Nitrogen and Sulphur in Coal

FUNASAKA, Wataru; YOKOKAWA, Chikao

FUNASAKA, Wataru ...[et al]. Nitrogen and Sulphur in Coal. Memoirs of the Faculty of Engineering, Kyoto University 1960, 22(1): 30-40

Nitrogen and Sulphur in Coal

By

Wataru FUNASAKA* and Chikao YOKOKAWA†

(Received October 31, 1959)

As it was considered that the origin of nitrogen in coal was protein, cellulose and lignin were coalified with protein (egg albumin) in water medium at 300°C under corresponding pressure. The behaviors of nitrogen in the artificial coalification processes were observed and the properties of thus obtained coals were examined. Nitrogen in protein is chemically combined with cellulose and lignin, and the proper amount of protein accelerates the huminification of cellulose and the bituminization of lignin. When these nitrogen containing artificial coals are oxidized with alkaline $KMnO_4$, nitrogen is recovered as NH_3 and NO_3' almost quantitatively, as same as in the case of natural coals. With this fact, it seems probable that nitrogen in artificial coal is in the same condition of that in natural coal.

Cellulose and lignin were artificially coalified in aqueous solutions or suspension of sulfides or sulfates to discuss the origin of sulphur in coal. Water soluble sulfides supply sulphur into artificial coal as organic sulphur, but water insoluble sulfides or sulfates (even water sobluble) do not. It can be concluded that the origin of organic sulphur in coal is water soluble sulfides and that the hypothesis, which explaines that iron sulfates are reduced to pyrite in the coal forming process, seems scarecely probable.

Introduction

The process of coal formation was discussed previously on the basis of the artificial coalification experiments 1) 2). In this paper, the origin of nitrogen and sulphur in coal are discussed on the same basis.

As these elements in coal scarecely exceed over several per cent., they are liable to be ignored in discussing the chemical constitutions of coal. But for the purpose to discuss the coal forming process, it seems very noticeable that the way in which these elements are combined in the molecule of coal is studied.

Nitrogen, which hardly exceeds 0.1% in living plants, can be usually identified as 1–2% in coal. This enrichment of nitrogen in coal should be a clew for our problem and is explained by the melanoid theory of L. C. Maillard 3) and C. Enders 4) and the ligno-protein theory of S. A. Waksman 5).

---

* Department of Industrial Chemistry
† Department of Fuel Chemistry

About sulphur in coal, which is discussed principally on the view of industrial application of coal, we have no definite knowledge not only of its combination but of its origin, excepting some conjectures.

I. Artificial Coalification of Protein and Cellulose or Lignin Mixtures

F. Bergius[6], E. Terres[7] and E. Berl[8] observed nitrogen behavior in the artificial coalification processes of protein, however, their discussions are all very brief. Therefore more detailed experiments were carried out to discuss the effects of protein on the artificial coalification of cellulose or lignin, i.e. on the quantity and quality of artificial coals.

Experiments and Results

As protein egg albumin was chosen, failing to get any pure vegetable material which seems more preferable. The moisture content (weight decrease by one hour drying at 105°C) and the nitrogen content (moisture free basis) of this albumin are 11.5% and 15.3%, respectively. As cellulose, filter paper (Toyo Roshi Co., Ltd., for qualitative use, N 0.00%) and as lignin thioalkali pine lignin (N 0.20%) were used, respectively. The materials, as shown in Table 1, were brought into an autoclave (capacity 1,000 cc) and submitted to the artificial coalificction for six hours at 300°C under 110–120 atm.

When protein was coalified alone, oily product was formed and it was gained by extraction with benzene and alcohol (1:1) mixture. In the other artificial

Table 1. Artificial Coalification of Protein and Cellulose (or Lignin) Mixture.

