CHAPTER 5

EXPERIMENTAL PROCEDURES

5. Experimental Procedures

5.1 Ball Clay Sample Preparation Procedure

Core Logging Samples

→ Wet Sieve Analysis on 120, 200 and 325 # mesh

Sampling

Grinding – 60 # mesh
- Chemical Analysis by XRF
- Mineral Analysis by XRD
- Microstructure by SEM and TEM
- P.S.D. by Sedigraph
- Organic Matter Analysis by Leco EC-12, and Extractable Humic Acid and Fulvic acid
- Soluble Salts Analysis by Water and Wastewater Analysis

Ball Slip Preparation Screen Sieve –120 # mesh
- Deflocculation Response
- Viscosity, Gelation and Relative Gel-strength
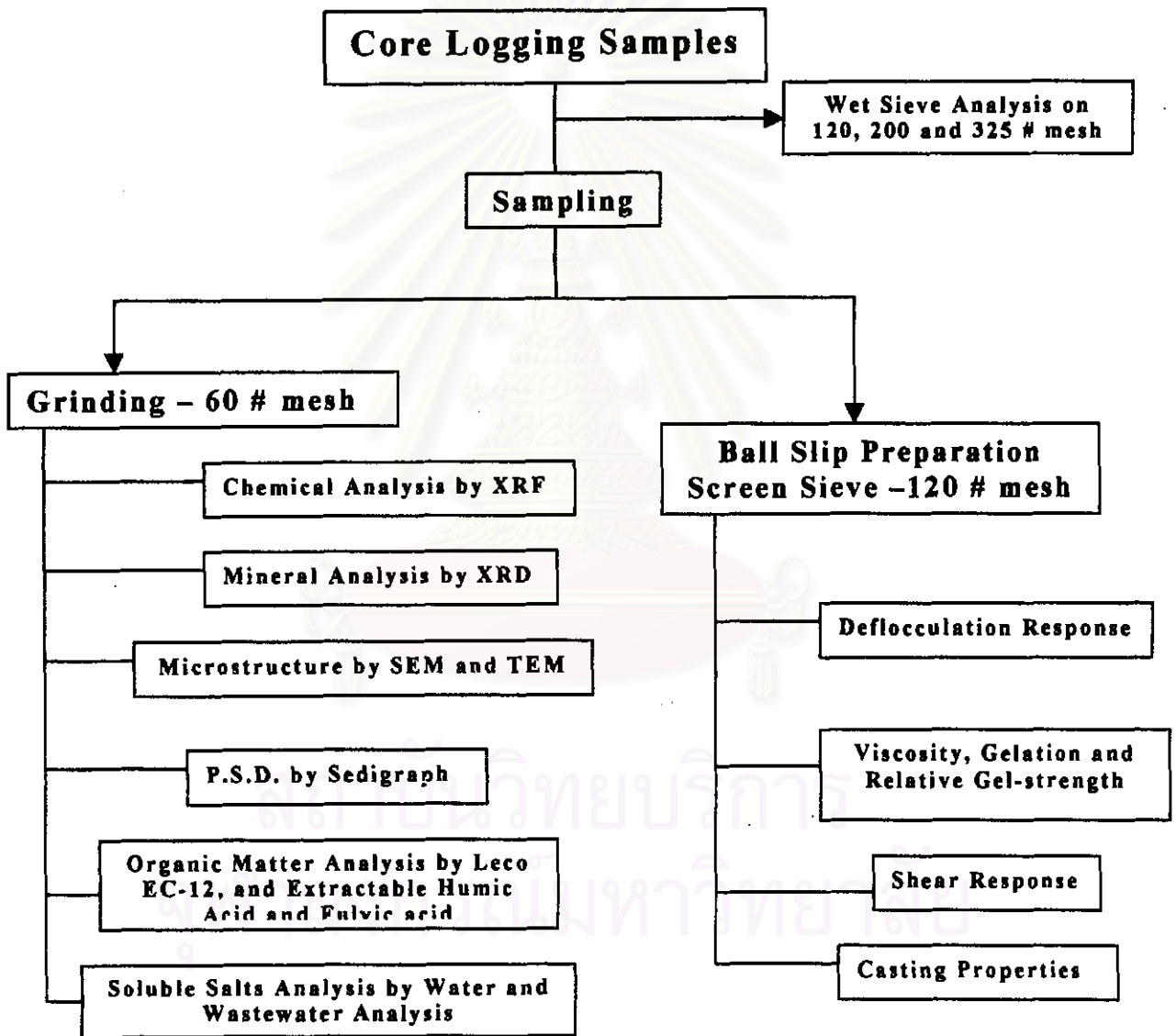- Shear Response
- Casting Properties

