Extraction and Characterization of Organic Fractions isolated from a China Ball Clay Quarried in Devon South West England

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1. INTRODUCTION

China Ball clay has been used for centuries in the tiling and pottery-ware industry. Because it is much finer than the other components in the casting slip the ball clay dominates the particle-particle interactions. Therefore, the ball-clays give the cast its plasticity and cohesion. The clay under investigation is a dark slightly sandy china ball (DSSCB) clay with a high content of finely divided kaolinite and is mixed with other substances for casting. Because of its surface area properties and its associated organic matter it has an important influence on the cohesiveness and visco-elastic properties of the clay bodies used in manufacturing pottery ware. The fine particles in the ball clays have an important influence on the rheology of the wholebody, and stabilise the flow and casting properties of the slip.

A number of analytical procedures have been used in this study in order to gain a better understanding of the clays and their associated organic materials. Identification of the amount and nature of the active organic fraction and of its mode of action is important. The work described here is part of a larger project that investigates the chemical properties and compositions of the clay and lignite materials, and the nature of clay-humic complexes and of lignite materials in clay and lignite deposits.

2. MATERIALS AND METHODS

The ball clay was pre-washed with 1 M HCl acid followed by washing with distilled water until the conductivity approached 200 µS. The ball clay was first exhaustively extracted with 0.5 M NaOH from which one fulvic acid and two humic acid fractions were isolated (samples FA1, HA1 and HA2), then (exhaustively) with 0.1 M NaOH plus 6 M urea to give a 'urea humic acid' fraction (sample HAU). All extractions were in an atmosphere of

N$_2$. The soluble fractions were separated from the insoluble clay material by centrifugation (15,000 g). The soluble fractions were then adjusted to pH 9 using 6 M HCl. These were then pressure filtered through 0.2 μm cellulose acetate membrane filters. The soluble fractions were then adjusted to pH 2 using 6 M HCl. The FA and HA was separated due to precipitation of the HA under acidic conditions. The FA fraction was pumped on to XAD-8 column, desalted, back eluted with 0.1 M NaOH and was ion exchanged with IR120 resin, and was then freeze dried. The HA fractions were dialysed in Visking tubing over 3 to 4 days using 0.3 M HF plus 0.1 M HCl acid. The conductivity of the HA solution was reduced to 200 μS using distilled water before freeze drying.

Characterisations of the series of organic fractions were carried out using Solid-state ^{13}C NMR spectroscopy using a VARIAN INOVA spectrometer at ^{13}C and ^{1}H frequencies of 100.5 and 400.0 MHz, respectively. Cross-polarization times of 1 ms, acquisition times of 13 ms, and recycle delays of 500 ms were used. For Variable Amplitude Cross-Polarization (VACP) experiments a Magic-Angle Spinning (MAS) frequencies of 13 kHz was used. Additional experiments using Chemical Shift Anisotropy (CSA) filter (C-sp^3 only spectra) and Dipolar Dephasing (DD) filter (non-protonated mobile C only spectra) were carried out. The spectral data along with a number of other ^{13}C NMR spectra along with thermogravimetry analyses (TGA) of the same samples were analysed using Partial Least Squares (PLS).

3. RESULTS AND DISCUSSION

The NMR spectra show high contributions from aliphatic functionalities. There are broad peaks in the aliphatic hydrocarbon region for both the FA and HA1 spectra (Figures 1a and 1b) corresponding to methylene carbons in alkyl chains, and CH$_3$ groups of acetyl groups attached to aliphatic structures. Evidence for CH$_3$ functionality is provided by the prominent resonance at 10-20 ppm in the DD spectrum. The broad resonance at about 30 ppm is characteristic of the significant contributions from methylene C. The peak centred around 32 ppm is characteristic of crystalline, or ordered methylene groups, and this feature is more pronounce for the HA2 and the HAU fractions. The HAU spectra show two distinct peaks at 30 and 34 ppm which is likely to indicate long chain amorphous and crystalline methylene structures, respectively.

The wide band at around 75 ppm for both the FA and HA samples (TOSS spectra) and the peaks at around 75 and 102 ppm (CSA filtered spectra) indicate the presence of sp^3-hybridized C, which are probably due to cellulose and other polymeric carbohydrates.