Code	Material (g)					Solid products			Nitrogen distribution (%)			Distribution of water-soluble-nitrogen (%)			
	Protein	Cellulose	Lignin	Water as medium	Nitrogen	Yield (g)	Yield (%)	N-Content (%)	in Solid	in Medium	Loss	NH_3 type	Humin	Diamino acid	Monoamino acid
P	50.0	0.0	0.0	500	7.65	14.0	28.0	5.79	10.6	70.9	18.5	53.4	0.9	2.3	11.4
CP 1	2.5	47.5	"	"	0.38	14.7	29.5	1.93	74.2	25.8	0.0	19.5	7.5	—	—
CP 2	5.0	45.0	"	"	0.76	14.5	29.1	3.32	63.0	27.9	10.1	13.1	5.1	8.8	3.5
CP 3	10.0	40.0	"	"	1.53	16.0	32.1	5.18	54.3	37.7	8.0	16.5	3.1	10.5	3.1
CP 4	15.0	35.0	"	"	2.29	15.7	31.4	5.46	37.4	46.9	15.7	25.5	1.4	12.5	—
LP 1	2.5	0.0	47.5	"	0.48*	25.8	51.6	1.27	68.6	31.4	0.0	23.3	6.1	—	—
LP 2	5.0	"	45.0	"	0.86*	27.6	55.3	1.65	53.2	36.0	10.8	24.0	6.2	2.3	3.6
LP 3	8.5	"	33.7	420	1.35*	20.6	49.0	2.42	37.0	47.4	15.6	27.8	3.6	12.4	2.7
CN	0.0	45.0	0.0	500	0.76	13.8	30.6	3.95	76.5	28.5	—	15.1	5.9	—	—
LN	0.0	0.0	45.0	"	0.86*	25.8	57.3	2.35	70.5	—	—	—	—	—	—

*: Nitrogen in Lignin is accounted.

coalification, black powder or granular coals coagurated with pitchy material were formed and they were air dried after filtering and washing. These artificial coals were tested according to the proximate analysis and rational analysis. Of nitrogen, all the fractions of rational analysis were measured their nitrogen content by Kjeldahl method and the coalification medium with washing solution was analyzed according to van Slyke's amino acid classification.

Table 1 shows the ratio of protein-cellulose (or protein-lignin) mixing and nitrogen distribution after coalification. P, C and L in the table indicate protein, cellulose and lignin, respectively. CN and LN mean that C or L are coalified in N/10 NH_4OH, respectively.

The yields for the CP, LP, CN and LN coals are all larger than that for cellulose or lignin alone. Most of mediums after coalification show alkaline reaction and include free ammonia, as shown in Table 1. According as the protein in starting materials increases, nitrogen contents of solid products increase, although the proportion of nitrogen distributed to the latters to the total nitrogen decreases.

Table 2 shows the results of proximate analysis of artificial coals. It can be said in general that CP, CN, LP and LN include more volatile matter than coals prepared from cellulose or lignin alone in water medium (C and L). As for CP series, much fluctuation of volatile matter content can be pointed out according to the amount of protein added. LP series show no fluctuation. Concerning with the quality of cokes, it is clear that addition of protein to cellulose causes distinct increase of caking property, although the coals of LP series show only strong sintering.

Table 2. Proximate Analysis of N-Artificial Coals (%)

Sample	Moisture	Volatile matter	Fixed carbon	Ash	Appearance of coke
CP 1	5.30	62.51	31.95	0.24	sintering
CP 2	3.16	50.36	45.71	0.77	caking
CP 3	5.56	53.26	39.76	1.42	"
CP 4	12.81	69.18	15.97	2.04	swelling, crust-like-coke
LP 1	7.15	41.30	50.35	1.20	not sintering
LP 2	6.45	40.78	51.14	1.63	sintering
LP 3	6.69	41.40	49.89	2.02	strongly sintering
CN	8.43	45.20	46.00	0.37	feebly sintering
LN	2.51	36.27	60.56	0.66	"
C	4.24	39.99	54.59	1.18	"
L	4.50	31.20	62.84	1.46	"

C and L indicate that cellulose and lignin are coalified in water, respectively.

Table 3 shows the result of rational analysis. As for CP series, with addition of protein the huminification of cellulose seems to be accelerated, however, with much protein bitumen rich product is formed. On the other hand, lignin seems to be bituminized by the addition of protein; although this bitumen is very unstable in benzene and can easily precipitate.

