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DEMINERALIZATION OF PETROLEUM COKES AND FLY ASH SAMPLES OBTAINED FROM
THE UPGRADING OF ATHABASCA OIL SANDS BITUMEN

BY

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INTRODUCTION

Today's commercially proved technology to recover oil from the Athabasca oil sands, as practiced by Suncor and Syncrude, involves two major operations, namely: separation of the bitumen from the sand and upgrading of the bitumen to refinery oil. Significant amounts of petroleum coke are produced during the bitumen upgrading process. Suncor burns the bulk of its petroleum coke in boilers to fulfill the energy requirements of the entire operation, still meeting government regulations restricting the amount of sulfur dioxide that can be released to the environment. In contrast, Syncrude is able to burn only 20% of its coke production because of high sulfur dioxide emissions from elsewhere in its operations (1). The boiler ash (Fly ash) which contains appreciable amounts of metals, such as vanadium, nickel, lithium, iron, aluminum and other elements, is collected in the boiler hoppers and cyclones of the petroleum coke fired steam generation plants.

There has been relatively little effort made towards the understanding of the chemical or physical nature of these materials (2-3). Knowledge of the physico-chemical properties of these materials will be helpful in assessing their beneficiation and potential use as fuel or metallurgical coke and the feasibility of extracting some metals, especially Ni and V. In this communication we report studies of acid demineralization as a means of reducing ash content of these materials for ^{13}C NMR spectroscopic investigations.

EXPERIMENTAL METHODS

Materials

Syncrude and Suncor refinery cokes and fly ash samples derived from Athabasca bitumen were obtained from the Alberta Research Council sample bank. Coke samples were ground to $\approx 40\mu\text{m}$ particle size using a Brinkman Centrifugal Grinding Mill ZM-1. Fly ash samples were used as received.

Ash Reduction of Coke and Fly Ash Samples

In order to reduce ash content of Athabasca bitumen derived cokes and fly ash samples, the mineral matter was selectively dissolved in various acids (4-6). The general procedure for mineral dissolution is presented in Figure 1.

In general, 20 grams of the sample were agitated at 70°C for two hours with 250 ml of $\sim 6\text{M}$ hydrochloric acid in a 500 ml glass beaker while stirring occasionally. The mixture of coke/Fly ash and hydrochloric acid was then filtered using a glass funnel with a fritted disc of medium porosity. The residue was separately washed with warm distilled water until the filtrate was completely free of chlorides (absence of white precipitate on the addition of AgNO_3 solution). On completion of the washing, the residue was transferred to the beaker and agitated with concentrated hydrochloric acid to dryness. About 200 ml of warm distilled water was added to the hydrochloric acid treated sample and after proper mixing the procedure for filtering and subsequent washing of the residue as described above was repeated.

The chloride free residue from above was then transferred to a 250 ml teflon beaker. About 100 ml of 35% hydrofluoric acid was slowly added over a period of ≈ 2 hours, while mixing the contents gently using a teflon rod. After the effervescence ceased, the contents were heated to dryness at 80°C . Another 50 ml of hydrofluoric acid was added to this treated sample and the entire procedure repeated.

About 200 ml of warm distilled water was added to the hydrofluoric acid treated sample and after proper mixing the contents were left to settle. After the solids settled down the clean

supernatant liquid was decanted. This procedure was repeated several times until the pH of the supernatant liquid was 4.0. From there on the contents were filtered using a glass funnel with a fritted disc of medium porosity.

Figure 1. Flowsheet for acid demineralization of Cokes/Fly Ashes

The residue was washed repeatedly with warm water until the washings became neutral. The residue of the demineralized sample of coke or fly ash was then dried in a vacuum oven at 70°C to a constant weight.