Fig. 5.1 Ball Clay sample Preparation chart.

Ball Slip preparation procedure is in Appendix A

5.2 Ball Clays General Characterization Method[4,6,20,2]

Test procedure for chemical analysis x-ray fluorescence, mineralogical analysis by XRD, microstructure analysis by SEM and TEM and particle size distribution analysis are shown in Appendix A.

5.3 Organic Matter Analytical Procedure

5.3.1 Total Carbon (TC), Inorganic Carbon (IC) and Organic Carbon (OC) by Leco EC-12 Carbon Analyser[28]
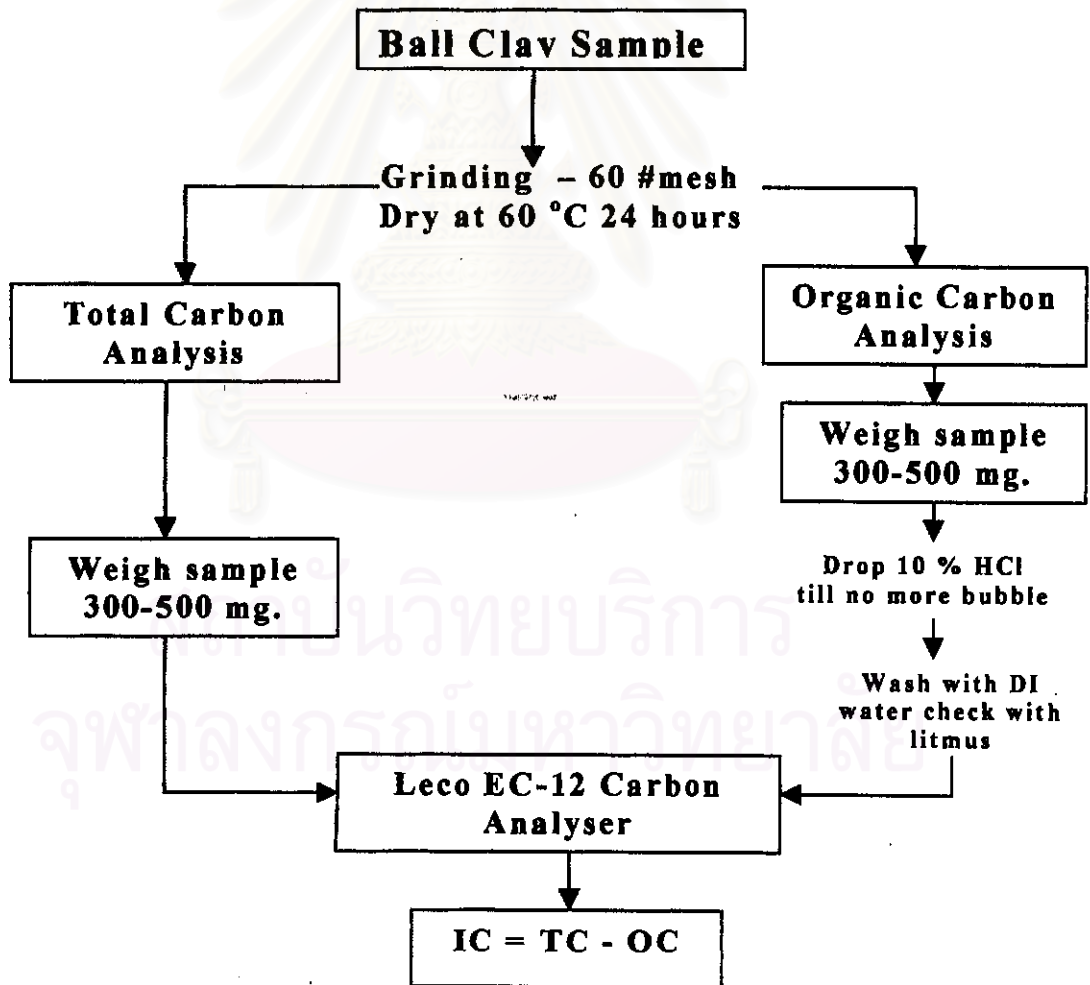