The broad peaks in the 125 ppm region are assigned to variety of aromatic structures, that may include C_1 quaternary carbons of guaiacyl and syringyl lignin units and the C_6 carbon of guaiacyl structures. The ratio of DD to TOSS in the aryl region (110-150 ppm) (Table 1) shows that there is a high degree of condensation in the aromatic structures. This may be attributable to lignite material.
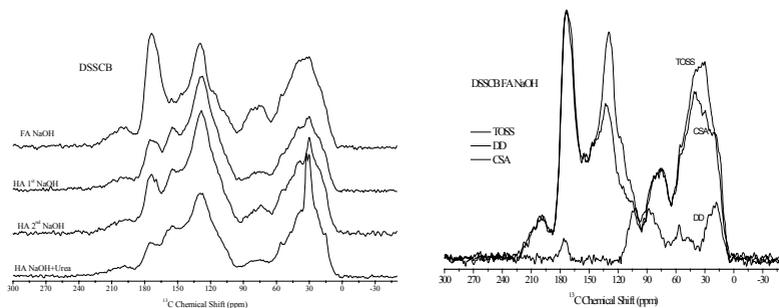

Figure 1a. ^{13}C NMR Spectra isolated from the DSSCB clay; from top to bottom: FA, HA1, HA2, and HAU fractions. Figure 1b. FA TOSS spectra, including the changes of the spectra due to DD and CSA experiments

Table 1. Relative values of the ^{13}C NMR spectra for TOSS, DD and CSA for the four organic fractions isolated from the DSSCB clay

| Samples		Alkyl 0-45 ppm	Methoxyl 45-65 ppm	O-Alkyl 65-90 ppm	di-O-Alkyl 90-110 ppm	Aryl 110-150 ppm	Aryl-O 150-160 ppm	Carboxyl 160-185 ppm	Carbonyl 185-225 ppm
FA	Abundance%[a]	23.5	9.5	8.4	4.6	26.1	4.4	18.6	4.9
	DD/TOSS[b]	21.7	21.4	41.3	85.2	75.6	103.0	102.5	92.7
	CSA/TOSS[c]	90.0	92.4	101.9	83.8	1.5	-0.0	4.4	7.0
HA1	Abundance %[a]	18.5	6.55	3.9	4.4	30.8	5.75	9.8	3.5
	DD/TOSS[b]	24.85	26.1	61.9	93.2	80.7	100.0	95.5	44.3
	CSA/TOSS[c]	83.6	79.65	101.8	38.1	0.2	-0.3	4.2	10.5
HA2	Abundance %[a]	22.5	7.7	5.45	5.1	33.0	6.0	10.7	3.9
	DD/TOSS[b]	22.7	21.3	38.2	67.1	69.9	90.8	98.1	99.1
	CSA/TOSS[c]	89.4	82.2	100.2	43.6	0.6	0.6	5.6	12.2
HAU	Relative %[a]	22.5	6.1	3.75	3.7	23.7	4.8	7.3	3.0
	DD/TOSS[b]	21.4	23.0	42.8	66.0	68.0	85.8	91.75	77.6

a; Abundance % is the percentage of the area of the different subsections of the spectra over the total area of the spectra
b; DD/TOSS is the ratio of DD (%) to the TOSS (%) for each subsection of the spectra
c; CSA/TOSS is the ratio of CSA (%) to the TOSS (%) for each subsection of the spectra

There are a number of similarities throughout, although some differences are apparent. The DD to TOSS ratio in the carbonyl group between the HA1 and HA2, 44.3 and 99.1 %, respectively, may indicate some protonated carbons in mobile macromolecules in the HA1 sample. The low CSA values in the aryl and O-aryl regions of the four spectra indicate that the peaks present in these regions are due to aromatic moieties.

The latent variable (60% of the variance from NMR data and 36% of TGA data) (Figures 2a and 2b) show the correlation between labile compounds and the thermal events at 352, 360, 386 and 407°C respectively. The latent variable from NMR have positive and negative signals, the positive signals are probably due mainly to crystalline polymethylene and carbohydrates which have a positive correlation with the exothermic thermal events and negative signals indicating a negative correlation with carboxyl and aryl groups present.
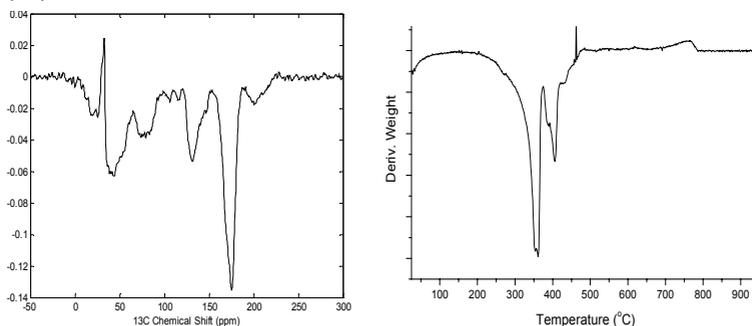
Figures 2 a and 2 b showing the latent variance from 60% of NMR data
and 36% of TGA data

4. CONCLUSIONS

^{13}C NMR has indicated compositional characteristics of the organic matter associated with the clay matrix in DSSCB, and in combination with TGA in the PTS given insights into their thermal properties.

REFERENCES

1. Keeler, C. and G. E. Maciel, 1999. 13C NMR spectral editing of humic material
2. Konta,1995. Clay and man: clay raw materials in the service of man. Applied Clay Science, 10(4), 275-335.

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