Chemical, Plastic, and Coking Properties of "Natural Bitumen"

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Abstract

In the course of evaluating potentially useful blending materials for improving the coking strength of coals, the Applied Research Laboratory of the United States Steel Corporation investigated the potentialities of a coal-like material identified only as "natural bitumen." From this study, the material has been tentatively identified as impsonite, probably resulting from the weathering of grahamite, both of which are asphaltites.

"Natural bitumen," found to be of very low fluidity, possessed coke-improvement properties similar to those of Lower Kittanning low-volatile coking coal and somewhat better than those of Pocahontas low-volatile coking coal. Coked alone, "natural bitumen" produced a carbonization pressure of over 40 psi and a volume expansion of about 32 per cent.

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Introduction

In the course of evaluating potentially useful materials for use in blending in coke manufacture and for improving the coking strength of coals, the Applied Research Laboratory of the United States Steel Corporation investigated the potentialities of impsonite, a coal-like material initially identified only as "natural bitumen." A preliminary examination was completed because of the unique properties possessed by this material.

The efficacy of pitches and asphaltic materials as coke-strengthening agents for the poorer coking coals has been known for many years. Coal-tar pitches have been used with Utah coals in commercial operations[1,2)] and in tests[3)] with poorly coking French and Italian coals. A highly fluid asphaltite from Argentina has been blended in carbonization tests with weakly coking Chilean coal.[4)] The effectiveness of these blending materials is usually attributed to their high fluidity, as compared with that of the poor or weakly coking coals with which they are blended.

In this article the chemical and physical properties of "natural bitumen" are described, its tentative identification is presented, and its coking properties when coked alone and in blends with good and poor coking coals are demonstrated.

Experimental

Three different samples of "natural bitumen" were received for study. The first sample, consisting of only a few grams of about 200-mesh by 0 material, was used in determining Gieseler Fluidity, Free Swelling Index, and Proximate Analysis. The other two samples, on which most of the evaluation was made, were received in 3-inch by 0 size. In this size, the "natural bitumen" could be easily mistaken for a bright coal, Figure 1.

Chemical and petrographic analyses were performed on representative samples of "natural bitumen." Proximate and ultimate analyses were determined, as were solubilities in selected organic solvents. The "bitumen" was carbonized in blends with several coals and coal blends in the 30-pound Pressure-Test and Sole-Heated Ovens for pressure and volume-change determinations, respectively; the resulting coke from the 30-pound Pressure-Test Oven was tested to provide comparative-strength data. The Laboratory's 30-pound Pressure-Test Oven has been described in several published papers;[5,6)] the Sole-Heated Oven used is similar to that developed by the U. S. Bureau of Mines[7)] and the first reported in 1938.

Coke strengths were determined by the Laboratory's Modified Tumbler Test, in which 10 pounds of 1-1/2 by 1-inch coke is tumbled for 500 revolutions in the standard ASTM Tumbler Drum. The tumbled coke is screened and the per cent retained on a 3/4-inch screen is designated as the Modified Tumbler Index.[6)]

Results and Discussion

Examination of the "natural bitumen" as received showed it to be coal-like and lustrous in appearance, extremely friable, greasy to the touch, and dirty to handle. Macroscopically, banding was not evident, but the presence of cleavage and the checkered appearance suggested some kind of structure. Microscopically, a conchoidal-like fracture was clearly identified, and the surface resembled that found on hard pitches and other similar amorphous organic materials. Smooth, irregular, jet-black, highly reflecting surfaces were prominent, Figure 1.

The physical properties of the "natural bitumen" were similar to those of Lower Kittanning low-volatile coal, Table I. In the 3-inch by 0 size, this material had a bulk density of 49 lb per cu ft, which is only a little lower than that of Lower Kittanning coal, and it floated at a specific gravity as low as 1.23. This "natural bitumen" was slightly soluble in carbon disulfide, but the insoluble residue disintegrated into a fine powder. The behavior in xylene was similar: a lump of "bitumen" disintegrated into an insoluble, fine powder, while the solvent became faintly straw-colored.

In the flame test, a lump of "natural bitumen" decrepitated and burned, and incipient fusion was detectable. Burning ceased when the lump was removed from the flame; this indicated a high-ignition temperature. When the "bitumen" was subjected to the ASTM Free-Swelling Index Test,[8)] in which the sample must be pulverized to 60 mesh, the resulting "button" was strong, coherent, dull black, and non-swollen, and had an index of 1-1/2, see Figure 2. However, when coarse, minus 1/4-inch particles (rather than the standard 60-mesh particles) were used in the ASTM Free-Swelling Index Test, a strong, dense, coherent, shiny black button was formed that had an apparent Index of 3 to 4. The outlines of the small lumps were still distinguishable on the outside surfaces of the Free-Swelling Index button, Figure 3.

