

STATE OF ILLINOIS

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O. W. Rees  
N. F. Shimp  
C. W. Beeler  
J. K. Kuhn  
R. J. Helfinstine

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John C. Frye, *Chief*

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### ABSTRACT

Retention of sulfur in bituminous coalashes prepared in the laboratory was shown to be related to ashing temperature and to amounts of sulfur and calcium present in the coal. Evidence also was obtained in support of the theory that catalytic oxidation of sulfur dioxide to sulfur trioxide influences retention of sulfur as calcium sulfate in coal ash. Iron oxide produced during coal combustion acts as a catalyst for this reaction.

Factors affecting sulfur retention in coal ash prepared in the laboratory at 800° C were not applicable to most industrial combustions because of the relatively higher temperatures (usually > 1000° C) involved in commercial applications. As these temperatures are above the thermal decomposition temperature of calcium sulfate, it does not form and hence cannot serve as a sulfur retaining agent. The small amount of sulfur found in power plant coal ashes was related to carbon remaining in the ash after combustion and was of no practical significance in reducing sulfur emission to the atmosphere.

### INTRODUCTION

From the viewpoint of the coal chemist, any retention of sulfur in coal ash is undesirable. The fact that not all of the sulfur is retained, but rather that the percentage retained is indefinite, is especially troublesome in determining the amount of ash and in preparing ash for complete analysis. This problem has concerned coal analysts for many years and is generally more pronounced in coals that contain the greater amounts of pyrite and calcite. Various approaches have been suggested for minimizing the difficulty. Parr (1916) treated laboratory ash with sulfuric acid to convert all calcium to calcium sulfate; excess acid was fumed off

and the sulfated ash ignited. Rees (1937) found that this procedure gave high values unless the sulfated ash was corrected for its sulfur trioxide content. Rees and Selvig (1942) demonstrated that a slow rate of heating during ashing lessened retention of sulfur in ash. For coal ash analysis, it has been proposed that sulfur trioxide be determined and all other items be calculated to the sulfur trioxide free basis.

There is ample evidence supporting the relation between the amount of sulfur retained in coal ash and the calcium oxide content of the ash; however, this relation is not quantitative. Because of this, consideration was given to other factors that might play a part in controlling sulfur retention. Nelson and Lisle (1964) have shown that catalytic production of sulfur trioxide is responsible for formation of corrosive complex alkali sulfates on tubes of coal-fired boilers. Consequently, a study was made to provide further information regarding a possible catalytic mechanism by which sulfur is retained in coal ash during laboratory ashing in the temperature range 750-850° C.

More recently, the possibility of government regulation of the permissible sulfur content of coal and other fuels, in connection with the control of atmospheric pollution, has emphasized the need for information on the fate of sulfur during combustion. Where atmospheric pollution is of primary concern, any retention of sulfur in coal ash could be beneficial because of the reduction in sulfur oxides liberated to the atmosphere. Some information regarding this serious problem is included in this report.

#### METHODS OF ANALYSIS

Coal ash was determined using ASTM Standard D 271-64 (1965), and coal sulfur determinations were made by the Eschka fusion method described in the same standard. Coal ash and synthetic ash mixtures were fused with sodium carbonate, and the sulfur in them was determined gravimetrically as barium sulfate; ASTM Standard D 1757-62 (1965). Calcium in coal ash was determined gravimetrically as the oxalate after fusion of the ash with sodium carbonate. Coal power plant ashes were analyzed for carbon utilizing a closed system high temperature (1250° C) combustion furnace with an oxygen atmosphere; British Standard 1016 (1958). After purification, the carbon dioxide emitted during combustion was absorbed and weighed.

