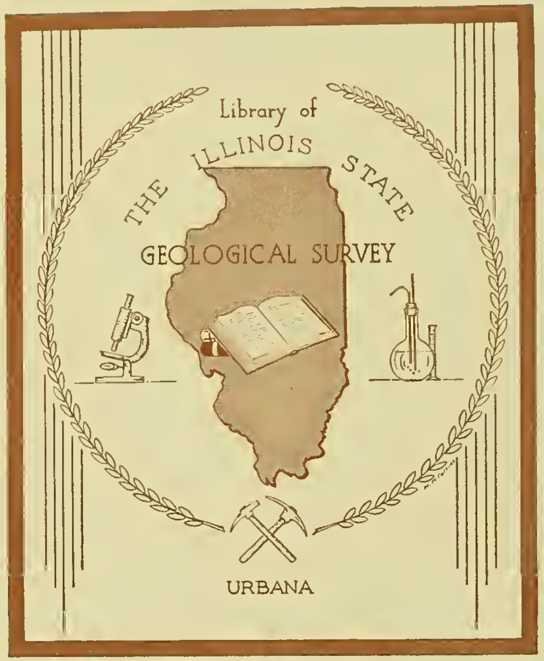

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M. M. LEIGHTON, *Chief*

REPORT OF INVESTIGATIONS—NO. 32

CONTRIBUTIONS TO THE STUDY OF COAL

A Proposed Simplification of the Parr Unit Coal Formula

BY GILBERT THIESSEN

Ash-to-Mineral Matter Correction in Coal Analyses

BY GILBERT THIESSEN

Unit Coal as a Basis of Coal Standardization as Applied to Illinois Coals

BY G. H. CADY AND O. W. REES

Studies of the Graphical Method of Calculating Pure Coal Calorific Value

BY GILBERT THIESSEN AND FRANK H. REED

AUG. 26TH 1818

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Preface

This report comprises a group of scientific papers that give the results of studies, made in the laboratories of the State Geological Survey, which contribute to a sounder basis for the classification and evaluation of Illinois coals. These papers are especially timely in view of the requirements of the Bituminous Coal Code of the National Recovery Act for information scientifically determined.

This work was undertaken in the first place to provide needed information on Illinois coals required by the Sectional Committee on Classification of Coals, of the American Society for Testing Materials, who have been engaged for the past six years in a careful study of the classification of all American coals.

(Signed) M. M. Leighton, *Chief,*
Illinois State Geological Survey.

August 30, 1934.

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Contents

A PROPOSED SIMPLIFICATION OF THE PARR UNIT COAL FORMULA*

By Gilbert Thiessen†

PURPOSE

The purpose of this paper is (1) to present a simplification of, not a substitution for, the Parr formula[1] for the calculation of unit coal calorific values; (2) to prove the validity of the simplification, both experimentally and mathematically, by showing that the corrections for the heat of combustion of sulfur, for the difference in quantity between ferric oxide and pyrites and for the water of hydration of the non-pyritic mineral matter may be mathematically combined into a single factor and that this factor is a function of the ratio of sulfur to ash and of the degree of hydration of the non-pyritic minerals; (3) to show that though this factor is also dependent upon the unit coal value, the dependence is so small that it may for practical usage on any individual rank be ignored; (4) to show that sulfur as well as ash must be considered in the calculation of unit or pure coal values; and (5) to show that the method of simplification may be applied to other correlative unit coal formulæ. Though no argument is presented relative to the validity of any hydration factor, it is assumed that the factor 0.08 is most satisfactory.

INTRODUCTION

It has been shown[2] that the Parr unit coal calorific value formula gives the most consistent "pure coal" calorific values of any method of calculation so far proposed. It has also been shown that unit coal calorific values are of great value in coal technology as a means of shortening analytical procedures and checking analytical results[3] and as a basis for coal classification.[4] The formula has the disadvantage of being somewhat complicated, even for machine computation. Substitutions have therefore been previously proposed in which the ash value as found on analysis is increased by a fixed amount, as one-tenth or one-eighth.[5]

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* Reprinted from "Fuel in Science and Practice," Vol. XII, No. 2, pp. 403-411, 1934.

† Associate Chemist, Fuels Division.

These formulæ do not give as consistent "pure coal" calorific values as does the Parr formula. For various reasons investigators have considered one or another of these substitutions to be most satisfactory. The difficulties encountered, it will be shown, are due to the fact that the ratio of apparent mineral matter to ash is not constant but is a function of both ash and sulfur. It is the first purpose of this paper to propose a modification of, not a substitute for, the Parr unit coal formula.

THE SIMPLIFIED PARR FORMULA

When coal is burned, the mineral matter is converted into ash, involving changes in composition and quantity and certain thermal effects. Of these, the loss in quantity due to the release of water of hydration and to the conversion of pyrites to iron oxide, and the heat effect due to the combustion of the pyrites, are the most important. The heat effect and the quantitative effect due to the change of calcium carbonate to calcium oxide, although appreciable when considered by itself, may be neglected in calculations of "pure coal" values,[6] except in the infrequent cases of the occurrence of calcite in coal in quantities greater than 1 per cent. Other quantity and heat effects are so small that they may be neglected and yet not affect the calculation to an amount approaching the allowable experimental errors.

All the corrections in the Parr formula for the calculation of unit coal calorific values may be combined mathematically into a single factor, "f", which combines the correction for the heat of combustion of pyrites, the water of hydration of the non-pyritic mineral matter, and the difference in quantity between pyrites and ferric oxide. The expression "f" × % ash represents a "modified mineral matter" value. The Parr formula

$$\text{B.t.u. unit coal} = \frac{\text{B.t.u. determined} - 50 \times \%\ \text{S}}{100 - (1.08 \times \%\ \text{ash} + 0.55 \times \%\ \text{S})} \times 100 \quad \text{(dry basis)}$$

becomes

$$\text{B.t.u. unit coal} = \frac{\text{B.t.u. determined}}{100 - (f \times \%\ \text{ash})} \times 100 \quad \text{(dry basis)}$$

The factor "f" is not 1.1 or 1.125 or some other constant value, but, as will be shown, is a variable depending upon the ratio of sulfur to ash in the coal for any given degree of hydration of the non-pyritic mineral matter.

The value of "*f*" for any coal can be calculated from analytical data which include values for moisture, ash, calorific value, and unit coal calorific value. Since

$$\text{Unit coal B.t.u.} = \frac{\text{B. t. u. determined}}{100 - (\text{“}f\text{”} \times \%\ \text{ash})} \times 100$$

$$\text{“}f\text{”} = \frac{\left\{1 - \dfrac{\text{B.t.u. determined}}{\text{Unit B.t.u.}}\right\} \times 100,}{\%\ \text{ash}}$$

The values of "*f*" calculated for a number of samples of coal prepared by gravity separation are given in Table 1.

These samples represent fractions of coals prepared by several float-and-sink procedures for a study of the agreement of "pure coal" calorific values obtained by various methods of calculations. These studies, the main conclusions of which were that the Parr unit coal formula gave the most consistent values, are also published herein (pp. 57-99). In Table 2 are presented analyses, "*f*" values, unit coal calorific values, and other values for a selected list of coals of various ranks taken from the published literature.

TABLE 1.—*Calculation of apparent mineral-to-ash ratios for Parr unit coal formula*

1	2	3	4	5	6	7	8	9	10
Sample No.	Ash	Sulfur	Sulfur / Ash	Determined B.t.u.	Unit coal B.t.u.	B.t.u. / Unit coal	Apparent mineral	Calculated "f"	Sulfur factor
Illinois No. 6 coal, Franklin County									
C- 56	1.5	0.84	0.560	14,329	14,593	0.9819	1.81	1.207	0.2268
C- 57	2.9	0.87	0.300	14,122	14,606	0.9669	3.31	1.141	0.2033
C- 58	5.0	1.01	0.202	13,827	14,642	0.9443	5.57	1.114	0.1683
C- 59	7.0	1.02	0.146	13,580	14,728	0.9221	7.79	1.113	0.2260
C- 60	10.5	1.02	0.097	13,050	14,752	0.8846	11.54	1.099	0.1959
C- 61	15.3	0.94	0.061	12,362	14,839	0.8331	16.69	1.091	0.1803
C- 63	20.7	0.82	0.040	11,592	14,955	0.7751	22.49	1.086	0.1500
C- 62	44.7	2.06	0.046	7,466	14,554	0.5130	48.70	1.089	0.1957
Illinois No. 6 coal, Franklin County									
C- 66	1.6	0.88	0.550	14,234	14,511	0.9809	1.91	1.194	0.2073
C- 64	6.2	0.96	0.155	13,629	14,639	0.9310	6.90	1.113	0.2129
C- 77	20.8	0.79	0.038	11,368	14,693	0.7737	22.63	1.088	0.2105
C- 78	40.3	2.40	0.060	8,245	14,730	0.5597	44.03	1.093	0.2167
C- 76	54.2	6.30	0.116	5,737	14,272	0.4020	59.80	1.103	0.1982
C- 65	24.6	2.10	0.085	10,737	14,711	0.7299	27.01	1.098	0.2118
Illinois No. 5 coal, Fulton County									
C- 81	2.3	2.5	1.087	14,102	14,538	0.9700	3.00	1.304	0.2061
C- 83	4.0	2.6	0.650	14,266	14,998	0.9512	4.88	1.220	0.2154
C- 85	5.2	2.7	0.519	13,920	14,840	0.9380	6.20	1.192	0.2158
C- 87	7.4	2.9	0.392	13,590	14,871	0.9139	8.61	1.164	0.2143
C- 82	15.9	4.8	0.302	12,092	14,780	0.8181	18.19	1.144	0.2119
C- 86	18.6	5.8	0.312	11,756	14,945	0.7866	21.34	1.147	0.2147
C- 84	23.2	6.4	0.276	10,827	14,712	0.7359	26.41	1.138	0.2101
C- 88	46.7	13.5	0.289	6,873	14,712	0.4672	53.28	1.141	0.2111
C- 79	13.8	4.4	0.319	13,067	15,538	0.8410	15.90	1.152	0.2257
C- 80	14.2	4.7	0.331	12,577	15,038	0.8363	16.37	1.153	0.2205
C- 39	14.40	4.93	0.342	12,306	14,754	0.8341	16.59	1.152	0.2105

TABLE 1.—Concluded

1	2	3	4	5	6	7	8	9	10
Sample No.	Ash	Sulfur	Sulfur / Ash	Determined B.t.u.	Unit coal B.t.u.	B.t.u. / Unit coal	Apparent mineral	Calculated "f"	Sulfur factor
Benches of Illinois No. 6 coal, Franklin County									
C- 48	9.7	1.21	0.125	13,021	14,577	0.8933	10.67	1.100	0.1600
C-126	9.5	1.0	0.105	13,040	14,564	0.8954	10.46	1.101	0.2100
C- 50	11.3	0.91	0.081	12,767	14,572	0.8761	12.39	1.096	0.1975
C- 51	3.8	1.38	0.363	13,916	14,554	0.9562	4.38	1.153	0.2011
Illinois No. 1 coal, Fulton County									
C-104	9.3	4.4	0.473	13,077	14,687	0.8904	10.96	1.178	0.2072
C-105	2.3	2.5	1.087	14,206	14,646	0.9700	3.00	1.304	0.2061
C-107	3.0	2.6	0.867	14,365	14,933	0.9620	3.80	1.267	0.2157
C-109	3.5	2.5	0.714	14,143	14,781	0.9568	4.32	1.234	0.2157
C-111	4.4	2.7	0.614	13,945	14,728	0.9468	5.32	1.209	0.2101
C-113	5.5	2.9	0.527	13,829	14,800	0.9344	6.56	1.193	0.2144
C-115	5.7	3.1	0.544	13,524	14,511	0.9320	6.80	1.193	0.2077
C-117	5.7	3.0	0.526	13,381	14,353	0.9323	6.77	1.188	0.2053
C-106	15.8	6.0	0.380	12,037	14,738	0.8167	18.33	1.160	0.2105
C-108	19.7	7.1	0.360	11,345	14,691	0.7722	22.78	1.156	0.2111
C-110	23.1	8.1	0.351	10,718	14,610	0.7336	26.64	1.153	0.2080
C-112	33.4	11.1	0.332	9,069	14,725	0.6159	38.41	1.150	0.2108
C-114	47.9	19.1	0.399	6,141	13,734	0.4471	55.29	1.154	0.1855
C-116	56.2	21.9	0.390	4,633	12,979	0.3570	64.30	1.144	0.1641
C-118	61.4	27.4	0.446	3,382	10,806	0.3130	68.70	1.119	0.874

Table 2.—*The analyses, calculated factors, and other*

(1) State	(2) County	(3) Town	(4) Mine	(5) Bed	(6) Sample No.
Illinois	Vermilion			No. 6	A 62,307
Kentucky	Harlan	Closplint	Closplint	Highsplint	A 61,047
Kentucky	Harlan	Closplint	Closplint	Highsplint	A 61,048
Kentucky	Letcher	Jenkins	204	Elkhorn	A 61,300
Kentucky	Letcher	Jenkins	204	Elkhorn	A 61,299
Maryland	Garrett	Wilson, W. Virginia	Arnold	Davis	A 60,320
Montana	Carbon	Red Lodge	No. 4	No. 5	A 64,310
North Dakota	Burleigh	Wilton	Trux Traer		A 67,054
North Dakota	Mercer	Beulah	Knife River		A 68,042
North Dakota	Morton	New Salem	McCormick		A 67,459
North Dakota	Ward	Velva	Trux Traer		A 67.838
Pennsylvania	Allegheny	New Kensington	Springdale	Thick Freeport	A 58,155
Pennsylvania	Luzerne	Jeddo	Highland 5	Gamma-top Split	A 71,098
Pennsylvania	Luzerne	Jeddo	Highland 5	Wharton-top B	A 71,095
Pennsylvania	Luzerne	Jeddo	Jeddo 4	Orchard	A 71,080
Pennsylvania	Luzerne	Jeddo	Jeddo 4 Slope	Mammoth Top 6 ft. bench	A 71,089
Pennsylvania	Washington	McDonald	Montour 9	Pittsburgh	A 58.606
West Virginia	Fayette	Kilsyth	Siltex	Sewell	A 59,370
West Virginia	McDowell	Berwind	Berwind 1	Pocahontas 3	A 59,378
West Virginia	McDowell	Caples	Caples	Pocahontas 3	A 59,382
West Virginia	McDowell	Pageton	Page	Pocahontas 3	A 59,374
West Virginia	Mercer	Freeman	Booth Bowen	Pocahontas 3	A 59,390
West Virginia	Mercer	McComas	Sagamore	Pocahontas 3	A 59,386
Wyoming	Carbon	Hanna	Hanna 4	No. 2	A 62,410
Wyoming	Sweetwater	Rock Spring	Rock Spring 4	No. 1	A 62,229
Wyoming	Sweetwater	Winton	Winton 3	No. 3	A 62,223
Washington	Lewis	Centralia	Salzer Valley King	Salzer Valley	A 55,443
Washington	Thurston	Tenino	Pleasant Hill	Black Bear	A 56,242
Washington	King	Renton	Renton Strain	No. 1	A 53,870
Washington	King	Renton	Renton Strain	No. 2	A 53,871
Washington	King	Renton	Renton Strain	No. 3	A 53,872
Illinois	Franklin	West Frankfort	Orient No. 1	No. 6	A 66,446
Illinois	Fulton	Thirteen mine averages		No. 5	Bull. 56 Rev.
Illinois	Knox	One mine		No. 4	Bull. 56 Rev.
Illinois	Bureau	Three mines		No. 2	Bull. 56 Rev.
Total					

The "*f*" values in Table 1 for the float-and-sink fractions are plotted against ash values (Fig. 1). It is seen that the curve for each set of fractions shows a rapid decrease in "*f*" values with increasing ash content when the ash figures are small, and that this change decreases in rapidity as ash values increase, until, for ash values above about 10 per cent the value remains practically constant for each set of fractions. It is seen that the high "*f*" factors occur when the sulfur-to-ash ratios are relatively large (around unity). In most coals this occurs with relatively low ash content.

relationships for a selected list of coals of all ranks

(7) Ash	(8) Sulfur	(9) B.t.u.	(10) Unit coal B.t.u.	(11) B.t.u./U.C.	(12) Apparent mineral	(13) Sulfur to ash ratio	(14) Apparent mineral to ash (f)	(15) Slope factor	(16) Rank	(17) Rank sulfur factor	(18) By simplified formula using 0.21 S	(19) By simplified formula using rank factor	(20) 18-10	(21) 19-10
7.6	1.3	13,210	14,432	0.9153	847	0.171	1.114	0.1988	B	0.21	14,434	14,434	+ 2	+ 2
3.1	0.5	14,190	14,697	0.9655	345	0.161	1.113	0.2050	Splint B	0.21	14,697	14,697	0	0
3.0	0.5	14,420	14,920	0.9665	335	0.167	1.117	0.2216	B	0.21	14,920	14,920	0	0
2.0	0.5	14,860	15,206	0.9772	228	0.250	1.114	0.1360	B	0.21	15,205	15,205	— 1	— 1
3.3	0.6	14,650	15,212	0.9631	369	0.182	1.118	0.2088	B	0.21	15,210	15,210	— 2	— 2
7.4	1.3	14,470	15,779	0.9170	830	0.176	1.122	0.2386	Sm. B	0.23	15,775	15,778	— 4	— 1
14.8	1.8	11,470	13,706	0.8369	1,631	0.122	1.102	0.1803	Sb. B	0.18	13,714	13,705	+ 8	+ 1
8.3	1.1	11,150	12,269	0.9088	912	0.133	1.099	0.1429	L	0.14	12,280	12,269	+11	0
8.7	1.1	11,060	12,228	0.9045	955	0.126	1.098	0.1429	L	0.14	12,239	12,228	+11	0
11.1	0.9	10,920	12,426	0.8788	1,212	0.081	1.092	0.1481	L	0.14	12,435	12,425	+ 9	+ 1
8.3	0.6	11,120	12,226	0.9095	905	0.072	1.090	0.1389	L	0.14	12,232	12,226	+ 6	0
8.0	0.9	14,120	15,491	0.9115	885	0.113	1.106	0.2301	B	0.21	15,488	15,428	— 3	— 3
18.5	0.7	12,040	15,076	0.7986	2,014	0.038	1.089	0.2368	A	0.22	15,074	15,074	— 2	— 2
8.9	1.9	13,560	15,072	0.8997	1,003	0.213	1.127	0.2207	A	0.22	15,068	15,072	— 4	0
14.5	0.6	12,620	14,986	0.8421	1,579	0.041	1.089	0.2195	A	0.22	14,986	14,986	0	0
6.6	0.6	13,850	14,934	0.9274	726	0.091	1.100	0.2198	A	0.22	14,933	14,934	— 1	0
6.3	0.7	14,010	15,058	0.9304	696	0.111	1.105	0.2252	B	0.21	15,056	15,056	— 2	— 2
3.8	0.9	15,020	15,697	0.9569	431	0.237	1.134	0.2278	Sm. B	0.23	15,693	15,697	— 4	0
4.3	0.6	14,980	15,732	0.9522	478	0.140	1.112	0.2286	Sm B	0.23	15,730	15,732	— 2	0
5.2	1.0	14,800	15,720	0.9415	585	0.192	1.125	0.2344	Sm. B	0.23	15,716	15,720	— 4	0
4.6	0.6	14,990	15,797	0 9489	511	0.130	1.111	0.2385	Sm. B	0.23	15,794	15,797	— 3	0
3.9	0.7	15,130	15,823	0.9562	438	0.179	1.123	0.2402	Sm. B	0.23	15,828	15,821	— 3	— 2
4.0	0.6	15,110	15,815	0.9554	446	0.150	1.115	0.2333	Sm. B	0.23	15,814	15,815	— 1	0
7.3	0.6	12,540	13,629	0.9201	799	0.082	1.095	0.1829	B	0.21	13,632	13,632	+ 3	+ 3
4.2	1.2	13,170	13,829	0.9523	477	0.286	1.136	0.1958	B	0.21	13,833	13,833	+ 4	+ 4
4.4	1.7	12,810	13,493	0.9494	506	0.386	1.150	0.1813	Sb. B	0.18	13,500	13,493	+ 7	0
11.3	3.6	11,190	12,829	0.8722	1,278	0.319	1.131	0.1599	Sb. B	0.18	12,856	12,840	+27	+11
30.4	3.2	8,600	12,903	0.6665	3,335	0.105	1.097	0.1619	Sb. B	0.18	12,932	12,915	+23	+12
11.5	0.7	11,840	13,539	0.8745	1,255	0.061	1.091	0.1803	Sb. B	0.18	13,542	13,539	+ 3	0
15.0	0.6	11,370	13,586	0.8369	1,631	0.040	1.087	0.1750	Sb. B	0.18	13,589	13,586	+ 3	0
7.5	0.6	12,550	13,673	0.9179	821	0.080	1.095	0.1875	Sb. B	0.18	13,675	13,673	+ 2	0
9.2	0.9	13,150	14,631	0.8988	1,012	0.098	1.100	0.2041	B	0.21	14,632	14,632	+ 1	+ 1
12.98	3.79	12,349	14,493	0.8521	1,479	0.292	1.139	0.2021	B	0.21	14,500	14,500	+ 7	+ 7
9.09	4.55	13,199	14,794	0.8922	1,078	0.501	1.186	0.2116	B	0.21	14,795	14,795	+ 1	+ 1
8.83	3.48	12,989	14,469	0.8977	1,023	0.394	1.159	0.2005	B	0.21	14,471	14,471	+ 2	+ 2
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If it is assumed that the factor for water of hydration is 1.08, the difference between "*f*" and 1.08 ("*f*" — 1.08) represents the numerical value, in terms of ash, of the heat of combustion of pyritic sulfur and the difference in the quantity between pyrites and ferric oxide. This relationship may be expressed thus:—

$$\text{“}f\text{”} - 1.08 = K \times S/A$$

"K" may conveniently be referred to as the sulfur factor. Its character and experimental value can be determined mathematically from analytical data. Inspection of Table 1 shows that the sulfur factor for the

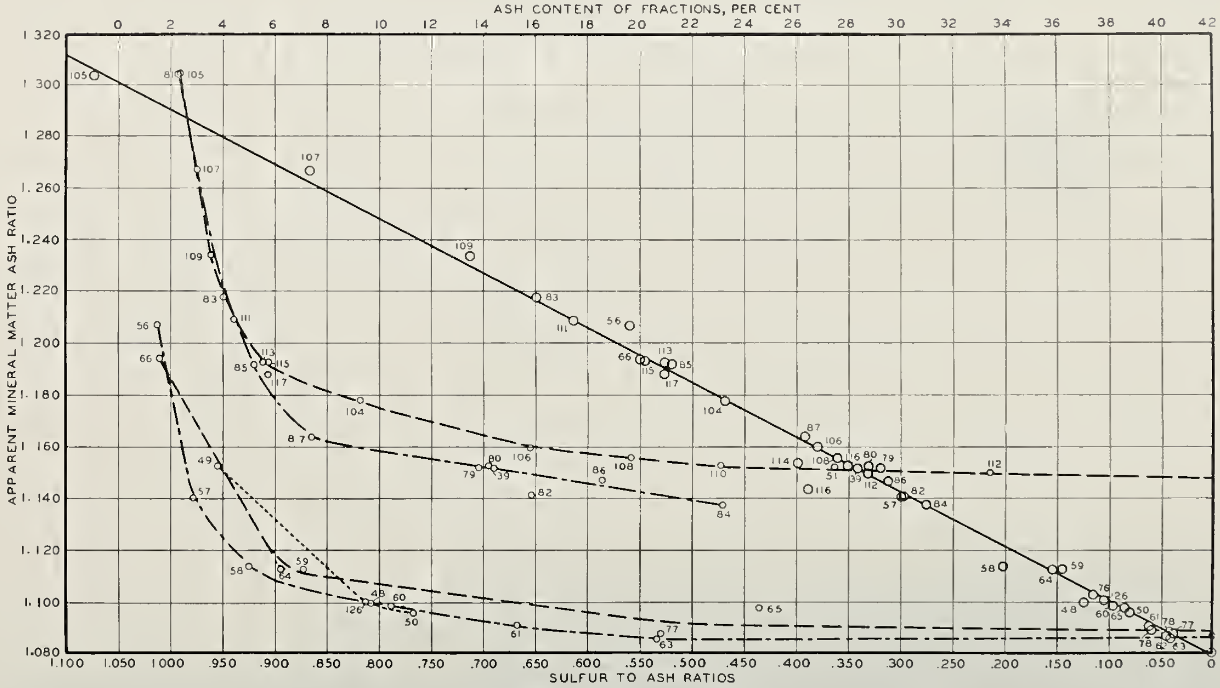

FIG. 1. Variation of "*f*" (apparent mineral matter-to-ash ratio) with ash content and with sulfur-to-ash ratios for fractions of several Illinois coals.

Illinois coals represented approximates very closely to 0.21. It is apparent, therefore, that if the values for "*f*", (or "*f*" — 1.08) are plotted against the values for S/A, the points will lie very close to a straight line. The relationship can be expressed in the slope-intercept form, $y = mx + b$, thus:

$$\text{"}f\text{"} = \text{K} \times \text{S/A} + 1.08, \text{ or}$$

$$\text{"}f\text{"} \times \%\ \text{ash} = \text{modified ash} = \text{K} \times \%\ \text{sulfur} + 1.08 \times \%\ \text{ash}.$$

This is similar to, but not the same as, the Parr formula: mineral matter = 0.55 × % sulfur + 1.08 × % ash. The difference between the two formulæ represents the difference between true mineral matter and modified mineral matter, which includes allowance in terms of ash of the heat of the sulfur.

Variation of Sulfur Factor "K" With the Rank of Coal

It should be possible, with experimental evidence, to determine whether or not the sulfur factor "K" varies from rank to rank among different coals. Investigation of this value for a considerable variety of coals shows that the factor varies from about 0.14 for lignites to 0.235 for semi-bituminous coals (Table 3). In figure 2 it is seen that when S/A is plotted against "*f*", for a large variety of coals, the coals of the same rank tend to lie along straight lines, the slopes of which increase with the value of "K" or the rank of the coal. It will be shown in the mathematical derivation of the simplified formula that the sulfur factor "K" varies with unit coal calorific value.

Table 3.—*Unit coal and sulfur factor values found from analyses of coals of different ranks*

Rank	Average of unit coal values	Factor (K)
Anthracite	15,017	0.224
Semi-bituminous	15,766	0.235
Bituminous	14,681	0.209
Sub-bituminous	13,390	0.175
Lignite	12 287	0.143

It is apparent that, whatever the variations in "*f*", these are due to variations in the product K × S/A, and that this variation is contained in that part of "*f*" in excess of 1.08, or whatever value is taken to represent the original hydrated clay or shale in the coal. If 1.11 or 1.125 is taken, the residue of "*f*" is smaller than when 1.08 is taken; then obviously the value K × S/A is less, and since the ratio S/A does not change in this instance the value K must be smaller. By increasing the hydration factor, it would appear possible to diminish the K almost to 0, thus giving S little importance in the formula. However, whether or not such increase would be legitimate, depends entirely upon experimental evidence. The present weight of evidence seems to indicate that the value 1.08 most nearly fits the facts for Illinois coal, but the possibility of variation among even mid-western coals is recognized. Investigations now in progress, of the mineral constituents of Illinois coal, will probably throw some light on this problem.