The proximate analyses in Table II show that the ash content was low, but might be somewhat variable, whereas the sulfur content ranged from 1-1/2 to 2 per cent. Although this material could be designated in the ASTM classification as a medium-volatile coal on the basis of (1) its proximate analysis and (2) the fact that the material was agglomerating, petrographic examination, which revealed no plant structure visible by either transmitted or reflected light, indicated that the material is not of plant origin. None of the structures ordinarily found in coal of the same volatile matter and fixed carbon contents were present. The material appeared homogeneous, with no banding or recognizable cell structure being observed in either the polished or thin section; however, isolated masses and crystals of pyrite were noted.

Because of its poor solubility in carbon disulfide, high percentage of fixed carbon, and high specific gravity, and because no petrographic entities characteristic of coal could be found, this so-called "natural bitumen" has been tentatively identified as impsonite,[9)] one of the asphaltic pyrobitumens, which include elaterite, wurtzilite, and albertite, all characterized by infusibility and insolubility, or poor to slight solubility in carbon disulfide. Impsonite represents the final stage in the metamorphosis of asphaltites and asphaltic pyrobitumens. Outcrops of grahamite,[10)] which is an asphaltite, metamorphize readily into impsonite. "Weathered asphaltites ... closely resemble impsonite in their physical and chemical properties and may be classified as such."[9)] The softening and fusion exhibited by the "natural bitumen" upon being heated is the only property not characteristic of impsonite. This may indicate that the material is indeed weathered grahamite, since varieties of this asphaltite exhibit softening, possess good solubility in carbon disulfide, and contain less than 55 per cent fixed carbon.

Deposits of impsonite are reported[10)] in Oklahoma, Arkansas, and Nevada, and copper-bearing impsonite has been reported in Michigan. Deposits of grahamite are reported in West Virginia, Texas, Oklahoma, and Colorado. Dietrich, in a recent publication[11)] refers to impsonite from the Carboniferous Jackforth sandstone as originally being called "grahamite." Abraham cites[12)] the same deposits (LeFlore County, Oklahoma) and lists it as grahamite, but he notes that grahamite can weather into impsonite. Perhaps Dietrich may have obtained a sample of weathered grahamite.

"Natural bitumen" exhibits plastic properties and very low fluidity similar to those of Lower Kittanning seam low-volatile coking coal, Table II, and possesses good coke-improvement properties comparable with those of Lower Kittanning in blends with high-volatile coking coals, see Table III. This "natural bitumen," like Lower Kittanning coal, exhibits a prohibitively high coking pressure, Table III, when coked alone in the 30-pound Pressure-Test Oven. Also, the "bitumen" showed extremely high expansion; it has an estimated volume change (expansion in the sole-heated oven of approximately 32 per cent, whereas the Lower Kittanning low-volatile coal used for comparison in this evaluation showed expansion of about 14 per cent, at bulk densities of 55 to 58 pounds of dry coal per cubic foot.

A photograph of a lump of coke from "natural bitumen" that was coked alone, is shown in Figure 4. The extremely fine cell structure of the coke, as well as its fingery character, are evident. Chemical analysis and a sulfur balance made on "natural bitumen" and the resultant coke from the 30-pound Pressure-Test Oven indicate sulfur elimination from the "natural bitumen" during carbonization, Tables II and III, is relatively low. Forms of sulfur[13)] are listed in Table II for the raw "natural bitumen."

Carbonization in the 30-pound Pressure-Test Oven of blends containing "natural bitumen" showed that this material was as effective as Lower Kittanning coal in improving the strength of cokes from the highly fluid Pittsburgh Seam high-volatile coal, but somewhat less effective than Lower Kittanning in improving the strength of cokes from the low-fluidity Utah high-volatile coal, see Table III. Replacement of nearly half the Pocahontas low-volatile component by "natural bitumen" in a blend with Kentucky Splint Coal shows that the "bitumen" possesses greater strength-improving power than Pocahontas and that it increases the coking pressure of the blend.

