

**MACROMOLECULAR ORGANIC BAYER
PROCESS POISONS**

**by
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**This thesis is submitted in fulfilment of the
requirements for the degree of
Doctor of Philosophy**

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December 2000

CERTIFICATE OF AUTHORSHIP

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person. This thesis does not contain material which to a substantial extent has been accepted for the award of any other degree or diploma of a university or other institute of higher learning, except where due acknowledgment is made in the text.

Damian Edward Smeulders.

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“WATERGATE” NMR

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Acknowledgments

I would like to thank the following people for their help during this project:

- Professor Michael Wilson (principal supervisor)
- Dr Lyndon Armstrong and Vicki Mitchell from Queensland Alumina Limited
- Dr Kamali Kannangara
- Mr Jean-Pierre Guerbois
- Dr Craig Marshall
- and (almost Dr) Amanda Ellis

I would like to thank the present and past members of the research group, particularly Mick, Dennis, Harry, Adam, Craig and Amanda for their encouragement, friendship, and their purchase of liquid distractions. This also applies to non-group members - Frank and Aeron.

I would especially like to thank Vivien, Mum (aka Kath), Dad (aka Bill), Nathan, Narelle, Carl, Nicole and Kirsten.

ABSTRACT

Sodium hydroxide is used at elevated temperatures to separate aluminium hydroxide from ferric oxide (red mud) in bauxite by the Bayer process. During the processing of the bauxite, the organic material that it contains is extracted into the Bayer liquor where it interferes with the precipitation of aluminium hydroxide. The organic material present in the Bayer process liquor from a high temperature alumina refinery operating at 250-255°C was examined in this study. Under these conditions large amounts of the acidified organic material was volatile (approximately 89% at 100°C, 0.1atm pressure under rotary evaporation). The non-volatile organic material obtained by rotary evaporation was fractionated by dialysis to produce different molecular weight fractions. These fractions have been analysed by thermal and spectroscopic methods (thermogravimetric analysis and calorimetry, nuclear magnetic resonance, infrared spectroscopy, pyrolysis gas chromatography mass spectrometry). It was discovered that the smallest molecular weight fraction (<1.2kD) appears to yield mainly hydroxybenzene carboxylic acids on pyrolysis and structurally resembles the highly oxidised humic acids that are found in the group of soils known as podsols. The 12-25kD and 25-50kD fractions appear to resemble material more akin to oxidised kerogen. The highest molecular weight material (>300kD) behaves as a soluble char.

Dialysis separates the organic material into molecular weight fractions, or more correctly fractions which can pass through specifically sized pores. As a result of the study of high temperature Bayer humic substances, it was discovered that the dialysis process appeared not to discriminate against certain small molecules. These small molecules, termed “guests”, appear to be bound to larger macromolecules, “termed hosts”, by physical entrapment. This may or may not also involve hydrogen bonding. Evidence for this supposition was obtained by proton nuclear magnetic resonance and by derivatisation of polar groups. Derivatisation released the entrapped small molecules which could then be detected and identified by gas chromatography mass spectrometry. It is suggested that host-guest humic complexes may also be prevalent in nature, where they have wide ramifications for the transport of organic matter in natural aqueous solutions such as streams, rivers and seas.

Prior to this study little was known about which molecular weight ranges of Bayer humic substances are particularly detrimental to the precipitation of aluminium hydroxide and sodium oxalate. The effects of the various molecular weight fractions (<1.2kD to >300kD) of organic matter introduced into alumina refineries with bauxite have been studied by precipitation testing. It was discovered that the effects produced by the organic materials were maximised under system stress, such as when there is competition for the number of sites at which new alumina carrying species or humic material can bind. The preparation of seed crystal is therefore very important and because of competition, effects are concentration dependent. Different molecular weight fractions of the humic substances were found to have different detrimental effects on precipitation yields of aluminium hydroxide and these did not correlate to changes in crystal surface area. While yields may be affected by ionic strength changes, it is clear that the higher molecular weight organics (>50kD), although present in low concentrations in Bayer process liquor, have particularly strong adverse affects on the dynamics of the precipitation of aluminium hydroxide. These larger molecular weight organics (>50kD) were also found to increase the stability of sodium oxalate in solution by about 20%. The impact of the organic fractions on the precipitation of aluminium hydroxide was found to be minimised through the use of caustic washed aluminium hydroxide seed.

In addition to the organic materials present in the Bayer process liquor, a number of insoluble organic materials are also produced from organic material entering the refinery with the bauxite. These insoluble organic materials appear in the waste solids termed "red mud", in the shell-side of the heat exchangers, on sodium oxalate crystals, on precipitated aluminium hydroxide "gibbsite", in precipitation tank scale, and on oxalate-gibbsite co-precipitation fines. These materials were analysed by pyrolysis gas chromatography mass spectrometry with in-situ methylation and by nuclear magnetic resonance spectroscopy to determine their compositions. Differences in composition can give information on the selectivity of the dissolution process and hence help in enhancing yields of alumina from the process. It was discovered that on pyrolysis each insoluble material produced different products. The pyrolysis products for the bauxite and red mud were found to differ considerably, with the red mud pyrolysates consisting mainly of aromatic polycyclics. However part of this difference was due to the red mud catalysing pyrolysis leading to the production

of simple aromatic compounds. Nevertheless methanol soluble products were also found to be different in the red mud and bauxite.

The organic material recovered from the heat exchanger was found to be different to both the above materials, having characteristics similar to those of a light pitch or tar. The organic deposits in sodium oxalate and aluminium hydroxide crystals were also different, however they produced several common pyrolysis products including alkanes, alkenes, and long chain aliphatic carboxylic acids, predominantly with C₁₄ to C₁₆ carbon chain lengths, as well as short chain (C₄-C₇) aliphatic mono- and di-carboxylic acids. Not unexpectedly the organic material on the precipitation tank scale was similar in composition to soluble organic material in the process liquor.

As a result of this study we now have an understanding of the composition of both the soluble and insoluble organic materials present in a high temperature (250-255°C) Bayer alumina refinery. In addition we now know the molecular weight ranges of organic material responsible for many of the detrimental impacts on the operation of the Bayer process and we have a new concept in binding of humic materials, namely the "host-guest theory".

CHAPTER ONE
INTRODUCTION

The Australian alumina industry

1.1 Alumina Production

In a relatively short period of time Australia has developed into the world's leading producer of both bauxite and alumina. In 1971 Australia took over the leadership as the world's largest bauxite producing country with an output of 12.7 million tonnes (Patterson *et al.*, 1986), this figure is dwarfed by the current bauxite production which is in excess of 48.4 million tonnes (Australian Aluminium Council, 2000).

Earlier this century Australia was reliant on imports of alumina from Indonesia for the operation of its first aluminium smelter at Bell Bay in Northern Tasmania. Bauxite deposits of sufficient size and grade to support an aluminium industry were discovered in 1955 near Weipa on the Cape York Peninsula in Queensland and in the Darling Range in Western Australia in the late 1950's. The deposits on the Weipa peninsula are now known to be amongst the largest in the world. Five bauxite mines are operated around Australia at Weipa, Gove, and in the Darling Ranges of Western Australia.

The first alumina refinery in Australia was commissioned in 1963 at Kwinana in Western Australia. The QAL refinery at Gladstone was constructed shortly afterwards, and was commissioned in early 1967. In total, Australia has six alumina refineries producing nearly 14.5 million tonnes of alumina annually, making Australia the world's largest alumina producer, a position that it has held since 1976 (Australian Aluminium Council, 2000).

Since the opening of the aluminium smelter at Bell Bay, a further five primary aluminium smelters have come into operation. The Australian aluminium industry produces almost 1.72 million tonnes of aluminium annually or approximately 10% of the world's total aluminium production (Australian Aluminium Council, 2000).

The Australian aluminium industry generated export earnings of over \$6 billion in 1998, and it is Australia's fourth largest commodity exporter (Australian Aluminium Council, 2000).

1.1.1 Overview of the Bayer Process.

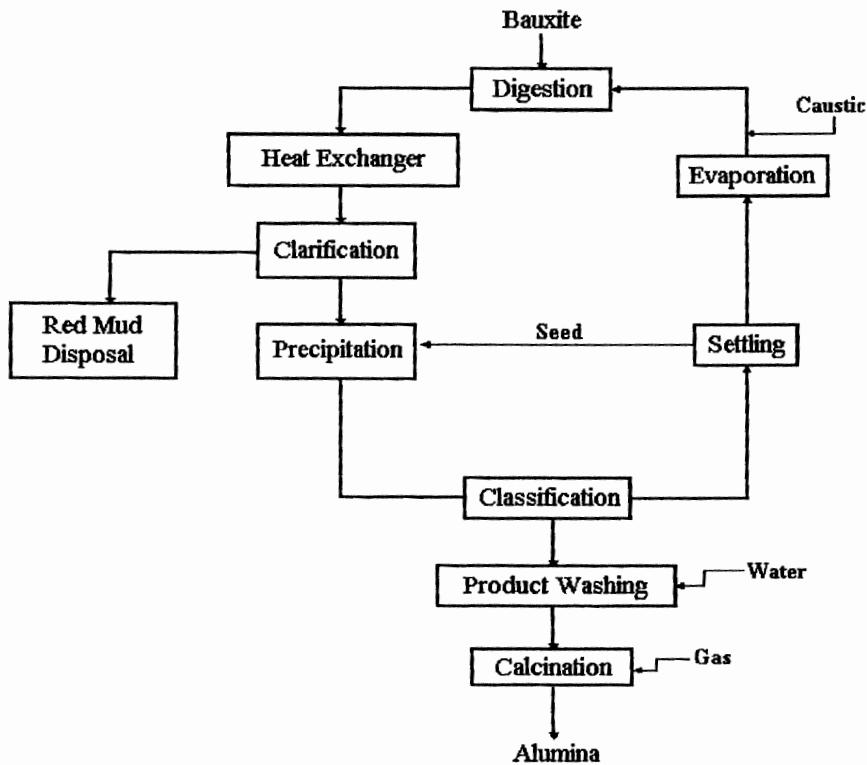
The Bayer process is used to produce smelter grade alumina (aluminium oxide Al_2O_3) from its main ore, bauxite. Most of the alumina produced is converted into aluminium metal via reduction using the Hall-Heroult process. Alumina is also produced for the abrasives, ceramics and refractory industries.

The Bayer process was discovered by the Austrian chemist Karl Bayer and patented in 1887. The Bayer process involves four main stages: digestion, clarification, precipitation and calcination. The Bayer process uses a concentrated sodium hydroxide solution, heat and pressure to extract soluble aluminium species from bauxite. After filtering to remove undissolved impurities, the saturated liquor is cooled in a series of settling tanks to which fine seed crystals of aluminium hydroxide are added. Over a period of time the crystals of aluminium hydroxide grow and settle out of solution. After removal from the precipitation tanks, the aluminium hydroxide is converted into alumina by calcination. The Bayer process is cyclic, and a schematic diagram of the stages of the Bayer process is shown in Figure 1.1. All Bayer refineries follow this general arrangement but the technical and engineering methods vary with the type of ore being used.

The digestion stage of the Bayer process varies considerably around the world depending on the composition of the bauxite. The three main aluminium minerals present in bauxite are gibbsite (aluminium hydroxide $\text{Al}(\text{OH})_3$), boehmite and diasporite (aluminium oxyhydroxides). The degree of hydration of the mineral determines the extraction conditions required, with the monohydrate minerals, diasporite and boehmite, requiring higher digestion temperatures and higher sodium

hydroxide concentrations then those required for ores containing the trihydrate mineral gibbsite.

Figure 1.1 Schematic diagram of the Bayer process



The samples for this project were sourced from Queensland Alumina Limited (QAL) which operates a refinery near Gladstone in Queensland processing Weipa bauxite, the bulk of which is made up of boehmite, a monohydrate form of bauxite. A second type of bauxite is also used at the refinery containing a higher gibbsite content. Average analyses of the two grades of Weipa bauxite are detailed in Table 1.1.

Boehmite in the monohydrate grade bauxite requires elevated temperatures above 200°C to dissolve readily in the process liquor. The gibbsite in trihydrate grade

bauxite dissolves readily at temperatures below 150°C. Consequently the monohydrate grade bauxite undergoes a high temperature and high pressure extraction (250-255°C, 3500kPa) in digesters, while the trihydrate grade bauxite is added to the process liquor when the temperature is below 200°C.

Table 1.1 Average analyses of Weipa bauxites

Constituent	Monohydrate Grade %	Trihydrate Grade %
Al ₂ O ₃	55	50
Available Al ₂ O ₃	50*	44 [#]
Fe ₂ O ₃	12	17
SiO ₂	5	4
TiO ₂	3	3
Other (mainly H ₂ O)	25	26

* 40% from gibbsite and 10% from boehmite

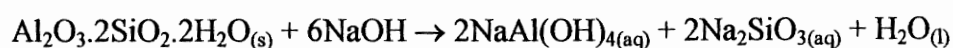
[#] Gibbsite is only extractable in sweetening.

The Bayer process conditions employed by the QAL refinery are detailed in the next section.

1.1.2 Digestion

The extraction of the sodium aluminate from the bauxite occurs during the digestion stage. Pisolitic, monohydrate grade bauxite, with a maximum size of 20mm, is ground in two-stage ball / rod mills with recycled spent process liquor. Lime is introduced to the resultant slurry for the control of phosphate and for red mud conditioning.

The clay mineral kaolinite dissolves in the caustic solution forming soluble sodium silicate (Na₂SiO₃) by the following reaction:

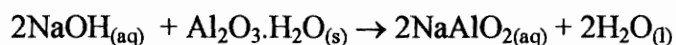
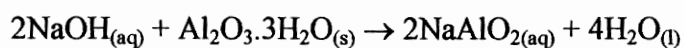


The soluble sodium silicate is not stable in solution, precipitating as an insoluble complex sodium aluminosilicate. This solid desilication product results in the loss of alumina and sodium hydroxide and it is therefore an additional cost in the production process, and can be represented by the following equation:



The slurry is desilicated prior to digestion by heating the slurry from the grinding mills at atmospheric pressure in pre-treatment tanks for a period of time between 10 and 30 minutes. The solid desilication products are not a single compound, but a series of insoluble zeolites, which may also contain other ions including SO_4^{2-} , Cl^- , OH^- , and AlO_2^- . The majority of the silica content passes out of the process as sodium aluminium silicate compounds as part of the red mud.

The formation of soluble sodium aluminate occurs in the digestion units. The monohydrate slurry is pumped through two agitated, vertical digestion vessels operating in series. When mixed with steam and hot concentrated caustic solution, the alumina in the bauxite is converted into soluble sodium aluminate leaving undissolved impurities containing mainly titanium dioxide, iron oxides and silica compounds. The reaction to extract monohydrate ore proceeds at approximately 250-255°C at a pressure of about 3500kPa. The reactions that proceed at this stage are represented below:



By the correct sizing of the reactor vessels for the optimum holding time, approximately 97% of the total available alumina can be extracted from the bauxite.

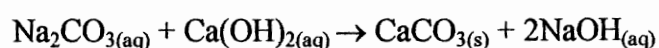
About 30% of the initial weight of the bauxite remains suspended in the liquor as a thin red mud slurry. The mud laden liquor leaves the digestion vessels and is flash

cooled to atmospheric boiling point by flowing through a series of flash tanks operating at successively lower pressures. The steam generated is used to heat recycled caustic liquor flowing through tubular heat exchangers, minimising the energy usage of the plant. The condensate is also recycled for use in the plant.

The trihydrate ore is ground and pre-treated in a separate facility. As the monohydrate ore passes through the flash tanks, the trihydrate ore slurry is injected to maximise the alumina content of the liquor stream. This process is known as 'sweetening'. The trihydrate slurry is added to the appropriate flash vessels when the slurry has been cooled to below 200°C.

1.1.3 Clarification

The next stage of the Bayer process is clarification. Clarification is a purification process used to remove solid material from the Bayer process liquor. Flocculents such as starch are added to the stream feed to improve settling rates, and the clarity of overflow liquor. The separation of the solid material from the Bayer process liquor must be as efficient as possible, as any solid material remaining after clarification will contaminate the product material. Most clarification occurs in single deck, 40 metre diameter settling tanks. The underflow from the settling tanks has sand removed, which is recycled to the grinding mills. The remaining red mud is washed in fresh water to recover the sodium hydroxide and alumina content of the mud. The washed mud is then disposed of in large disposal ponds. Slaked lime is added in the washing process to precipitate carbonate, aiding in its removal from the process. Carbonate reduces the effectiveness of the liquor to dissolve the alumina content of the bauxite reducing the efficiency of the plant. The addition of lime leads to the formation of insoluble calcium carbonate, which precipitates and is discarded with the waste mud. This reaction is represented by the equation:

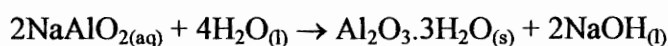


The overflow from the settling tanks contains fine mud particles. The small amounts of solid remaining in the overflow liquor are removed from the process liquor by filtering on Kelly-type constant pressure filters, with polypropylene filter cloths. Slaked lime slurry is used as a filter aid on these filters. The lime forms a porous filter cake that traps the fine mud particles.

The liquor after clarification is supersaturated with sodium aluminate. The liquor is cooled further before going to the precipitation tanks.

1.1.4 Precipitation

In the precipitation stage, aluminium hydroxide crystals are precipitated from the process liquor. Alumina precipitates as the trihydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which is the reverse of the initial digestion reaction. This reaction is shown by the following reaction:



The cooled pregnant liquor flows to rows of precipitation tanks, the solution is seeded with aluminium hydroxide crystals of a fine or intermediate size to encourage crystal growth. Each precipitation tank is agitated, and the solution is held for approximately three hours in each tank. The total holding time is between 25 and 30 hours, during which time various sized crystals of aluminium hydroxide are produced. The temperature, temperature gradient across each row, seeding rate and caustic concentration are all carefully controlled to achieve the desired size distribution of the crystalline product. The seed area is very important, for the system to remain balanced the number of particles leaving the system must equal the number of new particles being generated. New nuclei do not form rapidly in the absence of seed crystals, so the maximum amount of seed is kept in contact with the solution to keep the precipitation rate high. The production capacity of an alumina refinery is largely dependent upon the size and yield of the precipitation tanks.

The precipitation of aluminium hydroxide crystals proceeds via several mechanisms including nucleation, growth, agglomeration, and attrition.

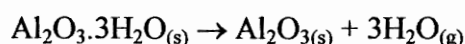
- **Nucleation:** occurs in the presence of seed crystals, and is the spontaneous formation of new crystals of very small size.
- **Growth:** is the process of deposition of aluminium hydroxide onto existing crystals.
- **Agglomeration:** proceeds via an unknown mechanism. It is the process where small particles come together to form larger particles, reducing the amount of fine crystals.
- **Attrition:** is the wearing down of particles due to inter-particle collisions and collisions between crystals and the walls of the precipitation tank, leading to an increase in the amount of fine crystals.

The solution then proceeds from the precipitation tanks to a series of classification tanks. Here the range of crystal sizes are settled from the process liquor and classified into three size ranges in three stages of gravity classification tanks. In the primary classifiers the coarse fraction, which becomes the product is separated. This coarse material is transferred to the calciners for conversion into alumina. The intermediate and fine crystal sizes, obtained from the secondary and tertiary classifiers, are washed and returned to the precipitation tanks as seed.

The spent process liquor overflows from the tertiary tanks and is returned through an evaporation stage where it is reconcentrated, heated and recycled to dissolve more alumina in the digesters. Additional sodium hydroxide is added to the liquor to make up for process losses.

1.1.5 Calcination

The slurry of coarse aluminium hydroxide from the primary classifiers is filtered and washed on horizontal table vacuum filters to remove the process liquor. The filter cake is fed to a series of calcining units, either rotary kilns or fluidised bed calciners. The aluminium hydroxide is calcined at temperatures exceeding 1100°C to remove both free moisture and chemically bound water to produce alumina (Al₂O₃). The reaction occurring here is shown by the equation:



The product alumina is cooled in fluidised bed coolers to temperatures less than 90°C. The alumina is then stockpiled in storage sheds ready for distribution.

1.1.6 The Bayer process in Australia

In this thesis we term alkali soluble organic material "humic substances". The definition of humic substances varies from one group to another, and within and outside the alumina industry. We use the term here operationally defined as sodium hydroxide soluble organic material.

Unfortunately most Australian bauxites contain high levels of organic matter, approximately 0.15 to 0.3% (w/w) total organic carbon, which is considerably higher than found in bauxite ore bodies elsewhere in the world (Hind *et al.*, 1999). In addition, many of the Australian bauxite ore bodies lie buried close to the surface, as a result many of the trees which contribute to the forest cover above the ore send out large tap roots which penetrate the bauxite. Although the forest cover is cleared before mining some of the roots that have penetrated the ore remain in the bauxite and they contribute to the organic matter entering the refinery.

The majority of the organic carbon present in the bauxite is extracted into the process liquor, where it contributes to numerous operational problems. The organic matter in bauxite consists of two main types:

- material that is largely unchanged from its natural form, such as tree roots and plant debris
- material which is derived from the chemical and microbiological decomposition of plant matter, which is known as humic substances.

The humic substances introduced with the bauxite are highly soluble in the caustic Bayer liquor, where they undergo partial decomposition or oxidation, leading to the production of simpler organic molecules such as oxalic acid. In Bayer liquor, oxalic acid is converted into sodium oxalate, this is a major impurity present in process liquor (Grocott, 1988). Other organic compounds such as low molecular weight sodium carboxylates, fulvics, humics and other organic species are also formed.

The dissolved organics interfere with plant operation in many ways. At sufficiently high concentrations sodium oxalate and other salts may precipitate as fine needles onto which the aluminium hydroxide co-precipitates. The sodium oxalate contaminated aluminium hydroxide is destroyed during calcination, causing dusting of the alumina and results in a product with a high sodium content. The increase in sodium content and the fine crystal structure make the alumina less suitable for smelting and other applications, decreasing the value of the alumina (Grocott and Rosenberg, 1988; Atkins and Grocott, 1988). More sodium hydroxide must also be added to make up for the loss of sodium from the process.

The presence of organics at lower concentrations is also undesirable, the main problems occur during the precipitation stage. The dissolved organics decrease the rate of growth of alumina hydroxide crystals while increasing the proportion of very fine crystals, decreasing the yields of acceptable quality alumina. As a result, the cooling supersaturated liquor must be held in the precipitation tanks for longer

periods, reducing the throughput of the plant and the level of liquor productivity (Mitchell *et al.*, 1991).

Other problems caused by the presence of the dissolved organics include a poor red mud settling rate during clarification, liquor and product coloring, foam formation, loss of caustic due to the formation of sodium ions of organic acids, a distinctive odour, increased liquor density and viscosity, and increased plant scaling. These problems are costly to both the alumina industry and the environment.

The build up of organics is a problem for all alumina plants, but it tends to be a particularly serious one for Australian plants due to the high organic content of our bauxite (Mitchell *et al.*, 1991). Synthetic and natural flocculants, as well as other chemical additives are added to process liquors to improve plant operation, these along with lubricants and other chemicals can act to increase the organic carbon content of the Bayer liquor. Carbohydrates such as starch are sometimes added during processing as a flocculant, this is despite the fact that polyalcohols are known to be poisonous to the process (Ryles and Avotins, 1996).

As the Bayer process is cyclic, the recirculating liquor acquires new organic species when in contact with fresh bauxite. This constant input increases the levels of the dissolved organic content until a steady state concentration is attained. Concentrations of up to 30g/L of total organic carbon have been reported in process liquors (Atkins and Grocott, 1988). Concentrations this high impose significant limitations on alumina refineries. It has been estimated in earlier studies that the decrease in production due to the presence of organic compounds costs the Australian alumina industry at least \$150 million annually (Atkins and Grocott, 1988; Hind *et al.*, 1997; Hind *et al.*, 1999). Indeed, the accumulated organics have the potential to make some alumina refineries unproductive unless the sodium hydroxide is recharged with new liquor, or organics are removed from the process by the expensive combustion of process liquor.

Presently we have a good knowledge of the structures of the thousands of simple organic compounds present in Bayer liquors and which of these compounds actively retard the precipitation of aluminium hydroxide. However little is known about the larger molecules collectively known as humic substances, these are compounds of molecular weight of 500 Dalton and above and are not simple oxidation products such as benzene carboxylic acids. In addition, we have only a limited understanding of the mechanisms involved during the inhibition of precipitation.

1.2 Humic Substances

1.2.1 Structure and functional groups

Humic substances are loosely defined as the organic material widely distributed in natural waters, marine and lake sediments, peat, soil and other sources where varying degrees of decomposition of plant and animal residues by soil bacteria have taken place (MacCarthy and Rice, 1985).

While the exact structure of humic substances remains unknown, modern analytical instrumentation has allowed the elemental composition and functional group content to be determined for humic substances from several environments. The results of these findings are best summarised by Vassallo and Attalla (1992), who stated that humic substances are comprised of a complex and variable structure based upon an aromatic or aliphatic backbone, depending on their origin, highly substituted with carboxylic acids and oxygen functionalities.

Traditionally humic substances have been classified into three main groups, humic acids, fulvic acids and humin depending on their solubility in water.

1. Humin: The fraction of humic substances that is insoluble in water at any pH value. The compounds in this chemical class are dark brown to black in colour.

2. Humic acid: The fraction of humic substances that is insoluble in water under acidic conditions (below pH=2), but becomes soluble at higher pH values. The compounds in this chemical class are brown to dark brown in colour.
3. Fulvic acid: The fraction of humic substances that is soluble under all pH conditions. The compounds in this chemical class are lightest in colour, being yellow to brown in colour.

These various fractions are not individual compounds, but groups of compounds with various compositions, properties and structures covering a wide range of molecular weights. The major elements present in humic substances are carbon, oxygen, hydrogen and nitrogen.

Humic substances play an important role in soil fertility as well as in the remediation of pollutants in soils and natural waters (Shevchenko and Bailey, 1996). Despite the fact that humic substances have been studied for over two hundred years their exact composition, structure, and origins are still poorly understood.

Numerous pathways for the formation of humic substances have been postulated during the last few centuries. Many of the very early studies realised that soil humic substances were mainly derived from lignin and proteins (Hoppe-Seyler, 1889; Fischer and Schrader, 1921; Wehmer, 1915; Waksman, 1938). These early studies suggested that during the fungal and bacterial degradation of wood, the lignocellulose is attacked, the cellulose is metabolised and the lignin is incompletely degraded, with the residual moiety becoming part of the soil humic material. These theories arose due to the chemical similarities between lignin and humic substances and the resilience of these compounds to degradation by fungi and bacteria.

There is still considerable debate over the modes of formation of humic substances, with two different pathways having major support (Swift, 1999). The first pathway involves the progressive oxidation, biochemical transformation and degradation of pre-existing plant components, particularly lignin, by microorganisms. In the second

pathway humic substances are synthesised from a range of molecules derived from plant precursors (phenols, saccharides and peptides) producing a new class of compounds. These compounds in turn are oxidatively degraded over time.

Most recent studies support the first pathway of formation, with the structural features and the composition of humic substances being related to the original macromolecules from which they were derived (Hayes and Swift, 1990; Lichtfouse *et al.*, 1998). Components such as carbohydrates and amino acids support microbial attack introducing polar groups into the structures. The less reactive macromolecules synthesised by plants including lignins, tannins, algaenans, cutins, suberins, terpenoids, polyphenols, polyisoprenes and proanthocyanidins represent the material progressively transformed in these processes into humic substances, as they constitute the bulk of organic matter preserved in soils and sediments (Shevchenko and Bailey, 1996).

The structural aspects of the humic materials have been shown to vary with the environment of diagenesis (Hatcher *et al.*, 1983). Studies have found that the phenolic content of humic substances varies with soil type, with the phenolic content being low in aerated soils while in peat soils the content of phenolic and methoxyl groups was seen to be quite high. This is thought to be due to the selective preservation of lignin under anaerobic conditions (Haider, 1992). Other soil factors also determine the structure of humic substances. Soil enzymes mainly promote the oxidative degradation of soil organic matter to form humic substances, as well as promoting condensation reactions. Numerous non-enzyme redox reactions also proceed in soils during humification (Deng and Stumm, 1993; Shindo, 1992). Inorganic oxides, such as manganese dioxide, the redox potential and the pH of the soil are also important factors in the transformation of organic matter into humic substances (Deng and Stumm, 1993; Shindo, 1992).

The composition of humic substances is also determined by the origin of the organic matter that is being degraded. The humic materials recovered from soils from Antarctica are derived from mosses, lichens and algae. The humic material contains

no organic matter derived from lignin (Wilson *et al.*, 1986; Wilson, 1990; Beyer *et al.*, 1995). The resultant humic material is rich in carbohydrates, alkylic compounds, fatty acids, sterols, and has a low aromatic content, making it very distinct from soil humic substances from other environments.

Despite the application of the most sophisticated chemical and analytical techniques available, the information that can be attained relating to the chemical structure of humic substances is severely limited compared to other areas of chemistry. The difficulty in determining the structures of humic materials is also due to the huge amount of variability in the structures of the parent biopolymers from which humic materials are derived. This variability produces macromolecules with little chemical or structural uniformity. Although accurate structural formulae cannot be attained, estimates of the composition and functional group content of humic substance mixtures can be made which is useful in predicting the properties and reactions of humic materials. These composition estimates are particularly useful in predicting the effects of humic materials on chemical systems such as the Bayer process.

1.2.2. Structural concepts of humic substances as determined by degradative techniques

Chemical degradation methods have been employed on humic materials with the aim of creating compounds that could be identified and related back to the structure of the original starting material.

Oxidative degradation has been used to study the structures of humic substances and provide structural information. Various reagents have been used including permanganate, persulphate, CuO and H₂O₂ in alkali, revealing many of the basic structural units present in humic substances (Hayes and Swift, 1978; Martin *et al.*, 1981; Schnitzer and Oritz de Serra, 1973; Hedges and Ertel, 1982). Oxidative degradation using CuO revealed typical lignin-type structures as products. These lignin-type compounds found in the oxidation products are now routinely used as

biomarkers to determine the relative amounts of vascular plant tissues in the humic materials (Hedges *et al.*, 1984, Hedges *et al.*, 1988).

Reductive splitting of humic substances gives lignin-derived phenols as major products. The products of the reductive splitting of humic substances are very similar to those obtained when lignin is degraded (Chen, 1991). Martin *et al.* (1974) employed reductive degradation using sodium amalgam to study a variety of soil humic substances and phenolic polymers. Most of the compounds identified in humic substances were found to be similar to those obtained from degradation of lignins or microbial phenolic polymers, suggesting that these types of compounds are also present in soil humic substances. A study by Jackson *et al.* (1972) which chemically degraded humic substances in the presence of phenol, identified several polymeric linkages associated with points of branching and/or cross linking. The abundance of tertiary and quaternary carbon bridging units suggests that the humic substances studied had a heavily branched, three-dimensional structure. The strength of these types of bond, together with this type of structure, may contribute to the stability of humic substances. A study conducted by Jahnel and Frimmel (1996) detected several protein-forming amino acids in hydrolysed humic substances. These results suggest that amino acid building blocks are also present in humic substances.

Dixon *et al.* (1997) looked at the degradation products obtained from humic substances sourced from the Bayer process. These humic materials were degraded with either sodium amalgam, or sodium in liquid ammonia. The compounds obtained from these reductive digestions were mainly substituted benzene carboxylic acids and hydroxybenzene carboxylic acids. Some longer chain fatty acids were also observed.

The results obtained from the oxidative and reductive degradation of humic substances were remarkably similar, with both methods revealing lignin-type units among the degradation products.