Table 3. Rational Analysis of N-Artificial Coals (d.a.f. %)

Sample	Bitumen	Cellulose	Humic acid	Lignin	Humin
CP 1	46.1	0.53	1.62	—	51.75
CP 2	28.6	8.83	1.34	—	61.26
CP 3	64.5	2.59	1.28	—	31.63
CP 4	78.1	0.09	1.21	—	20.60
LP 1	25.4	—	5.17	22.2	47.23
LP 2	25.6	—	4.58	17.0	52.82
LP 3	22.5	—	2.80	12.3	62.40
CN	40.6	2.66	1.28	—	55.46
LN	28.8	—	0.95	—	—
C	52.6	6.7	8.7	—	32.0
L	5.1	1.1	0.1	23.6	70.1

Table 4 shows nitrogen distribution for each fraction of rational analysis. As mentioned above, CP and LP coals contain much or less bituminous material derived from protein, however, it is clearly said that nitrogen is chemically combined in the residual coal, debituminised with benzene-alcohol mixture (1 : 1), humic acid and humin.

Table 4. Nitrogen Content and Distribution for Each Fraction of Rationd Analysis (%)

Sample	Original sample	Bitumen	Extracted residue	Cellulose	Humic acid	Lignin	Humin
CP 1	1.93(100)	1.40(33.4)	2.21(61.9)	3.48(15.9)	5.13(4.3)	—	1.71(45.8)
CP 2	3.32(»)	3.54(30.5)	2.99(64.4)	0.00	4.67(1.9)	—	3.62(66.1)
CP 3	5.18(»)	4.37(54.4)	3.50(37.7)	1.80(0.9)	5.01(1.2)	—	5.67(34.6)
CP 4	5.46(»)	5.57(79.7)	4.90(19.7)	0.00	4.23(0.9)	—	4.55(17.1)
LP 1	1.27(»)	1.55(31.0)	1.09(64.0)	—	2.18(8.9)	1.17(2.1)	1.56(58.0)
LP 2	1.65(»)	1.64(25.0)	1.79(80.5)	—	3.67(10.0)	5.51(5.7)	1.71(54.7)
LP 3	2.42(»)	2.60(24.2)	2.43(77.8)	—	5.45(6.3)	4.25(21.7)	1.94(49.8)
CN	3.95(»)	2.68(27.6)	4.04(61.0)	0.00	2.35(3.0)	—	4.19(58.7)
LN	2.35(»)	2.12(26.2)	2.74(82.8)	—	2.27(0.9)	2.96(32.2)	2.62(49.8)

( ) : Distribution %

Consequently it can be concluded as follows.

1) Some portion of nitrogen in protein is fixed chemically in coal with limited extend, i.e. 5% for cellulose coal and 2% for lignin coal, roughly.

2) With addition of protein, bituminization of lignin increases, but this bitumen seems not to be caking constituent.

3) Suitable amount of protein accelerates huminification of cellulose.

4) Protein seems not always to be necessary component for caking property of coal, but it accelerates the caking property.

II. Oxidation of Nitrogan containing Artificial Coals with Alkaline Permanganate Solution

Many experiments to discuss the combination of nitrogen in coal have been studied without any decisive conclusion to explain it clearly. C. R. Kinney and his coworkers[9) have discussed this problem, comparing natural coal and regenerated humic acid with known constitutional chemicals by tracing nitrogen distribution during oxidative degradation process. To compare the nitrogen in artificial coal with that of natural one, both were oxidized with alkaline $KMnO_4$ and behavior of nitrogen was traced.

Experiments and Results

0.3 g of samples (passing 60 mesh sieve, Table 6) were put in 500 cc five necked flask and 10 cc of 30% KOH, then 50 cc of water, with which the flask wall rinsed, were added. Agitator, dropping funnel, reflux condenser and air blasting pipe were equiped on the flask and a trap, filled with N/100 H_2SO_4, was provided at the top of the condenser. To fully wetted sample in heated flask, 300 cc of boiling N/2 $KMnO_4$ solution were added quantitatively, and the air blasting was started. After necessary boiling for reaction, the content in flask was put on ice to cool rapidly. After filtering off thus produced MnO_2 and unaffected coal, permanganate, NH_3 and NO_3' were determined. For the determination of residual coal, MnO_2 was reduced with oxalic acid and washed from the former off. Nitrate was determined as NH_3 after reduction with Devarda's alloy. Blank test with ammonium oxalate shows no loss of NH_3 and no oxidation of NH_3 to NO_3' in above-mentioned procedure.

Table 5 shows that the results of oxidation of artificial coals, and the results of compared samples are given in Table 6. In these tables, the quantity of nitrogen, NH_3 and NO_3' are expressed with corresponding cc of N/100 NaOH solution.