Fig. 5.2 Total carbon, organic carbon and inorganic carbon analytical procedure chart.

5.3.2 Extractable humic and Fulvic acid by Gross chemical fractionation of Organic matter
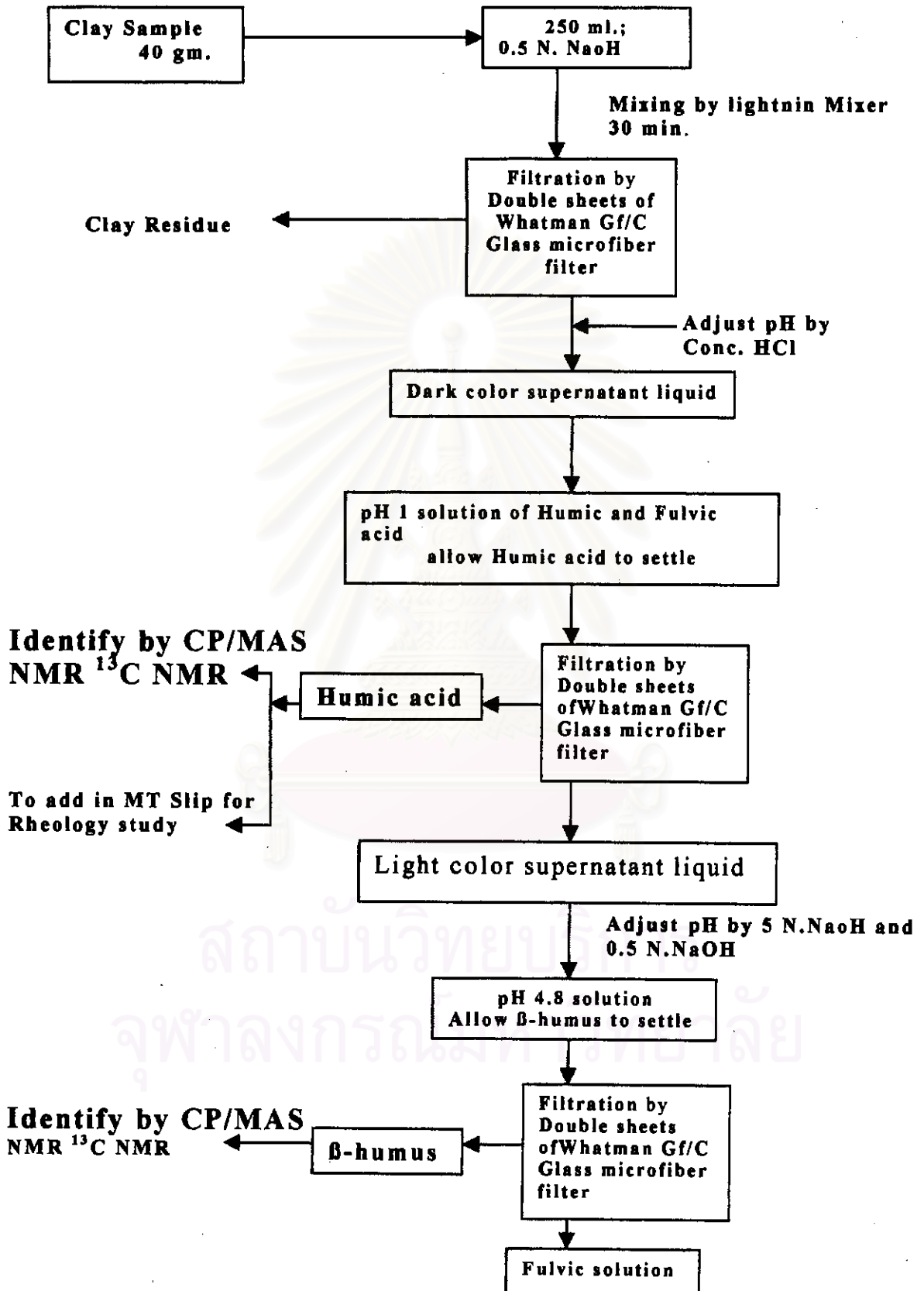
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┌─────────────────┐                    ┌─────────────────┐
│  Clay Sample    │───────────────────▶│   250 ml.;      │
│   40 gm.        │                    │  0.5 N. NaoH    │
└─────────────────┘                    └─────────────────┘
                                                │
                                       Mixing by lightnin Mixer
                                       30 min.
                                                │
                                                ▼
                                       ┌─────────────────┐
                                       │  Filtration by  │
                  Clay Residue ◀───────│  Double sheets of│
                                       │  Whatman Gf/C   │
                                       │  Glass microfiber│
                                       │  filter         │
                                       └─────────────────┘
                                                │
                                       ◀── Adjust pH by
                                           Conc. HCl
                                                │
                                                ▼
                                       ┌──────────────────────────┐
                                       │ Dark color supernatant liquid │
                                       └──────────────────────────┘
                                                │
                                                ▼
                                       ┌──────────────────────────────┐
                                       │ pH 1 solution of Humic and Fulvic│
                                       │ acid                           │
                                       │   allow Humic acid to settle   │
                                       └──────────────────────────────┘
                                                │
                                                ▼
Identify by CP/MAS                     ┌─────────────────┐
NMR ¹³C NMR ◀──────┌──────────────┐◀──│  Filtration by  │
                   │  Humic acid  │    │  Double sheets  │
                   └──────────────┘    │  ofWhatman Gf/C │
                                       │  Glass microfiber│
                                       │  filter         │
To add in MT Slip for                  └─────────────────┘
Rheology study ◀───                             │
                                                ▼
                                       ┌──────────────────────────┐
                                       │ Light color supernatant liquid │
