cu^{+2} are found. At the reaction temperature (563K), Co° on the surface can be partially oxidized by CO and CO_2 , with CO_2 as a stronger oxidizing agent. But syngas (H_2/CO=2) is a reducing agent. In contrast, Cu°on the surface is not affected by those gases. Cu/Co ratio on the surface is higher than that in the bulk (see Table 1) and can be affected by ambient gases. Cu enrichment on the surface is considerable, and can be weakened by the ambient gases (CO, CO_2, and Syngas). this is due to Cu having a lower surface energy than Co and the ambient gases having a stronger adsorption on Co than that on Cu[3].

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3. Ponec, V., Catal. Rev. -Sci. Eng. 11(1),41-70(1975).

●CO Hydrogenation

The main products of CO hydrogenation on Raney Cu-Co catalysts are C1-C8 normal alcohols and normal aliphatic hydrocarbons. For Cu/Co=0. 2 - 1. 5(atomic ratio) , the product distribution of alcohols and hydroncarbons follows the Schulz-Florry equation, but the carbon chain growth probability for alcohols (0. 3- 0. 5) is less than that for hydrocarbons(0.6-0.7). The test results are listed in Table 3. With Cu/Co increasing , the activity , C_2OH, and carbon chain growth probability all decrease, but methanol increases. The stable alcohol yield of the Raney Cu-Co catalysts with Cu/Co=0.3-1.5(atomic ratio) are higher than those of the coprecipitated Cu-Co catalysts. At Cu/Co= 0. 8 (atomic ratio), the stable alcohol yield of the catalyst reaches 0. 57 g/g/h, much higher than that of the IFP coprecipitated Cu-Co catalyst (0.2 g/g/h).

Table 3. Results of reaction tests

Cat.	Cu/Co	Stable Zone						React. Time 3-5 hrs				
	atom	A(a)	Sa	Ya	C_2	P	Sa(C_2)	Aa	Sa	Ya	C_2	P
R2	0.4	74	5	0.15	76	0.48	3.8	87	40	1.6	78	0.49
R3	0.8	70	33	0.57	75	0.44	24.8	86	55	2. 6	76	0.47
R4	1.2	69	22	0.39	63	0.43	13.9	69	45	0.6	67	0.46
R5	23.1	19	12	0.03	21	0.38	2.52	39	12	0.05	27	0.34

Aa : CO conversion (%)
Sa : selectivity to total alcohols (%)
Ya : yield of total alcohols (g/g/h)
C_2 : fraction of C2OH in total alcohols (wt. %)
P : probability of carbon chain growth for alcohols
Sa(C_2): selectivity ton C_2OH (%)

●Characterization by H_2-TPD

☆Low Temperature Adsorption

The H_2-TPD spectra on Raney Cu-Co catalysts with H_2 adsorption at RT(298K) are shown in Fig. 3. On Co-containing catalysts (R-Co and R_1- R_4), two peaks are observed at 344-476K and 623-657K, while on R-Cu,

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4. Wang, F. Y., Huang, J. S., Xu, Y. D., Dai, L. Z., Lu, D. X., and Peng, S. Y., J. Catal. (Chinese) 15(6), 426-431(1994).

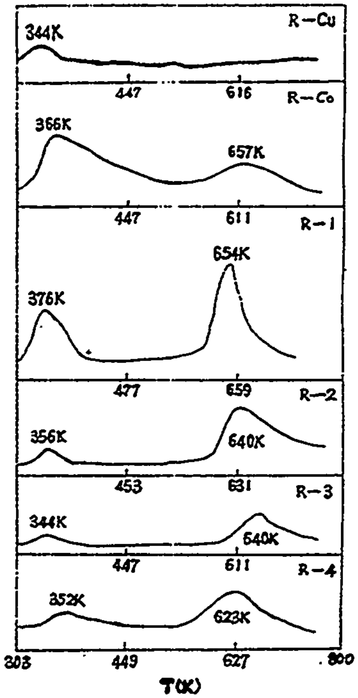

Fig. 3 H_2-TPD spectra on Raney Catalysts(catalyst: 0.3g ad. temp.: 298K)

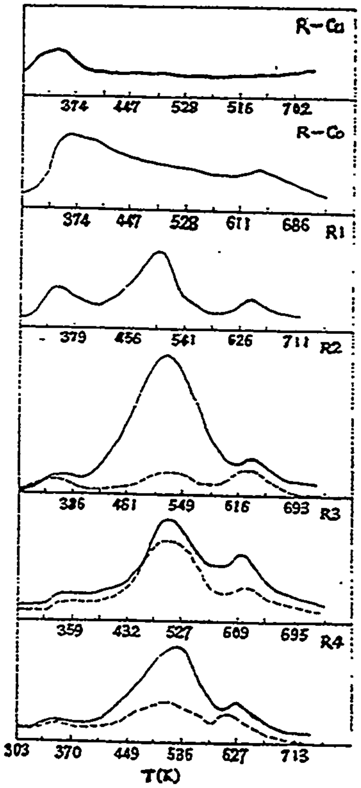

Fig. 4 H_2-TPD spectra on Raney Catalysts(catalyst:0.3g ad. temp.: 563->298K) only one peak is observed at 344 K. Similar H_2- TPD experiments have been carried out in our laboratory on coprecipitated Cu-Co catalysts[4]. In the low temperature zone (320-380K), two partially overlapped peaks rather than one peak have been observed and attributed to Cu (the lower temperature peak) and high-coordinated Co sites respectively. Similarly, the low temperature peak on R_1-R_4 can be attributed to Cu and high coordinated Co sites. The formation of Cu-Co solid solution in the Raney Cu-Co catalysts might lead to strong interaction between Cu and Co sites on the surface , and this interaction might lead to the totally overlapping of the two peaks (responsing to Cu and high coordinated Co sites respectively). The sites for the high temperature peaks have not been clarified yet.

☆High Temperature Adsorption

H_2-TPD spectra on Raney Cu- Co catalysts with H_2 adsorption temperature changing from 563 to 298K are shown in Fig. 4. The spectra on R-Cu is similar to the case of the low temperature adsorption (see Fig. 3) The spectra on R-Co is also similar to the case of the low temperature adsorption (see Fig. 3) except that a small amount of hydrogen seems to be desorbed gradually in the mid-temperature zone(493 -563K). In contrast, the spectra on R_1-R_4 are obviously different from the cases of the low temperature adsorption (see Fig. 3) . In addition to the low temperature peak and the high temperature peak , a much stronger peak is observed in the mid-temperature zone(493- 563K) . This mid-temperature peak emerges only in the case of the high temperature adsorption, indicating that it results from the activatedly adsorbed H_2. Because similar mid-temperature peak can be found in the H_2- TPD spectra on Co powder and Co/Al_2O_3 [5],but nothing can be found on Cu catalysts[6], the sites responsing to the mid-temperature peak can be attributed to the Co sites adsorpting H_2 activatedly. Reul etal.[7] found that hydrogen adsorption on Co is activated and reversible. If the activatedly adsorbed H_2 is considered, the H_2 adsorption stoichometry reaches 1.0 (H/Co_s), otherwise, less than 1.0, indicating that the Co sites on which H_2 adsorption is activated are surface sites. They also found that the proportion of the activatedly adsorbed H_2 on Co/Al_2O_3 catalysts decreases with the Co crystal size increasing. Besides, we found that the mid-temperature peak is much more sensitive to the high temperature treatment. The above results indicate that the mid-temperature peaks (see Fig.4·) correspond to the surface low-coordinated Co sites on which H_2 adsorbed activatedly.

The area fractions of the mid-temperature peaks (marked as β(i) for fresh catalysts and β (s) for used catalysts) are in proportion to the concerntration of the low-coordinated Co sites on the surface of the catalysts. Some area fractions of the mid-temperature peaks (β (i)

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5. Zowtiak, J. M., and Bartholomew, C. H., J. Catal. 83,107(1983).
6. Robert, D. L., Griffin, G. L., J. Catal. 110,117-126(1988).
7. Ruel, R. C., and Bartholomew, C. H., J. Catal. 85,63(1984).

Table 4. Relations between the activated adsorption of hydrogen and alcohol selectivity

Catalysts	Activated Adsorption		Alcohol selectivity	
	β (i) (%)	β (s) (%)	Sa(i) (%)	Sa(s) (%)
B2	82.1	41	42	5
B3	66.7	70	10	33
B4	75.6	61	32	22

☆ β (i) and Sa(i): obtained with fresh catalysts.
☆ β (s) and Sa(s): obtained with used catalysts.

and β (s)) obtained from Fig. 4 are listed in Table 4 along with the initial alcohol selectivities[Sa(i)] and the stable alcohol selectivities[Sa(s)]. It is clear that β (i) changes with catalysts in the same order as that of Sa(i), β (s) also changes with catalysts in the same order as that of Sa(s), but these two orders are different. We also noticed that these two orders are all different from that of the catalyst Cu/Co.

Raney Cu–Co catalysts are composed of two kinds of Cu– Co solid solution phases (A and B). For different catalysts, phase A has different composition, and so does phase B. Therefore, the surface structure of phase A as well as phase B for different catalysts may be different. Furthermore, because of the phenomena of surface enrichment, the proportion of phase A and phase B on the surface for different catalysts may be different. Therefore, the surface micro- structure of the catalysts may not have a linear relation with their bulk Cu/Co. β (i), β (s), Sa(i), and Sa(s) are only relative to the surface micro -structure of the catalysts, So they do not have a linear relation with the catalyst Cu/Co, either.

●5. CO Insertion Site

Since the selectivity to C_2 OH [$Sa(C_2)$] changes with catalysts in the same order as that of the total alcohol selectivity (Sa) (see table 3), the concentration of the low–coordinated Co sites on the catalysts surfaces must also changes with catalysts in the same order as that of $Sa(C_2)$.

According to the mechanism proposed by Xu Xiaoding etal.[1], the key step for higher alcohol formation is CO insertion. The higher the concentration of the CO insertion sites , the higher the alcohol selectivity is . Here we found that the higher the concentration of the low–coordinated Co sites, the higher the alcohol selectivity is. Apparently, low–coordinated Co sites are most likely the CO insertion sites. This inference is in accordance with the IR results[8].

CONCLUSIONS

Raney Cu–Co catalysts are composed of two kinds of Cu–Co solid solutions. One is enriched in Cu, The other is enriched in Co. The surface composition of the Raney Cu–Co catalysts is different from the bulk. Cu enrichment on the surface is intensive.

Raney Cu–Co catalysts are very active and selective for the synthesis of higher alcohols. The low-coordinated Co sites on the catalyst surface are most likely the CO insertion sites.

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BOILER FLUE GAS CLEANING BY LIQUEFACTION

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INTRODUCTION

Abdelmalek & Associates, Inc. is an Engineering and Construction Management Company located in St. Louis, Missouri. Abdelmalek's flue gas cleaning by liquefaction utilizes thermodynamic cryogenic process for removing NO_x, SO_x and CO_2.

ABSTRACT

A flue gas stream emitting from a boiler after removing the flyash and fine particulate matter is cooled in a reversible condensing heat exchanger to drop its temperature from approximately 270° F to near ambient temperature and to preheat a combustion air stream to approach the flue gas entering temperature. Sensible and latent heat from the flue gas stream is recovered by the combustion air stream causing condensation of acidic water vapor and removal of hazardous trace metals vapors. The cooled flue gases then undergo steps of compression, cooling, expansion and heat exchanging to reach thermodynamic equilibrium conditions for liquefaction of SO_2, and CO_2. Expanded and cleaned flue gas stream is then diffused through a cooling tower structure to disburse the flue gases into the atmosphere. Liquefied SO_2 and CO_2 by-products are then removed for further processing and for possible manufacturing for a wide range of well known chemical products.

THE PROCESS

Abdelmalek's thermodynamic process for cleaning the boiler flue gas stream is firstly through flue gas cooling and condensing at atmospheric conditions, and secondly by utilizing compression and cryogenic open cycle, where heat exchanging steps take place between a polluted relatively hot and compressed flue gas stream, and a cleaned relatively cold and expanded flue gas stream. SO_2 and CO_2 contained in the flue gas stream and other hazardous flue gas components, can be removed at predetermined thermodynamic equilibrium points.

Although SO_2 emissions are the primary focus of acid rain control methods; scrubbing systems and fluidized bed combustion has dominated the market and are proven for SO_2 reduction, these systems use massive and very expensive for handling and processing the raw materials and for disposal of the solid wastes. Wet scrubbers are not effective in removing nitrogen oxides and are characterized by the high environmental direct impact because of the acid mist discharged in the scrubber exhaust. On the other hand, the fluidized bed combustion process requires excessive energy use for calcining the lime stone, and requires increased costs for dust collection, lime stone handling and solid waste disposal. These reasons, in addition to the inefficient, cumbersome, unduly expensive process are the stumbling blocks for these systems to continue dominating the flue gas cleaning market.

The first step of Abdelmalek's process is to reduce the acidic vapor emissions, to eliminate deleterious environmental hazards, and to recover wasted heat energy otherwise rejected into the atmosphere; in a non-corrosive manner; by cooling the flue gases to condense its vapors, to recover its heat energy and to produce additional electric power.

The flue gas stream is cooled utilizing a condensing heat exchange process where concurrent chemical reactions could occur between the nitrogen oxide (NO), sulfur dioxide (SO_2), oxygen (O_2) and water vapor (H_2O) at relatively low temperature conditions, which otherwise take place in the atmosphere over a much longer period of time and contribute to acid rain.

The hot flue gas stream flowing from a coal fired boiler after removing the fine particulate matter; in a dust collector, a bag house or an electro-static precipitator; passes through an electro-static gas treater to neutralize the ion electrostatic charges of the ultrafine particulate matter and mist particles that escaped the dust collector, this step starts a coagulation process enhancing the removal of these materials in the condensing step. Cooling of the gas stream is achieved by recovering sensible and latent heat to pre-heat the combustion air stream of the high efficiency thermal power cycle to substantially increase the electric power plant capacity.

The cooling of the flue gas stream takes place in a non-corrosive condensing heat exchanger, where heat energy is recovered. Upon reaching lower temperature levels, the water vapor condenses and concurrent and consecutive reactions take place to produce nitric acid (HNO_3), sulfurous acid (HSO_3) and sulfuric acid (H_2SO_4) in aqueous water solution, in addition the radical acidic components of the condensate particulate reacts with the hazardous trace metal spices, and with other organic volatiles, they end down in the waste water stream, which can be treated to meet the waste water discharge requirements.

When a relatively hot flue gas is cooled to lower temperatures, nitric oxide (NO) reacts readily with the excess oxygen in the flue gases to form nitrogen dioxide (NO_2) as follows:

$$2NO + O_2 = 2NO_2$$

At lower temperatures NO_2 becomes very soluble in water to form nitric acid (HNO_3) and nitric oxide (NO) as follows:

$$3NO_2 + H_2O = 2HNO_3 + NO$$

The nitric oxide formed being oxidized to nitrogen dioxide, and recycled the total reaction is

$$4NO + 3O_2 + 2H_2O = 4HNO_3$$

under the same circumstances of low temperature, a small part of the sulfur dioxide (SO_2) dissolves in water to form sulfurous acid (HSO_3) and in the presence of trace metal pieces; which act as an oxidation catalyst for the SO_2; it forms an aqueous sulfide ion SO_3, which is very soluble in water, the total reaction is as follows:

$$SO_2 + H_2O = HSO_3 + H^+$$

Having nitrogen dioxide in the presence of the sulfurous acid, concurrent and consecutive reactions can take place and result in the production of intermediates including: Hydroxyiomidodsulfate [$HON(SO_3)2$]; hydroxysulfamate [$HONHSO_3$]; Nitridotisulfate [$N(SO_3)_3$]; Imidodisulfate [$HN(SO_3)2$] and sulfamate [H_2NSO_3]; in the presence of excess HSO_3, the latter is converted to sulfonate ion, which then hydrolyzes to produce (NH_4^+) ion in acidic medium, these reactions are expressed as follows:

$$NO_2 + 2HSO_3 = HON(SO_3)^{2}{}_{2}^{-} + OH^-$$
$$HON(SO_3)^{2-}{}_2 + HSO_3 = N(SO_3)^{3-}{}_3 + H_2O$$
$$N(SO_3)^{3-}{}_3 + H_2O = HN(SO_3)^{2-}{}_2 + SO^{2-}{}_4 + H^+$$
$$HN(SO_3)^{2-}{}_2 + H_2O = H_2NSO^-{}_3 + SO^{2-}{}_4 + H^+$$
$$H_2NSO^-{}_3 + H^+ = H_2NSO_3H$$
$$HNSO_3H + H_2O = NH^+{}_4 + SO^+{}_4 + H^+$$
$$N(SO_3)^3{}_3 + H_2O = HN(SO_3)^2{}_2 + SO^{2-}{}_4 + H^+$$

The overall reaction is:

$$NO^-{}_2 + 3HSO^-{}_3 + H_2O = NH^+{}_4 + 3SO^{2-}{}_4 + H^+$$

The combination of the above reactions may be represented as follows:

$$SO_2 + 4NO + 3O_2 + 3H_2O = 4HNO_3 + HSO_3 + H^+$$

In summary, it could be said that the reactions of the nitrogen oxide, sulfur dioxide, oxygen and water in the presence of thermodynamic energy removal (cooling) and trace heavy metal spices act as oxidizing catalysts, the reaction of these radical compounds will take place and for every 4 molecules of NO only one molecule of SO_2 is removed. In the flue gas cooling process for a typical boiler flue gas stream which contains 500 ppm NO, 6000 ppm SO_2. 3.5% H_2O, all these chemical reactions will take place to result in removing mostly all the nitrogen oxide (NO), but only less than 2.0% of sulfur dioxide, which will contribute to form sulfurous acid (HSO_3) in aqueous solution of the water vapor condensate.

The second step of Abdelmalek's process is to remove SO_2 and CO_2 by liquefaction at their thermodynamic equilibrium points. Depending on the particular conditions of the heavier stream fraction of the flue gas, the equilibrium point for sulfur dioxide liquefaction will occur at temperatures below -40°F and partial pressure above 1.2 psia, which will require a flue gas total pressure above 30 psia. Liquefaction of the carbon dioxide will occur at temperatures below -60°F and at CO_2 partial pressure above 92 psia, which will require a system pressure above 200 psia. To avoid forming solids or dry ice in the gas expander the minimum system pressure and the amount of carbon dioxide liquefied, must be controlled to maintain CO_2 partial pressure above its sublimation point.

The cryogenic effect of the uncondensed gases, and of the refrigeration effect of the liquefied by-products are utilized to provide cooling required for condensing the gas components.

Fig. 1 indicates a schematic block diagram for a flue gas cleaning system 10. The flue gases flowing from a boiler, incinerator of other fossil fuel burning facility 1, is received after removing its particulate mater in an electrostatic precipitator, or a dust collector 2, and conducted to enter an electrostatic gas treater 3, where the electromagnetic charges of its ultra-fine sub-micron particulate matter is neutralized to enhance coagulation of the particles, and prevent its adherence to the metallic surfaces of the heat exchanger elements.

