

SURFACE CHARACTERIZATION OF  
IRON OXIDE DISPERSED ON SUBBITUMINOUS COAL.

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**ABSTRACT**

The preparation and characterization of Wyodak subbituminous coal impregnated with 0.1-1.0 wt% iron by the incipient wetness technique have been studied. X-ray photoelectron spectroscopy (XPS) was used to examine the surface chemistry versus the bulk composition of the iron oxide loaded on the coal particles. The effects of Fe concentration,  $\text{NH}_4\text{OH}/\text{Fe}$  ratios and coal drying on the speciation of Fe are reported. The relative concentration of  $\text{FeOOH}$  and  $\text{Fe}_2\text{O}_3$  on the surface is a function of coal drying. The direct liquefaction performance of the different Fe loaded coal samples is related to the specific Fe concentrations.

**INTRODUCTION**

Small particle iron oxide catalyst precursor deposited on coal by an incipient wetness (IW) technique provided improved conversion and distillate yields in direct liquefaction.<sup>1</sup> In this technique coal is impregnated with a metal salt solution which when added to the coal reaches the point where unbound moisture begins to form drops.<sup>2</sup> In the case of iron salts, addition of base produces finely divided iron oxyhydroxide. SEM analysis showed that iron impregnated by IW using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was primarily deposited on the surface of the coal.<sup>3</sup> Subsequently, coal is dried to remove the excess moisture before subjecting it to liquefaction. Sulfidation that occurs during liquefaction presumably does not result in any significant growth of the iron particles upon conversion to pyrrhotite,<sup>4</sup> although recent results indicate that pretreatment at lower temperatures provide increased liquefaction performance because of more efficient conversion of the precursor oxide to pyrrhotite.<sup>5</sup> Distillate yields from liquefaction of 5000 ppm Fe-impregnated Wyodak coal were greater than from the corresponding liquefaction when using pigment grade iron oxide plus added sulfur.<sup>6</sup>

Impregnating coals by IW is a multi-step process involving first the distribution of the metal solution onto the coal, after which the oxide is formed, presumably at the point of contact with the base material. Since preparation proceeds through a series of steps involving coal preparation, metals impregnation, base precipitation, filtration, washing, and drying, all which may alter the subsequent liquefaction performance of the impregnated coal.

This paper describes the results of a study to evaluate the performance of an Fe-impregnated Wyodak coal. The effects of several independent variables in the preparation scheme on metal dispersion and chemical form were investigated using XPS. This technique has been used not only to analyze the surface composition of coals<sup>7</sup> but also to characterize the surface composition, elemental distribution and chemical state of the Fe-O system, including  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ , and  $\text{FeOOH}$ .<sup>8</sup> In addition, the conversion and product distribution from liquefaction of several of

these Fe-impregnated coals are discussed.

#### EXPERIMENTAL

Impregnated Coals - Wyodak coal from the Black Thunder Mine in Wright, Wyoming, which was provided by CONSOL, Inc., was ground to -200 mesh, riffled and stored under nitrogen at 4°C. Proximate and ultimate analyses of the coal are presented in Table 1. IW-coal samples were prepared starting with either as-received coal or coal predried at 110°C/10 Torr/20 hrs. The moisture content and the volume of water used in the IW-impregnation of as-received coal were 21 wt% and 0.75 ml/g dry coal, respectively, and for impregnation of predried coal were 2-3 wt% and 0.90 ml/g dry coal, respectively. Solutions containing  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , purchased from Aldrich Chemical Co., were slowly added in a dropwise manner to the coal while mixing to assure even distribution. 1.5M  $\text{NH}_4\text{OH}$  was added to these samples at a  $\text{NH}_4\text{OH}/\text{Fe}$  mole ratio from 31 to 138. The aqueous slurries were filtered and the samples were dried at 40°C/20 hrs/10 Torr, unless otherwise specified. Water washing, if performed, preceded the drying step.

XPS Measurements - The XPS of the various samples of Fe impregnated coal was carried out with the LHS-10 Leybold-Heraeus Spectroscope using Mg K $\alpha$  radiation with 15 Kv, 20 mA and pass energy of 100 ev. The powdered samples were mounted on the XPS sample probe with Double-Stick Scotch tape. The sample powders were gently pressed and covered all of the Scotch tape attached on the stainless steel foil. The analysis chamber vacuum was about  $5 \times 10^{-9}$  Torr. The C $_{1s}$ , O $_{1s}$ , Fe $_{2p}$ , Fe $_{3p}$ , N $_{1s}$ , Ca $_{2p}$ , Al $_{2p}$ , Si $_{2p}$ , and S $_{2p}$  elemental spectra and the survey spectra of the coal samples were obtained under the above working conditions and corrected with the hydrocarbon C $_{1s}$  binding energy 284.6 ev. The elemental concentrations were calculated and the peak deconvoluted with a computer aided program of damped non-linear least squares curve fitting, using mixed Gaussian/Lorentzian profiles.<sup>9</sup>