                                       └──────────────────────────┘
                                                │
                                       Adjust pH by 5 N.NaoH and
                                       0.5 N.NaOH
                                                │
                                                ▼
                                       ┌──────────────────────┐
                                       │  pH 4.8 solution     │
                                       │ Allow ß-humus to settle │
                                       └──────────────────────┘
                                                │
                                                ▼
Identify by CP/MAS                     ┌─────────────────┐
NMR ¹³C NMR ◀──────┌──────────────┐◀──│  Filtration by  │
                   │   ß-humus    │    │  Double sheets  │
                   └──────────────┘    │  ofWhatman Gf/C │
                                       │  Glass microfiber│
                                       │  filter         │
                                       └─────────────────┘
                                                │
                                                ▼
                                       ┌─────────────────┐
                                       │  Fulvic solution │
                                       └─────────────────┘
```

Fig. 5.3 Extraction of Humic substance Chart

5.3.3 Humic and Fulvic acid Identification by NMR

- Nuclear Magnetic Resonance or NMR[30]

NMR as it is abbreviated by scientists, is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin. Most of the matter you can examine with NMR is composed of molecules. Molecules are composed of atoms. Here are a few water molecules. Each water molecule has one oxygen and two hydrogen atoms. If we zoom into one of the hydrogens past the electron cloud we see a nucleus composed of a single proton. The proton possesses a property called spin which:

1. can be thought of as a small magnetic field, and
2. will cause the nucleus to produce an NMR signal.

When placed in a magnetic field of strength B, a particle with a net spin can absorb a photon, of frequency v. The frequency v depends on the gyromagnetic ratio, γ of the particle.

$$v = \gamma\ B$$

For hydrogen, $\gamma = 42.58$ MHz / T

Not all nuclei possess the property called spin. Almost every element in the periodic table has an isotope with a non zero nuclear spin. NMR can only be performed on isotope whose natural abundance is high enough to be detected. Some of the nuclei routinely used in NMR are listed in Table 5.1.

Table 5.1 Some of the nuclei routinely used in NMR

Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin	γ (MHz / T)
^{1}H	1	0	1/2	42.58
^{2}H	1	1	1	6.54
^{31}P	0	1	½	17.25
^{23}Na	0	1	3/2	11.27
^{14}N	1	1	1	3.08
^{13}C	1	1	1/2	10.71