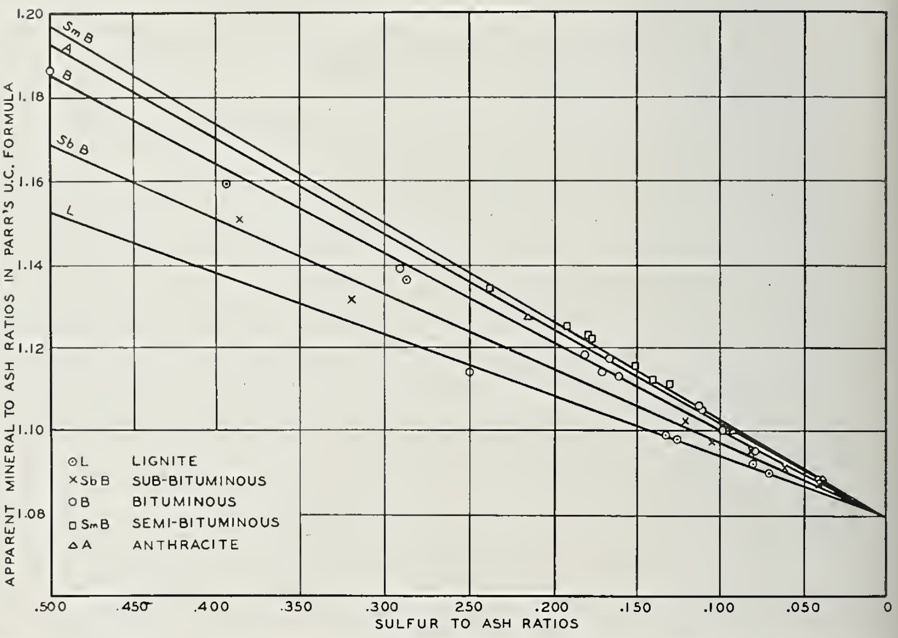

FIG. 2. Variation of "f" values with sulfur-to-ash ratios for coals of various ranks.

THE SIMPLIFIED PARR FORMULA AND ITS EXPERIMENTAL VERIFICATION

Since "f" $= \text{K} \times \text{S/A} + 1.08$, the unit coal formula,

$$\text{Unit coal B.t.u.} = \frac{\text{B.t.u. (dry)}}{100 - (\text{“}f\text{”} \times \%\ \text{ash})} \times 100,$$

becomes Unit coal B.t.u. =

$$\frac{\text{B.t.u. (dry)}}{100 - (1.08 \times \%\ \text{ash} + \text{K} \times \%\ \text{sulfur})} \times 100$$

This formula has been found to give results which agree to within a few B.t.u. of those given by the original unit coal formula when the sulfur factor which corresponds to the rank of the coal is used, and to within the experimental error of a calorimetic determination when the value 0.21 (correct for bituminous coals, 14,700 B.t.u.) is used. The values found by using the average factor 0.21 and also the values found using the factor appropriate to the rank of the coal may be found in Tables 2 and 4. In the case of the samples high in ash and sulfur (Nos. 114, 116, and 118), the simplified formula gives results which correspond more nearly to the average unit coal value for the group of fractions than do the values obtained by Parr's original formula.

Table 4.—*Comparison of calorific values calculated by regular and simplified Parr unit coal calorific value formula*

Illinois bituminous coals—float-and-sink separation samples

Sample No.	Unit coal calorific values		Difference
	Parr formula	Simplified formula K = 0.21	
56	14,593	14,592	− 1
57	14,606	14,605	− 1
58	14,642	14,649	+ 7
59	14,728	14,724	− 4
60	14,752	14,754	+ 2
61	14,839	14,844	+ 5
63	14,955	14,963	+ 8
62	14,554	14,556	+ 2
66	14,511	14,511	0
64	14,639	14,639	0
77	14,693	14,693	0
78	14,730	14,731	+ 1
76	14,272	14,292	+ 20
65	14,711	14,710	− 1
Average			3.8
104	14,607	14,608	+ 1
105	14,646	14,647	+ 1
107	14,933	14,931	− 2
109	14,781	14,780	− 1
111	14,728	14,729	+ 1
113	14,800	14,798	− 2
115	14,511	14,512	+ 1
117	14,353	14,356	+ 3
106	14,738	14,737	− 1
108	14,691	14,690	− 1
110	14,610	14,612	+ 2
112	14,725	14,722	− 3
114	13,734	13,875	+ 41 (*a*)
116	12,979	13,352	+ 373 (*a*)
118	10,806	12,109	+1,303 (*a*)
Average			1.6

(*a*) Omitted in average.

TABLE 4.—Concluded

Sample No.	Unit coal calorific values		Difference
	Parr formula	Simplified formula	
81	14,538	14,540	+ 2
83	14,998	14,996	— 2
85	14,840	14,837	— 3
87	14,871	14,869	— 2
82	14,780	14,779	— 1
86	14,945	14,940	— 5
84	14,712	14,711	— 1
88	14,712	14,708	— 4
79	15,538	15,525	— 13
80	15,038	15,030	— 8
39	14,754	14,754	0
48	14,577	14,586	+ 9
126	14,564	14,565	+ 1
50	14,572	14,574	+ 2
51	14,554	14,555	+ 1
Average			3.6

MATHEMATICAL DERIVATION OF THE SIMPLIFIED FORMULA

The Parr unit coal formula,

$$\text{Unit coal} = Q = \frac{H - 5{,}000\,S}{1 - (1.08\,A + 0.55\,S)},$$

when S and A represent respectively fractions of sulfur and ash in the coal and H the heating value in B.t.u. per pound, may be put in the forms,

$$Q\,(1 - 1.08\,A - 0.55\,S) = H - 5{,}000\,S$$

$$Q\,(1 - 1.08\,A) - 0.55\,S.Q + 5{,}000\,S = H$$

$$Q\,(1 - 1.08\,A) - Q\,(0.55\,S + \frac{5{,}000\,S}{Q}) = H$$

$$Q\left\{1 - [1.08\,A + (0.55 - \frac{5{,}000}{Q})\,S]\right\} = H$$

The factor for sulfur is "K" $= (0.55 - \frac{5{,}000}{Q})$. Its values for various values of Q are given in Table 5 and the variation of K with Q is shown graphically in figure 3. The unit coal values corresponding to the indicated coal rank are mean values for each rank and are taken from Parr's system of coal classification based on unit coal calorific values and unit volatile matter contents.

TABLE 5.—*Solutions for equation* $K = 0.55 - \frac{5{,}000}{Q}$

Coal rank	Unit coal B.t.u. (Q)	Calculated factor	Factor found experimentally
	10,000	0.050	
	11,000	0.096	
Lignite (P)	11,750	0.114	
	12,000	0.133	
Lignite (A)	12,287	0.143	0.143
	13,000	0.165	
Sub-bituminous (P)	13,250	0.173	
Sub-bituminous (A)	13,390	0.177	0.175
	14,000	0.193	
Bituminous (A)	14,700	0.209	0.210
Bituminous (P)	15,000	0.217	
Anthracite (A)	15,017	0.217	0.224
Anthracite (P)	15,500	0.227	
Semi-bituminous (P)	15,500	0.227	
Semi-bituminous (A)	15,766	0.233	0.235

(A)—mean of samples selected.
(P)—mean of Parr class range.

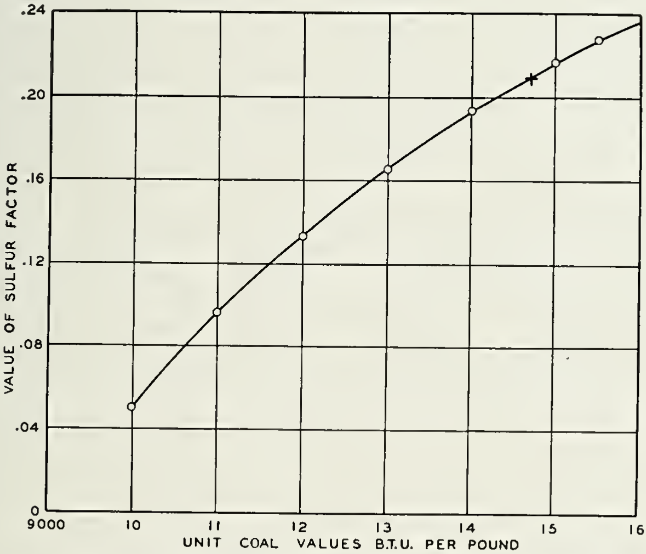

FIG. 3. Variation of sulfur factor "K" with unit coal values.

The value 0.21 will, however, be found satisfactory as a universal value and is especially satisfactory for bituminous coals. If greater accuracy is required for calculating the unit coal values of low rank coals (lignite or brown coals), it would be preferable to use the value 0.14.

Choice of a Standard Sulfur Factor (K)

An intermediate sulfur factor, such as 0.21, is satisfactory for general use.

Variations in the sulfur factor will increase or decrease unit coal values, depending upon whether these variations increase or decrease the value of "*f*". However, since the amount of this increase must always be measured in comparison with that portion of "*f*" below which no decrease can take place (1.08, 1.11, 1.125 as the case may be) it is always relatively small, since S/A rarely equals ½, and K, for all except lignite coals, varies within the narrow range of from 0.17 to 0.23. Hence the value "*f*" — 1.08 is always small, rarely more than 0.12 and commonly less than 0.08. If 0.21 is used as the value of K, with S/A equal ½, "*f*" would be 1.185; if S/A equal 1/10, "*f*" would be 1.10. This represents about the range of probabilities, the extreme values lying about equal amounts above and below the position of the average value. It is quite apparent, however, that the higher the permissible value that can be used for moisture correction, the less the amount of the sulfur factor. The present argument, however, assumes that 1.08 is the most suitable factor.

When using 0.21 as the sulfur factor, the greatest deviation from the unit coal value as calculated by the Parr formula was + 27 B.t.u. for a sub-bituminous coal from Lewis County, Washington, which has 11 per cent ash and 3.6 per cent sulfur on the dry basis, and 29 per cent moisture (Table 2.).

Variations in pure coal calorific values with sulfur constant for two bituminous coals are as follows:

(1) A bituminous coal from the Pittsburgh bed (Sample A58,606) containing 6.3 per cent ash, 0.7 per cent sulfur as determined, calorific value of 14,010 B.t.u. per lb., and a unit coal value of 15,058 B.t.u. per lb., when calculated to unit coal calorific value using the factors 0.19, 0.21, and 0.23 gives 15,055, 15,056, and 15,060 B.t.u. per lb. respectively. These values differ from the unit coal value by 3, 2 and 2 units respectively.

(2) A sample of Illinois coal No. 4, from Knox County, with 9.09 per cent ash, 4.55 per cent sulfur, 13,199 B.t.u. per lb. heating value, all on dry basis, and 14,794 B.t.u. per lb. unit coal calorific value, when calculated to pure coal calorific value by the simplified Parr formula using sulfur factors of 0.14, 0.19, 0.21 and 0.23 respectively, gives values of 14,739, 14,777, 14,792, and 14,807, being differences from the unit coal values of — 55, — 17, — 2, and + 13 units respectively. This is a range of only 68 B.t.u. units between values calculated using sulfur factors for coals at each end of the scale of rank and for a coal

with a high sulfur-to-ash ratio (0.501). Such a high sulfur ratio does not commonly accompany an ash content as low as 10 per cent. The difference in calculated calorific values, using sulfur factors of 0.19 and 0.23, is only 30 B.t.u.

The writer concludes, therefore, that the use of the factor 0.21 is permissible in all cases.

OTHER COAL FORMULÆ

Knowing the unit coal calorific value for coal from a given seam over a delimited area, the calorific value of any sample of known moisture, ash and sulfur content may be found from the following formula:

B.t.u. = unit coal $\times$ $(1 - 1.08A - 0.21S - W)$ when A, S, W are ash, sulfur, and moisture respectively expressed fractionally. This is the simplified form of the original Parr expression:

B.t.u. = Unit coal $\times$ $(1 - 1.08A - 0.55\ S - W) + 5{,}000\ S$, in which again A, S, and W respectively, are ash, sulfur, and moisture in fractions present in the coal.

CORRESPONDING FORMULÆ IN CALORIES

If calories per gram are used in place of British thermal units per lb. (B.t.u. / lb.), the simplified formulæ may be used without further change, whereas in the original Parr formulæ the value 5,000 S had to be changed to $\frac{5{,}000}{1.8}$ S or 2,778 S. The simplified formulæ have therefore the advantage that the same formula may be used no matter what heat units are used, as the ratio of heat from the ashing of the pyrites to the unit coal value remains constant.

IMPORTANCE OF BOTH SULFUR AND ASH

The sulfur and the ash contents of coals must be considered as independent variables even though some dependencies are generally evident. Any formula or system of calculation which considers only one of these variables will be in error, as may be readily seen from consideration of the formula "f" $= K\ S/A + 1.08$; particularly when values of S/A exceed ¼, as is likely to be the case when S exceeds 2 per cent.

The simplified formula here presented involves the use of each of these variables but once, and is therefore in the most simplified form.

VARIATION OF HYDRATION FACTOR IN UNIT COAL FORMULÆ

The original Parr unit coal formula assumes that the non-pyritic minerals contain 8 per cent of combined water. It was realized that this value was low when only clay minerals were considered, but that it approximated the facts as an over-all factor in the majority of cases. There has been considerable discussion concerning the correct value of this hydration factor. It is not in place here to discuss the relative merits of any specific factor, since any value which is chosen may be used in either the original Parr formula or the proposed simplification.

The general formula and its derivation follow: Mineral matter = ash + ⅝ sulfur + h (ash — 10/8 sulfur)

$$= (1 + h)\ \text{ash} + (5/8 - \frac{10\,h}{8}\ \text{sulfur})$$

The values for mineral matter for several values of hydration factors which have been given consideration elsewhere are:

$h = 0.08 \quad M = 1.08\ A + 0.55\ S$
(Adjusted by Parr from 0.525)
$h = 0.10 \quad M = 1.10\ A + 0.500\ S$
$h = 0.11 \quad M = 1.11\ A + 0.487\ S$
$h = 0.125 \quad M = 1.125\ A + 0.469\ S$

when M is the actual mineral matter.

In the unit coal calorific value formulæ, the corresponding values of apparent mineral matter for a unit coal value of 14,700 B.t.u. per lb. are:

$h = 0.08 \quad \text{Apparent } M = 1.08\ A + 0.21\ S$
$h = 0.10 \quad \text{Apparent } M = 1.10\ A + 0.16\ S$
$h = 0.11 \quad \text{Apparent } M = 1.11\ A + 0.15\ S$
$h = 0.125 \quad \text{Apparent } M = 1.125\ A + 0.13\ S$

corresponding to the general formula,
Unit coal calorific value =

$$\frac{\text{Determined calorific value}}{100 - [(1 + h)\ \%\ A + \left\{\frac{5}{8} - \frac{10\,h}{8} - \frac{5{,}000}{\text{U.C. B.t.u.}}\right\}\ \%\ S]} \times 100$$

A very useful and simple formula for obtaining mineral matter-free calorific values which very closely approximate Parr unit coal values in most cases is:

$$\text{MM-free calorific value} = \frac{\text{Determined calorific value}}{100 - (1.1 \times \%\ \text{Ash} + 0.1 \times \%\ \text{Sulfur})} \times 100$$

This formula was suggested by Dr. A. C. Fieldner on the basis of these discussions.

The other unit coal formulæ considered below may be similarly altered to take care of any desired hydration value for the non-pyritic minerals.

Other Unit Coal Formulæ

The Parr unit coal formula for use with coals high in carbon dioxide makes correction only for the quantitative effects. As the author has shown (pp. 82-87), correction must also be made for the heat of decomposition of the calcium carbonate. This amounts to 1,750 B.t.u. per lb. of carbon dioxide. The formula recommended was:

Unit coal B.t.u. =

$$\frac{\text{B.t.u. determined} - 50 \times \%\ S + 17.50 \times \%\ CO_2}{100 - (1.08\ [(\%\ \text{ash} - 1.27\ \%\ CO_2)] + 2.27\ \%\ CO_2 + 0.55 \times \%\ S} \times 100 \text{ (dry basis)}$$

Just as the 50 × per cent S and 0.55 × per cent S were combined to give the value 0.21 × per cent S, so the values 17.50 × per cent CO_2, 2.27 × per cent CO_2 and 1.08 × 1.27 × per cent CO_2 may be combined to give the value + 1.02 × per cent CO_2. The simplified formula would then be:

Unit coal calorific value =

$$\frac{\text{Heat of combustion determined}}{100 - (1.08 \times \%\ \text{ash} + 1.02 \times \%\ CO_2 + 0.21 \times \%\ S)} \times 100 \text{ (dry basis)}$$

The ash analysis, of course, is to be made by the Parr modified ashing procedure for coals high in calcite.

The unit volatile matter equation

Unit volatile =

$$\frac{\text{Determined volatile} - 0.08 \times \%\ \text{ash} - 0.4 \times \%\ S}{100 - (1.08\ \%\ \text{ash} + 0.55\ \%\ S)} \times 100$$

cannot be simplified by the above method because of the fact that the term $(0.55 - \frac{40}{U.V.})$ S is negative and not constant for all values of U.V. The term $(1.08 - \frac{8}{U.V.})$ A also does not become constant.

The same reasoning applied to the simplification of the unit fixed carbon formula,

$$\text{Unit F.C.} = \frac{\text{F.C.} - 0.15}{100 - (1.08\ \%\ A + 0.55\ \%\ S)} \times 100$$

shows that simplification by elimination of the term -0.125 S is not possible since $(0.55 - \frac{15}{U.F.C.})$ does not become constant. For low sulfur and high fixed carbon values the 0.15 S term becomes relatively small and the formula

$$\text{Unit F.C.} = \frac{\text{F.C. determined}}{100 - (1.08 \times \%\ \text{ash} + 0.55 \times \%\ \text{S})} \times 100$$

will give unit fixed carbon values approximating the values of the original formula to within the experimental error of volatile determinations. This formula is not recommended.

CONCLUSION

It has been shown that an apparent mineral matter value exists which when used to calculate coal calorific values to a mineral-free basis, gives the same pure coal calorific value as the Parr unit coal calorific value formula, and may be found from the expression,

$$M = 1.08\ \text{ash} + K\ \text{sulfur}.$$

It has been further shown that the value "K" varies with the value for unit coal, being 0.14 for lignites and 0.23 for semi-bituminous coals; but that for practical purposes the use of the value 0.21 gives results well within the experimental error.

A mathematical derivation of the value K has been presented, showing

$$K = 0.55 - \frac{5{,}000\ \text{B.t.u. /lb.}}{\text{Unit coal in B.t.u. /lb.}}$$

Simplified forms of the Parr unit coal formulæ have been presented. In the case of calorific values these are,

$$\text{Unit coal} = \frac{\text{Determined heat of combustion}}{100 - (W + 1.08\%\ A + 0.21\%\ S)} \times 100$$

when W, A and S are respectively moisture, ash and sulfur contents expressed in percentages of the coal; and the unit coal and heat of combustion are respectively the heat of combustion of the moisture- and mineral-free coal, and the determined heat of combustion expressed in any units desired, consistency in the use of units being implied. Tables are presented showing that values calculated by the original Parr formula and by the simplified formula are equivalent within the experimental errors inherent in the analytical values. Calculations of heats of combustion of coal to dry, mineral-free basis must take into account corrections due to the heating effects of the sulfur in the coal as well as of the quantitative changes occurring during the formation of ash from the mineral matter originally in the coal. The Parr unit coal formula was developed on a sound basis and has been proved many times to give the most satisfactory pure coal values. The simplified form here presented takes into account both ash quantity variations and ashing heat effects, but contains only one term for ash and one term for sulfur. The simplified formulæ have the advantage that the same expression may be used no matter in what units the heats of combustion are expressed. The same scheme of simplification applied to the Parr formulæ for calculating unit fixed carbon and unit volatile matter shows that simplification is not possible.

ACKNOWLEDGMENT

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ASH-TO-MINERAL MATTER CORRECTION IN COAL ANALYSES*

A Study Based Upon Coal-ash Analyses

By Gilbert Thiessen†

The purposes of this paper are (1) to show that the mineral matter content of coal is satisfactorily represented by the Parr formula, that is,

$$\text{Mineral matter} = 1.08 \times \text{Ash} + 0.55 \times \text{Total sulfur};$$

(2) to compare ash-to-mineral-matter ratios with factors by which ash values must be multiplied in order that dry, factor-times-ash-free values shall equal Parr unit coal values; (3) to examine such ash-correction factors and to compare them with similar factors corresponding to certain simplifications or modifications of the Parr formulas; and (4) to show that ash-correction factors used for simplification in calculating approximate unit coal calorific values cannot be correctly used for the conversion of other determined values in an analysis to the unit coal basis, but that each type of calculation requires separate treatment in simplification.

THE UNIT COAL CONCEPT

Calculation of coal analyses to the moisture-and-ash-free basis does not result in values accurately indicative of the composition or properties of the dry mineral-free coal. This is due not only to the fact that coal ash is not equal in quantity to the original coal mineral matter, but also to the further fact that, in the laboratory determination, effects due to certain parts of the mineral matter are included with effects due to the coal substance. In order to obtain values which represent the composition and properties of the pure coal substance, it is necessary first to correct the determined values to eliminate the effects of the mineral matter, and then to convert these corrected values to a mineral-matter-free basis. This is essentially the procedure in the unit coal calorific formula as developed by the late Dr. S. W. Parr. Professor Parr realized that his formulas were approximations. Both for that reason, but mainly because "pure coal" had previously been used to designate

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moisture-and-ash-free coal, he chose the name "unit coal" for his approximation to theoretical pure coal. The Parr formulas are:

For calorific value (in English units):[1]

$$\text{Unit coal B.t.u.} = \frac{\text{Determined B.t.u.} - 50 \times \%\ \text{sulfur}}{100 - (1.08 \times \%\ \text{ash} + \%\ \text{moisture} + 0.55 \times \%\ \text{sulfur})} \times 100$$

For volatile matter:[2]

$$\text{Unit Volatile}\ \% = \frac{\text{Determined volatile} - (0.08 \times \%\ \text{ash} + 0.4 \times \%\ \text{sulfur})}{100 - (1.08 \times \%\ \text{ash} + \%\ \text{moisture} + 0.55 \times \%\ \text{sulfur})} \times 100$$

As far as the author can discover, Professor Parr published no corresponding formula for unit fixed carbon. A formula which gives values comparable to the above unit volatile matter formula, and is developed upon the same assumptions, is:

$$\text{Unit fixed carbon} = \frac{\text{Determined fixed carbon} - 0.15 \times \%\ \text{sulfur}}{100 - (1.08 \times \%\ \text{ash} + \%\ \text{moisture} + 0.55 \times \%\ \text{sulfur})} \times 100$$

The factor 0.15 is changed from the theoretically calculable one of 0.125, which gives too high a value for the fixed carbon, since the sum of unit volatile matter and unit fixed carbon must equal 100.

Estimation of the accuracy with which these formulas furnish values truly representing the pure coal substance is made difficult because of the hypothetical nature of pure coal. The methods that have been used to test them, more particularly the calorific value formula, have been of three types:

1. Investigation of the constancy of values obtained by calculating analytical values for coal samples from a limited area of a given seam by the Parr or alternatively proposed formulas. This method rests upon the theory that the pure coal substance of a coal seam is constant in composition and properties within a limited area.

2. Comparison of values obtained by formula with values obtained by extrapolating, to zero ash, on such curves as represent the variations in composition or properties of coals with ash content.

3. Calculation of mineral content of a coal, from ash content of the coal and the analysis of the ash.

Very little may be found in the literature referring to tests of the accuracy of volatile-matter or fixed-carbon formulas.

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CONSTANCY OF UNIT COAL VALUES

Examination of large numbers of calorific value determinations on coals leads to the conclusion that the calorific value of the dry, mineral-free substance in coal from any one seam is quite uniform over considerable areas of geological uniformity; for example, in Illinois, a county. Examination of other analytical values leads to the same conclusions. If these conclusions are correct, then that formula or method of computation which gives the most consistent "pure coal" values for samples from within a limited area of a given coal seam must be the closest approximation to the correct method. Such tests, at least for Illinois coals, show that the Parr unit coal calorific value formula gives the most consistent results.[3, 4]

GRAPHICAL PURE COAL VALUES, FLOAT-AND-SINK SEPARATIONS

This method consists in taking a coal sample and so separating it that portions having different ash contents are obtained. Ordinarily, this is done by placing the sample in a liquid of such density that the low-ash coal floats while the higher-ash material sinks. By separating several portions of the same sample on liquids of different density or by successively separating the coal sample with liquids of increasing (or decreasing) gravity, a series of samples increasing in ash content may be obtained. Calorific or other analytical values may be plotted against ash values and the curve may be extrapolated to zero ash. The value so obtained may be compared with the values obtained by the formula method from analyses of the individual fractions, and the formula methods may be examined for constancy. Such tests also show that the Parr formulas give more consistent results than do other formulas and that the values obtained by Parr formulas correspond, within the limits of experimental error, to the values obtained graphically.[5,6,7,8]

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CALCULATION OF MINERAL MATTER FROM ASH ANALYSES

Mineralogical examination has shown that the mineral matter in coal is composed mainly of pyrite, calcite, clay minerals, particularly kaolinite,[9] and quartz, with minor amounts of a large variety of other minerals. Assuming that all of the ash-forming material is inorganic and present in these minerals, it is possible to calculate the theoretical composition of the mineral matter from the results of ash analyses. In the Parr unit coal formulas, the coal mineral matter is assumed to equal 1.08 × % ash + 0.55 × % sulfur. Comparison of values obtained by this expression with values obtained by calculation from ash analyses provides a method of determining the accuracy of the former.

In view of the present great interest in methods for calculating coal analyses to mineral-matter-free bases, it seemed desirable to use this method for checking the validity of the more important methods of calculation, more so in view of the scarcity of such checks to be found in the literature. Published analyses were used.

CALCULATION OF MINERAL MATTER CONTENT OF COAL AND OF MINERAL MATTER—ASH RATIOS FROM ASH ANALYSES

Table 1 presents the results of the calculation of the mineral matter content and mineral-matter-to-ash ratios from ash analyses, and proximate analyses of the corresponding coals, based upon the analyses of 21 coals published in U. S. Bureau of Mines *Bulletin* 364, "Clinker Formation as Related to the Fusibility of Coal Ash." The calculations by which the table was constructed are as follows:

Since the ash analyses were given in percentages of the various components in the ash, these were converted to the percentages of the respective components in the coal by multiplying the percentage of the component in the ash by the percentage of the ash in the coal. These values having been obtained, the following series of calculations was made:

(*a*) Pyritic sulfur values (col. 11) were converted to pyrite values (col. 15). Per cent pyritic sulfur times 1.8709 equals per cent pyrite.

(*b*) Iron oxide in ash (col. 3) minus iron oxide corresponding to pyritic sulfur equals excess iron oxide (col. 16). Per cent pyritic sulfur times 1.2452 equals iron oxide.

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[9] C. G. Ball and G. H. Cady: Evaluation of Ash Correction Formulae Based on Petrographic Analysis of Mineral Matter in Coal. Read before the Society of Economic Geologists, Dec. 28, 1933. Economic Geology (In press); Illinois State Geol. Survey Report of Investigations No. 33.

(*c*) Assuming that the clay mineral kaolinite, $Al_2O_3.2SiO_2.2H_2O$, represents the clay minerals in the coal, either silica or alumina may be in excess.

(1) When silica is in excess, the value for SiO_2 (col. 17), corresponding to the kaolinite represented by the Al_2O_3 values (col. 2), is found from $Al_2O_3 \times 1.1783 = SiO_2$ in kaolinite. The water of hydration (col. 19) is found from $Al_2O_3 \times 0.3535 =$ water of hydration in kaolinite. Column 18 represents the Al_2O_3 in the kaolinite. The kaolinite in the coal (col. 22) is found by adding the values for Al_2O_3 (col. 18), SiO_2 (col. 17), and H_2O (col. 19). The difference between the total SiO_2 in the coal (col. 1) and the SiO_2 in the kaolinite (col. 17) gives excess SiO_2 (col. 20).