#### RESULTS AND DISCUSSION

Data for part of this work were obtained for two 1½ in. x 0 samples of coal, one representing the No. 5 Coal from Sangamon County and the other representing No. 6 Coal from Williamson County. Each of these was screened into five sizes, and each size was further separated into six specific gravity portions by float and sink procedure. Ash and total sulfur were determined on all samples, including the original or head samples, the sized portions, and the specific gravity portions. In addition, all were ashed and analyzed for calcium oxide and retained sulfur expressed as sulfur trioxide. Values for these two items were then calculated to the coal basis. These data permitted calculation of the percentage of coal total sulfur

retained in the ashes, and the sulfur retaining capacity of calcium oxide, assuming that all of it reacts with sulfur trioxide to form calcium sulfate.

Results for the No. 5 and No. 6 Coals are shown in tables 1 and 2, respectively. In general, trends are similar for the two series of samples. Attention is called first to column 6, which shows amounts of sulfur retained in the ashes expressed as percentages of the coal total sulfur. Percentages of sulfur retained were definitely lower for the larger sizes and lighter specific gravity portions, rarely exceeding 10 percent. Furthermore, appreciable sulfur retention is shown for the small sizes and heavy specific gravity portions. Greater sulfur retention in the ashes usually occurred where the total sulfur and calcium oxide contents were higher—note especially the higher specific gravity portions. While there is a relation between the CaO content and the percentage of coal sulfur retained in the ash, it is quite variable, as described below.

Column 7, tables 1 and 2, shows calculated values for the sulfur retention potential of the CaO present, assuming complete conversion to calcium sulfate. These values are expressed as percentages of the coal total sulfur. Comparison of columns 6 and 7 shows that in no case was this retention potential entirely utilized. This suggests that some factors other than the CaO content may influence the amount of sulfur retention in the ash.

Various factors could be involved. For example, the surface or contact area of the calcium oxide and the contact time of sulfur oxide gases with the ash could be important. Another factor that seems most pertinent is the extent to which sulfur trioxide is formed during ashing. When sulfur containing materials are burned, sulfur is converted primarily to sulfur dioxide. This is true whether sulfur is elemental or combined, as long as it is not in its highest oxidation state. Although sulfur dioxide is an acid gas that can react with calcium oxide to form calcium sulfite, this compound is not thermally stable at the temperatures involved here and would not contribute to sulfur retention in ash. On the other hand, calcium sulfate is relatively stable at these temperatures and would contribute to retention if formed during ashing. For calcium sulfate to form, the sulfur dioxide first produced must be oxidized to sulfur trioxide. Thus, the amount of sulfur trioxide formed would influence the amount of sulfur retained in ash.

Oxidation of sulfur dioxide to sulfur trioxide is rather difficult, but it can be accomplished catalytically. Iron oxide ( $\text{Fe}_2\text{O}_3$ ) is known to catalyze this reaction, although it is not the best catalyst for the purpose. It occurred to us that the iron oxide derived from pyrite during ashing might catalyze the formation of sulfur trioxide. This theory was tested as follows.

Synthetic mixtures were prepared, each containing a known amount of calcium carbonate as a source of calcium oxide. Mixtures with known amounts of pure sulfur-containing compounds, either organic (cystine) or inorganic (pyrite), with and without known amounts of iron oxide, were prepared and subjected to the ashing procedure. In addition, mixtures containing calcium carbonate and both organic and inorganic sulfur in equal amounts with and without iron oxide were ashed. The synthetic mixtures were ashed at a rapid rate to promote sulfur retention and the ashes analyzed for retained sulfur. Results of these tests are shown in table 3.