Elemental Analyses

C, H and N analyses were performed using a Perkin Elmer model 240 CHN analyser. Sulfur was analysed as total sulfur using X-ray fluorescence spectroscopy. Oxygen was determined directly by pyrolyzing the sample in nitrogen with subsequent formation of carbon monoxide by contact of the pyrolysis products with platinumized carbon at 950°C (7). Analytical results were confirmed from the results of duplicate analyses done at the Energy Mines and Resources Laboratory using ASTM procedure D271.

SiO₂ and Al₂O₃ content of the ashed samples was determined using x-ray fluorescence spectrometry. Quantitative Inductively Coupled Plasma Atomic Emission spectroscopic methods (ICP-AES) were used to analyze the ash from these samples for Ti, Zr, Fe, Ni, V, Cu and Cr.

Ash Content

Ash content of cokes and fly ash samples both before and after acid demineralization was determined by heating at 400 ± 10°C to constant weight (8).

¹³C NMR Measurements

Solid state ¹³C NMR spectra were obtained at 45.28 MHz on a Bruker CXP 180/90 NMR spectrometer using a Doty Scientific Magic Angle Spinning (MAS) probe. For both coke samples the cross polarization (CP) technique (9) was used with a contact time of 1 ms for spectra obtained with MAS at 3 kHz and 2 ms at 5 kHz. Spectra run at 5 kHz had better signal to noise ratios, but unfortunately at this speed the spinning side-bands seriously overlapped the aliphatic region. Each spectrum was the Fourier transform of 2000-4000 free induction decay curves. The dipolar dephasing technique (10) was used to distinguish the non protonated carbons (except groups in motion, e.g. CH₃) from those with attached hydrogens. All chemical shifts (in ppm) are referenced to tetramethylsilane.

The fly ash samples posed a few problems. Both Syncrude and Suncor fly ash seriously detuned the probe and although it was found possible to retune the ¹³C channel it was not possible to retune the ¹H channel. The problem was presumably caused by quantities of graphitised carbon forming conducting areas within the samples. When the Syncrude fly ash was diluted 1:1 with sodium polyphosphate it was possible to tune the ¹H channel, but unfortunately no CP signal could be found. Instead a simple Bloch decay ¹³C spectrum was obtained with ¹H

decoupling. The Suncor fly ash had to be diluted to 1:4 in sodium polyphosphate before the ^1H channel could be tuned, but even then there were serious noise problems when the ^1H radio frequency was pulsed. Consequently the Suncor fly ash sample was studied neat using a Bloch decay experiment without ^1H decoupling.

RESULTS AND DISCUSSION

A considerable reduction in the ash content of cokes and fly ash samples derived from Athabasca bitumen was achieved as a result of acid treatment. However, the reduction in the ash content of Suncor coke and fly ash samples was considerably greater than for the corresponding samples from Syncrude (80 and 92% compared with 52 and 76% respectively). This difference in mineral dissolution reflects the difference in severity of conditions under which the cokes are produced. The flexicoking process used by Syncrude produces graphitized carbon as compared with the delayed coking process used by Suncor that produces amorphous carbon. This is supported by the ash reduction trends for the two cokes which lead to the conclusion that the acids can penetrate relatively easily through the pores of Suncor coke compared with the Syncrude coke. Ash reduction for the fly ash samples follows the same trend as the parent cokes because the carbon associated with these samples is essentially the same as in the unburnt coke.

Ultimate analysis of these samples both before and after demineralization are given in Table I. There is no satisfactory method for the determination of the elemental composition of the organic matter associated with inorganic or mineral matter (4). This is because of the contribution of inorganic or mineral components to the organic elemental analyses. For such systems the determination of the elemental compositions, particularly with combustion techniques, reflects total rather than organic analyses. The best route for determining the average composition of the organic matter in such systems, is to remove as much of the inorganic material as possible (11). Hence, the analyses of the demineralized samples should be more representative of the compositions of the cokes and fly ashes than the parent samples.