Equipment and Procedures - Liquefaction experiments were performed in 50 ml microautoclaves to which were added 3 grams of coal, 5.4 grams of tetralin, and 1.2 mol dimethyl disulfide/mole added Fe. The reactors were sealed, pressurized with hydrogen to 1000 psig, and leak tested. Reactions were carried out in a fluidized sandbath set at the specified temperature while the reactors were continuously agitated at a rate of 400 cycles per minute. Reactors were then quenched to ambient temperature, the gaseous products collected and analyzed, and the products separated into THF insoluble (IOM), THF soluble-pentane insoluble (PA+A), and pentane soluble (oils+water) fractions. The product distribution was calculated assuming complete recovery of ash and conversion of catalyst to pyrrhotite ( $\text{Fe}_{0.9}\text{S}$ ). The total of the net products equals the amount of maf coal in the feed and reflects the net make of each of the solubility fractions; coal conversion equals 100 minus the yield of IOM.

#### RESULTS AND DISCUSSION

The volume of water used in the IW-impregnation of as-received coal containing 21 wt% moisture was 0.75 ml/g, which was 20% less than for dry coal (0.90 ml/g). Ferric nitrate has sufficient solubility that this difference in the volume of water was not limiting. The incorporation of the metal onto the coal was essentially quantitative as determined by analysis of filtrates collected during preparation. The analysis of filtrates from addition of 1.5M  $\text{NH}_4\text{OH}$ , which causes precipitation of Fe as  $\text{FeOOH}$ , and filtrates from subsequent water

washes, indicated negligible Ca exchange and Fe bypass (see Table 2). In the  $\text{NH}_4\text{OH}$  treatment, only 0.1 wt% of the Ca originally in the coal was removed with about the same amount recovered in a subsequent water wash. Less than 0.01 wt% of the Fe added to the coal was found in both filtrates. The extent of  $\text{NH}_4^+$  exchange corresponding with formation of ammonium carboxylates is presumably quite small.  $\text{NO}_3^-$  recoveries in the  $\text{NH}_4\text{OH}$  filtrates ranged from 83 wt% up to 119 wt% and were accurate only to  $\pm 20\%$ . The absence of  $\text{NO}_3^-$  ions in the washwater filtrate indicates substantially complete removal in the  $\text{NH}_4\text{OH}$  filtrate which makes water washing unnecessary.

Fe Distribution - Surface and bulk concentrations determined for metals (Fe, Ca, Al, Si), C, O, N and S for both impregnated as-received and predried coals are presented in Table 3. The surface of the dry as-received Black Thunder coal without any added Fe is enriched in the concentration of Fe, O, Al and Si, which reflects particle fracturing along the mineral surfaces during grinding. In the impregnated samples, the Fe concentration on the surface was significantly higher than in the bulk and increased with the amount of added Fe. In those samples that were final dried at  $40^\circ\text{C}/10$  Torr/20 hrs, the concentration on the surface reached 6.3 wt% (CH-41) at the 1.0 wt% Fe addition level versus 12.5 wt% (CH-45) in the sample dried in flowing nitrogen at  $40^\circ\text{C}/20$  hrs, the maximum observed in this study. This difference in surface Fe concentration suggests significant penetration of the iron within the cracks, crevices and pores of the coal particles. For each of these samples the relative concentration of oxygen on the surface increased as the iron concentration increased. Carbon fluctuated between samples and sulfur was generally lower at the surface relative to the bulk.

The increased surface Fe concentration of two impregnated predried samples suggests that diffusion of the Fe salt into these coals was hindered. Thermal pretreatment apparently results in sufficient transformation within the coal structure to block diffusion of the Fe-containing aqueous phase into the particle. Maintaining the integrity of the aqueous phase within the particle, as in the as-received samples, promotes diffusion of the Fe ions into the particle.