TABLE 1 -- NO. 5 COAL, SANGAMON COUNTY

Column 1	2	3	4	5	6	7
Lab. No.	Description	Coal analyses moisture free			Sulfur retained in ash - % of coal sulfur	Sulfur holding capacity CaO - % of coal sulfur <sup>a</sup>
		% Ash	% Total S	% CaO		
C-1085	head (1½" x 0)	13.8	5.3	1.16	9.5	12.5
C-1086	1½" to ¾"	12.8	5.2	0.66	4.9	7.3
C-1087	¾" to 3/8"	14.1	5.5	0.84	4.3	8.8
C-1088	3/8" to 10 mesh	13.8	5.3	1.19	9.4	12.8
C-1089	10 to 48 mesh	17.3	5.4	3.29	27.2	34.9
C-1090	minus 48 mesh	20.2	5.0	4.65	30.8	53.2
1½" to ¾"						
C-1219	1.30 float	7.0	3.5	0.23	2.0	3.8
C-1220	1.30 - 1.35	12.0	4.2	0.59	3.0	8.0
C-1221	1.35 - 1.40	16.3	5.8	0.71	5.6	7.0
C-1222	1.40 - 1.50	22.1	7.1	1.29	5.9	10.4
C-1223	1.50a- 1.70	31.0	11.6	2.46	9.6	12.1
C-1224	1.70 sink	51.2	25.0	3.73	5.9	8.5
¾" to 3/8"						
C-1225	1.30 float	6.2	3.4	0.21	1.0	3.5
C-1226	1.30 - 1.35	11.0	4.0	0.44	3.0	6.3
C-1227	1.35 - 1.40	16.0	5.7	0.77	4.3	7.7
C-1228	1.40 - 1.50	21.6	7.5	1.25	6.0	9.5
C-1229	1.50 - 1.70	31.9	10.0	3.19	10.4	18.2
C-1230	1.70 sink	54.4	25.6	5.36	9.1	12.0
3/8" to 10 mesh						
C-1198	1.30 float	6.5	3.5	0.22	2.5	3.6
C-1199	1.30 - 1.35	9.2	3.9	0.40	4.0	5.8
C-1200	1.35 - 1.40	12.8	4.6	0.56	4.6	7.0
C-1201	1.40 - 1.50	18.1	6.1	1.04	7.1	9.7
C-1202	1.50 - 1.70	29.4	8.5	3.16	13.2	21.2
C-1203	1.70 sink	60.3	15.5	10.01	21.3	36.9
10 to 48 mesh						
C-1192	1.30 float	3.5	3.2	0.11	0.4	2.0
C-1193	1.30 - 1.35	5.7	3.3	0.17	0.7	2.9
C-1194	1.35 - 1.40	10.4	3.9	0.24	2.1	3.5
C-1195	1.40 - 1.50	15.8	4.9	0.54	4.7	6.3
C-1196	1.50 - 1.70	27.5	7.1	2.16	10.2	17.4
C-1197	1.70 sink	61.7	12.7	19.37	51.7	87.2
Minus 48 mesh						
C-1508	1.30 float	2.2	3.1	0.14	2.3	2.6
C-1509	1.30 - 1.35	2.5	3.0	0.13	1.4	2.5
C-1510	1.35 - 1.40	5.2	3.1	0.32	2.9	5.9
C-1511	1.40 - 1.50	10.7	2.9	0.68	6.8	13.4
C-1512	1.50 - 1.70	18.8	3.2	1.43	18.0	25.6
C-1513	1.70 sink	58.6	11.6	20.25	33.2	99.8

<sup>a</sup> Sulfur holding capacity of CaO =  $\frac{\text{CaO as Mole \%}}{\text{Total S as Mole \%}} \times 100$