The hydrogen and nitrogen contents of the demineralized samples are essentially the same as for the parent samples indicating that there is no significant contribution of these elements from mineral constituents. The carbon content of all demineralized samples is slightly higher compared with the parent samples. This could be due to the better carbon combustion in the demineralized samples compared with the original samples. The oxygen content of the demineralized samples is lower compared with the original samples. The reduction in the oxygen content is more pronounced in the fly ash samples than in the coke samples. This clearly demonstrates that the part of the oxygen determined is from the inorganic part of the samples that constitutes ash. The oxygen content of the demineralized samples is more representative of the oxygen associated with the organic matter of the cokes and fly ash samples. Higher sulfur content of the original samples of Syncrude fly ash and Suncor coke and fly ash compared with the demineralized samples indicates the presence of inorganic sulfur in these samples.

The higher H/C ratio of the Suncor coke indicates the more severe conditions to which the fluid coking coke (Syncrude coke) was subjected. This is supported also by the relatively unchanged H/C ratio in the Syncrude fly ash as compared with the coke. Since the Suncor coke is a product of a less severe process (delayed coking process) it burns efficiently as is indicated from the very low H/C ratio of its fly ash compared with the coke.

Table II lists the results for the analyses of the ash from cokes and fly ash. An examination of this data leads to the following observations:

- 1) Suncor fly ash is quite amenable to the acid leaching of silica, alumina, vanadium, nickel, iron and titanium. The almost quantitative recovery of vanadium and nickel from Suncor fly ash by acid leaching in the present investigation is contrary to the published reports (1, 12, 13) regarding the dilute HCl and H_2SO_4 leaching studies. It has been suggested that the poor response to leaching of Suncor fly ash was due to the fact that vanadium and nickel were associated with the aluminosilicate shperes (1, 13). At the high temperature of combustion, the aluminosilicates contained in the coke particles form a glassy phase in which metals such as vanadium and nickel become physically or chemically entrapped (14). It appears that the HF treatment destroys the aluminosilicate matrix, thus releasing these metals in a form which is readily soluble.

- 2) Fluid coking coke from Syncrude is least amenable to acid leaching among the four samples investigated. Fluid coking coke particles are known to be non-porous and these particles are said to have a vanadium rich core ensheathed by a surface zone quite low in vanadium content (15). This particle structure would render the metals unavailable to the largely surface-effective leaching technique employed here. In addition, the actual chemical composition of the cokes may play an important role in the retention or release of metals in a leaching experiment. Although the actual chemical form of the metals in the coke is not known, it is noteworthy that delayed coker coke (Suncor) which is amenable to acid leaching has a lower heteroatom content (O,S) than the fluid coking coke from Syncrude which resists leaching (Table I). Heteroatoms,

such as oxygen and sulfur, are suitable donor atoms for the complexation of transition metals.

3) Extraction of vanadium and nickel from syncrude fly ash and the two coke samples is much less efficient than for silica, alumina, iron and titanium. Both of these metals are primarily found in the asphaltene fraction of the bitumen in the form of very stable complexes such as porphyrins (16). It is probable that at least part of these metals remain bound to the heteroatoms in coke and thus are not susceptible to acid leaching. Combustion of the coke particles might render these metals in a form that could be extracted in acids. This is supported by the higher solubility of vanadium and nickel from the fly ash samples compared with their respective coke samples. The difference in behavior of the two fly ash samples on acid leaching could be due to the relative severity of the coking processes.

4) The vanadium leached from the delayed coking coke (Suncor) was about 40% lower than the amount leached from the fluid coking coke (Syncrude). However, this trend is reversed for the two fly ash samples where almost quantitative extraction resulted from the Syncrude fly ash. Because of the lesser severity of the delayed coking process, there is greater probability of vanadium being complexed with the heteroatoms in the delayed coking coke as compared to the fluid coke. On combustion to produce fly ash while vanadium could have been converted to a form more amenable to acid leaching. On the other hand the intractability of vanadium in fluid coke may be a consequence of the inaccessibility of this element in the coke particles because of the non-porous nature of the carbon. On combustion the non-porous nature of the residual carbon in fly ash remains unchanged. Hence, there is not as significant a change in the extent of vanadium release from Syncrude fly ash compared with the coke as for the corresponding Suncor samples.