Surface Chemistry - Fe-IW impregnated coals show XPS spectra with  $\text{Fe}_{2p}$  peaks appearing at 711.2 eV ( $\text{Fe}_{2p\ 3/2}$ ) and 725.1 eV ( $\text{Fe}_{2p\ 1/2}$ ),  $\text{Fe}_{3p}$  at 56.6 eV and  $\text{O}_{1s}$  at 531.3 eV. The known spectra of  $\text{FeOOH}$  provides a good fit with the observed spectra. For those coals having low Fe loadings the  $\text{O}_{1s}$  peak is shifted to a higher binding energy of 532.4 (CH-20, CH-11) which approaches that of the  $\text{O}_{1s}$  binding energy in the spectra of the starting coal. This higher binding energy is consistent with greater participation of the  $\text{O}_{1s}$  peaks for  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , which are located at 531.8 and 532.8 eV, respectively. The binding energy of the  $\text{N}_{1s}$  peak was found to be 399.5 eV which is consistent with organic nitrogen in the coal which precludes the presence of any significant amount of  $\text{NH}^+$  or  $\text{NO}_3^-$ . Interpretation of the form of the added Fe is not complicated by the iron in the original coal since the  $\text{Fe}_{2p\ 3/2}$  peak at 709.3 eV and a  $\text{Fe}_{3p}$  peak at 52.3 eV are considerably lower than observed. These lower binding energies are consistent with Fe-O and Fe-S structures. For the samples dried at about  $110^\circ\text{C}$  (CH-2), the decrease in the  $\text{Fe}_{3p}$  binding energy to 56.0 eV indicates the appearance of  $\text{Fe}_2\text{O}_3$ , that occurs as the  $\text{FeOOH}$  particles on the surface agglomerate. Likewise, deconvolution of the  $\text{O}_{1s}$  envelope indicates a lower binding energy peak at 530.0 eV consistent with the presence of the  $\text{Fe}_2\text{O}_3$  species. In general, the  $\text{Fe}_{2p}$  spectra are broadened and highly complex due to multiplet splitting

effects which are characteristic of oxides. The samples developed significant electrical charge during analysis consistent with the low electrical conductivity of Fe oxyhydroxide.

Liquefaction of Impregnated Coals - No significant effect on THF conversion or product distribution was observed as a result of varying the  $\text{NH}_4\text{OH}$  treatment over a range of  $\text{NH}_4^+/\text{Fe}$  ratios from 31 to 138. Likewise, subjecting the coals to a final wash also had no effect on liquefaction. Fe, however, had a definite effect on both oil yield and THF conversion as shown in Table 4. A sharp increase in both THF conversion and oil yield occurred with addition of 2800 ppm Fe; conversion increased from 81 wt% to 86 wt% while oils+water increased from 38 wt% to 44 wt%. Further addition of Fe up to 1.0 wt% resulted in smaller increases in both conversion and oil+water yields.

#### CONCLUSIONS

XPS spectra show a high degree of Fe dispersion on the coal surface with significant diffusion of Fe into the cracks, crevices and pore structure of the coal. The surface Fe concentration was higher on coals predried at 110°C before adding the Fe salt, indicating reduced metal diffusion into the coal. XPS supports Fe being present both as  $\text{FeOOH}$  and  $\text{Fe}_2\text{O}_3$ . Addition of 2800 ppm Fe causes a sizable increase in both THF conversion and oils+water yield. Increasing the Fe concentration up to 1 wt% causes still further increases in both conversion and oil+water yield, though to a lesser extent.

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Table 1. Proximate, Ultimate and Ash Analysis of Black Thunder Wyodak Coal

	As Received <sup>a</sup>	Dry <sup>b</sup>
Proximate, as-received basis		
Moisture	22.4	2.63
Ash	5.46	5.66
Volatile Matter	34.4 <sup>c</sup>	45.47
Fixed Carbon	39.8 <sup>c</sup>	46.2
Ultimate, Dry		
Carbon	70.32	72.15
Hydrogen	4.68	4.34
Nitrogen	1.04	1.23
Sulfur	0.50	0.53
Chlorine	0.035	-
Oxygen	16.74	15.93
Ash	6.69	5.81
Ash Composition, wt%		
Fe <sub>2</sub> O <sub>3</sub>	5.48	-
CaO	21.34	-
Al <sub>2</sub> O <sub>3</sub>	15.76	-
SiO <sub>2</sub>	31.48	-
MgO	4.3	-
Na <sub>2</sub> O	0.48	-
K <sub>2</sub> O	0.49	-
TiO <sub>2</sub>	1.14	-
P <sub>2</sub> O <sub>5</sub>	0.96	-
SO <sub>3</sub>	17.26	-

<sup>a</sup> Analysis provided by Consol, Inc. <sup>b</sup> Dried 110°C/20 hrs/10 Torr. <sup>c</sup> Determined at UK/CAER.