1.2.3 Instrumental methods for the analysis of humic materials

As instrumentation has developed, new techniques have been employed to provide information on the structures of humic substances including mass spectrometry, X-ray methods, NMR spectroscopy, infrared spectroscopy and functional group analysis techniques. Undoubtedly pyrolysis GC/MS and NMR spectroscopy are the two instrumental techniques that have allowed the largest amount of information to be determined about the nature of humic materials.

1.2.3.1 Pyrolysis GC/MS analysis of humic substances

Pyrolysis techniques have proved to be particularly useful in studying humic materials, due to the detailed information obtainable at the molecular level and the ease of sample preparation with this technique. Large macromolecules are not volatile and hence conventional GC/MS is of limited use in determining structural information. Pyrolysis thermally degrades the macromolecules to smaller structural units more amenable to GC/MS analysis.

The most significant early discoveries using pyrolysis GC/MS were made by Saiz-Jimenez and de Leeuw (1984a, 1984b, 1986a, 1986b) who revealed that humic substances contain groups originating from lignins, polysaccharides, proteins and lipids in their structures. Later studies by Saiz-Jimenez and de Leeuw (1987a, 1987b) suggested that humic substances can also contain highly aliphatic plant biopolymers originating from plant cuticles, which are resistant to chemical attack and which possibly contribute to the resistant part of the humic substances. The chief pyrolysis products from humic substances are methoxyphenols, which are typical structural units of lignin. Studies have determined that the number of methoxyl units depends on the origin of the lignin (Bracewell and Robertson, 1981).

Numerous other studies have used pyrolysis GC/MS to examine the structural aspects of soil organic matter, humic substances and related compounds such as lignins and carbohydrates. A study by Sihombing *et al.* (1996) related the chemical composition

of organic matter to the molecular weight of the material, and examined the origin of the organic matter by comparison with the results of earlier published pyrolysis studies (Saiz-Jimenez and de Leeuw, 1984a). The study by Sihombing *et al.*, (1996) determined that compounds derived from carbohydrates and lignin accumulated in certain molecular weight ranges in the humic substances extracted from swamp water.

Many of the pyrolysis studies that have been performed suggest that humic materials consist of aromatic rings that are connected by long, flexible aliphatic chains. These aliphatic chains may be significantly carboxylated and are possibly derived from oxidative ring opening processes on lignin (Schulten *et al.*, 1991; Schulten and Schnitzer, 1992; Umezawa, 1988; Bracewell *et al.*, 1980; Shevchenko and Bailey, 1996). These networks of aliphatic structures in humic substances can have varying degrees of aromaticity (Hatcher *et al.*, 1980; Hatcher *et al.*, 1981; Almendros *et al.*, 1996).

Several advances have been made in the study of soil organic matter and humic substances using pyrolysis GC/MS during the last decade. During pyrolysis, benzenecarboxylic acids undergo dehydroxylation and decarboxylation allowing few carboxylated pyrolysis products to be detected (Del Rio *et al.*, 1994). To prevent this from occurring in humic materials, pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) was proposed by Martin *et al.*, (1994). The development of this method was based on work by Challinor (1989), who had used TMAH to produce methyl esters of carboxylic acids and methyl ethers of hydroxyl compounds during pyrolysis.

The use of TMAH to provide in-situ methylation during pyrolysis was shown by Hatcher *et al.* (1995) to produce many of the same degradation products as are produced by CuO oxidation, with the new technique providing higher sensitivity and easier sample preparation. Methylation with TMAH has now been extensively employed in the study of natural and synthetic polymers, as well as humic substances, lignin and geochemical samples including low rank coals (Anderson and Winans,

1991; de Leeuw and Baas, 1993; Filley *et al.*, 1999; McKinney *et al.*, 1995; Saiz-Jimenez, 1995; Del Rio *et al.*, 1994).

Pyrolysis GC/MS is a very powerful degradative technique, however it can produce a distorted picture due to the selective thermal degradation of some structures, although the use of TMAH offers some protection from major structural change (Saiz-Jimenez, 1995). The complexity of the organic matter in humic substances often prevents researchers from relying solely on one instrumental technique to characterise the material, as the results can become distorted due to various factors including the low concentrations of organic material often present in geochemical samples. Typically pyrolysis GC/MS is employed with a combination of other techniques, such as ^{13}C NMR, to allow conclusions on the structures of humic materials to be made.

1.2.3.2 ^{13}C Nuclear magnetic resonance spectroscopic analysis of humic substances

It has now been over twenty years since solid state ^{13}C NMR with cross polarisation and magic angle spinning (CP/MAS) was first applied to soil organic matter (Barron and Wilson, 1981; Hatcher *et al.*, 1980; Wilson *et al.*, 1981; Preston and Ripmeester, 1982). This technique has now been applied to numerous related organic samples, such as plant litter, organic wastes, whole soils, and physical and chemical fractions of soils, including humic substances (Hedges and Oades, 1997; Baldock and Preston, 1995; Baldock *et al.*, 1997; Frund *et al.*, 1994; Knicker and Skjemstad, 2000; Kogel-Knabner, 1997; Mahieu *et al.*, 1999; Preston, 1996; Wilson, 1987; Wilson, 1991; Zech *et al.*, 1997).

The use of ^{13}C NMR has greatly added to the understanding of soil organic matter, even though the quality of ^{13}C NMR spectra of soil organic matter are normally poor due to low concentrations of organic carbon and poor resolution. The characteristic regions of the NMR spectra of humic materials and soil organic matter are 0-50 ppm (aliphatic carbon), 50-60 ppm (methoxyl C-O carbon), 60-100 ppm (carbohydrate C-

O carbon), 100-150 ppm (aromatic carbon), 145-160 ppm (phenolic and aromatic ether carbon), 160-190 ppm (C=O carbon of carboxyl and ester groups), and 190-210 ppm (C=O ketonic carbon). ^{13}C CP/MAS NMR of solid humic materials has revealed that they contain structures related to lignins, however the spectra show intensity differences in various areas, such as in the carbonyl and aliphatic carbon regions (Frund and Ludemann, 1989; Petsom and Steelink, 1987; Petsom and Steelink, 1988; Schnitzer and Preston, 1986).

There have been a tremendous number of studies examining the transformation of organic matter into humic substances in both cultivated and undisturbed soils using ^{13}C NMR. This technique has allowed the determination of the stages of organic matter transformations. In the initial stages of decomposition of organic matter the most noticeable change is the decrease in O-alkyl carbon with respect to alkyl carbon (Amalfitano *et al.*, 1995; Baldock and Preston, 1995; Beyer *et al.*, 1993; de Montigny *et al.*, 1993; Del Rio *et al.*, 1994; Kogel-Knabner and Ziegler, 1993; Preston *et al.*, 1989; Zech *et al.*, 1987). This decrease in methoxyl carbon is attributable to the loss of easily metabolised carbohydrates and an accumulation of alkyl carbon. The alkyl carbon comes from the selective preservation of alkyl polymers and from newly synthesised biomass, appearing at about 30 ppm in the ^{13}C NMR spectrum. As decomposition continues, the long alkyl chains and plant biopolymers are modified, the alkyl region broadens and the dominance of the CH_2 peak decreases. As the aromatic rings of lignin are modified, the phenolic region and the shoulders at 112 to 120 ppm decrease, and the aromatic region becomes dominated by a single broad peak at around 130 ppm (Newman and Tate, 1991). With further degradation the humic material may become highly aromatic with the development of polycondensed rings (Chen and Pawluk, 1995; Olk *et al.*, 1995).

The climatic factors during the humification process can have an enormous impact on the nature of the humic substances produced (Preston, 1991). High rainfall leads to excessive leaching which can lead to the removal of lignin moieties from the organic matter and hinder aromatisation processes. On the other hand, the rapid removal of plant litter, for example by termites, can produce highly aromatic humic substances.

Alteration of soil organic matter by fire and the incorporation of charcoal also leads to highly aromatic humic substances (Almendros *et al.*, 1992; Haumaier and Zech, 1995). Humic materials of low aromaticity have been derived from sources without lignin, from mosses and algae (Beyer *et al.*, 1995; Wilson *et al.*, 1986). With the mosses producing some aromatic material possibly due to the presence of tannins (Wilson *et al.*, 1989). All of these transformations have been monitored using ^{13}C NMR.

The ^{13}C NMR experiment is the most widely used in the study of humic materials, however ^1H , ^{15}N and ^{31}P NMR have also been used to examine humic materials. ^1H NMR was the first form of NMR used for the study of humic materials. Schnitzer and Barton (1963) were the first to use ^1H NMR to study the structure of humic material, by examining the structure of a methylated soil humic acid. The application of ^1H NMR spectroscopy to humic materials has been limited due to broad resonances relative to the chemical shift range, and the presence of a large residual water peak. However effective techniques have been developed to suppress the water signal allowing the distribution of hydrogen types to be determined (Wilson *et al.*, 1983; Lee *et al.*, 1998).

^{15}N and ^{31}P NMR have been relatively under utilised in the study of soil organic matter, with few studies being published using these techniques. ^{15}N NMR is particularly useful in the study of soil organic matter as it can be used to determine the form of nitrogen in the samples. A study by Knicker and Ludemann (1995) observed nitrogen in amide, indole, pyrrole and amino structures in various fractions of soil organic matter. A recent study by Zang *et al.* (2000) using ^{15}N NMR in conjunction with pyrolysis GC/MS revealed that nitrogen in humic substances can exist as amide functional groups, as a result of the survival of proteins in humic substances by encapsulation in hydrophobic domains.

1.2.4 Organic matter in bauxite

Australian bauxite ore bodies generally lie buried close to the surface, the humic substances produced from the decomposition of plant material on the surface, are leached into the bauxite. As a result, Australian bauxites contain significant levels of organic matter with typical total organic carbon contents in the range of 0.15 to 0.3% (w/w) (Hind *et al.*, 1999). The majority of the organic carbon present in the bauxite is extracted into the Bayer process liquor during the digestion stage. The extracted organic materials contribute to numerous problems in the operation of Bayer refineries.

While the dissolved organic matter in the Bayer process liquor has been extensively studied (see for example Lever, 1978; Wilson *et al.*, 1999; Smeulders *et al.*, 2000 (Appendix A)) relatively few studies have examined the chemical composition of organic matter in bauxite. Bauxite is a difficult material to study primarily because the organic material is in trace quantities; in addition bauxite is not directly amenable to NMR analysis due to the presence of magnetic iron species. As a result little is known about the nature of the humic material that it contains.

In a study by Baker and Greenaway (1998), extracted humic material from Jamaican bauxite and the humic substances found in the corresponding low temperature (140°C) Bayer liquor were compared using ^{13}C CP/MAS NMR. It was discovered that the humic substances in the Bayer process had significant structural differences to those found in the bauxite. The main finding was that the Bayer humic substances were more aromatic than the humic material obtained from the bauxite. The study did not elucidate any other details about the structure or identities of the humic substances present in the Bayer liquors.

No other studies have been published on the characterisation of bauxite organic matter.

1.2.5 Organic matter in the Bayer process

The nature of the compounds present in Bayer liquors may vary with each refinery, but little is in the open literature due to industrial confidentiality. This is particularly true for the structure and nature of the higher molecular weight humic substances which have a weight greater than 1200 Daltons, which are known to be important in the Bayer process during crystallisation and agglomeration (The, 1980; Grocott and Rosenberg, 1988).

Only a few studies have been published concerning the identification and measurement of organics in Bayer liquors. The composition of the small molecular weight species present in Bayer liquors by GC/MS and the weight distribution of other Bayer organic species have been examined in various studies (Lever, 1978; Yamada *et al.*, 1981; Guthrie *et al.*, 1984; Baker *et al.*, 1995). These studies have shown that the organic matter present in Bayer liquors can vary depending on the conditions employed at the refinery and the organic matter present in the bauxite. Other studies have looked at methods of determining other organic levels in the Bayer process, particularly the total organic content, sodium oxalate content and carbonate levels (Solymar *et al.*, 1996; Jackson, 1995; Grocott, 1988).

Determining which of the multitude of organic compounds present in Bayer liquor that act as poisons is difficult. Recent studies have found that often the poisonous compounds preferentially adsorb onto the aluminium hydroxide during crystallisation (Coyne *et al.*, 1994; Mitchell *et al.*, 1991). Wilson *et al.* (1998) studied compounds that preferentially adsorb onto aluminium hydroxide. By acidifying the Bayer liquor to pH=7, rather than pH=2 which is conventionally used, the humic substances remain in solution but the aluminium hydroxide precipitates, allowing only the aluminophilic material to adsorb. The preferentially adsorbed compounds were studied by pyrolysis gas chromatography/mass spectrometry after methylation and by ^{13}C NMR. Five types of organic carbon were identified in the humic substances by solid state ^{13}C NMR, and various small molecular weight benzenecarboxylic acids were identified by pyrolysis GC/MS.

A study by Dixon *et al.* (1997) looked at the degradation products obtained from humic materials sourced from the Bayer process. The humic materials were degraded with either sodium amalgam, or sodium in liquid ammonia, to allow analysis of the small degradation products from the macromolecules. The compounds obtained from these reductive digestions were mainly substituted benzene carboxylic acids and hydroxybenzene carboxylic acids. Some longer chain fatty acids were also observed.

Norman *et al.* (1997) analysed the humic substances present in spent Bayer liquor, the sodium oxalate cake, as well as those present in the mining overburden by ^{13}C CP/MAS NMR and size exclusion chromatography. The study found that the humic macromolecules undergo changes during the Bayer process, producing smaller molecules with fewer types of functional groups than what is present in natural soil humic substances.

An earlier study performed in our laboratories characterised all of the organic matter recovered from a low temperature alumina refinery. The organic material was separated into molecular weight fractions for analysis (Wilson *et al.*, 1999). Each molecular weight fraction was analysed by several analytical techniques, revealing that each fraction had different chemical characteristics. The higher molecular weight fractions were found to be more aromatic with a lower content of carboxylic acid units than what is seen for the lower molecular weight ranges. Lignin derived humic material was seen to accumulate in the 6-12kD weight range, while the largest molecular weight range, the >300kD fraction, was seen to behave as a soluble char which was able to hold occluded water at temperatures in excess of 200°C (Wilson *et al.*, 1999). The findings of the earlier study of the material from a low temperature refinery will be contrasted with the results obtained for the analysis of material obtained from a high temperature alumina refinery examined in the present study.

It can be seen from these studies that there is a vast knowledge on the small molecular weight species found in Bayer process liquors, and the concentrations at which these compounds are present. This is due to fact that these compounds are relatively simple to analyse, particularly by techniques such as gas chromatography/mass spectrometry

(GC/MS). What these studies also demonstrate is that the amount of information in the open literature relating to the structures of the larger molecular weight Bayer humic substances is very limited.

1.2.5.1 Sodium Oxalate in the Bayer process

The presence of sodium oxalate in the Bayer process originates in digestion due to the degradation of organic compounds present in the bauxite. There are numerous references in the literature detailing the effects of sodium oxalate on the precipitation of aluminium hydroxide in the Bayer process (Lever, 1978; Sato and Kazama, 1971; Brown and Cole, 1980; Sang, 1988; The and Bush, 1987; Calalo and Tran, 1993; Violante and Huang, 1985; Wang *et al.*, 1983; Grocott and Rosenberg, 1988). Uncontrolled crystallisation of sodium oxalate in the Bayer process is highly undesirable for several reasons. The oxalate crystals co-precipitate with the aluminium hydroxide producing crystals that have a lower tendency to agglomerate and have a high attrition rate, reducing yields from the Bayer process. These crystals are highly fragile and decompose during calcination, leaving small alumina particles that are high in sodium (Sang, 1988; Brown and Cole, 1980; Stahlin *et al.*, 1985).

Studies on sodium oxalate have found that needle fine crystals of sodium oxalate precipitate after saturation and act as nuclei for the formation of fine crystals of aluminium hydroxide (Satapathy and Vidyasagar, 1990; Lever, 1983; Pohland and Tielens, 1983). The presence of sodium oxalate needles in an alumina refinery, can result in a 'fines shower', where aluminium hydroxide is precipitated onto the sodium oxalate nuclei producing very fine crystals. These events are thought to be the result of a surplus of nuclei in the liquor and a deficit in agglomeration (Power and Tichbon, 1990; Power, 1991). Unfortunately no mechanism has been developed to adequately explain the processes by which sodium oxalate interferes with the processes occurring during the precipitation of aluminium hydroxide.

1.2.6 Mechanism of interaction of precipitation poisons

The detrimental effects of organic impurities on the precipitation of aluminium hydroxide from Bayer liquors are well documented. Certain low molecular weight organic impurities such as formate, acetate and simple benzenecarboxylic acids have little impact on the precipitation of aluminium hydroxide in the Bayer process (Lever, 1978). However some compounds clearly affect the process, creating problems such as suppressing precipitation yields, altering product size distributions by reducing agglomeration, or increasing the amount of impurities present (Grocott and Rosenberg, 1988; Armstrong, 1993). Species that possess hydroxycarboxylic acid functionalities and alcohols have been implicated (Grocott and Rosenberg, 1988; Armstrong, 1993; The, 1980; Alamdari *et al.*, 1993; Coyne *et al.*, 1994; Tran *et al.*, 1996).

Grocott and Rosenberg (1988) conducted a study with model compounds that are typical of organic impurities present in Bayer liquors. The experiments identified a strong relationship between the poisoning of crystallisation with increased levels of incorporated sodium in the aluminium hydroxide crystals. It was found that compounds with acidic, adjacent hydroxyl groups significantly increased levels of sodium in precipitated crystals. Armstrong (1993) extended this study using sodium tartrate and five model compounds with the main configuration of di- and tri-hydroxyl groups on an aromatic carbon backbone to study effects on the crystallisation kinetics, yield and level of sodium incorporation. The study determined that the compounds modify the precipitation kinetics of aluminium hydroxide and enhance sodium incorporation by up to 100%, the relative poisoning effects of each compound was found to vary with concentration and configuration of the hydroxyls relative to the carboxylic acid group on the aromatic ring.

Various organic compounds have been investigated for their impacts on the precipitation of aluminium hydroxide including compounds based on carbohydrates. Some of the model compounds studied include glucoisosaccharinate, gluconate, tartrate and mannitol (The, 1980; Coyne *et al.*, 1994; Rossiter *et al.*, 1996; Alamdari *et al.*, 1993). The model Bayer poison 3,4-dihydroxybenzoic acid has been examined

to determine the impact of oxidising the acid in the presence of various transition metal ion catalysts (Whittington *et al.*, 1994), which lead to an increase in the precipitation yield of aluminium hydroxide.

Other studies have looked specifically at the group of compounds known as polyhydric alcohols or polyols (Watling *et al.*, 1996, Smith *et al.*, 1996, Owen *et al.*, 1999). Polyhydric alcohols are compounds that show extensive variation in structural configuration. The longer chain alditols (C5 and C6) are straight chain alkanes with a hydroxyl group on each carbon. They possess multiple chiral centres giving them highly variable stereochemistry. These compounds are similar to simple sugars and are active in physiological processes (Owen *et al.*, 1999). It has been found that the poisoning strength of hydroxy compounds appears to increase as the number of hydroxyl groups increase, however there are some exceptions. The poisoning affects of the C-5 polyols, ribitol, arabinitol, and xylitol differ significantly and meso-tartaric acid is particularly active (Watling *et al.*, 1996; Smith *et al.*, 1996). The ease with which polyol poisons can form the configuration of three adjacent hydroxyl groups suggests that up to three hydroxyl groups could be involved in the poisoning process. The adsorption of these polyol poisons onto the aluminium hydroxide surface inhibits aluminium hydroxide crystallisation (Smith *et al.*, 1996). These linkages may be similar to those formed between organic poisons and aluminium hydroxide in Bayer process liquors during precipitation.

Industry sources also suspect that humic materials are responsible for the poisoning of the precipitation of sodium oxalate from the Bayer process, however little has been reported on what organics adsorb on oxalate surfaces, or the influence of organics on oxalate precipitation (Hind *et al.*, 1999).

1.3 The present study

Humic substances are among the most important species in Bayer refinery liquors as they cause a number of undesirable effects, however the interferences they cause are

poorly understood. Although humic substances are heterogeneous in nature, it is possible to determine certain structural features of these molecules, including their functionalities and elemental compositions.

Determining the structural features of Bayer humic substances, how the humic materials are altered during alumina processing, and the processes by which they interfere with the crystallisation of the aluminium hydroxide, are necessary in order to understand the effects of these materials on the operation of the Bayer process. An increased understanding would also help in determining ways to possibly negate their influence on the Bayer process.

The organic matter contained in high temperature Bayer alumina refineries (250-255°C digestion temperature) have not been separated on the basis of molecular weight to examine the mass distribution of the humic material that it contains. In addition, the humic materials in high temperature Bayer process liquor have not been characterised by modern instrumental techniques, such as ^{13}C NMR or pyrolysis GC/MS. The present study rectifies this by examining both of these areas of interest for alumina refining companies.

Furthermore the poisoning effects of the humic molecular weight fractions from Bayer liquor on the precipitation of aluminium hydroxide have been examined in this study. The impacts of the humic molecular weight fractions on sodium oxalate stability have also been examined in this study.

In addition to the study of the humic substances obtained from the Bayer process liquor, the organic matter present in bauxite, and the insoluble organic materials that are deposited in several areas of the high temperature Bayer alumina refinery were also characterised by several analytical techniques. This characterisation work provides an insight into the nature of the organic matter that enters the Bayer process, how it is altered in the process, and where different organic material exits the process.

CHAPTER TWO
EXPERIMENTAL

Bayer liquor humic substances

The following sections detail the methods employed to isolate, and then fractionate, the organic material contained in high temperature (250-255 °C) Bayer process liquors.

2.1 Extraction of humic substances from Bayer liquor

Isolating the humic substances from the Bayer process was carried out using a similar method to that described by Sihombing *et al.* (1996), and is displayed diagrammatically in Figure 2.1.

Aliquots of Bayer process liquor were diluted at a ratio of 1:5 (v/v) in singly distilled water. 1:1 (v/v) hydrochloric acid in water was added to the mixture dropwise with stirring to give a pH of approximately 1.5. The solution was then left for 24 hours to allow the aluminium hydroxide to settle to the bottom of the flask. The acidified solution was decanted, filtered through a glass microfibre filter (Whatman GF/D 15cm) and then filtered again through a sintered glass filter of porosity 4.

Affinity resin chromatography was used to separate the organic compounds out of the Bayer liquor. The column chosen was an Amberlite XAD-7 column with dimensions of 2cm x 60cm which separated the organics from the solution salts. The XAD-7 column was washed and acidified before use. The filtrate was passed through the column with a flow rate of approximately 1mL per minute. More filtrate was added until the eluant from the column developed a yellow tinge, signifying that the column was overloaded. The column was then rinsed with 2 litres of 0.1 molar hydrochloric acid, followed by 2 litres of distilled water to remove any salts. The solutions used to rinse the column were retained, and later passed through the XAD-7 column again to recover the dissolved organics that were eluted off the column.

After the removal of salts from the XAD-7 column, the Bayer organics were eluted by passing 500mL of 0.1 molar potassium hydroxide solution through the column. The

eluant was captured along with an additional 300mL of distilled water that was added to rinse the column.

The organic compounds contained in the eluant from the XAD-7 column were protonated using a cation exchange resin. The solution was passed through a column containing the resin IR-120(H) with dimensions of 2cm x 60cm. The organic compounds remaining on the IR-120(H) resin were removed by passing 300mL of distilled water through the column. This rinse water was also captured. The eluant from the column containing the protonated organics was concentrated by rotary evaporation.

The XAD-7 column was acidified after use, by passing 2 litres of 0.1 molar hydrochloric acid through the bed. The IR-120(H) cation exchange column was regenerated by rinsing the column with distilled water, then 3 molar hydrochloric acid to protonate the resin. The resin was then rinsed with distilled water until the pH of the eluant was neutral.

The process of obtaining the humic substances from the remainder of the Bayer liquor was continued. Water and hydrochloric acid was added to give a solution at pH=1.5. The solution was then treated as detailed previously. This process was repeated numerous times until all of the aluminium hydroxide had been dissolved.

The pH of the solution was gradually increased in order to dissolve the precipitated humic substances. After filtering the decanted solution, it was passed through the XAD-7 column with hydrochloric acid. The hydrochloric acid was added to the solution in order to retain the organics on the column head, as the organics are not retained by the column at pH greater than 4. This process was repeated until all of the Bayer liquor had been dissolved and passed through the columns.

The protonated humic substances obtained from the above procedure were concentrated by rotary evaporation and then freeze dried. This procedure was

performed on 10 litres of each of the spent and pregnant Bayer liquors from the QAL plant, Gladstone, Queensland.

2.2 Molecular weight fractionation of Bayer humic substances

The protonated organics from the spent Bayer liquor were separated into their molecular weight fractions using molecular-porous dialysis membranes constructed from cellulose and cellulose-ester with molecular weight cut-offs (MWCO) of 1 200, 6 000, 12 000, 25 000, 50 000, 100 000 and 300 000 Daltons. The dialysis membranes carry no fixed charge and they do not absorb most solutes.

Benzoylated dialysis tubing of MWCO of 1 200 and 12 000 Daltons were supplied by Sigma. Spectrum, which is distributed by Cole Parmer, supplied the other dialysis tubing. The dialysis membranes were of the following types:

Spectra/Por® 1	MWCO 6 000
Spectra/Por® 6	MWCO 25 000
Spectra/Por® 6	MWCO 50 000
Spectra/Por® CE	MWCO 100 000
Spectra/Por® CE	MWCO 300 000

The membranes were cut into 45 cm lengths and conditioned prior to use. Each membrane had to be rinsed under running tap water for two hours to remove heavy metals and added preservatives. The membranes were then left to soak overnight in distilled water before being given a final rinse with ultra high purity water.

Many of the Spectra/Por® membranes are preserved in a 0.05% solution of sodium azide. Sodium azide is an acute poison, so appropriate precautions have to be taken while handling membranes.

The 50 000 MWCO membranes were the first to be used. The membranes were treated as described above. One end of the membrane was tied in a knot and the

membrane was filled with the freeze-dried humic substances dissolved in doubly distilled water at a concentration of 5 mg/mL. The other end of the membrane was tied and the membrane was placed in a beaker to dialyse against doubly distilled water. Each membrane was secured in a beaker using an elastic band, ensuring that both ends of the membrane were on the outside of the beaker. This was to ensure that any solution which leaked from the interior of the membrane did not go into the water. Each beaker was covered with Parafilm to prevent contamination.

In total 29.59g of the whole organic fraction obtained from the spent Bayer liquor was added to the 50 000 MWCO membranes. This represented the organics present in almost six litres of spent process liquor.

The water surrounding each membrane was changed on a regular basis, approximately every two days. The frequency at which the water was changed depended upon the intensity of its colour. The water surrounding the membranes was changed until the water remained colourless. Usually the dialysis time for each membrane was between 15 and 21 days, however this varied depending on the initial membrane concentration and the frequency at which the surrounding water was changed. The collected water was stored in a clean glass bottle, then concentrated by rotary evaporation.

The solution which remains inside the membrane represents all of the compounds with a molecular weight above that of the MWCO of the membrane (>50 000). The compounds which passed through the membrane into the surrounding water, had molecular weights less than that of the membrane (<50 000). In this way two solutions were obtained from each membrane. The two solutions which were obtained in this way were treated differently.

The compounds which are released from the membrane and which are held in the surrounding water (<50 000) were concentrated using a Buchi R-114 rotary evaporator. The concentrated solution was then placed in the next membrane with a

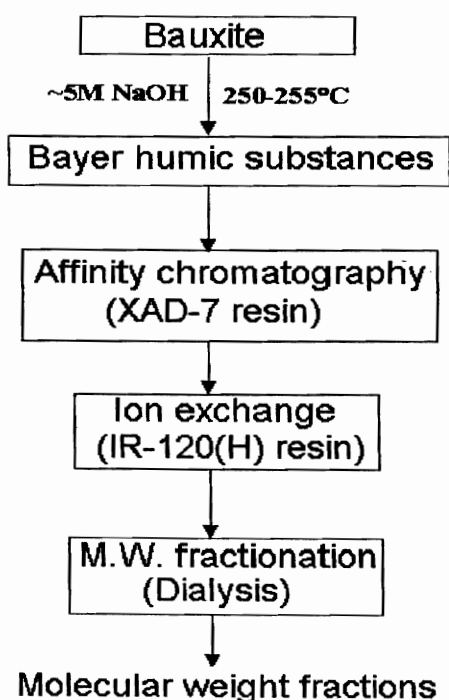
lower molecular weight cut-off value (the 25 000 MWCO membrane). The process was then repeated for that membrane using the dialysis procedure outlined above.

The solution that remained in the 50 000 MWCO membrane was concentrated by rotary evaporation before being placed in the next membrane with a higher MWCO (the 100 000 MWCO membrane). The dialysis process was performed on this membrane.

The dialysis was repeated for each of the 7 different membranes. This allowed eight different molecular weight fractions of the humic substances to be isolated. The eight fractions obtained by dialysis had the molecular weight ranges of <1.2kD, 1.2-6kD, 6-12kD, 12-25kD, 25-50kD, 50-100kD, 100-300kD, and >300kD.

As each fraction was isolated, it was freeze dried at 300 millitorr and -70°C. The freeze dried samples were stored in a desiccator over silica gel in a cool dark cupboard.

Figure 2.1 Diagram showing the isolation and fractionation of Bayer humic substances



Characterisation techniques

The following section details the techniques used to characterise the organic materials isolated from the Bayer process liquor.

2.3.1 Elemental analysis

C, N, H, S and O (by difference) analyses were performed on all Bayer humic substance samples. Analysis was performed by the Microanalytical unit, Research School of Technology, Australian National University, Canberra, Australia.

C, H and N analyses were performed on a Carlo Erba Elemental Analyser, model 1106. The procedure involves combustion of each sample in the presence of oxygen. Helium is used as the carrier gas to sweep the combustion products over several packings, removing excess oxygen and other elements (such as halogens and sulphur). The nitrogen, carbon dioxide and water peaks are separated on a GC column with quantities measured by thermal conductivity. The instrument is calibrated using known standards.

Sulfur analyses were performed using ion chromatography. Each sample was combusted in an oxygen flask, to convert all sulfur to sulfate. The sulfate produced was run through a Dionex AS14 column. The instrument was calibrated using known standards.

2.3.2 Ash analysis

The ash content was determined using a TA Instruments, SDT (simultaneous differential techniques) 2960.

9.2 mg of the spent liquor fraction was evenly packed into an open 170 μ L platinum crucible. The platinum crucible was placed in the furnace under an air atmosphere with a flow rate of 35 mL/minute. The furnace was programmed to rapidly heat to 600°C, then ramped at 30°C/minute to 1200°C. The furnace was held at 1200°C for 5 minutes. After this time, the furnace was cooled with air to 35°C. The ash content was found to be negligible.

2.3.3 pH measurement

Each of the organic fractions was pH tested. Each sample was dissolved in ultra high purity water at a concentration of 5g/L (50mg of each freeze dried humic fraction was dissolved in 10mL of water).

The pH of each sample was tested with a TPS (Australia) pH meter (model number: N427 900p) equipped with a glass electrode, at 25°C. The pH meter was calibrated before use with TPS buffer solutions at pH 4.00 and pH 7.00.

2.3.4 Fourier transform infrared transmission spectroscopy (FTIRTS)

Freeze dried sample (0.5 mg) was ground with 200 mg of potassium bromide in a dry agate mortar. Oven dried (120°C) BDH laboratory reagent grade KBr (for infrared spectroscopy) was used for these samples. The samples were pressed into 10mm diameter disks under 10 tonnes of pressure and high vacuum for 10 minutes.

