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ASHING INSOLUBLE OXIDATION RESIDUES TO DETERMINE PERCENTAGES OF COAL OXIDIZED BY AQUEOUS SODIUM DICHROMATE

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ABSTRACT

Illinois #6 bituminous coal, North Dakota lignite, Illinois #2 bituminous coal, a solvent-refined lignite (North Dakota) and a solvent-refined coal were oxidized with aqueous sodium dichromate. The insoluble residues were ashed and a correlation coefficient of 0.974 was obtained between the weight of ash obtained and the percent of carbon oxidized.

Sodium dichromate has been used extensively to oxidize different coals and lignite, e.g., Hayatsu *et al.* (Hayatsu, 1975, 1978, 1981) have oxidized Illinois #2 bituminous coal, North Dakota lignite and anthracite coal. Lignite coal and its solvent-refined product have been oxidized by sodium dichromate. (Duty, 1980), and from these studies a question has been raised about the percentage of coal oxidized by the authors (Duty, 1981). Consequently, we began this study to ascertain if ashing the insoluble residues from these oxidation experiments could be used with reasonable success.

In this study the following were oxidized; Illinois #6 bituminous coal, North Dakota lignite, and Illinois #2 bituminous coal. In addition, a solvent refined lignite (North Dakota) and a solvent refined coal were oxidized. All coals were dried in a vacuum desiccator over phosphorus pentoxide. The analytical data for these coals is found in Table 1.

One way to determine the extent of oxidation would be to determine the percent carbon in the insoluble oxidized residue and compare this with the percent carbon in the original coal. To avoid the analysis for the percent carbon in the insoluble residue, this study was undertaken to investigate the ashing of the insoluble residue from the dichromate oxidations to ascertain if these results could be used to predict the amount of coal oxidized. If a sufficiently high coefficient of correlation exists between the percent carbon oxidized in these reactions and the weight remaining in the ashing procedure, a yield percent should be predictable from the ashing weight. Therefore, this study set out to prove that this coefficient of correlation is sufficiently large to predict with reasonable accuracy the percentage of coal oxidized from the weight of the ash of the insoluble residue. Two coefficients of correlation were determined between the percent carbon lost (% C in raw coal minus % C in insoluble residue) and 1) the weight loss in ashing the insoluble residues and 2) the weight of the ashed insoluble residues.

The mineral content of the oxidized insoluble residue should remain reasonably constant throughout the ashing procedure, consequently, the loss in weight by ashing should correlate well to the carbon content oxidized, e.g., the amount of coal oxidized. Carbon dioxide is a known by-product from dichromate oxidations (Guyout, 1920), consequently, the inorganic carbonates could be generated by these oxidations and cause a weight increase in the ashed residues which would erroneously lower the oxidation yields. To ascertain if this were a source of error, the carbonate content of the oxidized insoluble residues was determined by measuring the carbon dioxide released when the residues were decomposed by hydrochloric acid. The percentage weights of the carbonates in the oxidized residues as measured by this technique were always less than 0.16% (Duty, 1981).

Since the residues also may contain unreacted sodium dichromate and chromium oxide, each of these was dried under the same conditions as the residues and ashed. These duplicate ashing experiments are shown in Table 1 which clearly show these compounds, as expected, would contribute very little to the weight loss of the ashed oxidation residues.

For the first coefficient of correlation measurement the percent of coal oxidized, taken as the difference in carbon content between the original (mf) coal and the insoluble residue, was compared to the weight lost in ashing. These values are shown in Table 2 for eight different reactions, and the coefficient of correlation between these two parameters was calculated and found to be a very low correlation, 0.774. This low coefficient of correlation is understandable because in the ashing procedure the hydrogen, nitrogen and sulfur are lost as well as carbon, and these values may well contribute to a low coefficient of correlation.