^{19}F	0	1	1/2	40.08

Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. As a consequence, NMR spectroscopy finds applications in several areas of science. NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules. These techniques are replacing x-ray crystallography for the determination of protein structure. Time domain NMR spectroscopic techniques are used to probe molecular dynamics in solutions. Solid state NMR spectroscopy is used to determine the molecular structure of solids. Other scientists have developed NMR methods of measuring diffusion coefficients. The versatility of NMR makes it pervasive in the sciences. Scientists and students are discovering that knowledge of the science and technology of NMR is essential for applying, as well as developing, new applications for it.

Many of the molecules studied by NMR contain carbon. Unfortunately, the carbon-12 nucleus does not have a nuclear spin, but the carbon-13 (C-13) nucleus does due to the presence of an unpaired neutron. Carbon-13 nuclei make up approximately one percent of the carbon nuclei on earth. Therefore, carbon-13 NMR

spectroscopy will be less sensitive (have a poorer SNR) than hydrogen NMR spectroscopy. With the appropriate concentration, field strength, and pulse sequences, however, carbon-13 NMR spectroscopy can be used to supplement the previously described hydrogen NMR information. Advances in superconducting magnet design and RF sample coil efficiency have helped make carbon-13 spectroscopy routine on most NMR spectrometers.

- The nondegradative approach to identify humic substance[30]

The nondegradative approach seeks to analyze isolated humic substances without chemical or physical alteration utilizing techniques which allow structural inference to be drawn. The techniques utilized include UV-visible and infrared spectrophotometry, electron spin resonance spectrometry and NMR, X-ray analysis, electron microscopy and electron diffraction, viscosity and surface tension measurements, and various titrimetric methods. It has become apparent in recent years that the most promising nondegradative technique for humic structural analysis is NMR.

The utility of NMR for humic structural analysis is primarily due to two fundamental instrumental advance. The first of these is the Fourier transform technique described in detail by Fukushima and Roeder[32]. Basically, the technique allows the rapid acquisition and averaging of many individual spectra to produce an average spectrum with greatly enhanced signal-to-noise ratio and thus, sensitivity. This is critical for samples such as humic substances which have limited solubility in NMR solvents. It is also important for the study of relatively dilute spin systems, such as ^{13}C Levy[33]. The second major instrumental advance is the crosspolarization/magic-angle spinning (CP/MAS) technique which