Prepared disks were stored in a desiccator over silica gel until the spectra were acquired. Disks were analysed shortly after preparation to avoid disks becoming contaminated with atmospheric water.

Spectra were obtained on a Nicolet Magna-IR 760 Fourier Transform spectrometer and were collected between 400 and 4000 cm^{-1} using 256 scans with 4 cm^{-1} resolution

in a dry nitrogen atmosphere. A spectrum of the air in the compartment was used for background correction to remove interfering peaks due to atmospheric water and carbon dioxide.

2.3.5 Pyrolysis-gas chromatography mass spectrometry.

A Hewlett Packard 5890 gas chromatograph interfaced with a JEOL JMS-DX303 mass spectrometer was used. The column was fused silica (60m x 0.25mm I.D), phase DB5MS (modified 5% phenyl, 95% methyl silicone) with 0.25 μ m film thickness. Spectra were obtained using a split injection technique. The helium flow rate through the pyroinjector was at 25ml/minute, split so that 10ml/min of helium passed through the column.

The gas chromatograph was programmed to have the following parameters:

Initial temperature: 40°C

Initial time: 2 minutes

Rate: 5°/minute

Final temperature: 230°C

After this program was completed, the GC heated to 290°C where it was held for ten minutes to remove contaminants from the column.

Each molecular weight fraction as well as the whole pregnant and spent fractions were analysed by pyrolysis-GC/MS.

5mg of each sample was dissolved in 100 μ L of 0.05M ammonia solution. An SGE spiral tip syringe was used for injection purposes. 5 μ L of the solution was deposited along the length of the spiral tip. The syringe was then positioned under a lamp to evaporate the water, leaving the solid sample on the syringe tip. The spiral tip was then withdrawn into the syringe barrel.

Injectons were performed with an SGE pyrojector at pyrolysis temperatures of 400, 425, 450, 475, and 500°C. When the pyrojector was at temperature the syringe was inserted through the septum and the plunger was depressed. The syringe was left for 5 seconds before the spiral tip was drawn into the syringe barrel and the syringe withdrawn from the pyrojector.

Mass spectra were recorded using an electron impact of 70eV. Assignment of compounds from the mass spectra data were based on searches of the mass spectral libraries contained within the instrument as well as by comparison with published collections of pyrolysis-GC/MS data performed on similar samples (Saiz-Jimenez and de Leeuw, 1984a, 1986a; Sihombing *et al.*, 1996).

As no internal standard was added for the analyses the abundance values are not absolute, instead the abundances of each compound have been calculated with respect to phenol. Phenol was used for this purpose as it was consistently detected in all samples in large amounts without overlap by other compounds.

2.3.6 Nuclear Magnetic Resonance spectroscopy

2.3.6.1 Solution 1-Dimensional ^1H NMR

Solution ^1H NMR spectra were recorded on a Bruker DRX 300 MHz instrument fitted with field gradient coils. Water suppression was accomplished using a modified WATERGATE pulse sequence (Lee *et al.*, 1998). This technique involves field gradient timed sequences to remove the water resonance from the spectra. Humic material (2 mg) was dissolved in either D_2O or a combination of D_2O and sodium deuterioxide (0.3 mL). The clear amber liquor was removed by pipette to a 5mm NMR tube. The normal non-decoupled experiment required 200 transients with a recycle delay of 2 s and a 1.02 s acquisition time. The WATERGATE experiment requires the carrier frequency to be set to the water resonance. The gradient field pulses were set to 2 ms in duration with a ring down delay of 100 μs . The selective 180° pulse was

broken down into 6 pulses of 5.775 μ s, 17.300 μ s, 36.550 μ s, 36.550 μ s, 17.300 μ s and 5.775 μ s in length with a 200 μ s delay between each. The spectra required 32 transients, 2 s delay, 4 dummy scans and a 1.02 s acquisition time. A 4000 Hz spectral width was used for all experiments. All the data were collected in 8K of memory and then Fourier transformed using a line broadening factor of 0.5 Hz. Tetramethylsilane TMS (0 ppm) was used as an external reference.

2.3.6.2 Solution 2-Dimensional ^1H -NMR

For one fraction (12-25kD in DMSO- d_6), ^1H - ^1H homonuclear correlation (COSY) (von Kienlin *et al.*, 1991; Hurd and John, 1991) and ^1H - ^{13}C heteronuclear multiple quantum coherence (HMQC) (Ruiz-Cabello *et al.*, 1992; Wilker *et al.*, 1993; Bax and Summers, 1986; Wilson, 1987) spectra were obtained to assist in assignments. In this case 3-(TMS)-propionic-2,2,3,3- d_4 acid, sodium salt (99.99% pure, Aldrich) was used as an internal reference. Typical acquisition parameters for 2D NMR experiments were as follows: ^1H - ^1H COSY – spectral width of 4000 Hz; recycle delay of 2 s; 2048 data points (time domain); 16 scans per experiment. For ^1H - ^{13}C HMQC – spectral width of 4000 Hz and 220 ppm for proton and carbon respectively; recycle delay of 2 s; 2048 data points (time domain); 16 scans per experiment.

2.3.6.3 Solid State ^{13}C NMR

NMR spectra were obtained on a Bruker DRX-300 MHz spectrometer at 75.48 MHz using cross polarisation (CP) and magic angle spinning (MAS) of 54.7° to the applied field. Approximately 200mg of each of the Bayer organic fractions were packed into 5mm zirconia rotors with Kel-F caps.

The ^{13}C NMR spectra were acquired using the following parameters: contact time of 1 ms, and a recycle delay of 1 s. Up to 10 000 scans were recorded for each spectrum and samples were spun at 8 kHz. Spectra were collected in 1K points, zero filled to

4K, and then Fourier transformed using a line broadening factor of 50 Hz to obtain the frequency domain spectra. The low field peak of adamantane was employed as a secondary reference (38.3 ppm).

Solid state ^{13}C CP/MAS NMR spectroscopy is a powerful non-destructive technique for the elucidation of bulk structural parameters of carbonaceous materials, however this technique does have significant limitations. Carbon nuclei with long T₁ρ values may not be seen if the recycle time is not correctly adjusted. In addition carbon in the presence of paramagnetic species may not be observed; this may mean that all carbon in a sample is not observed. The low abundance of carbon nuclei in many samples of geochemical origin decreases the signal to noise ratio obtained during the analysis of the samples by ^{13}C NMR, this significantly increases the error associated with this technique. ^{13}C CP/MAS NMR is an important technique for the experimental measurement of functional group content, notwithstanding the above listed factors, the experimental error is typically not above +/- 3%.

2.3.7 Thermal Gravimetry and Differential Thermal Analysis (TG, DTA)

TG/DTA analyses were performed on a TA Instruments, SDT (simultaneous differential techniques) 2960. Each sample was heated in an open platinum crucible from 25°C to 1000°C with a constant heating rate of 5°C/minute. An inert atmosphere of dry nitrogen was used with a gas flow rate of 140mL/minute.

Samples were placed into a platinum crucible of 170μL volume and evenly packed to ensure maximum contact between particles to allow heat transfer. Between 7.64mg and 10.08mg of each freeze dried sample were analysed by this technique.

2.3.8 Modulated Differential Scanning Calorimetry (MDSC)

The MDSC analyses were performed on a TA Instruments, DSC 2920 Differential Scanning Calorimeter. Between 2.69-5.73mg of each of the freeze-dried samples were evenly packed into disposable aluminium crucibles. Each sample was lightly pressed to ensure maximum contact of the sample with the bottom of the pan. Aluminium lids were placed over each pan and the edges were crimped to prevent loss of sample. However the crucible and lid were not airtight to allow evolved gases to escape from the crucibles.

Each sample was initially heated from 25-120°C at a heating rate of 10°C/minute to remove the surface water from the samples. The samples were cooled to 40°C then reheated to 600°C at a constant heating rate of 5°C/minute. Finally the sample chamber was air cooled to 30°C. The analyses were carried out in a dry nitrogen environment with a gas flow rate of 140 mL/minute.

2.3.9 Methylation procedure

The organic fractions were methylated according to the procedure described by Hatcher *et al.* (1995). Approximately 0.5mg of each dry sample was placed in a 2mL glass ampoule and 100µL of a solution (made from 5mL of 25% tetramethylammonium hydroxide in methanol (Sigma) and 1mL of 0.05% (w/v) of an internal standard, *n*-eicosane, in methanol) was added. The methanol was evaporated under vacuum to dryness and the ampoules were flame sealed under vacuum. The ampoules were placed in an oven at 200°C for 30 minutes. After cooling the ampoules were opened and thoroughly washed out with dichloromethane. The solution was concentrated by evaporation to approximately 100µL then analysed by gas chromatography-mass spectrometry. A Hewlett Packard 5890 gas chromatograph interfaced to a Hewlett Packard 5970 mass selective detector was used. 1µL of the solution was injected onto a DB5MS capillary column (30m x 0.25mm I.D.). The oven was programmed to have an initial temperature of 60°C. After an initial holding time of 5 minutes, the oven was heated at a rate of 5°/minute to 240°C, then at 20°C/minute to 280°C.

Precipitation experiments

In this section, the various molecular weight fractions of organic matter obtained from the high temperature Bayer alumina refinery were tested for their impacts on the precipitation dynamics of aluminium hydroxide and sodium oxalate from synthetic Bayer liquor. These tests were performed to determine which molecular weight ranges of organic matter are particularly detrimental to the operation of the Bayer process.

2.4.1 Seed preparation

Two types of seed were used. The first seed called “water washed seed” was typical refinery seed. Seed crystals were prepared by washing with hot water, five liters of water was used for each kilogram of seed crystals. The second seed called “caustic washed seed” was prepared by obtaining the seed crystal slurry from the refinery and extensively washing (5 volumes) with hot caustic (~5M NaOH). Five liters of caustic was used for each kilogram of seed crystals. It was then water rinsed and air dried. Both types of seed crystals were dried in an oven at 65°C.

2.4.2 Precipitation experiments

Two sets of experiments were carried out to determine the impact of the organic molecular weight fractions on the Bayer process dynamics. The first set of experiments (Group A), were run with the organic fractions added at the concentrations recovered from the process (Table 3.19) and caustic washed seed was used. The second set of experiments (Group B) was performed with equal concentrations of each organic fraction (Tables 3.20 and 3.21) and hot water washed seed was used. All experiments were carried out in 250mL polypropylene bottles rotating end over end at 50 r.p.m. in a water bath for 22 hours.

Precipitation dynamics were measured using a Metrohm autotitrator. This instrument determines the alumina and caustic concentrations of the liquor based on the method developed by Watts and Utley (1956). The alumina concentration is determined by titration with gluconate solution. Sodium hydroxide concentration is measured by titration with hydrochloric acid. Sodium carbonate concentration is determined with an ion selective electrode sensitive to sodium ions, the contribution of sodium ions from sodium hydroxide removed by calculation.

The particle size distributions of the crystalline product were measured with a Malvern Mastersizer series 2600C instrument. This instrument employs the laser diffraction technique to determine the sizes of product crystals dispersed in water in an agitated vessel. This technique determined the proportion of crystals with a surface area $<20\mu\text{m}^2$ along with measurements of the surface areas of the crystals.

Oxalate concentrations in each solution were determined using ion chromatography. 50 μL of each sample solution was added to 5mL of a 1000 ppm solution of potassium fluoride, each solution was then accurately diluted to 500mL with water. These solutions were run on a Dionex DX-100 ion chromatograph to determine oxalate concentrations.

2.4.3 Group A Experiments

Synthetic liquor was prepared from Alcoa C31 hydrate, 149.5g/L (C31 defines a company product), sodium hydroxide pellets, 230g/L (Ajax chemicals AR grade). The impurities sodium carbonate (34.36g/L), sodium chloride (30.52g/L) and sodium oxalate (1.09g/L) were added to the synthetic liquor, which was then filtered through two glass filters (Whatman GF/C) to remove any solid impurities.

Litre aliquots (1L) of the synthetic Bayer liquor were heated to 65°C in stainless steel beakers. To each beaker was added a sample of an organic molecular weight fraction at various doses with stirring. Four 200mL samples of each of these solutions were

then placed into individual 250mL polypropylene bottles in a water bath maintained at 65°C.

Two bottles from each sample set were charged with caustic washed coarse secondary seed (300g/L) containing 0.2% (w/w) sodium oxalate to monitor the impacts on precipitation yields. The other two bottles from each sample set were used to monitor impacts on agglomeration. These bottles were charged with caustic washed fine tertiary seed (150g/L). Bottles were rotated end over end in a water bath maintained at a constant temperature of 65°C for 22 hours.

Agglomeration was tested after 2 and 4 hours. Precipitation yields were tested after 2, 4, 8 and 22 hours. To perform these tests the seed was allowed to settle, then 10mL aliquots of solution were removed and syringe filtered through a Millipore (Millex-HN) 0.45µm nylon syringe filter to prevent further precipitation. The filtered solutions were analysed for oxalate, alumina, sodium hydroxide and soda concentrations. The slurries from the agglomeration samples (2 and 4 hours) and the precipitation samples (after 22 hours) were vacuum filtered and hot water washed. The precipitated material was oven dried at 105°C and weighed. The crystal sizes of the dried samples were determined. The results of these tests including the percent changes in the surface area of the crystals and the percentage change for the crystals with a surface area less than 20µm² are shown in the Results and Discussion section in Table 3.19. The changes in the yield of alumina from these tests under ideal conditions are shown in Figure 3.32.

2.4.4 Group B Experiments

For Group B experiments, synthetic liquor was prepared from Alcoa C31 hydrate, 165.6g/L (C31 defines a company product), sodium hydroxide pellets, 230g/L (Ajax chemicals AR grade). The impurities sodium carbonate (34.34g/L), sodium chloride (9.98g/L) and sodium oxalate (3.0g/L) were added to the synthetic liquor, which was

then filtered through two glass filters (Whatman GF/C) to remove any solid impurities.

Group B tests were performed with the samples containing the organic fractions at constant dosage rates of 5g/L and 0.1g/L. Several organic fractions were not available in sufficient quantities to conduct these tests.

Hot water washed seed was used in these experiments instead of caustic washed seed. The water bath was programmed to simulate the precipitation conditions encountered during the Bayer process, with the water bath having an initial temperature of 75°C decreasing to the final temperature of 60°C over the 22 hour run time. Agglomeration tests were performed under isothermal conditions for 2 hours at 75°C. The sampling procedures and hot water washed seed dosage rates were the same as those previously described (Section 2.4.3). The results for Group B experiments are shown in the Results and Discussion section in Tables 3.20 and 3.21. The changes in the yields of alumina under these conditions, which simulate industrial processing, are shown in the Results and Discussion section in Figure 3.35.

Insoluble organic carbon samples obtained from the Bayer process

During the dissolution of bauxite in a high temperature (250-255 °C) Bayer alumina refinery, a number of insoluble materials are produced from organic material entering the refinery with the bauxite. These organic materials are deposited in several areas of the refinery (see Figure 2.2), however prior to this study these materials had not been extensively characterised, primarily because they are insoluble or are in trace quantities. The section below details the procedures used to characterise the organic matter contained in these insoluble materials. These materials were characterised to provide information on the selectivity of the dissolution and degradation processes for the organic matter, with the ultimate aim of enhancing alumina yields from the refinery.

2.5 Insoluble organic carbon samples from the Bayer process

Weipa Bauxite (Weipa, North Queensland, Australia) was feed material to a refinery operating at 250-255°C. Red mud, hand picked aluminium hydroxide i.e gibbsite (prepared by auto-precipitation from saturated (“pregnant”) plant liquor), precipitation tank scale (sometimes called “pea gravel”), the organic scale which accumulates on the shell-side of heater tubes in the heat exchanger units, and oxalate-gibbsite co-precipitation fines (sometimes called “non settling hydrate”) were collected from the same refinery (QAL, Gladstone, Queensland). Sodium oxalate was prepared under organic-free laboratory conditions with the same acicular morphology as plant samples and then contacted with pregnant plant liquor to adsorb organics from solution. Samples were dried for chemical characterisation. Figure 2.2 shows the locations where each of these products were obtained from the Bayer process.

Inorganic compositions were determined by QAL. Carbon, nitrogen and hydrogen analyses were carried out by the Microanalytical unit, Research School of Technology, Australian National University, Canberra, Australia.

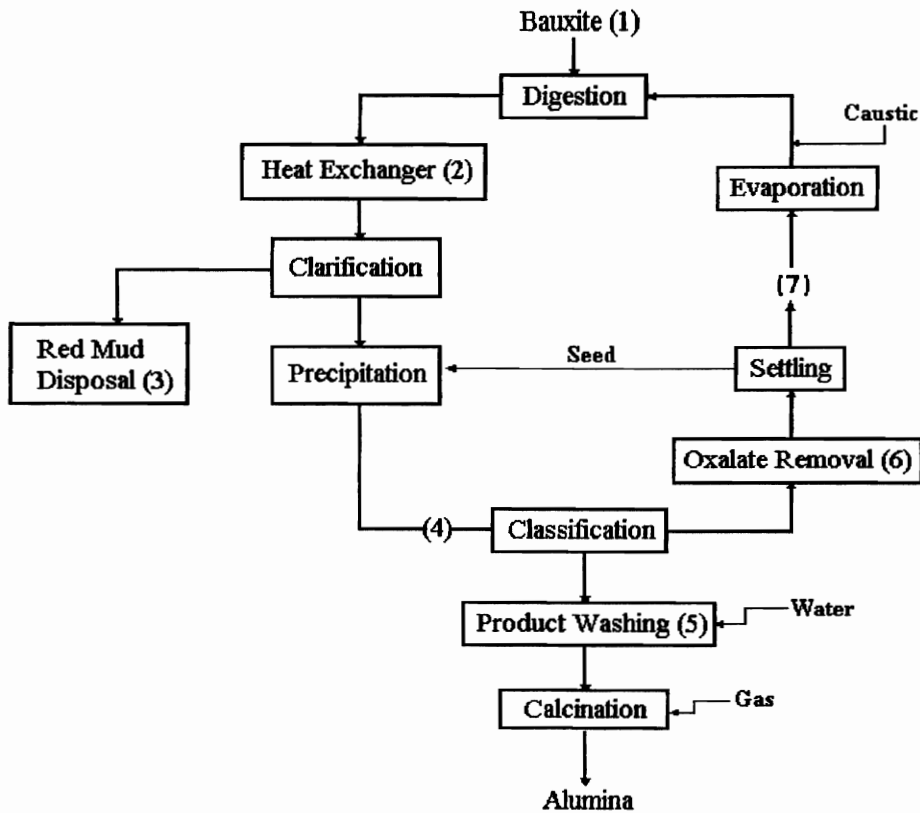
2.5.1 Methylation and pyrolysis GC/MS

Samples were initially methylated. Each sample was finely ground in an agate mortar and pestle. The ground samples (250mg) were placed in scintillation vials with 200 μ L of tetramethylammonium hydroxide (TMAH) in methanol (Sigma 25% w/v). Methanol was then evaporated under vacuum.

Following methylation, up to 10mg of each finely ground sample was injected into a SGE pyrojector at a pyrolysis temperature of 475°C on a Shimadzu GC17A gas chromatograph interfaced with a Shimadzu QP5050A mass spectrometer. The column used was fused silica (60m x 0.25mm I.D), phase DB5MS (modified 5% phenyl, 95% methyl silicone) with 0.25 μ m film thickness. The gas chromatograph was programmed to have an initial temperature of 40°C, where it was held for 2 minutes; followed by heating at 5°/minute to 290°C, with 8 minutes at this temperature. The mass spectrometer was programmed to scan for ions between m/z 60 - 600. Details of the pyrolysis products for each of the samples analysed are given in the results and discussion section (Tables 3.3 and 3.4) and are listed by number in the text (e.g methyl benzoate, compound 148, Table 3.3).

Figure 2.2 The Bayer process with the source of insoluble organic materials sampled.

1) Bauxite; 2) Heat exchanger organic scale; 3) Red mud; 4) Precipitation tank scale; 5) Aluminium hydroxide; 6) Sodium oxalate 7) Oxalate-gibbsite co-precipitation fines.



2.5.2 Examination of catalytic affects of iron oxide

Pregnant Bayer liquor organic material (loosely defined as humic substances) (10mg) obtained from the same plant and prepared as described previously (Section 2.1) were dissolved in 2mL of methanol. 1mL aliquots of solution were placed on individual 0.5g samples of iron oxide (Technical grade, Ajax chemicals) and calcined alumina (LR grade, Ajax chemicals). Methanol was evaporated to dryness. The dried samples (2mg), as well as the Bayer humic substances alone, were formed into pellets in an SGE pelletiser with 2 μ L of TMAH in methanol (Sigma 25% w/v). The samples were analysed by pyrolysis-GC/MS using the previously described method.

2.5.3 Soxhlet extraction of samples

The ground insoluble samples from the Bayer process (1g) were placed in cellulose extraction thimbles. The samples were extracted in a soxhlet with methanol (200mL) for 24 hours. The methanol was evaporated to dryness on 20mg of calcined alumina. Each sample (2mg) was formed into a pellet in an SGE pelletiser with 2 μ L of TMAH in methanol (Sigma 25% w/v). The samples were analysed by pyrolysis GC/MS using the method described above.

2.5.4 Nuclear Magnetic Resonance Spectroscopy

Solid state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DPX200W Advance 200 MHz instrument operating at 50.33 MHz. Approximately 200 mg of the organic scale from the heat exchangers, sodium oxalate, aluminium hydroxide, precipitation tank scale and oxalate-gibbsite co-precipitation fines were analysed by ^{13}C NMR using the cross polarisation technique with magic angle spinning (CP/MAS). Pulse widths of 4 μ s were used, with a 2 s recycle time and a contact time of 1 ms. Spectra were collected in 1K points, zero filled to 4K, and

Fourier transformed with a line broadening factor of 50 Hz to obtain the frequency domain spectra. A spinning speed of 8 kHz was used.

Spectra for the Bauxite and Red mud samples could not be obtained due to the presence of paramagnetic species (Fe_2O_3). Integrated areas corresponding to different functional groups measured by NMR are given in the Results and Discussion section in Table 3.2. The low signal to noise ratios obtained for many of these samples allowed only qualitative estimates of the functional group content to be obtained, these values are not absolute however they remain useful for comparative purposes.

CHAPTER THREE

RESULTS AND DISCUSSION

PART A

***Insoluble organic products
of the Bayer process***

The following section details the results from the analysis of insoluble organic materials obtained from the Bayer process. These materials were characterised by both ^{13}C NMR and pyrolysis-GC/MS. The experimental procedures for the analysis of these materials are detailed in Section 2.5.

3.1 Analysis of insoluble organic materials in the Bayer process

As previously noted in the introduction, during the digestion stage the organics contained in the bauxite enter the refinery where they can influence the yield and quality of the alumina product. Most organics dissolve and are degraded in the sodium hydroxide to form sodium salts of organic carboxylates including humic substances, but some are insoluble. The insoluble organic matter is removed from the process with the red mud, as an organic rich material on heater tubes in the shell-side of heat exchangers, or adsorbed on aluminium hydroxide precipitate and the sodium oxalate by-product. Sometimes organic matter is also observed in precipitation tank scale and with oxalate-gibbsite co-precipitation fine particles.

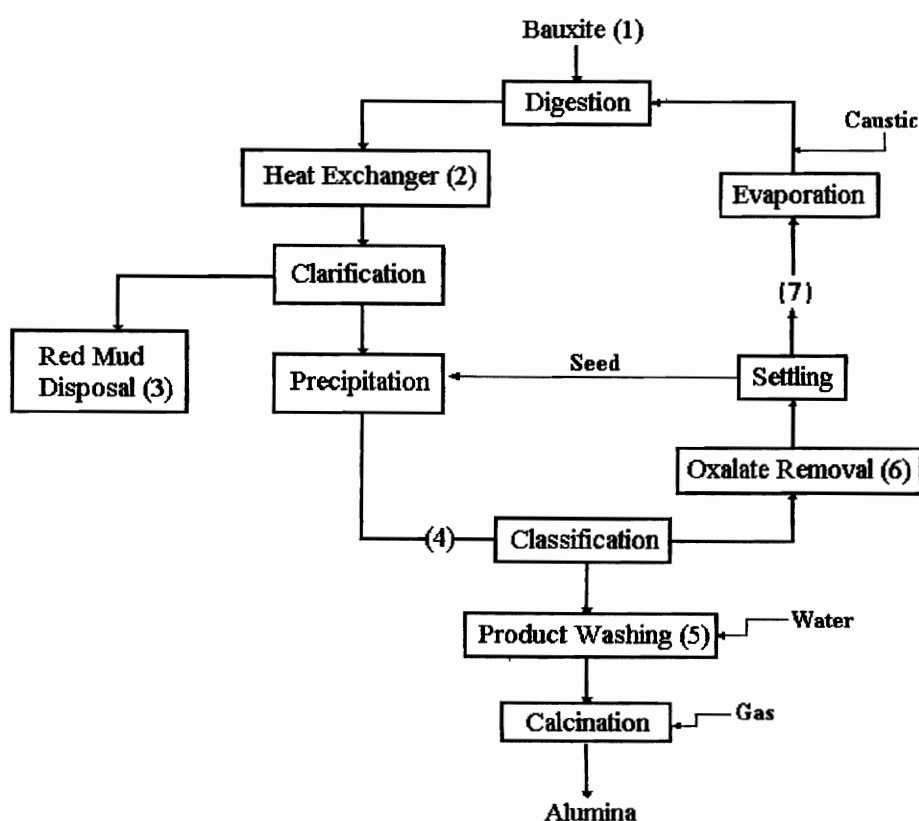
The structure of the dissolved organic material is studied later in this thesis. Here we discuss the composition of insoluble materials. These materials are difficult to analyse because of their intractability. However, pyrolysis-GC/MS with in-situ methylation is useful for the analysis of intractable insoluble amorphous solids (Hatcher *et al.*, 1995). It is important to realize that the analysis of macromolecular organic compounds by pyrolysis-GC/MS is only a qualitative technique. Due to the nature of pyrolysis-GC/MS the extreme heat treatment of samples during injection results in the conversion of some organic material into involatile coke and char compounds, these compounds will not be detected by this technique. In addition low molecular weight gases such as methane and carbon dioxide are produced during pyrolysis, however they will not be observed as they elute at very short retention times. We use pyrolysis-GC/MS here to distinguish between these amorphous materials and to draw inferences between their compositions. Differences in composition can give information on the selectivity of the dissolution process and hence help in enhancing yields of alumina in the Bayer process. All results obtained from the pyrolysis-

GC/MS experiments are expressed as the average of duplicate samples. In terms of experimental measured errors these were not above $\pm 5\%$.

The samples containing insoluble organic material were sourced from a high temperature Bayer alumina refinery. The locations at which the samples were removed from the Bayer process are shown in Figure 3.1.

Figure 3.1 The Bayer process with the source of insoluble organic materials sampled.

1) Bauxite; 2) Heat exchanger scale; 3) Red mud; 4) Precipitation tank scale; 5) Aluminium hydroxide; 6) Sodium oxalate 7) Oxalate-gibbsite co-precipitation fines.
(Repeated from Figure 2.2)



3.1.1 Bauxite and Red mud samples

It is worthwhile observing the differences in chemical structure between the organic matter that was insoluble in sodium hydroxide which ends up in the red mud, and that in the original bauxite, since this provides an insight to the changes in the organic matter during digestion. However we were able to show that simple pyrolysis GC/MS is insufficient to compare the two materials because the iron oxide, but not the alumina species, catalyse the decomposition of organics. Hence any differences may be due to the presence of iron oxide alone.

Figure 3.2 shows the simple pyrograms obtained for the red mud and bauxite samples. The most significant difference is the presence of small ring aromatic compounds (compounds 1,3-dimethyl-5-(1'-methylethyl)-benzene (56), 1,2-diethyl-3,4-dimethylbenzene (63), 1,2,4-trimethyl-5-(1'-methylethenyl)-benzene (64) and *m*-diisopropylbenzene (72)) in the bauxite but not in the red mud samples. In contrast, polycyclic aromatics are more predominant in the pyrolysates of the red mud fraction. Compounds fluorene (88), phenanthrene (104), 1-phenylnaphthalene (109), and 2-phenylnaphthalene (118) are more important in the red mud pyrolysates. The other compounds displayed in Figure 3.2 include styrene (6), ethoxybenzene (12), indene (20), 1,2,3,4-tetramethylbenzene (31), pentylbenzene (43), naphthalene (48), hexylbenzene (52), heptylbenzene (61), biphenyl (62), octylbenzene (74), nonylbenzene (82), 1,4,5-trimethylnaphthalene (83), 1-methyl-7-(1'-methylethyl)-naphthalene (108), pyrene (120), 2,3-dimethyl-2-heptene (181) and C₁₈ alkane (225).

Figure 3.3 shows pyrograms for Bayer humic substances, Bayer humic substances adsorbed onto Al₂O₃ and Bayer humic substances adsorbed onto Fe₂O₃. Pyrograms A and B for Bayer humic substances and Bayer humic substances adsorbed onto Al₂O₃ (Figure 3.3) are very similar, with the pyrolysis products consisting mainly of simple aromatic carboxylic acids, identified as their esters e.g. methyl benzoate (compound 148) and methyl 3-methoxybenzoate (compound 153). This indicates that alumina has a minimal catalytic effect during pyrolysis. The humic material in the presence of iron oxide (Pyrogram C) produced very different pyrolysis products, highly enriched in aromatic molecules including styrene (6), methoxybenzene (7), naphthalene (48), 2-

methylnaphthalene (58), 1-methylnaphthalene (59), biphenyl (62), fluorene (88) and phenanthrene (104). These pyrolysis products and the pyrograms are very different to those obtained from the original humic material, indicating that the iron oxide causes catalytic degradation of the humic material during pyrolysis. Moreover the pyrolysis products from the humic material on iron oxide are similar to those obtained from red mud samples, with both of these samples producing mainly aromatic pyrolysis products although the compounds are present in different yields. This result suggests that the pyrolysis products from the red mud, and the bauxite (as it also contains iron oxide), do not represent the types of organic materials actually in these samples prior to pyrolysis. It is for this reason that the samples from the Bayer process containing insoluble organic carbon were also analysed by pyrolysis GC/MS after soxhlet extraction with methanol, in order to remove the iron oxide, negating its catalytic effect.

Figure 3.2 Pyrograms for a) Bauxite and b) Red mud.