TABLE 2 - NO. 6 COAL, WILLAMSON COUNTY

Column 1	2	3	4	5	6	7
Lab. No.	Description	Coal analyses moisture free			Sulfur retained in ash - % of coal sulfur	Sulfur holding capacity CaO - % of coal sulfur <sup>a</sup>
		% Ash	% Total S	% CaO		
C-1689	head (1½" x 0)	10.4	1.9	0.48	10.3	14.5
C-1163	1½" to ¾"	9.8	1.7	0.23	3.3	7.7
C-1164	¾" to 3/8"	9.9	1.9	0.26	3.3	7.8
C-1165	3/8" to 10 mesh	10.8	2.2	0.40	6.1	10.4
C-1166	10 to 48 mesh	14.4	2.3	1.19	16.8	29.6
C-1167	minus 48	14.6	2.2	1.65	30.9	42.9
1½" to ¾"						
C-1245	1.30 float	4.4	1.3	0.11	0.0	4.9
C-1246	1.30 - 1.35	8.7	1.6	0.11	0.4	4.0
C-1247	1.35 - 1.40	14.9	1.7	0.16	2.2	5.5
C-1248	1.40 - 1.50	21.1	2.1	0.32	5.1	8.7
C-1249	1.50 - 1.70	34.3	3.5	1.88	20.0	30.7
C-1250	1.70 sink	67.5	10.3	1.63	3.9	9.1
¾" to 3/8"						
C-1257	1.30 float	3.7	1.3	0.12	0.7	5.2
C-1258	1.30 - 1.35	8.8	1.6	0.17	0.8	6.0
C-1259	1.35 - 1.40	14.5	1.7	0.28	0.9	9.4
C-1260	1.40 - 1.50	20.7	2.2	0.75	10.4	19.5
C-1261	1.50 - 1.70	35.2	3.1	2.28	35.8	42.1
C-1262	1.70 sink	67.7	10.4	1.73	4.4	9.5
3/8" to 10 mesh						
C-1502	1.30 float	4.6	1.4	0.12	1.4	4.8
C-1503	1.30 - 1.35	11.8	1.8	0.19	3.1	6.1
C-1504	1.35 - 1.40	16.5	2.0	0.32	4.6	9.1
C-1505	1.40 - 1.50	22.3	2.0	0.62	11.3	17.8
C-1506	1.50 - 1.70	35.2	2.9	2.07	20.7	40.8
C-1507	1.70 sink	67.9	12.1	3.17	8.1	15.0
10 to 48 mesh						
C-1239	1.30 float	3.5	1.1	0.14	1.9	7.3
C-1240	1.30 - 1.35	10.1	1.5	0.21	3.3	7.9
C-1241	1.35 - 1.40	14.1	1.7	0.28	4.5	9.4
C-1242	1.40 - 1.50	18.1	1.7	0.55	10.1	18.5
C-1243	1.50 - 1.70	30.3	2.1	1.97	24.6	53.6
C-1244	1.70 sink	71.1	10.5	6.93	26.4	37.8
Minus 48 mesh						
C-1427	1.30 float	1.7	0.9	0.15	6.6	9.7
C-1428	1.30 - 1.35	3.8	1.1	0.22	6.2	11.4
C-1429	1.35 - 1.40	6.4	1.1	0.25	3.3	13.1
C-1430	1.40 - 1.50	8.6	0.9	0.81	26.0	51.3
C-1431	1.50 - 1.70	10.4	0.9	0.45	8.8	27.9
C-1432	1.70 sink	62.5	9.3	8.89	35.3	54.7

<sup>a</sup> Sulfur holding capacity of CaO =  $\frac{\text{CaO as Mole \%}}{\text{Total S as Mole \%}} \times 100$

TABLE 3 - CATALYTIC EFFECT OF IRON OXIDE ON SULFUR  
RETENTION IN SYNTHETIC SAMPLES

0.9 g. CaCO <sub>3</sub> mixed with:	g. Sulfur in sample	g. Sulfur in ash	Percent sulfur retained
0.375 g. cystine	0.1	0.0067	6.7
0.375 g. cystine +0.1 g. Fe <sub>2</sub> O <sub>3</sub>	0.1	0.0364	36.4
0.1875 g. pyrite	0.1	0.0761	76.1
0.1875 g. pyrite +0.1 g. Fe <sub>2</sub> O <sub>3</sub>	0.1	0.0761	76.1
0.09375 g. pyrite +0.1875 g. cystine	0.1	0.0389	38.9
0.09375 g. pyrite +0.1875 g. cystine +0.1 g. Fe <sub>2</sub> O <sub>3</sub>	0.1	0.0659	65.9

Data for the synthetic mixtures reveal the following:

When the mixture of cystine (containing organic sulfur) with calcium carbonate was ashed, only 6.7 percent of the sulfur present was retained in the ash.

When this same mixture with added iron oxide was ashed, 36.4 percent of the sulfur was retained in the ash.