(2) When Al_2O_3 is in excess, calculations are similar; but starting with SiO_2 as the determining value, excess alumina (col. 21) is obtained in place of excess SiO_2, as above.

The assumption that all of the alumina or silica in excess of that calculated as existing combined in kaolinite is present as free silica or alumina is no doubt incorrect. For an accurate reconstruction of the mineral matter, a mineralogical examination of each coal would first be necessary. However, the present assumptions simplify calculation and still introduce but little error into the final result, since the purpose, here, of calculating the amount of clay mineral is to arrive at an estimate for water of hydration.

(*d*) Calcium oxide (col. 6) and magnesium oxide (col. 7) were converted to their respective carbonates (cols. 23 and 24).

(*e*) Titania (col. 4), phosphorus pentoxide (col. 5), sodium oxide (col. 8), and potassium oxide (col. 9), were summed up as "all others" (col. 25).

(*f*) The sum of pyrite (col. 15), excess iron oxide (col. 16), kaolinite (col. 22), excess silica (col. 20) or alumina (col. 21), calcium carbonate (col. 23), magnesium carbonate (col. 24), and all other components (col. 25), gives the mineral content of the coal on the basis of analysis of the ash and the ash content of the coal (col. 26); assuming that all of the ash-forming materials are inorganically combined and occur approximately as the minerals listed.

(*g*) As shown by the negligible sulfate sulfur content of the coal, the SO_3 in the ash is not a component of a definite sulfate mineral in the original coal. It is derived from the pyritic sulfur already taken into account in the value for pyrite. The value for SO_3 in the ash, therefore, must not be included in the mineral matter (col. 26). However, the SO_3 in the ash acts as a diluent for the other ash components derived from the mineral matter and, as such, must be corrected for by dividing

TABLE 1.—*Mineral matter contents of coals as calculated from ash analyses and comparisons with values obtained in other ways. (Original analyses taken from U. S. Bureau of Mines Bulletin 364)*

Percentages

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Coal	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3	Pyritic S	SO_4 S	Total S	Ash	FeS_2	Excess Fe_2O^3 in ash	SiO_2 in Kaolinite	Al_2O_3 in Kaolinite
A	40.4(2.87)	38.6(2.74)	4.7(0.33)	1.5(0.11)	4.0 0.28)	5.6(0.40)	0.5(0.04)	0.4(0.03)	0.9(.06)	2.6	0.19	0.02	.78	7.1	0.36	0.09	2.87	2.44
B	54.7(4.32)	33.7(2.66)	4.3(0.34)	1.8(0.14)	0.5 (0.04)	0.7(0.06)	0.5(0.04)	0.7(0.06)	1.8(.14)	0.8	0.18	0.01	.86	7.9	0.34	0.12	3.13	2.66
C	43.6(3.71)	29.3(2.49)	19.9(1.69)	1.3(0.11)	0.14(0.01)	1.4(0.12)	0.6(0.05)	0.3(0.03)	1.1(.09)	2.0	1.12	0.03	1.90	8.5	2.10	0.30	2.93	2.49
D	43.5(4.35)	27.1(2.71)	20.8(2.08)	1.3(0.13)	0.09(0.01)	2.1(0.21)	0.7(0.07)	0.4(0.04)	1.7(.17)	1.7	1.43	0.03	2.00	10.0	2.68	0.30	3.19	2.71
E	43.9(2.37)	33.4(1.80)	15.0(0.81)	1.3(0.07)	0.13(0.01)	1.9(0.10)	0.3(0.02)	0.3(0.02)	1.0(.05)	2.5	0.56	0.01	1.22	5.4	1.05	0.11	2.12	1.80
F	45.7(5.85)	24.2(3.10)	19.7(2.52)	1.0(0.13)	0.17(0.02)	3.6(0.46)	0.8(0.10)	0.4(0.05)	2.1(.27)	1.6	1.61	0.04	2.51	12.8	3.01	0.52	3.65	3.10
G	41.2(5.73)	15.9(2.21)	23.1(3.21)	0.8(0.11)	0.12(0.02)	9.4(1.31)	0.4(0.06)	0.6(0.08)	1.9(.26)	7.4	2.17	0.04	4.01	13.9	4.06	0.51	2.60	2.21
H	55.5(6.22)	26.6(2.98)	10.9(1.22)	1.5(0.17)	0.38(0.04)	0.9(0.10)	0.9(0.10)	0.7(0.08)	1.5(.17)	0.6	0.73	0.05	1.52	11.2	1.36	0.31	3.51	2.98
HW	53.8(4.47)	27.5(2.28)	13.0(1.08)	1.4(0.12)	0.30(0.02)	1.0(0.08)	0.4(0.03)	0.7(0.06)	1.3(.11)	0.5	0.64	0.05	1.63	8.3	1.20	0.28	2.69	2.28
I	50.8(3.71)	28.5(2.08)	13.4(0.98)	1.2(0.09)	0.13(0.01)	1.1(0.08)	1.0(0.07)	1.0(0.07)	2.3(.17)	0.3	0.39	0.03	0.99	7.3	0.73	0.49	2.45	2.08
J	51.2(3.17)	24.0(1.49)	10.6(0.66)	1.8(0.11)	0.09(0.01)	4.8(0.30)	2.0(0.12)	0.6(0.04)	1.7(.11)	2.5	0.06	0.01	0.59	6.2	0.11	0.59	1.76	1.49
K	47.2(4.30)	23.2(2.11)	21.9(1.99)	1.0(0.09)	0.22(0.02)	2.4(0.22)	0.6(0.05)	0.4(0.04)	1.6(.15)	1.6	1.20	0.07	2.28	9.1	2.25	0.50	2.49	2.11
L	53.5(3.85)	30.4(2.19)	9.4(0.68)	1.3(0.09)	0.18(0.01)	0.9(0.06)	1.0(0.07)	0.9(0.06)	2.1(.15)	0.3	0.22	0.01	0.81	7.2	0.41	0.41	2.58	2.19
M	47.4(5.12)	31.1(3.36)	10.3(1.11)	1.8(0.19)	1.9 (0.21)	2.7(0.29)	0.8(0.09)	0.5(0.05)	2.1(.23)	1.0	0.59	0.04	1.40	10.8	1.10	0.38	3.96	3.36
N	55.5(6.27)	22.7(2.57)	12.7(1.44)	1.0(0.11)	0.05(0.01)	2.1(0.24)	1.3(0.15)	0.5(0.06)	2.5(.28)	1.9	0.87	0.03	2.16	11.3	1.63	0.36	3.03	2.57
O	54.9(6.04)	26.3(2.89)	12.0(1.32)	1.3(0.14)	0.17(0.02)	0.5(0.06)	0.6(0.07)	0.9(0.10)	1.9(.21)	0.7	0.90	0.01	1.80	11.0	1.68	0.20	3.41	2.89
P	52.4(5.03)	23.3(2.24)	11.5(1.10)	1.0(0.10)	0.27(0.03)	3.7(0.36)	1.0(0.10)	0.6(0.06)	1.8(.17)	3.9	0.61	0.00	1.41	9.6	1.14	0.34	2.64	2.24
Q	55.7(3.73)	28.3(1.90)	7.3(0.49)	1.5(0.10)	0.62(0.04)	2.4(0.16)	0.8(0.05)	0.6(0.04)	0.9(.06)	1.3	0.11	0.01	0.82	6.7	0.21	0.35	2.24	1.90
R	38.6(3.63)	31.1(2.92)	24.2(2.27)	1.3(0.12)	0.3 (0.03)	1.6(0.15)	0.4(0.04)	0.5(0.05)	0.8(.08)	1.1	1.42	0.03	1.93	9.4	2.66	0.50	3.44	2.92
RW	41.3(3.30)	33.1(2.65)	19.3(1.54)	1.3(0.10)	0.35(0.03)	1.8(0.14)	0.3(0.02)	0.4(0.03)	0.8(.06)	1.4	1.02	0.02	1.47	8.0	1.91	0.27	3.12	2.65
S	41.2(7.62)	13.1(2.42)	14.9(2.76)	0.8(0.15)	0.22(0.04)	15.8(2.92)	0.6(0.11)	0.8(0.15)	1.8(.33)	10.1	1.76	0.06	3.67	18.5	3.29	0.57	2.85	2.42

All analytical values on dry basis.

Column 1. Silica content of coal ash. Values in parenthesis, content of component in the coal.

Column 2. Alumina content of coal ash. Values in parenthesis, content of component in the coal.

Column 3. Iron oxide content of coal ash. Values in parenthesis, content of component in the coal.

Column 4. Titania content of coal ash. Values in parenthesis, content of component in the coal.

Column 5. Phosphoric acid content of coal ash. Values in parenthesis, content of component in the coal.

Column 6. Lime content of coal ash. Values in parenthesis, content of component in the coal.

Column 7. Magnesia content of coal ash. Values in parenthesis, content of component in the coal.

Column 8. Sodium oxide content of coal ash. Values in parenthesis, content of component in the coal.

Column 9. Potassium oxide content of coal ash. Values in parenthesis, content of component in the coal.

Column 10. Sulfur trioxide content of coal ash.

Column 11. Pyritic sulfur content of coal.

Column 12. Sulfate sulfur content of coal.

Column 13. Total sulfur content of coal.

Column 14. Ash content of coal.

Column 15. Pyrite in coal corresponding to pyritic sulfur.

Column 16. Iron oxide in coal (excess over iron oxide from pyrite).

Column 17. Silica in coal present in kaolinite.

Column 18. Alumina in coal present in kaolinite.

TABLE 1.—Concluded

Coal	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
	$\frac{2H_2O}{Al_2O_3}$	"Free" Silica	Free Alumina	Kaolinite	$CaCO_3$	$MgCO_3$	All others	Preliminary total mineral value	1.08 ash + 0.55 sulfur (Parr)	$\frac{\text{Col. 26}}{100 - \text{Col. 10 Final M.}} \times 100$	Diff. A 27-26	Diff. B 27-28	Col. 28/ Col. 14 Ratio M to A	$\frac{1.1A + 0.1S}{A}$	Col. 27/ Col. 14 Ratio (Parr) M to A
A	0.86	--------	0.30	6.17	0.71	0.08	0.48	8.19	8.10	8.41	—0.09	—0.31	1.185	1.11	1.141
B	0.94	1.19	--------	6.73	0.11	0.08	0.38	8.95	9.01	9.02	+0.06	—0.01	1.142	1.11	1.141
C	0.88	0.78	--------	6.30	0.21	0.10	0.24	10.03	10.23	10.23	+0.20	0.00	1.204	1.12	1.204
D	0.96	1.16	--------	6.86	0.37	0.15	0.35	11.87	11.90	12.08	+0.03	—0.18	1.208	1.12	1.190
E	0.64	0.25	--------	4.56	0.18	0.04	0.15	6.34	6.50	6.50	+0.16	—0.00	1.204	1.12	1.204
F	1.10	2.20	--------	7.85	0.82	0.21	0.47	15.08	15.20	15.33	+0.12	—0.13	1.198	1.12	1.188
G	0.78	3.13	--------	5.59	2.34	0.13	0.47	16.23	17.22	17.53	+0.99	—0.31	1.261	1.13	1.239
H	1.05	2.71	--------	7.54	0.18	0.21	0.46	12.77	12.93	12.85	+0.16	+0.08	1.147	1.11	1.154
HW	0.81	1.78	--------	5.78	0.14	0.06	0.31	9.55	9.86	9.60	+0.31	+0.26	1.157	1.12	1.188
I	0.74	1.26	--------	5.27	0.14	0.15	0.34	8.38	8.43	8.41	+0.05	+0.02	1.152	1.11	1.155
J	0.53	1.41	--------	3.78	0.54	0.25	0.27	6.95	7.02	7.13	+0.07	—0.11	1.150	1.11	1.132
K	0.75	1.81	--------	5.35	0.39	0.10	0.30	10.70	11.08	10.87	+0.38	+0.21	1.195	1.13	1.218
L	0.77	1.27	--------	5.54	0.11	0.15	0.31	8.20	8.22	8.22	+0.02	+0.00	1.142	1.11	1.142
M	1.19	1.16	--------	8.51	0.52	0.19	0.68	12.54	12.43	12.67	—0.11	—0.24	1.173	1.11	1.151
N	0.91	3.24	--------	6.51	0.43	0.31	0.46	12.94	13.39	13.19	+0.45	+0.20	1.167	1.12	1.185
O	1.02	2.63	--------	7.32	0.11	0.15	0.47	12.56	12.87	12.65	+0.31	+0.22	1.150	1.12	1.170
P	0.79	2.39	--------	5.67	0.64	0.21	0.36	10.75	11.14	11.19	+0.39	—0.05	1.166	1.11	1.160
Q	0.67	1.49	--------	4.81	0.29	0.10	0.24	7.49	7.69	7.59	+0.20	+0.10	1.133	1.11	1.148
R	1.03	0.19	--------	7.39	0.27	0.08	0.28	11.37	11.21	11.50	—0.16	—0.29	1.223	1.12	1.193
RW	0.94	0.18	--------	6.71	0.25	0.04	0.22	9.58	9.45	9.72	—0.13	—0.27	1.215	1.12	1.181
S	0.86	4.77	--------	6.13	5.21	0.23	0.67	20.87	22.00	23.21	+1.13	- 1.21	1.255	1.12	1.189
										Average	0.26	0.20	1.182	1.117	1.175

All analytical values on dry basis.

Column 19. Water of hydration of kaolinite in coal.
Column 20. Silica in coal not combined in kaolinite.
Column 21. Alumina in coal not combined in kaolinite.
Column 22. Kaolinite in coal.
Column 23. Calcium carbonate corresponding to lime in coal.
Column 24. Magnesium carbonate corresponding to magnesium oxide in coal.
Column 25. Sum of titania, and phosphoric acid, sodium, and potassium oxides.
Column 26. Sum of columns 15, 16, 20, 21, 22, 23, 24 and 25.
Column 27. Mineral matter found by Parr formula, 1.08 ash + 0.55 sulfur.
Column 28. Total minerals (col. 26) corrected for SO_3 in ash. This is the final estimate in mineral matter.
Column 29. Difference between columns 27 and 26.
Column 30. Difference between columns 27 and 28, being the difference between mineral contents of coal estimated by Parr formula and from ash analyses.
Column 31. Ratio of calculated mineral matter to ash.
Column 32. Ratio of (1.1 × % ash + 0.1 % sulfur) to % ash.
Column 33. Ratio of (1.08 × % ash + 0.55 % sulfur) to % ash.

the sum of mineral components (col. 26) by 100 — % SO_3 in the ash (col. 10). Conditions are usually much more favorable for retention of SO_3 in ash when large quantities of coal are burned in a confined space than when small quantities, thinly spread out, are burned as in the standard method for determining ash.

COMPARISON OF PARR AND CALCULATED MINERAL VALUES

The difference between the preliminary mineral value (col. 26) and the Parr mineral value (col. 27) is shown in column 29. Similarly, the difference between the final mineral value (col. 28) and the Parr value (col. 27) is given in column 30. The final mineral value (col. 28) is generally a little higher than the Parr value (col. 27), whereas the preliminary value (col. 26) is lower. This may be due, in the case of the preliminary value, to the reduction in other values because of the excess of SO_3 in the analyzed ash over the SO_3 in the ash as obtained in the ash determination; and, in the case of the final value, to too great a correction for SO_3 made on the assumption that the ash from the ash determination contained no SO_3. Even so, there is a remarkable agreement between the three sets of values, the average arithmetical differences from Parr values being 0.26 and 0.20 per cent in the preliminary and final values respectively. In the case of the final values, the differences were 0.20 or less in 12 cases, less than 0.30 and more than 0.20 in 6 cases, and greater than 0.30 in 3 cases out of 21. The cases of greatest difference are almost always those in which the CaO content of the ash is high, cases for which Professor Parr recommended his modified ashing procedure.[10]

MINERAL MATTER-ASH RATIOS

In view of the fact that there is an increasing tendency to use the generalized mineral matter-ash ratio of 1.1 to 1 (or some similar ratio), it seemed important to determine the mineral matter to ash ratios given by the final reconstructed mineral matter values found in Table 1 and to compare these with the ratios of Parr mineral matter (1.08 ash + 0.55 sulfur) to ash. It is seen that the ratios of calculated mineral matter to ash, (col. 31, Table 1) and of Parr mineral matter to ash (col. 33, Table 1) are closer to 1.2 than to 1.1, the average being 1.182 for column 31 and 1.175 for column 33—both being 1.18 to two decimal places. The

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[10] S. W. Parr: Chemical Study of Illinois Coals. Illinois Coal Mining Investigation, Cooperative Agreement, *Bull.* 3 (1916) 34.

individual values range from 1.133 to 1.261 for the calculated mineral matter and from 1.132 to 1.239 for Parr values. It is apparent, therefore, that 1.1 × % ash does not give a value approximating the mineral matter content of the coal. Why, then, do calorific values corrected to a dry 1.1 ash-free basis correspond so closely to unit coal values? Because the factor 1.1 includes not only the quantitative correction for ash to mineral matter, but also the calorimetric correction for the heat of combustion of sulfur. While this factor 1.1 may be acceptable in the case of low-sulfur coals for calculating unit coal calorific values, it is far from correct for unit fixed carbon calculations and is entirely erroneous for unit volatile calculations. These facts are shown by the following discussion and calculations:

Ash Correction Factors Giving Equivalent Unit Coal Values

The Parr unit coal formulas may be expressed in the form,

$$\text{Unit coal value} = \frac{\text{Determined value}}{100 - \text{f} \times \%\ \text{ash}} \times 100$$

where f is the factor, different for each individual calculation, by which the ash value must be multiplied in order that experimental values corrected to an f times ash-free basis shall equal Parr unit coal values.

Calorific Value

Table 2 presents the proximate analyses, sulfur and calorific values, and the factor calculations for the same 21 coals (listed in U. S. Bureau of Mines *Bull.* 364) as those considered in Table 1. Solving the equation just given for f we get,

$$f = \frac{100 - \dfrac{100\ \text{Determined value}}{\text{U. C. value}}}{\%\ \text{ash}}$$

The values for f for calorific value calculation are given in column 10, averaging 1.1188 (1.12), ranging between 1.1016 and 1.1410, a difference of 0.0394 or 3.5 per cent of the average, the greatest deviation being 2 per cent of the average. The values are reasonably close to 1.1 but, it is pointed out, are lower than the actual ratio of mineral matter to ash.

Fixed Carbon

In the case of fixed carbon (col. 15), the average value is 1.1368 (1.14) ranging from 1.1145 to 1.1640, a difference of 0.0495 or 4.35

TABLE 2.—*Calculations of ash correction factors giving mineral-free coal analysis values corresponding to Parr unit coal values.* (*Original analyses from U. S. Bureau of Mines Bulletin 364*)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Coal	Volatile matter, per cent	Fixed carbon, per cent	Ash, per cent	Total S, per cent	B.t.u. per lb. experimental	Unit coal B.t.u. per lb.	$\frac{\text{Col. 6}}{\text{Col. 7}}$	100 (1 — Col. 8) f × ash	$\frac{\text{Col. 9}}{\text{Col. 4}}$ B.t.u. ash f	Unit fixed carbon, per cent	Unit volatile (100 — Col. 11) per cent	$\frac{\text{Col. 3}}{\text{Col. 11}}$	100 (1 — Col. 13) f × ash	$\frac{\text{Col. 14}}{\text{Col. 4}}$ F. C. ash f	$\frac{\text{Col. 2}}{\text{Col. 12}}$	100 (1 — Col. 16) f × ash	$\frac{\text{Col. 17}}{\text{Col. 4}}$ Volatile-ash f
A	16.2	76.7	7.1	0.8	14,520	15,758	.9214	7.86	1.1070	83.34	16.66	0.9203	7.97	1.1225	0.9724	2.76	0.3887
B	19.3	72.8	7.9	0.9	14,410	15,790	.9126	8.74	1.1063	79.88	20.12	0.9114	8.86	1.1215	0.9592	4.08	0.5165
C	24.5	67.0	8.5	1.9	14,330	15,856	.9038	9.62	1.1318	74.31	25.69	0.9016	9.84	1.1576	0.9537	4.63	0.5447
D	15.9	74.1	10.0	2.0	13,990	15,766	.8874	11.26	1.1260	83.77	16.23	0.8846	11.54	1.1540	0.9797	2.03	0.2030 L.
E	21.4	73.2	5.4	1.2	14,850	15,817	.9389	6.11	1.1315	78.09	21.91	0.9374	6.26	1.1593	0.9767	2.33	0.4315
F	39.6	47.6	12.8	2.5	12,470	14,558	.8566	14.34	1.1203	55.69	44.31	0.8547	14.53	1.1352	0.8937	10.63	0.8305
G	36.9	49.2	13.9	4.0	12,460	14,809	.8414	15.86	1.1410 H.	58.70	41.30	0.8382	16.18	1.1640 H.	0.8935	10.65	0.7662
H	32.8	56.0	11.2	1.5	13,600	15,532	.8756	12.44	1.1107	64.05	35.95	0.8743	12.57	1.1223	0.9124	8.76	0.7821
HW	34.0	57.7	8.3	1.6	14,070	15,518	.9067	9.33	1.1241	63.73	36.27	0.9054	9.46	1.1398	0.9374	6.26	0.7542
I	21.0	71.7	7.3	1.0	14,470	15,748	.9188	8.12	1.1123	78.14	21.86	0.9176	8.24	1.1288	0.9607	3.93	0.5384
J	21.2	72.6	6.2	0.6	14,750	15,832	.9317	6.83	1.1016 L.	77.99	22.01	0.9309	6.91	1.1145 L.	0.9632	3.68	0.5935
K	36.4	54.5	9.1	2.3	13,580	15,145	.8967	10.33	1.1352	60.91	39.09	0.8948	10.52	1.1560	0.9312	6.88	0.7560
L	17.9	74.9	7.2	0.8	14,520	15,776	.9204	7.96	1.1056	81.47	18.53	0.9194	8.06	1.1194	0.9660	3.40	0.4722
M	18.0	71.2	10.8	1.4	13,850	15,737	.8801	11.99	1.1102	81.07	18.93	0.8783	12.17	1.1269	0.9509	4.91	0.4546
N	35.4	53.3	11.3	2.2	12,850	14,714	.8733	12.67	1.1212	61.18	38.82	0.8712	12.88	1.1398	0.9119	8.81	0.7796
O	33.1	55.9	11.0	1.8	13,460	15,345	.8772	12.28	1.1164	63.85	36.15	0.8755	12.45	1.1318	0.9156	8.44	0.7673
P	35.0	55.4	9.6	1.4	13,600	15,226	.8932	10.68	1.1125	62.11	37.89	0.8920	10.80	1.1250	0.9237	7.63	0.7948
Q	34.2	59.1	6.7	0.8	14,280	15,424	.9258	7.42	1.1075	63.88	36.12	0.9252	7.48	1.1164	0.9468	5.32	0.7940
R	16.9	73.7	9.4	1.9	14,120	15,793	.8941	10.59	1.1266	82.67	17.33	0.8915	10.85	1.1543	0.9752	2.48	0.2638
RW	16.9	75.1	8.0	1.5	14,390	15,812	.9101	8.99	1.1238	82.70	17.30	0.9081	9.19	1.1488	0.9769	2.31	0.2888
S	37.7	43.8	18.5	3.7	11,640	14,689	.7924	20.76	1.1222	55.45	44.55	0.7899	21.01	1.1357	0.8462	15.38	0.8314 H.
Averages									1.1188					1.1368			0.5977
Range of values, per cent of average									3.5					4.35			105
Greatest deviation, per cent of average									2.0					2.4			66

All analytical values on dry basis.

H = High value.

L = Low value.

Column 1. Sample.
Column 2. Volatile matter in coal.
Column 3. Fixed carbon in coal.
Column 4. Ash in coal.
Column 5. Total sulfur in coal.
Column 6. Determined calorific value.
Column 7. Unit coal calorific value.
Column 8. Ratio determined to unit calorific value.
Column 9. 100 times 1 minus column 8.
Column 10. Ash correction factor for calorific value calculation to unit coal basis.
Column 11. Unit fixed carbon in coal.
Column 12. Unit volatile matter in coal.
Column 13. Ratio determined to unit fixed carbon.
Column 14. 100 times 1 minus column 13.
Column 15. Ash factor for fixed carbon calculation to unit coal basis.
Column 16. Ratio determined to unit volatile matter.
Column 17. 100 times - minus column 16.
Column 18. Ash factor for volatile-matter values.

per cent of the average, the greatest deviation being 2.4 per cent of the average. The average fixed carbon *f* value is 1.5 per cent greater than the average calorific value *f*. It will be noted that the range of variation in the individual fixed carbon *f* values is greater than the range of variation in the calorific value factor.

VOLATILE MATTER

When we consider the volatile-matter formula, we find an entirely different situation. Unit volatile matter values are always less than moisture-and-ash-free values, due to the corrections for water of hydration of the clay minerals and for the volatile sulfur. The factor is therefore less than unity (col. 18). We find that the factors range from 0.2030 to 0.8314. A formula for mineral-matter-free volatile matter in which no correction is made in the numerator and in which mineral matter values are used in place of ash values in the denominator is therefore incorrect. Furthermore, the variations are so great in the ash correction factor that no one value can be used. The formulas,

$$\%\ \text{Mineral-matter-free volatile} = \frac{\%\ \text{Determined volatile}}{100 - (\%\ \text{M} + 1.1 \times \%\ \text{ash})} \times 100$$

or,

$$\%\ \text{Mineral-matter-free volatile} = \frac{\%\ \text{Determined volatile}}{100 - f \times \%\ \text{ash}} \times 100$$

or similar ones, are entirely unacceptable, since the corrections that they make are in the wrong direction.

FORMULAS BASED UPON THE TERMS 1.1 ASH + 0.1 SULFUR

Recently proposals[11] have been made that coal analyses be corrected to mineral-matter-free values by means of the following fomulas:

Mineral-matter-free dry calorific value =

$$\frac{\text{Determined calorific value}}{100 - (\text{M} + 1.1 \times \%\ \text{ash} + 0.1 \times \%\ \text{sulfur})} \times 100$$

Mineral-matter-free dry fixed carbon =

$$\frac{\text{Determined fixed carbon} + \text{correction}}{100 - (\text{M} + 1.1 \times \%\ \text{ash} + 0.1 \times \%\ \text{sulfur})} \times 100.$$

The first formula includes, in the denominator, the correction made in the numerator of the Parr formula. The second formula assumes

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[11] Report No. 7, Subcommittee 11 on Origin, Composition and Methods of Analysis, Sectional Committee on Classification of Coal, A. S. T. M.

that 1.1 ash + 0.1 sulfur is equivalent to mineral matter. The ratio of 1.1 ash + 0.1 sulfur to ash was found for the 21 coals in Table 1 in order to compare them with the various ash-factor values previously mentioned. These values are compared in Table 3. For calculating mineral matter, the 1.1 ash + 0.1 sulfur formula gives low results compared with values reconstructed from ash analyses and from the Parr formula. The 1.1 ash + 0.1 sulfur values compare very well with the ash factor found in Table 1, which would give the same corrected calorific value as the Parr formula. Similarly, the value is low, compared with the corresponding factor for fixed carbon; and, as mentioned before, very much too large for mineral-matter-free volatile computations.

TABLE 3.—*Ash conversion factors found by or equivalent to corrections in various formulas*

(1.1 ash + 0.1 sulfur)/ash	1.117	(1.12)
(1.08 ash + 0.55 sulfur)/ash	1.175	(1.18)
Reconstructed mineral/ash	1.182	(1.18)
Calorific value *f*	1.1188	(1.12)
Fixed carbon *f*	1.1368	(1.14)

CONCLUSIONS

1. The Parr formula, Mineral matter in coal = 1.08 × % ash + 0.55 % sulfur, gives values that closely agree with mineral matter values found by calculation from ash analyses.