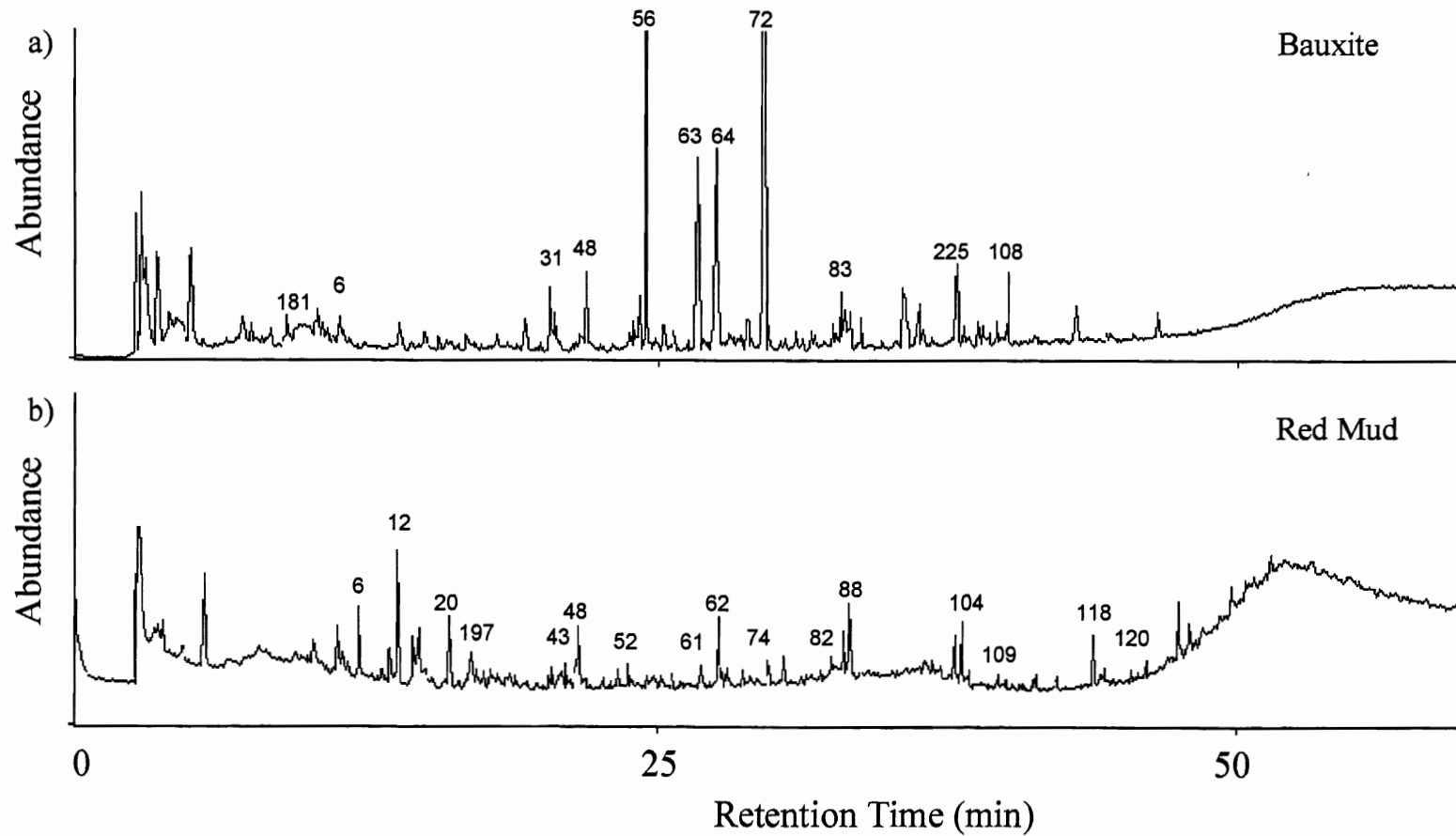


Figure 3.3 Pyrograms for A) Bayer humic substances B) Bayer humic substances adsorbed onto Al_2O_3 and C) Bayer humic substances adsorbed onto Fe_2O_3 .

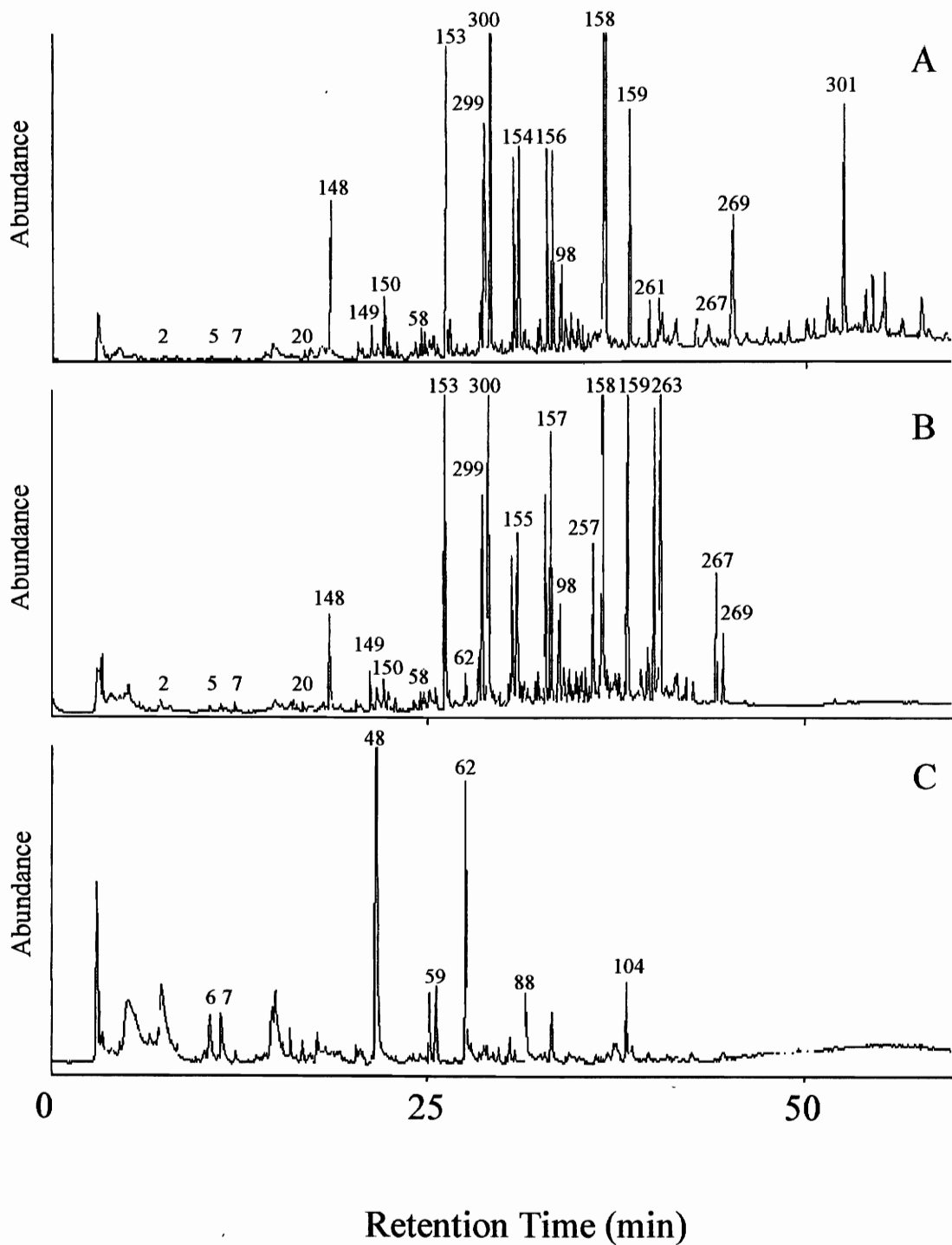


Figure 3.4 Pyrograms for analysis of methanol solubles of a) Red mud and b) Bauxite.

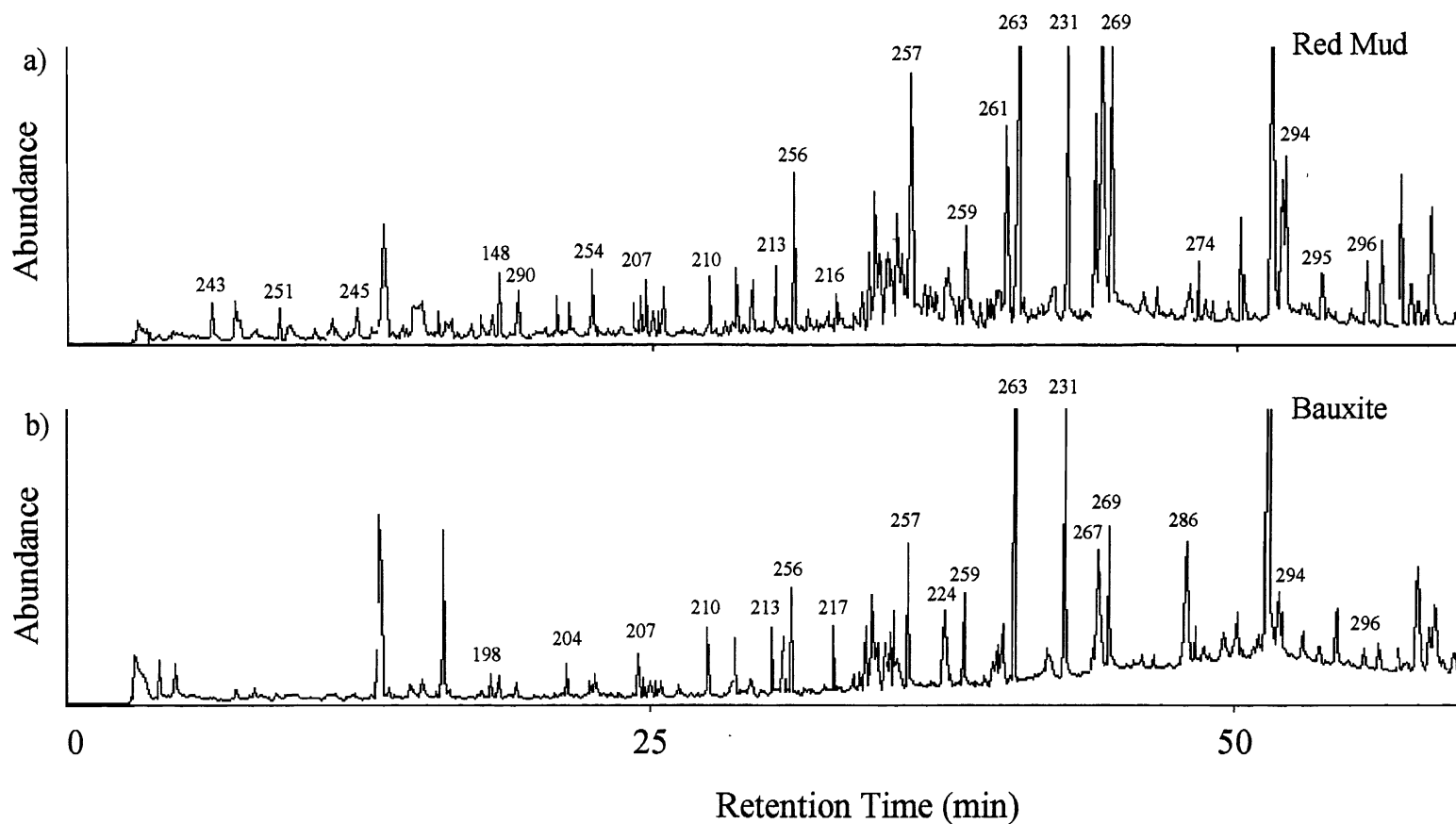


Figure 3.4 shows that the pyrolysis products from the methanol solubles from the red mud contain many of the same compounds released from the bauxite. Each sample was found to release various alkanes, alkenes, aromatic carboxylic acids, and aliphatic carboxylic acids (further information is given in Table 3.4). Some examples are methyl benzoate, methyl esters of saturated carboxylic acids (C_4 - C_{20}) and C_{11} - C_{23} alkenes. Few aromatic compounds were seen in the extracts (Table 3.4). Many of the alkenes and aliphatic carboxylic acids were common to the two samples. The exceptions included the short chain aliphatic carboxylic acids ($<C_{12}$, e.g. butanoic acid (243) (observed as the methyl ester), pentanoic acid methyl ester (251), nonanoic acid methyl ester (254)) which were absent from the chromatogram of the bauxite sample. Compounds 261 (11-hexadecenoic acid methyl ester), and 216 (C_{15} alkane) appear to be almost specific to the red mud while compounds 286 (C_{23} alkene) and 217 (C_{16} alkene) appear to be almost specific to the bauxite.

The other compounds identified in Figure 3.4 (listed in Table 3.4) include benzoic acid methyl ester (148), C_{11} alkene (198), C_{12} alkene (204), C_{13} alkene (207), C_{14} alkene (210), C_{15} alkene (213), C_{15} alkane (216), C_{16} alkene (217), C_{18} alkene (224), C_{21} alkene (231), butanoic acid methyl ester (243), hexanoic acid methyl ester (245), pentanoic acid methyl ester (251), nonanoic acid methyl ester (254), dodecanoic acid methyl ester (256), tetradecanoic acid methyl ester (257), pentadecanoic acid methyl ester (259), 11-hexadecenoic acid methyl ester (261), hexadecanoic acid methyl ester (263), 9-octadecenoic acid methyl ester (267), octadecanoic acid methyl ester (269), eicosanoic acid methyl ester (274), C_{23} alkene (286), docosanoic acid methyl ester (294), tricosanoic acid methyl ester (295), tetracosanoic acid methyl ester (296).

3.1.2 Shell-side heat exchanger organic scale material

After digestion, the first cooling event occurs at the heat exchanger units. Here an organic product forms on the shell-side of heater tubes and contains enough carbon to be analysed by ^{13}C CP/MAS NMR. Figure 3.5 shows two signals from aromatic carbon (centred at 130 ppm) and aliphatic carbon (centred at 40 ppm). The material is highly aromatic and the aromaticity (fraction of carbon that is aromatic, f_a) is 0.40.

The absence of carboxylic carbon at or around 175 ppm shows that this material is unhumic like.

Figure 3.6 shows pyrolysis GC/MS data on the same material. Carboxylic acid containing compounds, or their esters, were not identified in agreement with the NMR data. Few phenolic compounds were identified as well. These results are reflected in the low oxygen content of this material (Table 3.1). Important compounds are methylbenzenemethanol (11), 1,2,4-trimethylbenzene (13), 1,2,3-trimethylbenzene (14), divinylbenzene (44), (1'-methyl-1'-butenyl)-benzene (45), 1,2-dihydro-2-methylnaphthelene (55) and 2,4-dimethyl-1-heptene (182). Aromatic compounds containing between one and four fused aromatic rings (compounds benzene (1), fluorene (88), benzo-3,4-phenanthrene (132), and 6-methylchrysene (133)), as well as alkyl-substituted structures (compounds toluene (2), methylbenzenemethanol (11), 1,2,4-trimethylbenzene (13), 1,2,3-trimethylbenzene (14), divinylbenzene (44), (1'-methyl-1'-butenyl)-benzene (45), 2-methylnaphthalene (59), 1,4-dimethylnaphthalene (71), 9-methylfluorene (98), 2,3-dimethyl-9H-fluorene (106), and 2,5-dimethylphenanthrene (119)) were significant pyrolysis products. Nitrogen is present in the pyrolysates as pyrrole and pyrimidine compounds (eg 2,3-dimethylpyrrole (162), 2,4-dimethylpyrrole (163), 2,5-dimethylpyrrole (164), 2,3,4,5-tetramethylpyrrole (166) and 4-N,N-dimethylaminopyrimidine (167)) (Table 3.3). Alkanes with straight and branched alkyl chains containing between 8 and 29 carbons were one of the main chemical classes identified in the pyrolysates, their distribution in this material is shown by the ion $m/z = 85$ (Figure 3.6b and Table 3.3). Other compounds identified in Figure 3.6 are 2-ethenyl-1,4-dimethylbenzene (28), 4,5-dimethylnonane (200), 2-methyltridecane (209) and C_{14} alkene isomer (212). Clearly, as the heat exchangers are located directly after the high temperature digestion units, the effect of flashing conditions on the Bayer slurry causes carbonisation reactions on the surfaces of the heater tubes. This residue is hydrophobic, and thus does not contain polar carboxylic acid units or many phenolic groups.

Figure 3.5 ^{13}C CP/MAS NMR spectrum of organic scale from heat exchanger units.

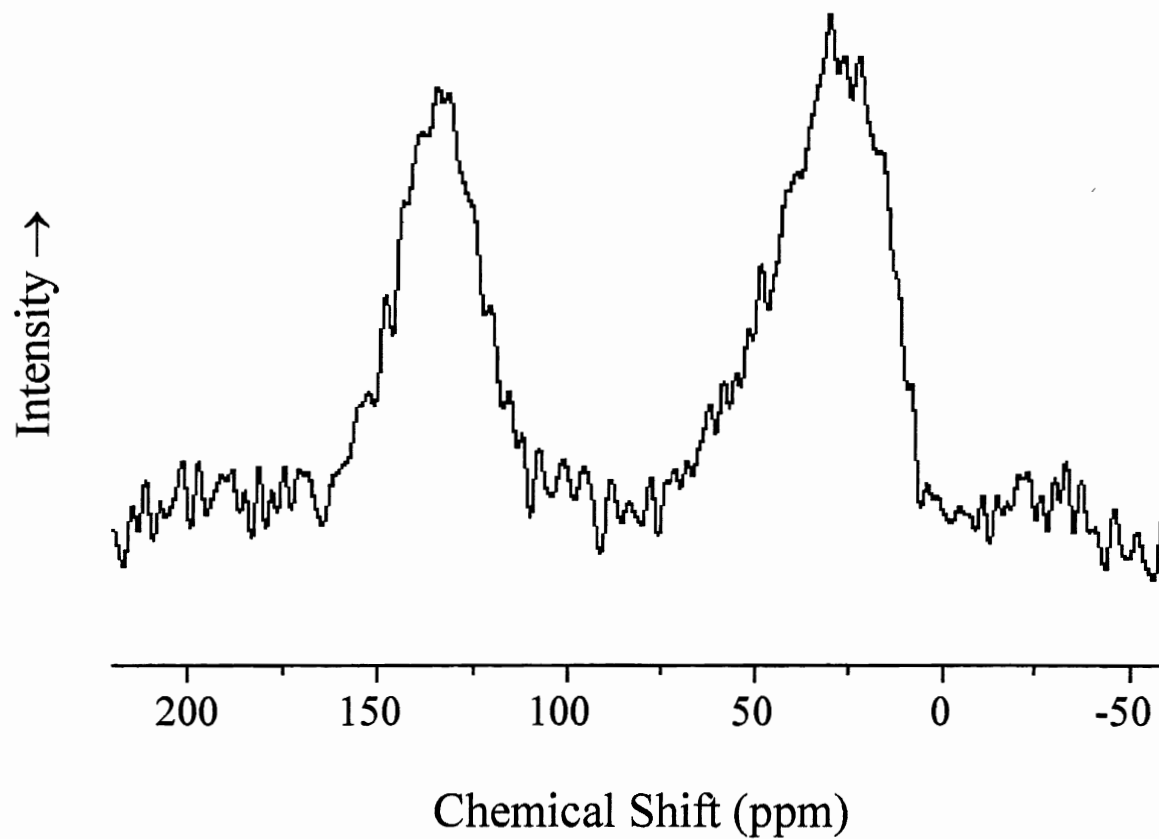
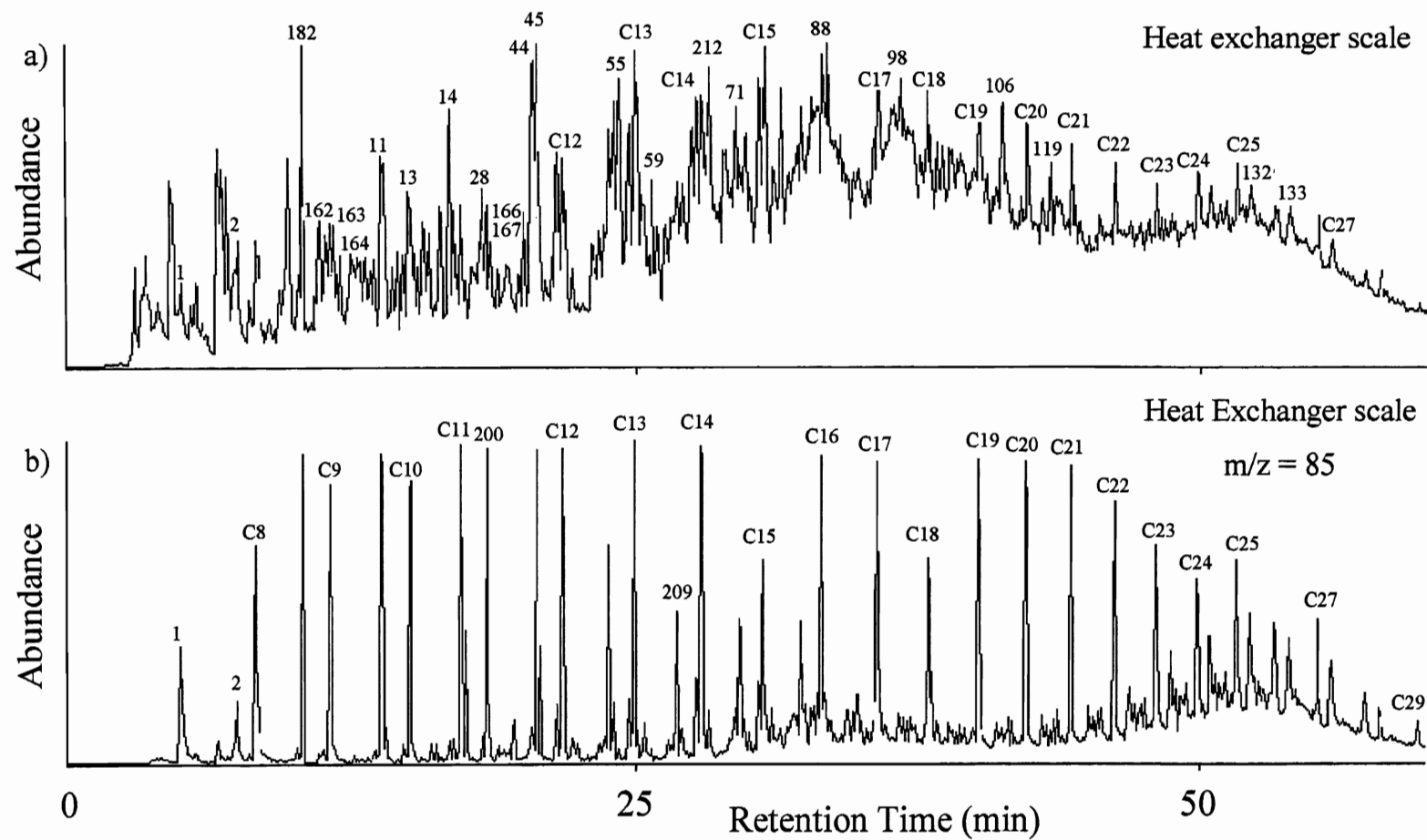


Table 3.1. Elemental composition (%) of materials studied by pyrolysis gas chromatography mass spectrometry

	Al	Fe	Ti	Si	C	H	N	O (by difference)	Ash
Bauxite	30.3	4.8	1.4	3.6	0.2	N/D	N/D	N/D	N/D
Red Mud	14.1	19.3	3.9	8.7	0.07	N/D	N/D	N/D	N/D
Shell-side Heat exchanger scale	N/D	N/D	N/D	N/D	39.5	4.9	0.8	10.0	44.7
Sodium oxalate	N/D	N/D	N/D	N/D	17.9	N/D	N/D	47.8	N/D
Aluminium hydroxide (gibbsite)	34.6	N/D	N/D	N/D	0.02	3.8	N/D	61.5	N/D
Precipitation tank scale	33.0	N/D	N/D	N/D	0.6	N/D	N/D	N/D	N/D
Oxalate-gibbsite co-precipitation fines	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D

N/D not determined

Figure 3.6 Pyrograms of heat exchanger scale a) Total pyrogram and b) Selected ion $m/z = 85$. The $C_8 - C_{29}$ series of n-alkanes are shown.



3.1.3 Sodium oxalate and aluminium hydroxide

Solid-phase sodium oxalate plays a minor role in the total sodium content of product alumina (Grocott and Rosenberg, 1988), but it plays a critical role in gibbsite nucleation and fines balance in precipitation operations, determining crystal size and particle numbers (Rehani *et al.*, 1999). Bayer alumina refineries typically operate an oxalate precipitation stage to control the level of oxalate build up in the liquor, so as to minimise the impact of this organic degradation product via precipitation at unwanted parts of the process. The presence of organic matter in the Bayer liquor stabilises the oxalate in solution to some extent (Lever, 1978). However, once oxalate precipitation begins the oxalate surface adsorbs some of the organics from the liquor promoting further precipitation. This phenomena, known as ‘oxalate showers’, disturbs the orderly precipitation of aluminium hydroxide causing excessive nucleation leading to fines in the circuit and poor quality alumina with a high sodium content (Grocott and Rosenberg, 1988; Rehani *et al.*, 1999).

The NMR spectra (Figure 3.7) of the insoluble carbon in the sodium oxalate and aluminium hydroxide appeared similar with each containing three main regions. Each sample contained a distinct aromatic region (100-150 ppm), a less intense aliphatic region from aliphatic carbon with substituted electron donating groups (50-100 ppm) and a series of peaks in the region between 160-180 ppm due to the presence of carboxylic carbon and oxalate. Oxalate carbon resonates at around 162 ppm and is seen, although not quantitatively, because of its relaxation properties. Aromatic carboxylic acids resonate at 172 ppm and aliphatic carboxylic carbon resonates at 181 ppm (Pouchert and Behnke, 1993). Both samples contained a peak at 172 ppm and a shoulder peak at 182 ppm, indicating the presence of carboxylic acids. Compounds of both these types were common pyrolysis products of the sodium oxalate and aluminium hydroxide samples (see below).

Figure 3.7 ^{13}C CP/MAS NMR spectra of insoluble organic matter from a) Sodium oxalate and b) Aluminium hydroxide.

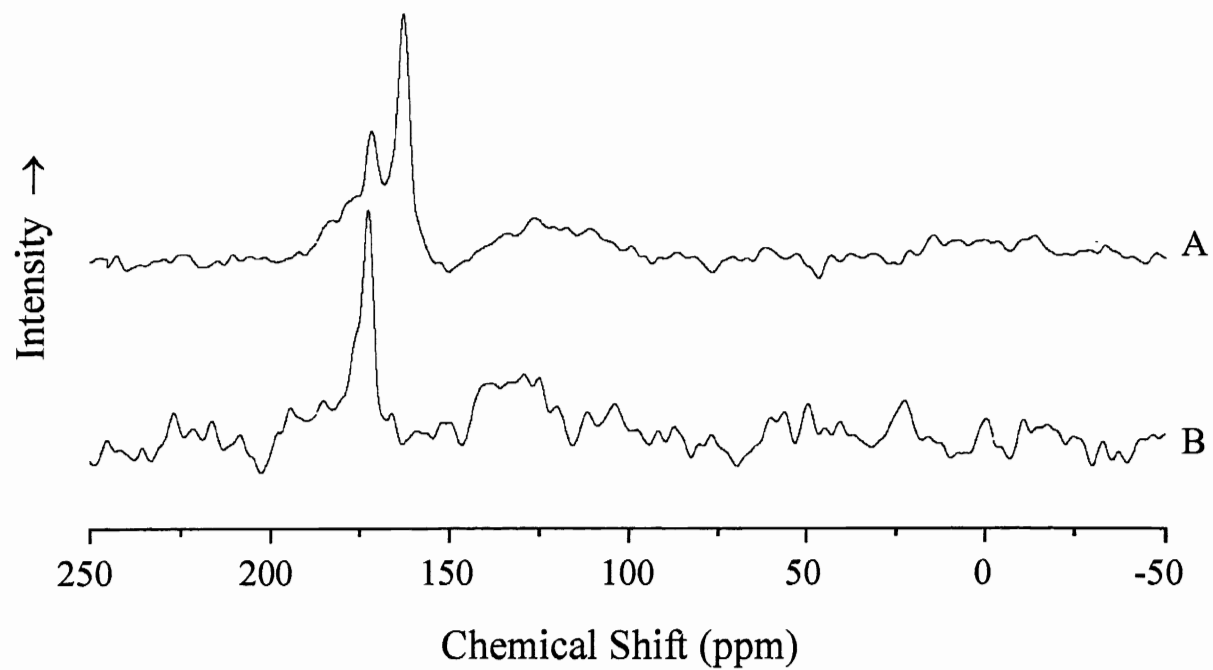
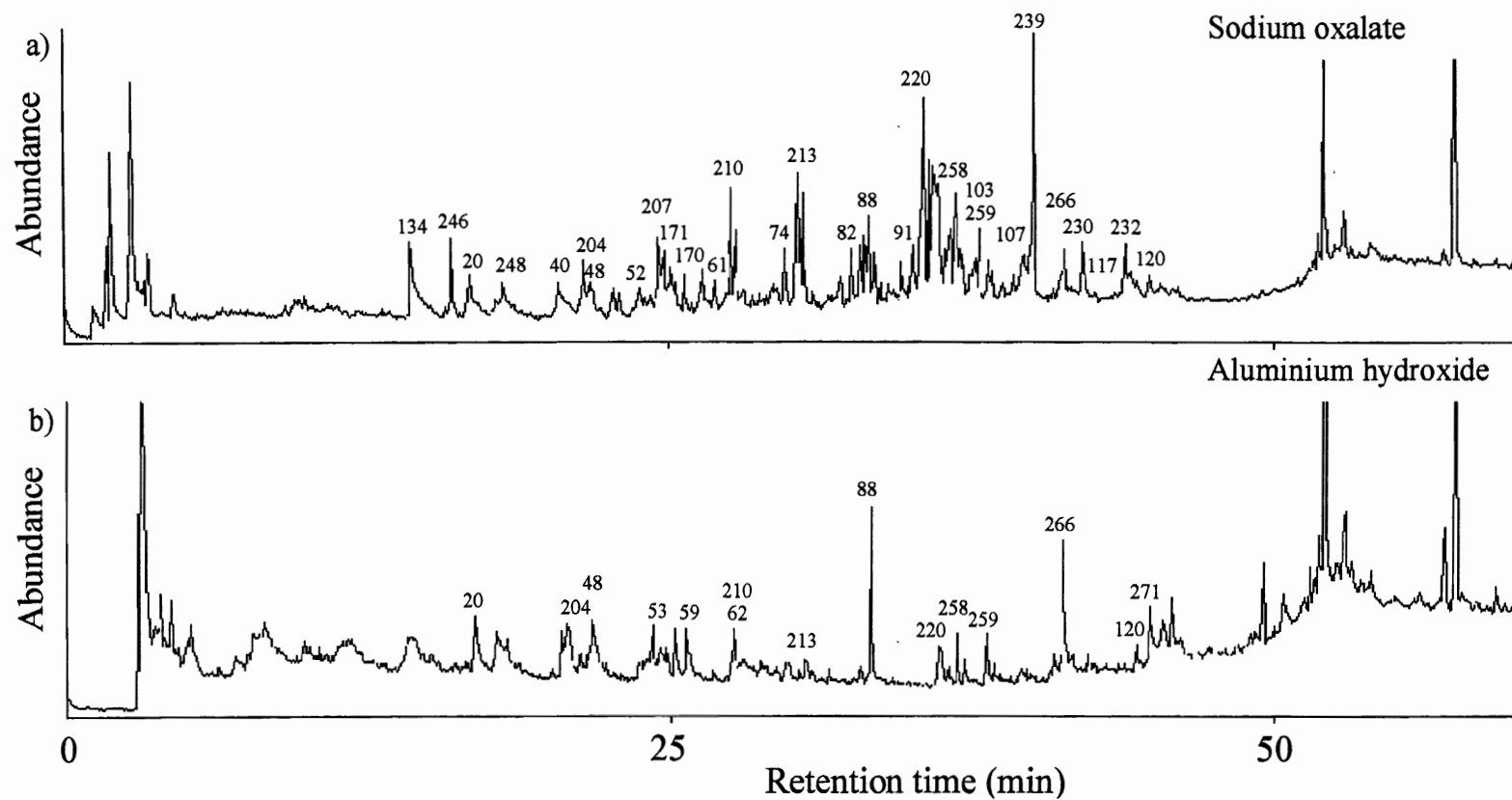


Figure 3.8 Pyrograms for a) Sodium oxalate and b) Aluminium hydroxide.