The flue gas cooler 4 is a reverse heat exchanger for flue gas cooling and to combustion air preheating, where a relatively hot flue gas stream flowing on one side of the heat exchanger is cooled to approach the ambient temperature, while a combustion air stream flowing at ambient temperature on the other side is heated to approach the hot flue gas stream entering temperature; depending upon the ambient conditions approximately 60 to 70% of the water vapor contained in the flue gas stream will condense. The heat recovered by the combustion air will contribute to approximately 8 to 9% reduction in the heat rate of the power plant heat cycle. Condensation of the vapors contained in the relatively higher temperature flue gas stream will occur on the relatively colder metal surfaces of the heat exchanger at temperatures below the dew point of the condensing vapor, even at gas temperatures higher than the vapor dew point, condensation will occur at the relatively colder metal surfaces of the heat exchanger elements. The heat exchanger structure can be divided into temperature condensing zones; a high temperature zone where the condensing temperature is above 200°F; a medium temperature zone between 200°F and 100°F, and a low temperature zone where the condensing temperature is below 100°F. The lower the temperature of the heat exchanger metal surfaces, the more condensate washing, and the lesser the corrosion effect will be. The higher the condensing temperature (above 200°F), the more aggressive corrosion environment will occur. The heat exchanger elements must be constructed from suitable high corrosion resistant materials, and must be protected by intermittent wash cycles, using high pressure water or steam spray nozzle system to keep the heat exchanger surfaces clean, to effectively reduce the corrosion, and to increase the life cycle of the heat exchanger. The interior of the flue gas cooler enclosure may be protected with corrosion resistant coating or maybe constructed from corrosion resistant materials. The mass flow rate of the cooled flue gases flowing to the liquefaction plant is controlled by a flue gas separator 5, where the gas stream is split into two gas streams; a heavier gas fraction, basically an enriched carbon dioxide mixture of gases, containing most of the sulfur dioxide and nitrogen oxides. The mass flow of the heavier gas fraction stream is a smaller fraction of the flue gas emitted from the boiler. The enriched heavier gas fraction is conducted to enter a gas liquefaction plant 6, where the gas is acted upon by compression, cooling, and expansion to co-generate useful power and cryogenic effect needed for condensing its acidic water vapor, sulfur dioxide, and carbon dioxide, at their corresponding equilibrium points. The cryogenic cooling effect of the liquefied by-products are used to provide the cooling required for the process. The reheated uncondensed cleaned gas stream, combined with the lighter gas fraction flowing from the gas separator, are vented into a cooling tower gas release system 7. The recirculating cooling tower water, and the oxygen rich ambient air in the cooling tower structure further permit reaction with trace nitrogen oxides which may escaped the cleaning steps of the process. The cleaned flue gas stream mixed with the ambient air is uplifted by the strong cooling tower air draft for an unembedded disbursement into the atmosphere.

Fig. 2 indicates a schematic diagram for a system 100 for a flue gas desulfurization by liquefaction of sulfur dioxide. Unit 101 consists of a gas compressor 101a, connected to a gas expander 101b, and driven by an electric motor or steam turbine prime mover 101c. The heavier gas fraction flowing from the gas separator enters the gas compressor 101a. The gas compressor 101a has a pressure ratio of up to 3:1 with a range between 2:1 to 2.5:1 will be preferred depending upon the concentration of the sulfur dioxide (SO_2). The heavier gas fraction flowing from the gas separator at near atmospheric pressure (P1), and near ambient temperature (T1), passes through line 11 to enter the gas compressor 101a, where the gas is compressed to a higher pressure level of above 30 psia (P2), and about 180°F (T2). The pressurized hot flue gas passes through line 12 to a first heat exchanger (after cooler) 102 to reduce its temperature to near 85°F (T3) using auxiliary cooling water circuit. The flue gas flowing from the after cooler heat exchanger 102 is then conducted through line 13 to a second heat exchanger 103, where its temperature is reduced to below 40°F (T4) to condense most of its water vapors, and to accelerate the oxidation of any remaining nitric oxide to form nitrogen dioxide which reacts readily with the water vapor condensate forming weak nitric acid. The pressurized gases, and the acidic water vapor condensate then passes through line 14 to a first moisture separator 104. In the moisture separator 104, the acidic water condensate is separated and removed from the bottom through line 15 and the gases are released from the top through line 16. The cleaned pressurized gas stream then enters a third heat exchanger 105 to further reduce its temperature to below -60°F (T5) to condense most of the sulfur dioxide in the gas mixture. The desulfurized gas, and the sulfur dioxide condensate then passes through line 17 to a second moisture separator 106. In the moisture separator 106, the liquid sulfur dioxide is separated and removed from the bottom through line 18, and the uncondensed gas stream is released from the top through line 19. The pressurized uncondensed gas stream is then conducted through the gas expander 101b, where the gas expands isentropically to a relatively lower pressure, and its temperature drops substantially to a much lower temperatures below -100°F (T6). The gases flowing from the expander passes through line 20 to enter the said third heat exchanger 105 to provide cooling needed for condensing the sulfur dioxide, while increasing its temperature to about 0°F (T7). The gas from the third heat exchanger 105 then passes through line 21 to enter the said second heat exchanger 103, to further provide cooling needed for condensing the acidic water vapor, while reheating the uncondensed gas back to near ambient temperature (T8). The expanded, cleaned and reheated gas stream is then conducted into the cooling tower gas release system. The refrigeration effect of the cold acidic water vapor condensate, and the liquid sulfur dioxide by-product is utilized to provide sub-cooling for the auxiliary cooling water stream 23, the sub-cooled water stream 24 is used for cooling the compressed gas stream in after cooler 102. The temperature of the acidic water, and the liquid sulfur dioxide is normalized to near ambient temperature. The sulfur dioxide by-product is pumped through line 18, and the acidic water condensate is pumped through line 15 to a water treatment facility and recycled into the cooling tower system.

Fig. 3 indicates a schematic diagram for a similar system 200, where carbon dioxide emissions can be reduced by liquefaction. Unlike system 100, the gas compressor-expander unit 101 will have much higher pressure ratio of up to 20:1 with a range of 13:1 to 15:1 is preferred to generate the cryogenic effect required for the liquefaction of as desired part of the carbon dioxide contained in the heavier gas mixture. In addition to the heat exchanging steps and embodiments indicated in system 100, a fourth heat exchanger 108 provides the cooling to the relatively high pressure gas stream to reach CO_2 equilibrium temperature of condensation. Moisture separator 109 separates the liquefied carbon dioxide from the uncondensed gas stream. At a system total pressure of above 210 psia, up to 50% of the carbon dioxide may be liquefied in heat exchanger 108 at a temperature below -60°F, most of the sulfur dioxide will be liquefied in the heat exchanger 105 at a temperature below 0°F and most of the acidic water vapor will condense in heat exchanger 103 at a temperature below 60°F. The refrigeration effect of the cold liquid carbon dioxide is utilized in the reversing heat exchanger 107 to provide the cooling needed for condensing the weak acidic water while restoring the temperature of the liquified carbon dioxide to near ambient temperatures before transferring into pipe lines or to a bulk storage facility.

The Abdelmalek's process shall effectively reduce the heat rate of the power plant heat cycle by employing a condensing flue gas cooler to preheat the combustion air, will reduce the power needed to clean the flue gas and also will produce useful liquefied gas by-products. It should be understood that the mass flow rates, operating pressures, and temperatures are given only to demonstrate the merits of the process, and the given values are based upon certain particulars which may vary. It is also understood that the quality of the by-products liquid sulfur dioxide, and liquid carbon dioxide shall be of commercial grade, and processes for refining these products for food or medical grades are well known and are out of the scope of the present paper.

Table 1 represents an estimate and analysis for the mass flow rates for Flue Gas Energy recovery (FGER), Flue Gas Desulfurization by Liquefaction (FGD-L), and Flue Gas Carbon Dioxide Liquefaction (CO_2-L) for a 500 M.W. Plant.

	DESCRIPTION	MASS FLOW 1000 LB/HR	PERCENT FLUE GAS MASS FLOW
I.	COAL FIRED BOILER PLANT		
	Coal Burned	428	
	Flue Gas Emitted,	5,000	100
	3.5% Sulfur Burned	15	
	SO_2	30	0.6
	CO_2	950	19
	H_2O	295	5.9
	N_2	3,550	71
	O_2	175	3.5
II.	FLUE GAS ENERGY RECOVERY (FGER)		
	Flue Gas Entering Cooler,	5,000	100
	Flue Gas Leaving Cooler,	4,813	96.3
	Acidic Water Condensed,	186	3.7
III.	FLUE GAS DESULFURIZATION-LIQUEFACTION (FGD-L)		
	a. Flue Gas Separator		
	Total Flue Gas Entering,	4,813	96.3
	CO_2 Enriched Gas Fraction	2,406	48.15
	N_2 Enriched Gas Fraction	2,407	48.15
	b. Sulfur Dioxide Liquefaction (SO_2-L)		
	Total Flue Gas Entering	2,406	48.15
	SO_2 Liquefied	28	0.55
	Flue Gas Leaving	2,378	47.6
	c. Carbon Dioxide Liquefaction (CO_2-L)		
	Total Flue Gas Entering	2,378	47.6
	CO_2 Liquefied	600	12.0
	Flue Gas Released	1,578	31.6
IV.	COOLING TOWER FLUE GAS RELEASE		
	Cleaned Flue Gas Released	3,984	79.7
	Ambient Air Entering to Cooling Tower	40,000	800
	Total Tower Plume Air Released	43,984	879.7

TABLE 2 Represents estimated electric power generated, and consumed by the Flue Gas Energy Recovery (FGER) and Flue Gas Desulfurization by Liquefaction (FGD-L) Process.

	DESCRIPTION OF PROCESS STEP	% OF FLUE GAS FLOW	ELC. PWR CONSUMED MW/HR	% OF ELEC. PLANT CAPACITY
I.	Flue Gas Cooler	100	1	0.2
II.	Flue gas separator	97	4	0.8
III.	SO_2 Liquefaction (SO_2-L)	48.5	36	7.2
IV	CO_2 Liquefaction (CO_2-L)	48.5	45	9.0
V.	Cooling Tower	80.0	4	0.8
VI.	Electric Power Required		90	18
VII.	Electric Power Produced		36	7.2
	Total Net Power Used		54	10.8

TABLE 3 represents an estimated annual operating cost for 500 MW power plant for wet lime scrubber flue gas desulfurization (WS-FGD) and Fluidized Bed Combustion (FBC) versus Flu Gas Energy Recovery/Flue Gas Desulfurization-Liquefaction (FGER/FGD-L) for SO_2-L and CO_2-L. All Quantity figures are in thousands and Cost Figures are in Million U.S. Dollars

In conclusion, the Abdelmalek's Flue Gas Desulfurization by Liquefaction (SO_2-L) will be less expensive to operate when compared with a wet lime scrubbing or fluidized bed combustion, and will be commercially profitable for Carbon Dioxide Liquefaction.

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TABLE 3: Cost Comparison for 500 M.W. power plant desulfurization systems

DESCRIPTION	WLS-FGD		FBC		SO_2-L		CO_2-L	
	QTY	COST	QTY	COST	QTY	COST	QTY	COST
I. CAPITAL COST MILLION $		90.0		100.0		110.0		140.0
II. ANNUAL OPERATION COSTS, MILLION $								
a. Raw material								
* Hydrated lime tons @ $40/ton	150.0	6.0						
* Limestone tons @ $20/ton			420.0	9.8				
* Other chemicals tons @ $100/ton	6.0	0.6			6.0	0.6	6.0	0.6
b. Solid waste disposal/treatment, tons @ $38/ton	405.0	15.4	945.0	17.0	105.0	1.9	105.0	1.9
c. Utilities								
* Limestone calcining coal, tons @ $30/ton			15.7	0.5				
* Process water, million gal	240.0	0.6			371	2.5	371.0	16.1
* Electric power, million KW	30.0	1.2	10.0	0.4				
* Steam, million lb	490.0	1.4						
d. Operating & Supervision		1.6		1.7		1.9		2.3
e. Maintenance		1.5		1.6		1.8		2.2
f. Depreciation (20 yr)		4.5		5.0		5.5		7.0
g. Capital recovery (10%)		9.0		10.0		11.0		14.0
Total operating costs $		41.8		46.0		25.2		44.1
III. ANNUAL OPERATION INCOME								
a. Liquefied SO_2 @ $40/ton					98.0	3.9		
b. Liquefied CO_2 @ $30/ton					2100.			63.0
IV. NET INCOME (EXPENSES)		(33.8)		(46.0)		(21.3)		22.8

STUDY OF AGGLOMERATION/CLINKER FORMATION PROBLEM IN FBC POWER PLANTS IN INDIA

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ABSTRACT

There are a number of small scale (10-20 MW) fluidised bed power plants in India. Occasionally these power plants face the problem of agglomeration. When agglomeration occurs the plants need to be shutdown resulting in economic loss. An investigation was undertaken to find out the reasons for agglomeration. Two sets of feed coal samples were collected from a typical FBC based power plant and analysed. It was observed that coarser particles had more ash content and as a result were denser. The smaller particles had better caking properties therefore had tendency to agglomerate due to stickiness. Agglomeration may occur due to excessive presence of either finer particles or too coarser particles or both. Coarser particles lead to defluidisation due to increased minimum fluidisation velocity. Defluidisation causes agglomeration.

INTRODUCTION

Fluidised bed combustion technique is being extensively used in India to generate power from coal washery rejects. This technique makes it possible to utilise high ash coal washery rejects in an environmental friendly manner. A number of small scale power plants (10-20 MW) have been installed in India near coal washeries to extract energy from this waste material. Almost all coal washeries in India clean the coal meant for the steel plants. Therefore the rejects from these washeries have some degree of caking propensity left in them. These small scale FBC power plants have been running successfully. However occasionally they face agglomeration problem. When this problem occurs due to the formation of very big size agglomerates, defluidisation takes place and the operation of the plant comes to a sudden halt. The plant can be restarted only after the agglomerates from the bed are removed which takes considerable time. The economic implications are quite obvious.

It is a well known fact that the melting of ash inside a boiler takes when the temperature generated by burning of coal exceeds the ash fusion temperature. The melting ash then engulfs the unburned coal particles and form a solidified mass which is known as clinker. Clinker inside a boiler generally occurs when coal contains ash of low fusion temperature. In addition, sintering and agglomeration of particles may occur in the lower portions. However this reasoning can not be extended to agglomerate formation in fluidised bed combustor because the temperature maintained inside the bed is around 850-900°C which is much below the ash fusion temperature.

Keeping the TISCO and other similar FBC power plants' problems in India in mind a study was undertaken to investigate the possible causes for agglomeration.

EXPERIMENTAL DETAILS

To find out the reasons for agglomeration two sets of feed coal samples were collected from TISCO, Jamadoba plant. The first set was collected when the plant was running smoothly and another set was collected when agglomeration occurred. Both sets were subjected to analysis. The proximate analysis and the particle size distribution, the density and ash of each size fraction were determined. The details of the same are presented in Tables 1-3. Further experiments have been conducted to find out the temperature and the fluidising conditions under which agglomeration is likely to occur. For this feed coal sample was heated in two experimental bowls, one with sufficient number of holes in its bottom for supply of air and other one without any holes for restricted air supply. The heating was done at different temperatures ranging from 300°C~600°C and for different particle fractions and for different duration of time. After the heating is over, samples from both bowls were taken out and the amount of loose material in each case has been measured and the agglomerate were subjected to shatter test. The agglomerates were dropped from a height of 6 feet onto a steel plate and the loose materials below the size of 2 mm has been measured. The agglomerate giving the least amount of loose material has been designated as the strongest and relative strengths of other agglomerates have been worked out. These experimental details have been presented in Table-3.

RESULTS AND DISCUSSION

The formation of agglomerate is mainly due to defluidisation that may occur due to the presence of moisture, binding agents or by the softening of particle with increasing temperature. Since the FBC at Jamadoba operates around 900°C, the possibility of moisture contributing to agglomerate formation is nil. Again no binding agents are used in the FBC plant at Jamadoba which rules out the possibility of agglomeration due to binding agent also. Hence softening of particles due to increased temperature is the main cause behind the defludisation. The plant in Jamadoba uses washery rejects of coking coal as feed which have softening tendency at higher temperature. When defluidisation occurs, the bed temperature decreases and also the fluidising gas escapes without fluidising the particles which start agglomerating.

The tendency for agglomeration in a bed of materials depends upon:

* The stickiness of the particles
* The available surface area
* The particle momentum

Fig.1 shows the relation between average particle diameter and ash percentage of feed coal sample. As the average particle diameter increases, the ash content in coal particle increases. From Fig.2, as the average particle size increases, the density also goes on increasing due to increase in ash content. Figures 3 and 4 represent the effect of particle size and density on minimum fluidisation velocity (U_{mf}) respectively. From Fig.3, it can be seen that as the particle size increases U_{mf} increases, coarser and denser particles offer more resistance to fluidisation.

The design of the gas distributor affects the physical and chemical performance of a fluidised bed[1-4]. One of the most important requirements of an effective gas distributor is that it must ensure uniform gas distribution throughout the bed.

To study the effect of minimum fludisation velocity upon the fraction of number of active holes, the approach given by Yue and Kolaczkowski[5] has been adopted. A partially operated multiorifice distributor plate is shown in Figure 5. Normally gas tends to flow preferentially through that part of bed which has a higher voidage and therefore low bed pressure drop. Thus two regions of different voidage exist as shown in Figure 5. Section 1 of the bed is freely bubbling and its voidage is greater than e_{mf}. The corresponding superficial gas velocities in the sections are U_1 and U_{mf}.

For the system shown in Figure 5 to be in equilibrium, the total pressure drop across the distributor and bed in both sections must be the same, i.e.

$$\Delta P_{D1} + \Delta P_{B1} = \Delta P_{D2} + \Delta P_{B2} \tag{1}$$

The pressure drop across a single orifice in the distributor plate is given as;

$$\Delta P_0 = \frac{\rho_f}{2gC_D^2} U_0^2 \tag{2}$$

Hence the difference between the distributor pressure drops of the two sections is given by:

$$\Delta P_{D1} - \Delta P_{D2} = \left(\frac{A_1}{N_1 a_0}\right)^2 \frac{\rho_f U_1^2}{2gC_D^2} - \left(\frac{A_2}{N_2 a_0}\right)^2 \frac{\rho_f U_{mf}^2}{2gC_D^2} \tag{3}$$

For a multiorifice distributor with a regular array of holes, each of the same dimension, we have

$$\frac{A_1}{N_1} = \frac{A_2}{N_2} = \frac{A_T}{N} \tag{4}$$

Therefore,

$$\Delta P_{D1} - \Delta P_{D2} = \frac{\rho_f}{2gC_D^2 \phi^2}(U_1^2 - U_{mf}^2) \tag{5}$$

where, $\phi = Na_o/A_T$ which may be called orifice density.

The overall increase in bed height can be obtained from a volumetric balance given below;

$$\Delta H = \frac{\bar{e}_B (N_1/N) H_{mf}}{1 - \bar{e}_B N_1/N} \tag{6}$$

The difference between the pressure drops across the two sections because of the presence of bubbles in Section 1 is given by

$$\Delta P_b = \rho_s g(1 - e_{mf})(H_{mf} + \Delta H)\bar{e}_B \tag{7}$$

Using ΔH from equation (6), equation (7) becomes

$$\Delta P_b = \bar{e}_B \Delta P_{Bmf} + \frac{\bar{e}_B^2 \Delta P_{Bmf} N_1/N}{1 - \bar{e}_B N_1/N} \tag{8}$$

where,

$$\Delta P_{Bmf} = \rho_s g(1 - e_{mf}) H_{mf} \tag{9}$$

Again the difference between the pressure drops across the two sections because of the spouts formed above the active orifices, according to Fakhimi and Harrison[6] is given by:

$$\Delta P_s = (1 - 2/\pi)\frac{h_s \Delta P_{Bmf}}{H_{mf}} \tag{10}$$

Combining the difference with that due to presence of the bubbles, we obtain:

$$\Delta P_{B2} - \Delta P_{B1} = \Delta P_b + \Delta P_s$$

$$= \bar{e}_B \Delta P_{Bmf} + \frac{\bar{e}_B^2 N_1/N}{1-\bar{e}_B N_1/N} \Delta P_{Bmf} + (1-2\pi)\frac{h_s \Delta P_{Bmf}}{H_{mf}} \tag{11}$$

The bubble voidage usually has a value of 0.1 to 0.2. Therefore, the second term in right-hand side of equation (11) is relatively small and can be neglected. Equating (5) and (11), we can get;

$$\frac{\rho_f}{2gC_D^2\phi^2}(U_1^2 - U_{mf}^2) = \bar{e}_B \Delta P_{Bmf} + (1-2/\pi)\frac{h_s \Delta P_{Bmf}}{H_{mf}} \tag{12}$$

Re-arranging the above equation, we can get

$$U_1 = [\frac{\Delta P_{Bmf}\{\bar{e}_B + (1-2/\pi)h_s/H_{mf}\}}{\rho_f/2gC_D^2\phi^2} + U_{mf}^2]^{1/2} \tag{13}$$

But

$$U = \frac{N_1}{N}(U_1 - U_{mf}) + U_{mf} \tag{14}$$

or,

$$\frac{N_1}{N} = (U - U_{mf})/(U_1 - U_{mf}) \tag{15}$$

Putting the value of U_1 from equation (13) in equation (15) we can finally get;

$$\frac{N_1}{N} = \frac{U - U_{mf}}{[\Delta P_{Bmf}\{\bar{e}_B + (1-2/\pi)h_s/H_{mf}\} \times 2gC_D^2\phi^2/\rho_f + U_{mf}^2]^{1/2} - U_{mf}} \tag{16}$$

Figure (6) shows a relation between fraction of active number of holes and U_{mf}. From the figure, as the minimum fluidisation velocity decreases, the number of active holes increases. In other words, the active number of holes in distributor plate decrease when the minimum fluidisation velocity of the feed coal increases. The minimum fluidisation velocity increases when the coarse content in the feed coal increases as shown in Figure 3. That means as the feed coal becomes coarser, the number of active holes in the distributor plate decreases and as a result there will be some spots in the fluidised bed very close to the distributor plate where there is improper supply of air. This may lead to a fall in temperature and consequent agglomeration.