5) Compared with vanadium the extent of nickel release was considerably greater for the delayed coking coke from Suncor and slightly greater for the fluid coke. This suggests that a greater part of nickel might be present in acid soluble form than vanadium.

The CP/MAS, ^{13}C NMR spectra of Suncor demineralized coke are shown in Figure 2. In Figure 2a the signal due to the aliphatic carbons is masked by the spinning side band at 5 kHz. By reducing the spinning frequency to 3 kHz the spinning side bands are removed and signals in the aliphatic region become visible (Figure 2b). These signals can be mainly ascribed to the methyl and methylene carbons (17-20). In order to distinguish ^{13}C directly bonded to a hydrogen from carbons not directly bonded to hydrogens, a dipolar dephasing experiment was also carried out (10,11). The dipolar dephased spectrum is shown in Figure 2c. Figure 2d is the difference between the normal spectrum of Suncor Coke (2b) and that obtained using a dipolar dephasing time of 40 μs (2c). The dipolar dephased spectra generally show quaternary aliphatic carbons, methyl carbons, and carbons in the interior of the aromatic rings. The carbons of rotating methyl groups can show about 60% of their intensity in the dephased spectra. The difference spectrum represents methyl, methylene and methyne carbons in the aliphatic region and perimeter carbons in the aromatic region. The signals for the non-protonated aromatic carbons are noticeably downfield from the protonated ones.

It is clear from the spectra (2c,d) that most of the signals in the aliphatic region are therefore due to methyl, methylene and methyne carbons. The distribution of the two different types of carbons in the aromatic region can be calculated from the integrated areas of the dipolar dephased and the difference spectra. Carbons directly bonded to hydrogen constitute about 50% of the aromatic carbons.

Aromaticity (f_a), as the ratio of the aromatic region and aliphatic region. The value of f_a determined suggests that 92% of total carbons in Suncor coke are in aromatic locations. This is consistent with the view that coke is a polymerized product of high boiling polyaromatics and hydrogen deficient fractions of bitumen (21).

Figure 3 shows the CP/MAS- ^{13}C NMR spectra of Syncrude coke. Unlike Suncor coke which has about 10% aliphatic carbons, it is apparent from the 3 kHz MAS spectrum (Figure 3a) that Syncrude coke consists only of aromatic carbons. This can be explained on the basis of the difference in severity of conditions under which the cokes are produced (22). The distribution of two types of carbons i.e. carbons directly bonded to hydrogens and those not directly bonded to hydrogens were again calculated from the integrated areas of the dipolar dephased and the difference spectra. This time the 5 kHz spectra, which have better signal to noise, could be used since there is no interference from aliphatic carbons. It can be determined from the dipolar dephased and difference spectra that carbons directly bonded to hydrogen constitute about 45% of the total carbons compared with 50% for Suncor coke. This is consistent with the lower hydrogen content of the Syncrude coke compared with the Suncor coke and is due to the severity of the process for the production of Syncrude coke.

Figure 4 shows the Bloch decay MAS ^{13}C NMR spectra of Fly ash samples obtained from the combustion of Suncor and Syncrude coke. The experimental problems encountered with these samples were mentioned earlier. Although considerably more scans were needed than for a CP experiment, the Bloch decay spectrum obtained with ^1H decoupling for the Syncrude fly ash (Figure 4 (a)) is quite respectable and clearly shows ^{13}C in the aromatic region. The result

TABLE I

ELEMENTAL ANALYSIS OF COKE AND FLY ASH SAMPLES
(In Percentage of Dry, Ash Free Basis)