2. If the formulas for calculating mineral-matter-free coal values are placed in the form,

$$\text{Mineral-matter-free value} = \frac{\text{Determined value}}{100 - f \times \%\ \text{ash}} \times 100$$

and the values of f are determined, it is found that the factors f required to give mineral-matter-free analytical values equal to unit coal values are of different magnitudes for the calorific value, fixed carbon, and volatile matter. In the following paragraphs, f will be referred to as the "ash factor."

3. The ash factor in the calorific value formula was found to average 1.1188 with a range of 3.5 per cent of this value for 21 coals.

4. The ash factor in the fixed carbon formula was found to average 1.1368 with a range of 4.35 per cent of this value for 21 coals.

5. The ash factor in the volatile matter formula was less than unity and ranged from 0.2030 to 0.8314 for 21 coals. The use of corrections which increase the ash values and which apply no corrections in the numerator are incorrect.

6. If calorific values are corrected to a dry, 1.1 ash + 0.1 sulfur-free basis (no heat correction), values approaching Parr unit coal values are obtained but the agreement is not always close enough to be satisfactory.

7. In unit coal formulas simplified to the extent of combining the corrections in the numerator terms with the terms in the denominator, it is erroneous to use the same denominator for calorific, fixed carbon and volatile matter values.

8. Because of the difference in the magnitudes of the correction terms in the numerator of unit coal formulas compared with the analytical values, only the calorific value formula can be simplified to the extent of combining the correction terms in the denominator and yet preserve a sufficient degree of approximation to the original formula. While for coals of certain analyses, such fixed carbon formula so simplified may give satisfactory results, the general uncertainty is so great as to rule out this possibility. It is impossible to simplify the volatile matter formula in this manner.

9. The original Parr unit coal formulas appear to be the most acceptable coal analysis correction formulas so far proposed.

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UNIT COAL AS A BASIS OF COAL STANDARDIZATION AS APPLIED TO ILLINOIS COALS*

By Gilbert H. Cady† and O. W. Rees°

ABSTRACT

Unit coal calorific values represent a close approach to pure coal values; they possess characteristics theoretically inherent in the latter values; they are essentially uniform in the same seam for areas possessing essentially uniform environment; they are higher in older than in younger coals in most cases, at least, and in deeper than in more shallow coals. In general, they display characteristics closely in accordance with expectation, assuming that they are essentially indices of rank. Because it possesses these characteristics, the unit coal value is essentially a standard value characteristic of each bed in each local region. Hence it can be used as a basis for determining the accuracy of results in newly established laboratories, or when new equipment is installed, or in checking the results of different laboratories, or even in determining the character of coal as mined or prepared, if ash, moisture, and sulfur values are known.

INTRODUCTION

Belief in the fundamental significance of the pure coal value as a basis of comparison and evaluation of coals originally led Professor Parr to the development of the unit coal formula,[1] which he believed would give values closely approximating those of theoretical pure coal. Unit coal values, particularly calorific values, have been in continuous use by the Illinois State Geological Survey since about 1909.[2]

Since a large body of analytical information about Illinois coals is now available, it should be possible to demonstrate the usefulness of unit coal values, particularly the calorific values, for the purposes for which they were originally devised. Two lines of demonstration are essential.

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[1] Parr, S. W., and Wheeler, W. F., Unit coal and the composition of coal ash: University of Illinois Eng. Exp. Sta. Bull. 37, pp. 2-5, 1909.

[2] DeWolf, Frank W., Introduction to studies of Illinois coal: Illinois State Geol. Survey Bull. 16, p. 178, 1910.

Parr, S. W., The chemical composition of Illinois coals: Illinois State Geol. Survey Bull. 16, pp. 203-243, 1910.

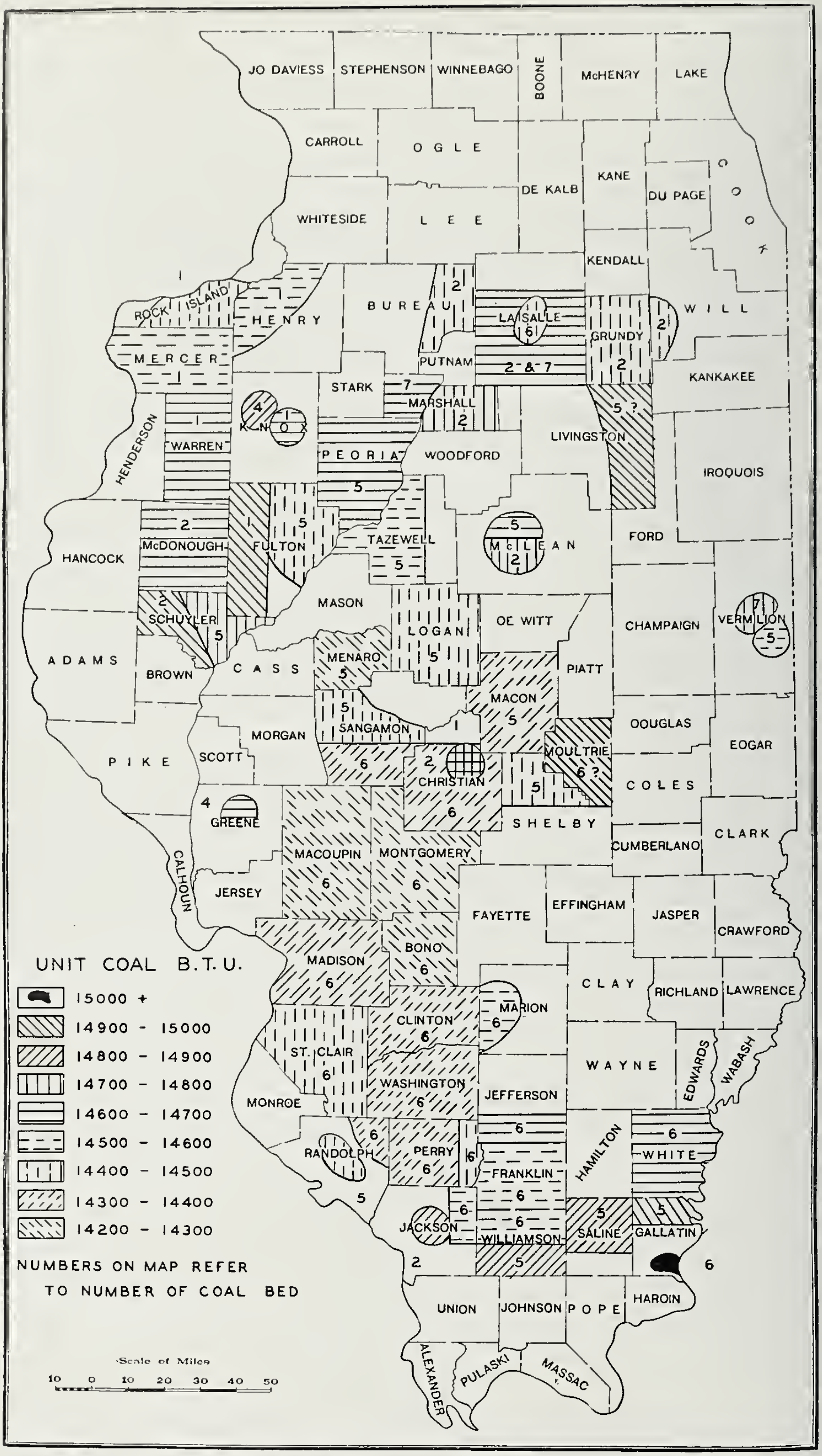

FIG. 1. Map of Illinois, showing the distribution of unit coal calorific values by county and seam. Data from Illinois State Geological Survey Bulletin 56, pages 90-94.

First, it must be shown that the variations in these values are regular and systematic, being in accordance with and in response to variations or differences in geological conditions, thereby showing that variations in unit coal values are indicative of variations in rank, and hence are fundamental in character. Second, it is necessary to show that within a local area possessing geological uniformity an individual coal seam is characterized by uniform unit coal values. If the unit coal values meet these two essential requirements, they would appear to be a suitable basis for coal standardization. If, on the other hand, variations in unit coal values of a uniform type of coal are not due to variations in rank, then the cause of variation is unknown and no special significance can be attached to erratic values; likewise, if individual coal beds in regions of geological uniformity, do not locally possess uniformity of fundamental character, as indicated by the unit coal values, these values are of no significance as indices of rank.

In line with the foregoing argument the present discussion will endeavor to show first, that the variations in unit coal values are in accordance with the variations in geological environment; second, that the unit coal values for local areas are essentially uniform, and third, that the standard values thus obtained are useful in checking chemical procedure and in other related ways. In the discussion only unit coal calorific values will be considered.

Variations in Unit Coal Values as Related to Geological Conditions

The general distribution of unit coal calorific values is shown by figure 1, which is based upon county average values. The simple geographic distribution of values shows considerable variation and rather heterogeneous distribution, although certain associated groups of counties evidently are in the same category with respect to heat value. However, any systematic variation in the values is difficult if not impossible to discover, and, without further analyses, there might appear to be little basis for believing that such variation exists. On the other hand, when the values are arranged as in Table 1, so that the geographic distribution of the calorific values for each seam can be readily seen, more definite relationships between the geological features and the unit coal values can be discovered. From the table it can be shown (1) that in general the older coals have the higher B.t.u. value, (2) that the calorific value in general increases with the increase in the probable original depth of burial, and (3) that there is a general tendency for each seam to increase in calorific value toward the areas of diastrophic instability.

TABLE 1.—*Geographic variation in the unit coal values for each seam*

B.t.u.	County
	Rock Island (No. 1) coal [a]
14,900 – 15,000	Fulton County
14,600 – 14,700	Knox and Warren counties
14,500 – 14,600	Henry and Mercer counties
14,400 – 14,500	Rock Island County
	LaSalle (Colchester) (No. 2) coal
14,900 – 15,000	Schuyler County
14,700 – 14,800	Marshall and McLean counties
14,600 – 14,700	LaSalle and McDonough counties
14,400 – 14,500	Bureau, Grundy, and Will counties
	Summum (No. 4) coal
14,800 – 14,900	Knox County
14,600 – 14,700	Greene County
	Harrisburg (No. 5) coal [b]
14,900 – 15,000	Gallatin County
14,800 – 14,900	Saline and Williamson counties
14,400 – 14,500	Randolph County
	Springfield (No. 5) coal (Grape Creek coal in Vermilion County)
14,700 – 14,800	Schuyler County
14,600 – 14,700	McLean and Peoria counties
14,500 – 14,600	Tazewell and Vermilion counties
14,400 – 14,500	Fulton, Logan, Sangamon, Shelby counties
14,300 – 14,400	Macon County
14,200 – 14,300	Menard County
	Herrin (No. 6) coal
+ 15,000	Gallatin County (Eagle Valley district)
14,900 – 15,000	Moultrie County
14,600 – 14,700	Jefferson and White counties
14,500 – 14,600	Franklin, Jackson, Marion, and Williamson counties
14,400 – 14,500	East Perry and St. Clair counties
14,300 – 14,400	Christian, Clinton, Madison, West Perry, Randolph, Sangamon and Washington counties
14,200 – 14,300	Bond, Montgomery, and Macoupin counties
	Danville (No. 7) coal
14,700 – 14,800	Vermilion County
14,600 – 14,700	LaSalle and Marshall counties

(*a*) It is possible that Murphysboro (No. 2) coal of Jackson County is the same as the Rock Island (No. 1) coal of northern Illinois. This coal has a unit coal calorific value of between 14,800 and 14,900.

(*b*) It is possible that the Harrisburg (No. 5) coal is not the same as Springfield (No. 5) coal. It may be the same as the Summum (No. 4) coal.

Preliminary to a brief discussion of each of these points, it is probably desirable to explain the general stratigraphic relationships with respect to the commercially important coals in the Illinois basin. The Pennsylvanian system in Illinois with a total original thickness probably in excess of 3,000 feet, contains six commercially important seams known from above downward as No. 7, No. 6, No. 5, No. 4, No. 2, and No. 1. No. 7 coal lies between 1,500 and 2,000 feet below the probable original top of the system; No. 1 coal lies about 750 feet above the base, and probably never more than 500 feet below coal No. 7. Both because of surface erosion and the thinning of individual beds, the "Coal Measures" thin in all directions away from the axis of the Illinois basin but particularly toward the north and west. Structural disturbances affected the "Coal Measures" notably (1) along the LaSalle anticline, which lies along the northeast side of the main Illinois basin and separates it from the Indiana basin, the western margin of which extends into Illinois, (2) along the DuQuoin anticline, a monoclinal fold extending about north and south from near Sandoval, Marian County, to near De Soto, Jackson County, and (3) in the Ozark province south of the present productive coal field. The coal in the southern counties, Perry, Jackson, Williamson, Saline, and Gallatin, was elevated to erosion level with the positive movements in the adjacent Ozark province.

Effect of Difference in Age on Unit Coal Values

From the data presented in Table 1, it appears that in central and northern Illinois the lower coals, particularly coals No. 1 and No. 2, show a relatively high unit coal value. Coal No. 1, in general, has a calorific value above 14,500 and coal No. 2, except for marginal areas in Bureau, Grundy, and Will counties, has a value exceeding 14,600. In contrast, it may be noted that much of Springfield No. 5 coal and Herrin No. 6 coal has a calorific value less than 14,500.

Further evidence that calorific quality improves with the age of the coal bed is the fact that in general the older or oldest of two or more coals in the same region has the higher or highest calorific value. The following table (Table 2) shows the different values given for different coals in the same counties. A positive or negative sign follows the value depending on whether it is larger or smaller than the preceding value representing the next lower coal. The fact that most of the signs are negative indicates a general decrease in calorific value for the higher and younger coals. In three instances the higher and younger coal has a higher calorific value than the lower coal or coals. It is noteworthy that in two instances the higher coal is coal No. 7. Recent tests on a coal from No. 7 seam in Vermilion County suggest that possibly the

Table 2.—*Unit coal values of different seams in the same county*

(+ or — sign follows the calorific value depending upon whether it is larger or smaller than the preceding value on the same line)

County	Coal below No. 2 (*a*)		Coal No. 1	Coal No. 2	Coal No. 4	Coal No. 5S (*b*)	Coal No. 5N (*c*)	Coal No. 6	Coal No. 7
	A	B							
Christian	14,756	14,690 (—)						14,389 (—)	
Fulton			14,956				14,493 (—)		
Jackson			14,820 (*d*)					14,584 (—)	
Knox			14,653		14,794 (+)				
LaSalle				14,599				14,399 (—)	14,684 (+)
Marshall				14,777					14,627 (—)
McLean				14,717			14,605 (—)		
Randolph						14,441		14,349 (—)	
Schuyler				14,973			14,737 (—)		
Vermilion								14,590	14,770 (+)
Williamson						14,818		14,598 (—)	

(*a*) Coals formerly mined at Assumption and called No. 1 and 2 but probably older than coal No. 2 and not certainly equivalent to coal No. 1.

(*b*) Coal 5S: Harrisburg No. 5 coal possibly not the same as Springfield No. 5 coal.

(*c*) Coal 5N: Springfield No. 5 coal.

(*d*) Murphysboro No. 2 coal is now regarded as possibly the same as the Rock Island No. 1 coal.

county average value, 14,770 is too high. Unfortunately, verification of the values for coal No. 4 in Knox County and coal No. 7 in LaSalle County are no longer possible.

EFFECT OF DEPTH OF BURIAL ON THE UNIT COAL VALUE

The data in Table 3 indicate the possible effect of differences in depth of burial upon the thermal value of a coal bed, but this can also readily be shown by observing the increase in this value for the same bed as depth of burial increases (Table 1 and Figure 1). As an individual bed is traced eastward from the west margin of the basin or southward from the north margin it becomes overlain by a greater and greater thickness of material which originally probably exceeded the thickness of the present overburden. The following table (Table 3) in which data given in Table 1 are specially arranged shows how values for two coals change as the trough of the basin is approached.

TABLE 3.—*County average unit coal values of the same seam arranged to show the change accompanying approach to the axis of the basin*

A Coal No. 6		B Coal No. 2	
County	Unit B.t.u.	County	Unit B.t.u.
West:		North:	
Randolph	14,349	Bureau	14,469
Western Perry	14,336	LaSalle	14,684
DuQuoin Anticline		Woodford	14,693
Eastern Perry	14,421	McLean	14,714
Franklin	14,598	South:	
East·			

The order in which the counties are listed under Rock Island (No. 1) coal in Table 1 is in general from south to north. The decline in B.t.u. value in the same direction shown by the figures in the table indicate the effect of approach to what was probably the original margin of the basin. Other examples than those given could be readily arranged.

EFFECT OF APPROACH TO AREAS OF DIASTROPHIC INSTABILITY UPON UNIT COAL VALUES

In Table 1 both the Harrisburg (No. 5) and the Herrin (No. 6) coals show by the arrangement of the counties with respect to calorific value the general effect of approach to the area of diastrophic instability at the southern border of the coal basin. This is particularly indicated by the high calorific value characteristic of both coals in Gallatin County and by the general increase in the values of the Harrisburg No. 5 coal toward the southeast from Randolph to Gallatin County.

Recent studies by Benson and Cady[3] of the relation between unit coal values of coal No. 6 and structural features in Franklin and Williamson counties have revealed a definite increase in calorific value in and adjacent to two zones of deformation as well as a regional southward increase.

It is not definitely apparent that deformation along the LaSalle anticline materially affected the character of the coals in or adjacent to this zone of movement. It has been observed that coals east of the anticline commonly have a higher unit coal calorific value than coals in the same latitude west of the anticline. Inspection of Figure 1 will show the relatively high unit coal calorific value of the coals in Livingston and Vermilion counties as compared with coals in counties directly to the west in each instance. This difference does not hold, however, with respect to LaSalle No. 2 coal in northern Illinois. (Compare the values for coal No. 2 in LaSalle and Grundy counties, Figure 1.)

It has long been known that the calorific value of Herrin No. 6 coal increases rather abruptly from between 14,300 and 14,400 west of the DuQuoin anticline (Table 1—Herrin (No. 6) coal) to above 14,500 in Williamson and Franklin counties.[4] This may be due to diastrophic instability, but it may also be partly or entirely due to increase in thickness of overburden from west to east across the general position of the anticline.

These relations of variations in unit coal calorific values to geological conditions indicate that the unit coal value is an index of the rank of a coal as determined by the geological vicissitudes to which it has been subjected. This being the case it is reasonable to believe that a coal of uniform type in a local area of geological uniformity will possess uniform calorific value which may be taken as a standard for classification and comparison. The facts appear to support this belief. It is the custom of the Illinois State Geological Survey to group mines by counties in compiling averages. In spite of the fact that this is not always the most natural grouping, the results are sufficiently satisfactory to establish the principle of uniformity (Table 4).

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[3] Benson, E. T., and Cady, G. H., Variations in the Chemical Character of Coal No. 6 in Franklin-Williamson District, Illinois. Presented before the Society of Economic Geologists, Chicago, December 30, 1933. Illinois State Geol. Survey. Rept. Inv. No. 35 (in press).

[4] Bement, A., Illinois Coal: Illinois State Geol. Survey Bull. 56, page 34, 1932.

Table 4.—*Maximum positive and negative deviations of mine averages from county average unit coal B.t.u. values for ten counties with ranges of deviation, average deviation and number of mines for each county for which the deviation is less than 100 units*

County	Bed	Number of mines	Maximum positive deviation B.t.u. units	Maximum negative deviation B.t.u. units	Range of deviation B.t.u. units	Average deviation B.t.u. units	Number of mines with deviation less than 100 units
Franklin...	6	21	136	151	287	67.3	16
Jackson....	2	5	68	115	183	47.0	4
Madison...	6	7	62	52	114	35.8	7
Marion....	6	3	40	25	65	27.0	3
Peoria.....	5	7	108	108	216	55.4	5
Perry (West) (*a*)	6	10	115	72	187	51.9	9
Saline.....	5	16	159	79	238	49.1	15
Sangamon.	5	9	48	43	91	22.1	9
Sangamon.	6	3	22	19	31	17.7	3
Vermilion..	6 (5?)	5	68	48	116	28.0	5

(*a*) West of the DuQuoin anticline.

Having shown the theoretical and actual validity of standard unit coal values as indices of geological rank and the consequent uniformity of such values in local areas possessing geological uniformity, thereby establishing the validity of the concept, it remains to show how such standard values, once accepted as representing the actual character of the coal, are a useful tool in chemical procedure.

APPLICATION OF UNIT COAL VALUES TO CHEMICAL PROCEDURE AND RESULTS

In spite of the standardization and perfection of methods of analyses and the check afforded by running analyses in duplicate both in the same and in different laboratories, some means of recognizing anomalous values requiring special substantiation is desirable, as there is always a possibility that unknown factors may have modified procedure and affected the results. This is particularly desirable when there is a change in personnel or a slight modification of conditions for experimental purposes. Such a means of checking results is found in well-established average unit coal values, particularly the calorific value.

A brief explanation of the use of unit coal values is possibly desirable. It should be realized that comparisons made in this discussion are between individual analyses of different samples of coal, not between analyses of duplicate samples of the same coal. The use of unit coal values in no way supplants the routine checking of analytical results by the use of such duplicate samples in the same or in different laboratories.

It often happens, however, during a period of years that a series of analyses is run on coal from the same general region, there being no means of checking earlier results with those subsequently determined except the means supplied by the analytical results themselves. It has been the experience of the Illinois Geological Survey that reducing values to the simple and theoretically sound basis of pure coal as represented by the unit coal values provides the best basis for such comparison. It is not contended that B.t.u. values calculated from unit coal values shall be substituted for direct determination for accurate scientific work. It will, however, be suggested as a substitute for direct determinations as a convenience in commercial work.

The use of standard unit coal calorific values in our laboratories is briefly described:

Use in Routine Analysis: In Table 5 will be found a comparison of unit B.t.u. values, as determined in this laboratory by analyses run in duplicate, with average values for the appropriate counties.[5] In column 4 appear the determined values; in column 5, the county averages; and in column 7, the differences between the determined values and the county averages. In twenty out of twenty-four cases, the determined unit B.t.u. value varies from the corresponding county average less than 100 units.

The table is introduced to bring out two points: First, the general close agreement of the individual values with the average values, although the averages are based upon analyses made at different times through a period of twenty years in two unrelated laboratories. Second is the importance of substantiating the values which are not in close agreement with the general values. It is our general practice to require substantiation of values departing more than 100 units from the average value, although this is not always done. Such values may not be wrong and if substantiated must be accepted as valid, although the reason for their anomalous character may not be apparent. In some instances county average values have been found unsatisfactory because of considerable local variations within the area of a county due to proximity of areas of diastrophic disturbance. Thus, the wide departure of the calorific value from the county average in the case of the two samples from Williamson County (Table 5) is due largely to the fact that the average for the county is compiled from mines located in the west half of the county, whereas in the east half of the county, for which there are few analyses, the unit coal calorific value is nearer 14,700 than 14,600. Analysis No. C-125 was made from a sample cut from a column of coal that had been in cold storage about one year.

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[5] Bement, A., Illinois coal: Illinois State Geol. Survey Bull. 56, pages 99-104, 1932.

The usefulness of the unit coal values to the chemist is determined by the representative character of the averages used. If the method has not been used and a start is to be made, the average must first be determined from available values. Although presumably all available analyses made in accordance with standard procedure will be used, none, of course, will have been checked against average values, so that the resulting averages may eventually require considerable modification as additional analyses, which may be checked against the average values, become available. Special assurance of the accuracy of anomalous values is provided if laboratories use this checking system. Unquestionably verified results will now and then depart more than the usual amount from the local average value; there should be special assurance that such values are accurately determined. Not uncommonly, it is found that anomalies disappear upon the redetermination of values.

TABLE 5.—*Comparison of determined unit B.t.u. values with county averages*

1	2	3	4	5	6	7
Lab. No.	Coal bed	County	Unit B.t.u. determined	Unit B.t.u. (county average)	Number mines averaged	Difference between determined and county average B.t.u.
C-48.....	6	Franklin......	14,577	14,554	22	+ 23
C-198....	6	Franklin......	14,557	14,554	22	+ 3
C-200....	6	Franklin......	14,560	14,554	22	+ 6
C-409....	6	Franklin......	14,609	14,554	22	+ 55
C-122....	6	Macoupin.....	14,195	14,259	11	— 64
C-123....	6	Montgomery...	14,313	14,288	6	+ 25
C-124....	6	Montgomery...	14,196	14,288	6	— 32
C-197....	6	Perry.........	14,231	14,336	10	—105
C-383....	6	Randolph.....	14,377	14,349	4	+ 28
C-33.....	6	St. Clair.......	14,377	14,458	10	— 81
C-34.....	6	St. Clair.......	14,517	14,458	10	+ 59
C-38.....	6	St. Clair.......	14,530	14,458	10	+ 72
C-119....	6	St. Clair.......	14,515	14,458	10	+ 57
C-120....	6	St. Clair.......	14,467	14,458	10	+ 9
C-121....	6	St. Clair.......	14,457	14,458	10	— 1
C-360....	5	Saline.........	14,842	14,818	16	+ 24
C-361....	5	Saline.........	14,895	14,818	16	+ 77
C-258....	6	Washington....	14,371	14,382	2	— 11
C-367....	6	Washington....	14,502	14,382	2	+120
C-368....	6	Washington....	14,349	14,382	2	— 33
C-369....	6	Washington....	14,367	14,382	2	— 15
C-415....	6	Washington....	14,465	14,382	2	+ 83
C-37.....	6	Williamson....	14,736	14,598	28	+138
C-125....	6	Williamson....	14,774	14,598	28	+176
Average.....						54

Use in a New Laboratory.—The unit coal value provides a useful means of checking analytical results in a new laboratory. In standardizing a recently purchased adiabatic calorimeter in 1931, excessive calorific values were obtained from standard benzoic acid. There was no apparent reason to suspect the water equivalent factor furnished by the makers of the instrument, so that the fault was thought to lie in the technique of the operator who was unfamiliar with the operation of the calorimeter. A procedure was then developed that appeared to overcome this supposedly faulty technique because it gave satisfactory results with standard substances furnished by the U. S. Bureau of Standards, such as benzoic acid, naphthalene, and sucrose. However, we found that when used in coal analyses the calorimeter gave values which, when calculated to the unit coal basis, were prevailing higher than the county averages.

TABLE 6.—*Comparison of unit B.t.u. values obtained with water equivalent factor supplied by the manufacturer of the calorimeter and those obtained by the corrected factor*

1	2	3	4	5	6	7	8	9	10	11
Column	Coal bed	County	County average unit B.t.u.	Number of mines averaged	Unit B.t.u. face sample old W. E.*	Variation from county average	Unit B.t.u. face sample new W. E.	Variation from county average	Unit B.t.u. column sample new W. E.	Variation from county average
1	6	St. Clair.....	14,458	10	14,887	+429	14,563	+105	14,515	+ 57
2	6	St. Clair.....	14,458	10	14,693	+235	14,574	+116	14,377	— 81
3	6	St. Clair.....	14,458	10	14,670	+212	14,532	+ 74	14,467	+ 9
4	6	St. Clair.....	14,458	10	14,712	+254	14,485	+ 27	14,457	— 1
5	6	St. Clair.....	14,458	10	14,740	+282	14,376	— 82	14,517	+ 59
6	6	St. Clair.....	14,458	10	14,899	+441	14,657	+199	14,530	+ 72
10	6	Macoupin...	14,259	11	14,535	+276	14,428	+169	14,195	— 64
11	6	Christian....	14,389	4	14,621	+232	14,386	— 3	14,272	—117
14	6	Montgomery	14,288	6	14,515	+227	14,300	+ 12	14,313	+ 25
15	6	Montgomery	14,288	6	14,408	+120	14,198	— 90	14,196	— 92
24	6	Franklin....	14,554	22	14,925	+371	14,579	+ 25	14,661	+107
30	6	Williamson..	14,598	28	14,943	+345	14,713	+115	14,774	+176
31	6	Williamson..	14,598	28	14,955	+357	14,737	+139	14,736	+138
Average variation..						291		89		77

* W. E. = Water equivalent.