When the mixture of pyrite with calcium carbonate was ashed, 76.1 percent of the sulfur was retained in the ash. The addition of pure iron oxide to this mixture had no effect on sulfur retention in the ash.

When the mixture of pyrite and cystine with calcium carbonate was ashed, only 38.9 percent of the sulfur was retained in the ash. It is interesting to note that about half as much sulfur was retained in this case as when the mixture of pyrite and calcium carbonate was ashed, even though the original total sulfur contents of the two mixtures were the same. The source of iron oxide was pyrite in both cases. It seemed reasonable that the sulfur in the cystine might be expelled before iron oxide could be formed from the pyrite. If this were true, addition of immediately available iron oxide to the mixture should increase sulfur retention in ash. This was tried and found to be true, 65.9 percent of the sulfur being retained in the ash.

Data for the synthetic mixtures support the theory of catalytic oxidation of sulfur dioxide to sulfur trioxide as a controlling factor in the retention of sulfur in coal ash at laboratory ashing temperatures. Furthermore, it appears that iron oxide, whether formed from pyrite during ashing or added as such initially, can exert this catalytic effect. Results for the mixture of cystine, pyrite, and calcium carbonate

indicate that cystine sulfur was not retained in the ash; however, it cannot be assumed that a similar reaction occurs in coal. The organic sulfur in coal is probably a portion of less volatile structures than is the case for cystine and would not be lost as readily during ashing. This could permit formation of iron oxide from pyrite in time to catalyze formation of sulfur trioxide and its retention as calcium sulfate in coal ash.

In summary, data obtained in this laboratory study permit proposal of the following mechanism for retention of sulfur in coal ash:

1. Pyrite + oxygen  $\longrightarrow$   $\text{Fe}_2\text{O}_3$  +  $\text{SO}_2$
2. Organic sulfur + oxygen  $\longrightarrow$   $\text{SO}_2$
3.  $\text{SO}_2$  + oxygen +  $\text{Fe}_2\text{O}_3$  (as catalyst)  $\longrightarrow$   $\text{SO}_3$
4.  $\text{CaCO}_3$  + heat  $\longrightarrow$   $\text{CaO}$  +  $\text{CO}_2$
5.  $\text{CaO}$  +  $\text{SO}_3$   $\longrightarrow$   $\text{CaSO}_4$ .

Without question step three is inefficient, and this may account in part for the indefinite and relatively low percentages of coal sulfur retained in laboratory ashes.

#### RETENTION OF SULFUR IN ASH FROM LARGE SCALE COMBUSTION UNITS

The problem of atmospheric pollution and its control is of very real concern today. The effect of coal combustion on this pollution is receiving considerable study. Of particular interest are the percentage of coal sulfur retained in the furnace ash and the percentage emitted to the atmosphere as sulfur oxides. The question arose as to how sulfur retention behavior in laboratory ashes might apply to large-scale combustion.

One distinct difference between laboratory ashing of coal and large-scale combustion is temperature. Laboratory ashing is accomplished at 750 to 850° C (1382 to 1562° F), while temperatures in large combustion units normally are well above these temperatures. To determine the effect of temperature on sulfur retention in ash, both raw and cleaned samples of two coals were ashed at three temperatures, 800, 950, and 1150° C (1472, 1742, and 2102° F), and the ashes were analyzed for retained sulfur. Results of these tests are shown in table 4.

TABLE 4 - EFFECT OF ASHING TEMPERATURE ON  
SULFUR RETENTION IN COAL ASH

Ashing temp. C	% of Total sulfur retained			
	Coal		Coal	
	Raw	Clean	Raw	Clean
800	17.8	6.1	7.5	4.8
950	12.3	5.5	6.7	5.2
1150	Nil.	Nil.	Nil.	Nil.