Rate of oxidation, i.e. velocity of $KMnO_4$ consumption, is larger for cellulose coal than for lignin coal, and is very large for artificial coal compared with natural coal. By the by, the amount of permanganate consumed is larger for lignin coal than for cellulose coal, and for the former is almost as same as that for natural coal, on the basis of unit weight of pure coal oxidized. As clearly shown in

Table 5. Alkaline-$KMnO_4$ Oxidation of N-Artificial Coal

Sample	Nitrogen		Reaction time (min)	Coal consumed (%)	$KMnO_4$ consumed per g of d.a.f. coal	Nitrogen recovered				NH_3/NO_3'
	%	Content in 0.3 g coal, as cc of N/100 solution				as cc of N/100 solution			%	
						NH_3	NO_3'	Total		
CP 2	2.99	64.18	5	100	7.19	24.45	—	—	—	—
”	”	”	10	”	7.63	31.94	13.02	44.96	70.1	2.54
”	”	”	20	”	7.77	35.02	14.30	49.32	76.9	2.54
”	”	”	60	”	8.42	39.16	23.00	62.16	96.8	1.70
”	”	”	120	”	8.91	40.74	25.21	65.95	102.8	1.61
LP 2	1.79	39.43	5	84.5	6.85	19.78	5.80	25.58	64.7	3.41
”	”	”	10	88.5	7.76	19.00	7.92	26.92	68.2	2.40
”	”	”	20	91.5	8.35	23.87	11.42	35.29	79.7	2.08
”	”	”	60	100	9.09	21.37	17.16	38.53	96.4	1.24
”	”	”	120	”	9.94	21.12	20.28	41.40	104.0	1.04
CN	4.04	80.35	5	—	—	32.22	13.03	45.23	55.2	2.47
”	”	”	40	100	9.33	33.65	16.20	49.85	62.1	2.08
”	”	”	60	”	9.74	37.83	21.30	59.13	73.7	1.76
”	”	”	120	”	—	39.80	22.85	62.65	78.0	1.74
”	”	”	180	”	9.56	39.60	21.56	61.16	76.1	1.83
LN	2.74	58.65	20	”	8.10	16.65	10.18	26.83	46.9	1.64
”	”	”	40	95.9	8.67	23.80	16.33	40.13	68.4	1.45
”	”	”	90	97.3	9.50	19.30	20.30	39.60	67.5	0.95
”	”	”	120	96.9	9.76	24.90	23.95	48.85	83.0	1.04

Table 5, regarding to the time elapse for oxidation, $KMnO_4$ consumption and production of NH_3 and NO_3' can be expressed by smooth curves to show a continuous reaction, and after all, nitrogen in samples are recovered almost quantitatively as NH_3 or NO_3'. Moreover it is very interesting to note that the production of NH_3 is predominant at the early stage of oxidation. This fact is a new evidence for discussion and is clearly shown by the values of NH_3/NO_3' in the tables, and is supported with the blank test which ensured that no further oxidation of NH_3 to NO_3' occured. The ultimate value of NH_3/NO_3' in Table 6 is roughly 1.5 for cellulose coal and 1.0 for lignin coal. It is 1.5 and 2.2 for bituminous coal and cannel coal (so-called Kabari in Fuchun, Manchuria), respectively. Considering the three experiments on ligno-protein and the values for natural coals proposed by C. R. Kinney and coworkers, it seems very noticeable to know that high NH_3/NO_3' values are observed for such kind of coals as considered to have been composed of more cellulose rich materials.

It is naturaly impossible to discuss the art of nitrogen linkage in coal with above experiments, however, two different combinations seem to be reasoned. One of them is more reactive to oxidizing reagent and gives NH_3 predominantly