Careful restandardization showed that the original water equivalent factor supplied by the manufacturer was too high by about 100 units. This discrepancy no doubt would have eventually been discovered without the use of pure coal values, but the relatively greater importance of variations in such value as compared with determined values made discovery much simpler and more probable.

In Table 6 will be found the calorific determinations made by using the water equivalent factor supplied by the maker of the calorimeter and those made using the corrected factor, the values being compared with the county average values. Analyses represented by columns 6 and 8 are of duplicate samples whereas the analyses represented by column 10 are samples of the same columns of coal cut separately. None of the samples were fresh coal, but the values in column 10 in general substantiate those in column 8, both being in fair agreement with the county average as compared with the wide disagreement with the county average of values obtained using the original water equivalent factor as shown in columns 6 and 7. The data are introduced to illustrate one use made of county average values, and not to demonstrate similarity of individual unit coal values to the county averages; for in this case all the samples were old and hence possibly more or less weathered so that there is considerable possibility of individual variation.

TABLE 7.—*Comparison of average fraction values, face values, county averages, and head sample values of certain coals used in running float-and-sink tests*

1	2	3	4	5	6	7	8	9	10
Column	Coal bed	County	County average unit B.t.u.	Average of fractions	Variation from county average	Face samples	Variation from county average	Reruns head samples	Variation from county average
1	6	St. Clair.....	14,458	13,958	—500	14,563	+105	13,953	—505
3	6	St. Clair.....	14,458	13,904	—554	14,532	+ 74	......	......
6	6	St. Clair.....	14,458	13,994	—464	14,657	+199	14,066	—392
10	6	Macoupin...	14,259	13,606	—653	14,428	+169	13,655	—604
15	6	Montgomery	14,288	13,531	—757	14,198	— 90	13,552	—736
18	6	Washington.	14,382	13,889	—493	13,961	—421	13,897	—485
21	6	Randolph...	14,349	13,902	—447	14,159	—190	......	......
22	6	Perry.......	14,336	14,135	—201	14,231	—105	......	......
24	6	Franklin....	14,554	14,326	—228	14,579	+ 25	......	......
27	6	Franklin....	14,554	14,330	—224	14,557	+ 3	14,450	—104
31	6	Williamson..	14,598	14,412	—186	14,737	+139	14,446	—152
33	5	Saline.......	14,818	14,526	—292	14,546	—272	......	......
Average variation.....					417		149		425

Use in Detecting Weathered Samples.—Analyses were made of certain fractions obtained by a series of float-and-sink tests run on several samples of coal that had been stored in the laboratory about two years. That the coal had suffered some deterioration seemed probable. Comparison was possible with analyses of samples of the same coal separated about a year earlier and with analyses of the head samples separated at the time the float-and-sink tests were made. The data are assembled in Table 7 which requires no explanation beyond stating that the values in column 5 represent the average of several fractions including all coal having a specific gravity of 1.5 or less. Here again because samples of old coal were used, no close agreement with county average values is to be expected, but the much greater departure from such averages of the older samples represented by values in columns 5 and 9, as compared with the usual better agreement displayed by the samples represented by the values in column 7, indicates a definite greater amount of deterioration of the float-and-sink and head samples, that is, the older coal.

Undoubtedly the probability of deterioration would have been suspected if determined values or ash-free values had been the only bases of comparison, but the use of pure coal value eliminates irregularities, giving more definite significance to variations and similarities.

TABLE 8.—*Comparison of calculated and determined moisture-free values of certain coals*

Lab. No.	Coal bed	County	Unit B.t.u. county average	Ash (moisture free)	Sulfur (moisture free)	Calculated B.t.u. (moisture free)	Determined B.t.u. (moisture-free)	Difference between calculated and determined B.t.u.
C-48	6	Franklin....	14,554	9.65	1.21	13,001	13,021	— 20
C-198	6	Franklin....	14,554	10.2	1.22	12,914	12,916	— 2
C-200	6	Franklin....	14,554	13.3	1.58	12,416	12,420	— 4
C-409	6	Franklin....	14,554	6.8	1.19	13,450	13,500	— 50
C-122	6	Macoupin...	14,259	12.0	4.6	12,280	12,226	+ 54
C-123	6	Montgomery	14,288	13.4	4.3	12,097	12,118	— 21
C-124	6	Montgomery	14,288	11.8	4.6	12,336	12,258	+ 78
C-197	6	Perry.......	14,336	14.8	1.10	12,013	11,925	+ 88
C-383	6	Randolph...	14,349	16.2	3.86	11,727	11,749	— 22
C-33	6	St. Clair.....	14,458	16.35	4.97	11,759	11,694	+ 65
C-34	6	St. Clair.....	14,458	15.54	4.94	11,886	11,933	— 47
C-38	6	St. Clair.....	14,458	13.03	5.38	12,265	12,324	— 59
C-119	6	St. Clair.....	14,458	13.5	4.0	12,232	12,279	— 47
C-120	6	St. Clair.....	14,458	13.9	5.6	12,123	12,130	— 7
C-121	6	St. Clair.....	14,458	13.6	4.4	12,204	12,203	+ 1
C-360	5	Saline.......	14,818	8.3	2.99	13,396	13,417	— 21
C-361	5	Saline.......	14,818	8.4	2.55	13,394	13,463	— 69
C-258	6	Washington.	14,382	16.2	4.1	11.747	11,738	+ 9
C-367	6	Washington.	14,382	14.6	5.10	11,966	12,064	— 98
C-368	6	Washington.	14,382	13.7	4.71	12,117	12,089	+ 28
C-369	6	Washington.	14,382	14.8	4.50	11,952	11,940	+ 12
C-415	6	Washington.	14,382	12.6	3.64	12,319	12,389	— 70
C-37	6	Williamson..	14,598	9.79	1.59	13,006	13,130	—124
C-125	6	Williamson..	14,598	12.0	2.5	12,530	12,773	—143
Average difference..								47

Use in Elimination of Calorific Determination.—With a local standard, pure coal calorific value established for a coal in a local area within which no important variations are likely to exist because of geological irregularities, it should be possible—knowing the ash, moisture, and sulfur content of a sample of such coal—to calculate the "as received" B.t.u. value. The accuracy of such calculated values is readily indicated by comparing the B.t.u. values obtained by such a method with those obtained by actual analysis, as is done in Table 8. In general, the difference between the calculated and determined values is surprisingly small, and consequently the usefulness of the unit coal values in checking coal analyses is apparent.

Such calculations as those suggested may be employed in lessening the expense of commercial analyses. For samples collected from localities or mines having well-established average unit coal values, only moisture, ash, and total sulfur determinations are necessary, since these provide the means of calculating the heat value on either the moist or dry basis. Such procedure would make necessary only an occasional B.t.u. determination as a precautionary check on the coal being sampled.

STUDIES OF THE GRAPHICAL METHOD OF CALCULATING PURE COAL CALORIFIC VALUE* †

By G. Thiessen[1] and F. H. Reed[2]

SUMMARY

The concept "pure coal" is defined as the organic combustible material, including organic sulfur, which is assumed to remain constant in average composition for a given coal seam over a delimited area, even though the proportion of ash associated with it changes. "Unit coal" values are the values obtained in an attempt to express "pure coal" quantitatively.

Two types of methods for finding pure coal values are used: (*a*) formula methods, as illustrated by the Parr unit coal formula; and (*b*) graphical methods, making use of analyses of float-and-sink fractions of coal samples.

Studies of the method for graphically determining pure coal calorific values and ash-mineral matter ratios by plotting the calorific values against ash contents of fractions of coal samples separated by float-and-sink procedure on liquids of different gravities, show that the calorific value / ash curve is usually, though not necessarily, a straight line. The ratio of ash to the amount of mineral matter obtained by the graphical method corresponds to the ratio as calculated from the ash analysis, provided that the heat of transformation of the mineral matter to ash is negligible.

If the mineral matter absorbs or evolves considerable heat in transformation, then the graphical method will not give the correct value unless the intercept of the curve with the ordinate representing the calorific value of the mineral matter is taken. This is illustrated in the case of mixtures of a low-ash coal with pyrites, with calcite, and with gypsum. Float-and-sink separation on liquids of low specific gravity can give a float coal of abnormal calorific value, due to concentration of a distinctive type of coal.

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† Paper presented before the eighty-sixth meeting of the American Chemical Society at Chicago, Sept. 10 to 15, 1933.

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A study of component bands hand-picked from a coal sample showed that the ash-calorific value and ash-specific gravity relationships were not linear, and that segregation of coal components in certain gravity fractions could be expected, making it impossible always to expect linear relationships between ash and calorific values for coal fractions separated on a gravity basis. Moisture and ash-free, dry 1.1 ash-free, and dry 1.125 ash-free, and unit coal calorific values were compared for the individual fractions of the coal separated by float-and-sink procedure. Least deviation of individual values from the average value for the series was always found in the case of the Parr unit coal values.

A comparison of the values obtained by the two methods shows close agreement between them. However, in view of the fact that Parr unit coal calorific values can be calculated from published proximate coal analyses, and that special procedures of analyses are not required, Parr's formula method is susceptible of much wider application than is the graphical method.

PURPOSE

The purposes of this paper are: (1) to report certain investigations and comparisons of graphical and formular methods of finding "pure coal" calorific values, and of determining ratios of coal ash to coal mineral matter; (2) to report studies on the effect of added mineral matter on the calorific values of coal samples; and (3) to discuss the effect of gravity separation by float-and-sink methods on the composition of the various fractions of coal samples.

INTRODUCTION

Coal is a solid, banded, combustible rock of limited heterogeneous constitution and of organic origin. It contains ash-forming substances, mainly minerals, which may or may not be combustible, and more or less extraneous uncombined moisture.

The quality of a coal, exclusive of the kind and quantity of the ash, is determined by the character of the combustible matter which, in turn, is determined partly by its original constitution or "type," and partly by its stage of coalification or "rank." The amount of combustible material is commonly but erroneously regarded as the coal exclusive of ash, moisture, and sulfur, and the quality of a coal is usually expressed in terms of the proximate analysis and calorific value. A "proximate analysis of coal" is expressed in terms of moisture, ash, volatile matter, and fixed carbon, and is usually accompanied by a figure representing the calorific value. The error in regarding the "pure coal" as equivalent to the ash-, moisture-, and sulfur-free coal lies in the fact that the ash resulting from combustion represents a quantity which is different from the mineral matter from which the ash was derived, and in the further fact that, in certain cases, appreciable heat effects are involved in the conversion of mineral matter to ash. Correction of analyses to a moisture- and mineral-free basis shows that the "pure coal" substance of any coal possesses a constancy of composition for limited areas exceeding that attained by the ash- and moisture-free values. With such definite regional pure coal heat values characterizing each coal, local variations in the heat value of the raw coal are determined by variations in the moisture and mineral matter content. Realization of these facts should eliminate much analytical labour since, if the moisture and mineral matter content of a particular coal are known, it is possible to calculate actual (as received) composition from the regional pure coal values. Standard pure coal values also provide a simple basis for checking the accuracy of determined values, for if determined heat values, as calculated to a pure coal basis. do not conform with the regional value for that particular coal, the accuracy of the determination is doubtful.

Classification of coal on a mineral-free basis is preferable to classification on an ash-free basis, whether or not moisture is included. "Pure coal" is a theoretical conception concerning the meaning of which there is disagreement, one of the main points of controversy being the relation of organic sulfur to pure coal. The concept of "pure coal" accepted by the present authors requires the inclusion of the organic sulfur with the organic matter, since it is believed that, like other organic matter, it is a component present in constant proportion in the pure coal. It will be understood, therefore, that in speaking of pure coal the authors refer to the theoretical coal substance including organic sulfur but excluding moisture and mineral matter.

DEFINITIONS

For the sake of clarity, the following terms are defined as used in this paper:

Ash.—The solid residue left after complete combustion of coal. Quantitatively, it is determined by the method described in A. S. T. M. method D271-30, Standard Methods of Laboratory Sampling and Analysis of Coal and Coke.

Mineral Matter.—The ash-forming materials as they exist in the original coal.

Pure Coal.—The non-mineral portion of the coal; the combustible organic portion of the original coal sample, including sulfur in organic combination.

Pure Coal Calorific Value.—The calorific value of "pure coal" as defined above.

Unit Coal (Parr).—An approximation to pure coal basis on the assumption that all the sulfur is present in the coal as pyrites and that all non-pyritic ash is derived from clay minerals.

Unit Coal Calorific Value.—An approximation to pure coal calorific value obtained by calculation from determined values using the Parr formula.

Unit coal calorific value in B.t.u. =

$$\frac{\text{Determined B.t.u.} - 50.0 \times \%\ \text{S}}{100 - (1.08 \times \%\ \text{ash} + 0.55 \times \%\ \text{S})} \times 100$$

METHODS OF OBTAINING PURE COAL VALUES

Pure coal cannot be obtained as a physical substance in the laboratory, but, having defined it, we can calculate its composition from an analysis. There are three possible methods of attacking this problem, all of which are, to some degree, approximations. These are:

(1) Calculation of the mineral matter from the proximate and ash analyses, assuming a distribution of elements among certain known mineral constituents of coal and making due allowance for analytical effects of the conversion of mineral matter into ash.

(2) Determination of the quantity and composition of the organic matter present by removing inorganic components by mechanical and chemical procedures and calculation of analytical results to an organic matter basis[3].

(3) Determination of the heat value and composition of a hypothetical ash- (or mineral matter-) free coal by ascertaining the proportional effect produced by known variations in the ash content upon the heat value and composition of a coal.

(4) Calculation of mineral matter-free values using determined ash values and assuming certain experimentally determined quantitative relationships between ash and mineral matter, with proper adjustment for the heat effects involved in the change. Of these relationships, the ones most commonly used are those given by the Parr unit coal formula.

Of these four methods, only the last has been widely used. For the most accurate results by the first method, a complete analysis of the ash and determinations of the amount of pyritic and sulfate sulfur and carbonate carbon dioxide are necessary, in addition to a proximate analysis of the coal. Such elaborate analyses are not usually practicable. By

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[3] Schuster, F., Asche, Elementarzusammensetzung und Heitzwert von Kohle, *G. W. F.*, 74 (27), 629-35 (1933).

the use of the fourth method, a satisfactory approximation to accuracy may, however, be obtained if the total sulfur and ash contents of the coal are known. Formulæ, by which such approximations are made, and of which the Parr unit coal formula is best known, make corrections for the change from mineral matter to ash, assuming in general that the mineral matter consists largely of clay and pyrites. These corrections provide for the dehydration of the clay minerals, for the conversion of pyrites to iron oxide, and for the heat of combustion of pyrites when calorific values are computed.

The direct determination of organic material by removal of inorganic matter, which constitutes the second method, is quite tedious and difficult and has therefore not found much use.

The third method, which involves the determination of the dilution effect of increasing quantities of ash upon the heat value of the coal, makes possible a graphical determination of pure coal values. Calorific values of samples from within a given seam and within a limited area for which the calorific value-ash relationship has been established, can then be read from the curve, if the ash content is known. Because of the supposed theoretical validity of the third method in determining the mineral matter-free calorific value of coal and the wide use of the Parr formula for Illinois coals for the same purpose, a comparative study of the results and procedures of the two methods has been made for the sake of testing the comparative accuracy and convenience of each. Before proceeding to the description of these experiments, reference should be made to two earlier series of tests on other coals, those by Brinsmaid in 1909 and those by Stansfield and Sutherland in 1930.

EARLIER TESTS OF THE GRAPHICAL METHOD

Brinsmaid, in 1909,[4] described a procedure by which he constructed calorific value/ash curves. His procedure was to place about 30 lb. of coal, in small lumps, on a table and pick high- and low-ash pieces from this pile as representatively as possible. A high-ash and a low-ash fraction were thus obtained. From these two samples, other samples of intermediate ash content were prepared. All the samples were analyzed for ash and calorific value, and calorific values were plotted against ash values. Since the intermediate fractions were prepared by mixing the originally hand-picked samples and not from the original coal, the curve obtained was of necessity a straight line. The slope of such a line would be fixed by the position of the points representing the values obtained by analyzing the high-ash and low-ash samples. Brinsmaid put his

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[4] Brinsmaid, W., *Ind. Eng. Chem.*, 1, 65 (1909).

results in their most usable form by calculating the calorific value of the "pure coal" and the decrease in calorific value due to each per cent ash.

In 1930 Stansfield and Sutherland[5] employed a procedure of this type based upon an improved method of sampling, whereby the sample was separated by gravity, rather than by hand, into several high- and low-ash fractions. From each of four portions of a coal sample, a high- and a low-ash fraction was prepared, yielding eight individual samples of different ash content for analysis, four high in ash and four low. Calorific values are then plotted against ash values, the eight determined points for each coal sample yielding a curve showing the relationship between calorific and ash values for that particular coal. Such curves are, or approximate to, straight lines. Extrapolation of this curve to intersection with the zero ash axis gives the theoretical pure coal calorific value; and to zero calorific value gives the ratio of ash to mineral matter.

The critical assumption of the graphical method, namely, that the curve provided by the gravity separation method is a true dilution curve which can be correctly extrapolated as a straight line to zero ash or zero heat value, rests upon two further assumptions: (1) That the "pure coal" and the mineral matter components of coal remain constant in composition and properties throughout the various fractions of the sample; and (2) that the transformation of mineral matter to ash involves no appreciable production or absorption of heat.

Available information in the literature throws doubt on the validity of these assumptions. Lessing[6] separated durain from vitrain and clarain using float-and-sink procedure and presented figures which show that these fractions differ both as regards ash and chemical composition. His work showed that the composition of the ash from the part of a coal sample which floats on a liquid of gravity 1.35 may be markedly different from that of ash from the portion of the sample which sinks in the same liquid. If the composition of both the coal substance and the ash differed in portions of different density, then it might be expected that the relationship between calorific value and ash content need not be linear. That this relationship is not always linear is shown by curves published by Gründer,[7] who concluded that so long as the ash contents of the fractions remained lower than about 20 per cent, the curves were practically linear; but that for values of ash above 20 per cent, deviations could be expected—more in some cases, of course, than in others.

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[5] Stansfield, E., and Sutherland, J. W., *Trans.* A. I. M. E., Coal Division, 1930, 614-26.

[6] Lessing, R., *J. Soc. Chem. Ind.*, 1925, 44, 277T.

[7] Gründer, W., *Glückauf,* 1932, 68, 114.

The second assumption, which deals with the calorific value of the mineral matter, is unimportant if only the heating value of the mineral-free (pure coal) material is wanted; but it must be considered for the ratio of ash to mineral matter. Of the individual minerals commonly occurring in coal, only pyrites and marcasite have considerable heats of combustion. Even though the heats of decomposition of the hydrated minerals may be high, most of this heat is recovered in the calorimeter when the moisture released on the decomposition of the mineral condenses in the calorimeter bomb. It has long been recognized that the heat of combustion of the sulfur minerals is important in the calculation of heats of combustion of coals. Carbonates, while having considerable negative heats of decomposition, are relatively unimportant sources of heat effects, due to their low concentrations in coal. Because of the foregoing considerations, examination of the validity of the gravity method for determining pure coal values of Illinois coals involved finding an answer to the following question:

Are there sufficient variations in the different fractions of coal obtained by gravity separation to invalidate the straight line relationship of the dilution curve? The answer to this question required, first, comparison of the pure coal values of the banded ingredients; and, second, comparison of the character and quantity of mineral matter, on the assumption that there is unequal concentration of the ingredients in different fractions. Incidentally, experimental evidence of the effect upon its heating value of the addition of different quantities of different minerals to a known quantity of coal is desirable as evidence of the disturbing effect upon the dilution curve of irregularities in the mineral content.

EXPERIMENTAL EXAMINATION OF GRAPHICAL METHOD FOR DETERMINATION OF PURE COAL HEAT VALUES FROM ILLINOIS COAL

The experimental work consisted of:

(1) A determination of the relationship of ash and calorific values for different fractions of each of several Illinois coals.

(2) A determination of the possible effect of variation in the amount and kind of sulfur in the different fractions.

(3) A determination of the possible effect upon the dilution curve of differences in the character of the coal in different benches of the same seam.

(4) A study of ash composition to determine the accuracy of the ratios of ash to mineral matter as found by the graphical method.

(5) Determination of the possible effect of unequal concentration of any of the banded ingredients in different fractions by studying the dilution curve of the individual ingredients.

(6) Determination of the effect of artificial mineral dilution upon the dilution curve and values derived by its extrapolation.

(7) Finally, as one of the main purposes of the paper, the values obtained by the graphical method are compared with those obtained by the Parr method, that is, the pure coal calorific values were compared (*a*) with the unit coal values. Incidentally, comparison is also made with calorific values calculated on a basis, (*b*) free from moisture and ash, (*c*) free from moisture and 1.1 × ash, and (*d*) free from moisture and 1.125 × ash, since these last three values have been proposed, and have had more or less use, as substitutes for the Parr unit coal values.

FIG. 1. Centrifuge cups, according to the design of Stansfield and Sutherland, for separating coal samples into fractions of different densities.

(1) *Evaluation of the Graphical Method for Illinois Coals.*—A sample of Illinois coal No. 5 from Fulton County was separated, according to the method of Stansfield and Sutherland, with mixtures of benzene and carbon tetrachloride of the following specific gravities: 1.30, 1.35, 1.40 and 1.50. Besides these, sink fractions were obtained in liquids of 1.20 and 1.25 sp. gr., but the corresponding float fractions were too small for analysis. The separations were made in centrifuge cups (fig. 1) similar to the design of Stansfield and Sutherland.

The separations were so carried out that the samples were exposed to the action of the separating liquid and to the air for the shortest possible period of time. Minus 20-mesh samples of coal were rapidly weighed out, introduced into the centrifuge cups, the proper liquid added, the cups closed, and immediately centrifuged for 15 min. Upon completion of the separation, the liquid was quickly removed from the coal portions by suction filtration on a Büchner funnel and the samples were freed from the separating medium by evacuation in a desiccator using paraffin wax shavings as an absorbent in the desiccator. The ball mills used for grinding the minus 20-mesh coal to minus 60-mesh were flushed with natural gas, as were all containers used for storing the samples. All grinding operations, such as sieving and riffling, were carried out as rapidly as possible. There was little solvent action of the organic liquids on the samples. A slight discoloration of the liquids occurred, but the amount of extracted material was negligible, as shown by the residue obtained on distillation of the liquids for purification.

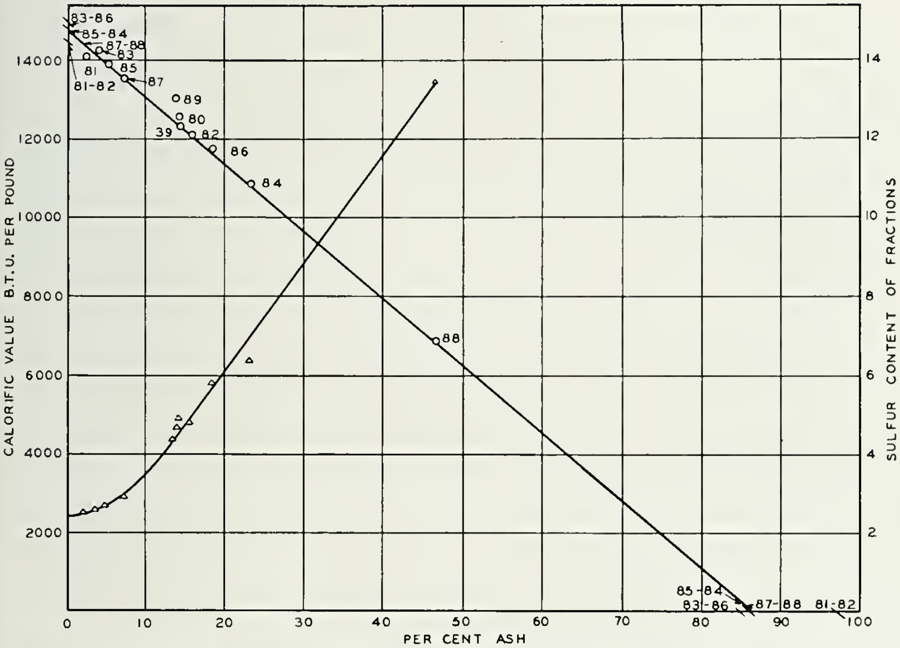

FIG. 2. **Relationships of calorific value to ash and of sulfur to ash for coal No. 5 from Fulton County.**

The samples of Illinois coals used in this investigation were as follows: (1) Coal No. 5, Fulton County; (2) Coal No. 1, Fulton County; (3) Coal No. 6, Franklin County; (4) Coal No. 6, Washington County.

The analyses of the original coal and of the fractions are given in Table 1. The calorific values of the fractions were plotted against the respective ash values, all calculated to the dry basis (fig. 2). Lines drawn through corresponding float-and-sink points and extended to the zero ash axis intercepted this axis at points varying from 15,000 to 14,500 B.t.u. per lb., with 14,800 as the most probable value. Parr unit coal values for these eight fractions varied over the same range, being from 14,998 to 14,538. The unit coal calorific value for the original coal sample was 14,754 B.t.u. per lb. This is 46 B.t.u. per lb. lower than the average of the unit coal values for the fractions and 4 B.t.u. per lb. higher than the mean of the range of pure coal calorific values for the four pairs of float-and-sink fractions. The average value for the ratios of ash to mineral matter is 0.89, individual values being 0.855, 0.865, 0.87 and 0.97.[8] This factor for converting ash to mineral matter becomes $\frac{100}{89}$ or 1.12 for this coal.

TABLE 1.—*Analyses of pairs of float-and-sink fractions and of original coal from coal No. 5 Fulton County, Illinois (on a dry basis)*

Sample No.	Coal fraction	Ash	Total sulfur	Pyritic and sulfate sulfur	Calorific value B.t.u. per lb.		
					Moisture-free	Moisture- and ash-free	Unit coal
C-81	Float 1.30........	2.3	2.5	0.52	14,102	14,430	14,538
C-83	Float 1.35........	4.0	2.6	0.61	14,266	14,860	14,998
C-85	Float 1.40........	5.2	2.7	0.66	13,920	14,685	14,840
C-87	Float 1.50........	7.4	2.9	0.95	13,590	14,677	14,871
C-82	Sink 1.30.........	15.9	4.8	3.39	12,092	14,374	14,780
C-86	Sink 1.35.........	18.6	5.8	4.28	11,756	14,442	14,945
C-84	Sink 1.40.........	23.2	6.4	5.14	10,827	14,100	14,712
C-88	Sink 1.50.........	46.7	13.5	12.91	6,873	12,891	14,712
						(a)14,307	(a)14,800
C-79	Sink 1.20.........	13.8	4.4	2.80	13,067	15,149	15,538
C-80	Sink 1.25.........	14.2	4.7	3.04	12,577	14,655	15,038
C-39	Original coal.....	14.4	4.9	3.2	12,306	14,376	14,754

(*a*) Average.

Similarly, a sample of Illinois coal, No. 1, from Fulton County, was separated in corresponding float-and-sink pairs by Stansfield and Sutherland's procedure on liquids from 1.30 to 1.70 gravity, to study the effect of separations in liquids of a wider range of specific gravity.

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[8] These values are obtained at the ash contents at which the curves relating calorific value and ash cut the zero calorific value abscissa.