The data show that, as temperature of ashing increases, the percentage of coal sulfur retained in the ash decreases. At 1150° C (2102° F), no sulfur was retained in the ash. This leads to the conclusion that most of the coal sulfur will be emitted to the atmosphere as oxides of sulfur due to the high temperatures used in power plant and other commercial combustion applications. The proposed mechanism for sulfur retention in laboratory ashes does not appear to be applicable in practical combustion, since at the higher temperatures calcium sulfate is thermally unstable and does not form.

The preceding discussion applies to a carbon-free inorganic ash; however, combustion in commercial units often results in an ash containing appreciable quantities of unburned carbon. To determine the effect of incomplete combustion upon the sulfur content, six ashes were obtained from a local power plant. The coals had been burned under varying load conditions in both chain-grate and spreader-type combustion units, and the resulting ashes were analyzed for carbon and sulfur. Results are given in table 5 and displayed graphically in figure 1.

TABLE 5 -- PERCENTAGES OF CARBON AND SULFUR  
IN POWER PLANT ASHES

Unit type and load	% Carbon	% Sulfur
Spreader, full load	1.45	0.17
Spreader, full load	1.83	0.19
Chain grate, full load	14.00	0.35
Chain grate, full load	14.97	0.37
Chain grate, banked	35.77	0.71
Chain grate, light load	53.47	0.97

The data show a direct relation between the amount of unburned carbon remaining in the ash and the sulfur content. Extrapolation of the line in figure 1 to zero carbon indicates that the true inorganic ash would contain about 0.15% sulfur. Coals from which the power plant ashes were derived contained 7 to 10% ash and 2 to 3% sulfur. Using these figures, 0.15% sulfur in the carbon-free ash is equivalent to less than 1% of the coal total sulfur. A similar calculation for the ash containing 53.47% carbon and 0.97% sulfur indicates retention of 5 to 10% of the total coal sulfur, of which nearly all is associated with the organic carbon. From these data, it is concluded that unburned carbon in coal ash indicates incomplete combustion and increased retention of sulfur, but the quantity is generally too small to be of practical significance for bituminous coals. Furthermore, it should be pointed out that unburned carbon in the ash required combustion of additional coal to achieve the necessary heat output. The net effect of this increased coal consumption would be increased sulfur emission.

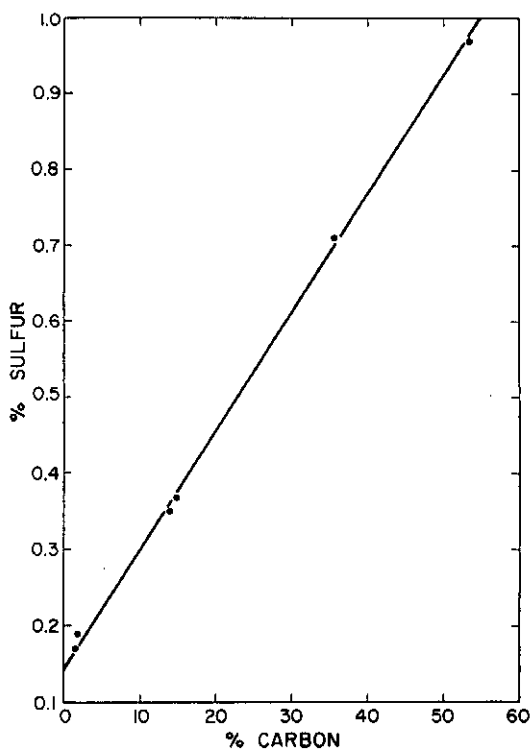


Figure 1. Relation between unburned carbon and sulfur in power plant ashes.

### CONCLUSIONS

1. In laboratory ashing, the percentage of coal sulfur retained in the ash is related to the total sulfur and calcium contents of the coal; however, this relation is not sufficiently constant to permit prediction of sulfur retention values in coal ash.

2. The data presented support the theory that the amount of sulfur trioxide formed during ashing through the catalytic action of iron oxide is an important factor in retention of sulfur in laboratory coal ashes.

3. Very little sulfur is retained in bituminous coal ash resulting from higher temperature combustion in industrial or power plant installations.

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