From Table 2 and Figures 7 and 8, the caking and swelling tendency of particle increases as the particle size decreases. The coarser particle have no caking tendency and the smaller ones below the size of 3 mm have considerable caking tendency. Obviously as the percentage of these fines in the feed coal increases, the tendency of agglomeration increases. Moreover the agglomeration tendency persists when there is inadequate supply of air, a condition similar to inside of a coke oven. When such particles are present near the inactive holes, due to inadequate air supply the particles start forming agglomerates. Once the agglomeration is initiated, it leads to further defludisation which in turn perpetuates the agglomeration ultimately leading to the collapse of the bed.

Table 3 gives a brief idea about the nature of agglomerates at different conditions of combustion. It has been observed that the agglomerates obtained from the bowl without holes are relatively harder than that of with holes at the same temperature and time. The conditions in the bowl without holes are similar to the conditions near an inactive hole in the distributor plate. There is a restricted supply of air to the coal sample in the bowl but the temperature of the sample is sufficient enough to make it soft and sticky leading to the formation of agglomerates whereas in case of bowl with holes due to some amount of air supply, some combustion takes place and the chances of particles becoming soft and developing stickiness are comparatively less. As a result the chances of agglomerate formation is also less. Table 3 indicates the strength of the agglomerates formed in both the bowls which increases with temperature.

The size distribution of the feed samples are shown in Fig. 9. The values of distribution modulus for these three samples are also given in Table 1. The distribution modulus in Rosin Rammler equation is a measure of spread of the sample. Higher the value of distribution modulus of the sample, narrower will be the particle size distribution and vice versa. From Fig. 9, the feed coal sample which was responsible for agglomeration in TISCO, Jamadoba plant has got the smallest size distribution modulus or widest distribution indicating that increase in coarse and fines content is responsible for agglomeration.

From Table 3, the agglomerates become stronger with time. That means the remedial measures to stop the agglomerate formation should start as soon as possible. The recommended average particle size is 4mm.

CONCLUSION

1. The tendency of agglomerate formation increases as the number of active holes decreases. The number of active hole decreases with the increase of minimum fludisation velocity. Minimum fluidisation velocity increases with particle size and density.

2. The finer particles have more tendency towards agglomerate formation. As the particles become finer, the available surface area increases. The caking index and swelling index also increase with the decrease in particle size.

3. The tendency of agglomerate formation increases with increase in softening property of particle, with increasing particle temperature, and when there is restricted air supply to the furnace. As the temperature and retention time increases, the hardness of agglomerates formation increases.

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NOMENCLATURE

Math. Symbols	Description
a_o	Area of orifice (cm^2)
A_1, A_2	Area of sections 1 and 2 in the model respectively (cm^2)
A_T	Total area of fluidized bed (cm^2)
d_o	Actual diameter of orifice (cm)
d_{or}	Diameter of distributor orifice (cm)
d_p	Average particle diameter (cm)
e_{mf}	Bed voidage at minimum fluidisation
e_b	Average bubble voidage in section 1 of the model
g	Acceleration due to gravity (cm/sec^2)
h_s	Height of spout or jet (cm)
H	Bed height at minimum fluidisation (cm)
N	Total number of orifices
N_1/N	Fraction of active number of orifice
P	Pitch of holes in distributor (cm)
P_{av}	Average pressure in the combustor (atm)
P_B	Pressure drop across the fluidized bed, subscripts 1 & 2 denote sections 1 & 2 respectively
P_D	Pressure drop across the distributor, subscripts 1 & 2 denote sections 1 & 2 respectively.
T_b	Absolute bed temperature (^oK)
U	Total superficial gas velocity (cm/sec)
U_1, U_2	Superficial gas velocity in sections 1 and 2 respectively (cm/sec)
U_{mf}	Minimum fluidisation velocity (cm/sec)
	Greek Symbols
ρ_g	Density of fluidising gas ($gram/cm^3$)
ρ_s	Density of fluidised solids ($gram/cm^3$)
ϕ	Orifice density (Na_o/A_T)
μ_v	Viscosity of fluidising gas (gram/cm-sec)

Table 1-Proximate Analysis of coal samples

Composition	Sample1	Sample2	Sample3
Moisture(%)	1.43	2.86	1.43
Ash(%)	55.05	59.96	53.05
VM(%)	28.23	15.18	30.23
FC(%)	15.285	22.0	15.28
Distribution Modulus (a_n)	0.699	1.1157	0.682
Absolute size constant(C_r)	0.174	0.378	0.296
Average particle diameter, d_{nav}(mm)	1.91	1.09	1.23

Table 2-Data on Feed Coal (Sample I)

Sieve Size (mm)	% wt. retained	Ash %	Sp.Gr.	FSI	CI	Umf (cm/sec)	N_1/ N
+ 5.6	3.88	68.889	1.88889	x	1	261.71	0.38
+4.0	11,48	63.887	1.88887	x	1	234.49	0.57
+3.535	9.27	63.586	1.88586	x	1	193.72	0.80
+2.3	15.5	63.275	1.88275	x	1	102.48	1.0
+1.7	17.31	63.135	1.88135	x	2	51.95	1.0
+0.85	12.2	62.453	1.87453	x	2	14.49	1.0
+0.42	11.34	61.342	1.86342	1	3	2.66	1.0
+0.125	10.6	57.310	1.82310	1.5	8	0.356	1.0
+0.076	3.04	53.965	1.78965	2	9	0.0505	1.0
+ 0.0	5.38	53.421	1.78421	2	9	—	1.0

Table 3-Results of the combustion test for agglomerates

Sample No.	Temp (^0C)	Heating time(min)	Bowl type	Nature of agglomerate
1	500	15	Without hole	Loose cake formation, very soft, 90% loose material.
2	500	15	With hole	Loose cake formation, softer than sample No.1, 95% loose material.
3	500	30	Without hole	Very less amount of cake formation, soft but harder than sample No.1&2, 80% loose material.
4	500	30	With hole	Very soft cake formation, harder than sample Nos.1&2, but softer than sample 3, 86% loose material.
5	600	15	Without hole	Harder cake formation than sample Nos. 1 to 4; 72% loose material obtained.
6	600	15	With holes	Harder cake formation than sample Nos. 1 to 4 but softer than sample 5; 77% loose material formation.
7	600	30	Without hole	Harder cake formation than sample No.1 to 6; 65% loose material formation.
8	600	30	With holes	Harder cake formation than sample Nos. 1 to 6 but softer than sample No.7; 70% loose material formation. 9
9	700	15	Without hole	Harder cake formation than sample Nos.1 to 8; 60% loose material obtained.
10	700	15	With holes	Harder cake formation than sample Nos.1 to 8 but softer than sample No.9; 63% loose material obtained
11	700	30	Without hole	Harder cake formation than sample Nos. 1 to 10; 50% loose material obtained.
12	700	30	With hole	Harder cake formation than sample Nos. 1~10 but softer than sample No.11; 53% loose material obtained.

13	800	15	Without hole	Harder cake formation than sample Nos. 1~12. 42% loose material obtained.
14	800	15	With hole	Harder cake formation than sample Nos.1~12; but softer than sample No.13. 48% loose material obtained.
15	800	30	Without hole	Harder cake formation than sample No.1~14. 35% loose material obtained.
16	800	30	With holes	Harder cake formation than sample Nos.1~14 but softer than sample No.15; 40% loose material obtained.
17	900	15	Without hole	Harder cake formation than sample Nos.1~16; 25% loose material obtained.
18	900	15	With holes	Harder cake formation than sample Nos.1~16; but softer than sample No.17; 30% loose material obtained.

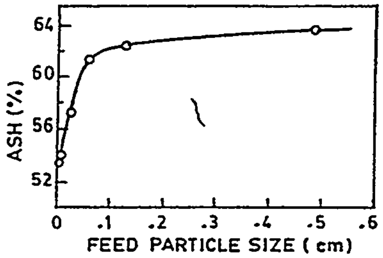

FIG.1 EFFECT OF FEED PARTICLE SIZE ON ASH PERCENTAGE

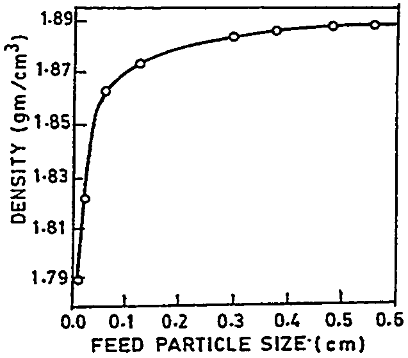

FIG.2 EFFECT OF FEED PARTICLE SIZE ON PARTICLE DENSITY

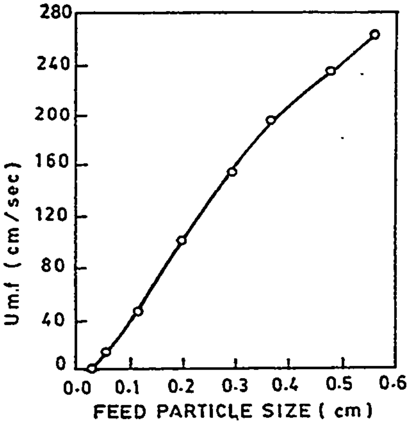

FIG.3 EFFECT OF FEED PARTICLE SIZE ON MINIMUM FLUIDIZATION VELOCITY

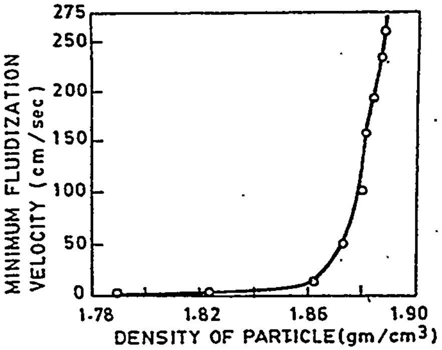

FIG.4 EFFECT OF PARTICLE DENSITY ON MINIMUM FLUIDIZATION VELOCITY

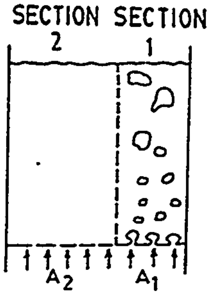

FIG.5 MODEL SHOWING PARTIAL OPERATION OF A MULTIORIFICE DISTRIBUTOR

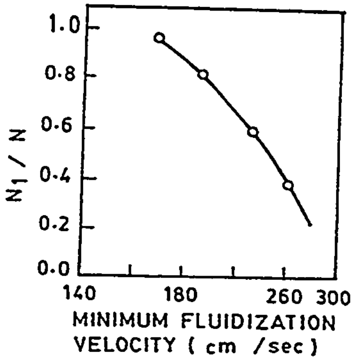

FIG.6 EFFECT OF FLUIDIZATION VELOCITY ON FRACTION OF ACTIVE NO. OF HOLES

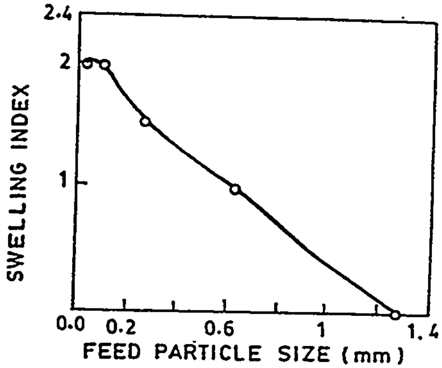

FIG.7 EFFECT OF FEED PARTICLE SIZE ON SWELLING INDEX

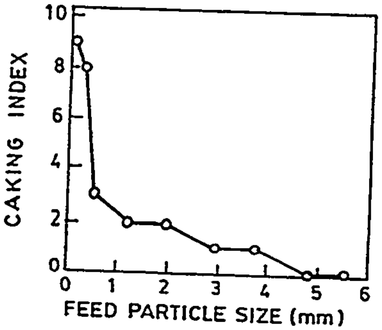

FIG.8 EFFECT OF FEED PARTICLE SIZE ON CAKING INDEX

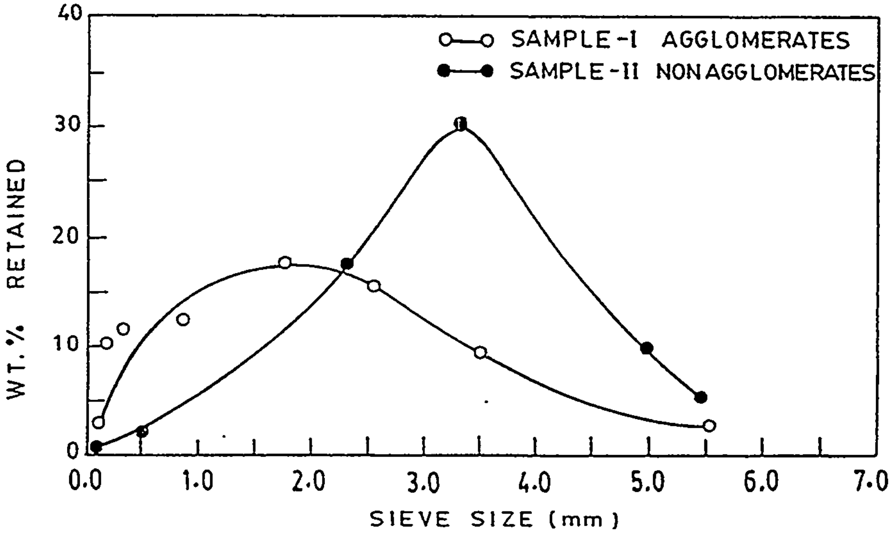

FIG. 9 SIZE DISTRIBUTION OF FEED COAL SAMPLES

Discussion of Some Aspects of Coal Tailings Slurry Combustion in Bubbling Fluidized Bed Boiler, *Wang Tao and Li Ru Ying, Coal Chemistry Research Institute, PEOPLE'S REPUBLIC OF CHINA*

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This paper was unavailable at the time of publication and may be obtained directly from the author.

UTILITY APPLICATIONS FOR COAL WATER SLURRY CO-FIRING

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"THE YEAR OF COMPLIANCE"

CLEARWATER, FLORIDA
MARCH 20-23, 1995

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UTILITY APPLICATIONS FOR COAL WATER SLURRY CO-FIRING

INTRODUCTION

In order for the electric utilities to continue to use coal and still meet environmental requirements, deeper cleaning of coal will be required. The downside to that cleaning is the increased generation of coal fines. These fines are produced from coal cleaning processes and are generally disposed of in settling ponds. This material represents a significant fuel loss for coal companies and an additional operating cost and environmental problem as ponds are filled and new pond permits become necessary.

If the coal pond fines can be economically recovered and used, the material is no longer a liability but represents a significant stockpile of fuel. Recovery of the fines for use as a low solids coal water slurry (CWS) is one means of utilizing this resource and is attractive from both an economic and an environmental standpoint. CWS from freshly produced coal fines have been successfully co-fired with pulverized coal in boilers at Penn State University and Penelec.

Penelec has recently completed formulation and combustion testing of this concept at a total boiler combustion rate of 20% on a 32 MWe boiler utilizing a slurry produced at the coal preparation facility at Homer City, PA. The objectives of the project were: 1) to determine the technical feasibility of co-firing; 2) to develop the design criteria for formulating low solids CWS without the need for costly additives; and 3) to utilize the fuel without the need for major boiler modifications. An additional benefit of this process is the reduction in NOx formation compared to firing with pulverized coal alone.

This paper presents the success to date of the co-firing of low solids CWS with pulverized coal in a utility scale boiler using "fresh" fines directly from coal cleaning circuits. The paper also outlines continuation work in progress and the future outlook on the effects of the implementation of the technology. The use of coal fines as a CWS feedstock has the potential to generate a new market for a material that is currently discarded as waste by coal producers and to provide possible savings in fuel costs to coal users.

BACKGROUND

Pennsylvania Electric Company (Penelec) is one of the operating companies for the General Public Utilities System (GPU) which includes the Pennsylvania Electric Company, Metropolitan Edison and Jersey Central Power and Light. GPU has a service territory which covers a large portion of the states of Pennsylvania and New Jersey.

Penelec's generating capacity is over 10,000 MWe and, in 1993, the Company burned more than 16 million tons of bituminous coal at facilities that are wholly-owned or operated by us as part of the Chestnut Ridge Energy Center. This is about one fourth of the coal mined in the state of Pennsylvania.

Together with New York State Electric and Gas Corporation, Penelec owns and operates the Homer City Coal Preparation Plant which cleans over 3,000,000 tons of coal per year. The facility currently generates more than 100 tons per hour of coal fines and extreme measures must be taken to burn those fines in the adjacent 1850 MWe power plant. This problem is shared by virtually all coal processing plants using advanced coal cleaning techniques. What do you do with the wet fines?

WET COAL FINES

Fine coal is very difficult to handle. It requires the use of thermal dryers which are costly to operate and maintain. When the material is stockpiled, it creates a fugitive dust problem and has a tendency to contaminate water runoff. It causes plugged chutes and hang-ups in coal transport systems and bunkers. It contributes to NOx and opacity problems as a consequence of running the thermal dryers. For coal producers, it results in a loss of product and it becomes a lifetime storage commitment as a waste in coal ponds.

In 1992, 998 million tons of coal were mined in the United States. According to various sources approximately half of that coal was cleaned in preparation plants resulting in anywhere from 40-100 million tons of additional fine coal refuse impoundments. In addition to this, there are estimates of two to five billion tons of this refuse currently impounded from past coal processing efforts over the last forty years. That's a lot of coal. That's also a potentially big environmental headache.

The mining industry is faced with ever increasing regulations for the production and use of coal. The electric utilities which purchase three fourths of that production are faced with ever increasing environmental regulations requiring deeper cleaning of coal. This will inevitably cause an increase in the production of coal fines waste and an increase in the problems associated with the disposal of that waste as water quality regulations become increasingly stringent.

These facts paint a gloomy picture for the future competitiveness and continued use of coal but it doesn't have to be.

SLURRY TEST PROGRAM

At Penelec, the Research and Development Department has focused on resolving the problem of dealing with wet coal fines through a series of four projects started in late 1990 with the help of the Pennsylvania Energy Development Authority (PEDA).

These four projects involved: 1) laboratory testing to determine the optimum slurry formulation; 2) small scale combustion testing of that fuel in various test combustors at the University of Alabama and Penn State University; 3) construction and operation of a pilot scale (3 tons per hour) fine coal cleaning and coal water slurry formulation circuit; and 4) performance of a series of low solids coal water slurry co-firing tests on a 32 MWe pulverized coal electric utility boiler at Seward Station, located in western Pennsylvania near Johnstown. The process we have developed consists of co-firing coal water slurry with a solids content of up to 50% by weight with pulverized coal in quantities of up to 50% fuel input.

The initial focus, in the development of this technology, has been with "fresh" fines. These fines are generated as the fine reject material from froth flotation operations or from classifying cyclones and vacuum filters. They can also be the finest fractions in the range of minus 100 and minus 200 mesh which are removed to enhance the handling and drying properties of commercial coarse coal products.

In addition, the largest source of fines is located in the thousands of coal waste ponds scattered across the United States. For those electric utilities located near these sources, the potential exists for recovering and utilizing them as a coal water slurry fuel, at an economic benefit to both the utility and the coal producer.