Pyrolysates from the oxalate and aluminium hydroxide show many similarities (Figure 3.8). Naphthalene (compound 48) was present in roughly equal amounts, as was pyrene (compound 120). Long chain C₁₄-C₁₆ aliphatic carboxylic acids (compounds tetradecanoic acid (258), pentadecanoic acid methyl ester (259), and hexadecanoic acid (266)), as well as short chain (C₄-C₇) aliphatic mono- and di-acids (compounds heptanoic acid methyl ester (246) and 2,2-dimethylbutanedioic acid dimethyl ester (248)) were present in both crystals but in different amounts. Many of the alkane and alkene pyrolysis products were common to the two materials (compounds C₁₂ alkene (204), C₁₃ alkene (207), C₁₄ alkene (210), C₁₅ alkene (213), C₁₇ alkene (220)). However the alkane and alkene pyrolysis products were released in much higher abundance from the sodium oxalate, with several of the alkene and alkane products released from the oxalate sample not being released from the aluminium hydroxide sample during pyrolysis. Fluorene and biphenyl were released in much larger amounts from the aluminium hydroxide (Figure 3.8, compounds 88 and 62 respectively) and also hexadecanoic acid (266). The aluminium hydroxide pyrolysates also contained methyl-substituted naphthalenes (compounds 1,2-dihydro-3-methylnaphthalene (53), 1-methylnaphthalene (59) and biphenyl (62)), as well as methyl-substituted phenanthrenes and anthracenes in low concentrations (Table 3.3) and two alkanes C₂₀ alkane (230) and C₂₁ alkane (232). These compounds were not released from the oxalate sample during pyrolysis. The compound hexadecanenitrile (239) predominates in the sodium oxalate crystals. Likewise, alkylbenzenes with alkyl chains containing up to 13 carbons were contained in the pyrolysis products from the sodium oxalate (hexylbenzene (52) to tridecylbenzene (117)), as were nitrogen containing quinoline compounds (4-methylquinoline (170) and 5-methylquinoline (171)). It is established that molecular weight fractions of the organics in the liquor all have nitrogen functionalities but they concentrate in higher (>50kD) molecular weight fractions (Smeulders *et al.*, 2000). These compounds were not released from the aluminium hydroxide during pyrolysis. It seems the nitrogen compounds have a propensity for the oxalate surface rather than the aluminium hydroxide. The sodium oxalate sample also released several aromatic carboxylic acids in trace amounts; many of these compounds were not detected on the aluminium hydroxide sample (Table 3.3).

The methanol solubles of the sodium oxalate and aluminium hydroxide produced the same trends that were seen for the whole samples by pyrolysis GC/MS. Again numerous aliphatic carboxylic acids were detected for both samples, and sodium oxalate contained more alkane and alkene pyrolysates. The main difference was that the sodium oxalate sample produced fewer aromatic di- and tri-carboxylic acids than released from the whole sample (Table 3.4). The aromatic di- and tri-carboxylic acids may bind too strongly to the sodium oxalate to be released during soxhlet extraction with methanol, preventing them from being detected.

3.1.4 Oxalate-gibbsite co-precipitation fines

Oxalate-gibbsite co-precipitation fines are a network of fine aluminium hydroxide and sodium oxalate crystals that do not settle from the Bayer liquor. These produced pyrolysis products including alkanes, alkenes, aromatic compounds including substituted benzene, alkylbenzenes, as well as substituted naphthalene, anthracene, phenanthrene and fluorene (Figure 3.9b and Table 3.3). This pyrogram is quite different from that shown for the oxalate and conventional aluminium hydroxide, although the importance of alkenes e.g compounds C₁₆ alkene (217) and C₁₀ alkene (192) (see Figure 3.9b) are significant and similar to oxalate. Aromatic and aliphatic carboxylic acids identified in the pyrolysis products from the sodium oxalate and aluminium hydroxide were not identified, nor were the compounds identified in an earlier study of aluminium hydroxide precipitated at neutral pH (Wilson *et al.*, 1998). However, these compound types were released from the material during soxhlet extraction with methanol (Table 3.4), the polar nature of carboxylic acids would have led to their concentration in the methanol and their subsequent detection. The detection of these compounds only after their concentration by soxhlet extraction indicates that these compounds must be present at quite low concentrations in the whole oxalate-gibbsite co-precipitation fines material. As noted for sodium oxalate above, di- and tri-carboxylic acids were not observed in methanol extracts.

The ¹³C NMR spectrum of the oxalate-gibbsite co-precipitation fines (Figure 3.10B) showed the presence of aliphatic carbon. The CP/MAS aromaticity at a contact time

of 1 ms was 0.35. The oxalate-gibbsite co-precipitation fines contained a large amount of oxalate carbon (162 ppm) (Wilson *et al.*, 1988; Stothers, 1972; Fernandes *et al.*, 1994), carbonate carbon (168 ppm) and a smaller amount of aromatic carboxylic carbon (175 ppm). Acetate (182 ppm) (Fernandes *et al.*, 1994) does not appear to be present probably because the sample was predried. A peak at 52 ppm in the oxalate-gibbsite co-precipitation fines spectrum is due to methoxyl carbon (Runge and Ragauskas, 1999). Methoxyl substituted aryl carbon is also visible in the aromatic region of the spectrum as a shoulder at 147 ppm. The presence of such a wide range of chemical groups in the oxalate-gibbsite co-precipitation fines may explain why the crystals were prevented from growing sufficiently large enough to be settled from the Bayer process liquor during gravity separation.

Figure 3.9 Pyrograms for a) Precipitation tank scale and b) Oxalate-gibbsite co-precipitation fines.

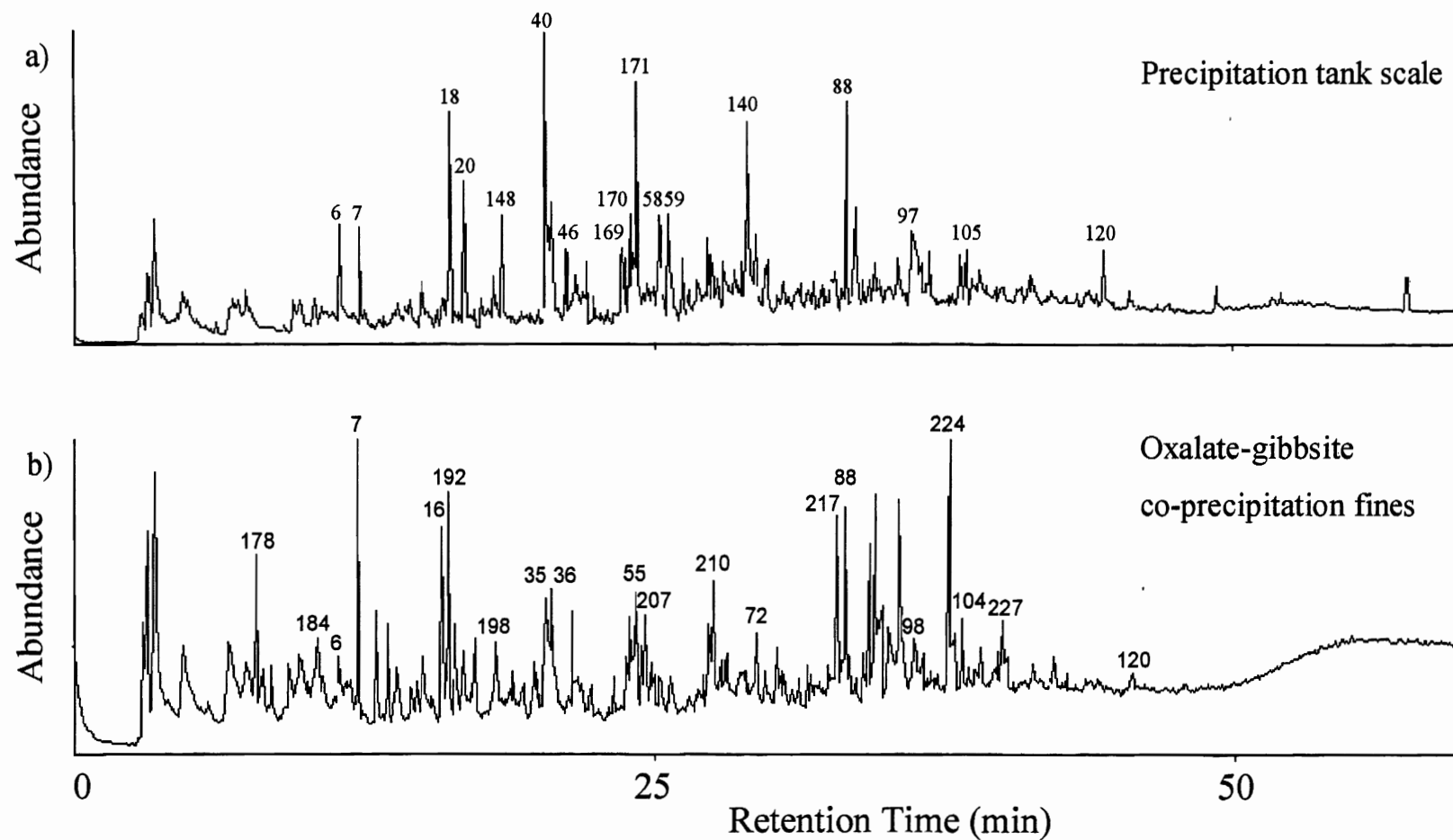
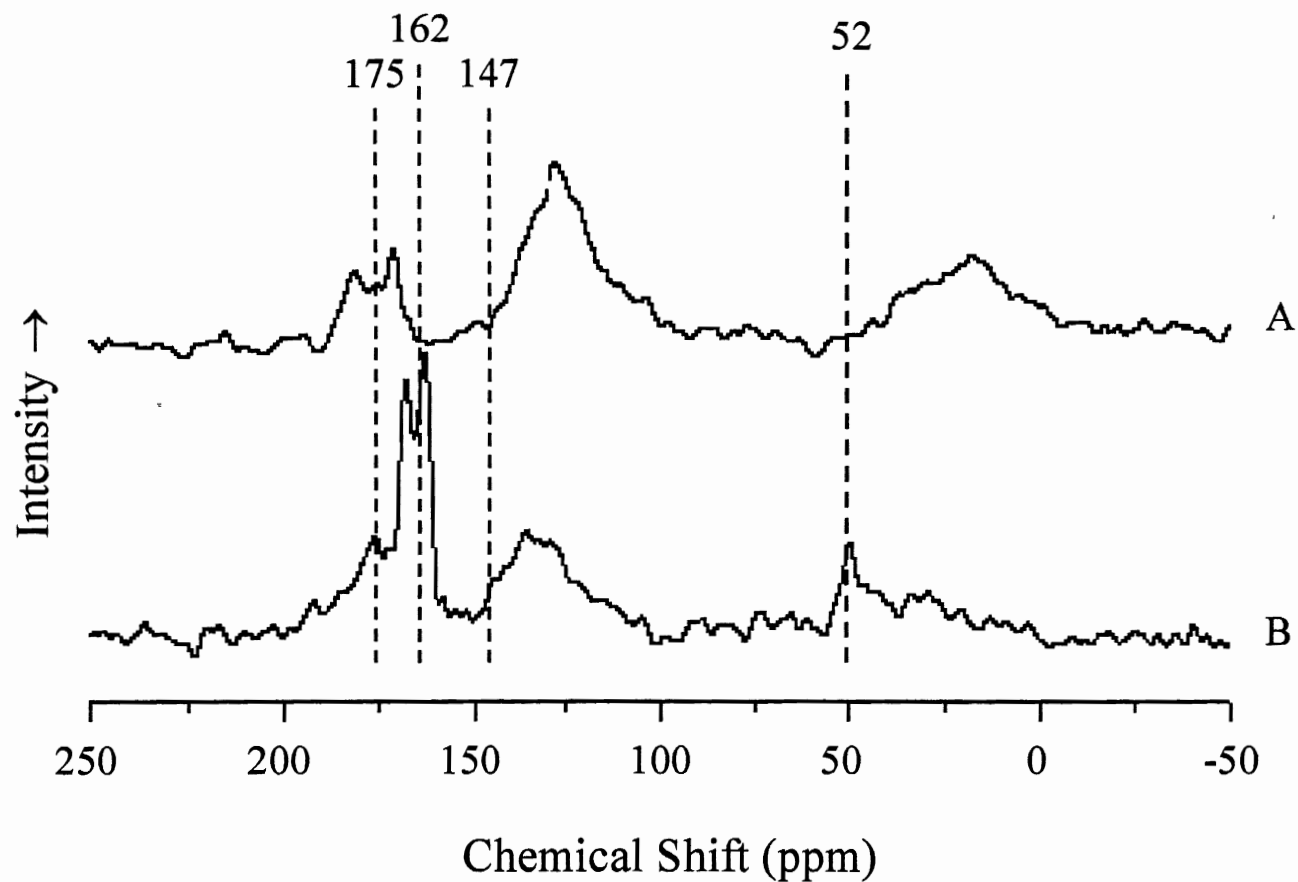


Figure 3.10 ^{13}C CP/MAS NMR spectra of insoluble organic matter a) Precipitation tank scale and b) Oxalate-gibbsite co-precipitation fines.



3.1.5 Precipitation tank scale deposits

A precipitation tank scale deposit, containing both precipitated sodium oxalate and aluminium hydroxide, produced a pyrogram (Figure 3.9a) consisting mainly of substituted aromatic, quinoline and phenolic compounds. The major pyrolysis products included the substituted aromatic compounds styrene (6), methoxybenzene (7), 4-ethyl-1,2-dimethylbenzene (18), indene (20), 1-methylindene (40), 1,1-dimethylindene (46), 2-methylnaphthalene (58), 1-methylnaphthalene (59), fluorene (88), various methylfluorenes (97-100), phenanthrene (104), anthracene (105) and pyrene (120). 2,3,6-trimethylphenol (140), benzoic acid (148), quinoline (169), 5-methylquinoline (170), and 4-methylquinoline (171) were the other major pyrolysates for this sample. The precipitator tank scale deposit is clearly different in organic matter content from that present in aluminium hydroxide, oxalate-gibbsite co-precipitation fines, or sodium oxalate.

Other compounds identified in Figure 3.9 include 1-methoxy-2-methylbenzene (16), (1'-methyl-1-propenyl)-benzene (35), 1-ethyl-2,3-dimethylbenzene (36), 1,2-dihydro-2-methylnaphthalene (55), *m*-diisopropylbenzene (72), C₈ alkene (178), 4-nonene (184), C₁₁ alkene (198), C₁₃ alkene (207), C₁₄ alkene (210), C₁₈ alkene (224) and C₁₉ alkene (227). The numbers shown represent the compounds listed Table 3.3.

The ¹³C NMR spectrum of the precipitation tank scale (Figure 3.10A) appeared quite similar to the NMR spectra obtained for dissolved humic substances, and the proportions of the different carbon types (Table 3.2) were also similar (see Section 3.5). The spectrum of the precipitation tank scale had a strong aromatic region ($f_a = 0.56$) and a distinct aliphatic region. The spectrum also displayed contributions from aliphatic carboxylic acids (181 ppm) and aromatic carboxylic acids (171 ppm). The scale material would contact humic material present in the Bayer process liquor leading to its adsorption and the appearance of the humic material in the ¹³C NMR spectrum. However pyrolysis GC/MS data (Figure 3.11) showed some significant differences. They include styrene (6), methoxybenzene (7), 4-ethyl-1,2-dimethylbenzene (18), indene (20), 1-methylindene (40), 1-methylfluorene (97), pyrene (120), methyl benzoate (148), and 4-methylquinoline (171). The results

suggest there is not selective adsorption of any particular structural group on a bulk scale, but that some more polar compounds may be selectively removed, possibly via the sodium oxalate in the scale sample. Other compounds identified in Figure 3.11 include 1-methylnaphthalene (59), fluorene (88), and 2,3,6-trimethylphenol (140).

Figure 3.11 Pyrograms for a) Bayer humic substances and b) Precipitation tank scale.

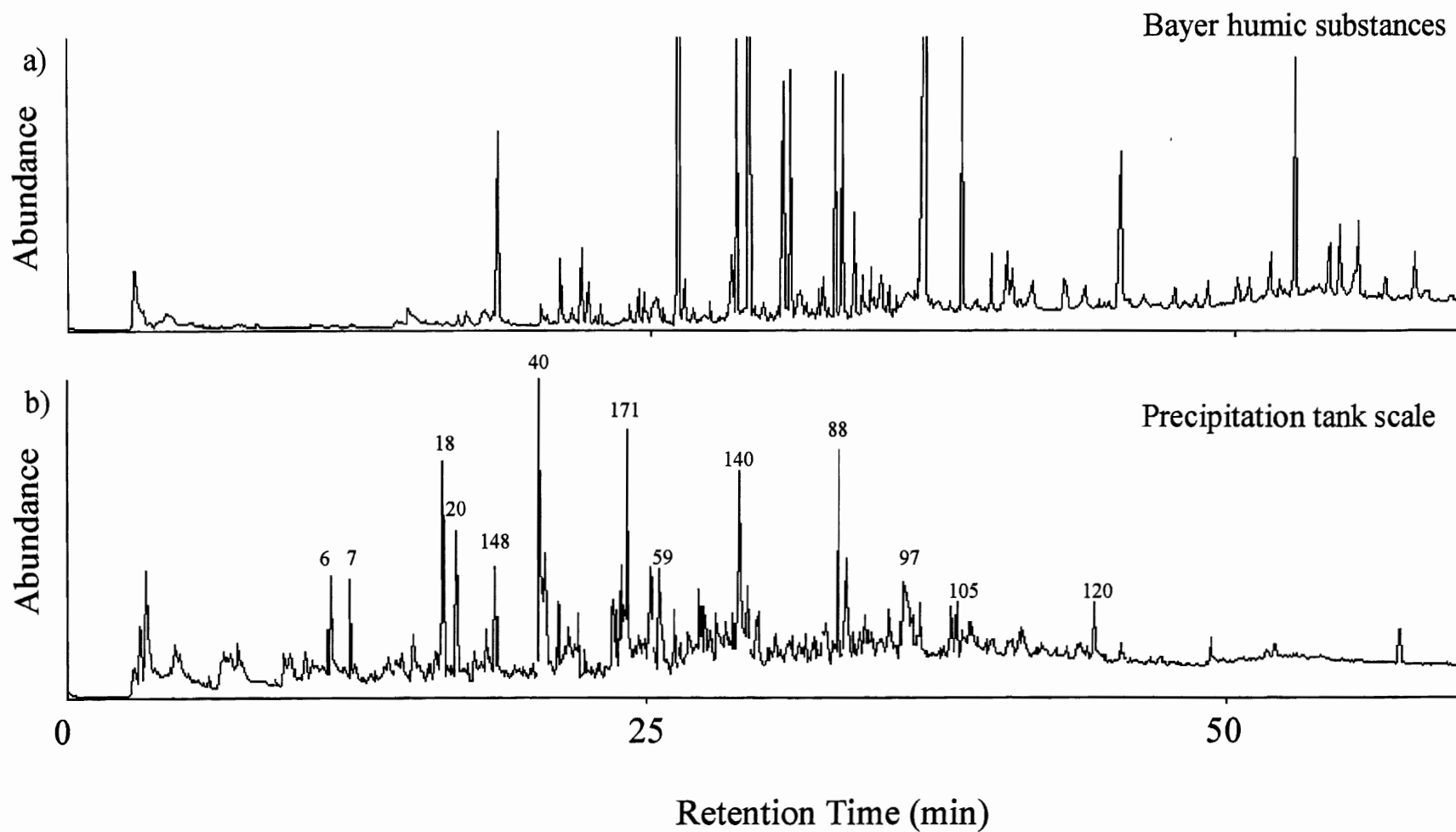


Table 3.2 ^{13}C NMR CP/MAS results

	C-Alkyl	O-Alkyl	Aromatic	Carboxylic	Carbonyl
	0-50	50-100	100-160	160-190	190-220
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
	%	%	%	%	%
Heat exchanger scale	60	0	40	0	0
Sodium oxalate	13	0	33	54	0
Aluminium hydroxide	22	0	36	42	0
Precipitation tank scale	28	0	56	16	0
Oxalate-gibbsite co-precipitation fines	26	0	35	39	0

3.1.6 Fate of the non soluble organic material in the Bayer process

It is clear from the above results that the dissolution of organic matter in the Bayer process is selective. That is, the molecular structure of the organic matter in the red mud differs from that in the bauxite and that which dissolves in sodium hydroxide. Surprisingly some of the most polar compounds (e.g short chain carboxylic acids) seem to concentrate in the red mud despite their obvious solubility in sodium hydroxide. This suggests that the red mud may act as an adsorbent. That is, the process is not purely controlled by solubility.

Nevertheless solubility is important during processing. At the heat exchangers non polar organic matter drops out of solution primarily because it does not contain carboxylic functionality. Moreover, when aluminium hydroxide or oxalate precipitates from solution polarity again becomes important. While the bulk organic matter that is co-precipitated with precipitation tank scale is similar to that in solution, polar compounds are adsorbed preferentially to some degree which produces some capacity to release polycyclic aromatics on pyrolysis. Not surprisingly these compounds are also found in more abundance on pyrolysis of the trace organics on aluminium hydroxide. The adsorption process on sodium oxalate appears to be different, since alkenes and alkanes are released in higher concentration on pyrolysis and some pyrolysates are quite different to those from aluminium hydroxide.

Simple hydroxyl substituted aromatic carboxylic acids have been implicated in the past as possible poisons to the precipitation of aluminium hydroxide from the Bayer process (Armstrong, 1993; Coyne *et al.*, 1994; Alamdari *et al.*, 1993; Tran *et al.*, 1996; The, 1980). However, little has been reported on what organics adsorb on oxalate surfaces, and the influence of organics on oxalate precipitation (Hind *et al.*, 1999). There are several possible models for the poisoning of the precipitation of the sodium oxalate by humic material. One model is that oxalate occupies adsorption sites on large humic macromolecules. The oxalate is aggregated with the macromolecules via hydrogen bonding. In doing so, oxalate needles may be prevented from agglomerating into normal morphology. Another model is that oxalate could be incorporated into humic macromolecules as guests (Sections 3.9-3.12 and Smeulders

et al., 2000, 2001) and thus is unavailable for precipitation. This would prevent oxalate from precipitating with aluminium hydroxide.

The pyrolysis products from the aluminium hydroxide (gibbsite) differed to those found on the aluminium hydroxide when it was precipitated at neutral pH (Wilson *et al.*, 1998), although some compounds were common including the short chain aliphatic dicarboxylic acids. No activity poisonous to the precipitation process was observed for the material selectively adsorbed at pH=7. Thus there appears to be little association between adsorbability and activity. Rather the functionalities that adsorb are determined by pH and inorganic composition. Current ideas on organic activity are based on a competitive model for sites on the seed surfaces required for growth, nucleation and agglomeration (Wilson *et al.*, 1998). If one organic poison is removed, another may take its place. Since the humic materials can store a wide range of smaller guest molecules inside voids caused by macromolecular intramolecular binding, any removal of poisonous material may set up a gradient which releases further poisons from the macromolecular humic host. Further studies are in progress to test this model.

3.2 Conclusions from the analysis of insoluble organic materials from the Bayer process

The pyrolysis products from bauxite and red mud were found to differ considerably, with the red mud pyrolysates consisting mainly of aromatic polycyclics. Iron oxide was found to have catalytic effects during pyrolysis leading to the production of simple aromatic compounds but the materials are intrinsically different.

The organic material recovered from the heat exchanger units was found to have characteristics similar to those of a light pitch or tar.

Sodium oxalate and aluminium hydroxide produced several common pyrolysis products including alkanes, alkenes, and long chain aliphatic carboxylic acids, predominantly with C₁₄ to C₁₆ carbon chain lengths, as well as short chain (C₄-C₇)

aliphatic mono- and di-carboxylic acids. Nitrogen containing compounds seem to favour the oxalate surface.

Organic material on the precipitation tank scale was similar in composition to Bayer humic substances. However differences in styrene (6), methoxybenzene (7), 4-ethyl-1,2-dimethylbenzene (18), indene (20), 1-methylindene (40), 1-methylfluorene (97), pyrene (120), methyl benzoate (148), and 4-methylquinoline (171) concentrations in pyrolysates were observed.

The oxalate-gibbsite co-precipitation fines surprisingly produced very different pyrolysis products to those from the sodium oxalate and aluminium hydroxide.

Table 3.3 Pyrolysis products of Bayer process materials.

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
Aromatic Hydrocarbons								
1	Benzene	✓	✓	✓			✓	
2	Toluene	✓✓	✓	✓✓			✓	
3	o-Xylene			✓				✓
4	m-Xylene			✓✓				✓
5	p-Xylene	✓	✓✓✓	✓✓			✓	✓
6	Styrene	✓	✓✓✓			✓	✓✓	✓✓
7	Methoxybenzene	✓	✓✓			✓	✓✓	✓✓✓
8	1-Ethyl-3-methylbenzene						✓	
9	1,2,5-Trimethylbenzene	✓						✓
10	Benzaldehyde	✓						
11	4-Methylbenzenemethanol			✓✓				
12	Ethoxybenzene	✓	✓✓✓					
13	1,2,4-Trimethylbenzene	✓✓	✓	✓✓			✓	✓✓
14	1,2,3-Trimethylbenzene	✓✓		✓✓			✓	✓
15	1-Methoxy-3-methylbenzene						✓	
16	1-Methoxy-2-methylbenzene	✓	✓				✓	✓✓
17	1,3,5-Trimethylbenzene	✓					✓	✓
18	4-Ethyl-1,2-dimethylbenzene	✓					✓✓✓	
19	Indane			✓✓				✓
20	Indene	✓✓	✓✓		✓✓	✓✓	✓✓	✓✓
21	Acetophenone						✓	
22	Butylbenzene	✓	✓					
23	1,2,3,4,5,8-Hexahydronaphthalene	✓	✓					
24	1-Phenyl-1,2-butandiol		✓					
25	N-Methylbenzenamine	✓						
26	1-Methyl-2-propylbenzene	✓						
27	1,2-Diethylbenzene			✓				
28	2-Ethenyl-1,4-Dimethylbenzene			✓✓				
29	2,3-Dimethyl-methoxybenzene						✓	
30	1,2,4,5-Tetramethylbenzene	✓✓		✓			✓	
31	1,2,3,4-Tetramethylbenzene	✓✓		✓			✓	✓
32	2,4-Dimethylmethoxybenzene						✓	
33	3,4-Dimethylmethoxybenzene						✓	

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
34	1,3-Diethyl- 5-methylbenzene			✓				
35	(1'-Methyl-1'-propenyl)-benzene							✓✓
36	1-Ethyl-2,3-dimethylbenzene	✓						✓✓
37	1,2,3,5-Tetramethylbenzene	✓		✓				
38	2-Phenyl-1,3-butadiene	✓						✓
39	(1'-Methylene-2'-propenyl)-benzene			✓				
40	1-Methylindene	✓			✓✓		✓✓✓	
41	2,3-Dimethoxytoluene						✓	
42	3-Methylacetophenone						✓	
43	Pentylbenzene	✓	✓✓					
44	Divinylbenzene			✓✓✓				
45	(1'-Methyl-1'-butenyl)-benzene			✓✓✓				
46	1,1-Dimethylindene						✓✓	
47	2-Methyl-1-phenyl-1-butene			✓				
48	Naphthalene	✓✓	✓✓✓	✓	✓	✓✓	✓	✓
49	1-Isopropyl-2-methoxy-4-methylbenzene						✓	
50	1,3-Dihydro-inden-2-one				✓			
51	1,4-Dimethoxy-2-methylbenzene						✓	
52	Hexylbenzene	✓	✓✓		✓✓			
53	1,2-Dihydro-3-methylnaphthalene	✓✓		✓✓	✓	✓✓	✓	✓
54	1,2-Dihydro-6-methylnaphthalene	✓✓		✓✓		✓	✓	✓✓
55	1,2-Dihydro-2-methylnaphthalene			✓✓			✓	✓✓
56	1,3-Dimethyl-5-(1'-methylethyl)-benzene	✓✓✓						✓
57	4-(2'-Butenyl)-1,2-dimethylbenzene			✓				
58	2-Methylnaphthalene	✓✓	✓✓	✓	✓	✓✓	✓✓	✓
59	1-Methylnaphthalene	✓✓	✓✓	✓	✓✓	✓✓	✓✓	✓
60	1,4-Dimethyltetralin			✓				
61	Heptylbenzene		✓✓		✓✓			✓
62	Biphenyl	✓	✓✓✓	✓		✓✓	✓	✓
63	1,2-Diethyl-3,4-dimethylbenzene	✓✓✓	✓					
64	1,2,4-Trimethyl-5-(1'-methylethenyl)-benzene	✓✓✓	✓					
65	Diphenyl ether		✓					
66	Diphenylmethane	✓	✓					✓
67	1,5-Dimethylnaphthalene	✓✓				✓	✓	✓

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
68	1,7-Dimethylnaphthalene					✓	✓	✓
69	1,6-Dimethylnaphthalene			✓		✓	✓	
70	2,6-Dimethylnaphthalene	✓✓		✓			✓	
71	1,4-Dimethylnaphthalene	✓✓		✓✓		✓	✓	
72	<i>m</i> -Diisopropylbenzene	✓✓✓						✓✓
73	(1'-Methylheptyl)-benzene		✓					
74	Octylbenzene	✓	✓✓		✓✓			✓
75	Acenaphthene			✓✓			✓	
76	2,4,6-Triethyltoluene						✓	
77	1,2-Dihydro-2,5,8-trimethylnaphthalene			✓				✓
78	1,2-Dihydro-3,5,8-trimethylnaphthalene			✓				
79	1,2,3,4-Tetrahydro-1,4,6,7-tetramethylnaphthalene			✓✓				
80	1,4-Dihydro-2,5,8-trimethylnaphthalene	✓✓		✓			✓	
81	1,4,6-Trimethylnaphthalene	✓✓		✓			✓	✓
82	Nonylbenzene	✓✓	✓✓		✓✓			
83	1,4,5-Trimethylnaphthalene	✓✓		✓✓			✓	✓
84	1,6,7-Trimethylnaphthalene	✓✓		✓✓			✓	✓
85	3-Methyl-1,1-biphenyl			✓				
86	2-Methyl-1,1-biphenyl			✓				
87	2,3,6-Trimethylnaphthalene	✓✓		✓✓			✓	✓
88	Fluorene	✓✓	✓✓✓	✓✓✓	✓✓	✓✓✓	✓✓✓	✓✓✓
89	Phenalene			✓			✓	
90	Diphenylamine				✓			
91	Decylbenzene				✓✓			✓
92	2-Ethyl-1,1'-biphenyl			✓				
93	4-Isopropyl-1,6-dimethylnaphthalene			✓				
94	4-Methylfluorene			✓		✓	✓✓	✓
95	2,4-Dimethylbiphenyl			✓				
96	2,3-Dimethylbiphenyl			✓		✓	✓	✓
97	1-Methylfluorene			✓		✓	✓✓	✓✓
98	9-Methylfluorene	✓	✓	✓✓	✓	✓✓	✓✓	✓
99	2-Methylfluorene					✓✓	✓✓	✓
100	2,3-Dimethylfluorene						✓✓	
101	9-Methylene fluorene							✓