allows the acquisition of ^{13}C NMR spectra from solid samples, somewhat alleviating the sensitivity and other problems inherent in solution NMR experiments. A more detailed discussion of the CP/MAS ^{13}C NMR technique is beyond the scope of this chapter. The interested reader is advised to consult the monographs by Levy et al[33]. and Fukushima and Roeder[32].

To date, CP/MAS ^{13}C NMR spectra have been obtained from humic substances isolated by a variety of procedures from numerous matrices and environments. Hatcher and co-workers[34] at the U.S. Geological Survey have published such spectra of aquatic and marine sedimentary humic substances, and isolated aquatic humic substances.

Fig. 5.4 shows three spectra acquired by this group including a humic acid derived from Everglades peat, a humic acid derived from a Histosol soil, and a humic acid derived from a Mollisol soil. The signals in these NMR spectra represent the different types of carbon atoms present in these materials. Further, CP/MAS spectra are generally taken to be quantitative, that is, the relative intensities of the various resonance signals are proportional to the relative amounts of the various carbon atoms in the material under investigation.
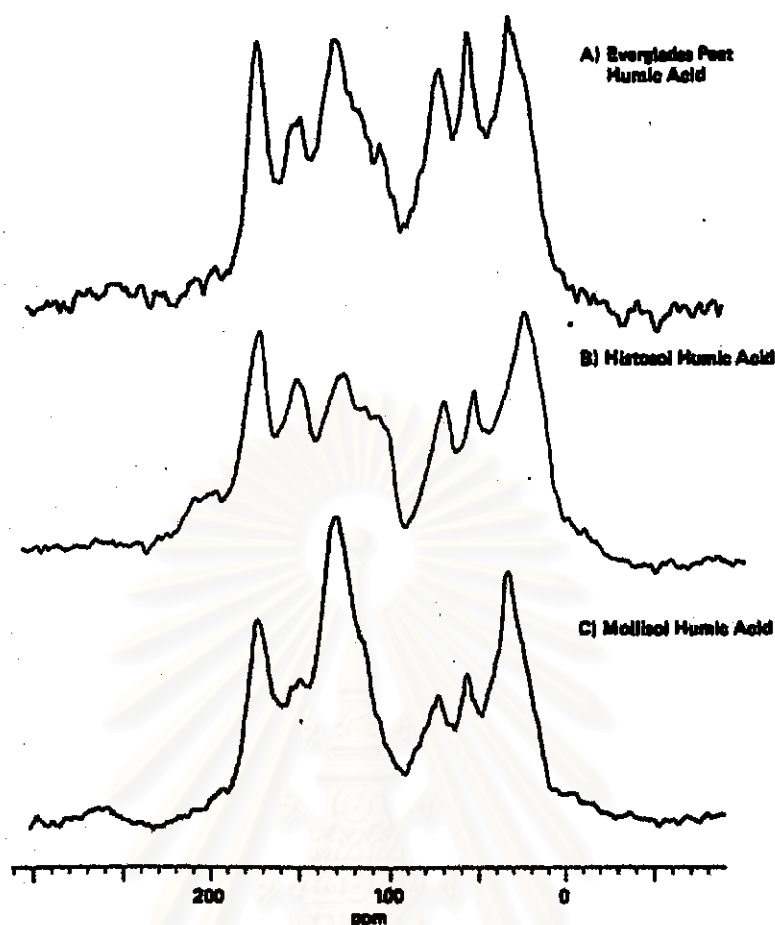
Fig. 5.4 CP/MAS ^{13}C NMR spectra of three isolated humic acids

For example, Fig. 5.5 shows a spectrum Norwood[35] of an aquatic fulvic acid (Singletary Lake, North Carolina) which can be divided into four principal resonance regions. The relative intensities, as represented by peak areas integration, coupled with the positions of the resonance signals in each region allow structural inferences to be drawn. First, it is apparent that this humic substance is highly aliphatic in nature (regions I and II) as well, but relatively little of this carbon appears to be substituted with heteroatoms such as oxygen. This implies that intact lignin and other phenolic units are only minor structural components of this material. Note, however, that this is not the case for certain soil-derived humic substance such as those shown in Fig. 5.4
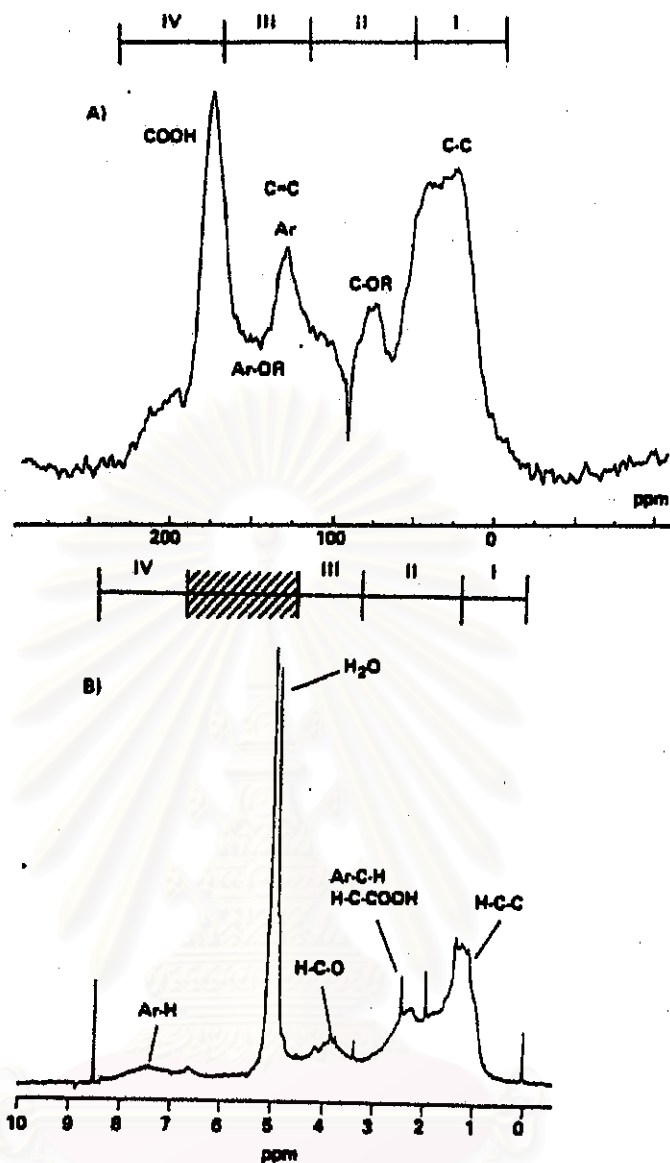
Fig. 5.5 CP/MAS (A) and ^{1}H (B) NMR spectra of Singletary Lake fulvic acid

Further structural inference can be derived from the ^{1}H NMR spectrum Norwood[35] shown in Fig. 5.5. This spectrum was obtained from an NaOD/D$_2$O solution of the humic substance. Four spectral regions are again apparent which represent the types and relative amounts of all non-deuterium exchangeable protons in the aquatic fulvic acid. As in the CP/MAS spectrum, aliphatic structures are shown to be of significance. The lack of significant