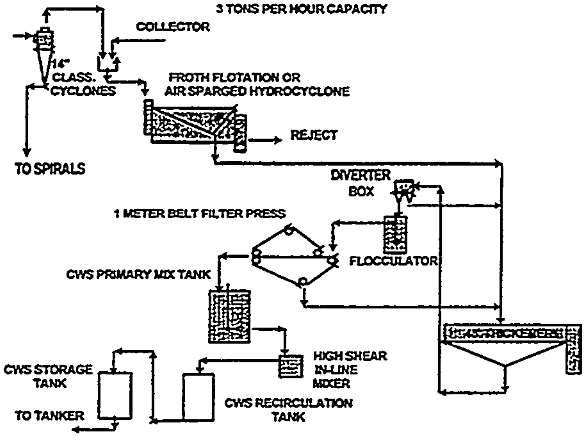
FORMULATING COAL WATER SLURRY

Early on, we recognized the difficulty in formulating a high solids slurry for 100 percent Btu input due to the high costs of additives, the difficulties in maintaining stability, the problems with atomization and so forth. We elected to pursue co-firing a low solids slurry with pulverized coal, which is less expensive and more easily accomplished. The slurry characteristics are 50% solids by weight with a target viscosity of less than 200 centipoise at 100 reciprocal seconds and a stability of one week at static conditions. This is based on a coal feed with a dry basis heating value of 14,000 Btu/lb, ash content of 10% and sulfur content of 1%.

Figure 1 is a schematic of the 3 ton per hour CWS pilot plant consisting of circuits for fine coal cleaning and coal water slurry formulation. This plant was constructed at the Homer City Coal Preparation Plant. Starting at the top left of the figure and going clockwise, we took the minus 100 mesh classifying cyclone overflow in the cleaning circuit. We cleaned it with froth flotation, thickened it in an Enviroclear thickener and further increased the solids content in a Parkson filter press. The filter cake was then thinned with water to the desired solids content in a mixing tank, run through a high shear mixer to break up the floc and recirculated until thoroughly blended. The slurry for our combustion testing was then stored temporarily or loaded directly into a tank truck and transported 35 miles to Seward Station. A commercial plant design would eliminate the filter press and directly thicken the froth to the required 50% solids.

Figure 1. CWS Pilot Plant

3 TONS PER HOUR CAPACITY



UTILITY SCALE CO-FIRING COAL WATER SLURRY

Successful completion of the first three projects enabled Penelec to proceed with the utility scale combustion testing of the concept. A project was initiated by Penelec and supported by PEDA, the Electric Power Research Institute (EPRI), the Pennsylvania Electric Energy Research Council (PEERC) and others.

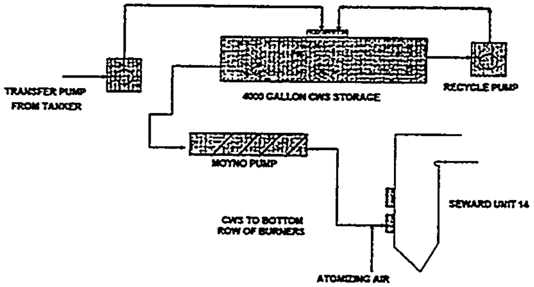
The objectives of this combustion test program were to determine the problems associated with co-firing low solids coal water slurry in a pulverized coal boiler. Specifically, we intended to: 1) determine the effect of such co-firing on the boiler performance, SO_2, NOx, carbon monoxide and opacity; 2) evaluate the stability of low solids coal water slurry during handling, transport and short term storage; 3) measure the ability of the boiler control system to handle slurry co-firing in meeting load demands and 4) evaluate the various production parameters in maintaining the quality of low solids coal water slurry.

At Seward Station, there is one 147 MWe tangentially-fired pulverized coal boiler (#15) and two 32 MWe front-fired pulverized coal boilers (#12 and #14). We chose #14 Boiler for the testing.

The #14 Boiler at Seward Station was manufactured in 1950 by Babcock and Wilcox and is capable of generating 330,000 pounds of steam per hour at 700 psi and 845°F. There are two B&W model E-56 pulverizers on this boiler. Each pulverizer has a capacity of approximately 8-10 tons/hour. The boiler is front-fired with two levels of three burners. The capacity of each pulverized coal burner is approximately 3 tons/hour. The bottom three burners were modified to accept slurry.

Figure 2 is a schematic of the original Seward slurry handling system used for the parametric test program. Starting from the left, the slurry was off-loaded from a tanker by an air-operated positive displacement pump to a storage tank, through a Moyno pump and strainer assembly and into the boiler through three air-atomized slurry guns. The Moyno pump was rated at 25 gpm and it delivered the slurry to the burner. Instrumentation in this delivery system included a mass flow meter and a density meter. In addition, the new burner control system was designed to include direct control of the slurry delivery system.

Figure 2. Seward Parametric CWS System



SUMMARY PARAMETRIC TEST RESULTS

The combustion testing recently completed at Seward involved burning over 100,000 gallons of 50% solids slurry by weight at Btu input rates as high as 40% on a per burner basis. Much of the testing consisted of three to four hour test burns with baseline testing before and after for comparison. These tests culminated in long term tests of about sixteen hours in duration.

The long duration CWS co-firing tests were conducted in June 1994 at Seward Station. The tests consisted of a series of co-firings using the bottom three rows of Unit 14 burners. The tests were run with CWS produced at the Homer City Coal Processing slurry pilot plant. The test conducted on June 1, 1994 utilized a mobile lab supplied by EER to collect continuous emission data. Data collected using the mobile lab included SO_2, CO, O_2, CO_2 and NOx data. In addition, data normally collected by the boiler data retrieval system was collected and reduced to a spreadsheet file for use in reports. The two additional long duration tests retrieved data from the boiler data retrieval system only.

Test 1 was run using a feed rate of 125 pounds of slurry per minute. Test 2 was run at 150 pounds per minute. The pounds of NOx were calculated from CEM data. The tests were completed successfully and the results of the June 1 test showed a reduction in NOx ranging from 7% to 20% depending on operating conditions. The higher slurry feed rate produced the greatest NOx reduction. Other operating parameters such as SO_2, steam rate, Opacity, O_2 , CO_2 and CO levels weren't significantly affected by slurry co-firing. A summary of the June 1 test data is shown in Table #1.

Table 1 Long Duration Test #1 - June 1, 1994

(Time,Min.)	O_2%	CO2, %	NOx#/MM	CO, ppm	Steam, k#/HR
Baseline (0-40):					
Average	5.90	12.43	0.549	26	302
St. Dev.	0.22	0.2	0.014	6	4
Maximum	6.31	12.80	0.581	56	311
Minimum	5.53	12.10	0.520	21	297
Test 1 (41 - 540):					
Average	5.70	12.58	0.544	33	320
St. Dev.	0.28	0.28	0.018	10	5
Maximum	6.76	13.87	0.614	89	335
Minimum	4.54	11.74	0.499	19	302
Test 2 (541-980):					
Average	5.65	12.79	0.511	30	322
St. Dev.	0.28	0.32	0.020	11	5
Maximum	6.02	13.74	0.545	85	334
Minimum	4.72	12.26	0.467	23	315

The following figures were derived from the collected data. Figure 3 shows that opacity and slurry density were constant throughout the test (the slurry flow rate change was a deliberate change). Figure 4 shows the variability of the NOx level reported as pounds of NOx per million Btu. This was calculated from the CEM data using the EPA methods published in the January 11, 1993 Federal Register. The NOx levels are typically reduced by 20 to 25% in most of the tests run at the Seward Station. Figure 5 shows that O_2 and CO_2 were constant throughout the test program. Figure 6 shows a spike in CO levels during start up, otherwise the CO level is significantly less than 100 ppm.

Figure 3. Opacity & CWS Density

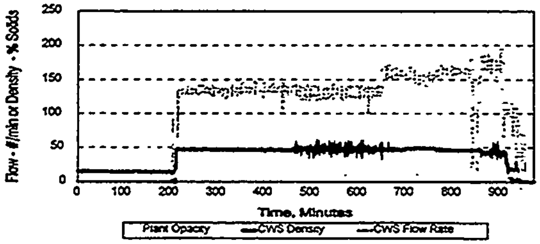


Figure 4. NOx Levels

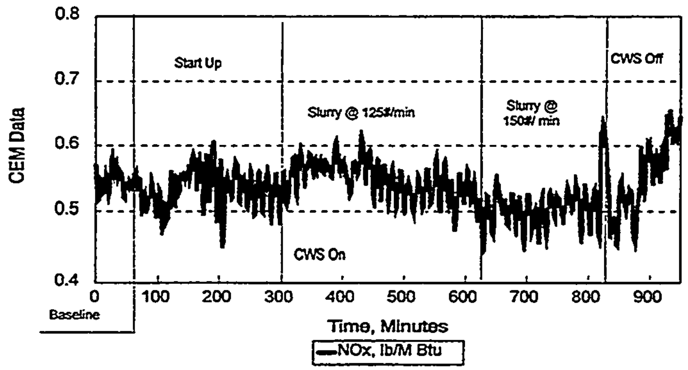


Figure 5. O2 & CO2 Levels

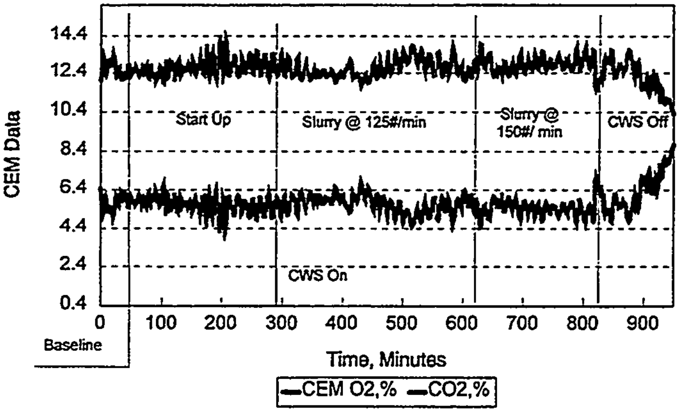
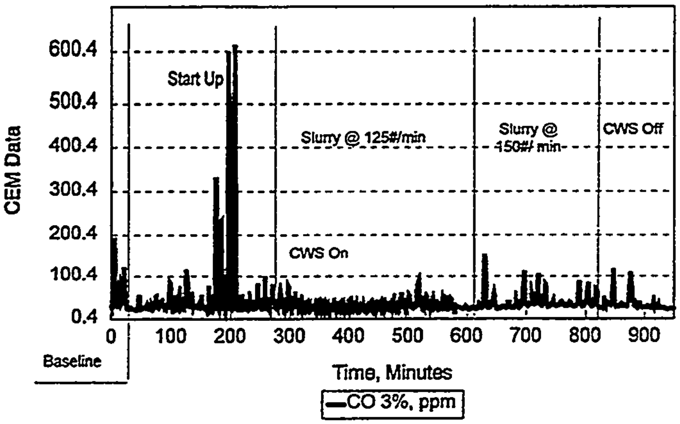


Figure 6. CO Levels



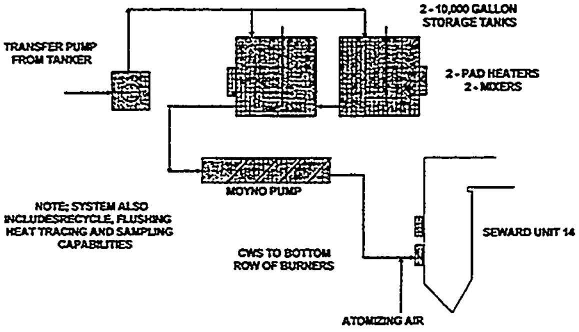
The results of the entire test program are summarized here: 1) low solids coal water slurry can be successfully co-fired in a 32 megawatt utility boiler with no adverse effects on boiler performance; 2) co-firing this fuel with pulverized coal results in a reduction in NOx of 15 to 20% under the conditions tested at the Seward Station; 3) emission levels of carbon monoxide, SO_2 and opacity, are essentially the same when co-firing with low solids coal water slurry as with normal pulverized coal firing levels when using the current slurry quality; 4) slurry handling and feed systems installed at the Seward plant performed within design parameters and are not difficult to operate or maintain; 5) low solids coal water slurry co-firing can be successfully integrated into the boiler control system; and 6) Seward Station plant operators readily accepted slurry co-firing as a routine procedure once the test program got underway.

RECENT WORK

In order for Penelec to move forward, it was determined that a continuous burn, twenty-four hours per day and seven days per week, was required. That made it necessary to develop an outside source of low solids coal water slurry. The maximum capacity of the formulation plant at Homer City was only 700-800 gallons per hour and the continuous requirements for 20% Btu input on #14 Boiler is 1200-1500 gallons per hour. As a result of this, Penelec issued a request for proposals to supply up to 2,500,000 gallons of slurry to our specifications over a three to six month period on a continuous basis. We were successful in getting a supplier in place, Washington Energy Processing (WEP), out of Coraopolis, PA, and they are currently supplying slurry to Seward Station by tank truck..

We also needed to modify the system to allow continuous operation. Figure 7. is a schematic of the new installation. It was determined that additional tank storage was needed and that the test program should incorporate weatherization testing. The previous test program verified the fact that mixing was effective in ensuring slurry stability when the slurry quality varied. With the help of EER Corporation, the system has been modified by employing the use of two 10,000 gallon storage tanks along with mixers and pad heaters at the Seward site. In addition, heat traced supply and recirculation lines were added and the transfer and supply pumps were installed outdoors to enable a determination of weatherization requirements in winter.

Figure 7. Seward Continuous CWS System



In December 1994, a test burn was conducted on the original test equipment using the slurry provided by WEP. The slurry quality was very good and the test burn was completed without incident. In early February 1995, a test burn of 4,800 gallons of slurry was conducted using the newly modified and installed system. This test was also successful. As of this writing, plans are in place to start up the continuous test burns immediately after the plant corrects an unrelated problem with the boiler which is projected to be by the end of February. In the interim, two loads of slurry will be off-loaded into one storage tank to determine weatherization requirements on long term storage in winter.

FUTURE WORK

The question you may now ask is, "where do we go from here?". As mentioned earlier, Penelec has awarded a contract for an independent supplier of 2,500,000 gallons of slurry to be utilized in a six-month test burn at Seward Station to determine the final design requirements, weatherization of equipment, transportation logistics and long term combustion characteristics of utility scale slurry co-firing. The slurry will be formulated from feedstock derived from Pittsburgh Seam coal ponds. Near the end of this test program, we intend to complete the modification of the upper three burners on #14 Boiler and implement several parametric test burns with the total boiler conversion to determine the maximum NOx reduction effects.

Successful completion of this work will result in the modification of a second boiler (#12 Boiler) at Seward and the issue of a request for proposals for a long term contract for the purchase of up to 40,000 tons of coal as slurry (8,000,000 gallons) per year. This will also spur the development and utilization of various types of feedstock and will encourage the development of variations in the slurry delivery systems to reduce transportation costs. One likely outgrowth of this need for continuous slurry is the possible construction of a slurry formulation plant at the Seward site which could eventually be expanded to supply slurry to all three boilers at the station and could also be used as a permanent slurry test facility.

Continuous delivery of slurry to Seward Station's #12 and #14 Boilers will give Penelec the logistical capability to consider testing the concept on #15 boiler which is a 147 MWe tangentially fired pulverized coal boiler. Successful testing on #15 boiler will result in requiring the delivery of an additional 90,000 tons of coal (18,000,000 gallons) per year as slurry to Seward and we will begin transferring the technology to the other power plants in our system.

Penelec is currently participating with Penn State University, PEDA and the DOE in a study to produce coal water slurry fuel from four Pennsylvania coal fines ponds. This project will determine the characterization and variability of the ponds and the washabilities of the material. The project will also essentially replicate laboratory combustion work done previously on fresh fines which will allow direct comparisons with that work. It is anticipated that this will result in a larger scale project later this year involving utility scale combustion testing at Seward Station of slurry made from one of those coal ponds.

Penelec is also working with the EPRI through the Upgraded Coal Interest Group (UCIG) to test slurry burning in TVA's large cyclone boilers in Paradise, Kentucky. Also initial test results by EER Corporation on coal water slurry reburning at their test facility in Irvine, CA are very promising and warrant further study.

We are in the initial stages of proposing a project to the UCIG to test various types of additives to the slurry to gain additional NOx or SO_2 capture such as urea or ground limestone.

We are looking into the area of toxic elements as another area in which the co-firing concept may show promise. The coal water slurry system can be considered a material delivery system. Sorbents of various kinds could easily be delivered to the furnace by this method. Some sorbents could even be coated to delay exposure of the sorbent's availability to the proper temperature range or location in the furnace for maximum reactivity and effectiveness.

In addition to front-fired, tangential, cyclone and fluidized bed pulverized coal boilers, we plan to explore the slurry co-firing concept on oil and gas boilers and consider replacing some of their primary fuel with low solids coal water slurry. Due to the narrower gas passes, shorter residence times and lack of ash handling equipment, there will be limits to the amounts of slurry they can accommodate but we believe that we can exceed 20% Btu input without negative effects.

Various types of fine coal cleaning processes result in various size distributions and various coal qualities. Our testing to date seems to indicate that there are no serious barriers to developing systems which will enable the formulation of acceptable quality slurries from those processes. One area requiring additional research by others is to determine the effect on traditional coal cleaning processes when the need to minimize fines is reduced. If a coal processor has an outlet for the fines he generates, he should be free to fine-tune his conventional feed coal cleaning circuit to make a higher quality feed coal and recover the additional fines as a high quality slurry by-product.

We have only begun to scratch the surface of a technology which has a potential to revolutionize the way we view coal combustion in this industry. As systems are built and operated, an experience curve will develop which should propel our knowledge of the process to ever greater levels and could ultimately lead to cost effective high density slurry for stand alone combustion systems.

CONCLUSION

In conclusion, an economic alternative fuel in the form of low solids coal water slurry can be produced from clean coal fines derived from fine coal streams in conventional coal cleaning processes, from reclaiming coal ponds or from fine coal streams resulting from advanced coal cleaning processes. There is an economic justification and an environmental benefit for fuel suppliers to develop and improve such processes and there is a significant economic justification for utilities to purchase and utilize this fuel.

It is essential for the electric utilities, coal producers and researchers to become more knowledgeable and more deeply involved in the development of this technology as an important, economically sound, first step toward the introduction of high solids slurry combustion. The current political and economic climates mandate greater efficiency in energy production and use. One current cause of inefficiency in the area of coal processing is the production of waste coal fines during cleaning. As increasingly stringent environmental regulations take effect over the next few years, deeper cleaning of coal will be required which will result in a dramatic increase in the generation of coal fines. In order for coal to remain a competitive fuel for the utility industry, several means must be found for dealing with these fines and utilizing the Btu currently lost to coal fines ponds. There are many possibilities for dealing with this problem. Co-firing low solids coal water slurry with pulverized coal is certainly one of the most promising.

The Utilization of Coal Pond Fines as Feedstock for Coal-Water Slurry Fuels

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INTRODUCTION

It has been reported that coal slurry fuels were first introduced in the 1870's in the form of coal-oil mixtures[1]. In the 1950's, coal-water mixtures were investigated as a supplement to fuel oil[1]. However, because of the low price, abundant supply, and convenience of fuel oil, interest in substitute fuels waned in the U.S. It was the fuel oil supply shortages and price increases of the 1970's that created an economic incentive for the development of fuel oil-replacement fuels. The envisioned applications of coal-water slurry fuels (CWSFs) through the 1980's were essentially the same as those for fuel oil: industrial and utility steam boilers, blast furnaces, process kilns, and diesel engines[2]. The concept involved substituting CWSF for fuel oil with minimal retrofitting of the existing oil-fired system. Such fuels require fairly stringent quality restrictions: low ash, high solids loading and low viscosity, which resulted in significant problems with stability. In many cases, the use of additives was required, thereby increasing the cost of the fuel. When oil prices fell during the 1980's, CWSFs lost economic viability due to the cost of production and the capital intensive modifications required to retrofit oil-designed boilers[3].

One approach to lowering the cost of CWSFs is to use coal refuse as the feedstock and to cofire the CWSF with pulverized coal. The utilization of coal fines, both freshly produced and impounded, is potentially economically and environmentally beneficial. Coal fines (generally minus 28 mesh) are produced during wet cleaning of coal. Waste coal fines can account for up to 20 % of the total coal cleaned in a preparation plant. The use of fines, therefore, has the potential to reduce the amount of coal discarded and to lower overall fuel costs. The environmental impact of impoundments is also of concern. Problems associated with the surface disposal of coal waste include: the nonproductive use of land, the loss of aesthetic value, the danger of slides, dam failure, significant permitting costs, and water pollution. It is estimated that 2 billion tons of coal refuse are contained in impoundments in the U.S. Over 75 % of these fines are in states east of the Mississippi River. The current annual production of coal fines at preparation facilities exceeds 50 million tons[4, 5]. This does not include anthracite fines, which could account for additional 100 million tons in eastern Pennsylvania.