Table 6. Alkaline-$KMnO_4$ Oxidation of Related Substances

Sample	Nitrogen		Reaction time (hr)	Coal consumed (%)	$KMnO_4$ consumed per g of d.a.f. coal (g)	Nitrogen recovered				NH_3/NO_3'
	(%)	Content in 0.3 g coal, as cc of N/100 solution				as cc of N/100 solution			(%)	
						NH_3	NO_3'	Total		
Lignoprotein	2.39	51.25	9	100	10.85	36.65	15.21	51.86	101.2	2.41
Lignoprotein coal	1.85	39.71	6	"	6.39	22.70	14.89	37.59	94.7	1.52
Lignoprotein coal (Extracted residue)	1.78	38.20	6	"	10.88	18.50	18.78	37.28	97.5	0.99
Albumin*	12.4	266.50	9	"	8.13	197.90	69.05	266.95	100.1	2.86
CP 2	2.99	64.18	2	"	8.91	40.74	25.21	65.95	102.8	1.61
LP 2	1.79	39.43	2	"	9.94	21.12	20.28	41.40	104.0	1.04
CN	4.04	80.35	3	"	9.56	39.60	21.56	61.16	76.1	1.83
LN	2.74	58.65	2	96.9	9.76	24.90	23.95	48.85	83.0	1.04
Lignite	1.20	25.70	15	—	—	17.28	11.16	28.44	110.0	1.55
High volatile bituminous coal	1.52	32.50	9	—	—	19.89	10.76	30.65	94.5	1.84
Medium volatile bituminous coal	1.33	28.57	"	—	15.92**	16.89	10.95	27.84	97.8	1.54
"	1.80	38.57	15	—	10.00**	22.48	13.68	36.16	93.7	1.64
"	1.88	41.15	"	—	9.02**	22.77	16.90	39.67	96.4	1.35
"	2.14	45.71	9	—	9.85**	27.85	15.81	43.66	95.5	1.76
Low volatile bituminous coal	1.55	32.14	"	—	—	20.25	12.30	32.55	101.5	1.65
Cannel coal "Kabari" Fuchun	2.06	44.75	15	—	11.26**	31.38	14.16	45.54	101.8	2.22
Medium volatile bituminous coal (Extracted residue)	1.75	37.86	"	—	14.96**	21.61	17.04	38.65	102.1	1.27
"	1.49	32.14	9	—	10.76**	16.57	15.41	31.98	99.5	1.08

* Albumin contains 12.5% moisture. ** Dry coal basis

and the other is rather resistant and gives NO_3' predominently. On the other hand, as the behaviors of nitrogen in artificial coal and natural coal against oxidative degradation are comparable, it seems likely that these nitrogen combinations in artificial coal are the same to them in natural coal, in their character.

III. Effects of Sulphur Compounds on Artificial Coal

We have no accurate knowledge of organic sulphur in natural coal excepting a report by I. Y. Postovskii and A. B. Harlampowich[10], though its origin is supposed and discussed without any experimental evidence[11].

The following experiments were carried out to examine how sulphur compounds, especially H_2S, other sulfides and sulfates of iron give sulphur to artificial coal, and to know their effects on the nature of artificial coal.

Experiments and Results

Besides filter paper and thioalkali pine lignin, which were already mentioned above, Willstätter's lignin was used as starting material, because thioalkali lignin contains 2.39% of sulphur and is unsuitable for present purpose. The sulphur content of filter paper and Willstätter's lignin gained from saw-dust of an acerose-tree is 0.00 and 0.04%, respectively.

Twenty grams of starting materials were heated with 200 cc of aqueous solution of sulphur compounds for 6 hours at 300°C in an 400 cc capacity autoclave. Sulphur in all the solid matters was determined by the bomb method gravimetrically. Hydrogen sulfide and other sulfides in solution were also determined iodometrically, but organic sulphur compounds which would be formed and be soluble in aqueous medium were not estimated.

Table 7 shows all sulphur behaviors in artificial coalification. With addition of sulphur compounds, no special phenomena were observed during the artificial coalification processes. Speaking of sulphur distribution, a clear difference should be pointed out between sulfides and sulfates. Water soluble sulfides, i.e. H_2S, Na_2S and $(NH_4)_2S$, are supposed to combine easily with organic materials and scarecely left unchanged in aqueous medium or in gaseous state. As much as 30–40% of total sulphur added in this form is fixed in coal and the rest, i.e. 60–70%, of them seem to be water soluble organic sulphur compounds chiefly, or some will be combined with autoclave wall and packing parts. On the other hand, pyrite (S 22.08%), which was suspended in the aqueous coalfication medium,