Conclusions

Coking tests reported by Thompson[1)] showed that a 15 per cent addition of coal-tar pitch to Utah coal significantly increased the Stability Factor of this coke over that of coke containing no pitch (24 as opposed to 11). As shown in Table III, similar additions of "natural bitumen," and of Lower Kittanning low-volatile coal, both having low fluidity, upgraded the strength of the coke from Utah high-volatile coal to a degree comparable with that found for coal-tar pitch additions in the earlier work cited. Consequently, these results lend no support to the long-held hypothesis that improvement of poorer coking coals is best accomplished by the addition of "fluid" components. It appears, therefore, that coke-strengthening power may be more dependent on some combination of optimum coking pressure and fluidity, rather than on fluidity alone. Also, the high fixed-carbon content of "natural bitumen" (76%) contributes to coke improvement: after the "bitumen" has passed through the fluid state, sufficient carbonaceous residue remains, adding to the strength of the cell walls of the resultant coke, and not much material is lost by devolatilization (which promotes shrinkage).

The following three factors, then, probably explain the success of "natural bitumen" as a coke-improvement additive: (1) coking pressure, that helps consolidate the mass during the coke-formation process, (2) sufficient fluidity, that agglomerates the non-coking entities of the coal in the cell walls of the resultant semi-coke and (3) a comparatively large amount of carbon remaining after decomposition and solidification of the fluid material (compared to that of pitches and asphaltites), that contributes strength to the cell walls of the final, finished coke and thus minimizes the weakening effect of shrinkage.

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Erratum: On page 115, paragraph 4, the first 3 words of line 7 should be changed to read ... "Coal-like in fine structure."

Table I

Characteristic Properties of "Natural Bitumen" Compared with Lower Kittanning Seam Low-Volatile Coal

	"Natural Bitumen"	Lower Kittanning Seam Low-Volatile Coking Coal
Bulk Density (Modified ASTM)	49 lb per cu ft	52 lb per cu ft
Color in Mass	Black	Black
Fracture	Subconchoidal (conchoidal to hackly)	Cubic
Luster	Bright	Dull to bright
Specific Gravity	Floats at 1.23	Approximately 1.3
Solubility in Carbon Disulfide*	2.3% at 25 C. Lumps disintegrate to a fine powder, which forms a dull black, coherent, non-swollen button in the Free-Swelling Index test similar to that from the original pulverized bitumen.	0.3% at 25 C
Solubility in Xylene	Lumps disintegrate into a fine powder, with pale-straw coloration of solvent	--
Solubility in Benzene **	3.6%	0.6%
Flame Test	Lumps decrepitate violently and burning ceases upon removal of material from flame. Fusion of particles is evident.	Lumps burn slowly, soften, and harden into a semi-coke.
ASTM Free-Swelling Index	1-1/2	2-1/2
Fixed Carbon (from proximate Analysis), %	74 to 78	75
Ash Content, %	1 to 4	7.5
Sulfur Content, %	1 to 2	0.8

* See Reference 14)
** See Reference 15)

Table II

Chemical, Plastic, and Free-Swelling Properties of "Natural Bitumen"

(A) Proximate Analysis, Ultimate Analysis, Sulfur Content, and Heating Value of "Natural Bitumen," all on the dry basis:

Sample No.	1	2	3	Lower Kittanning Low-Volatile Coal
Proximate Analysis, % dry basis:				
Volatile Matter	21.6	21.7	22.0	15.1
Fixed Carbon	77.6	74.3	76.3	76.8
Ash	0.8	4.0	1.7	8.1
Ultimate Analysis, %				
Carbon	-	-	85.7	83.4
Hydrogen	-	-	5.3	4.3
Nitrogen	-	-	1.9	1.2
Oxygen	-	-	3.6	3.0
Ash	-	-	1.7	8.1
Sulfur	1.66	2.05	1.82	1.01
Heating Value, BTU per lb	-	15,120	-	

(B) Gieseler Fluidity and Free-Swelling Index of "Natural Bitumen", and Lower Sunnyside Seam (Utah and Lower-Kittanning Seam Coals):

	Natural Bitumen (Sample No. 1)	Lower Sunnyside High-Volatile Coal	Lower Kittanning Low-Volatile Coal
Plastic Properties:			
Softening Temperature, C	435	377	449
Solidification Temperature, C	480	453	504
Plastic Range*, C	45	76	55
Maximum Fluidity, dial div. per min.	0.6	3	1.1
Temperature of Maximum Fluidity, C	458	413	477
Free-Swelling Index	1-1/2	2-1/2	2-1/2

* Solidification temperature minus softening temperature

(C) Forms of Sulfur in "Natural Bitumen"

Sulfate Sulfur	0.04%	3.0%
Pyritic Sulfur	0.57%	43.5%
"Organic" Sulfur	0.70%	53.5%
Total	1.31%	100.0%