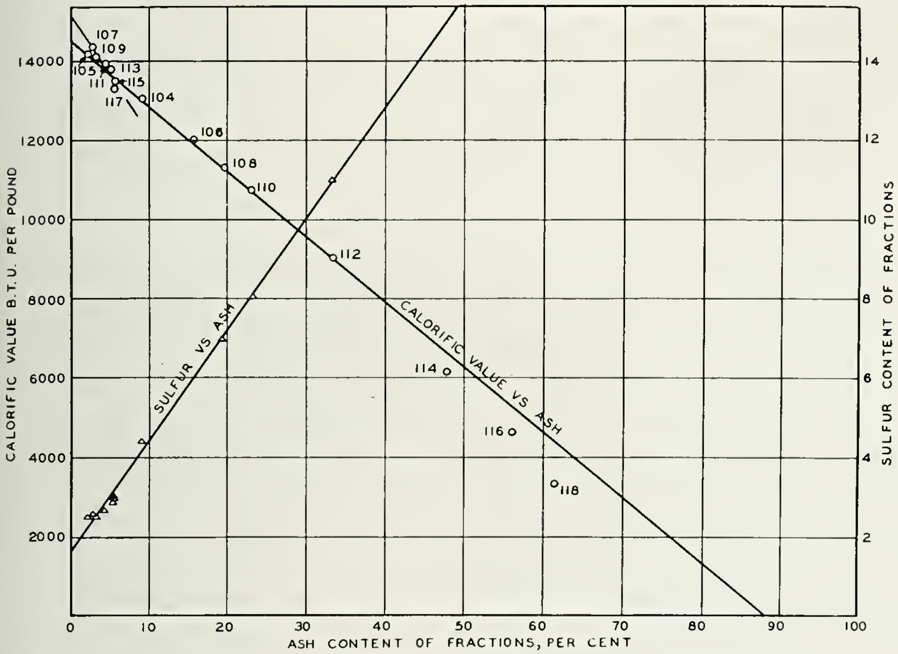

FIG. 3. Calorific values and sulfur variations with ash in fractions from Illinois coal No. 1, Fulton County, Illinois.

TABLE 2.—*Analyses of coal fractions from Illinois coal No. 1, Fulton County (dry basis)*

Sample No.	Fraction	Ash	Sulfur	Calorific value B.t.u. per lb.		
				Moisture-free	Moisture- and ash-free	Unit coal
C-104	Entire	9.3	4.4	13,077	14,410	14,687
C-105	Float 1.30	2.3	2.5	14,206	14,536	14,646
C-107	Float 1.33	3.0	2.6	14,365	14,807	14,933
C-109	Float 1.35	3.5	2.5	14,143	14,653	14,781
C-111	Float 1.40	4.4	2.7	13,945	14,591	14,728
C-113	Float 1.50	5.5	2.9	13,829	14,628	14,800
C-115	Float 1.60	5.7	3.1	13,524	14,345	14,511
C-117	Float 1.70	5.7	3.0	13,381	14,189	14,353
C-106	Sink 1.30	15.8	6.0	12,037	14,294	14,738
C-108	Sink 1.33	19.7	7.1	11,345	14,130	14,691
C-110	Sink 1.35	23.1	8.1	10,718	13,941	14,610
C-112	Sink 1.40	33.4	11.1	9,069	13,611	14,725
C-114	Sink 1.50	47.9	19.1	6,141	11,796	13,374
C-116	Sink 1.60	56.2	21.9	4,633	10,574	12,979
C-118	Sink 1.70	61.4	27.4	3,382	8,773	10,806

TABLE 3.—*Sulfur relationships in fractions of Illinois coal No. 5 from Fulton County (dry basis)*

Lab. sample No.	Fraction	Ash	1.12 ash	Total sulfur	Organic sulfur	Pyritic sulfur	Organic sulfur in pure coal	Ratio of organic to total sulfur	Ratio of total sulfur to ash	Ratio of pyritic sulfur to ash	Ratio of pyritic sulfur to total sulfur
C-39	Original coal......	14.4	16.1	4.9	1.73	3.17	2.06	0.35	0.34	0.22	0.65
C-81	Float 1.30........	2.3	2.6	2.5	1.98	0.52	2.03	0.79	1.09	0.23	0.21
C-83	Float 1.35........	4.0	4.5	2.6	1.99	0.61	2.08	0.77	0.65	0.15	0.23
C-85	Float 1.40........	5.2	5.8	2.7	2.04	0.66	2.17	0.76	0.52	0.13	0.24
C-87	Float 1.50........	7.4	8.3	2.9	1.95	0.95	2.13	0.67	0.39	0.13	0.33
C-82	Sink 1.30.........	15.9	17.8	4.8	1.41	3.39	1.71	0.29	0.30	0.21	0.71
C-86	Sink 1.35.........	18.6	20.8	5.8	1.52	4.28	1.92	0.26	0.31	0.23	0.74
C-84	Sink 1.40.........	23.2	26.0	6.4	1.26	5.14	1.70	0.20	0.28	0.22	0.80
C-88	Sink 1.50.........	46.7	52.3	13.5	0.59	12.91	1.24	0.09	0.29	0.28	0.96
					(*a*) 1.59		(*a*) 1.87				

(*a*) Average.

Seven separations were made with liquids of 1.30, 1.33, 1.35, 1.40, 1.50, 1.60 and 1.70 sp. gr. The analyses of the original coal and of the 14 fractions for ash, sulfur, and calorific value (all on the dry basis) are given in Table 2. Calorific values and sulfur contents of the fractions were plotted against corresponding ash values in figure 3. The relationships between calorific and ash values, and between sulfur and ash values are linear. The points representing the calorific values of the float fractions are scattered and apparently tend to fall on a more sloping line than that formed by the points representing sink fractions. The pure coal calorific value obtained by extrapolating to zero per cent the central portion of the curve showing the ratio of calorific value to ash is about 14,600 B.t.u. per lb., which compares with a Parr unit coal calorific value for the original coal of 14,687 B.t.u. per lb. If the curve showing ratios of sulfur to ash (fig. 3) is extrapolated in a straight line, a sulfur content of 1.7 per cent is obtained for the pure coal.

Attention is especially called to the uncertainty of the points representing the low-ash fractions. The curve in this region should, therefore, be drawn with critical regard for the direction of the curve as indicated by points representing fractions with intermediate ash contents.

(2) *Study of the Distribution of Varieties of Sulfur in Fractions of Coal Separated by Float-and-sink Methods.*—The fractions from the sample of coal No. 5 from Fulton County were analyzed for organic, pyritic, and sulfate, as well as for total sulfur. The results of these analyses, together with various sulfur relationships, are presented in Table 3 and figure 4. The average organic sulfur content of the pure coal for eight fractions was found to be 1.87 per cent; for the four float fractions, 2.10 per cent; for the four sink fractions, 1.64 per cent; and for the original coal sample, 2.06 per cent. These values were found by calculating organic sulfur values to a mineral-free basis, using 1.12 times ash as being equal to mineral matter, the value 1.12 being the ratio of mineral matter to ash as found from figure 2. Considering the wide variation in ash content, and the fact that the value for organic sulfur includes all of the experimental errors in all of the determined sulfur values, it seems reasonable to conclude that the organic sulfur content of the pure coal components of the various fractions remained constant at approximately 2 per cent for this particular coal. It therefore follows for this coal that since organic sulfur is a constant proportion of the pure coal, and pyritic sulfur bears a constant relation to the ash, the ratio of pyritic sulfur to total sulfur increases as the ash increases.

Sulfur would not be expected to disturb the linearity of relationship between calorific and ash values of fractions separated from the coal by float-and-sink method. Where deviations might be expected, ash and sulfur values are low and of small importance. For coals whose pyrite content can be concentrated in the heavier fractions, disturbing effects would be expected.

It may also be seen from Table 3 that the ratio of total sulfur to ash decreases with increasing ash content, and that the ratio of pyritic sulfur to total sulfur increases with increasing ash content. For this coal the ratio of pyritic sulfur to ash remained fairly constant, ranging from 0.13 to 0.28.

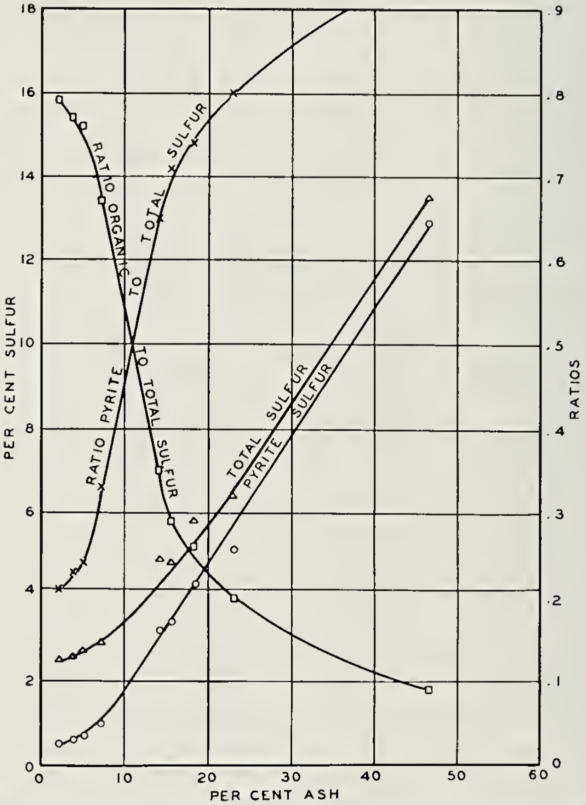

FIG. 4. Sulfur relationships in fractions of Illinois coal No. 5, from Fulton County.

(3) *Comparison of Analyses of Coal Samples from Different Benches of a Seam and of Float-and-sink Fractions from a Sample of the Entire Seam.*—During the course of cutting a columnar sample of coal for petrographic examination, the opportunity was taken to obtain samples from three benches of the same seam. Separation into benches was made after inspection of radiographs of the entire column. Three distinct regions of ash variation were noticeable. The results of the analyses of the original coal and of the three benches, all on the dry basis, are presented in Table 4.

Table 4.—*Analyses of coal from entire seam and three benches, Illinois coal No. 6 from Franklin County (dry basis)*

Analysis	Entire seam	Bench 1	Bench 2	Bench 3
Ash	9.7	9.5	11.3	3.8
Volatile	34.3	34.8	34.0	36.6
Fixed carbon	56.0	55.7	54.7	59.6
Total sulfur	1.21	1.0	0.91	1.38
Pyritic sulfur	0.66	....	0.38	0.66
Sulfate sulfur	0.05	....	0.03	0.04
Organic sulfur	0.50	....	0.50	0.68
Organic sulfur/total sulfur	0.41	....	0.55	0.49
Calorific value B.t.u. per lb.—				
(*a*) Dry coal	13,021	13,040	12,767	13,916
(*b*) Unit coal	14,577	14,564	14,572	14,554
Lab. No	C-48	C-126	C-50	C-51

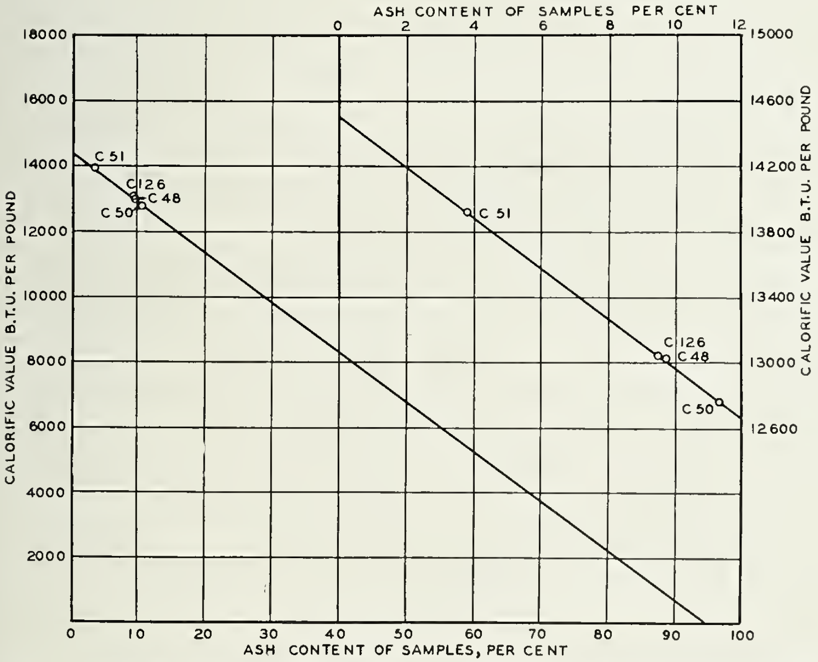

Fig. 5. Calorific values-ash content relationships in benches from Illinois coal No. 5, Franklin County.

The calorific values of the four samples were plotted against their respective ash contents (fig. 5, lower curve). The values were also plotted on an enlarged scale so that variations could be made more apparent (fig. 5, upper curve).

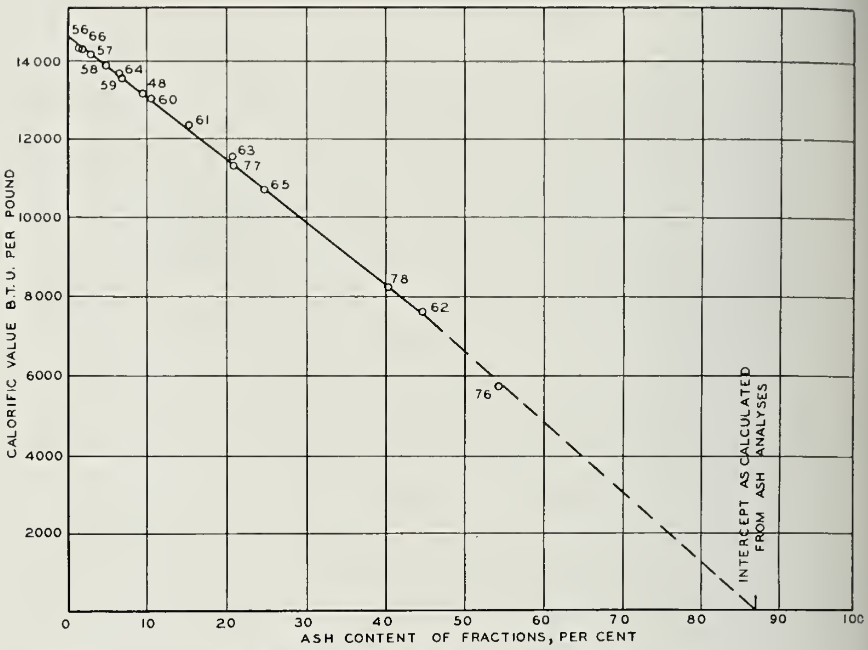

Fig. 6. Relationship of calorific value to ash content for coal No. 6, from Franklin County, Illinois. Successive separations.

Table 5.—*Coal No. 6 from Franklin County, Illinois, separated into fractions of increasing density (dry basis)*

Lab. No.	Separation	Ash	Sulfur	Calorific value B.t.u. per lb.		
				Dry coal	Unit coal	Moisture- and ash-free
C-56	Float 1.25..............	1.5	0.84	14,329	14,593	14,550
C-57	Sink 1.25 Float 1.30....	2.9	0.87	14,122	14,606	14,554
C-58	Sink 1.30 Float 1.33....	5.0	1.01	13,827	14,642	14,546
C-59	Sink 1.33 Float 1.35....	7.0	1.02	13,580	14,728	14,606
C-60	Sink 1.35 Float 1.40....	10.5	1.02	13,050	14,752	14,577
C-61	Sink 1.40 Float 1.45....	15.3	0.94	12,362	14,839	14,591
C-63	Sink 1.45 Float 1.50....	20.7	0.82	11,592	14,955	14,609
C-62	Sink 1.50..............	44.7	2.06	7,466	14,554	14,502
					(*a*) 14,709	(*a*) 14,567
C-48	Original................	9.7	1.21	13,021	14,577	14,420

(*a*) Average.

These curves show that the points representing the relationships between calorific value and ash for the entire seam and benches 1, 2 and 3 lie on a straight line. The conclusion is that for this coal at least, a determination of the pure coal values by the graphical method would not be invalidated by excess of any part of the seam in a sample since the coal in all the benches is essentially alike. The calorific value for pure coal indicated by the curve is 14,500 B.t.u. per lb. The average unit coal value for the entire seam and benches is 14,567 B.t.u.

Effect of Progressive Gravity Separation on the Graphical Method of Pure Coal Calculation.—Coal from the entire seam thickness of the coal, previously studied by benches, was separated with liquids of increasing gravity, by the method previously used. The coal was first separated on a benzene-carbon tetrachloride mixture of 1.25 sp. gr. The sink fraction from this separation was further separated on a mixture of 1.30 sp. gr. and so on for liquids of 1.33, 1.35, 1.40, 1.45 and 1.50 sp. gr. until a final fraction sinking in 1.50 sp. gr. was obtained. These fractions were analyzed for moisture, ash, calorific value, and total sulfur. The results of the analyses, calculated to the dry basis, are shown in Table 5, and calorific values were plotted against ash contents in figure 6.

The same coal was also separated in larger quantities by float-and-sink procedures by allowing 20-mesh coal to separate in carbon tetrachloride-benzene or carbon tetrachloride-bromoform mixtures overnight in battery jars about 8 in. high and 6 in. in diameter. The float coal was skimmed off the surface with a dip net made of bolting cloth. The analyses of the fractions are given in Table 6.

The calorific values shown in Tables 5 and 6 were plotted against their respective ash values on the same graph (fig. 6). The points lay along the same smooth curve. The following conclusions may be drawn from an examination of this curve:

(*a*) The curve approximates to a straight line but shows deviation downward for ash values above 45 per cent.

(*b*) The calorific value of the pure coal obtained by extrapolating the low-ash portion of the curve to zero ash is 14,550 B.t.u. per lb. The unit coal calorific value for the original sample was 14,577 B.t.u. per lb.

(*c*) Extrapolation of the central portion of the curve to the zero calorific value axis gives an intercept close to that calculated from ash analysis which will be shown later.

(4) *Comparison of Ratios of Ash to Mineral Matter Obtained by Calculation from Ash Analyses With Ratios Obtained Graphically.*—The ash-to-mineral matter ratios obtained graphically were compared

for two coals with the ratios obtained by calculation from the results of analyses of the ashes of the coals. The ashes analyzed were from Fulton County No. 5 and Franklin County No. 6 coals. The analyses of the ashes and the percentages of each mineral assumed to be present on the basis of the ash analyses are shown in Tables 7 and 8. Calculation of the mineral matter was made as follows: Pyritic sulfur was calculated to pyrites and the corresponding amount or iron oxide in the ash accounted for. The pyrite was also considered to account for the

TABLE 6.—*Illinois coal No. 6 from Franklin County separated by float-and-sink procedure (dry basis)*

Lab. No.	Separation	Ash	Sulfur				Calorific value B.t.u. per lb.		
			Total	Organic	Sulfate	Pyritic	Dry coal	Unit coal	Moisture and ash-free basis
C-48	Original............	9.7	1.21	0.50	0.05	0.66	13,021	14,577	14,420
C-66	Float 1.30..........	1.6	0.88	0.62	0.03	0.23	14,234	14,511	14,461
C-64	Sink 1.30 Float 1.40.	6.2	0.96	0.52	0.05	0.39	13,629	14,639	14,525
C-77	Sink 1.40 Float 1.60.	20.8	0.79	0.22	0.57		11,368	14,693	14,362
C-78	Sink 1.60 Float 1.70.	40.3	2.40	0.78	1.62		8,245	14,730	13,813
C-76	Sink 1.70..........	54.2	6.30	0.38	5.92		5,737	14,272	12,529
C-65	Sink 1.40..........	24.6	2.10	0.17	0.09	1.86	10,737	14,711	14,232

TABLE 7.—*Analysis of ash from coal No. 5; coal column 37-A, Lab. No. C-39, Fulton County, Illinois*

Ash sample No. C-91

	Analysis per cent	Ingredient in coal per cent	Mineral in coal per cent	Minerals assumed present
SiO_2........................	57.20	8.24	7.29	Quartz
Fe_2O_3......................	27.25	3.92	5.90	Pyrites
Al_2O_3......................	5.61	0.81	2.42	Kaolinite
CaO..........................	4.68	0.67	1.20	$CaCO_3$
MgO..........................	0.57	0.08	0.17	$MgCO_3$
Alkali as Na_2O..............	2.57	0.37	....	In clay
Loss on ignition..............	1.01	0.15	....	Neglected
SO_3.........................	1.76	0.25	....	In pyrites
Total..................	100.67	14.40	16.98	

Ratio of ash to mineral by calculation—0.84.
Ratio of ash to mineral by graphical method—0.86(0.89).

TABLE 8.—*Analysis of ash from coal No. 6, Franklin County, Illinois*

Ash sample No. C-92

	Analysis	Ingredient in the coal	Minerals
	Per cent	Per cent	Per cent
SiO_2	40.89	3.97	0.26 quartz
Fe_2O_3	7.68	0.75	1.23 FeS_2
Al_2O_3	32.48	3.15	7.97 kaolinite
CaO	9.63	0.93	1.66 $CaCO_3$
MgO	0.07	0.01	0.02 $MgCO_3$
Alkali as Na_2O	Not determined		
Loss on ignition	Nil.		
SO_3	8.53	0.83	
P_2O_5	0.00	0.00	
Total	99.28	9.7 ash	11.14 minerals

Ratio ash to mineral matter calculated—0.87.
Ratio ash to mineral matter by graphical method—indeterminate.

sulfate in the ash. Calcium and magnesium oxides were calculated to the corresponding carbonates. The ash contains a much larger proportion of silica to alumina than exists in hydrous alumina silicate minerals commonly found in clays. It was assumed that all the alumina existed as a component of the clay mineral kaolinite[9] whose composition is $Al_2O_3.2SiO_2.2H_2O$, and that the alkalies were also contained by this clay mineral. The amount of silica indicated by this formula as existing in the kaolinite was calculated and subtracted from the total silica. The remaining silica was then assumed to exist in the coal uncombined as a form of the mineral quartz.

Calculations for the values given in Table 7 are:

Pyrites:

$$\left.\begin{array}{l}\text{3.16 per cent. pyritic sulfur} = \\ \quad\text{5.91 per cent pyrites.} \\ \text{3.92 per cent } Fe_2O_3 \times 1.5025 = \\ \quad\text{5.89 per cent pyrites.}\end{array}\right\} \begin{array}{l}\text{Average} \\ \text{5.90} \\ \text{per cent} \\ \text{pyrites.}\end{array}$$

Calcium carbonate:

0.67 per cent CaO × 1.7847 = 1.20 per cent $CaCO_3$.

Magnesium carbonate:

0.08 per cent MgO × 2.0913 = 0.17 per cent $MgCO_3$.

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[9] According to a personal communication from R. E. Grim, the clay mineral most commonly found in Illinois coals is kaolinite.

Clay:

Clay =

$$\left\{\frac{2\ SiO_2}{Al_2O_3} \times Al_2O_3\right\} + Al_2O_3 +$$

$$\left\{\frac{2\ H_2O}{Al_2O_3} \times Al_2O_3\right\} + Na_2O \text{ or}$$

$(1.1783 \times 0.81) + 0.81 + (0.3531 \times 0.81)$
$+ 0.37 = 2.42$ per cent clay.

Silica:

The SiO_2 in the clay $= 1.1783 \times 0.81$ or 0.95.
The non-clay $SiO_2 = 8.24 - 0.95 = 7.29$ per cent.

The total mineral content is found to be 16.98. The ratio of ash to mineral matter, 14.40 to 16.98, is then 0.84, which is a fair agreement with the average (0.89) of the values obtained from the four pairs of analyses of fractions. The individual values were 0.855, 0.865, 0.87 and 0.97 (see fig. 2). Excluding the value 0.97, which is questionable due to sample C-81 being the lightest fraction, the average becomes 0.86.

Calculation of the values in Table 8 were made in the same manner as for those in Table 7. Alumina and silica were present in almost the ratio for kaolinite, 1-Al_2O_3 to 2-SiO_2.

In this case also, the iron was found to correspond closely to that required to combine with the pyritic sulfur in the coal to form pyrite. The total of the mineral quantities was found to be 11.14 giving a ratio of ash to mineral of 9.7 to 11.1 per cent or 0.87. In the case of these two calculations, the graphical method gives ratios of ash to mineral matter corresponding to those obtained by calculation from ash analyses.

(5) *Possibility of Irregularities in the Ash Dilution Curve Due to Difference in the Character of the Banded Ingredients.*—When coal is artificially separated into its banded ingredients the portions no longer possess the similarity of composition characteristic of coal separated by quartering, riffling, or to large extent by gravity methods. Although the different portions may be classified on the basis of their ash contents, a series of such samples does not represent a true dilution curve since some represent one kind of coal and some another. It would, in general, not be expected that such a series would be in straight line when heat value is plotted against ash. To determine the extent of the variations in the dilution curve caused by segregation of the ingredients, samples of anthraxylon (vitrain), attritus (clarain), splint (durain), and fusain were picked by hand from a columnar sample of Washington County coal No. 6. Specific gravities, proximate analyses, and calorific values were determined for each sample, results being given in Table 9.

TABLE 9.—*Analyses of components in coal No. 6, Washington County, Illinois*

Sample No.	Description	Specific gravity	Moisture-free					Unit coal		
			Ash	Volatile	Fixed carbon	Sulfur	B.t.u. lb.	B.t.u.	Volatile	Fixed carbon
C-127	Splint......	1.59	31.7	34.2	34.1	2.2	9,710	14,873	47.6	52.4
C-128	Splint......	1.60	31.1	30.5	38.4	4.1	9,423	14,370	41.0	59.0
C-129	Anthraxylon	1.30	1.5	45.1	53.4	2.6	13,956	14,261	45.3	54.7
C-130	Anthraxylon	1.30	2.5	45.5	52.1	3.1	13,824	14,300	45.9	54.1
C-131	Attritus....	1.35	3.8	50.1	46.1	3.8	13,749	14,454	51.4	48.6
C-133	Attritus....	1.35	5.2	48.9	45.9	3.9	13,755	14,702	50.8	49.2
C-320	Fusain.....	1.62	16.2	21.1	62.7	1.6	11,900	14,482	23.4	76.6
C-258	Original coal	1.42	16.2	40.8	43.0	4.1	11,738	14,371	47.1	52.9

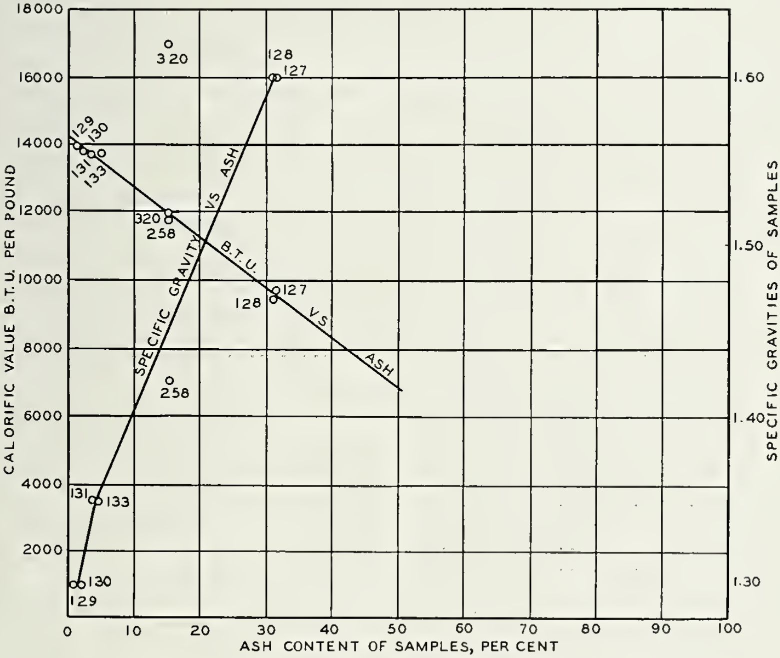

FIG. 7. Calorific value-ash content and specific gravity-ash content relationships in lithological components of coal No. 6, Washington County, Illinois.