Table 7. Sulphur Behavior in Artificial Coalification

Code	Medium	Sulphur added (g)	Coal yield (%)	Sulphur in coal (%)	Sulphur distribution (%) in			
					Medium	Gas	Coal	Diff.
C-H_2S	0.1 N H_2S	0.402	36	1.89	0	0.8	33.9	65.3
C-Na_2S	0.2 N Na_2S	0.789	18	7.50	H_2S 16.5	12.1	34.2	37.2
C-$(NH_4)_2S$	0.2N $(NH_4)_2S$	0.620	29	2.29	Sulfide 4.2	1.3	21.4	73.1
C-$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	0.866	29	0.58	Sulfate 88.2	0	4.0	7.8
C-FeS_2	Water + FeS_2	0.254	32	2.95	Sulfate 5.8	0	74.3	19.9
C-$FeSO_4$	$FeSO_4$	0.805	30	0.45	Sulfate 90.3	0	3.4	6.3
TL-H_2S	0.1 N H_2S	0.495 0.399	57	2.32	—	2.5	32.7	64.8
TL-Na_2S	0.2 N Na_2S	0.478 0.786	70	3.96	—	7.1	43.9	49.0
L-H_2S	0.1 N H_2S	0.442	54	1.46	0	0	35.7	64.3
L-Na_2S	0.2N Na_2S	0.588	54	0.84	Sulfide trace	trace	16.4	83.6
L-$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	0.866	57	0.36	Sulfate 96.3	0	4.7	—
L-FeS_2	Water + FeS_2	0.254	56	1.89	Sulfate 1.6	0	83.4	15.0

TL and L indicate Thioalkali-lignin and Willstätter's lignin, respectively.

produced some sulfate but most of which was left unchanged in artificial coal as mentioned latter. Sulfates, more than 90% of which existing in medium after coalification as SO_4'', neither gives sulphur to coal nor produces sulfide.

Table 8 presents characteristics of artificial coal. It shows the same tendency of previously mentioned artificial coal without any specialities caused by the addition of sulphur compounds, but it is noticeable that bituminization of lignin is accelerate by sulfides.

Table 8. Characteristics of Artificial Coal

Sample	Proximate Analysis (%)				Fuel ratio	Sulphur content (%)	Bitumen (%)	Appearance of artificial coal	Appearance of coke
	Moisture	Volatile matter	Fixed carbon	Ash					
C-H_2S	3.02	40.97	54.46	1.55	1.33	1.89	33.7	brown, powder	not sintering
C-Na_2S	2.50	75.80	20.00	1.70	0.26	7.50	100	almost asphalt like	swelling, crust like coke
C-$(NH_4)_2S$	3.97	66.50	26.39	3.14	0.40	2.29	62.7	partly pitch like	caking, swelling, metallic luster
C-$Fe_2(SO_4)_3$	4.97	52.33	41.64	1.06	0.80	0.58	53.3	black, powder	strongly sintering
C-FeS_2	2.21	48.44	25.90	23.45	0.54	2.95	71.7	″ , sand	coking
TL-H_2S	5.96	42.48	48.16	3.40	1.13	2.32	38.2	″ , ″	strongly sintering
TL-Na_2S	6.16	28.62	59.15	6.07	2.06	3.96	15.4	″ , powder	not sintering
L-H_2S	7.78	31.80	55.67	4.75	1.75	1.46	13.2	″ , ″	″
L-Na_2S	6.06	29.29	56.86	7.79	1.94	0.84	10.0	″ , ″	″
L-$Fe_2(SO_4)_3$	5.36	35.84	53.99	4.81	1.52	0.36	10.4	″ , ″	″
L-FeS_2	3.57	30.66	48.92	16.85	1.59	1.89	19.2	″ , ″	″

In Table 9, classification of sulphur in artificial coal are presented. The sulphur content of each ingredient and the sulphur distribution to each of them, although they may contain some error according to such experimental procedure, seem to be concluded as follows.

