ARC DESULFURIZATION OF COAL

S. Korman, T. J. Dougherty and C. Sheer
Chemical Engineering Research Laboratory, Columbia
University, New York, NY, U. S. A. 10027

Keywords: Gasification, Desulfurization

ABSTRACT

FCC arc treatment of coal causes decomposition and substantial vaporization of the associated complex iron aluminum silicates. These metals effectively fix the sulfur as sulfides or sulfates, when the transport gas is steam or air respectively. Fly ash, limestone, or lime FCC air arc products are very efficient SO_2 absorbers.

INTRODUCTION

A stringent environmental requirement for the utilization of coal, whether in conversion to gas or in the direct combustion for electric power generation, is the production of effluents free from gaseous sulfur compounds; e.g. H_2S or SO_2. Coal is invariably associated with sulfur, partly as inorganic mineral such as iron pyrite FeS_2 or in combination with carbonaceous organic portion. Both sources contribute significantly to the presence of gaseous sulfur compounds in gasification technology or in combustion.

In gasification, not only must the end product be sulfur-free for environmental reasons, but also the poisoning of methanation catalysts must be avoided. In combustion, the SO_2 formed is required to be removed before the combustion gases are released to the atmosphere.

RATIONALE OF ARC DESULFURIZATION

In the gasification process reported by us in a collateral paper of this Round Table (1) we described the method of treating the coal by feeding it into the fluid convection cathode (FCC) arc. This produces a gas free of sulfur directly from the arc. This gas is then combined with additional sulfur-free gas which is the product of steam treatment of the coal fume arc effluent solid.

The final residual solid consists mainly of inorganic mineral products. These include sulfides, -- a result not obtainable without the specific arc treatment; the treatment of coal to produce gaseous product by a conventional high intensity arc does not accomplish the fixation of sulfur in the residual solids (2). The form in which the sulfur has been fixed is believed to be metal sulfides; e.g., this is shown by adding hydrochloric acid to the residual solid and noting the evolution the H_2S.

Since this result is not achieved without the specific arc treatment, it is apparent that the mineral content of the coal provides metal cations capable of forming stable sulfides in quantity sufficient to fix virtually all the sulfur in the arc feed. Such metals are originally present in complex non-reactive form as complex silicates, such as kaolin, shale, etc. It is therefore evident that the effective introduction of coal into the region of the arc conduction column exposes the coal minerals to a temperature sufficient to decompose the complex silicates very rapidly. Upon leaving the arc, the liberated metals on cooling can combine readily with sulfur, forming stable sulfides.

In the combustion process, where coal is fed into the FCC arc column, using air to transport the coal, the effluent solids demonstrably contain metal sulfates.

Although direct arc combustion of coal is effective for producing a sulfur-free gas effluent, it may be economically difficult to justify this use of expensive electric power. However, by limiting the use of the arc to the production of a highly efficient absorbent for SO_2, we have found that the power consumption with feeds such, for example, as fly ash, limestone, or lime, is small (<3 kwh per lb.). The arc product in each case is fine particulate, high surface area, dispersible powder. In this form the stoichiometric requirement per unit of sulfur absorbed, as well as the absorption contact time, is minimal.

TEST CONDITIONS

Arc Gasification Process. Detailed description of the steam-coal arc used in these tests is given in our associated paper in this Round Table (1). Coal analysis is given in Table 1. Typical gas composition is shown in Table 2.

Arc Coal Combustion. Three series of tests were run, as follows:

A. 150 KW Open Arc; coal + steam feed.
B. 150 KW Open Arc; coal + air feed.
C. 50 KW Enclosed Arc; coal + air.

Typical gas composition in each case are shown in Tables 3, 4, and 5 respectively. Although the coal-steam open arc was run for other reasons (related by familiarization of steam arc operational characteristics on the 150 - 200 KW scale), gas samples taken from the effluent flame just beyond the arc were analyzed for composition as shown in Table 3. The low sulfur content found led to arc combustion tests, using air as transport gas in place of steam. Typical results are shown in Table 4.