aromatic proton (Ar-H) coupled with the amount of aromatic carbon indicates that aromatic structures are highly substituted, most likely with aliphatic side chains. These data and structural inference are supportive of those of Liao et al. (1982) described earlier in this paper. It is thus apparent that the degradative and nondegradative approaches are complementary

Schnitzer and his co-workers[36] have also employed numerous nondegrasative techniques to examine soil-derived humic substances. Preston and Schnitzer[37] acquired ^{13}C NMR spectra of several methylated soil humic and fulvic acids dissolved in deuterochloroform. They interpreted resonance signals in the aromatic carbon region of these spectra to be indicative of aromatic carbons substituted by methylated carboxyl groups. These signals were correlated with others in the aliphatic region due to added methyl groups on these carboxyls. They concluded that carboxyl groups in these humic substances are almost exclusively attached to aromatic rings and suggested that these data were support of the "building block" model for soil humic macromolecular structure.

5.4 Soluble Salts Analytical Procedure[32]

Filtrate preparation:
Mix 300 gm. of Ball clay sample in 1200 ml. of deionized water by using High speed mixer ; then filtrated it with Baroid filter, passed through Whatman filter paper no. 5 . Attained 1 lit of filtrate ,sending it to have soluble salts analysis at Department of Mineral Resources.

Soluble Salt Analytical Procedure shows in appendix B. that follow by Standard Methods for the Examination of Water and Wastewater 18th Edition 1992; Edited by Arnold E. Greenberg, Lenor S. Clesceri, Andrew D. Eaton.

5.5 Rheological and Casting Properties Determination

5.5.1 Flow Characterization

5.5.1.1 Deflocculation Response

Deflocculation curves were performed on each slip, starting at approximately 1.55 gm/ml for local ball clays or 1.60 gm/ml for imported ball clays and the minimum viscosity obtained on the deflocculation curve was about 100 and 140 cps. The powder was first, dispersed in distilled waster with just the necessary amount of dispersant (Na_2SiO_3) required only to disperse all the solids. The slip were then aged for 24 hours and then deflocculated.

For each slip, defloculant was gradually added, viscosity at each point was recorded until flocculation occurred, corresponding to increasing levels of dispersant. Thus, for the rest of the testing experiments, humic added MT ball slips were prepared at the selected specific gravity (1.60) to study the effect of humic on deflocculation curve.

5.5.1.2 Thixotropy

1. Viscosity Evaluation
Using Brookfield Viscometer model RV DV II$^+$ spindle no. 02 ; speed 20 rpm. Record the value after start to rotate spindle for 15 sec.
2. Gelation Evaluation
Using Brookfield Viscometer spindle no.02 ; speed 0.5 rpm. Record the values every minute for 10 min.