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
102	9-Fluorenone	✓	✓		✓✓	✓✓	✓	
103	Undecylbenzene				✓			
104	Phenanthrene	✓	✓✓	✓	✓	✓	✓✓	✓✓
105	Anthracene	✓	✓	✓	✓✓	✓	✓✓	✓
106	2,3-Dimethyl-9H-fluorene			✓✓				
107	Dodecylbenzene				✓✓			✓
108	1-Methyl-7-(1'-methylethyl)-naphthalene	✓✓						
109	1-Phenylnaphthalene		✓✓					
110	1-Methylanthracene	✓		✓		✓	✓	
111	2-Methylanthracene	✓						
112	1-Methylphenanthrene	✓				✓		✓
113	9-Methylphenanthrene	✓				✓		✓
114	3-Methylphenanthrene			✓				✓
115	4-Methylphenanthrene			✓			✓	✓
116	2-Methylphenanthrene	✓		✓			✓	✓
117	Tridecylbenzene				✓			✓
118	2-Phenylnaphthalene		✓✓			✓	✓	
119	2,5-Dimethylphenanthrene	✓		✓			✓	
120	Pyrene	✓✓	✓✓	✓	✓✓	✓✓	✓✓	✓✓
121	2,3-Dimethylphenanthrene	✓						
122	Naphthacene				✓			
123	2,3,5-Trimethylphenanthrene			✓				
124	3-Methylpyrene			✓				
125	7H-Benzofluorene			✓				
126	2-Methylpyrene			✓				
127	4-Methylpyrene			✓				
128	1-Methylpyrene			✓				
129	1,3-Dimethylpyrene			✓				
130	Chrysene			✓				
131	Isochrysene			✓				
132	Benzo-3,4-phenanthrene			✓				
133	6-Methylchrysene			✓				
	Phenols							
134	Phenol	✓			✓✓		✓	
135	2-Methylphenol						✓	

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
136	3-Methylphenol						✓	
137	2,4-Dimethylphenol			✓				
138	2,5-Dimethylphenol			✓				
139	2-Ethylphenol			✓			✓	
140	2,3,6-Trimethylphenol						✓✓✓	
141	<i>m</i> -Isopropylphenol				✓			
142	2-(1',1'-Dimethylethyl)-5-methylphenol							✓
143	4-(1-Methylpropyl)-phenol				✓			
144	3-(1,1-Dimethylethyl)-5-methylphenol				✓			
145	4-Dodecylphenol		✓					
146	Dodecylphenol		✓		✓✓			✓
147	Nonylphenol		✓		✓✓			
	Aromatic carboxylic acids							
148	Benzoic acid methyl ester				✓	✓	✓✓	
149	2-Methylbenzoic acid methyl ester					✓	✓	
150	3-Methylbenzoic acid methyl ester						✓	
151	4-Methylbenzoic acid methyl ester						✓	
152	4-Ethylbenzoic acid methyl ester						✓	
153	3-Methoxybenzoic acid methyl ester				✓	✓	✓✓	
154	2,3-Benzenedicarboxylic acid dimethyl ester				✓			
155	2,5-Benzenedicarboxylic acid dimethyl ester				✓			
156	4-Methyl-1,2-benzenedicarboxylic acid dimethyl ester				✓			
157	4-Methyl-1,3-Benzenedicarboxylic acid dimethyl ester				✓			
158	4-Hydroxy-2-methoxy-3,5,6-trimethylbenzoic acid methyl ester				✓	✓		
159	1,2,4-Benzenetricarboxylic acid trimethyl ester				✓			
160	2,4,6-Benzenetricarboxylic acid trimethyl ester				✓			
	Heteroaromatic Hydrocarbons							
161	2,4-Dimethylfuran					✓	✓	✓

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
162	2,3-Dimethylpyrrole			✓				
163	2,4-Dimethylpyrrole			✓				
164	2,5-Dimethylpyrrole			✓				
165	2,3,5-Trimethylpyrrole						✓	
166	2,3,4,5-Tetramethylpyrrole			✓				
167	4-N,N-Dimethylaminopyrimidine			✓				
168	4-Pyridine carboxylic acid methyl ester				✓			
169	Quinoline						✓✓	
170	5-Methylquinoline				✓		✓✓✓	✓
171	4-Methylquinoline				✓		✓✓✓	✓
172	Benzothiofuran		✓					
173	Dibenzofuran	✓	✓					
174	Dibenzothiophene		✓		✓			
175	9-Methylcarbazole	✓						
	Aliphatic Hydrocarbons							
176	C4-alkene	✓	✓					
177	2-Octene	✓	✓					✓
178	C8-alkene	✓	✓					✓✓✓
179	3-Octene	✓	✓					✓
180	C8-alkane			✓✓				
181	2,3-Dimethyl-2-heptene	✓✓	✓					
182	2,4-Dimethyl-1-heptene	✓	✓	✓✓✓				
183	4-Ethyl-3-heptene	✓	✓	✓				
184	4-Nonene	✓✓	✓					✓
185	3-Nonene	✓✓	✓					✓
186	C9-alkene	✓	✓					✓✓
187	cis-3-Nonene	✓	✓					✓
188	C9-alkane			✓✓				
189	1-(1'-Methylethyl)-cyclopentene							✓
190	5-Decene			✓				
191	3-Decene			✓				
192	C10-alkene			✓				✓✓✓
193	C10-alkane			✓✓				
194	4-Undecene			✓				
195	2-Methyldecane			✓✓				

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
196	3-Methyldecane			✓				
197	5-Undecene			✓				
198	C11-alkene		✓✓	✓				✓✓
199	3-Undecene	✓						
200	4,5-Dimethylnonane			✓✓				
201	C11-alkene isomer			✓				
202	C11-alkane	✓						
203	9-Methyl-3-undecene			✓				
204	C12-alkene	✓	✓✓	✓✓	✓	✓		✓✓
205	C12-alkane		✓	✓✓		✓		✓
206	3-Dodecene	✓		✓				✓
207	C13-alkene	✓	✓	✓✓	✓✓	✓		✓✓
208	C13-alkane	✓	✓✓	✓✓✓	✓✓	✓		✓
209	2-Methyltridecane			✓✓				
210	C14-alkene	✓	✓	✓✓	✓✓	✓		✓✓
211	C14-alkane	✓	✓✓	✓✓	✓✓			✓
212	C14-alkene isomer			✓✓	✓			✓
213	C15-alkene	✓	✓	✓	✓✓	✓		✓
214	C15-alkene isomer			✓✓				
215	4,8-Dimethyltridecane			✓				
216	C15-alkane	✓	✓✓	✓✓	✓✓	✓		✓
217	C16-alkene			✓				✓✓✓
218	C16-alkane	✓		✓✓	✓			✓
219	C16-alkene isomer			✓				✓
220	C17-alkene	✓	✓	✓	✓✓✓	✓		✓
221	C17-alkane	✓	✓	✓✓	✓✓	✓		✓
222	Pristane			✓				
223	8-Heptadecene				✓			
224	C18-alkene	✓		✓✓	✓✓			✓✓✓
225	C18-alkane	✓✓		✓✓	✓✓			✓
226	Phytane			✓				
227	C19-alkene					✓		✓✓
228	C19-alkane	✓	✓	✓✓		✓		✓
229	C20-alkene	✓						
230	C20-alkane	✓		✓✓	✓✓			

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
231	C21-alkene	✓						
232	C21-alkane	✓	✓	✓✓	✓✓			
233	C22-alkane			✓✓	✓			
234	C23-alkane			✓✓				
235	C24-alkane			✓✓				
236	C25-alkane	✓		✓✓				
237	C27-alkane	✓		✓✓				
238	C29-alkane			✓✓				
	Aliphatic Nitriles							
239	Hexadecanenitrile				✓✓✓	✓		
240	Octadecanenitrile					✓		
	Aliphatic alcohols							
241	Octadecanol	✓						
	Aliphatic Fatty Acids							
242	2-Methylpropanoic acid methyl ester				✓	✓		
243	Butanoic acid methyl ester				✓	✓	✓	
244	Pentanoic acid methyl ester					✓		
245	Hexanoic acid methyl ester				✓	✓	✓	
246	Heptanoic acid methyl ester				✓✓	✓		
247	3-Ethylhexanoic acid methyl ester				✓			✓✓
248	2,2-Dimethylbutanedioic acid dimethyl ester				✓	✓		
249	Butanedioic acid dimethyl ester					✓		
250	Methylbutanedioic acid dimethyl ester				✓			
251	Pentanedioic acid dimethyl ester				✓			
252	Hexanedioic acid dimethyl ester				✓			
253	2-Methylpentanedioic acid dimethyl ester				✓			
254	Nonanoic acid methyl ester				✓		✓	
255	Decanoic acid methyl ester				✓			
256	Dodecanoic acid methyl ester				✓		✓	
257	Tetradecanoic acid methyl ester				✓	✓✓		
258	Tetradecanoic acid				✓	✓✓	✓	
259	Pentadecanoic acid methyl ester	✓			✓	✓✓		
260	Pentadecanoic acid					✓	✓	
261	11-Hexadecenoic acid methyl ester	✓			✓			

Table 3.3 continued

	Compound	Bx	Mud	OrgS	Ox	Hyd	Scale	OGF
262	9-Hexadecenoic acid methyl ester				✓	✓		
263	Hexadecanoic acid methyl ester				✓✓	✓		
264	14-Methylpentadecanoic acid methyl ester						✓	
265	9-Hexadecenoic acid					✓		
266	Hexadecanoic acid	✓	✓			✓✓✓	✓	
267	9-Octadecenoic acid methyl ester				✓	✓		
268	1-Octadecenoic acid methyl ester					✓		
269	Octadecanoic acid methyl ester					✓		
270	10-Heptadecanoic acid methyl ester				✓		✓	
271	9-Octadecenoic acid					✓✓		
272	8-Octadecenoic acid	✓						
273	Octadecanoic acid	✓	✓					
274	Eicosanoic acid methyl ester					✓✓		
275	Eicosanoic acid					✓✓		
276	13-Docosenoic acid methyl ester					✓✓		

Bx = Bauxite; **Mud** = Red mud; **Hyd** = Aluminium hydroxide; **Ox** = Sodium Oxalate;
OrgS = Heat Exchanger Organic Scale; **Scale** = Precipitation tank scale; **OGF** =
Oxalate-gibbsite co-precipitation fines

✓ = low abundance (0-20% height); ✓✓ = medium abundance (20-50% height);
✓✓✓ = large abundance (50-100% height)

Table 3.4 Pyrolysis products of soxhlet extracted Bayer insoluble organics

	Compound	Bx	Mud	Ox	Hyd	Scale	OGF
Aromatic Hydrocarbons							
2	Toluene	✓					
3	<i>o</i> -Xylene					✓	
6	Styrene	✓	✓	✓	✓	✓	
7	Methoxybenzene		✓				
10	Benzaldehyde	✓					
14	1,2,3-Trimethylbenzene					✓	
20	Indene					✓	
21	Acetophenone		✓	✓			✓
48	Naphthalene					✓	
53	1,2-Dihydro-3-methylnaphthalene					✓	
54	1,2-Dihydro-6-methylnaphthalene					✓	
58	2-Methylnaphthalene					✓✓	
59	1-Methylnaphthalene					✓	
68	1,7-Dimethylnaphthalene					✓	
70	2,6-Dimethylnaphthalene					✓	
81	1,4,6-Trimethylnaphthalene					✓	
88	Fluorene					✓	
98	9-Methylfluorene				✓	✓	
277	3-Phenyldodecane			✓			
278	2-Phenylpentadecane			✓			
104	Phenanthrene	✓				✓	
279	5-Phenyltridecane			✓			
280	4-Phenyltridecane			✓			✓
281	3-Phenyltridecane			✓			
282	2-Phenyltridecane			✓			
Aromatic carboxylic acids							
148	Benzoic acid methyl ester	✓	✓	✓	✓✓	✓✓	✓
149	2-Methylbenzoic acid methyl ester			✓	✓	✓✓	✓
150	3-Methylbenzoic acid methyl ester				✓		✓
283	2,6-Dimethylbenzoic acid methyl ester				✓		
153	3-Methoxybenzoic acid methyl ester	✓		✓	✓	✓✓	✓✓
154	2,3-Dimethylbenzoic acid methyl ester					✓✓	
155	2,5-Dimethylbenzoic acid methyl ester				✓	✓✓	
284	3,5-Dimethylbenzoic acid methyl ester					✓	
160	2,4,6-Trimethylbenzoic acid methyl ester					✓	

Table 3.4 continued

	Compound	Bx	Mud	Ox	Hyd	Scale	OGF
Aliphatic Hydrocarbons							
186	C9-alkene	✓	✓				
198	C11-alkene	✓	✓	✓✓	✓		✓
204	C12-alkene	✓	✓	✓✓	✓	✓	✓
207	C13-alkene	✓	✓	✓✓	✓		✓
210	C14-alkene	✓	✓	✓✓	✓	✓	✓
213	C15-alkene	✓	✓	✓✓	✓	✓✓	
216	C15-alkane		✓	✓			
217	C16-alkene	✓		✓	✓	✓✓	✓
220	C17-alkene	✓		✓✓			
224	C18-alkene	✓		✓		✓	
225	C18-alkane					✓	
227	C19-alkene	✓		✓	✓		✓
228	C19-alkane			✓		✓	
229	C20-alkene	✓					
230	C20-alkane	✓		✓		✓	
231	C21-alkene	✓	✓✓	✓	✓	✓	✓✓
285	C22-alkene		✓				
233	C22-alkane					✓	
286	C23-alkene	✓✓	✓	✓			
234	C23-alkane					✓	
235	C24-alkane		✓	✓		✓	✓
287	C28-alkane	✓	✓			✓	✓
238	C29-alkane		✓			✓	
Aliphatic Fatty Acids							
242	2-Methylpropanoic acid methyl ester				✓		
243	Butanoic acid methyl ester		✓	✓	✓	✓	
288	3-Methylbutanoic acid methyl ester				✓	✓	
251	Pentanoic acid methyl ester		✓		✓		
245	Hexanoic acid methyl ester		✓	✓	✓	✓	✓
246	Heptanoic acid methyl ester		✓	✓	✓	✓	✓
249	Butanedioic acid dimethyl ester		✓				
289	2-Methylhexanoic acid methyl ester		✓	✓			✓
251	Pentanedioic acid dimethyl ester				✓✓		
290	Octanoic acid methyl ester		✓	✓	✓	✓	✓
254	Nonanoic acid methyl ester		✓	✓	✓	✓	✓
255	Decanoic acid methyl ester		✓	✓	✓	✓	✓

Table 3.4 continued

	Compound	Bx	Mud	Ox	Hyd	Scale	OGF
291	Undecanoic acid methyl ester		✓				✓
256	Dodecanoic acid methyl ester	✓	✓✓	✓✓	✓✓		✓
292	Nonanedioic acid dimethyl ester						✓
257	Tetradecanoic acid methyl ester	✓	✓✓	✓✓	✓✓	✓✓	✓✓
259	Pentadecanoic acid methyl ester	✓	✓	✓	✓✓	✓	✓✓
261	11-Hexadecenoic acid methyl ester	✓	✓✓	✓	✓✓		✓✓
263	Hexadecanoic acid methyl ester	✓✓	✓✓✓	✓✓✓	✓✓✓	✓✓✓	✓✓✓
266	Hexadecanoic acid				✓		
267	9-Octadecenoic acid methyl ester	✓	✓✓	✓	✓✓	✓	✓✓
269	Octadecanoic acid methyl ester	✓	✓✓	✓	✓✓	✓✓	✓✓
272	8-Octadecenoic acid methyl ester		✓✓✓		✓		✓
274	Eicosanoic acid methyl ester		✓	✓		✓	✓
293	Heneicosanoic acid methyl ester			✓		✓✓	✓
276	13-Docosenoic acid methyl ester	✓✓✓	✓✓	✓			
294	Docosanoic acid methyl ester	✓	✓	✓		✓✓	✓
295	Tricosanoic acid methyl ester		✓			✓	
296	Tetracosanoic acid methyl ester	✓	✓			✓	✓
297	Pentacosanoic acid methyl ester		✓				
298	Heptacosanoic acid methyl ester					✓	

Bx = Bauxite; **Mud** = Red mud; **Hyd** = Aluminium hydroxide; **Ox** = Sodium Oxalate;
OrgS = Heat Exchanger Organic Scale; **Scale** = Precipitation tank scale; **OGF** =
Oxalate-gibbsite co-precipitation fines

✓ = low abundance (0-20% height); ✓✓ = medium abundance (20-50% height);

✓✓✓ = large abundance (50-100% height)

PART B

Characterisation of Bayer liquor humic substances

This section of the thesis deals with the results from the characterisation of the molecular weight fractions of humic materials obtained from the Bayer process. Techniques including pyrolysis GC/MS, ^{13}C NMR, FTIR, Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and elemental analysis were all used to determine the composition of the organic fractions. The experimental methods for the isolation and analysis of the organic matter are detailed in Sections 2.1-2.3 of Chapter 2.

3.3 Yields from molecular weight fractionation of Bayer humic materials

Table 3.5 lists the yields, elemental and acidity data for each molecular weight fraction. Low molecular weight material (<1200 Daltons) comprises 87.0% of the recovered organic matter from a high temperature (250-255°C) alumina refinery (QAL, Gladstone, Queensland). By comparison, in a plant producing material at 145-150°C, 75.1% of the recovered organic matter has a molecular weight lower than 1.2kD (Wilson *et al.*, 1999).

The yields of other molecular weight fractions from the high temperature refinery were much smaller. The yield of the 50-100kD fraction is larger than any other fraction with molecular weight >1.2kD. Although the organic matter in bauxite used at different plants can differ, these changes are those expected for processes operating at different temperatures. In particular, higher yields of smaller molecular weight and highly volatile material are to be expected when the digestion temperature is increased by of the order of 100°C.

3.4 Elemental composition

Table 3.5 shows that the percent nitrogen and the nitrogen to carbon ratio (N/C) ratio tend to increase with increasing molecular weight. For example the N/C ratio is 0.1 for the 100-300kD fraction and 0.0095 for the <1.2kD fraction. The trend is not uniform since the nitrogen content of the 6-12kD fraction is particularly high. These results also mirror those obtained at 145-150°C (Wilson *et al.*, 1999). They

indicate that nitrogen containing compounds concentrate in higher molecular weight fractions and are less degradable both in the lower temperature process and the higher temperature process reported here. Bearing in mind the severity of reaction conditions, these compounds will not be nitrogen containing amides such as in proteins, but heterocyclic nitrogen compounds such as pyrimidines and pyrazine structures. These compounds are derived from enzymes and nucleotides or pyrolysis products of proteins.

Table 3.5 also shows that there is no correlation of the O/C mole ratio with increasing molecular weight. This differs from the results obtained for the low temperature (145-150°C) Bayer liquors described before. Presumably the harsher conditions result in the introduction of a lot more oxygen.

Unlike the low temperature Bayer organics, the percent hydrogen and H/C ratio do not decrease with increasing molecular weight (Wilson *et al.*, 1999). These results demonstrate that Bayer organics from the two processes are significantly different in molecular weight composition, and the molecular weight fractions themselves also differ in molecular structure.

Table 3.5 Yields, acidity and elemental analysis of the Bayer humic substance fractions (dry ash free basis)

Fraction No.	Molecular weight fraction (kD)	%C	%H	%N	%S	%O Difference	O/C	H/C	N/C	S/C	pH at 5g/litre in water	Mass yield (%) ^a
PL ^b	<1.2 to >300	56	3.7	0.41	0.21	39	0.53	0.78	0.0055	0.0015	2.4	100
SL ^b	<1.2 to >300	53	3.6	0.11	0.11	43	0.61	0.80	0.0018	0.00078	2.4	100
1	<1.2	50	4.2	0.56	0.17	44	0.65	0.99	0.0095	0.0013	2.5	87
2	1.2-6	48	3.8	1.9	0.32	46	0.71	0.93	0.033	0.0025	2.9	3.3
3	6-12	54	4.2	3.2	0.60	38	0.52	0.93	0.051	0.0041	3.4	0.6
4	12-25	54	3.7	1.4	0.44	41	0.57	0.81	0.022	0.0031	2.9	1.6
5	25-50	56	5.4	3.7	0.42	35	0.47	1.2	0.057	0.0028	3.8	1.0
6	50-100	49	4.1	4.9	0.68	42	0.64	0.99	0.086	0.0052	4.0	3.8
7	100-300	49	4.9	5.9	0.99	39	0.60	1.2	0.10	0.0075	4.6	0.7
8	>300	55	3.8	2.1	0.42	39	0.54	0.83	0.032	0.0029	4.4	2.0

a) The weight of fraction over total weight of material recovered. b) PL = pregnant liquors, SL = spent liquors

3.5 Analysis of molecular weight fractions by solid state ^{13}C NMR and FTIR

Table 3.5 lists the pH of the various fractions. The pregnant and spent fractions have similar acidities. The <1.2kD fraction is similar in acidity to the spent liquor because it is the largest constituent of the spent liquor. There is a trend to decreased acidity with increasing molecular weight, although the 12-25kD fraction is slightly anomalous. These results could be interpreted as different acidities of different functional groups in the fractions. However the infrared and NMR evidence (Figures 3.12 and 3.13, and Table 3.6) show that the change in acidity is due to different concentrations of carboxylic acid groups in the fractions. The most acidic fraction (<1.2kD) contains the most carboxylic carbon and the least acidic fraction (>300kD) contains the least (Table 3.6). This is also reflected in the size of the 1700cm^{-1} absorption ($\text{C}=\text{O}$ stretching vibration) in the infrared spectrum (Figure 3.12) (Painter *et al.*, 1981). In fact, excluding the 12–25kD fraction, there is a good correlation of acidity with carboxyl content. This is a similar trend to what was observed for low temperature processed Bayer organics (Wilson *et al.*, 1999).

In the infrared spectra aliphatic CH absorptions are present at around $1390\text{--}1400\text{cm}^{-1}$ (resulting from contributions of symmetrical CH_3 bending vibration at 1375cm^{-1} , CH deformation and terminal CH_3 groups around $1360\text{--}1400\text{cm}^{-1}$, as well as antisymmetrical bending vibration of CH_3 near 1450cm^{-1}) (Painter *et al.*, 1981). The spectra for the pregnant liquor, spent liquor and <1.2kD fraction showed medium intensity absorptions between $800\text{--}950\text{cm}^{-1}$ resulting from *o*, *p* and *m* interactions from multiple substitutions on aromatic rings. The aromatic absorption is also present in the infrared spectra at 1600cm^{-1} (carbon-carbon aromatic ring stretching) (Painter *et al.*, 1981). The NMR data suggests all materials are quite highly aromatic (Table 3.6), with aromaticity (f_a) varying from 0.53 to 0.67. These values are much higher than the equivalent fractions produced by low temperature Bayer processing. There is not a simple trend of increased aromaticity with increased molecular weight as was observed with the low temperature fractions (Wilson *et al.*, 1999).

The change in magnitude of the C-O stretching vibrations centred at 1260cm^{-1} (which includes contributions from aryl ethers) appears to coincide with the change in intensity with the carbonyl vibration at 1700cm^{-1} . If these differed, it would show the presence of other C-O functionality such as ether linkages. Thus there does not seem to be much additional oxygen in ethers in higher molecular weight fractions. This is in contrast to results obtained for Bayer organics produced at lower temperatures, where higher molecular weight material contained substantially larger amounts of ether materials (Wilson *et al.*, 1999). Presumably, notwithstanding differences in vegetation matter in the different bauxites, the harsh high temperature conditions aids in the cleavage of ether linkages in the humic materials.

Table 3.6 Estimates of proportions of different carbon types in molecular weight fractions of Bayer humic substances as measured by solid state ^{13}C NMR.

Molecular weight fraction (kD)	C-Alkyl	O-Alkyl	Aromatic $100f_a$	Carboxylic	Carbonyl
Chemical shift (ppm) →	0-50	50-100	100-160	160-190	190-220
<1.2	21	2	53	23	1
1.2-6	22	4	56	17	1
6-12	19	11	57	12	1
12-25	13	7	63	16	1
25-50	12	8	58	21	1
50-100	15	1	66	17	1
100-300	23	7	59	10	1
>300	26	7	58	8	1

Figure 3.12 Infrared spectra of Bayer humic molecular weight fractions. A) Pregnant liquor organics; B) Spent liquor organics; C) <1.2kD; D) 1.2-6kD; E) 6-12kD; F) 12-25kD; G) 25-50kD; H) 50-100kD; I) 100-300kD; J) >300kD.

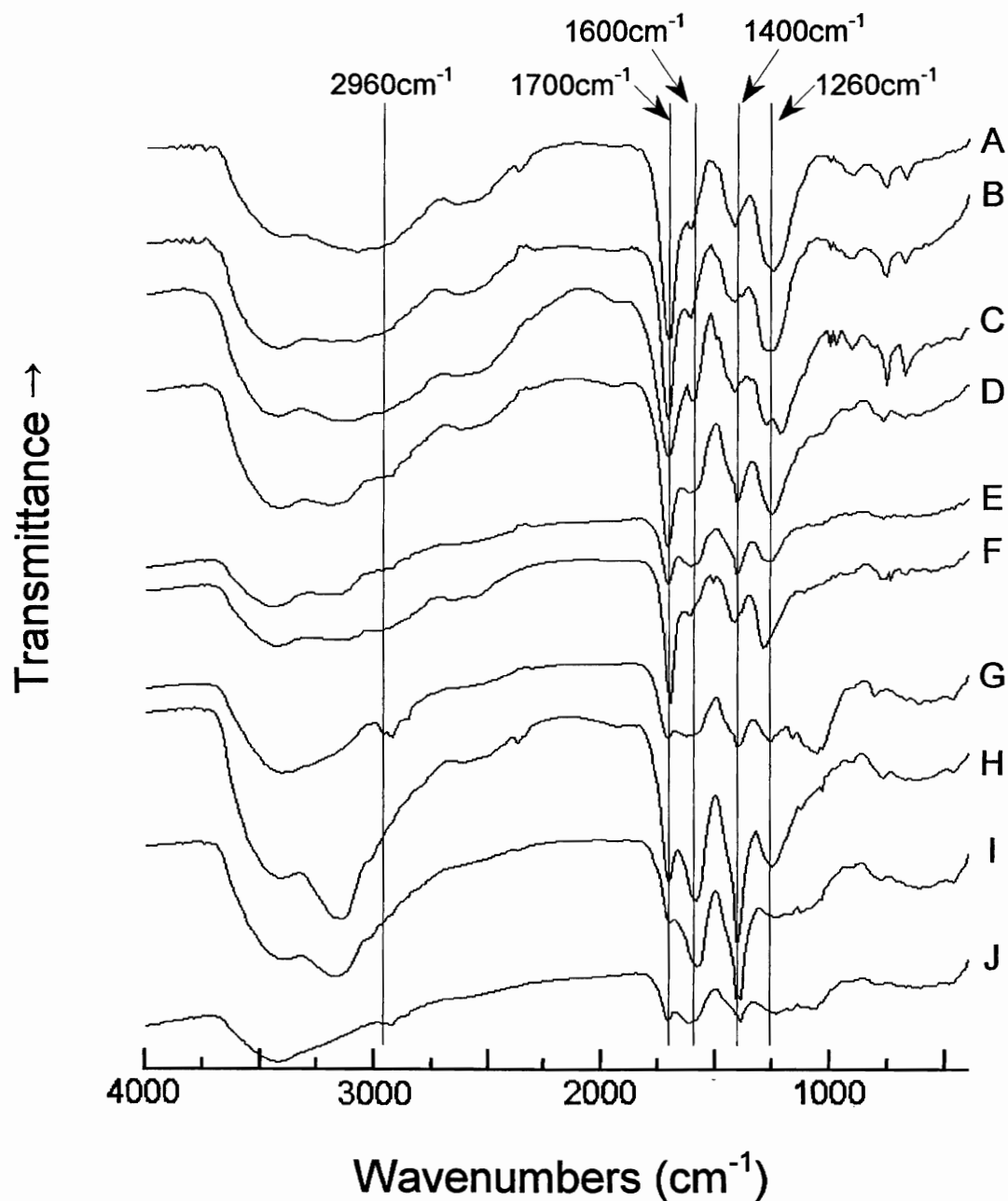
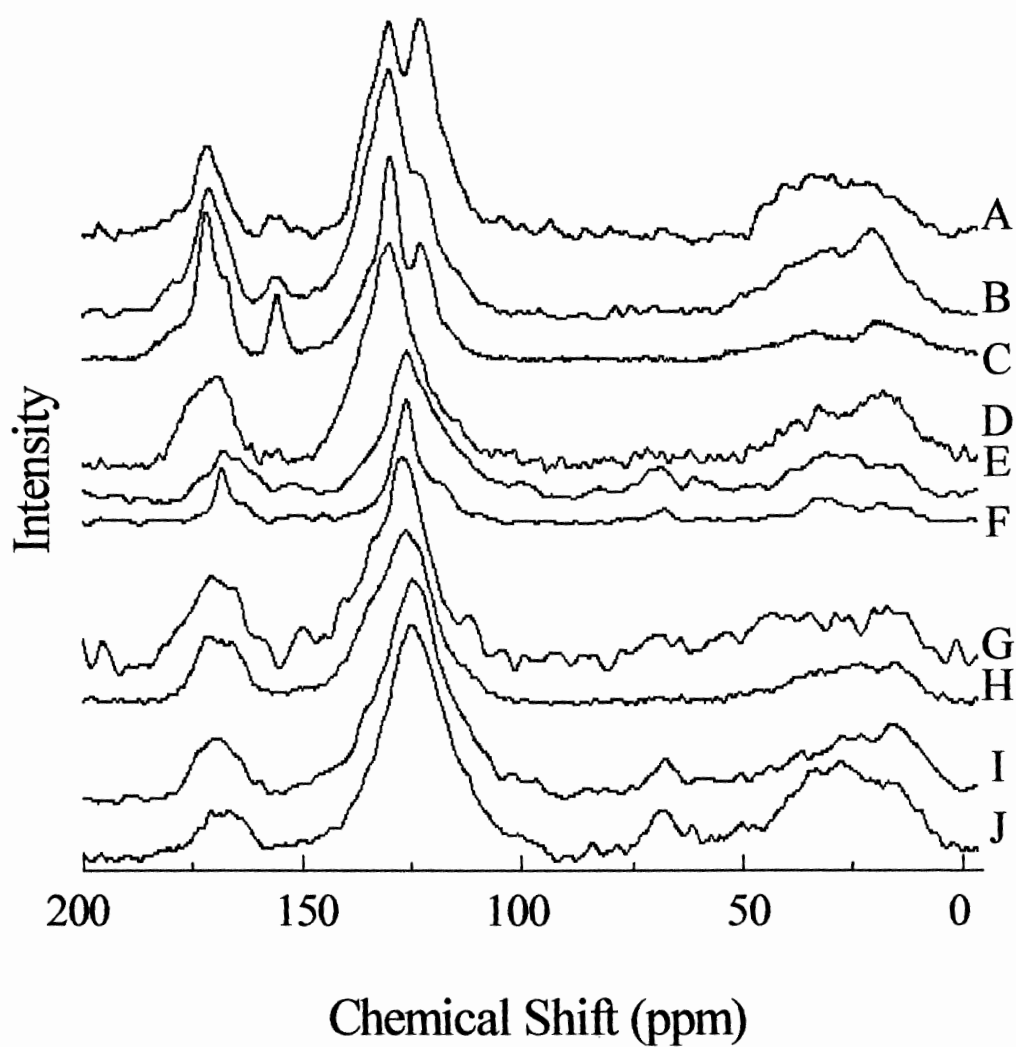


Figure 3.13 ^{13}C NMR spectra of Bayer process humic substances. A) Pregnant liquor organics; B) Spent liquor organics; C) <1.2kD; D) 1.2-6kD; E) 6-12kD; F) 12-25kD; G) 25-50kD; H) 50-100kD; I) 100-300kD; J) >300kD.