By microscopic examination of the entire column it was determined that the columnar sample was composed of approximately 37 per cent anthraxylon, 47 per cent attrital coal, 13 per cent splint coal, and 3 per cent fusain. Specific gravities and calorific values were plotted against ash values (fig. 7). The table and figure show lack of linear arrangement of the values with respect to both of the relationships plotted. The variations in the ash-heat value ratio are, however, relatively small, indicating that considerable variation in the quantity of the ingredients would be necessary to modify the linear value of a dilution curve beyond practical usefulness as a means of deriving the pure coal value. However, since many coals contain these constituents, a gravity separation would tend to effect their concentration according to their densities, absolutely straight-line relationships between calorific value and ash could not be expected. Thus one of the requisites for the complete validity of the Stansfield and Sutherland method cannot be perfectly met, at least in the case of this Illinois coal.

The ash contents of the splint samples are abnormally high, splint coals rarely contain more than 10 per cent. It would seem that these samples are bony splint coals.

(6) *Effect of Artificial Mineral Dilution on the Dilution Curve and Extrapolated Values.*—The accuracy of the graphical method of determining the ratio of ash to mineral matter was tested by adding a pure mineral in varying proportions to a relatively low-ash coal. Pyrites was used in one case and calcite in another. References in the literature were also found to similar work where gypsum and coal ash[10] had been added to coal.

TABLE 10.—*Analysis of pyrites used in investigation*

Sample No. R-385

SiO_2	9.83
Al_2O_3	1.65
Fe_2O_3 (HCl soluble iron)	3.26
MgO	0.29
CaO	0.88
Loss on ignition	(*a*) 5.12
Fe (HCl insoluble)	36.87
Sulfur, total	42.40
Total	100.30
Calculated pyrites	79.22
(*a*) Total loss on ignition	31.62
Loss due to pyrites	26.50
Net loss on ignition	5.12

The Effect of Pyrites.—Pyrites was added to coal from the third bench of Illinois coal No. 6 from Franklin County, corresponding to sample No. C-51 in the series of analyses of benches of coal from the same seam reported previously in this paper. A large portion of this coal was ground to pass a 60-mesh screen, a sample was taken for

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[10] Stumper, R., *Brennstoff-Chemie,* 1927, 8, 261; 33.

analysis, and three mixtures were made so that the added crude pyrites contents were 4, 10, and 20 per cent, respectively. The pyrites was obtained from a pyrites lens from coal. It was ground to pass a 100-mesh screen and analyzed (Table 10). The results of the analysis of the coal and coal/pyrites mixtures are presented in Table 11.

An attempt was made to reconstruct the mineral matter in the samples by calculation from analytical results in order that the ratio of ash to mineral matter as found graphically might be compared with the calculated ratio. The method of calculation was as follows: The non-pyritic ash from the coal portion of the sample was found by subtracting from the ash of the coal (item 8) the amount of Fe_2O_3 corresponding to the pyritic sulfur in the coal. This was increased by 15 per cent, accounting for water of hydration, assuming all non-pyritic mineral as clay mineral to give non-pyritic mineral in the coal portion (item 9).[11] The pyrites corresponding to the pyritic sulfur in the coal portion was next found (item 10). Since the crude pyrites added to the coal consisted of 79 per cent FeS_2 and 21 per cent non-pyritic matter, the added FeS_2 (item 11) and the non-pyritic matter (item 12) were found. The sum of the coal pyrites plus the added pyrites gave the total pyrites in the mixture (item 13). The non-pyritic mineral from the coal (item 9) plus the added non-pyritic mineral (item 12) gave the total non-pyritic mineral in the sample (item 14). The total mineral content of each mixture (item 15) was then found by adding the quantities of pyritic and non-pyritic mineral matter. To obtain the heat of combustion of the sulfur-free coal (item 17), the heat due to the combustion of sulfur (item 16) was found, using 5,247 B.t.u. per lb. as the heat of combustion of the sulfur and the values for total sulfur; and was subtracted from the heat of combustion as determined, calculated to a dry basis (item 4). These values were converted to dry mineral-free heats of combustion (item 18), using the previously found values for total mineral matter (item 15). The value 5,247, taken as the heat of combustion of the sulfur, is the heat of combustion of pyrites per lb. of sulfur present and is not strictly correct since a small part of the sulfur is present as organic sulfur. However, since the heats of combustion of pyritic and organic sulfur are of the same magnitude and the quantity of organic sulfur present is relatively small, the value is a sufficiently close approximation for the present purpose.

The values for dry sulfur, and mineral-free coal (pure coal) ranged from 14,357 to 14,446 B.t.u. per lb., averaging 14,410 B.t.u. per lb., the

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[11] Selvig, W. A., and Pohle, W. D., "Loss of Water of Hydration and CO_2 of Mineral Matter in Coal in the Standard Method for Determination of Volatile Matter." Mimeographic Circular by U. S. Bureau of Mines, 6-8-32.

TABLE 11.—*Analyses and calculations for coal-plus-pyrites mixtures*
(Moisture-free basis)

Lab. No.	Sample composition	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
		Ash	S_T	S_p	B.t.u.	Unit coal B.t.u.	Ash from coal portion	Fe_2O_3 corresponding to coal pyrites	Coal ash less Fe_2O_3	Non-pyritic mineral from coal	Coal pyrites	FeS_2 added	Non-pyritic mineral added	10 + 11 total pyrites	9 + 12 non-pyritic mineral	13 + 14 total mineral	52.47 × S_T sulfur heat	4 — 16 sulfur-free B.t.u.	$\frac{\text{Mineral-free B.t.u. 17}}{\text{100-col. 15}}$	Deviation from average	$\frac{\text{Ash}}{\text{mineral}}$
C-70	100 p. c. coal	3.9	1.4	0.72	13,811	14,461	3.9	0.9	3.0	3.5	1.35	—	—	1.35	3.5	4.9	73	13,738	14,446	+36	0.80
C-67	96 p. c. coal 4 p. c. pyrites	6.7	3.0	2.49	13,311	14,445	3.7	0.8	2.9	3.3	1.30	3.2	0.8	4.5	4.1	8.6	157	13,154	14,392	—18	0.78
C-68	90 p. c. coal 10 p. c. pyrites	10.9	5.6	5.08	12,672	14,553	3.5	0.8	2.7	3.1	1.22	7.9	2.1	9.1	5.2	14.3	294	12,378	14,443	+33	0.76
C-69	80 p. c. coal 20 p. c. pyrites	18.0	9.8	9.33	11,440	14,567	3.1	0.7	2.4	2.8	1.08	15.8	4.2	16.9	7.0	23.9	514	10,926	14,357	—53	0.75
Average						14,507													14,410	35	0.76

Column No. 1.—Ash. Ash as determined, moisture-free.
Column No. 2.—S_T. Total sulfur, moisture-free.
Column No. 3.—S_p. Pyritic sulfur, moisture-free.
Column No. 4.—B.t.u. B.t.u. as determined—moisture-free.
Column No. 5.—Unit coal B.t.u. Calculated by Parr formula.
Column No. 6.—Ash from coal portion of mixture.
Column No. 7.—Fe_2O_3 corresponding to pyrites in coal portion of sample.
Column No. 8.—Coal ash less Fe_2O_3. Ash from non-pyritic coal mineral.
Column No. 9.—Non-pyritic mineral from coal. Non-pyritic ash (8) × 1.15.
Column No. 10.—Coal pyrites—calculated from pyritic sulfur content of coal portion.
Column No. 11.—FeS_2 added. Crude pyrites added × 0.79.
Column No. 12.—Non-pyritic mineral added. Crude pyrites added times 0. 1
Column No. 13.—Total pyrites. FeS_2 added (11) plus coal pyrites (10).
Column No. 14.—Non-pyritic mineral. Coal mineral (9) plus non-pyritic mineral added (12).
Column No. 15.—Total mineral. Total pyrites (13) plus non-pyritic mineral (14).
Column No. 16.—52.47 × S_T. Heat of combustion due to sulfur in samples.
Column No. 17.—Sulfur-free B.t.u. Heat of combustion (B.t.u.) (4) minus heat due to sulfur (16).
Column No. 18.—Mineral-free B.t.u. Sulfur-free B.t.u. over 100 — total mineral percentage.
Column No. 19.—Deviation from average of group.
Column No. 20.—Ash/mineral. Ratio of ash to mineral. (Average for last three values only.)

value 14,446 being for the original coal. The Parr unit coal calorific value for the original coal is 14,461 B.t.u. per lb. Deviations of the individual values from the average (item 19) are within the experimental errors of calorimetric determinations for coal. The ratios of ash to mineral matter calculated for the various samples is given as item 20 and averages 0.76 for the three coal-plus-pyrites mixtures.

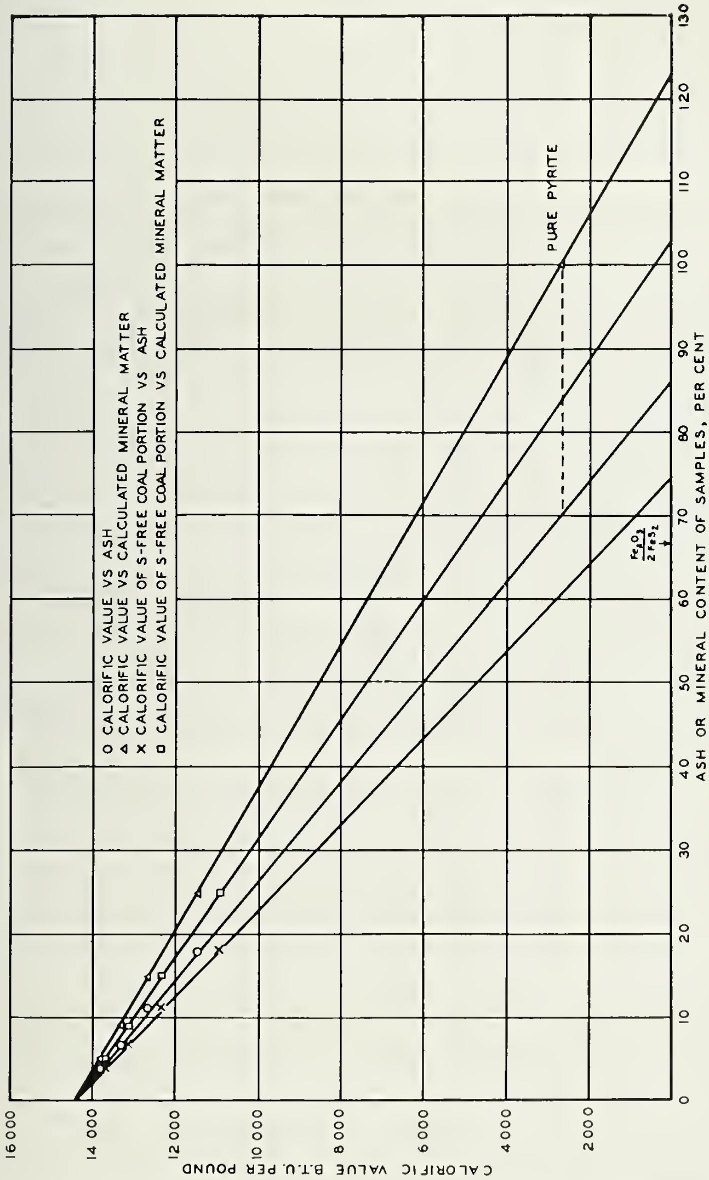

Fig. 8. Calorific value-ash content relationships for coal-plus-pyrites mixtures.

TABLE 12.—*Analyses of coal-calcite mixtures*

Lab. No.	Sample	1 Ash	2 B.t.u.	3 Parr unit coal	4 Sulfur	5 % A° coal ash	6 1.08 % A° + 0.55 % S	7 1.8 % A° + 0.55 % S + % CaCO$_3$	8 B.t.u. − 50 × % S	9 $\frac{\text{B.t.u.} - 50 \times \% \text{S}}{100 - \text{M}}$	10 Deviation	11 Mineral-free B.t.u. (9) + heat of decomposition of CaCO$_3$	12 Deviation	13 Parr unit coal corrected for CO$_2$	14 Deviation	15 Parr unit coal corrected for CO$_2$ and for heat of ashing CaCO$_3$	16 Deviation
C-70	100 p. c. coal	3.9	13,811	14,461	1.4	3.9	4.98	4.98	13,741	14,461	+150	14,461	−25	14,461	−129	14,461	−303
C-71	96 p. c. coal 4 p. c. CaCO$_3$	7.4	13,289	14,486	1.3	3.7	4.71	8.71	13,224	14,486	+175*	14,520	+34	14,537	−53	14,571	−193
C-72	90 p. c. coal 10 p. c. CaCO$_3$	11.0	12,426	14,130	1.1	3.5	4.39	14.39	12,371	14,450	+139	14,549	+63*	14,606	+16	14,705	−59
C-73	80 p. c. coal 20 p. c. CaCO$_3$	16.4	10,941	13,319	0.84	3.1	3.81	23.81	10,899	14,305	− 6	14,507	+21	14,612	+ 22	14,814	+ 50
C-73	60 p. c. coal 40 p. c. CaCO$_3$	27.1	7,960	11,260	0.30	2.3	2.65	42.65	7,945	13,854	−457*	14,391	−95*	14,732	+142	15.269	+505
	Average pure coal									14,311	185	14,486	48	14,590	72	14,764	222
	Range of deviations										632		158		271		804

Column No. 1.—Ash. Ash as determined, moisture-free.
Column No. 2.—B.t.u. B.t.u. as determined, moisture-free.
Column No. 3.—Parr unit coal. Calculated, using Parr unit coal formula.
Column No. 4.—Sulfur. Total sulfur as determined, moisture-free.
Column No. 5.—% A° — coal ash. Ash from coal portions of mixture.
Column No. 6.—1.08 % A° + 0.55 % S. Mineral matter in coal portion of mixture.
Column No. 7.—1.08 % A° + 0.55 % S + % CaCO$_3$. Total mineral matter in mixtures.
Column No. 8.—B.t.u. — 50 × % S. Moisture and sulfur-free heat of combustion.
Column No. 9.—B.t.u. — 50 × % S 100 — M. Dry, sulfur, and mineral-free heat of combustion.
Column No. 10.—Deviation. Deviation of individual values from average.
Column No. 11.—Mineral-free B.t.u. (9) plus heat of decomposition of CaCO$_3$ in mixture.
Column No. 12 —Deviation. Deviation of individual values from average.
Column No. 13.—Parr unit coal corrected for CO$_2$. Calculated from Parr formula.
Column No. 14.—Deviation. Deviation of individual values from average.
Column No. 15.—Parr unit coal corrected for CO$_2$ and for heat of decomposition of CaCO$_3$.
Column No. 16.—Deviation. Deviation of individual values from average.

The heats of combustion of the coal samples were plotted against ash values and against calculated mineral matter values, and the total B.t.u. minus pyritic B.t.u. was plotted against ash and against calculated mineral matter values (fig. 8).

The following observations may be made from the graph: (1) The curve relating B.t.u. and ash values cuts the zero B.t.u. line at 86.5, which is neither the experimentally determined ratio of ash to mineral matter nor the theoretical ratio with allowance made for the heat of the sulfur. We would expect a ratio slightly larger than 0.67, since the ash is to a considerable extent derived from pyrites in the high-ash samples.

(2) The curve relating B.t.u. and calculated mineral matter crosses the zero calorific value line at 124, and the 100 per cent ash axis at 2,800 B.t.u., which is the heat of combustion of the pyrites. This being so, it is apparent that the ratio of ash to mineral matter will be given by the intercept of the determined calorific value versus ash curve with the 2.800 B.t.u. ordinate, or at 70.

(3) If the ash were all derived from pyrites, the ratio of ash to mineral matter would theoretically be 0.67; by determination, we obtain the value 0.76 as the average value for the mixtures. This higher value is obtained because the ash is not entirely derived from pyrites.

(4) If the calorific value of the sulfur-free coal is plotted against ash (curve 3), thereby eliminating the heat effect due to sulfur, the ratio of ash to mineral matter is found to be 0.745, which is in good agreement with the value 0.76 obtained by calculation from the composition of the samples and with the value 0.70 found above.

(5) If the calorific value of the sulfur-free coal is plotted against mineral matter (curve 4), the heat due to sulfur again being eliminated, the curve intersects the zero calorific value axis at 103, very close to the theoretically correct position at 100.

These relationships show very definitely that the presence of pyrites in the mineral matter affects the dilution curve in a manner which accords very closely to theoretical expectancy, and that only as the amount of pyritic sulfur is known can the ash-mineral matter relationship be correctly determined from such a dilution curve.

The Effect of Calcite.—The same coal used in the pyrites experiment was used to make four mixtures of coal with 4, 10, 20, and 40 per cent calcite, respectively (Table 12).

The B.t.u. values were plotted against ash values to give a curve (fig. 9) whose extensions to the zero axis gave a ratio of ash to mineral matter of 55.5 and a pure coal heat value of 14,400 B.t.u. per lb. as against a calculated ratio of 56.03 and a unit coal value of 14,461 B.t.u.

per lb. This curve bends in the region of 7.5 per cent ash, due to the fact that the type of mineral matter in the samples is changing. Above this value the coal ash predominates, below this the calcite. The extrapolations were therefore made in the directions in which the curve was going after passing this point. This series of samples illustrates the effects of the changes in ash composition on the shape of the curve. If the upper portion of the curve is extrapolated to zero B.t.u., the intersection of the extrapolated curve with the zero B.t.u. axis is found to be the ratio of ash to mineral matter of the coal in the mixture. The values are 96.5 as against 97.0, found in the study of coal from different benches of the same seam; and around 91, from a recalculation of the ash analyses figures.

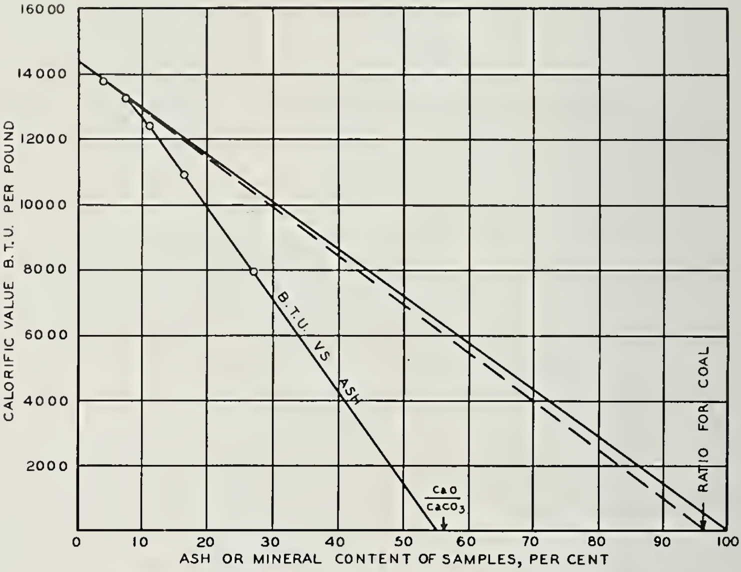

FIG. 9. Calorific value-ash content relationships for coal-plus-calcite mixtures.

Parr unit coal values calculated by the regular Parr unit coal formula, are seen to be too low and become increasingly lower with increasing calcite contents.

The following calculations were then made to convert the determined calorific values to mineral-free values. The ash derived from the coal was found from the ash content of the original coal and from the proportion of coal present in the mixture. This ash, together with the sulfur present, was calculated to mineral matter by means of the Parr formula—mineral matter = 1.08 ash + 0.55 sulfur. The total mineral matter in each sample was then found by adding the quantity of calcite in each mixture to the corresponding coal mineral matter content as calculated above. The dry determined calorific values were decreased by 50 times the sulfur content, as is usual in the calculation of unit coal values, and the resulting values were calculated to a mineral-free basis. It is seen that these values, while more consistent than unit coal values, also decrease with increasing calcite content. This is due to the endothermic decomposition of $CaCO_3$ to CaO and CO_2, which absorbs 770 B.t.u. per lb. of $CaCO_3$. When the values last calculated are each increased by 7.70 times, the per cent of $CaCO_3$ present in the respective mixtures, the values become still more consistent; the average deviation of the individual values from the average pure coal value being only 48 B.t.u. with a range of 158 B.t.u. as against an average deviation of 185 B.t.u. with a range of 632 B.t.u. for the values without the correction for heat of decomposition of the calcite. This indicates that the corrections should include one for the heat of ashing of calcite. It would be most convenient to express this value in terms of CO_2 content of the coal. If the heat of decomposition of calcite is taken as 770 B.t.u. per lb., the corresponding value will be 1,750 B.t.u. per lb. of CO_2 (or 17.50 B.t.u. for each per cent on a lb. basis).

Advantage was taken of these data to check the accuracy of unit coal calorific values calculated by use of the modified Parr formula for coals high in calcite. This formula states,

Unit coal calorific value =

$$\frac{[\text{B.t.u. det.} - 50 \times \%\ \text{S}]\ 100}{100 - (1.08\ [\%\ \text{Ash} + \%\ \text{CO}_2] + 0.55 \times \%\ \text{S})}$$

where Ash, S, CO_2 signify the percentages of these components in the coal.[12]

In order to make a more precise check on this formula, it was considered that the term "ash + CO_2" in the case of the samples tested was equal to the ash from the coal portion of the sample plus the calcite added. Errors due to incomplete evolution of CO_2 from the calcite during ashing and to absorption of sulfur oxides by the lime in the ash were thus avoided. These calculations were made to show in particular that it is not correct to add an hydration correction for the ash due to calcite and that the ash before hydration must be decreased by an amount corresponding to its "calcium oxide from calcium carbonate" content in the corrected formula, just as in all Parr formulæ the ash is decreased by an amount corresponding to the "iron oxide from pyrites." Results of these calculations are also given in Table 12.

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[12] Parr, S. W., Illinois Coal Mining Investigations Bull. 3, 1916.

TABLE 13.—*Analyses of mixtures of gypsum and coal*

(After Stumper) (Dry basis)

Coal	Gypsum	Ash from coal	Theoretical ash	Found ash	Difference	Loss of gypsum	Calories			B.t.u.		
							Calorific value found	Ash-free using ash + gypsum	Ash-free using found ash	Found	Ash- and gypsum-free	Found ash-free
Per cent	Per cent	Per cent	Per cent	Per cent		Per cent						
100	0	4.85	4.85	4.85	....	....	8,070	8,481	8,481	14,526	15,266	15,266
99	1	4.80	5.80	5.50	0.30	30.0	8,003	8,479	8,470	14,405	15,262	15,246
98	2	4.75	6.75	6.05	0.70	35.0	7,956	8,530	8,467	14,321	15,354	15,241
95	5	4.61	9.61	8.47	1.14	22.8	7,654	8,467	8,363	13,777	15,241	15,053
90	10	4.36	14.36	12.15	2.21	22.9	7,300	8,524	8,309	13,140	15,343	14,956
85	15	4.12	19.12	15.78	3.34	22.4	6,875	8,501	8,164	12,375	15,302	14,695
80	20	3.88	23.88	18.98	4.90	24.4	6,495	8,530	8,016	11,691	15,354	14,429
70	30	3.40	33.40	86.85	5.55	21.8	5,550	8,333	7,587	9,990	14,999	13,657
60	40	2.91	42.91	34.42	8.49	21.2	4,725	8,276	7,204	8,505	14,897	12,967

For coals high in calcite, the Parr unit coal formula should be,

B.t.u. unit coal =

$$\frac{[\text{B.t.u. det.} - 50 \times \%\ \text{S} + 17.5 \times \%\ \text{CO}_2]\ 100}{100 - (1.08\ [\%\ \text{Ash} - 1.27 \times \%\ \text{CO}_2] + 2.27 \times \%\ \text{CO}_2 + 0.55 \times \%\ \text{S})}$$

which simplifies to,

B.t.u. unit coal =

$$\frac{[\text{B.t.u. det.} - 50 \times \%\ \text{S} + 17.5 \times \%\ \text{CO}_2]\ 100}{100 - [1.08\ \%\ \text{Ash} + (0.90 \times \%\ \text{CO}_2) + (0.55 \times \%\ \text{S})]}$$

As has been shown elsewhere[13] the terms for sulfur and CO_2 may be combined to give a simplified formula which is a sufficiently good approximation for general use. This approximation formula is,

B.t.u. unit coal =

$$\frac{\text{B.t.u. determined} \times 100}{100 - (1.08\ \%\ \text{Ash} + 1.02 \times \%\ \text{CO}_2 + 0.21 \times \%\ \text{S})}$$

When using the unit coal formula, as modified by Parr for coals high in CO_2, for coals only moderately high in CO_2 (up to 2 per cent), the errors inherent in it are not evident because the heat effect due to the ashing of the calcite, which must be added, is compensated for by the fact that an over-correction is made in changing ash to mineral matter. When using the unit coal formula for coals high in CO_2, as revised in this paper, the ash must be determined by Parr's method for ash determination for coals high in CO_2. In this procedure, after the coal has been ashed, the ash is treated with a drop of sulfuric acid, ignited, and correction applied on the basis of the CO_2 content of the coal to convert the $CaSO_4$ in the ash to CaO.

The results of these tests show that the calorific values versus ash content dilution curve is affected by the presence of calcite according to theoretical expectancy, and that correction must be made for the heat of decomposition of calcite in the calculation of mineral-free coal values. The Parr unit coal formula modified for coals high in calcite should include a term for the heat of decomposition of calcite. Such a revised formula was presented.

The Effect of Gypsum.—No original work was done under this project on the influence of gypsum on coal analyses, since a study of this phase of the work by R. Stumper was found in the literature. Stumper's figures for the analyses of mixtures of a Saar coking coal containing 4.85 per cent ash with varying proportions of Kahlbaum's gypsum, which contained 20.75 per cent water of hydration, are reprinted in Table 13.

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[13] See this report, page 23.