In these oxidation experiments with sodium dichromate, an insoluble chromium oxide is produced, and consequently, if the coal is oxidized, the generation of chromium oxide should parallel the extent of coal oxidized. The water soluble sodium dichromate should not interfer because the water soluble compounds are removed, along with the carboxylic acids produced, when the residues are extensively washed with water. Therefore, a second correlation of coefficient was calculated for the percentage of coal oxidized (the weight of the carbon lost between the original coal and the insoluble residue) compared to the weight of the ash obtained from the insoluble residues. This coefficient of correlation for this comparison came out to be 0.974. The standard error of estimate was calculated to be 2.9%, and the probable error was 1.96%, i.e. if one uses the weight of ash in the insoluble residues, he has a 50% chance of predicting the percentage of coal oxidized within a 2% error.

In these oxidation experiments, the reactions were run with an excess of dichromate and a limited amount of dichromate. This was done to duplicate the experimental runs with dichromate in previous experiments (Duty, 1980, 1981). Excess dichromate was indicated by an orange filtrate, and limited dichromate was determined by a green filtrate at the completion of each experiment. To ascertain whether limited or excess dichromate would make a difference in predicting the oxidation yields from their ashed residues, a coefficient of correlation was determined for each. The excess had a 0.985 coefficient of correlation and the limited dichromate coefficient was 0.939. Evidently, the generation of chromic oxide enhances the predictably of ascertaining the precentage of coal oxidized.

The coefficient of correlation calculations were determined by using the equation: coefficient of correlation

$$= \frac{\Sigma x_i y_i}{\sqrt{\Sigma x_i^2 \Sigma y_i^2}}$$

This coefficient of correlation (Laitinen, 1975) has its y intercept fixed at zero which corresponds with our date; e.g. when there is no coal oxidized the chromium oxide is zero.

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Table 1. Elemental Analysis for Coals

	%C	%H	%N	%S	%O[a]	%Ash
Ill. No. 2 Coal	69.4	5.81	1.27	2.11	11.4	3.34
Ill. No. 6 Coal	69.2	4.72	—	4.42	8.46[b]	12.4
North Dakota Lignite	65.71	3.77	0.78	0.89	19.90	8.95
Solvent Refined Lignite	89.3	5.8	1.1	0.9	2.9	~0.0
Solvent Refined Coal	87.2	5.5	1.8	1.2	4.3	~0.0

[a] oxygen was determined by difference

[b] oxygen was determined by difference assuming a nitrogen content of 1.00%. The dmmf coal had a nitrogen content of 1.29%.

Table 2. Ash Content Versus Quantity of Coal Oxidized

Oxidation Reaction	g. of carbon in coal sample (mf)	g. of carbon in insoluble residue	% Loss of Original C.	g. of carbon oxidized	g. of insoluble residue	% Ash of insoluble residue[a]	g. of Ash of insoluble residue
IL#6 (limited)	6.9	5.9	14.5%	1.0	26.97	70.23 ± 1.15	18.94
IL#6 (excess)	6.9	6.2	10.1%	0.7	15.04	41.52 ± 0.15	6.14
NDL (limited)	6.6	4.9	25.8%	1.7	30.76	61.03 ± 1.02	18.77
IL#2 (limited)	7.4	7.3 ± 0.07[a]	13.5%	0.1	14.17	31.45 ± 0.18	4.46
SRC (excess)	7.4	6.5	12.2%	0.9	26.19	61.64 ± 0.14	16.14
SRL (limited)	8.8	4.2 ± 0.08[a]	52.3%	4.6	39.45	75.08 ± 0.01	29.62
SRL (excess)	8.9	4.2 ± 0.08[a]	52.8%	4.7	43.56	80.19 ± 0.01	34.93
SRL (excess)	8.9	6.0 ± 0.09[a]	32.6%	2.9	34.71	69.62 ± 0.90	24.16
Cr_2O_3 (expt. std.)						98.73 ± 0.90	
$Na_2Cr_3O_7$ (expt. std.)						97.03 ± 0.90	

[a] duplicate determinations