In order to establish the fate of the sulfur in the coal feed, the next series of tests were run in an enclosed system, using a coal-air arc at 50 KW level, with provision for downstream solids collection. Gas composition is shown in Table 5. Samples of solid effluent were taken from the effluent duct and cyclone, from a bag fabric filter beyond the cyclone and then from a two-stage electrostatic precipitator. The latter was introduced after it had been noticed that the downstream gas sample contained a pale yellow smoke exhibiting a Tyndall effect and which had escaped collection in the cyclone and bag filter.

Typical effluent solids analysis is shown in Table 6.

The two precipitator products were taken from the collecting plates and housing hopper respectively. Comparing these with the ash composition in the coal feed, as shown in Table 7, suggests selective enrichment of the metal cations as against silica, with the probability that they are present as sulfates. The observations leading to the method of their collection further implies that they were present in the arc effluent as a colloidal smoke. The origin of these metals and their reactivity implies that the silicates in the coal were dissociated to metal oxides by the arc, and condensed from vapor in the arc effluent.

SULFUR ABSORBENT ARC PRODUCTS

As a result of the arc tests with coal, and especially the finding that coal mineral arc effluent solids contain metal sulfates derived by dissociation of silicates in the coal, suggested that arc treatment of coal minerals could produce efficient and relatively inexpensive sulfur absorbents. This idea was pursued in three separate series of tests, involving fly ash, limestone, and lime feeds respectively.

Fly Ash. Using a fly ash product of coal combustion in a commercial steam boiler of power generating station, this material was fed to the 150 KW open arc using air as transport gas. The composition of the fly ash is given in Table 8. Immediately downstream of the arc, SO_2 was fed into the arc effluent at a controlled rate to produce approximately 1600 ppm of SO_2 when no fly ash was added. The effluent was sampled at a point where the temperature of the gas was below 550° F (288° C) and tested for SO_2 content. The SO_2 concentration was continuously monitored by using an MSA LIRA Model 202 infra-red meter to which the sample stream was sent after passing through a filter and drier, ahead of the meter. A schematic diagram of the arrangement is shown in Figure 1. A typical result is shown graphically in Figure 2.

The results indicate that a set of conditions existed which could produce a chemical reaction removing sulfur dioxide from an air mixture containing that gas the arc effluent of a complex silicate coal mineral feed which itself is not reactive.

Limestone. A sample of limestone was obtained which was in use in a fluidized bed combustion unit to absorb SO_2 at 1500° F (815° C). At ¼-inch particle size, in the fluidized combustion application, the CaO/S ratio required for effective desulfurization was reported to be = 3 (3). Under equivalent temperature and contact time (3 seconds), the arc product showed an absorption stoichiometric ratio CaO/S approaching unity, in the temperature range 1500° - 1100° F (815° - 590° C).

Lime. Substituting lime for limestone as an arc feed also resulted in a similar CaO/S ratio; however, this was obtained uniquely at 350° F (177° C), a temperature characteristic of steam boiler effluent flue gas.

Surface area measurements for these arc products are shown in Table 9.

SUMMARY

1. The FCC arc provides an efficient means of desulfurizing the gases produced when coal is fed to the arc with steam or with air as transport gases.
2. In a reducing environment, where the principal gas components are hydrogen and carbon monoxide, the H_2S is less than the detectable limit (4 ppm). The sulfur compounds COS and CS_2 appear in relatively low amount.
3. In an oxidizing environment, such as produced by feeding coal and air to the arc, SO_2 is less than the detectable limit (4 ppm), while COS and CS_2 are present in low parts per million. The solids produced are shown to contain a significant quantity of stable metal sulfates, principally in submicron size.
4. The metal cations, especially aluminum and iron, liberated by arc dissociated coal mineral silicates, form effective sulfur absorbents. Arc treatment of the coal minerals, or of limestone or lime, produce reactive submicron sulfur absorbents. These are more efficient than their coarser feed counterparts at temperatures of interest in coal-fired steam boilers.

ACKNOWLEDGEMENTS

The authors are endebted to the Consolidated Natural Gas Company and to its Vice-President for Research, Dr. Robert C. Weast, for their encouragement and support in this investigation.

REFERENCES

(1). C. Sheer, S. Korman and T. J. Dougherty, "Arc Gasification of Coal", IUPAC 4th International Symposium on Plasma Chemistry, Round Table on Thermal Plasma Processing (1979).

(2). R. E. Gannon and V. Krukonis, "Arc Coal Process Development", Final Report September 1972, Office of Coal Research, Washington, D. C., Contract DI-14-01-0001-493, NTS PB-235 300/1.