Penn State University, in conjunction with Pennsylvania Electric Company (Penelec), has evaluated the handling and combustion characteristics of CWSFs formulated from fines from Penelec's Homer City Cleaning Plant (HCCP). The CWSFs were successfully cofired with pulverized coal in Penn State's 1,000 lb steam/hr research boiler. The ratio of pulverized coal to CWSF was varied from 80:20 to 59:41, based on thermal input. The CWSFs contained no additives and the solids loading ranged from 48 to 55 %. The coal combustion efficiency for the cofiring tests ranged from 75 to 94 %. This range is a consequence of the variable nature, *e.g.*, solids loading, particle size, and ash content, of the CWSFs prepared at the HCCP. A value of 94 % for combustion efficiency is acceptable for the burner currently in use.

Penelec subsequently cofired the CWSF in a 360,000 lb steam/hr utility boiler (Unit 4, Boiler No. 14, Seward Station, Seward, PA). The unit contains six front wall burners located at two levels. Three dual fuel, low NO_x burners designed by Energy and Environmental Research, Inc. (EER), were installed in the unit, replacing the lower three burners. The CWSF was prepared in a 3 ton/hr pilot plant from cleaned minus 100 mesh waste coal from the HCCP. The coal was obtained from the classifying cyclone overflow in the B stream. An Air Sparge Hydrocyclone, that utilizes both flotation and centrifugal force, was used to clean the fine coal. The clean coal was sent to a static thickener to concentrate the solids (35-40 %), and the thickened clean coal then pumped to a filter press (65-70 % solids). The filter cake was then fed to a stirring tank and dispersed to produce a 40-50 % solids CWSF. Penelec cofired 20 % CWSF with a solids loading of 50 % with pulverized coal without derating the boiler.

In an attempt to lower the cost of CWSFs even further, interest in their formulation from impounded fines has emerged. Penelec has begun procuring and firing CWSF produced from impounded coal fines at the Seward Station[6]. Cofiring with pulverized coal permits the use of relatively low quality CWSF. Less stringent fuel quality standards, *i.e.* ash content, solids loading, and particle size, result in fewer viscosity and stability problems then are experienced with high solids CWSFs. CWSFs having ash contents of 10 to 15 %, with 50 % solids loading have been successfully cofired by Penelec.

CQ Inc. evaluated the economic and technical constraints of producing coal-derived fuels from coal refuse using advanced coal cleaning and slurry technologies[5]. They concluded that the use of advanced coal cleaning technologies has sufficient economic potential to warrant further investigation. The two fuels identified by CQ Inc. as "premium" fuels were compliance steam coal producing less than 1.2 lbs SO_2 per million Btu and coal water/oil slurries with low sulfur content and less than 5 % ash. Cleaning strategies recommended for the production of CWSFs were chemical extraction and selective agglomeration. This recommendation was based on the assumption that the costs of other fossil fuels and SO_2 compliance coal continue to rise as forecasted.

Hanna and Kalathur sampled impounded coal fines and plant discharge streams in Alabama to study the recovery of coal by sizing, gravity and flotation techniques[4]. The raw coal wastes had ash contents from 24 to 41 percent. Fine wastes from preparation plants had ash contents from 31 to 52 percent. Yields for a plus 200 mesh float at 1.6 specific gravity (ash content 4 to 11 %) ranged from 24 to 56 percent. In general, the yield from impounded fines taken from a site was the same or greater than, that for fresh fines[7].

Penn State is currently relating the characteristics of recovered coal fines to their suitability for use as CWSF feedstocks, investigating formulation strategies and determining the combustion behavior of the CWSFs. Four bituminous coal refuse sites with different characteristics (*i.e.*, age, active status, source of material, and composition) are being evaluated. Site samples are being characterized for cleanability and washability. This information, along with particle size distribution and compositional data, is being used to formulate CWSFs from the coal fines. The combustion performance of the CWSFs will be determined in Penn State's research boiler (1,000 lb steam per hour). One CWSF will be included in the Department of Energy's Alternative Fuel Evaluation Program at ABB Combustion Engineering. This same fuel will be burned at Penelec's Seward Station (Unit 4, Boiler No. 14).

According to CQ Inc., "... insufficient information was available for determining production and associated environmental costs. It is recommended that a case study be completed that involves a survey of potential sites, selection of one or more promising impoundments, and determination of an expected clean coal quality and production cost for each favorable site. This information will allow a more realistic appraisal of the potential of this feedstock source"[5]. The program at Penn State is generating the data to compare the economic viability formulation strategy and combustion performance of fresh and impounded fines at various scales.

FRESH COAL FINES

Combustion Behavior of CWSFs Formulated from Fresh Fines in Cofiring Applications

Penn State has been studying the character and combustion behavior of CWSFs formulated from fresh coal fines for over 5 years. Fifteen CWSFs formulated from fresh fines have been cofired with pulverized coal in the Penn State research boiler. The boiler is a 200 psig watertube boiler of A-frame construction, which was designed and built by Cleaver Brooks. The combustion chamber is 3 ft x3 ft x7 ft (63 ft^3) with a maximum heat release rate of 42,000 Btu/ft^3 h. The CWSFs were produced at the Homer City Processing Plant during cleaning of Upper Freeport coal. The coal was obtained from the classifying cyclone overflow (minus 100 mesh) in the B stream. An Air Sparge Hydrocyclone or a conventional froth flotation cell was used to clean the fine coal. The clean coal was sent to a static thickener to concentrate the solids (35-40 %), then pumped to a filter press (65-70 % solids), and then dispersed to produce a 40-50 % solids CWSF.

The CWSFs had a variety of particle size distributions, solid loadings, and ash contents. The majority of the fuels did not contain dispersants or stabilizers. Analyses of the pulverized coal and selected CWSFs are given in Table 1. Included are the ash, sulfur, and solids percentages, calorific value, selected particle size parameters, and viscosity at 100 s^{-1}. Table 1 also summarizes the combustion test results. Given is the coal combustion efficiency for each test fuel based on the char collected in the ash hoppers and the baghouse. Four samples were collected from the hopper and the baghouse. Each test was conducted firing 80 % pulverized coal and 20 % CWSF. A firing rate of 2MM Btu per hour was used for each test. In some cases, the combustion efficiency on cofiring was greater than that when firing 100 % pulverized coal. This may be attributed to the finer coal particle size in some of the CWSFs, the smaller particles requiring less time for burnout, and enhanced mixing during cofiring. Upon introducing the CWSF into the pulverized coal flame, the flame became more compact. This is attributed to the lower pressure region produced in the center of the flame that resulted from the high velocity of the CWSF/atomizing air mixture. In general, this produced a stable flame during each cofiring test. This is significant in that a stable flame could not be maintained when firing 100 % CWSF because of the low solids loading of the CWSF and the low volatile matter of the coal[8].

Table 1. Characterization and Combustion Results of Selected Coal-Water Slurry Fuels Tested in Penn State's Research Boiler

Test Fuel	Ash (db,wt%)	Sulfur (db,wt%)	Solids (%)	BTU/lb (db)	Particle Size (µm)			Viscosity @100/s (cp)	Coal Combustion Efficiency (%)	
					d90	d50	d10		Hopper	Baghouse
Pulverized Coal 2	12.7	1.7	NAp	13,168	NAv	NAv	NAv	NAp	86.8	91.4
No. 1	10.6	1.3	52.0	13,899	138.0	35.6	5.4	150	81.3	89.4
No. 2	16.9	1.4	52.1	12,764	106.7	19.1	1.8	145	73.3	89.2
No. 3	5.4	1.2	49.1	14,731	90.8	26.2	4.8	310	88.1	91.7
No. 4	8.9	1.3	48.0	14,130	109.3	34.5	3.6	117	84.8	92.2
No. 5A	5.5	1.1	50.8	14,660	95.1	27.5	4.7	333	91.9	93.4
No. 6[a]	8.9	1.2	41.8	14,071	92.0	27.3	4.6	60	93.8	94.1
No. 7	16.6	1.2	50.1	12,840	98.8	29.6	4.0	147	89.1	94.4
No. 8[b]	9.7	1.3	53.5	14,023	92.4	24.0	3.7	164	92.1	93.5
No. 13	8.4	NAv	44.1	NAv	29.7	10.7	2.6	43	NAv	
No. 14	8.3	NAv	47.2	NAv	33.4	10.8	2.5	63	NAv	

aParticle size determined on CWSF that had formed hard pack.

b Contained an undisclosed amount and type of dispersant

NAp Not Applicable

NAv Not Available

Relationship of Viscosity and Solids Loading to Particle Size Distribution

Viscosities, solids loadings, and particle size distributions of the various fuels were determined. All of the test fuels displayed pseudoplastic or shear thinning behavior. The viscosities ranged from 43 to 600 cP at 100 s^{-1}. Based on solids loadings the viscosity of Fuel No. 2 would be expected to be similar to, or slightly higher than, that of Fuel No. 3. However, the viscosity of Fuel No. 2 at 100s^{-1} was 145 cP compared to 310 cP for Fuel No. 3. There is no clear relationship between solids loading and viscosity. However, there is a theoretical relationship between particle size distribution and CWSF viscosity based on packing density. Skolnik et al. concluded that the established packing theory of Furnas, developed in 1931 and expanded by Farris in 1968, can be used to maximize the solids loading of CWSFs[9]. Farris expanded upon the work by Furnas to include the effect of a particle size distribution on viscosity and solids loading. The mathematical relationship is as follows:

$$CPP = (100)(D^n - Ds^n)/(Dl^n - Ds^n)$$

where CPP = Cumulative weight percentage of particles smaller than a given size
D = Particle diameter
Dl = Largest diameter coal particle
Ds = Smallest diameter coal particle
n = Distribution modulus
Farris value - 0.19
Furnas value - 0.25

The distribution modulus values of 0.19 and 0.25 are based on a CWSF having 70 % solids loading. The equation generates a theoretical particle size distribution for a coal with given top and bottom sizes that maximizes solids loading based on classical packing theory. A plot of the theoretical particle size distributions obtained using both distribution moduli and the actual particle size distributions of Test Fuels No. 2 and No. 3 are shown in Figures 1 and 2, respectively. A Dl value of 188 µm and Ds value of 0.5 µm were used to generate the Farris and Furnas curves.

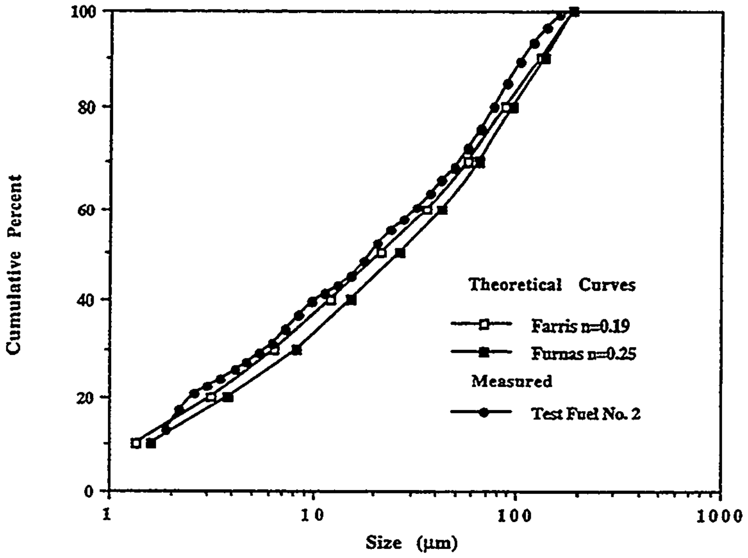

Figure 1. Theoretical Versus Measured Particle Size Distribution Curves for Test Fuel No. 2

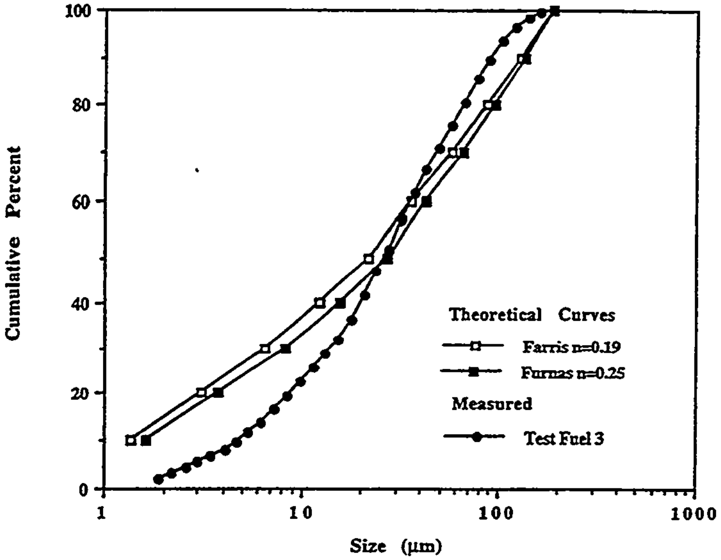

Figure 2. Theoretical Versus Measured Particle Size Distribution Curves for Test Fuel No. 3

The particle size distribution of Test Fuel No. 2 approximates that suggested by the Farris model for maximum packing density. Test Fuel No. 2 had the highest solids loading of the CWSFs that did not contain additives, *i.e.* 52.1 %. Test Fuel No. 3 had approximately 49.1 % solids loading. The particle size distribution of Test Fuel No. 3 is coarser than those suggested by both the Farris of Furnas models for maximum packing density. Test Fuel No. 3 has significantly fewer fines than both of the two theoretical distributions. These results emphasize the importance of the particle size distribution. The Furnas theory has some limitations in that discrepancies with experimental data have been documented. In addition, it is necessary to calculate the very complicated integer constant n . Further discussion of a new approach being developed at Penn State to applying packing theory to the formulation of CWSFs can be found in Painter et al[10].

Jim Walters Resources, Inc. (JWR) conducted formulation tests on the Penelec cleaned fine coal. Of particular interest were the properties of the CWSFs produced without additives compared to those of highly loaded CWSFs. Low density CWSF (50 % solids) containing no additives had a viscosity 112 cP at a shear rate of 100 s^{-1}. CWSFs containing approximately 60% solids had a viscosity 750 cP. Handling and combustion tests suggest that viscosities less than 300 cP are desirable. A CWSF having 60 % solids required the addition of 1 % dispersant to obtain a viscosity ≤ 300 cP.

As a result of these tests and those conducted by Penelec, the following specifications have been established by Penelec for CWSFs formulated from impounded fines: solids loading of approximately 50 %, particle size distribution of 100 % minus 60 mesh and 80 % minus 100 mesh, viscosity of 100-200 cP at 100 s^{-1}, ash content ≤ 12 % and sulfur content of ≤ 1.2 %.

IMPOUNDED FINES

Three impoundments within Pennsylvania have recently been cored using a split-spoon sampler. Selection of the specific impoundments was based on the quality of the impounded material, the impoundment size, status (*i.e.* active or inactive), and accessibility. The sites are located within a 60 mile radius of Penelec's Seward Station which is a viable customer or host site for cofiring CWSFs formulated from impounded coal fines. A tractor/truck-mounted split-spoon sampler was used at each impoundment. Four to five, six-inch diameter cores were drilled at each site totaling 160 to 180 feet.

Core liners 2.5 feet in length were used by the split-spoon sampler. Each core was extruded from the core liner and logged, *i.e.* macroscopic description of textural and structural features and color. Sample splits (approximately 1/8 to 1/16 of each core section) from each 5 foot core interval were taken for ultimate, proximate, sulfur, pH, alkali extraction and particle size distribution analyses. The remaining portions of the cores were combined to make a composite sample for each site. This sample was homogenized in a ribbon mixer and subsequently stored in two plastic 55-gal barrels. Two 5 gallon buckets were filled with the composite sample for washability and froth flotation analyses. The material in the 55 gallon barrels will be used for the formulation study and to prepare CWSF for combustion testing in the research boiler.

Character and Quality of Impounded Fines

Variation of the Quality of Coal Fines - Monongahela, PA Site

The variability in quality of the material contained in impoundments and its impact on fuel quality have been raised as possible roadblocks to the commercial use of refuse fines for CWSF. As previously discussed and demonstrated at Penn State, the specifications for fuel quality in a cofiring application are less stringent than for high density CWSFs fired in retrofitted oil-fired boilers. Still it is necessary to address the variability issue and its impact on formulation strategy.

The Monongahela site contains three inactive impoundments produced during cleaning of Pittsburgh Seam coal. The preparation facility at this site was the last Chance Cone plant built and went on line in 1959. One of the inactive sites was drilled. Four cores, 6 inches in diameter, were obtained accounting for a total of 180 feet. According to information provided by the owners, the impoundment was active from 1959 to 1977 and contains approximately 3.8 million tons of coal refuse. The estimated depth is from 50 to 70 feet. Cores obtained at the site were 40 to 60 feet in length.

Proximate and ultimate analyses of the composite material on a dry basis are as follows: ash 41.3 %, volatile matter 22.1 %, fixed carbon 36.6 %, carbon 48.7 %, hydrogen 3.4 %, nitrogen 0.9 % and sulfur 1.1 %. Approximately 84 % of the material is minus 100 mesh in size and contains 0.8 % sulfur and 48.7 % ash. Particle size, higher heating value, and proximate and ultimate analyses of the material as a function of depth are given in Tables 2 and 3.

Table 2. Coal Sediment Particle Size Distribution and Higher Heating Values for the Monongahela, PA Site

	Particle Size Distribution (Percent Passing) U.S. Standard Mesh						HHV
Depth	10M	30M	60M	100M	200M	400M	(Btu/lb)
0-5'	100.0	98.8	77.3	69.2	63.7	50.8	8,407
5-10'	100.0	99.0	87.6	80.6	71.9	62.1	7,831
10-15'	100.0	99.6	94.4	90.6	83.4	73.6	7,057
15-20'	99.8	99.6	95.8	92.9	86.7	77.1	7,318
20-25'	100.0	99.7	95.4	86.5	79.9	70.4	7,235
25-30'	100.0	99.9	98.1	95.6	89.7	85.1	7,468
30-35'	100.0	99.7	98.0	96.0	87.8	73.2	9,410
35-40'	100.0	99.8	95.0	91.4	84.4	75.7	8,311
40-45'	100.0	100.0	98.6	95.0	86.1	74.7	8,853
45-50'	100.0	99.9	96.9	90.8	79.5	69.7	9,514
50-55'	100.0	99.7	93.0	85.7	75.9	65.6	9,354
55-60'	100.0	99.9	94.9	86.5	72.4	54.6	10,720
60-65'	100.0	99.4	71.9	55.4	42.3	32.7	11,718

Table 3. Proximate and Ultimate Analyses (Dry Basis) for the Monongahela, PA Site

	Proximate Analysis (db, wt%)				Ultimate Analysis (db, wt %)			
Depth	Volatile Matter	Ash	Fixed Carbon	Total Sulfur	Carbon	Hydrogen	Nitrogen	Oxygen
0-5'	22.8	39.9	37.3	0.9	48.5	3.3	1.0	6.4
5-10'	22.4	44.1	33.6	1.0	45.5	3.1	0.9	5.4
10-15'	21.1	48.5	30.4	0.9	41.3	2.8	0.8	5.7
15-20'	21.8	46.7	31.5	1.0	43.1	2.8	0.9	5.5
20-25'	21.2	47.8	30.9	1.1	41.8	2.8	0.8	5.7
25-30'	20.8	46.5	32.7	1.0	43.7	3.0	0.9	4.9
30-35'	24.0	35.4	40.6	1.0	54.0	3.6	1.0	5.0
35-40'	22.2	42.6	35.2	1.2	47.9	3.3	1.0	4.0
40-45'	22.5	38.7	38.8	1.1	51.0	3.4	1.0	4.8
45-50'	23.5	34.7	41.8	1.1	54.7	3.6	1.1	4.8
50-55'	23.7	35.5	40.8	1.0	54.0	3.7	1.0	4.8
55-60'	26.2	27.7	46.1	1.0	61.3	4.1	1.1	4.8
60-65'	28.6	21.6	49.9	1.1	66.8	4.4	1.3	4.8

The amount of minus 100 mesh material ranges from 69 to 96 %, by weight. The total sulfur varies from 0.9 to 1.1 %, by weight (db), however, the percent ash varies from 21 to 49 % , by weight (db). In general, as the percent of minus 100 mesh material in the sample increases, the ash content increases. This is due to the concentration of ash in the fines during the cleaning of the original coal. The sulfur content of this material is within the limit set by Penelec. Therefore, cleaning of this material would concentrate on removal of ash, possibly by froth flotation as discussed by Hanna and Kalathur[4].