Table 9. Distribution of Sulphur in Artificial Coal (%)

Sample	Total S	Combustible S	Incombustible S	in Volatile matter	in Coke	in Bitumen	in Extracted residue
C-H_2S	1.89	95.0	5.0	47.5	52.5(1.77)	40.0(2.24)	60.0(1.71)
C-$(NH_4)_2S$	2.29	94.3	5.7	—	—	62.2(2.28)	37.8(2.32)
C-$Fe_2(SO_4)_3$	0.58	88.4	11.6	13.2	86.8(1.18)	12.0(0.13)	88.0(1.19)
C-FeS_2	2.95	95.8	4.2	—	—	—	—
TL-H_2S	2.32	95.7	4.3	57.3	42.7(1.92)	45.5(2.78)	54.5(2.04)
L-H_2S	1.46	93.2	6.8	26.0	77.0(1.79)	22.0(2.43)	78.0(1.31)
L-Na_2S	0.84	94.0	6.0	19.8	80.2(1.04)	3.6(0.29)	96.4(0.90)
L-$Fe_2(SO_4)_3$	0.36	85.1	14.9	41.2	58.8(0.36)	11.8(0.41)	88.2(0.35)
L-FeS_2	1.89	92.4	7.6	36.2	63.8(1.84)	0.7(—)	99.3(2.32)

( ): Sulphur content (%) of individual fraction.

Incombustible sulphur is about 5% of total sulphur of coal derived with addition of sulfide, and is 10–15% for sulfate. By washing C–FeS_2 and L–FeS_2 with HCl until no iron ion is identified in filtrate, the sulphur content of these coals becomes almost zero. This fact shows that nearly all of FeS_2 is mixed in coal by the artificial coalification, and this consideration is supported by the existence of almost all sulphur of L–FeS_2 coal in its extracted residue. Sulphur content of coke and extracted residue are almost the same to that of their pearent coal, so it is said that organic sulphur seems to be distributed relatively uniformly among the coal constituents, i.e. volatile matter and fixed carbon or bitumen and extracted residue.

Consequently, organic sulphur in coal is supposed to be derived from sulphur which may exist as soluble sulfide at moor area, because soluble sulfide can easily combine with organic material and insoluble sulfide or sulfate, even soluble one, seem not to have capability to combine with organic material during coal forming process. This consideration also may lead a conclusion that there will be less reliability of concept, in which FeS_2 in coal is explained to have been formed from iron sulfates by the reducing action of intermediate organic compounds in coal forming process.

Summary

Cellulose-protein and lignin-protein mixtures were artificially coalified and the nitrogen behavior and effect of protein to the characteristics of coal were considered. That is, nitrogen in protein combines chemically with cellulose or lignin with limited value of 5% or 2%, respectively. Protein is not always necessary for caking property of coal, but it seems to accelerate this property. Moreover, proper quantity of protein accelerates huminification of cellulose and bituminization of lignin.

Secondly, to check behaviors of nitragen in artificial coal and to compare it with that in natural coal, both coals were oxidized with alkaline permanganate. Nitrogen fixed in artificial coal acts similarly to that in natural coal and it is recovered as NH_3 or NO_3' quantitatively, where value of NH_3/NO_3' differs distinctly according to the original materials.

Finally, cellulose or lignin was artificially coalified in aqueous solution of sulfides or sulfate, to check sulphur behaviors and sulphur distribution in coal. It is concluded that organic sulphur in coal is derived from water soluble sulfides, and it seems to be scarecely probable that iron sulfate is reduced to pyrite in coal forming process.

References

1) W. Funasaka and C. Yokokawa, This Memoirs, **12**, 128 (1950)
2) W. Funasaka, C. Yokokawa and S. Kajiyama, ibid., **15**, 116 (1953)
3) L. C. Maillard, Compt. rend., **154**, 66 (1912) ; **155**, 1554 (1912) ; **157**, 860 (1913)
4) C. Enders, Brenn, Chem., **19**, 360, 402, 439 (1938) ; D. H. Bangham's "Progress in Coal Science" p. 189, London (1950)
5) S. A. Waksman, Soil Science, **34**, 44 (1930)
6) F. Bergius, Z. Elektrochemie, **18**, 660 (1912)
7) E. Terres, Gas- u. Wasserfach, 8-H, 1 (1930)
8) E. Berl, Z. angew. Chem., **45**, 517 (1932)
9) C. R. Kinney et al., J. A. C. S., **67**, 625 (1945) ; **70**, 392 (1948)
10) I. Y. Postovskii and A. B. Harlampovich, Fuel, **15**, 229 (1936)
11) G. Thiessen, "Chemistry of Coal Utilization" vol., 1, p. 425, New York (1945)