Table 2. Filtrate Analysis<sup>a</sup>

Coal Sample No.	NH <sub>4</sub> OH Filtrate		Washwater Filtrate	
	CH-3	CH-21	CH-4 <sup>b</sup>	CH-22 <sup>c</sup>
Fe <sup>+3</sup> Added, wt% dry coal	1.0	0.55	1.0	0.55
Ca, wt% dry coal	1.0	1.0	-	-
Calcium Recovery, wt% Ca in dry coal	0.10	0.11	0.12	0.02
Fe Recovery, wt% Added Fe ( $\times 10^2$ )	0.1	3.0	9.8	3.1
NO <sub>3</sub> <sup>-</sup> Recovery, wt% <sup>d</sup>	83	93	<sup>e</sup>	<sup>e</sup>

<sup>a</sup> Direct Current Plasma Emission Spectrometry (DCP). <sup>b</sup> CH-4 originated from CH-3.

<sup>c</sup> CH-22 originated from CH-21. <sup>d</sup> Measured using ion specific electrode; values  $\pm 18\%$ .

<sup>e</sup> NO<sub>3</sub><sup>-</sup> was not detected in these solutions.

Table 3. Surface Concentration of Elements as Determined by XPS<sup>a,b</sup>

As Received	Starting Coal <sup>c</sup>	Moisture wt%	Added Fe	Fe	C	O <sup>d</sup>	N	Ca	Al	Si	S
	-	22.4		(0.19)	(57.8)	(29.6)	(1.2)	(0.75)	(0.56)	(1.1)	(0.46)
CH-BT	AR	2.6	0	0.33	71.1 (70.3)	20.6 (17.8)	1.3 (1.2)	0.5	2.0	4.0	0.2 (0.5)
CH-10	AR	3.6	0.15	1.0	62.3	25.5	1.4	1.0	3.4	3.5	n.a. <sup>e</sup>
CH-11	AR	1.8	0.28	1.4	66.2	23.5	1.7	1.0	2.4	3.5	0.3
CH-13 <sup>f</sup>	AR	5.4	0.28	1.9	64.1	23.9	1.7	1.2	3.1	3.8	0.3
CH-1	PD	1.4	0.28	2.7	63.5 (67.4)	24.7 (19.4)	1.7 (1.5)	1.0	2.5	3.6	0.4 (0.4)
CH-20	AR	0	0.55	2.4	63.5	25.2	1.5	1.0	2.9	3.3	0.2
CH-8 <sup>g</sup>	AR	5.4	0.77	3.2	66.8 (68.1)	20.2 (19.2)	0.8 (1.8)	0.7	1.9	4.6	n.a. (0.4)
CH-31	AR	2.9	0.77	4.2	62.4	24.8	1.2	1.0	2.5	3.3	0.6
CH-41	AR	2.7	1.0	6.3	59.6	25.6	1.6	1.0	3.8	3.4	0.3
CH-3	PD	3.9	1.0	8.3	54.2 (65.4)	28.2 (21.2)	1.0 (1.6)	0.8	3.8	3.1	0.4 (0.5)
CH-45 <sup>f</sup>	AR	6.1	1.0	12.5	49.3	30.7	0.8	0.3	3.8	2.5	0.1

a. ( ) Bulk composition, wt% of sample.

b. Starting coal impregnated with Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 0.74 ml water/g for as-received coal and 0.90 ml/g for predried coal, treated with 1.54M NH<sub>4</sub>OH at 138 NH<sub>4</sub><sup>+</sup>/Fe ratio, vacuum filtered, and dried at 40°C/10 Torr/20 hrs.

c. AR is as-received coal, PD is predried coal at 110°C/10 Torr/20 hrs.

d. Includes oxygen associated with moisture in sample.

e. n.a., not available

f. Dried at 40°C/1 atm/flowing N<sub>2</sub>/20 hrs.

g. Washed with 1.54M NH<sub>4</sub>OH at 31 NH<sub>4</sub><sup>+</sup>/Fe ratio.

Table 4. Product Distribution from Liquefaction of Fe IW-Impregnated Coals

Sample No.		CH-11	CH-20	CH-8	CH-41	CH-45
Fe Added, wt% dry coal	0 <sup>a</sup>	0.28	0.55	0.77	1.0	1.0
S/Fe <sup>b</sup>	0	2.9	1.0	1.3	1.2	1.3
Moisture, wt%	1.8	2.5	0	3.4	2.7	6.1
Product, wt% maf coal						
HC Gases	1.0	1.1	1.1	1.1	1.2	1.2
CO <sub>2</sub> +CO	4.0	3.7	3.6	4.1	3.9	3.8
Oils + Water	38.3	44.1	44.9	45.1	46.4	48.0
PA + A	37.9	37.5	37.0	38.7	37.9	36.1
IOM	18.8	13.6	13.4	11.0	10.6	10.9
THF Conv	81.2	86.4	86.6	89.0	89.4	89.1
mg H <sub>2</sub> /g maf coal	26	38	40	36	40	45

a. Coal dried 90°C/125 Torr/20 hrs.

b. Mole ratio of added S in DMDS to added Fe.