Comparison between the organics in the liquors from the two plants yields a picture of higher degradation of aliphatic material at higher temperature in all molecular weight fractions. During the Bayer process, aromatic material and aliphatic material are degraded, but the aromatic material to a lesser extent. There does not appear to be any significant increase in carboxylation or decarboxylation at the higher temperatures of the remaining more thermally stable material. However the higher temperatures destroy a lot more ether linkages.

In addition, ^{13}C NMR revealed that the high temperature Bayer process produced a much higher phenolic carbon content (Figure 3.13, 145-160 ppm) in the humic material than what was observed in the low temperature processed material (Wilson *et al.*, 1999).

3.6 Thermal analysis for determination of gross chemical structure

Figure 3.14 shows the effect of temperature on weight loss by gravimetric thermal analysis. The Pregnant liquor and Spent liquor organic materials behave almost identically (Figure 3.14, Traces A and B), thereby demonstrating similar behaviour during pyrolysis. This shows that these two fractions have similar structures.

The individual molecular weight fractions of the spent liquor behave differently from each other. The loss of mass up to 200°C can be attributed to the loss of surface and bound water and volatile organics trapped in the macromolecular matrix (Van Krevelen, 1993). This mass loss was found to be between 9.3% and 17.6%, depending on which fraction was being examined. The water and organic content of the whole spent liquor organics cannot be calculated by summing the yield mass losses for each of the molecular weight fractions adjusted for mass. This shows that the water and volatile organic holding capacity for the different fractions changes when the different molecular weight materials are separated. It suggests that the various humic molecular weight fractions agglomerate together in structures where some water or volatile organic binding sites on each humic substance (rectangles) are held by other humic species. This is depicted in Figure

3.15 (left side), where both water and small organic volatiles (circles) occupy binding sites and the bound molecules can bridge macromolecules. After separation by dialysis (Figure 3.15, right side) the large molecules are separated and this process generates more sites for adsorption of small molecules. Thus the water content of the unseparated material is not the same as the mass weighted sum of the water content of the separated materials. Elsewhere we will present substantially more evidence for this model (Sections 3.9-3.11).

Further mass loss was seen between 200°C and 350°C. The largest losses are for the <1.2kD fraction and the 12-25kD fraction. Carboxylic acids are the least stable of the functional groups and they are the first structures to decompose at temperatures between 200-350°C (Wilson *et al.*, 1985). Other materials that volatilise at this temperature are aliphatic biopolymers such as those present in kerogen (Wilson *et al.*, 1985; Evans *et al.*, 1985), which distil just before the decomposition temperature of most geoorganic matter (400°C). Hence the spectroscopic data and mass loss data correlate well and suggest that these two fractions contain highly substituted aromatic polycarboxylic acids and kerogen like aliphatic biopolymers respectively.

Between 350-500°C most organic bonds are cleaved, and traditionally this is the region in which most volatile matter is evolved from humic substances and carbonaceous materials such as kerogens or coals (Wilson *et al.*, 1985; Evans *et al.*, 1985; Collin *et al.*, 1980; Vassallo and Codd, 1988). The mass loss is almost constant for each of the fractions up to molecular weight of 50kD (Table 3.7). The highest molecular weight fractions (>50kD) have low volatile contents, which is characteristic of chars or coals of very high rank (Van Krevelen, 1993). These chars can have high oxygen contents (as observed here) if they derive from carbohydrates rather than aromatic material (Vassallo and Codd, 1988).

Figure 3.14 Weight loss data for humic molecular weight fractions during pyrolysis.

A = Pregnant liquor organics; B = Spent liquor organics; C = <1.2kD; D = 1.2-6kD; E = 6-12kD; F = 12-25kD; G = 25-50kD; H = 50-100kD; I = 100-300kD; J = >300kD (Top figure displays stacked results).

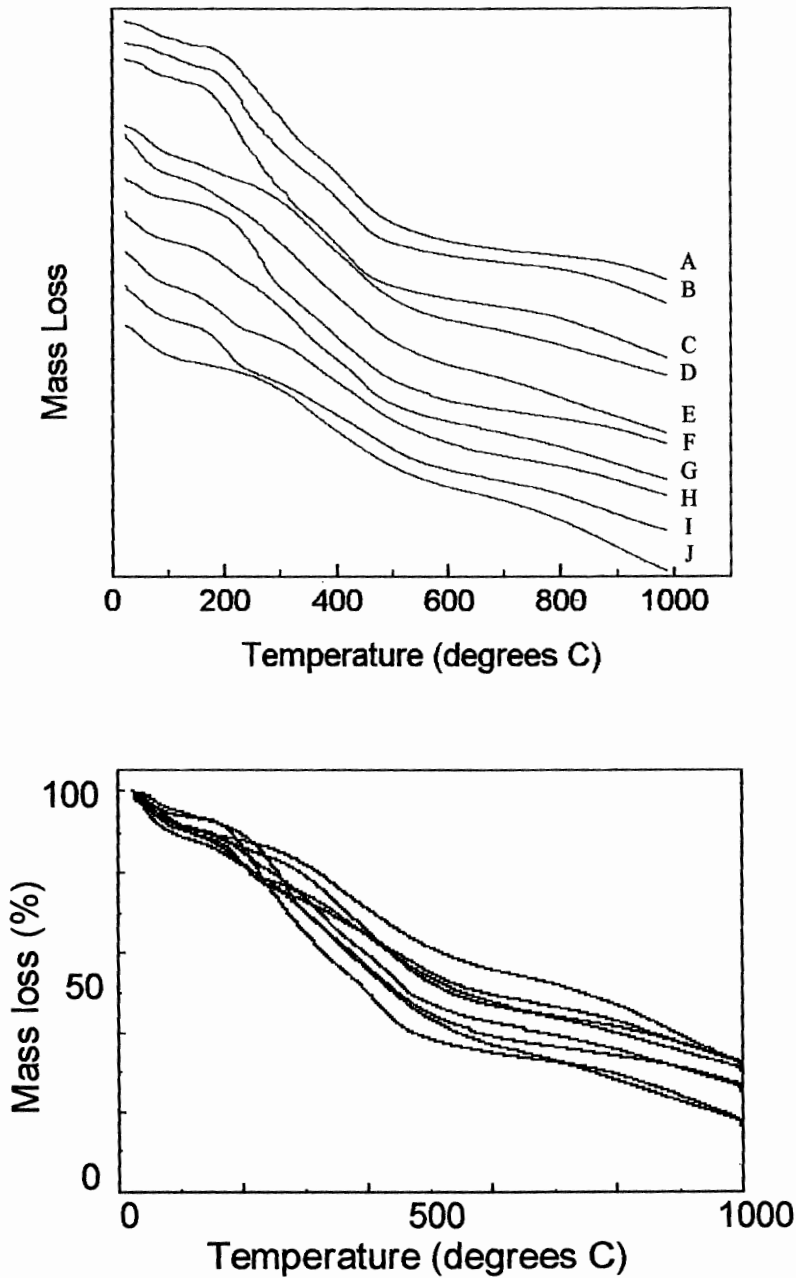


Figure 3.15 Model to explain the water and volatile holding capacity of humic substances before and after fractionation. Rectangles = humic substance, length equivalent to molecular weight, o = water, • = organic volatile. The arrow represents the process of dialysis.

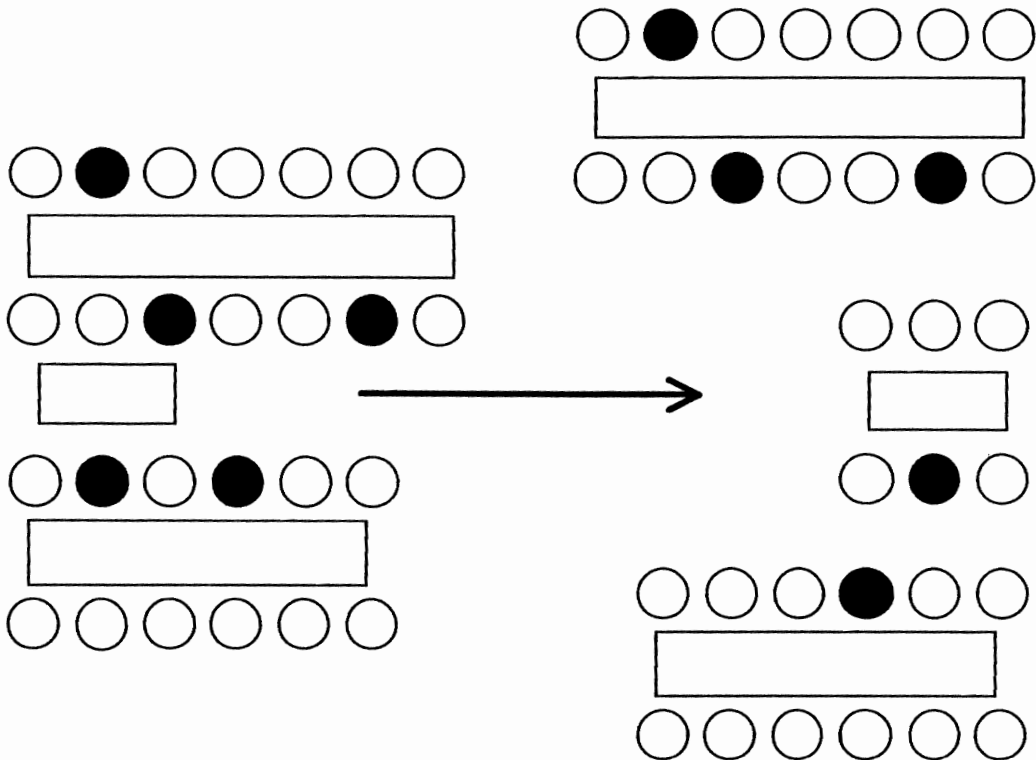


Table 3.7 Thermogravimetric analysis of organic Bayer fractions

Molecular weight fraction (kD)	% Mass loss to 200°C	% Mass loss 200°-350°C	% Mass loss 350°-500°C	% Mass loss 500°-600°C	% Mass loss 600°-1000°C	Residual %	Total % mass loss
Pregnant	9.32	25.6	20.2	4.61	14.2	25.9	74.1
Spent	9.31	25.6	19.0	3.48	16.8	25.5	74.4
<1.2	11.5	30.3	19.4	3.64	19.7	15.3	84.6
1.2-6	13.6	13.6	20.1	5.84	17.7	29.0	70.9
6-12	17.4	18.8	19.8	6.72	21.7	15.4	84.5
12-25	10.3	26.3	18.7	5.59	14.2	24.7	75.2
25-50	13.7	19.4	19.1	4.95	18.4	24.2	75.7
50-100	17.6	12.4	16.1	6.08	16.9	30.7	69.2
100-300	17.0	13.8	13.7	5.78	19.2	30.3	69.6
>300	11.7	11.3	15.3	5.57	26.8	29.0	70.9

Mass loss data expressed as first derivative plots (DTG) indicate temperatures at which rapid mass loss occurs and this allows further information to be gathered. These plots are given in Figure 3.17 for the molecular weight fractions. For all fractions there is clearly a free water fraction below 100°C, and then a continuous bleed of volatiles that for all fractions maximises at 400-500°C where as already noted, maximum C-C bond cleavage is expected. However plots for some fractions show that secondary volatile material is present which gives superimposed inflections in DTG plots. The <1.2kD fraction (Figure 3.17 top plot) clearly has secondary material which has maximum volatility at 235°C, plus three distinct more homogeneous materials which volatilise at 271-278, 295, 320°C respectively. The 12-25kD fraction clearly has some additional volatile material that has maximum volatility at or around 402°C, which we have assigned as an aliphatic biopolymer. The 25-50kD fraction also contains some additional material volatilising at around 342°C as well as material volatilising around 452°C. The spent liquor and pregnant liquor organics (Figure 3.16) have DTG curves that, as expected, are similar. The DTG plots

for these fractions appear most similar to the <1.2kD fraction, which comprises a large percentage of the material in these fractions. Figure 3.16 shows that both the pregnant liquor and spent liquor organic fractions had several large mass losses between 230-350°C, due to the evolution of volatile material.

Figure 3.16 Differential Thermal Gravimetric (DTG) analysis plots of Pregnant liquor and Spent liquor Bayer humic fractions.

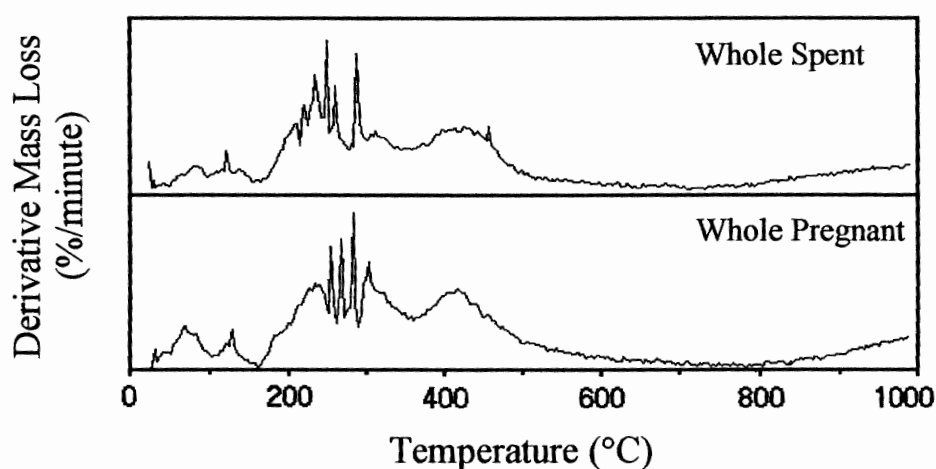
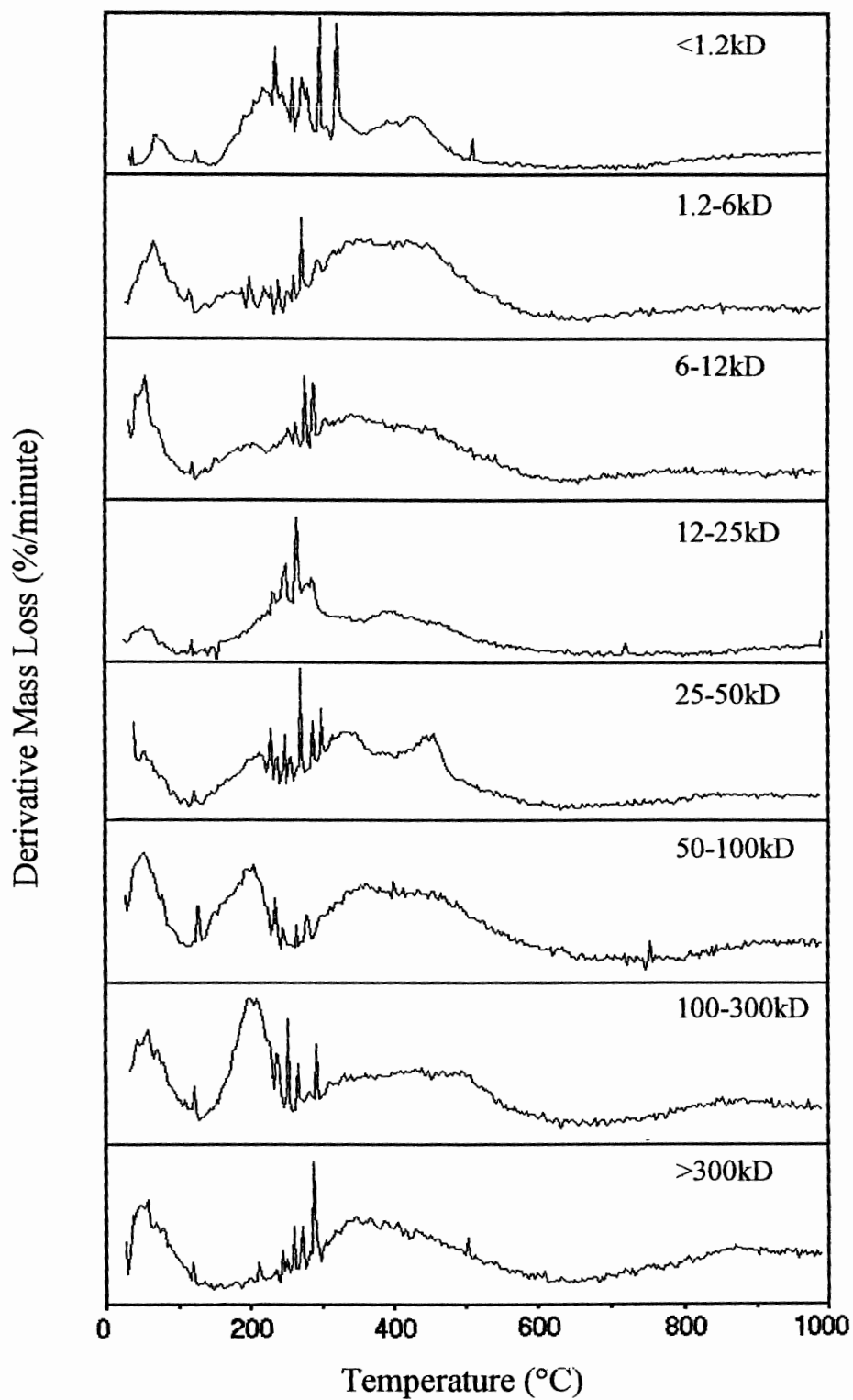


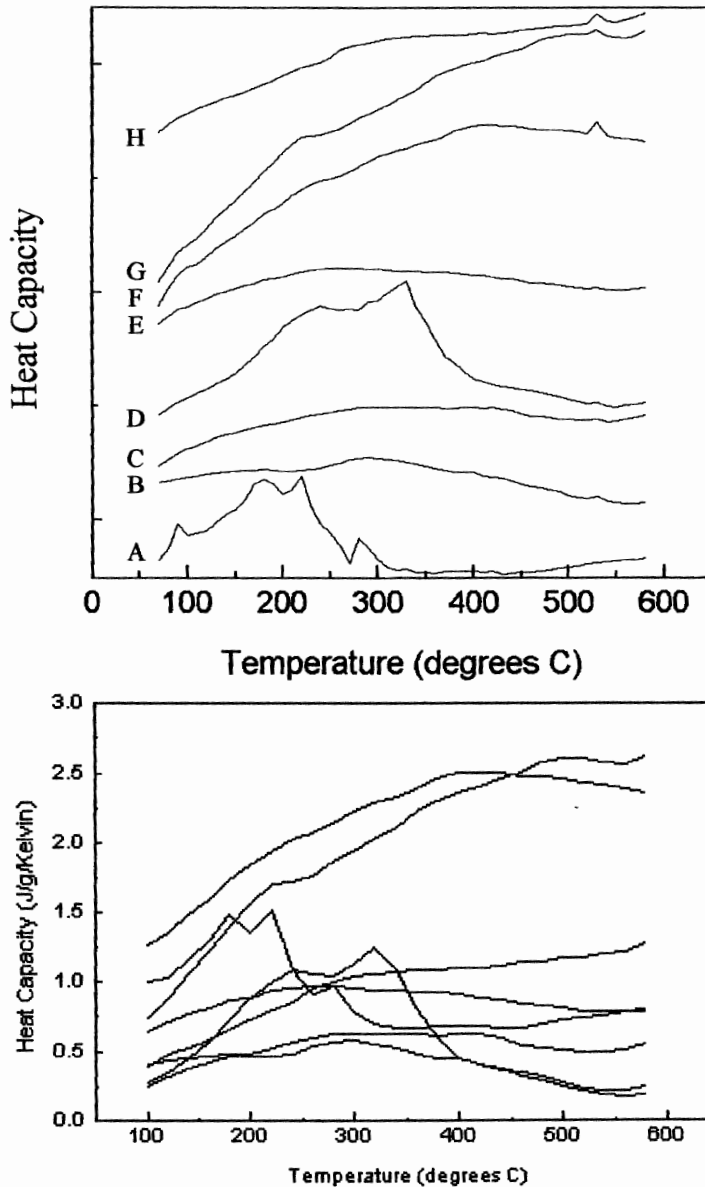
Figure 3.17 Differential Thermal Gravimetric (DTG) analysis plots of Bayer humic fractions.



3.6.1 Heat capacities

Heat capacities can give insights into functional group content, as well as being useful for determining thermal requirements in plant processing. Selected heat capacity data is shown and compared in Figure 3.18.

Figure 3.18 Plot of heat capacity versus temperature for molecular weight fractions of Bayer humic substances. A = <1.2kD; B = 1.2-6kD; C = 6-12kD; D = 12-25kD; E = 25-50kD; F = 50-100kD; G = 100-300kD; H = >300kD (Top figure is a stack plot)



While the heat capacity increases steadily with temperature for the fractions above 50kD, eventually levelling off at high temperatures, the other fractions behave differently. In general heat capacities of carbonaceous materials increase with degree of carbonisation, and with temperature (Van Krevelen, 1993). This reflects the initial loss of carboxylic functionality, followed by aliphatic side chain loss, and then condensation of aromatic rings to form extensive fused polycyclic aryl structures. At low temperatures ($<300^{\circ}\text{C}$) values for coals containing 81.5% carbon are around $1.18 \text{ J g}^{-1} \text{ K}^{-1}$ decreasing to 0.69 for material containing 100% carbon, such as graphite and chars (Van Krevelen, 1993). At 100°C the heat capacity for the 50-100kD fraction (Table 3.8) is around the heat capacity value obtained for coal containing 81.5% carbon, suggesting that this humic fraction contains structures similar to coals of that rank, containing a 2 to 4 aromatic ring structure. These coals, and hence the humic materials, have been modified by the coal formation process to the extent that the aliphatic chains are mainly cleaved and replaced by protons. The values for the 100-300kD fraction are much lower, for example at 100°C the heat capacity is around the value for graphite. The heat capacity value for the $>300\text{kD}$ fraction is lower still, but is supportive of a highly condensed char like structure, not necessarily as ordered as graphite, but containing extended aromatic ring structures. These can contain thousands of carbon atoms (Van Krevelen, 1993).

Figure 3.18 shows the variation in heat capacity with temperature in graphical form. The heat capacity of the 1.2-6kD and 25-50kD fractions (Traces B and E in Figure 3.18), increase much less with temperature than the higher molecular weight fractions discussed above. The different nature of the 12-25kD fraction (Trace D) is also evident. In this fraction there is evidence for at least two types of material that behave in a different thermal manner on top of a third material. This could be the biopolymer described previously. As expected, the lowest molecular weight material ($<1.2\text{kD}$) has wildly changing heat capacities as various molecules are volatilised below 300°C , (Figure 3.18, Trace A) but after this temperature the values are constant.

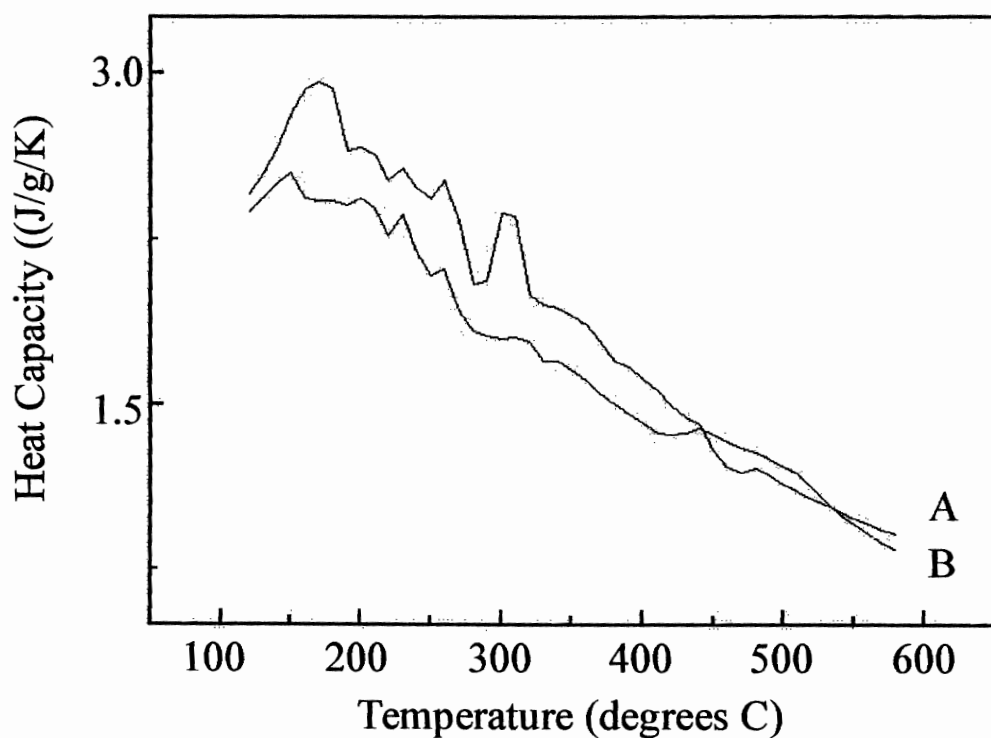
The heat capacities of the organic material obtained from the pregnant and spent liquors (Figure 3.19, Traces A and B) are almost identical. It is noteworthy that the Spent liquor organic material does not have the same heat capacity as the mass

weighted sum of the heat capacities of the various molecular weight fractions obtained from this material. This is due to the fractions having variable water contents, the loss of volatiles, and because the packing of each fraction is unique. This is further support for the model in Figure 3.15.

Table 3.8 Selected heat capacity data for Bayer humic materials (J/g/°C).

Temp (°C)	Whole Spent	Whole Pregnant	<1.2kD	1.2-6kD	6-12kD	12- 25kD	25- 50kD	50- 100kD	100- 300kD	>300kD
100			1.00	0.40	0.25	0.27	0.63	1.26	0.74	0.39
120	2.46	2.37	1.03	0.43	0.31	0.35	0.70	1.35	0.89	0.47
140	2.67	2.50	1.17	0.45	0.37	0.44	0.76	1.48	1.06	0.53
160	2.93	2.43	1.29	0.46	0.41	0.56	0.81	1.59	1.21	0.58
180	2.94	2.42	1.48	0.47	0.46	0.72	0.86	1.72	1.39	0.65
200	2.66	2.44	1.34	0.46	0.48	0.89	0.89	1.82	1.55	0.73
220	2.52	2.26	1.51	0.46	0.53	1.00	0.94	1.94	1.70	0.80
240	2.48	2.19	1.09	0.48	0.56	1.08	0.96	2.02	1.72	0.85
260	2.51	2.11	0.91	0.53	0.58	1.05	0.97	2.0	1.76	0.96
280	2.04	1.83	0.97	0.57	0.61	1.05	0.97	2.18	1.86	1.00
300	2.37	1.79	0.78	0.57	0.62	1.13	0.96	2.24	1.93	1.04
320	2.00	1.78	0.69	0.55	0.61	1.25	0.95	2.29	2.02	1.06
340	1.94	1.70	0.67	0.51	0.62	1.08	0.94	2.34	2.11	1.07
360	1.87	1.61	0.66	0.48	0.61	0.79	0.93	2.38	2.23	1.08
380	1.70	1.51	0.68	0.45	0.61	0.58	0.93	2.46	2.30	1.09
400	1.62	1.41	0.68	0.44	0.62	0.45	0.91	2.50	2.35	1.10
420	1.49	1.36	0.68	0.41	0.61	0.40	0.89	2.51	2.40	1.10
440	1.41	1.39	0.66	0.37	0.59	0.37	0.87	2.50	2.45	1.12
460	1.21	1.33	0.67	0.31	0.54	0.34	0.84	2.48	2.51	1.14
480	1.21	1.28	0.69	0.29	0.53	0.31	0.83	2.47	2.57	1.15
500	1.14	1.21	0.72	0.24	0.51	0.27	0.80	2.46	2.60	1.17
520	1.07	1.12	0.74	0.21	0.50	0.23	0.79	2.43	2.60	1.18
540	1.01	1.00	0.76	0.18	0.49	0.21	0.78	2.41	2.58	1.21
560	0.95	0.91	0.78	0.17	0.51	0.21	0.78	2.39	2.57	1.21
580	0.91	0.83	0.79	0.18	0.55	0.23	0.80	2.36	2.63	1.28

Figure 3.19 Plot of heat capacity versus temperature for Pregnant liquor and Spent liquor Bayer humic substances. A) Pregnant liquor organics; B) Spent liquor organics.



3.6.2 Enthalpies

With pure compounds, enthalpies can assist in identification. However, thermal events are not discrete here, since a variety of materials may be volatilising at the same time or changing phase in some other way. Enthalpy data can still be useful however in understanding molecular structure as shown below. During heating, the area under a plot of difference in power (heat flow, W/g) against temperature is directly proportional to the heat of reaction and is given by

$$\Delta H = K \Delta T \int dt = K.(\text{peak area}) \quad \dots\dots\dots \text{eq 1}$$

where K is a thermal factor to convert area into joules, its value may change with temperature and its value is found by calibration. Values of ΔH for thermal events are listed in Table 3.9.

The <1.2kD fraction displayed a complicated DTG plot (Figure 3.17) due to the evolution of volatile species between 260-350°C. As a result the plot of the heat flow (Figure 3.20, Trace A) for this fraction is equally complicated showing numerous thermal events. Since the ΔH of vaporisation of water is known to be 44 kJ mol⁻¹ (Aylward and Findlay, 1991) it should be possible to determine whether the thermal events at lower temperatures are due to loss of water or not (Berkovich, 1999). As noted, it is difficult to get accurate values for endotherms for individual events but those below 250°C can be summed. Values calculated as kJ mole⁻¹, assuming the vaporised material is water, are also shown in Table 3.10. The <1.2kD fraction produced two separate endotherms at 140°C and 210°C ($\Delta H = 21.69$ kJ mol⁻¹ if calculated as water). This is a lot lower than that expected for water ($\Delta H = 44$ kJ mol⁻¹) (Aylward and Findlay, 1991). Moreover, a further endotherm was observed at about 250°C–272°C (see arrow Figure 3.20), a temperature unlikely to be due to volatilisation of bound water, and an event that has an inappropriate ΔH . Thus there is considerable evidence for volatile material other than water being present.

The heat flow plot (Figure 3.20, Trace B) for the 1.2-6kD was almost identical to the 6-12kD fraction (Figure 3.20, Trace C). Each of these fractions showed endothermic

events due to volatilisation up to 250°C. This is not bond breaking, which for macromolecules of this type is exothermic and occurs at temperatures much higher than 250°C. For example, the most likely bond cleavage event is decarboxylation which normally occurs well above 250°C (Van Krevelen, 1993). Thus this event is due to the evolution of both free and bound water mixed with volatile organics. Since the molecular weight of this material is far in excess of anything that should be volatile at this temperature, this is evidence for the model in Figure 3.15.

There were further small mass losses for the 1.2-6kD and 6-12kD fractions at higher temperatures, with a mass loss accompanied by an exotherm observed at around 392-500°C resulting from the cleavage of aliphatic chains in this temperature region. Similar but less definitive behaviour was observed for the 12-25kD, 25-50kD, 50-100kD and 100-300kD fractions; each of these fractions showed small exothermic events that could not be analysed with the present data.

The >300kD fraction (Figure 3.20, Trace H) showed an endotherm at 140°C due to the evolution of free water. The ΔH value was 44.8 kJ mole⁻¹ identical to that expected for water (Aylward and Findlay, 1991). In this fraction there were no volatile organics but there is clearly bound water boiling above 100°C. We observed similar results for organics obtained from the refinery operating at lower temperature (Wilson *et al*, 1999).

The Modulated Differential Scanning Calorimetry (MDSC) plots for the heat flow during the pyrolysis of the Spent liquor and Pregnant liquor organic fractions were identical and are shown in Figure 3.21.

In summary, the thermal analysis results confirm the presence of a kerogen like material in the 25-50kD fraction and they support the supposition of a host guest model for the Bayer process humic materials.