Sample*	wt. %						
	C	H	N	O	S	H/C	Ash
Syncrude Coke	B 84.2	1.72	1.68	4.82	7.58	0.245	8.0
	A 84.6	1.73	1.67	4.37	7.61	0.245	3.8
Suncor Coke	B 85.92	3.49	1.58	3.00	6.14	0.487	3.4
	A 86.86	3.72	1.54	2.81	5.11	0.513	0.7
Suncor Fly Ash	B 90.12	0.18	0.56	4.31	5.37	0.024	39.7
	A 93.84	0.19	0.74	1.86	3.38	0.024	3.0
Syncrude Fly Ash	B 81.34	1.28	1.93	7.65	8.04	0.189	17.7
	A 84.43	1.33	1.91	6.17	6.16	0.189	3.7

B = Before demineralization

A = After "

TABLE II

CHEMICAL ANALYSES OF ASH FROM COKES AND FLY ASH SAMPLES

Sample	SiO ₂		Metal Concentrations w/w%				Ti		Ni		V	
	B	A	B	A	B	A	B	A	B	A	B	A
Suncor Coke	41.7	21.7 (89)	19.2	8.6 (91)	16.0	6.6 (93)	1.5	0.95 (86)	1.6	4.5 (42)	2.8	11.8 (13)
Syncrude Coke	40.6	36.7 (57)	21.5	20.3 (55)	8.4	9.1 (45)	2.0	1.7 (60)	0.7	1.1 (29)	1.8	3.0 (21)
Suncor Fly Ash	45.1	30.9 (95)	23.0	17.6 (95)	7.5	4.0 (96)	1.5	1.4 (94)	1.2	1.9 (89)	2.9	3.3 (92)
Syncrude Fly Ash	45.4	30.8 (86)	21.3	22.1 (78)	8.5	8.2 (80)	1.9	1.8 (80)	0.4	1.2 (35)	1.0	3.1 (35)

* Values in parenthesis represent % of material leached out from original material.

A = After acid demineralization, B = Before acid demineralization.

Figure 2. CP/MAS- ^{13}C NMR spectra of Suncor Coke.
 (a) 2000 scans, MAS at 5 kHz.
 (b)-(d) 3700 scans, MAS at 3.02 kHz.
 (c) 40 μs dipolar dephasing delay.
 (d) difference spectrum (b-c).
 * spinning side bands.

Figure 3. CP/MAS- ^{13}C NMR spectra of Syncrude Coke.
 (a) 2000 scans, MAS at 3.0 kHz.
 (b)-(d) 3000 scans, MAS at 5.0 kHz.
 (c) 40 μs dipolar dephasing delay.
 (d) difference spectrum (b-c).
 * spinning side bands.

Figure 4. a) Bloch decay ^{13}C NMR spectrum of syncrude fly ash diluted 1:1 with sodium polyphosphate (with ^1H decoupling). NS=27,500; spinning frequency=4.36 kHz; * spinning side bands.
 b) Bloch decay ^{13}C NMR spectrum of Suncor fly ash without ^1H decoupling NS=33,000; spinning frequency=3.08 kHz. * spinning side bands.

for the Suncor fly ash (Figure 4 (b)) obtained without ^1H decoupling is much poorer but again shows aromatic carbons. Both spectra are thus consistent with the graphitised nature of the samples, further evidence of which had been obtained from X-ray diffraction studies.

CONCLUSIONS

Acid demineralization techniques successfully reduced the ash content of Suncor delayed coking coke, Syncrude fluid coke and the two fly ash samples derived from these cokes, thus rendering the elemental analyses of all samples more representative. There are significant differences in the composition of these samples. Further, the metal recovery by acid leaching is also different. Part of this variation may be due to the different coking processes employed.

Ash reduction by acid demineralization technique rendered the two coke samples amenable to CP/MAS, ^{13}C NMR spectroscopic investigation. This study suggests that all carbons in the Syncrude fluid coke are of aromatic type compared with 92% aromaticity of the Suncor delayed coking coke. Further, the carbons bonded directly to hydrogens constitute 50% of the total aromatic carbons in the Suncor delayed coking coke and 45% in the Syncrude fluid coke.

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