It seemed that Stumper was not justified in considering the theoretical ash to be the ash from the coal fraction plus the gypsum added, and therefore a recalculation was made in which the theoretical ash was considered to be the ash from the coal fraction plus the anhydrous $CaSO_4$ added (Table 14). From Table 14 we see that the difference between the theoretical ash and the ash as determined is, with few

TABLE 14.—*Behavior of anhydrite on ashing mixture of coal and gypsum*

Calculated from Stumper's values (per cent, dry basis)

Coal	Gypsum	Ash from coal	$CaSO_4$ added	Theoretical ash	Found ash	Difference	Loss $CaSO_4$
100	0	4.85	0.0	4.85	4.85	....	....
99	1	4.80	0.79	5.59	5.50	—0.09	11.4
98	2	4.75	1.59	6.34	6.05	—0.29	18.2
95	5	4.61	3.96	8.57	8.47	—0.10	2.5
90	10	4.36	7.93	12.29	12.15	—0.14	1.77
85	15	4.12	11.89	16.01	15.78	—0.23	1.93
80	20	3.88	15.85	19.73	18.98	—0.75	4.73
70	30	3.40	23.78	27.18	26.85	—0.33	1.39
60	40	2.91	31.70	34.61	34.42	—0.19	0.60

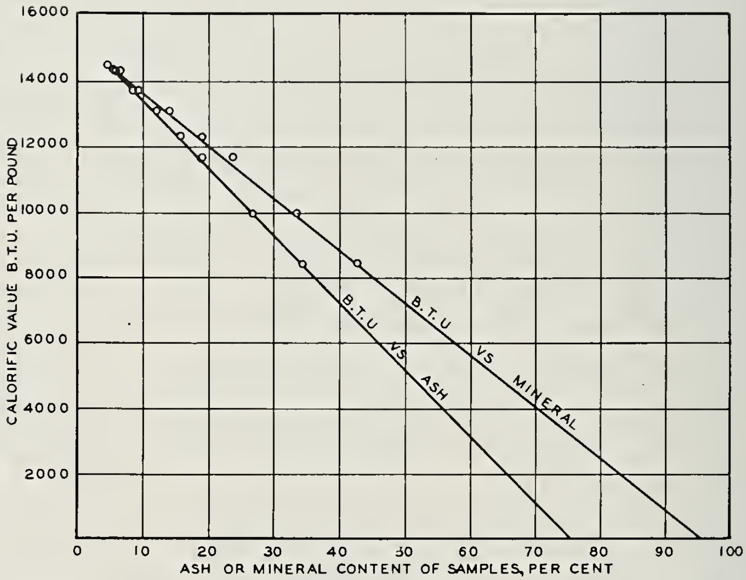

FIG. 10. Calorific value-ash content relationships for coal-plus-gypsum mixtures.

exceptions, within the range of experimental error; and that the difference expressed as percentage of the calcium sulfate, although high for mixtures containing but little gypsum, is low where appreciable amounts of gypsum are present. This leads to the conclusion that the loss of calcium sulfate by volatilization during ashing is not very appreciable. According to Parr,[14] the dissociation of calcium sulfate into CaO and SO_3 at 750° C. is about 25 per cent.

Calorific values (in B.t.u. per lb.) have been plotted against values for ash as found and ash-plus-gypsum (fig. 10). An extrapolation to zero ash was not made, since there is no change in the relationship between the coal ash and coal in any of the mixtures. Extrapolations of the curves relating (1) B.t.u. and ash as found; and (2) B.t.u. and coal ash plus gypsum cut the zero B.t.u. axis at 76 and 96.5 respectively. The B.t.u. ash plus gypsum curve should cut the zero B.t.u. curve at approximately 100, since the heat of decomposition of gypsum is very small if the water of hydration is considered to recondense. The fact that the curve cuts the axis at a value less than 100 leads us to believe that the calorific values are low. In that case the curve showing B.t.u. versus ash as found also lies lower than it should and the intercept with the zero B.t.u. axis gives too small a ratio of ash to mineral matter. If, therefore, the ratios of the intercepts are taken, we obtain the value 0.76/0.965 or 0.788. The ratio of $CaSO_4$ to $CaSO_42H_2O$ is 0.8003, a good agreement considering the uncertainty of the extrapolation. The heats of decomposition of $CaSO_42H_2O$ to $CaSO_4$ and water, and of $CaSO_4$ to CaO and SO_3 are 7 and 595 B.t.u. per lb. of decomposing substance respectively. The results may be low, due to decomposition of some of the $CaSO_4$, but it hardly seems possible that that is the case. The effect of gypsum may, in general, be neglected, since the gypsum content of coals is usually low and the heat effects small.

(7) *Comparison of Graphically Found "Pure Coal" Calorific Values with "Pure Coal" Calorific Values Calculated as Dry, Ash-free; Dry,* 1.1 *Ash-free; and Dry,* 1⅛ *Ash-free; and Parr Unit Coal Values.*—Whether or not the graphical method such as that employed by Brinsmaid or Stansfield and Sutherland for determining pure coal values is to be preferred to an empirical formula such as those proposed by Parr or others, depends largely upon the agreement which is found in the values obtained by the two methods. Theoretically, making due allowance for possibilities of error due to slight variations in the character of the coal substance in standard samples and to the presence of heat-

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[14] Parr, S. W., "Chemical Study of Illinois Coals," Illinois Coal Mining Investigation, Co-operative Bulletin No. 3 (1916), p. 35.

producing substances in the ash, the graphical method must be regarded as essentially correct and therefore a basis for evaluating the results obtained by formula. If the values by the two methods are found to be essentially in agreement, then brevity and relative ease of determining pure coal values by formula methods commends them to general use. The individual determined calorific values for the various samples used in this study were calculated to so-called pure coal values by converting

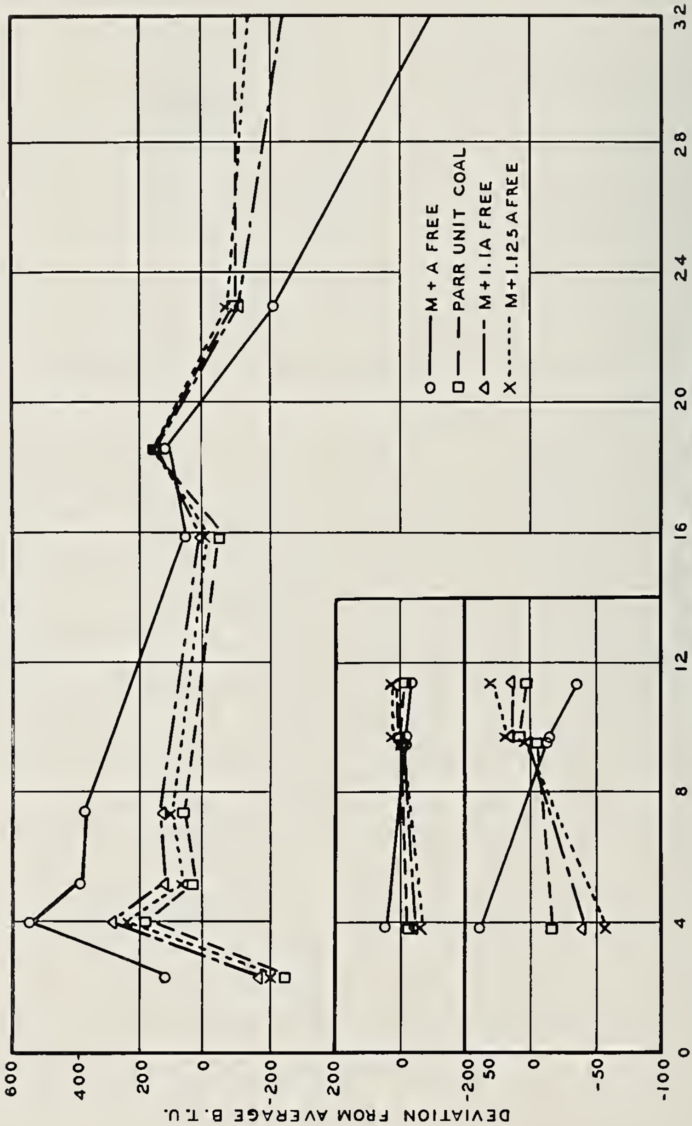

Fig. 11. Deviations from average of variously calculated "pure coal" values plotted against ash contents of samples. Large curve, coal No. 5, Fulton County, samples C-39, C-81-88; small curves, benches from coal No. 6, samples C-48, C-50, C-51, and C-126.

them to dry, ash-free; dry, 1.1 × ash-free; dry, 1⅛ × ash-free, and Parr unit coal values. The values so obtained and their averages were compared with the values obtained graphically, and the values were compared with themselves for constancy in any given series of fractions.

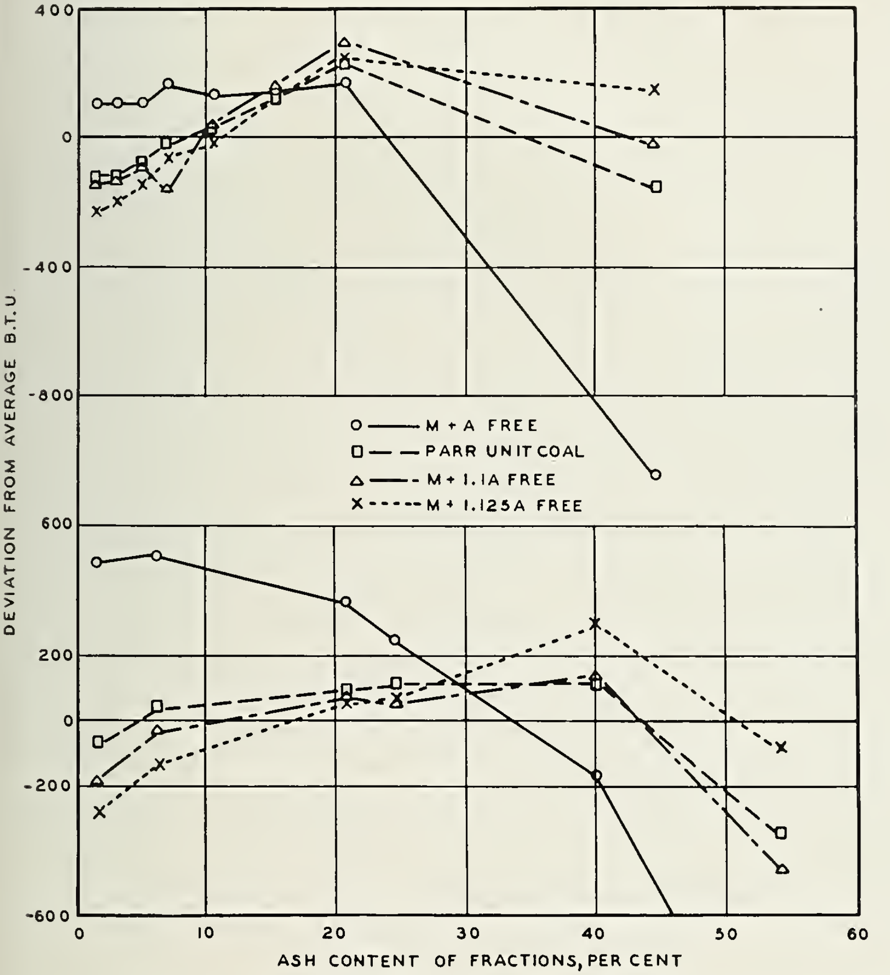

Fig. 12. Deviations of "pure coal" calorific values obtained by various formulæ from averages of such values plotted against ash contents of fractions. Successive gravity separations. Samples: Upper, C-56 to C-63; lower, C-64 to C-66, C-76 to C-78.

The dry, 1.1 ash-free and dry, 1⅛ ash-free values were included, since there is a considerable tendency towards their use in place of Parr unit coal values on the basis of simplicity. The values are given in Table 15.

In order to show more clearly the way in which the individual values in a series of fractions deviate from the average value for that

TABLE 15—*Comparison of various "pure coal" calorific values*

Sample C-39, Fulton County

Sample	Fraction	Sulfur	Ash	Dry calorific value B.t.u.	Moisture and ash-free calorific value B.t.u.	Deviation from average	Parr unit coal B.t.u.	Deviation from average	1.1 ash-free dry B.t.u.	Deviation from average	1.125 ash-free dry B.t.u.	Deviation from average
C- 81	F — 1.30	2.5	2.3	14,102	14,430	+ 123	14,538	—262 (*a*)	14,468	—164	14,477	—240
C- 83	F — 1.35	2.6	4.0	14,266	14,860	+ 553 (*a*)	14,998	+198 (*a*)	14,923	+291 (*a*)	14,938	+221 (*a*)
C- 85	F — 1.40	2.7	5.2	13,920	14,685	+ 378	14,840	+ 40	14,761	+129	14,793	+ 76
C- 87	F — 1.50	2.9	7.4	13,590	14,677	+ 370	14,871	+ 71	14,788	+156	14,820	+103
C- 82	S — 1.30	4.8	15.9	12,092	14,374	+ 67	14,780	— 20	14,657	+ 25	14,728	+ 11
C- 86	S — 1.35	5.8	18.6	11,756	14,442	+ 135	14,945	+145	14,787	+155	14,862	+145
C- 84	S — 1.40	6.4	23.2	10,827	14,100	— 207	14,712	— 88	14,533	— 99	14,651	— 66
C- 88	S — 1.50	13.5	46.7	6,873	12,891	—1,416 (*a*)	14,712	— 88	14,142	—490 (*a*)	14,469	—248 (*a*)
	Average pure coal by formulae	.....	.....	.....	14,307	406	14,800	114	14,632	189	14,717	139
	Value obtained graphically	.....	.....	.....	14,800	+ 493	14,800	00	14,800	+168	14,800	+ 83
C- 39	Original	4.9	14.4	12,306	14,377	+ 70	14,754	— 46	14,622	— 10	14,685	— 32
	Range of deviations					1,969		460		781		469
	Samples from benches of same seam No. 6 coal, Franklin County											
C- 48	Entire	1.2	9.7	13,021	14,412	— 13	14,577	+ 10 (*a*)	14,578	+ 17	14,615	+ 20
C-126	Bench 1	1.0	9.5	13,040	14,413	— 12	14,564	— 3	14,562	+ 1	14,601	+ 6
C- 50	Bench 2	0.9	11.3	12,767	14,393	— 32 (*a*)	14,572	+ 5	14,579	+ 18 (*a*)	14,626	+ 31 (*a*)
C- 51	Bench 3	1.4	3.8	13,916	14,466	+ 41 (*a*)	14,554	— 13 (*a*)	14,523	— 38 (*a*)	14,538	— 57 (*a*)
	Average pure coal by formulae	.....	.....		14,425	27	14,567	8	14,561	19	14,595	29
	Value obtained graphically	.....	.....		14,500	+ 75	14,500	— 67	14,500	— 61	14,500	— 95
	Range of deviations	.....	.....			73		23		56		88

Illinois coal No. 6, Franklin County

C- 56	F — 1.25	0.8	1.5	14,329	14,550	+ 109	14,593	—116	14,569	—138	14,575	—228 (a)
C- 57	S — 1.25 F — 1.30	0.9	2.9	14,122	14,554	+ 113	14,606	—103	14,587	—120	14,598	—205
C- 58	S — 1.30 F — 1.33	1.0	5.0	13,827	14,546	+ 105	14,642	— 67	14,632	— 75	14,650	—153
C- 59	S — 1.33 F — 1.35	1.0	7.0	13,580	14,606	+ 165	14,728	— 19	14,555	—152 (a)	14,742	— 61
C- 60	S — 1.35 F — 1.40	1.0	10.5	13,050	14,577	+ 136	14,752	+ 43	14,754	+ 47	14,798	— 5
C- 61	S — 1.40 F — 1.45	0.9	15.3	12,362	14,591	+ 150	14,839	+130	14,864	+157	14,932	+129
C- 63	S — 1.45 F — 1.50	0.8	20.7	11,592	14,609	+ 168 (a)	14,955	+246 (a)	15,010	+303 (a)	15,111	+246 (a)
C- 62	S — 1.50	2.1	44.7	7,466	13,502	— 939 (a)	14,554	—155 (a)	14,688	— 19	15,019	+155
Average pure coal		......	......	....	14,441	236	14,709	110	14,707	126	14,803	163
Value obtained graphically					14,550	+ 109	14,550	—159	14,550	—157	14,550	—253
Range of deviations						1,107		401		455		474
C- 66	F — 1.30	0.9	1.6	14,234	14,461	+ 474	14,511	— 82	14,489	—170	14,495	—275 (a)
C- 64	S — 1.30 F — 1.40	1.0	6.2	13,629	14,525	+ 538 (a)	14,639	+ 46	14,627	— 32	14,652	—118
C- 77	S — 1.40 F — 1.60	0.8	20.8	11,368	14,362	+ 375	14,693	+100	14,741	+ 82	14,841	+ 71
C- 78	S — 1.60 F — 1.70	2.4	40.3	8,245	13,813	— 174	14,730	+137 (a)	14,810	+151 (a)	15,084	+314 (a)
C- 76	S — 1.70	6.3	54.2	5,737	12,529	—1,458 (a)	14,272	—321 (a)	14,208	—451 (a)	14,703	— 67
C- 65	S — 1.40	2.1	24.6	10,737	14,232	+ 245	14,711	+118	14,720	+ 61	14,847	+ 77
Average pure coal		......	......	....	13,987	544	14,593	134	14,659	158	14,770	154
Value obtained graphically					14,550	+ 563	14,550	— 43	14,550	—109	14,550	—220
Range of deviations						1,996		458		602		589
C- 48	Original	1.2	9.7	13,021	14,412		14,577		14,578		14,615	

(a) Maximum and minimum values.

TABLE 15.—Concluded

Sample	Fraction	Sulfur	Ash	Dry calorific value B.t.u.	Moisture and ash-free calorific value B.t.u.	Deviation from average	Parr unit coal B.t.u.	Deviation from average	1.1 ash-free dry B.t.u.	Deviation from average	1.125 ash-free dry B.t.u.	Deviation from average
	Illinois No. 1 coal, Fulton County											
C-105	F — 1.30	2.5	2.3	14,206	14,536	+197	14,646	— 37	14,575	+ 31	14,584	— 12
C-107	F — 1.33	2.6	3.0	14,365	14,807	+468 (*a*)	14,933	+250 (*a*)	14,855	+311 (*a*)	14,868	+272 (*a*)
C-109	F — 1.35	2.5	3.5	14,143	14,653	+314	14,781	+ 98	14,709	+165	14,723	+127
C-111	F — 1.40	2.7	4.4	13,945	14,591	+252	14,728	+ 45	14,654	+110	14,671	+ 75
C-113	F — 1.50	2.9	5.5	13,829	14,628	+289	14,800	+117	14,727	+185	14,741	+145
C-115	F — 1.60	3.1	5.7	13,524	14,345	+ 6	14,511	—172	14,429	—115	14,450	—146
C-117	F — 1.70	3.0	5.7	13,381	14,189	—150	14,353	—330 (*a*)	14,276	—268 (*a*)	14,297	—299 (*a*)
C-106	S — 1.30	6.0	15.8	12,037	14,294	— 45	14,738	+ 55	14,571	+ 27	14,640	+ 44
C-108	S — 1.33	7.1	19.7	11,345	14,130	—209	14,691	+ 8	14,484	— 60	14,575	— 21
C-110	S — 1.35	8.1	23.1	10,718	13,941	—398	14,610	— 73	14,369	—175	14,482	—114
C-112	S — 1.40	11.1	33.4	9,069	13,611	—728 (*a*)	14,725	+ 42	14,336	—208	14,529	— 67
C-114	S — 1.50	19.1	47.9	6,141	11,796	......	13,734	......	12,980	......	13,318	......
C-116	S — 1.60	21.9	56.2	4,633	10,574	......	12,979	......	11,825	......	12,600	......
C-118	S — 1.70	27.4	61.4	3,382	8,773	......	10,806	......	10,419	......	10,938	......
	Average pure coal by formulae	......	......		14,339	278	14,683	112	14,544	151	14,596	120
	Value obtained graphically	......	......		14,600	+261	14,600	— 83	14,600	+ 56	14,600	+ 4
C-104	Original	4.4	9.3	13,077	14,410	+ 71	14,687	+ 4	14,567	+ 23	14,605	+ 9
	Range of deviations	......	......			1,196		580		579		571

(*a*) Maximum and minimum values.

series, the deviations from the average have been plotted against ash values in figures 11, 12 and 13. From these figures and from the tables, it is seen that the mean of the deviations from the group average is least for the values derived by the Parr unit coal formula. The range of deviations is also least in the case of the Parr unit coal calorific values, in all cases except that of the coal from Fulton County.

The averages of the pure coal values for the various series of float-and-sink fractions, and the corresponding pure coal values for the original coals are compared in Table 16 with the corresponding pure coal values found graphically. The best agreement with the graphical values was found in the case of the unit coal values, and while the unit coal values were not always closest to the graphical values, the average of the differences between the unit coal and graphical values was the smallest; and the maximum difference between unit coal and graphical value was also less than the maximum difference between some other pure coal value and the graphical value. If maximum values are considered as essentially correct, then the unit coal calorific value more nearly approaches the true state of affairs than do the values obtained by the other three formulæ.

TABLE 16.—*Comparisons of calorific values obtained graphically and by formulae*

Graphical	Ash-free	Difference	Unit coal	Difference	1.1 ash-free	Difference	$1\frac{1}{8}$ ash-free	Difference
14,800	14,307	493	14,800	000	14,632	168	14,717	83
14,800	14,377	423	14,754	46	14,622	178	14,685	115
14,500	14,425	75	14,567	67	14,561	61	14,595	95
14,550	14,441	109	14 709	159	14,707	157	14,803	253
14,550	13.987	563	14,593	43	14,695	145	14,770	220
14,550	14 412	138	14,577	27	14,578	28	14,615	65
14,600	14,339	261	14,683	83	14,544	56	14,596	4
14,600	14,410	190	14,687	87	14.567	33	14.605	5
Average difference		282		64		103		105

Concerning the oft-stated objection to the Parr unit coal calorific value formula on the basis of cumbersomeness, it may be stated that we have shown elsewhere that this formula may be simplified to the form,

B.t.u. unit coal =

$$\frac{\text{B.t.u. determined} \times 100}{100 - (1.08 \times \%\ \text{Ash} + 0.21 \times \%\ \text{S})}$$

which is an approximation within the range of experimental errors of coal calorimetry to the original Parr unit coal formula. By its use, only slightly more time is required for the calculation of unit coal calorific values than for the calculation of 1.1 ash- and moisture-free values, especially if a calculating machine is used.

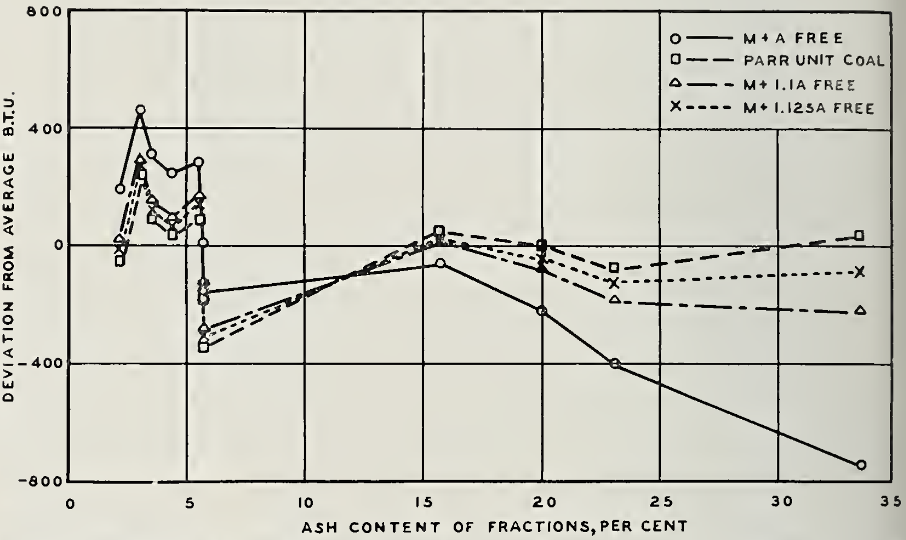

FIG. 13. Deviation of "pure coal" calorific values calculated by various formulæ plotted against ash contents of fractions, coal No. 1, Fulton County, Illinois; samples C-104 to C-118 inclusive.

SUMMARY

The ash or combustion residue obtained when coal is burned does not correspond in quantity nor composition to the mineral matter present originally in the coal. Calculations of coal analyses to an ash-free basis in order to obtain analyses of "pure coal" are therefore in error by an amount proportional to the ratio of ash to mineral matter. The concept of "pure coal" itself offers difficulties. In this paper, pure coal is considered to be organic combustible material, including organic sulfur assumed to remain constant in average composition for a given seam over a delimited area, as the proportion of ash associated with it changes.

The method of determining pure coal calorific values and ash-mineral matter ratios by plotting the calorific values against ash contents of fractions of a coal sample separated by float-and-sink procedure on liquids of differing gravities was studied. It has been shown that the curve relating calorific value and ash is usually, but not necessarily, a straight line. The mineral matter in the coal may be reconstructed from the ash obtained by analyses. The ratio of the ash to the amount of this reconstructed mineral matter corresponds to the ratios obtained by the graphical method, providing that the heat of transformation of mineral matter to ash is negligible. This was shown to be true in the case of two coals. If the mineral matter evolves or absorbs considerable heat in transformation, then the graphical method will not give the correct value unless the intercept of the curve with the ordinal representing the calorific value of the mineral matter is taken. This is illustrated in the case of mixtures of a low-ash coal with pyrites and with calcite. A similar study found in the literature, using gypsum which has but little heat of transformation, is also reviewed. The extrapolation of the calorific value/ash curve to the zero ash axis to give a pure coal calorific value must be made with the realization that the very light coal may have a characteristically different calorific value from the rest of the coal, because it consists of a different type of coal material; and with the realization that the curve may change direction in the region of high-ash value, due to a change in the nature of ash with specific gravity. This is of especial importance in the case of curves plotted from analyses of fractions of coal separated successively on heavier liquids, as for example, samples obtained in float-and-sink washability tests. The calorific values obtained in this manner do not necessarily need to correspond to "unit coal" values calculated by the Parr formula. A study of component bands hand-picked from a coal sample showed that the ash/calorific value or ash/specific gravity relationships were not linear and that a segregation of coal components in certain gravity fractions could be expected. Since these components may have different "pure" or "unit" coal composition, their segregation would make it impossible always to expect linear relationships between ash and calorific values for coal fractions separated on a gravity basis. However, the actual variations from a straight-line relationship due to the causes suggested are small and the values obtained by the graphical method are a close approach to accuracy and provide a satisfactory means of testing the adequacy of empirical formulæ, such as the Parr formula, for arriving at a value for mineral-free coal. Since comparison of results obtained by the two methods indicates that the Parr formula gives values in essential agreement with those obtained by the graphical method, the Parr method, because of its greater simplicity of application, is more suitable for general use. In the case of high-ash, high-sulfur coals, neither method possesses conspicuous advantage over the other.

CONCLUSIONS

(1) Coal is not a homogeneous material.

(2) "Pure coal" or "unit coal" values are average values dependent upon the properties of the coal components and upon the relative amounts of the individual components.

(3) The pure coal substance (coal free from mineral matter) is also a composite material. Its average composition for a given seam over a delimited area may remain constant for all practical purposes. Segregation or local concentration of certain of the components of pure coal in the coal seam or in the preparation of the coal sample may give values which differ from average values for the coal as a whole.

(4) Curves, representing variations in calorific value with ash content for fractions of a coal sample separated on the basis of specific gravity, were essentially straight lines for the coals studied until the ash content became high in the fractions (40 per cent).

(5) For the coal so studied, the organic sulfur content of the mineral matter-free coal remained constant. The pure coal calorific values obtained by the graphical method will include a correct value for the calorific effect of organic sulfur, provided the ratio of organic sulfur to pure coal remains constant with change in the ash content of the samples.

(6) The quantity and probable constitution of the mineral matter in a coal may be calculated from the ash and pyritic sulfur contents of the coal and an analysis of the ash. The ratio of the quantity of ash formed on combustion of a coal to the quantity of mineral matter contained in the coal may also be found from the analysis of the coal ash and the ash and sulfur content of the coal.

(7) A separation of a coal sample into fractions on the basis of physical properties may tend to concentrate certain pure coal components in certain fractions.

(8) The calorific effect due to pyritic sulfur will be excluded from the pure coal calorific value found by the graphical method, provided there is a constant ratio of pyritic sulfur to ash in the fractions.

(9) Pure coal calorific values obtained by the graphical method correspond closely to the average of the Parr unit coal values of the fractions used in the graphical method.

(10) The graphical method provides no advantage over the Parr unit coal formula for the calculation of "pure" or "unit" or similar coal calorific values from the standpoint of accuracy.

(11) The graphical method of pure coal calorific value calculation involves too great an amount of work for each value obtained to make its use very common.

(12) Published analyses cannot be converted to pure or unit coal values except by formulæ such as that of Parr.

(13) Any system of coal classification which will be practicable will not make division into classes or groups on analytical differences which are smaller than the differences between Parr unit coal values and graphically determined pure coal values.

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