(3). Foster Wheeler Corporation - Private Communication.

Table 1. Coal Feed Composition - Sewickley Coal

Proximate		Ultimate		Mineral	
Moisture	1.33%	C	70.77%	P_2O_5	.28% dry
----------------------		H	4.83	SiO_2	58.21
VCM	34.17dry basis	O	6.72	Fe_2O_3	10.69
Ash	15.51	N	1.48	Al_2O_3	24.93
Fixed Carbon	50.32	S	1.82	TiO_2	.50
Sulfur	1.82			Na_2O	.51
BTU/lb.	12792			K_2O	1.90
				CaO	1.15
				MgO	.82
				SO_3	.99

Table 2. 50 KW Enclosed Coal-Steam Arc: Gas Composition

CO	32.1 vol. %
CO_2	4.1
A	3.4
H_2	59.6
CH_4	.054
C_2H_2*	.052
$(CN)_2$	ND**
COS	.020
CS_2	.0017
C_6H_6	.0010
Toluene	.0020
H_2S	ND
SO_2	ND
Thiophene	ND

* Includes also C_2H_4 and C_2H_6.

** Not detected (less than 4 ppm).

Table 3. Typical Gas Composition; Coal-Steam 150 KW Open Arc
(750 amps., 200 volts, Coal 3 lb./min., Steam 4 lb./min.)

CO	26.1 vol. %
CO_2	4.46
H_2	26.59
CH_4	1.22
C_2H_2	.99
$(CN)_2$	.0016
COS	.016
CS_2	.014
C_6H_6	.027
Argon	3.29
H_2S	ND*
SO_2	ND
HCN (and/or C_2H_4)	.32
CS	ND

* ND - Less than 4 ppm.

Table 4. 150 KW Coal-Air Arc Gas Effluent
(750 amps., 200 volts, 22.63 cfm air, 477 gms./min. coal)

Nitrogen	78+ vol. %
Oxygen	2.8
Argon	2.3
CO_2	16.3
Hydrogen	0.056
CO	ND*
CS_2	0.0017
COS	ND
SO_2	ND

* ND - Less than 4 ppm.

Table 5. 50 KW Enclosed Coal-Air Gas Effluent
(450 amps., 110 volts, Coal 11.8 gms./min., Air .75 cfm)

Nitrogen	74+ vol. %
Oxygen	9.3
Argon	7.3
CO_2	7.4
Hydrogen	0.58
CO	.80
COS	.0017
CS_2	.0007
Mass 78 (C_6H_6?)	.0034
SO_2	ND

Table 6. 50 KW Enclosed Coal-Air Solids Effluent

	% Sulfur	% Ash
Cyclone + Duct	1.38	69.12
Bag Filter	2.09	82.90
Precipitator A	5.55	41.17
Precipitator B	6.90	48.52
Coal Feed	1.82	15.51