Table III

Coke Strength and Carbonization Pressure from 30-pound Pressure-Test Oven Tests with "Natural Bitumen" and Coking Coals

Blend*	Modified Tumbler Index, cum % plus 3/4 in.	Approximate ASTM Stability Factor	Carbonization Pressure, psi
100% "Natural Bitumen"	--**	--	40
100% Lower Kittanning Seam Low-Volatile	--	--	30
45% Kentucky Splint High-Volatile 55% Pocahontas Low-Volatile	55	--	3.5
55% Kentucky Splint High-Volatile 45% "Natural Bitumen"	62	--	6.7
50% Kentucky Splint High-Volatile 30% Pocahontas Low-Volatile 20% "Natural Bitumen"	63	--	4.5
80% Kentucky Splint High-Volatile 20% "Natural Bitumen"	59	--	2.3
100% Pittsburgh Seam High-Volatile	43	--	1
80% Pittsburgh Seam 20% "Natural Bitumen"	63	--	1
80% Pittsburgh Seam 20% Lower Kittanning Seam	61	--	1.5
100% Lower Sunnyside Seam High-Volatile	21	2	1
90% Lower Sunnyside Seam 10% "Natural Bitumen"	31	13	1.4
80% Lower Sunnyside Seam 20% "Natural Bitumen"	43	27	2.2
90% Lower Sunnyside Seam 10% Lower Kittanning Seam	41	25	1.1
80% Lower Sunnyside Seam 20% Lower Kittanning Seam	50	35	1.8

* Bulk Density as charged 50 to 53 lb per cu ft

** Proximate analysis and sulfur content of coke per cent (dry basis):

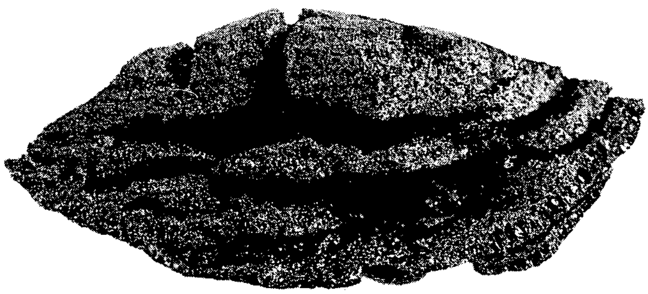
Volatile Matter	3.0
Fixed Carbon	92.7
Ash	4.3
Sulfur	2.12

SURFACE MAGNIFIED 5x
Negative No. 2-3578B-2

LUMP MAGNIFIED 1x
Negative No. 2-3578B-1

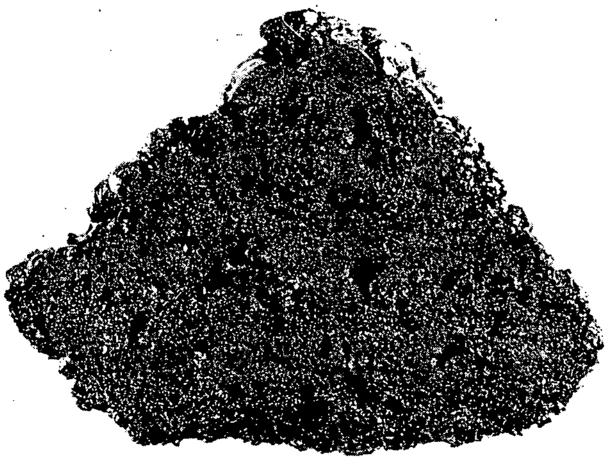
Figure 1. LUMP OF "NATURAL BITUMEN", AS RECEIVED

MAGNIFIED 1x
Negative No. 2-3574B-1



CROSS-SECTION, MAGNIFIED 5x
Negative No. 2-3574B-2

Figure 2. FREE-SWELLING INDEX BUTTON - INDEX 1-1/2 - FROM "NATURAL BITUMEN" PULVERIZED TO MINUS 60 MESH



CROSS-SECTION MAGNIFIED 5x
Negative No. 2-3573B-2

Figure 3. FREE-SWELLING INDEX BUTTON - INDEX 4 - FROM MINUS 1/4 INCH "NATURAL BITUMEN" PARTICLES

FULL LUMP MAGNIFIED 1x
Negative No. 2-3577B-1

SECTION OF LUMP MAGNIFIED 5x
Negative No. 2-3577B-2

Figure 4. LUMP OF COKE FROM "NATURAL BITUMEN" CARBONIZED IN 30-POUND TEST OVEN