Quality of Coal Fines as a Function of Particle Size - Eighty Four, PA Site

The following discussion focuses on a site located near Eighty Four, Pennsylvania. The Eighty Four Site contains one active and one inactive impoundment containing fines produced during cleaning of Pittsburgh Seam coal. The impoundments date from the 1950's and were active until 1987. One site is completely reclaimed and is adjacent to a community golf coarse. Reclamation was completed in 1989. Chance Cones were installed in the original preparation facility. Froth flotation was introduced into the plant in 1965. This impoundment was abandoned between 1965 to 1967. The estimated depth of the impoundment is 100 feet. A second impoundment site was begun in 1967. At this time two-stage froth flotation was being used at the preparation facility. Approximately 60 % of the surface of the active impoundment is dry with the remaining surface covered with water. A 120 foot earthen dam is located at one end of the impoundment. The material contains a significant amount of water, possibly due to the presence of a perched watertable. Four cores were drilled comprising a total of 150 feet. Three of the cores ranged in depth from 40 to 55 feet. One core was only 15 feet due to the excessive amount of water encountered.

The composite sample contains 34.7 % ash, 24.4 % volatile matter, 41.0 % fixed carbon, 53.3 % carbon, 3.5 % hydrogen, 1.0 % nitrogen, and 1.5 % sulfur on a dry basis. The particle size distribution of the as-received material is shown in Figure 3. The distribution of ash and sulfur as a function of particle size is shown in Figure 4. Approximately 64 % of the material is minus 100 mesh in size. The ash is concentrated in the minus 400 mesh size fraction while the sulfur is concentrated in the 100x400 size fraction. Washability curves, *i.e.* specific gravity yield, cumulative float ash and cumulative float sulfur, for the 28x100 material are given in Figures 5 and 6. The 28x100 size fraction accounts for 30 %, by weight, of the composite sample. According to the washability curves, 81 % of the material is recovered at a specific gravity of 1.6. The 1.6 float contains 1.4 % sulfur and 6.13 % ash. The minus 100 mesh material contains 1.6 % sulfur and 42.7 % ash.

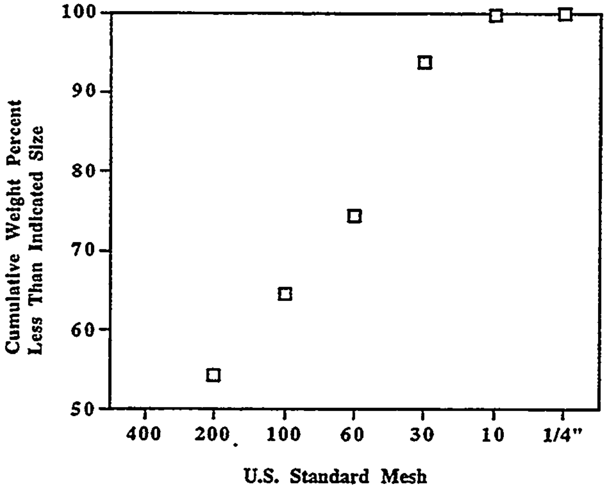

Figure 3. Particle Size Distribution of Material Collected at Eighty Four, PA Site

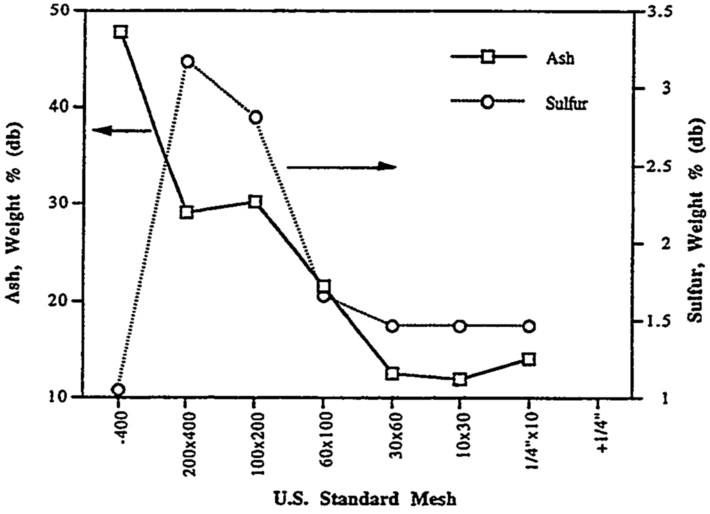

Figure 4. Ash and Sulfur Contents as a Function of Particle Size for the Eighty Four, PA Site Material

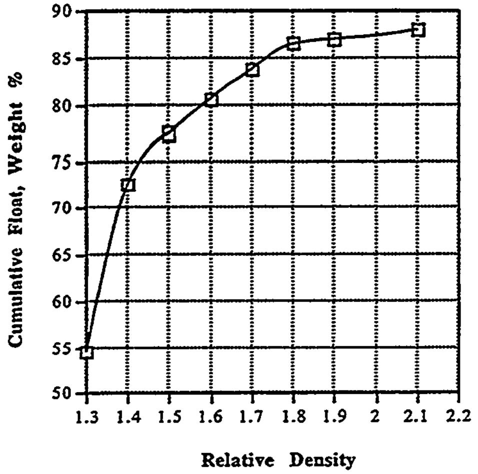

Figure 5. Eighty Four Washability Curve for 28x100 Mesh Size Fraction

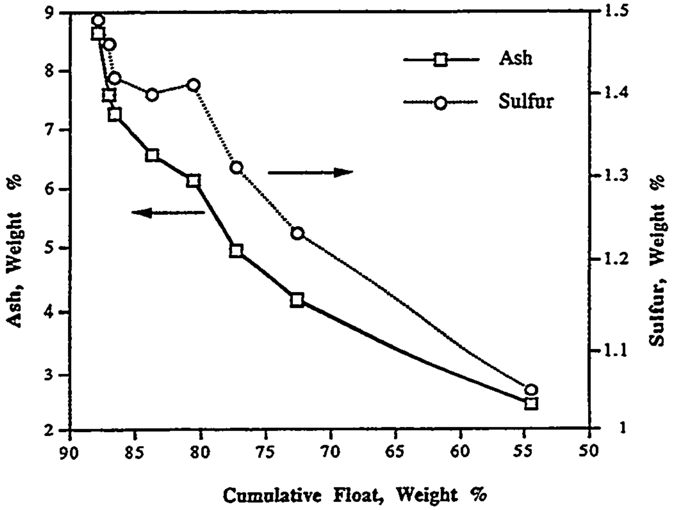

Figure 6. Cumulative Float Ash and Sulfur Curves for the Eighty Four Site

COMPARISON OF FRESH AND IMPOUNDED COAL FINES

The feedstock for the Penelec CWSFs successfully cofired at Penn State was obtained from the minus 100 mesh waste stream at the HCCP. The Penelec CWSF fuel contained 1.4 % sulfur and 16.9 % ash. In general, the particle size distribution of the minus 100 mesh Eighty Four material is finer than that in the Penelec CWSFs formulated from fresh coal fines (Figure 7). The minus 100 mesh size fraction accounts for 64 % of the total material in the Eighty Four sample. Forty-seven percent of the total material is minus 400 mesh. The minus 100 mesh material contains 1.6 % sulfur and 42.7 % ash. A direct comparison between the two materials is of questionable value since the fresh fines underwent cleaning prior to formulation whereas the impounded fines have yet to be cleaned. It is planned to clean the samples by froth flotation, even though the high percentages of fines and slimes may produce low yields. It is difficult to predict the effectiveness of froth flotation on such material, although the CWSF currently being used by Penelec was cleaned in this way resulting in a 50 % reduction in the ash content. Of concern also is the effect of a high percentage of fines on the stability of the CWSF and the solids loading for the required viscosity. A possible strategy would be to adjust the particle size distribution by adding material from the 28x100 mesh size fraction to obtain a distribution of 80 % minus 60 mesh.

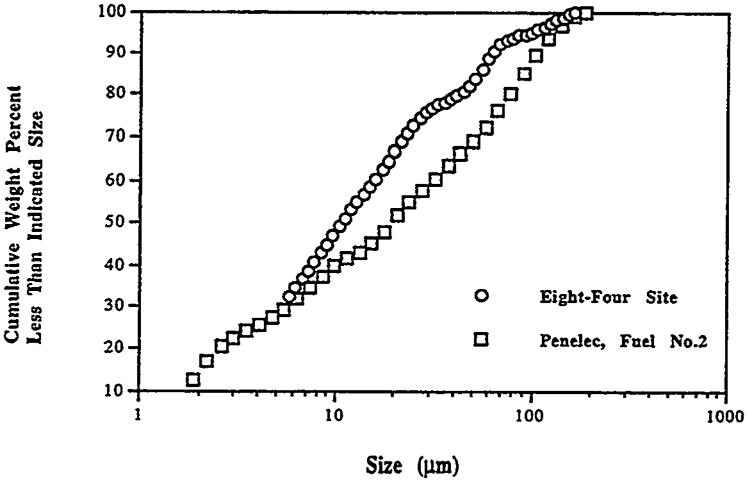

Figure 7. Particle Size Distribution of Eighty Four Site Fines and Penelec CWSF No. 2 Prepared from Fresh Fines (Minus 100 Mesh)

CONCLUDING REMARKS

The successful cofiring of CWSFs produced from fresh fines has presented an opportunity to expand the application of CWSF technology. The concept of cofiring with pulverized coal is attractive because the stringent quality standards traditionally placed on a CWSF in a fuel oil retrofit application can be relaxed. In cofiring applications the following apply:

- Stability beyond 2 weeks is not required since the CWSF is not the prime fuel and need not be stockpiled
- Solids loading may be low since the CWSF comprises only 20 % of the thermal input. Flame stability is promoted by the presence of the pulverized coal flame.
- The particle size distribution is not as critical as for high density CWSFs. This is related to the lower solids loading requirements. However, viscosity in the range of 100 to 200 cP is still desirable.
- Ash content is not critical from the standpoint of accumulation and deposition since the boiler is designed to fire pulverized coal. The CWSF should have an ash content similar to that of the pulverized coal fired in the boiler.
- Atomization performance is not as critical as in a total fuel replacement situation and the use of additives may not be necessary.

The less stringent fuel quality requirements for cofiring applications open the possibility for the use of fresh and impounded coal fines in the form of CWSFs. The potential benefits are lower emissions (particularly NOx) levels and the ability to use CWSF to increase the firing rate of a boiler when the capacity of the pulverizers has been reduced by wear. The key to the commercial success, however is to minimize the processing required to meet fuel specifications and to utilize coal cleaning equipment commonly found in coal preparation facilities.

ACKNOWLEDGMENTS

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PROSPECTS FOR RECLAIMING FINE COAL FROM SLURRY PONDS

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ABSTRACT

Although 400-500 million tons of coal are washed in the U.S. each year, less than half of the fine fraction [minus 28 mesh (0.6 mm)] is subjected to cleaning; a similar figure applies to other coal mining countries around the world. As a result, large quantities of fine coal have accumulated in slurry disposal ponds. In the U.S. alone, more than 2 billion tons of fine coal is estimated to reside in slurry ponds due to coal mining operations throughout the 1900s. Historical reasons for disposal of this potentially valuable material include (1) lack of effective cleaning processes to treat fine coal particles, (2) excessive costs and difficulties associated with dewatering fine particles, (3) absence of a reliable market for fine coal fractions, and (4) lack of regulatory impetus for waste minimization and secondary recovery. For both environmental and economic reasons, interest in the reclamation of fine coal from slurry impoundments has increased in recent years. Many of these impoundments contain high-quality coal that could be relatively easily cleaned to meet customer specifications. Tapping this huge resource, however, requires a clearer definition of its potential; estimates of the amount and quality of coal in slurry ponds are necessary to encourage increased industrial development. To address this need, this paper summarizes data, gathered from the literature and from private communications, concerning slurry pond quantity estimates, quality trends, washability relationships, material recovery, and case studies.

INTRODUCTION

In many countries, coal is extensively utilized for electricity generation, steel production, and home heating. The mining and cleaning processes associated with the preparation of this coal generate huge quantities of wastes. In the U.S., an estimated 174,000 acres of land that was used for coal refuse disposal remain unreclaimed.[1] In the member states of the European Union, this figure is approximately 100,000 acres.[2]

Disposal of coal mining and coal cleaning wastes can have serious environmental and social impacts if not properly conducted and controlled. Water quality is of particular concern. Under certain conditions, the sulfides (pyrite and marcasite) present in coal waste depositories can oxidize to sulfuric acid and significantly lower the pH of local water bodies; also, toxic metal species can be leached from refuse piles, endangering the surrounding ecosystem. Air quality may suffer in the vicinity of refuse areas from the generation of airborne dust and from the release of harmful gases arising from in-pile spontaneous combustion of the carbonaceous matter. Land degradation, beyond the decrease in land value, often accompanies the existence of refuse piles. Fine particle runoff, for example, can cause soil erosion, diminish ground stability, and hamper reclamation efforts.

The coal companies responsible for creating waste depositories incur substantial costs in complying with the regulations governing their use and upkeep. The activities involved in assuring safe and responsible operation of a waste disposal site—obtaining permits, conducting soil surveys and overburden analyses, drafting disposal and water management plans, preparing pond designs, and securing reclamation bonds—are labor intensive and entail significant expense. An estimated \$5 billion in reclamation bonds is currently held by various Federal and state agencies to comply with the provisions of the Surface Mining Control and Reclamation Act,[3] and individual site reclamation costs range from \$5,000-40,000/acre.[4] In West Virginia alone, during 1991-1992, the coal industry spent about \$1 million per day to neutralize acid mine drainage.[5]

The environmental and economic impacts discussed above can be significantly diminished by the development of cost-effective methods for reducing the amount of waste that is impounded. Secondary recovery of fine coal from slurry ponds is one promising waste minimization technique. Because coal preparation has been practiced primarily on the coarser fractions of the feed material, the fine streams in coal preparation plants (approximately minus 28 mesh) have often been discarded to slurry ponds without treatment. These fines contain considerable quantities of valuable combustible matter and make slurry ponds a significant coal resource. To assess the full potential of this resource, a systematic analysis of the nation's coal impoundments would be needed. Such an analysis is unrealistic, however, because it would require a monumental drilling and sampling campaign. Smaller-scale studies are of more practical significance; therefore, this paper discusses various data collected from localized exploratory programs regarding slurry pond sizes, impounded coal quality, and cleaning potential. It also includes descriptions of several commercial secondary coal recovery operations in coal-mining countries around the world.

SECONDARY RECOVERY OF FINE COAL FROM SLURRY PONDS

Quantity of Material in Slurry Ponds

In 1993, there were over 400 permitted fine-coal slurry impoundments in the eastern U.S.[6] In addition, Doyle[7] estimates that 3,000-5,000 sizable active (in use or actively maintained) and abandoned (not in use, not maintained) waste piles and impoundments exist in the eastern coal fields. Predicting the amount of material impounded in these waste depositories is often complicated by several factors: record-keeping practices at coal mines have historically been minimal, accurate maps of pre-deposition topography are not available, remote pond locations and difficult terrain confound drilling and sampling campaigns, and waste disposal regulatory issues make coal companies reluctant to release refuse data.

Despite the complicating factors, several estimates of coal refuse tonnages have been made. Extrapolating data obtained from drilling programs in Illinois and Alabama, CQ Inc.[8] estimated that there were 2.3 billion tons of fine coal in abandoned and active slurry ponds. The National

Academy of Sciences[9] estimated that nearly 3 billion cubic yards (2.3 billion cubic meters) of carbonaceous wastes had accumulated in the U.S. by 1975 due to coal mining and processing. At a bulk density of 60 pounds per cubic foot (0.96 grams per cubic centimeter), this equals about 2.4 billion tons of refuse material, a figure that is undoubtedly much higher today. Finally, Doyle[7] has placed the amount of refuse material in active and abandoned waste piles and impoundments in the eastern U.S. at more than 3 billion tons. It is also important to realize that considerable quantities of fine coal refuse continue to be disposed of by coal preparation plants each year. Estimates by CQ Inc.,[8] and calculations by the authors, indicate that 30-50 million tons of fine coal are added to impoundments annually.

Factors Influencing Coal Fines Quality

The existence of large quantities of impounded fine coal in the eastern U.S. does not necessarily indicate that secondary recovery is justified. The quality of the waste material must be high enough to enable coal cleaning processes to yield a marketable product. Ash content, sulfur content, and heating value are some of the important parameters to consider. It is impossible to derive general quality correlations because of the site-specific nature of coal mining operations. Many factors impact the quality of the fine coal that is disposed of in a given impoundment, including the following:

(1) Parent coal characteristics - The quality of the parent coal is typically reflected in the fine coal. If the parent coal is high in sulfur, it is likely that the fines will also be high in sulfur.

(2) Mining technique - Different mining methods produce run-of-mine coal with varying characteristics. Longwall mining, for example, may generate greater quantities of fines than continuous miners, but rock dilution may be less.

(3) Preparation procedures - The crushing technique employed, the type of cleaning equipment used, the presence or absence of a fines cleaning circuit, the method of dewatering, and the application of reagents are all factors that can influence the final quality of coal fines. A plant with dense-medium vessels and cyclones, for example, will produce fines of different quality than a plant with jigs and flotation cells.

(4) Efficiency of the preparation plant - Plants that do not practice quality control, have not instituted preventive maintenance programs, and do not seek continuous process improvement are destined to operate inefficiently and impound good-quality coal.

(5) Degree of oxidation - Depending on the method of deposition, geologic conditions, and the climate, coal fines may become oxidized in slurry ponds. Exposure of coal fines to ambient air can result in oxidation, which reduces the quality and cleaning potential of impounded coal.

(6) Product specifications - Final product specifications, either imposed directly by customer needs or indirectly through Federal regulations, can have a bearing on fine coal quality. Electric utilities, for example, may require compliance coal to meet Clean Air Act constraints or require a coal with different characteristics to conform to their equipment. Either way, the preparation plant would be forced to make process changes, impacting the fines quality as a result.

Quality Trends in Slurry Ponds

Several trends have been identified in the makeup of slurry impoundments. Quality tends to increase (lower ash, higher energy content) with increasing depth in the slurry pond. This is because, years ago, preparation plants did not operate efficiently, resulting in the disposal of good quality coal. Today, in an effort to optimize energy recovery from coal, plant efficiencies are much higher, so the slurry pond material is of much lower quality (higher ash, lower energy content). Figure 1 depicts this quality-depth relationship trend for a slurry pond in eastern Kentucky.[10] For both the fine fraction (minus 28 mesh) and the composite sample (nominal 3/8" x 0), the ash content generally decreases with increasing depth, indicating that higher quality coal was disposed of in the past.

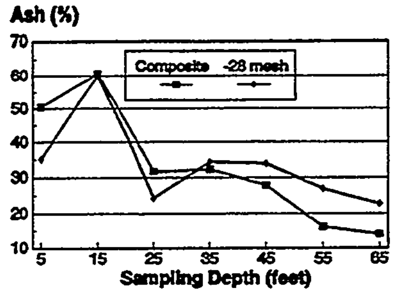

Figure 1 Variation of Impounded Coal Quality with Sampling Depth

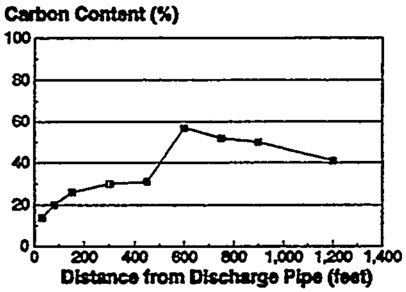

Figure 2 Spatial Distribution of Coal in an Illinois Refuse Impoundment

A second trend is that a spatial quality distribution often exists in slurry ponds. If the point of material discharge has not changed significantly during the formation of a slurry pond, the larger, denser mineral matter particles will often be found near the discharge location, having quickly settled out upon deposition. The lighter coal particles, on the other hand, are usually carried farther away from the discharge point and concentrate in certain portions of the pond. These concentration points may be ideal locations for secondary recovery of fines from slurry ponds. Cobb et al.[11] reported the data that are portrayed in Figure 2. Based on a series of drilled samples from an impoundment in Illinois, this figure corroborates the expected spatial quality distribution, showing that carbon content generally increases with distance from the refuse slurry discharge point. The dropoff in quality beyond 600 feet is likely the result of ultrafine clays that were carried along with the lighter coal.