Table 7. 50 KW Enclosed Coal-Air Arc P'P'tor Products

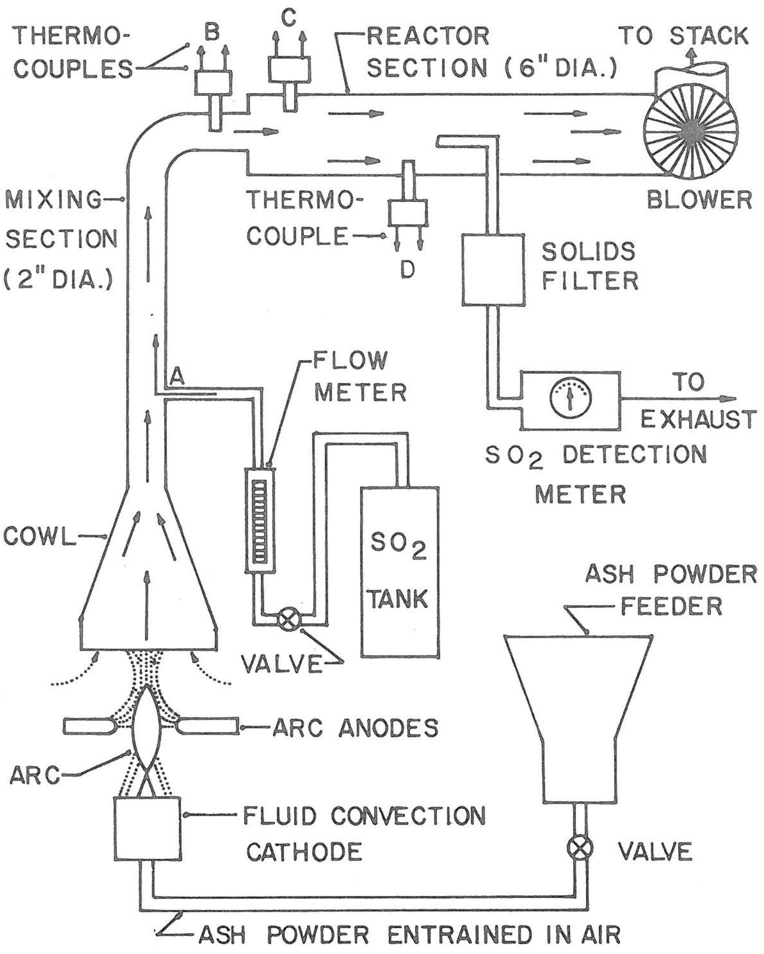
	Product A	Product B	Coal Feed Ash
Ash	41.17%	48.52%	15.51%
Total Sulfur	5.55	6.90	1.82
Al	2.56	20.88	13.20
Fe	0.54	4.53	7.48
SiO_2	0.12	0.09	58.21
SO_4 - Sulfate	16.92	19.55	1.19
Ca	0.95	0.08	0.82
Mg	0.11	0.13	0.49
Na_2O	0.18	0.05	0.51
K_2O	0.10	0.06	1.90
SO_3 - Sulfite	0.08	0.07	----

Table 8. Fly Ash Arc Feed Composition (Elrama Power Station)

SiO_2	42.56%
Fe_2O_3	17.24
Al_2O_3	22.72
CaO	0.98
MgO	0.63
Na_2O	0.27
K_2O	1.48
Sulfur	0.32
Loss on Ignition	13.80

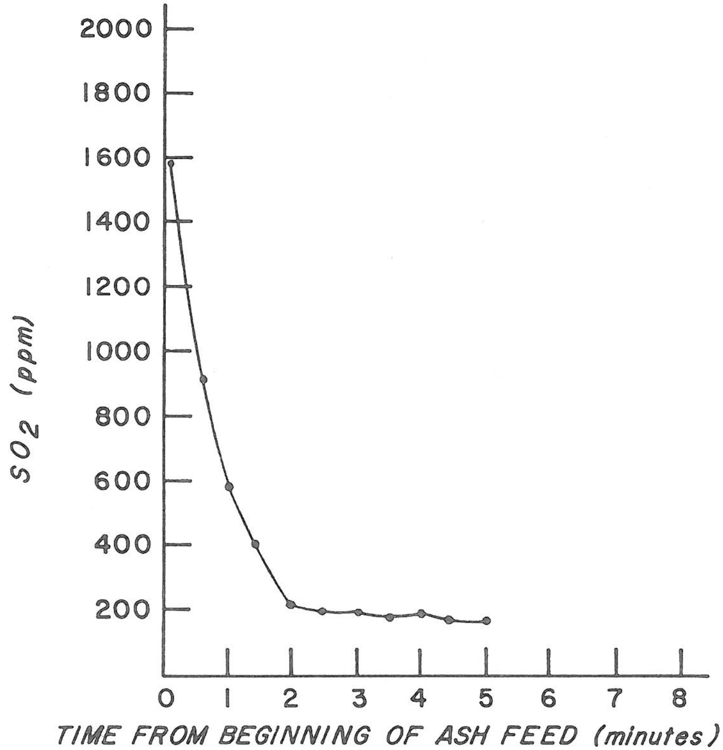
Table 9. Surface Area of Arc Products (Arc Feed = minus 100 mesh)

Fly Ash	91.3 m^2/gm.
Limestone	54.4
Lime	78.1



SET-UP FOR TESTING ARC DESULFURIZATION

FIG. 1



SO_2 ABSORPTION IN ARC EFFLUENT

(ASH FEED: 35.2 GRAMS/MINUTE)

FIG. 2