3. Gel-strength Characteristic can be evaluated by gel-strength relation, using Brookfield Viscometer spindle no.02 ; speed 0.5 rpm. To record the viscosity at each 30 sec.for 10 min., after that turned the power off for 5 min. and then start again at

the same speed for 5 min. Discussion were made on the gelling characteristics.

5.5.1.3 Flow Measurement by Brookfield viscometer

Using Brookfield Model RV DVII$^+$ Viscometer, obtain one liter of the ball slip to be tested and mixed with Lightnin mixer for 2 min., using optimum speed, low enough to avoid air entrainment in the sample but high enough to develop a vortex. Screw the no.2 spindle on to the viscometer shaft level the viscometer and set the speed at 20 rpm. . At the end of two minute mixing transfer the sample with minimum delay (set at 30 sec.) to the 600 ml. Beaker, filling the beaker to level 3 cm of top. Lower the viscometer into the beaker until the slip is at the immersion groove of the spindle. Turn on the switch and record the value at 15 sec. after start.

5.5.1.4 Flow Measurement by Gallenkamp Viscometer

Before measuring with Gallenkamp Universal Torsion Viscometer with # 30 SWG wire and 11/16 " diameter cylinder Stir 750 ml. of ball slip in a one liter container for 2 minutes with the mixer set at a speed low enough to avoid air entrainment in the slip and high enough to develop a vortex and visible movement then fill it in the stainless steel beaker with mark 1 cm. below rim. Place the beaker on the support stand of the viscometer, completely submerging the cylinder in the slip. Rotate and set the flywheel to the correct position, pull the release pin and note the degree of overswing. This reading is initial reading or "Overswing." Reset the pointer to 360° clockwise again, activate the stopwatch and take another reading at the end of 1 minute. The

difference of 1 minute reading and initial reading is called "thixo at 1 minute."

5.5.2 Casting Properties Measurement

5.5.2.1 Cast Rate by Baroid Filter

As mentioned before, 175 ml of each slip was filter pressed with BaroidΦ Filter Press, at 58 psi for 30 min., after that open the Baroid and drain slip for 5 min., which the excess slip was poured off and weighed. Filter press continue until no more water was filtrate. Finally, the filtered cake wall thickness was measured and its weight recorded. The cake was then dried at 105°C for 48 hours and stored in a dessicator. For this data, its water retention was calculated. The water retention of the cake was calculated by:

$$\% \text{ Water Retention } = \frac{H_w - D_w}{D_w} x 100\%$$

H_w = Humid weight

D_w = Dried weight

5.5.2.2 Cast Rate by Plaster Mold

Using American Standard "Half Moon" plaster mold, conditioning the mold until sponged-on water is adsorbed 10 seconds, pour slip into the mold, left for 10 minutes then drain the mold. After the clay cast is set, cut it sharply with a cutter and measure by a ruler that has 0.5 mm. Reading accuracy.