Quality Data

Quality data from a wide variety of sources, in terms of ash and sulfur content, are summarized in Table 1. Some of these data were obtained from actual slurry impoundments, while others were obtained from operating plant discharge streams destined for slurry ponds. Taken together, they constitute a fairly representative cross-section of the quality of material that makes up slurry ponds.

Table 1
Quality Data for Fine Coal from Various Disposal Sources

Reference	Source of Data	Ash Content Range (%)	Sulfur Content Range (%)
Choudhry et al.[12]	Plant effluent	44-61	1.8-4.3
Hanson Wilson[13]	Slurry pond	48-72	1.1-7.1
Rossmeissl et al.[10]	Slurry pond	17-25	0.7-1.1
Bradley et al.[14]	Plant effluent	20-70	0.6-2.7
Rackers[15]	Slurry pond	40 (avg.)	4.0 (avg.)
Browning and Hilleke[16]	Slurry pond	15-45	0.4-2.1
Lowe et al.[17]	Plant effluent	51 (avg.)	2.2 (avg.)
Chen et al.[18]	Plant effluent	14-41	2.0-4.3

The data in Table 1 emphasize the highly variable nature of the quality of fine coal in slurry impoundments. Ash contents range from 14 to 72% and sulfur contents range from 0.4 to 7.1%.

The data in Table 1 show that some of the sources contain coal of fairly high quality. For example, the data reported by Rossmeissl et al., obtained from three abandoned slurry ponds, indicate ash and sulfur levels of around 20% and 1.0%, respectively.[10] These values are better than the run-of-mine quality of many coals in the eastern U.S. The data reported by Chen et al. for effluents from seven plants are also indicative of relatively high-quality coal.[18] The ash values range from 14 to 41%, but if two of the high-ash samples are not considered, the range is only 14-21% ash. The preparation plant is discarding a fairly high-quality fraction of its feed coal.

In general, the data in Table 1 corroborate what is already assumed to be true regarding slurry ponds. Because of the wide variability in quality, some slurry impoundments will contain better material and be more amenable to fines recovery than others. There are many other factors to consider, but based only on the ash and sulfur data in Table 1, an interested company would certainly investigate the ponds with 17-25% ash material before the ponds with 48-72% ash material.

Cleaning Potential of Slurry Pond Material

The quality of fine coal in slurry ponds, while giving an indication of how dirty the impounded material *is*, does not reveal how clean the impounded material can *become* through coal preparation. This information is obtained from a washability test, which, by subjecting a given coal sample to a density-based separation, provides an indication of the theoretical quantity and quality of clean coal that could be obtained. Coal preparation plant circuits are designed primarily based on the washability characteristics of a chosen coal. Washability data enable engineers to select the most applicable equipment and circuitry to achieve fixed product specifications (considering both the desired quantity and quality of clean coal) and to determine the economic feasibility of a potential cleaning/recovery operation.

A given piece of coal preparation equipment is most effective over a finite particle size range. In general, the size distribution of coal in most slurry ponds or plant effluents would necessitate the use of cleaning technologies designed for fine particle sizes, although there are certainly some ponds that would require intermediate or coarse coal cleaning as well. Several researchers have investigated the size makeup of preparation plant effluent streams and slurry pond samples.[10,13,15,19] Some of these data are illustrated graphically in Figure 3, in terms of log percent finer as a function of log particle size.

As with the *quality* of the material in the slurry ponds and plant effluent streams (Table 1), the *size* is also quite variable. The data points with the lines drawn through them in Figure 3 (open square, diamond, and star) demonstrate the wide differences that exist in size distribution for slurry pond samples; at 100 mesh (0.150 mm), for example, the percent finer values are 28%, 38%, and 50%. The two filled squares plotted on Figure 3 are single-point data from slurry pond samples that indicate even more extreme particle size variations. The left-hand square corresponds to a sample with 86% of the material finer than 325 mesh (0.045 mm), while the right square portrays a sample with only 45% of the material finer than 28 mesh (0.6 mm). These two samples, if subjected to cleaning, would require quite different circuitry to accommodate the large difference in particle size distributions.

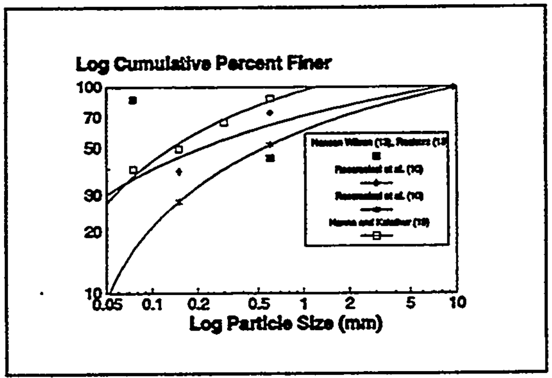

Figure 3 Particle Size Variation of Slurry Pond Material

Cleaning devices applicable to the finer particle sizes, such as dense-medium cyclones, spirals, concentrating tables, froth flotation, and selective agglomeration, would be the most likely candidates for upgrading of the material represented in Figure 3. Cyclones, spirals, or tables would probably be used for the top end of the particle size distribution, around plus 100 mesh, and froth flotation or selective agglomeration would be used for the rest of the material.

Little washability data for slurry pond material and plant effluent streams are readily available. Coal companies have no reason to obtain such data unless they are seriously considering recovery of this resource, and the government has not supported any national efforts to catalog the quality and cleaning potential of slurry pond fines to date. Some actual washability data exist for slurry ponds and plant effluents, but such data have been restricted to individual attempts to recover this material and to a few Federally sponsored studies.

Figures 4 and 5 illustrate the recovery potential of fine coal from several slurry ponds in the eastern U.S., based on washability data obtained from drilled samples. The figures show the theoretical yield and ash rejection levels that could be achieved at a given clean coal ash content. Ideally, both of these values would be high, indicating significant liberation and a high separation efficiency. For the Alabama pond samples (Figure 4), ash rejections are generally high and yields low (e.g., 4.0% clean coal ash at 40% yield and 95% ash rejection).[19] For the Appalachian pond samples (Figure 5), the yields are generally higher, but at lower ash rejection levels (e.g., 7.5% clean coal ash at 64% yield and 82% ash rejection).[10] It is important to realize that these values correspond to the relative density values utilized in the washability study; optimization procedures could likely be applied in practice to obtain a product with a market-acceptable clean coal ash level at higher yield and/or ash rejection levels.

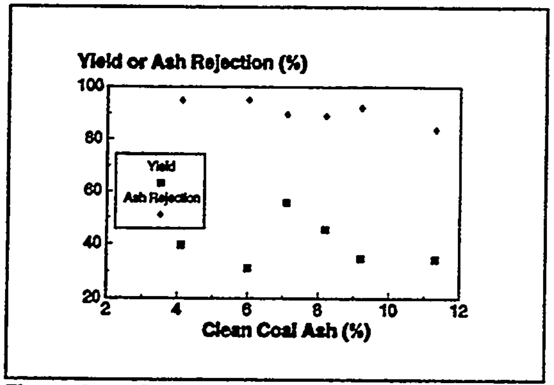

Figure 4 Recovery Potential of Fine Coal from Alabama Impoundments (based on 8 x 200 mesh washability data)

Case Studies

The most effective illustrations of the potential for exploiting the resources found in slurry ponds are commercial secondary recovery applications. Several such facilities have operated, or are in operation, in the U.S. and abroad. They will be described in detail below. In most cases, the coal that is recovered from these operations is blended with coarser coal from nearby mines and sold through normal commercial outlets (i.e., steam coal and metallurgical coal buyers).

(1) Associated Electric Cooperative, Inc. (AECI) operated a slurry pond recovery system at its Bee Veer mine near Moberly, Missouri, between 1987 and 1993.[15] Fine coal material from a 125-acre slurry pond, with estimated reserves of 1.5 million tons, was dredged and pumped to a preparation plant constructed at the site. Screens, classifying cyclones, spirals, and centrifuges were used to process 200 tph of 3/8" x 150-mesh material. Average plant production for a

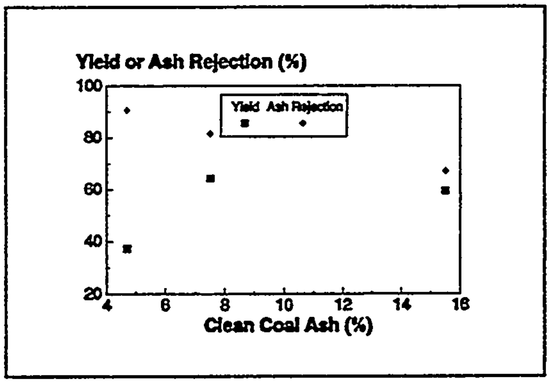

Figure 5 Recovery Potential of Fine Coal from Various Appalachian Refuse Impoundments (based on 3/8" x 0 washability data)

single month's operation was nearly 130 tph, representing a 65% yield. For one 12-month period of operation, the slurry pond recovery circuit produced 192,951 tons of clean coal averaging 8.41% ash, 3.53% sulfur, and 10,205 Btu/lb (2.37 MJ/kg). Quality of the raw coal from the slurry pond averaged 40% ash and 4% sulfur.

Because of diminishing reserves, high post-recovery reclamation costs, and Clean Air Act compliance decisions, AECI decided to shut down the secondary recovery operation in February 1993. From a technical standpoint, however, the operation was a complete success, and demonstrated the viability of recovering valuable fine coal from a waste impoundment.

(2) A slurry pond in the southern Appalachian coal fields is currently being re-mined by a major coal company to recover fine coal.[20] The slurry pond contained an estimated 6 million tons of material when recovery operations began in 1987. A dredge is used to "mine" the impounded material and pump the slurry to a nearby preparation plant. At the preparation plant, spirals and Microcel™ column flotation cells are employed to clean the plus 100-mesh and minus 100-mesh fractions, respectively. The plant is fed at a rate of about 120 tph with a feed ash of 35-50% and dry heating value of 9,000 Btu/lb (2.09 MJ/kg). The cleaning circuits achieve 35-45% yields and produce a clean coal with 8% ash, 14,000 Btu/lb (3.25 MJ/kg), and 17-27% moisture. Plant product is blended with the coarser cleaned fraction from a nearby coal mining/cleaning operation. The use of column flotation units at the preparation plant has resulted in a concentrate ash reduction of 7 percentage points and a combustible recovery increase of 15 percentage points compared to conventional flotation cells. During its seven years of operation, this plant has processed 4.5 million tons, producing 1.8 million tons of clean coal. Remaining lifetime of the project is two to three years. From an economic standpoint, this project has been a great success; the company's investment was recouped within the first few years of operation.

(3) Mineral Development Corporation (MDC), a U.S. firm specializing in secondary coal recovery operations, recently completed an extensive re-mining and reclamation project in southern Illinois at Arch Mineral's Streamline mine.[21] This project demonstrated the applicability of MDC's general technical approach for producing a consistent high-quality coal from a waste resource. In typical situations (as at Streamline), MDC first conducts a thorough drilling and sampling campaign to gauge the quality and quantity of impounded coal. A

proprietary computer simulator is then used to predict coal recovery from the slurry pond. Cutoff points are established for slurry pond size, coal recovery, and impounded coal quality to ensure the economic viability of the project. In actual operation, a remote-controlled floating dredge equipped with a high-pressure water jet collects the refuse material from an exposed slurry pond face. This material is then pumped to a preparation plant for treatment, which can be designed to accommodate feed rates of 70-500 tph. Screens, sieve bends, and classifying cyclones are utilized at the plant to scalp the oversize and deslime the ultrafines from the feed material. The sized feed coal (3/8" x 200 mesh) is delivered to a bank of concentrating spirals for cleaning. Centrifuges and cyclones are employed after the spirals for dewatering and secondary desliming.

Results from the Streamline site were encouraging during the 18 months of operation. A clean coal product averaging 7-8% ash, 2.20-2.35% sulfur, 10,500 Btu/lb (2.44 MJ/kg), and 16-18% moisture was obtained at the 150 tph plant. Additionally, the reject material from the secondary recovery circuit proved to be excellent for subsequent seeding and reclamation activities. MDC is exploring other sites at which to apply their expertise; their second slurry pond recovery project is to be commissioned in the spring of 1995 at a former U.S. Steel Mining property in West Virginia.

(4) German technology is currently being used to recover coal from slurry ponds in eastern Europe.[22] The Dębieńsko coal preparation plant in Czerwionka-Leszczny, Poland, has been utilizing German-developed Hoelter technology since 1991 to treat pond sludge. This plant won the prestigious "Building of the Year" award in Poland in 1992. Pond material is excavated and transported by truck to the plant for treatment. The plant processes refuse material (48% ash, 1% sulfur) using a two-step spiral circuit and froth flotation. Two products are generated: a 2.5 mm x 0.3 mm product containing 9% ash, 0.8% sulfur, 10-12% moisture, and 11,200 Btu/lb (2.60 MJ/kg); and a 0.3 mm x 0 product containing 14% ash, 1% sulfur, 10-12% moisture, and 9,000 Btu/lb (2.09 MJ/kg) (because this is a European plant, it is assumed that the coal heat contents are on a lower heating value basis). Overall yield from the 100 tph circuit is approximately 46%. Two other fine coal slurry pond recovery plants based on Hoelter technology, in Russia and China, are under construction or under development.

(5) HALDEX technology, a waste treatment system developed by Haldex Ostrava, a joint Czech-Hungarian mining venture, is being used in the Ostrava-Karviná coal field.[23] About 18 million tons of coal preparation waste is impounded in this area of the Upper Silesian coal basin. HALDEX technology treats about 500,000 tons of refuse material annually; about 20% of this quantity is recovered as coal fuel, and much of the rest is utilized in the building industry. The process relies on hydrocyclones to separate coal from waste in the 31.5 x 0.5 mm fraction and flotation to clean the 0.5 mm x 0 fraction.

(6) The Republic of South Africa is also becoming more interested in the recovery of coal from slurry ponds. Rand Mines Ltd., for example, ceased underground disposal of the fine coal slurry stream from their Zimbutu Mine in order to stockpile the material for subsequent recovery.[24] Although not operating a secondary coal recovery facility at this time, Rand Mines Ltd. intends to do so when the economics are favorable.

The preceding case study descriptions focused on the technical coal recovery issues associated with various slurry pond reclamation schemes. There are many other factors, however, that must be addressed in order to have a successful secondary recovery operation. These factors will not be discussed in detail here, but include handling of the fine coal product; securing necessary exploration, excavation, operation, and reclamation permits; instituting procedures to ensure that the relevant local, state, and Federal regulations are adhered to; providing road access to the site, electricity, and water; surveying the surrounding terrain for potential obstacles to site development; and determining the disposal method for wastes from the secondary recovery operation.

With the demonstrated success of these case studies, it is reasonable to question why there aren't many more such operations. One of the primary historical impediments to secondary recovery—the absence of reliable, effective fine coal cleaning processes—has been eliminated, due in large part to Department of Energy efforts, and should spur increased activity in fine coal recovery. The most imposing impediment remaining today is economics: many coal companies are convinced that the low price of coal can not justify the additional costs incurred in implementing a secondary coal recovery operation. Admittedly, not every slurry pond in the eastern U.S. is amenable to re-mining, but the case studies cited here demonstrate that secondary coal recovery is both technically and economically feasible.

SUMMARY

Vast quantities of fine coal are impounded in slurry ponds in the eastern U.S.; several estimates indicate more than 2 billion tons. In addition, coal preparation plants continue to send 30-50 million tons of fine material to slurry ponds each year. These slurry ponds present many problems and challenges with respect to permitting, maintenance, and environmental control, but promising opportunities exist as well. Although extremely variable, the quality of material in many slurry impoundments is often such that little cleaning would be required to recover a coal stream of significant commercial value. In the near term, the most likely candidates for slurry pond reclamation projects are those slurry ponds located near operating preparation plants, where existing infrastructure could be used to facilitate fine coal recovery. Several entities have capitalized on this opportunity, demonstrating the technical and economic viability of secondary recovery operations. As the success of these ventures becomes widely known, and as pressures to minimize surface landfilling mount, more and more companies will recognize the genuine value of these resources.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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COAL FINES UTILIZATION TECHNOLOGIES
"Emerging Low Cost - Low Polluting Fuels"

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INTRODUCTION

Electric utilities are being faced with significant challenges for meeting environmental regulations for its coal fired generation units, and at the same time must stay cost competitive in an industry that appears to be heading for deregulation. In tomorrow's power generation arena, to be competitive, utilities must find ways to reduce the cost of electrical power generation. When a station manager starts looking at what operating cost reductions might be made to lower the cost of power, it is quickly seen that the most significant impact occurs with a reduction in the cost of purchased fuel, which is typically 60 to 70% of the cost of power generation.

Decisions concerning the fuel to be purchased, centers primarily on delivered cost and the ability of that fuel to meet sulfur dioxide emission limits. Systems required to meet nitrogen oxide and particulate emissions limits are not as onerous on a utility; therefore, these potential pollutants usually do not impact the fuel selection process. Each power station; however, will have its own specific set of parameters for the selection of fuels and the following considerations will generally impact such selections:

- Fuel Switching Switch from the use of non-compliance high sulfur local coals to more distant sulfur compliance coals. Selecting this option obviates the need for installing an SO_2 scrubber.
- Flue Gas Desulfurization/Fluid Bed Boilers Use non-compliance high sulfur local coals and install stack gas scrubbers to meet the SO_2 emission limits, or retire old smaller units and replace them with a larger new fluid bed boiler.
- Sulfur Credits If a station is incrementally over its regulated sulfur dioxide emission limit, the option of purchasing sulfur credits to put it into compliance, may a low cost choice.

- Low Cost Fuels Power generation units that have stack gas scrubbers or stations with fluid bed boilers have the option of using potentially lower cost fuels such as slack coal, coal pond fines, petroleum coke, Orimulsion™, etc. These low cost fuels may be fired separately, but in most cases will probably be co-fired with a conventional fuel to effect an incremental cost reduction in purchased fuel.

With the pressures imposed on the electric utility industry, high on a utility's wish list would be to have an assured long term supply of low cost, low polluting fuels. The authors are working together on several projects to commercially develop low cost, low polluting fuels to meet this need. These technologies, when implemented, will provide such fuels using local fuel resources that are in close proximity to power plants. The technologies being developed will not solve the fuel problems for all power plants, but will be an answer or partial answer for specific plants. These technologies can be applied, under favorable situations to provide the low cost, lower polluting fuels the electric utilities are looking for.

The fuel technologies being offered are:

- Coal-Fiber Pellets A fuel that can be supplied at a cost less than the cost of an equivalent quality fuel for reducing SO_2, NO_x, and CO_2 emissions.

- Advanced Coal Water Slurry (ACWS) A low cost fuel, using coal pond fines to produce a 50/50 weight ratio coal/water slurry fuel, that can be fired in such a way to reduce NO_x emissions.

- Coal Filter Cake A low cost coal filter cake, from coal ponds or preparation plants can be made which effects easier handling, via addition of inexpensive chemicals.

- Microbial Sulfur Reduction A novel microbiological system that removes pyritic and organically bound sulfur from coal. This technique can be used with advanced physical cleaning to provide sulfur compliance coals. It can also be applied to produce a sulfur compliance coal-fiber pellet, coal water slurry or coal filter cake.

- Coal Water Slurry Co-Firing A novel technique of co-firing coal water slurry through low NO_x burners for further reduction of nitrogen oxides emissions. This is a low cost technique for providing a compliance comfort margin for low NO_x burners. If nearby low cost coal pond fines can be used to make the slurry, there could be a payback on the capital for the CWS co-firing system.

- Coal Water Slurry Reburning A novel technique of using coal water slurry as a reburn fuel to achieve NO_x reduction. This is another low cost technique for meeting NO_x compliance regulations. If nearby low cost coal pond fines can be used to make the coal water slurry, although more expensive than CWS co-firing, there could also be a small payback on the capital for the CWS reburning system.

COAL-FIBER PELLETS

This engineered fuel being developed by Alternate Fuels Incorporated (AFI) consists of coal that is blended with waste fiber material that contains little fuel bound sulfur and nitrogen. The coal and fiber, at a weight ratio of approximately 50/50, are blended and then extruded into coal fiber pellets that can be easily handled and co-fired in pulverized coal and stoker coal fired boilers, see Figure 1.

The fuel pellets, when fired, can yield lower emissions of sulfur dioxide, nitrogen oxides, carbon dioxide, and possibly particulate (including trace metals) than the parent coal used to make the pellet. The feedstock can be a waste, such as that found in coal preparation plant ponds, or it can be a freshly mined coal, petroleum coke, or combinations thereof. The fiber feedstock will normally be a waste product from domestic, commercial and/or industrial sources. A 3 TPH coal fiber pellet plant is now in startup near Canton, Ohio and combustion tests have been scheduled for several electric utility and industrial heating applications.

A comparison of a 50/50 weight ratio coal/fiber fuel, made with an Ohio High Volatile B Bituminous parent coal and a paper based fiber, is shown in Table 1.

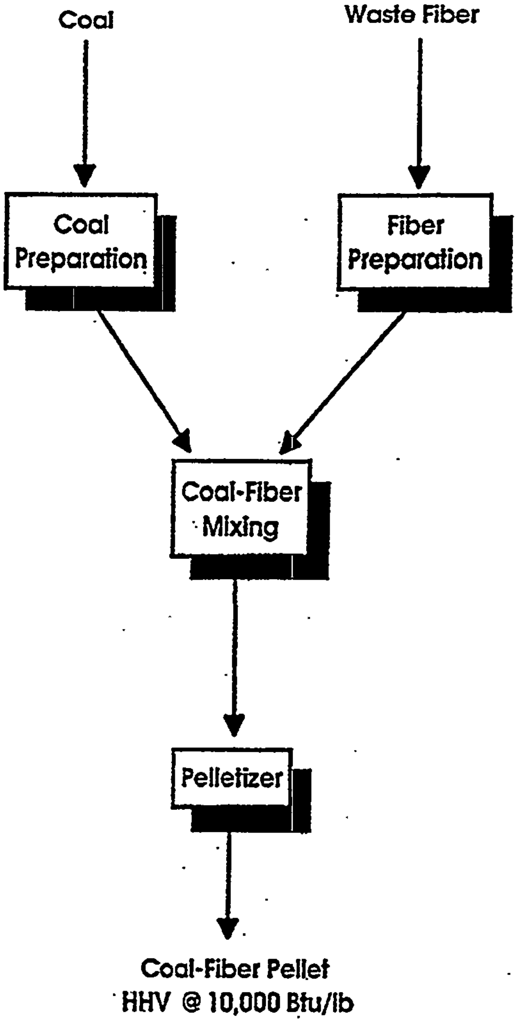
Table 1. Coal-Fiber Pellets

Ultimate Analysis:	Coal	Paper Fiber	50/50 Coal-Fiber
Carbon	66.21	41.68	53.95
Hydrogen	4.94	5.87	5.40
Oxygen	11.15	35.76	23.46
Nitrogen	1.23	0.29	0.76
Sulfur	1.93	0.20	1.06
Chlorine	0.00	0.00	0.00
Moisture	3.80	10.20	7.00
Ash	10.74	6.00	8.37
Total	100.00	100.00	100.00
HHV, Btu/lb	12,254	7,572	9,913
SO2, lb/MM Btu	3.15	0.53	2.13
Ash, lb/MM Btu	8.76	7.92	8.44

As can be seen in Table 1, a coal-fiber pellet fuel will emit lower sulfur dioxide emissions than the parent coal. It will also have less fuel bound nitrogen, and since a portion of the fuel bound nitrogen goes to the production of NO_x, a coal-fiber pellet should also yield lower nitrogen oxide

Figure 1

Coal Fiber Product



emissions compared to the parent coal. The ash content of the coal-fiber pellet could be greater or less than the parent coal depending on the parent coal ash content.

ADVANCED COAL WATER SLURRY (ACWS)

The principal barrier to the use of cleaned fine coal, historically has been the handling of the coal fines after processing. Such coal fines are usually filtered or dried and then are blended with the main coal stream for transport to the end user. When the fines arrive at the user's site, they can create both operational and environmental problems. Wet coal fines reduce coal pulverizer capacity and dry fines on a coal pile can create a dust problem. The ACWS technology eliminates the fine coal handling problem at the user's site. The ACWS is pumped like a heavy fuel oil, and is fired as a 50/50 liquid blend of coal and water.

The novelty of the advanced coal water slurry technology is its low production cost. Coal fines, from impounded ponds or from a preparation plant fine coal circuit, are used as the ACWS feedstock. Management and Technical Systems (MATS) has developed this advanced coal water slurry fuel.

In Figure 2, a production flow schematic is shown for an advanced coal water slurry system to convert coal pond fines into an upgraded coal water slurry. Coal will be dredged from the pond and pumped through hydroclones for the separation of a plus 200 mesh size and a minus 200 mesh size. The plus 200 mesh size will be sent to a spiral cleaner for the removal of pyritic sulfur and will then be centrifuged and blended with the processed minus 200 mesh fraction to produce an advanced coal water slurry fuel. The minus 200 mesh fraction will be processed through a froth flotation column for pyrite and ash removal. Optionally, the fines product from the froth column could be fed to a chemical or microbial sulfur reduction process for further removal of sulfur.

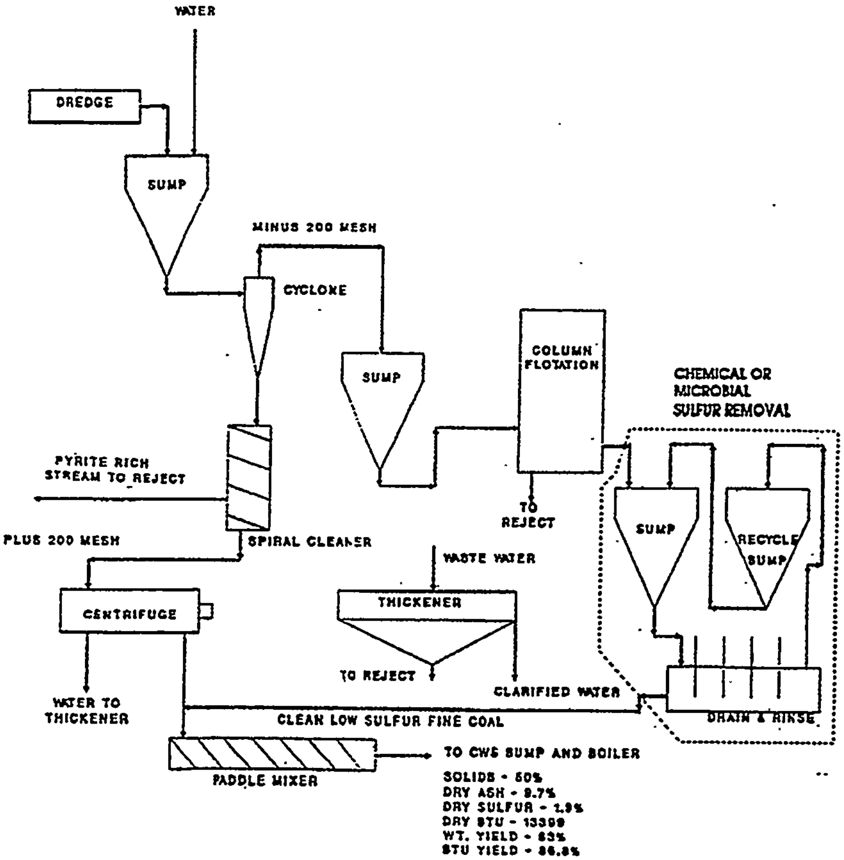
COAL FILTER CAKE

This process includes the use of proprietary additives to condition a coal filter cake so that it can be easily handled; having good flow characteristics but still containing a high moisture content. It can be burned without further drying. MATS is working on the development of this filter cake fuel.

MICROBIAL SULFUR REDUCTION

A novel microbiological system that removes pyritic and organically bound sulfur from coal is being developed by the Consolidated Sulfur Reduction Corporation (CSRC). The technology was first applied to remove sulfur from petroleum. Following that success, the technology is now being applied to coal. This technology can be used with advanced physical cleaning to provide sulfur compliance coals. It can be applied to produce a sulfur compliance coal-fiber pellet, coal water slurry or coal filter cake. The technology that is being developed is similar to that used by mother nature to produce low sulfur coals. The differences in the sulfur content of coals scattered throughout the world are believed to be condition specific. The mechanism that produced low sulfur coal at one location and not at another is believed to be due to the action

Figure 2
Advanced Coal Water Slurry Preparation Plant



or inaction of bacteria. Bacteria attacks sulfur and releases post-digestion hydrogen sulfide gas. Where seams of coal were vented, the process continued and the sulfur level in the coal was reduced. If the coal seam was not vented, the bacteria action slowed, then stopped.

In the microbial sulfur reduction process, the developers are duplicating the technique used in nature. Not having a million years to work with, to have an effective microbial reduction process it must designed to take place in a matter of hours, or at the most in a few days. In the Consolidated Sulfur microbial process the coal size, the temperature of the process, the degree of agitation, and specific etiology of the bacteria mutations are controlled. In addition, the reaction off-gases from the processing of the coal are continuously removed. In this process, pyritic, organic and sulfate sulfur are removed from the coal. By-products from this process, which may be sold on the open market, include elemental sulfur and sulfuric acid.

The process has been applied to Western Kentucky, Illinois, and Ohio Coals. Pyritic sulfur reduction has been performed on particles up to 1/2 inch in size with removals of up to 80 wt%. Organic sulfur reduction has been accomplished on minus 18 mesh particles and removals of 8% to 29% have been achieved. Table 2 shows the organic and pyritic sulfur reduction for the several coals that have been tested. The process will also reduce sulfate sulfur; in the coals tested, sulfate sulfur was reduced from 0.35 wt% down to less than 0.10 wt%.

Table 2. Microbial Sulfur Reduction

Sulfur Reduction:	Organic Sulfur, wt%	Pyritic Sulfur, wt%	Total Sulfur, wt%
Sample 1	24.4	66.0	44.6
Sample 2	28.6	76.3	47.7
Sample 3	8.1	81.4	44.8
Sample 4	23.3	77.5	49.3

Because the microbial sulfur reduction process actually alters the coal structure by attacking the organic sulfur, this technology would qualify for a tax credit under Section §29 of the U.S. Internal Revenue Code. The value of this tax credit in 1993 was $0.95/MM Btu. Under the current code, the microbial process facility would have to be placed in service before January 1, 1997, pursuant to a binding written contract in effect before January 1, 1996.

Assuming that the Ohio High Volatile B Bituminous Coal shown in Table 1 was used as a feedstock, in Table 3, one can see the synergy of combining conventional coal cleaning techniques with the microbial process to produce a low sulfur coal from a high sulfur coal feedstock and/or produce a sulfur compliance coal-fiber pellet.

Table 3. Technology Synergies to Yield Lower Sulfur Fuels

Coal:	Ash	Pyritic S	Organic S	Total S	HHV Btu/lb	lb SO2/ MM Btu
Raw	19.7	2.64	0.97	3.73	10,851	6.87
Physically Clean*	11.2	0.66	1.01	1.76	12,254	2.87
Bacterially Cleaned**	8.9	0.13	0.76	0.90	12,570	1.43
Coal-Fiber Pellets	7.45	0.065	0.38	0.45	10,071	0.89

* 96% Btu yield
** 93% Btu yield

COAL WATER SLURRY (CWS) CO-FIRING

Coal water slurry has been co-fired through low NO_x burners with good success on Penelec's Seward Unit #14, a 34 MW_e wall-fired unit. Currently, long term co-firing tests are being run. This testing is being completed by Penelec with assistance from the Energy and Environmental Research Corporation (EER) and MATS. Six new FlamemastEER^{TM} low NO_x burners were provided with three of these burners incorporating the dual fluid VEERjet^{TM} nozzles for CWS co-firing. The slurry nozzle design has resulted in a nozzle that has very low erosive wear, doesn't plug, and has superior atomization characteristics compared to commercially available dual fluid nozzles, see Figure 3. This slurry nozzle was designed and tested by EER on a 4 MM Btu/hr fire tube boiler, under a U.S. DOE project at the University of Alabama, prior to scale up to the Seward application. When co-firing up to 40% of the heat input via CWS through pulverized coal (PC) fired low NO_x burners, no significant operational problems have been experienced with the slurry nozzles. T

he characteristics of the slurry nozzle, plus co-firing orientation, were set to reduce NO_x emissions, and such reduction occurred. Overall NO_x emissions were reduced 15 to 20% over baseline low NO_x burner operation although slurry was being co-fired on only three of six low NO_x burners, see Figure 4. EER is currently applying for a patent for the novel introduction of coal water slurry to effect NO_x reduction. When co-firing CWS, it was found that nitrogen oxide emissions did not increase as rapidly with increased excess air as that for 100% PC firing. It was also found NO_x emissions decreased with increased heat input from CWS co-firing. These observations indicate that when co-firing CWS, there will be more flexibility in boiler operation for meeting NO_x emission compliance limits.

It was confirmed that the NO_x reduction experienced with CWS co-firing was a burner phenomenon and not simply the result of a cooler furnace caused by water evaporation. This was

Figure 3
Atomization Comparison

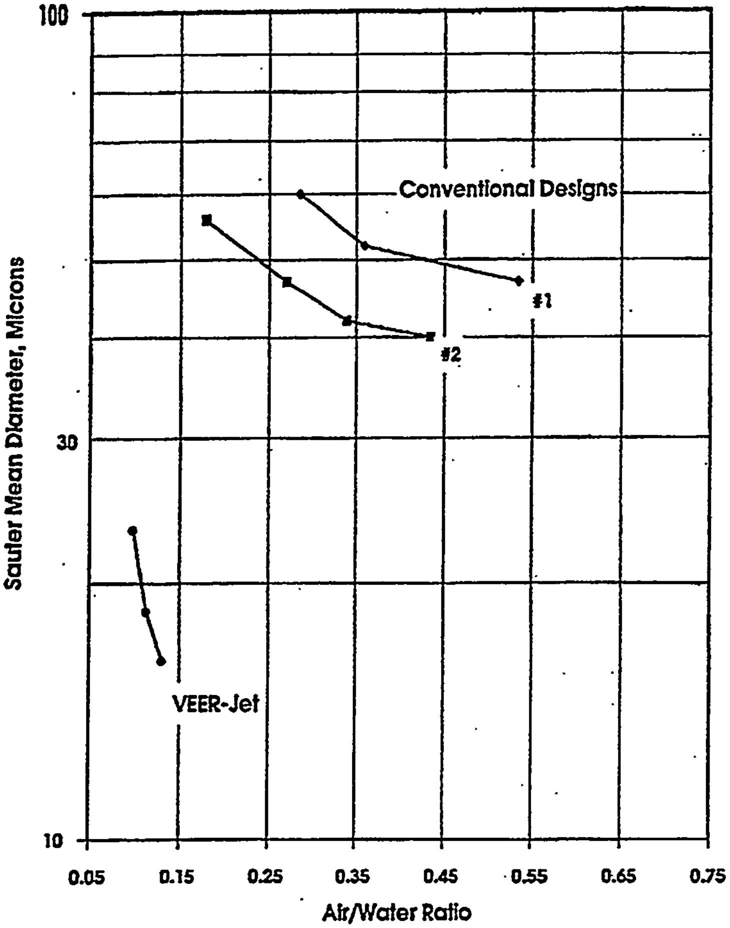
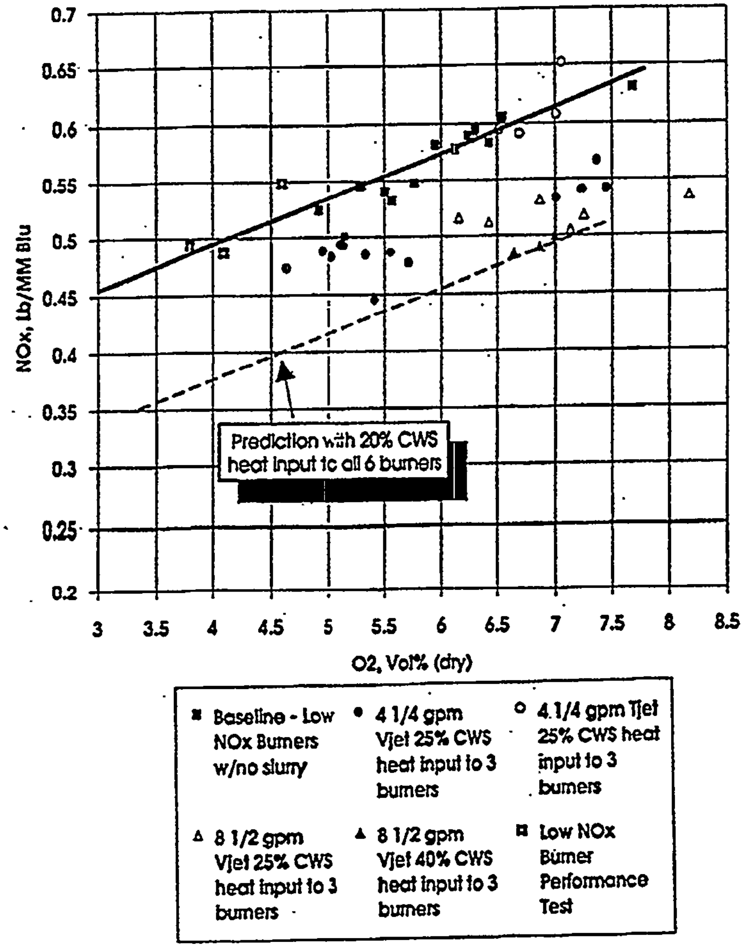


Figure 4
Penelec Seward Unit #14
NOx vs. O2 (Baseline & w/Slurry)



Prediction with 20% CWS heat input to all 6 burners proved by removing the VEERjet™ nozzles and replacing them with T-jet nozzles. As was expected, with the T-jet nozzle testing nitrogen oxide emissions were not reduced.

In March of 1995, it is expected that all six low NO_x burners on Penelec's Seward Unit #14 will be equipped with CWS co-firing capability. With all six low NO_x burners co-firing 20% of the heat input as CWS through the VEERjet™ nozzles, it is projected that NO_x reduction will be some 30 to 35% lower than that achieved with 100% PC firing alone.

This technology can be inexpensively added to first generation low NO_x burners that have marginal compliance performance to provide a healthy comfort margin on NO_x emissions. For example, if a utility's installed low NO_x burners are yielding a NO_x emission rate of 0.55 lb/MM Btu, which is higher than the 0.50 lb/MM Btu future limit for wall-fired units; with CWS co-firing, NO_x emissions could be reduced to 0.4 lb/MM Btu or less. The use of CWS as a co-fired fuel also assists those plants that are pulverizer limited and under wet weather conditions have to operate at a lower load than that desired.

COAL WATER SLURRY REBURNING

A novel technique of using coal water slurry as a reburn fuel to achieve NO_x reduction. Because of limited options for cyclone boiler operators in regard to reducing NO_x emissions, this technology may provide the low cost solution for reducing such emissions on cyclone units. This would be especially true for those units that have nearby coal preparation plants. When using CWS as a reburn fuel in a cyclone fired boiler, over 60% reduction of nitrogen oxides can be achieved, see Figure 5. EER conceived the CWS reburn approach some two years ago and patent filing is in progress.

This is another low cost technique for meeting NO_x compliance regulations. If nearby low cost coal pond fines can be used to make the slurry, there can be a payback on the capital required for the CWS reburning system, and the cost per ton NO_x removed would not be a cost, but instead could yield a slight savings. Although this may sound too good to be true, in the several studies completed it appears to be very real; it now needs only to be implemented.

The CWS reburn system has an advantage over pulverized coal or natural gas reburn systems in that a flue gas recycle (FGR) system is not required for furnace penetration. The momentum of the dual fluid slurry spray will be sufficient for penetration across the furnace. Further, because the mass flow rate is less, the reburn temperature is higher and rates of partial oxidation greater than that for coal reburn systems. Rates of reaction are very important in the reburn zone, for the level of NO_x reduction achieved is dependent on residence time.

Testing has been completed on coal water slurry reburning on a 1 MM Btu/hr Boiler Simulator Facility (BSF), and plans are underway to scale up testing to a 10 MM Btu/hr unit. These two test units were used by EER to successfully scale up natural gas reburning to a 40 MW_e cyclone unit, an 80 MW_e tangentially fired unit and a 172 MW_e wall-fired unit. The recently completed CWS reburn testing on the BSF was completed under co-sponsorship of the Electric Power Research Institutes' Upgraded Coal Interest Group.

Figure 5

NOx Reduction via CWS Reburn