Table 3.9 Enthalpy changes during thermal treatment of Bayer organic fractions

Fraction	Temperature Range (°C)	ΔH (J/g)
Whole Spent	40-250	188.2
Whole Spent	280-345	-24.51
Whole Spent	375-406	2.31
Whole Spent	406-500	-44.13
Whole Pregnant	40-250	191.1
Whole Pregnant	305-343	-10.11
Whole Pregnant	352-411	10.38
Whole Pregnant	411-500	-20.49
<1.2kD	40-250	286.1
<1.2kD	250-272	12.07
<1.2kD	293-309	1.91
<1.2kD	309-323	2.10
<1.2kD	356-382	2.61
<1.2kD	392-500	-42.13
1.2-6kD	40-250	288.6
1.2-6kD	258-368	18.79
1.2-6kD	420-530	34.29
6-12kD	40-250	409.5
6-12kD	250-287	-6.61
6-12kD	345-455	-23.55
6-12kD	429-524	32.31
12-25kD	40-250	203.7
12-25kD	300-340	-7.81
12-25kD	547-586	3.21
25-50kD	40-250	326.3
25-50kD	250-277	-1.01
25-50kD	400-440	-3.21
50-100kD	40-250	365.9
50-100kD	275-311	-4.89
50-100kD	390-435	-1.63
100-300kD	40-250	1582
100-300kD	250-303	74.35
100-300kD	426-559	20.97
>300kD	40-250	346.7
>300kD	250-321	3.79
>300kD	328-400	3.57
>300kD	448-502	2.72
>300kD	523-531	0.55
>300kD	570-585	0.056

Table 3.10 Enthalpy values for volatiles below 250°C for Bayer organic fractions assuming volatiles are water

Fraction	ΔH (J/g)	Mass loss (%)	ΔH (kJ/mol)
Spent liquor	188.2	20.08	21.77
Pregnant liquor	191.1	17.60	19.56
<1.2kD	286.1	23.76	21.69
1.2-6kD	288.6	16.28	31.94
6-12kD	409.5	22.44	32.87
12-25kD	203.7	18.63	19.70
25-50kD	326.3	19.45	30.23
50-100kD	365.9	22.18	29.73
100-300kD	1581	23.42	28.50
>300kD	346.7	13.94	44.80

Figure 3.20 Modulated Differential Scanning Calorimetry plots for molecular weight fractions. A = <1.2kD; B = 1.2-6kD; C = 6-12kD; D = 12-25kD; E = 25-50kD; F = 50-100kD; G = 100-300kD; H = >300kD. (Top figure is a stack plot)

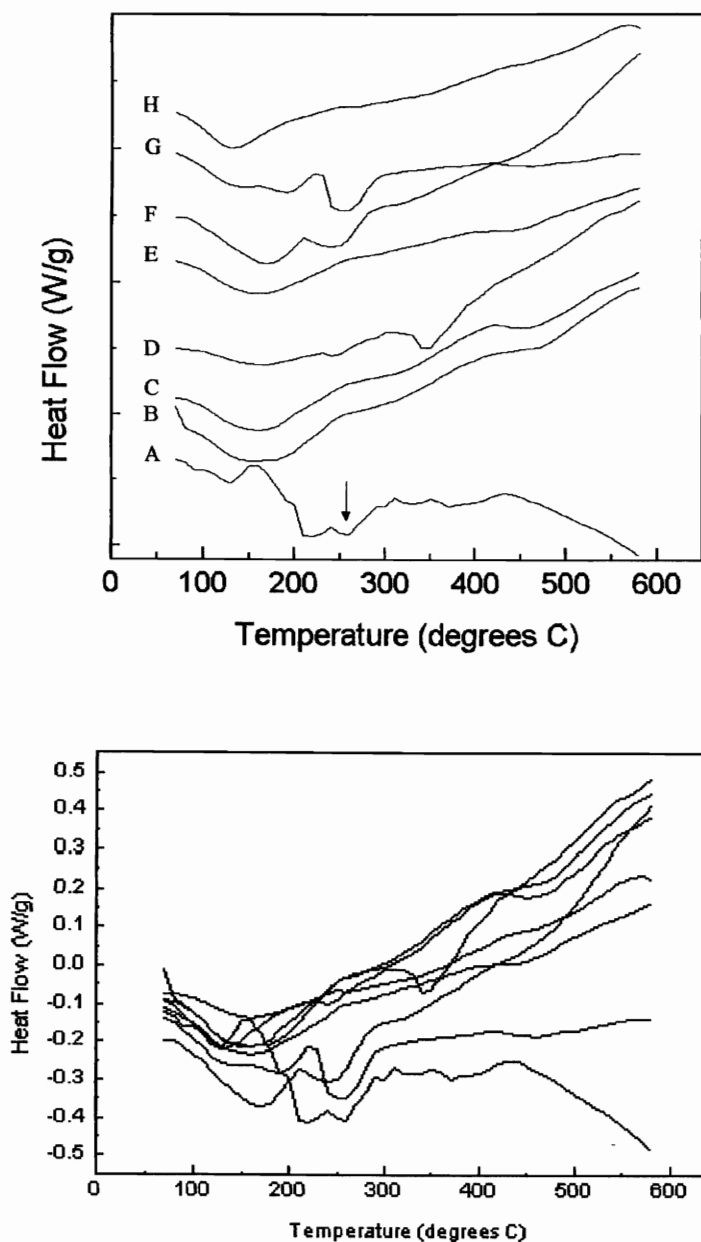
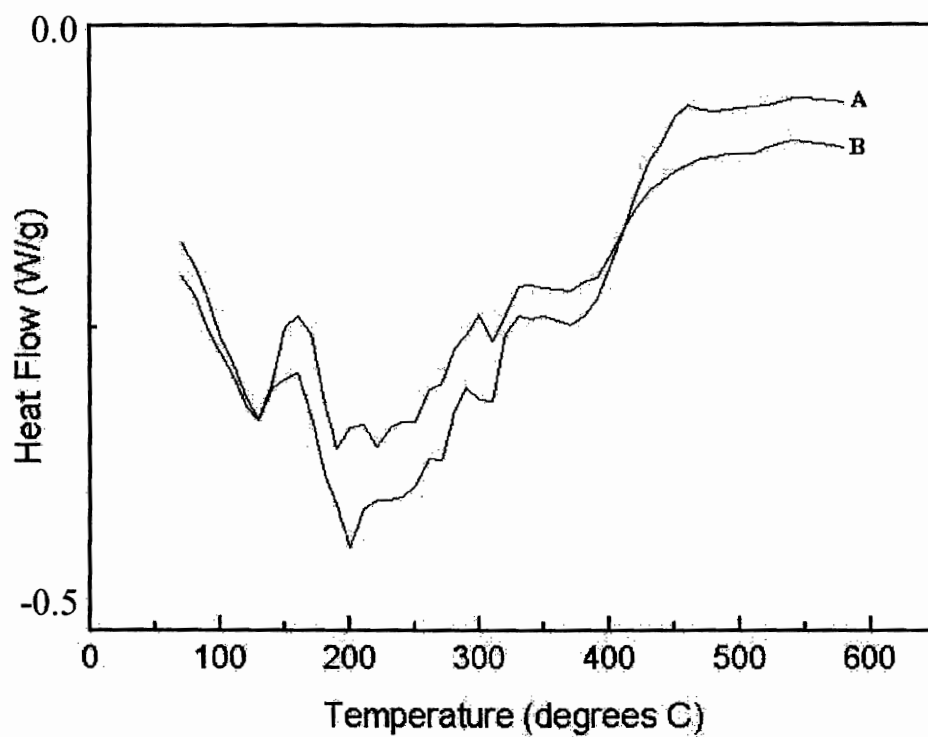


Figure 3.21 Modulated Differential Scanning Calorimetry plots for molecular weight fractions. A = Pregnant liquor organics; B = Spent liquor organics.



3.7 Pyrolysis GC/MS and effects of changing pyrolysis conditions on the nature of organics in pyrolysates.

Pyrolysis products are not necessarily simple functions of structure since they can contain a large number of rearrangement products. However comparison of products still tells us about differences in structure. Compounds identified in the pyrolysates from the molecular weight fractions are listed in Tables 3.11-3.15. The identified compounds include aromatic hydrocarbons, heteroaromatic hydrocarbons, aliphatic hydrocarbons, aromatic nitriles, phenols, alcohols, aromatic carboxylic acids and carboxylic anhydrides, aldehydes, ketones and esters. We have grouped compounds into three classes, with each class correlating with potential usefulness and also occupational health desirability (Clayton and Clayton, 1994; Chemwatch Australia - Material Data Safety Sheets, 1999; National Occupational Health and Safety Commission, 1991). Group 1, includes aromatic hydrocarbons, heteroaromatic hydrocarbons, aromatic nitriles and phenols. Group 2 includes aliphatic hydrocarbons, alcohols, aldehydes and ketones. Group 3 includes aromatic carboxylic acids which are generally non toxic.

Details of the effect of changing the pyrolysis temperature on yields relative to phenol are also given in Tables 3.11-3.15. All results obtained from the pyrolysis-GC/MS experiments are expressed as the mean values obtained from duplicate samples. In terms of experimental measured errors these were not above $\pm 5\%$. At any given temperature the nature of the pyrolysis products varies with molecular weight. In the 400°C pyrolysis results (Table 3.11), the 6-12kD fraction produced the most aromatic hydrocarbons and heteroaromatic hydrocarbons as well as significant amounts of the less toxic materials such as aromatic carboxylic acids, alcohols, aldehydes and ketones. The less toxic materials are also produced by the fractions of lower molecular weight than the 6-12kD fraction. The higher molecular weight material is less volatile, producing little identifiable matter at this temperature. These results are in general agreement with the DTG data. Interestingly, the data from the spent liquor organics and pregnant liquor organics are different, in that more aromatic hydrocarbons are produced from the pregnant liquor. Few of the macromolecules will have weak enough bonds to be pyrolysed at 400°C and the differences probably

represent very small amounts of volatile matter lost through downline processing. We note that the pyrolysis products of the <1.2kD fraction were not identical to the spent or pregnant fractions despite the fact that it contributes by far the major proportion of these materials, suggesting that molecules interact with each other and effect pyrolysis. This supports our structural model in Figure 3.15.

At 425°C weak aliphatic linkages between aromatic units are cleaved and many of the higher molecular weight materials start yielding simple aromatic and heteroaromatic hydrocarbons. The 6-12kD fraction now has reduced amounts of these materials relative to phenol (Table 3.12), which suggests they can be involved in recombination reactions at higher temperatures. All fractions start yielding significant amounts of aldehydes and ketones, and the <1.2kD fraction produces large amounts of hydroxybenzoic acids. As the temperature is raised further to 450°C (Table 3.13) volatiles from the 25-50kD fraction become important, particularly alcohols and aliphatic hydrocarbons. At this temperature all fractions show a range of volatiles, and nitriles common for kerogens are particularly important in the 12-25kD fraction (Evans *et al.*, 1985), although it should be noted that they are also important in the 25-50kD fraction. However simple aromatics are still not observed from the <1.2kD fraction. The behaviour of spent liquor and pregnant liquor organic fractions are still unlike but they are becoming similar and this is more so at 475°C and 500°C (Tables 3.14 and 3.15). By 500°C all fractions contain significant quantities of all materials apart from aliphatic hydrocarbons which only dominate the 25-50kD fraction and to a lesser extent the 12-25kD fraction.

3.8 Conclusions on the structures of molecular weight fractions of Bayer humic substances

In summary it appears that if molecular weight fractions of Bayer liquor organics can be obtained, then during processing by pyrolysis different products can be isolated. The pyrolysis data is in agreement with all the other suppositions discussed previously. The <1.2kD fraction appears to yield mainly hydroxybenzene carboxylic acids and its behaviour is much like that predictable of highly oxidised humic acids

that are found in the group of soils called podzols which are described in the literature (Hatcher *et al.*, 1989). The 12-25kD fraction appeared to be somewhat special and resembled material that is more akin to oxidised kerogen. The highest molecular weight material is more coal or char like and behaves accordingly on thermal treatment.

As already noted, these fractions from a high temperature Bayer refinery appear to be different in structure to those obtained from refineries operating at lower temperatures (Wilson *et al.*, 1999). Not unexpectedly, the high temperature material has a lower average molecular weight because many of the larger molecules are thermally degraded to small molecular weight species, these highly degraded products with molecular weights <1.2kD appear structurally similar for both refineries. However, some small molecular weight material from the high temperature refinery was observed to form molecular aggregates which behave during dialysis as if they have larger molecular weights, these aggregates also effect the water holding capacity of the humic materials. This is discussed further in the following section.

An important industrial consideration is that because the organic fractions have different structures, the fractions will have different reactivities and possibly different poisoning activities in sodium oxalate and aluminium hydroxide precipitation in the Bayer process. The poisoning effects of these fractions are detailed later in this thesis (Section 3.13). Moreover under different processing conditions, the poisoning activity could differ from one refinery to another for each fraction. The >300kD fraction organic matter is similar under both refinery conditions and would be expected to behave similarly. Similar behaviour might also be expected for the low molecular weight fractions (e.g <1.2kD). However the 12-25kD fraction and 25-50kD fractions are unique and may therefore be processing temperature dependant and thus plant specific.

[illegible]

Table 3.11 continued

4,7-Dimethyl-1,3-isobenzofurandione								51	42	97
5,6-Dimethyl-1,3-isobenzofurandione								24	23	60
Benzophenone		70		72		124				
Fluoren-9-one	9									52
GROUP 3										
AROMATIC CARBOXYLIC ACIDS AND ANHYDRIDES										
Benzoic acid				86	228	391	261		78	128
2-Methylbenzoic acid					5				25	24
3-Methylbenzoic acid									14	69
4-Methylbenzoic acid									23	
Phthalic anhydride				1161	72	489	138	42	29	24
2,4-Dimethylbenzoic acid									9	19
2,5-Dimethylbenzoic acid									14	
2,3-Dimethylbenzoic acid										40
2,6-Dimethylbenzoic acid									12	
4-Methyl-1,2-benzenecarboxylic acid								66	34	25
3-Hydroxybenzoic acid			534		11				36	79
2-Hydroxybenzoic acid					9			50		47
4-Hydroxybenzoic acid								23	189	
4-Methoxybenzoic acid			119							
3-Hydroxy-4-methylbenzoic acid									102	
Naphthalic anhydride	5									

NB. Values are averages obtained from duplicate runs. Typical errors were less than +/- 5%.

Table 3.12 Relative yields of humic pyrolysis products from different molecular weight fractions at 425°C

[illegible]

Table 3.12 continued

Group 3										
Aromatic carboxylic acids and anhydrides										
Benzoic acid		24		115	58	325	169	105		
2-Methylbenzoic acid					4					
3-Methylbenzoic acid					16	98		72		
Phthalic anhydride		79		979	7	309	219	131		
4-Methyl-1,2-benzenecarboxylic acid		8						210		
4-Hydroxybenzoic acid								1352		
3-Hydroxy-4-methylbenzoic acid								192		

NB. Values are averages obtained from duplicate runs. Typical errors were less than +/- 5%.

Table 3.13 Relative yields of humic pyrolysis products from different molecular weight fractions at 450°C

Compound	>300 kD	100 – 300 kD	50 – 100 kD	25 – 50 kD	12 – 25 kD	6 – 12 kD	1.2 – 6 kD	<1.2 kD	Spent	Pregnant
Group 1										
Aromatic hydrocarbons										
Pyridine	44									
Benzene	47	104	42		9	28	47			24
Toluene	15	27	35	369		72	39			11
p-Xylene		11	13				28			
Styrene		9	9		5					
Dimethylbenzenes							21			
Trimethylbenzenes						110				
Naphthalene	27	29	8		15	67	32		51	8
1,3-diethylbenzene										4
Biphenyl	21	24							6	7
Heteroaromatic hydrocarbons										
2-Methylfuran			36		1		44		8	
2,4-Dimethylfuran	31	43	30		6		21		21	
2,5-Dihydropyrrole							30			
3,4-Dihydropyran		19			12					
Dibenzofuran					3		18			16
5-Methoxy-2-methyl-1H-indole							27	99		
Aromatic nitriles										
Benzonitrile	15	50	70	218	281	76	73		18	
1,3-Benzenecarbonitrile					14	72	55			
1,2-Benzenecarbonitrile			12							
4-Hydroxybenzonitrile					10	65	40	51	19	
Phenols										
Phenol	100	100	100	100	100	100	100	100	100	100
2-Methylphenol	8								11	10
3-Methylphenol					4		22		12	8
2-Naphthalenol								125		
Group 2										
Aliphatic hydrocarbons										
5-Methylhexene				230						
3,4-Dimethylhexene			43							
4-Octene				2		35	31			
2-Octene				231			19			
Alcohols										
C8 alcohol				281						
Iso-octanol				95						
6-Methylheptanol				343	3					
1-Octanol				558						
2-Furanmethanol				171	2				5	
Aldehydes and ketones										
2(3H)-furanone		6								

Table 3.13 continued

5-Methyl-2-furancarboxaldehyde		14	7				28		10	
3,4-Dimethyl-2,5-furandione							24			
2-Coumaranone					2		18	63	10	4
4-Methyl-1,3-isobenzofurandione							21	61	25	
4-hydroxyphenyl-1-pentanone								23		
1H-isoindole-1,3(2H)-dione		21	41	965		78	73	87		
4,7-Dimethyl-1,3-isobenzofurandione								170	32	69
5,6-Dimethyl-1,3-isobenzofurandione								59	50	30
Fluoren-9-one	7						101		11	69
Group 3										
Aromatic carboxylic acids and anhydrides										
Benzoic acid		17			56	340	241	83	51	30
2-Methylbenzoic acid					4				31	
3-Methylbenzoic acid								41	19	5
4-Methylbenzoic acid									27	
Phthalic anhydride		16		1125	8	283	140	67	34	
2,4-Dimethylbenzoic acid									8	
2,5-Dimethylbenzoic acid									15	
4-Methyl-1,2-benzenecarboxylic acid							33	100	37	
3-Hydroxybenzoic acid					9					
1-Hydroxybenzoic acid					7					
3-Ethoxybenzoic acid										106
4-Hydroxybenzoic acid									139	16
3-Hydroxy-4-methylbenzoic acid								287	35	
2-Naphthalenecarboxylic acid					7					
1,2,4-Benzenetricarboxylic acid									30	

NB. Values are averages obtained from duplicate runs. Typical errors were less than +/- 5%.

Table 3.14 Relative yields of humic pyrolysis products from different molecular weight fractions at 475°C

Compound	>300 kD	100 – 300 kD	50 – 100 kD	25 – 50 kD	12 – 25 kD	6 – 12 kD	1.2 – 6 kD	<1.2 kD	Spent	Pregnant
Group 1										
Aromatic hydrocarbons										
Benzene	63	112	76	196	13	38	26		40	18
Toluene	15	25	61	328	5		16		27	7
p-Xylene		9	25	110		21	12		17	
Styrene		4					16		27	
Dimethylbenzenes		4	26	106	2	25				
Trimethylbenzenes						60	31		47	
Naphthalene	30	32	28		27	68	35		69	13
1-Methylnaphthalene							11		9	5
2-Methylnaphthalene			16		2					
1,3-Diethylbenzene										12
Biphenyl	26	29			3		10		9	8
Anthracene	5						15			
Phenanthrene							8			
Heteroaromatic hydrocarbons										
Pyridine										14
2-Methylfuran		16				38	27			
3-Methylfuran			52							
2,4-Dimethylfuran		22	19				14			
Dibenzofuran	6				6		9			
5-Methoxy-2-methyl-1H-indole							9	109	37	
Aromatic nitriles										
Benzonitrile	12	52	145	161	5	71	75	77	20	
1,3-Benzenecarbonitrile			15		25		11			
1,2-Benzenecarbonitrile		85	37				14			
4-Hydroxybenzonitrile					15	84	24	70	26	
Naphthalenecarbonitrile							11			
Phenols										
Phenol	100	100	100	100	100	100	100	100	100	100
2-Methylphenol	5				7		19		19	13
3-Methylphenol	4	7	17	35	9	28	20	25	20	13
2-Naphthalenol								61		
Group 2										
Aliphatic hydrocarbons										
2,4-Hexadiene				100						
Cyclohexadiene							15			
5-Methylhexene		5		164		4	25			
3,5-Dimethylhexene			43	181						
3,4-Dimethylhexene						76	13			
3-Octene			28							
Trimethylcyclopentane				174		30	23			

Table 3.14 continued

4-Octene				243		38	58			
2-Octene				275		25	7			
Alcohols										
Iso-octanol				37						
6-Methylheptanol				148						
1-Octanol		9	16	229						
5-Methylheptanol				73						
Aldehydes and ketones										
5-Ethyl-2(5H)-furanone				208		32				
2-Furancarboxaldehyde					6	41			21	
5-Methyl-2-furancarboxaldehyde									14	6
3,4-Dimethyl-2,5-furandione							15			
2-Coumaranone							12	50	15	12
3,4-Dihydro-2H-benzopyran-2-one										5
3-Hydroxyphenyl-1-ethanone								55	16	
4-Methyl-1,3-isobenzofurandione							11	50	24	
4-Hydroxyphenyl-1-pentanone								25		7
1H-isoidole-1,3(2H)-dione		30	130	587	12	79	49	85	15	
4,7-Dimethyl-1,3-isobenzofurandione							13	178	37	45
5,6-Dimethyl-1,3-isobenzofurandione								75	32	18
Fluoren-9-one	6						19	86	62	13
Group 3										
Aromatic carboxylic acids and anhydrides										
Benzoic acid		19	23	94	101	97	119	87	69	61
Benzoic acid ammonium salt							39			
2-Methylbenzoic acid					7	42	12		42	12
3-Methylbenzoic acid						25		98	28	9
4-Methylbenzoic acid						75			26	10
Phthalic anhydride		22		7	6	226	63	59	31	
2,4-Dimethylbenzoic acid									12	14
4-Methyl-1,2-benzenecarboxylic acid							20	95	35	6
2-Hydroxybenzoic acid					14					66
3-Ethoxybenzoic acid								427		
4-Hydroxybenzoic acid									120	23
3-Methoxybenzoic acid										20
3-Hydroxy-4-methylbenzoic acid									39	
Dimethoxybenzaldehyde							12			
2-Naphthalenecarboxylic acid					22	108			32	

NB. Values are averages obtained from duplicate runs. Typical errors were less than +/- 5%.

Table 3.15 Relative yields of humic pyrolysis products from different molecular weight fractions at 500°C

Compound	>300 kD	100 – 300 kD	50 – 100 kD	25 – 50 kD	12 – 25 kD	6 – 12 kD	1.2 – 6 kD	<1.2 kD	Spent	Pregnant
Group 1										
Aromatic hydrocarbons										
Benzene	167	125	94	154	11	122	58	21	25	35
Toluene	89	30	68	82			25		15	14
p-Xylene		8	26	66		126	11		8	
Styrene	38		16				7			
Dimethylbenzenes	38	11	16	8			7		13	
Trimethylbenzenes			30				19			
Naphthalene	49	36	8		9	259	41	11	11	15
1-Methylnaphthalene									10	5
2-Methylnaphthalene			10		2					
1,3-Diethylbenzene										6
Biphenyl	50	29			5	189	8		9	13
Anthracene				151						4
Heteroaromatic hydrocarbons										
Pyridine									18	10
2-Methylfuran		8	41	92	6	136				
2,4-Dimethylfuran			21		9	212				
Dibenzofuran					5				38	10
5-Methoxy-2-methyl-1H-indole						178		73		
Aromatic nitriles										
Benzonitrile		54	161	270	37		72	45	26	9
1,3-Benzenecarbonitrile			10				12			
1,2-Benzenecarbonitrile			19							
4-Hydroxybenzonitrile							37	59	22	
Phenols										
Phenol	100	100	100	100	100	100	100	100	100	100
2-Methylphenol		5						13	15	15
3-Methylphenol		9	14	37	4		16	18	16	12
2-Naphthalenol								34		
Group 2										
Aliphatic hydrocarbons										
2,4-Hexadiene							9			
5-Methylhexene		6		244						
3,5-Dimethylhexene			27							
3,4-Dimethylhexene			74	181						
Trimethylcyclopentane				141						
4-Octene				173						
2-Octene				118						
Alcohols										
Isooctanol				38						

Table 3.15 continued

6-Methylheptanol				122						
1-Octanol				202						
2-Furanmethanol					24	111				
Aldehydes and ketones										
5-Ethyl-2(5H)-furanone				163						
5-Methyl-2-furancarboxaldehyde			13			141				
2-Coumerone								36	10	4
3,4-Dihydro-2H-benzopyran-2-one								59	9	
4-Methyl-1,3-isobenzofurandione							10	46	14	
4-Hydroxyphenol-1-pentanone									9	
2-Hydroxyphenyl-1-ethanone								18		
1H-isoindeole-1,3(2H)-dione		12	27	448	4		36	76	18	
4,7-Dimethyl-1,3-isobenzofurandione						182		105	24	10
5,6-Dimethyl-1,3-isobenzofurandione								40	15	
Fluoren-9-one		6				341		49	22	10
Group 3										
Aromatic carboxylic acids and anhydrides										
Benzoic acid		12	7	112	197	391	128	83	67	43
2-Methylbenzoic acid					4			24	13	4
3-Methylbenzoic acid					37			41	12	7
4-Methylbenzoic acid									16	9
Phthalic anhydride				503	57	489	31	58	20	3
2,4-Dimethylbenzoic acid									11	
4-Methyl-1,2-benzenecarboxylic acid								75	18	
3-Hydroxybenzoic acid	174				4			910	222	14
2-Hydroxybenzoic acid	46									
3-Ethoxybenzoic acid	53									
4-Hydroxybenzoic acid					15					7
3-Methoxybenzoic acid										22
3-Hydroxy-4-methylbenzoic acid						68		152	47	

NB. Values are averages obtained from duplicate runs. Typical errors were less than +/- 5%.

PART C

Host-Guest interactions in humic materials

This section examines the behaviour of the Bayer organic fractions during analysis by several analytical techniques. The organic fractions appear to form host-guest complexes, a phenomenon not previously observed in humic substances. The existence of such complexes may help to explain the behaviour of humic materials observed by other researchers, these complexes may also be the means by which organic pollutants are transported in the environment.

3.9 Nuclear Magnetic Resonance spectroscopy (NMR) characterisation of Bayer humic materials

3.9.1 ^1H NMR characterisation of Bayer humic materials

Table 3.16 shows NMR data for the Bayer molecular weight fractions. Integration of the various spectral areas in the ^{13}C and ^1H spectra allows the fraction of carbons which are aromatic (f_a) and the fraction of protons which are aromatic (H_{Ar}) to be calculated. From this, the aromatic ring substitution parameter $H_{Ar}H/f_aC$ can be calculated where H/C is the hydrogen to carbon mole ratio obtained from elemental data.

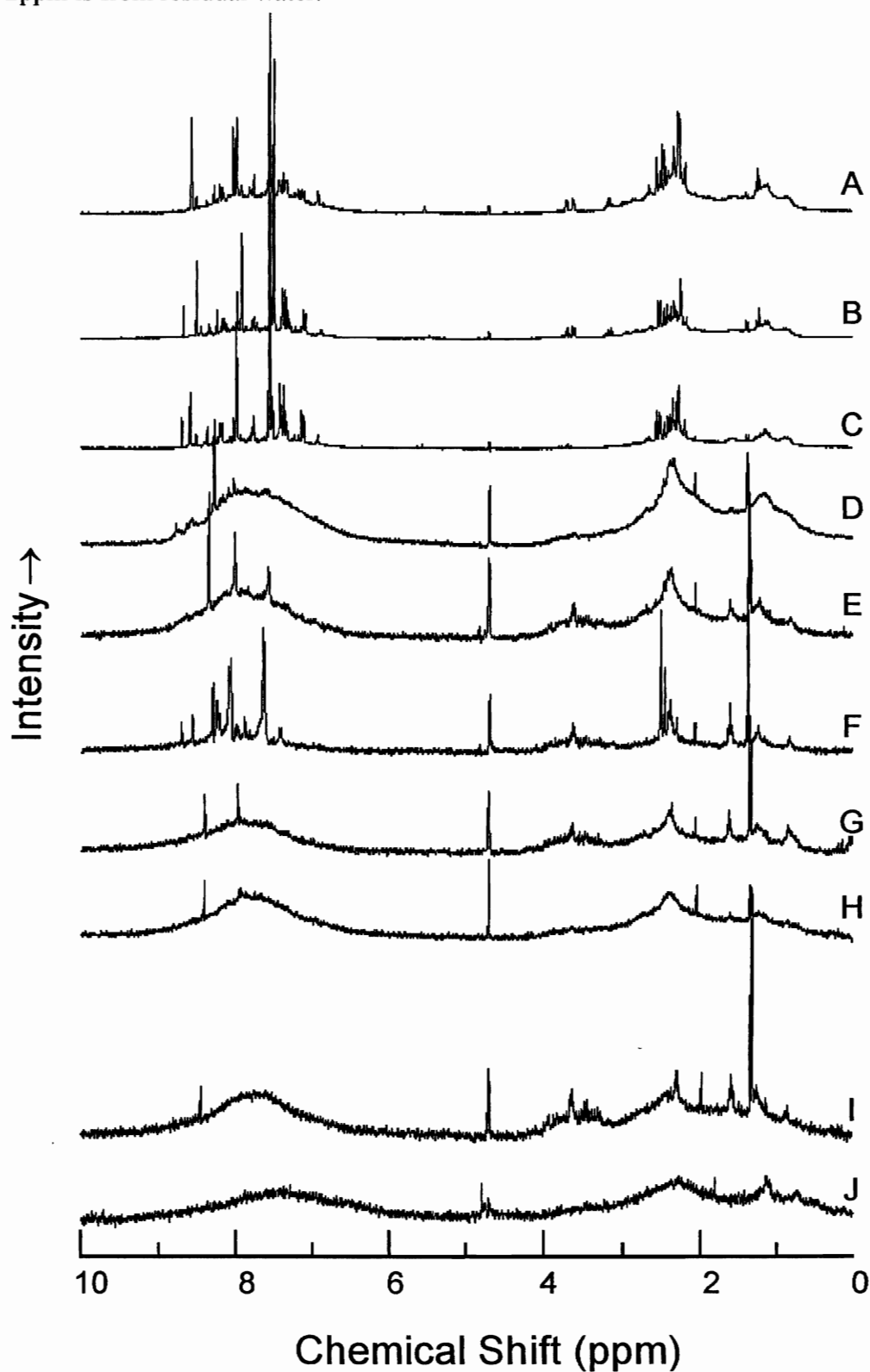
Table 3.16 Estimates of proportions (%) of different carbon types in different molecular weight fractions of Bayer humic substances as measured by solid state ^{13}C NMR and ^1H solution "WATERGATE" NMR.

Fraction No.	Molecular weight fraction (Daltons)	C-Alkyl	O-Alkyl	Aromatic (100f _a)	Carboxyl	Carbonyl	H _{Ar}	H _{Ar} /f _a	H _{Ar} H/f _a C ^a
	Chemical shift (ppm) →	0-50	50-100	100-160	160-190	190-220	6-9		
1	Spent	24	2	60	13	1	0.46	0.76	0.61
2	Pregnant	24	2	56	17	1	0.41	0.73	0.57
3	<1200	21	2	53	23	1	0.50	0.94	0.94
4	1200-6000	22	4	56	17	1	0.43	0.77	0.72
5	6000-12000	19	11	57	12	1	0.46	0.81	0.75
6	12-25000	13	7	63	16	1	0.52	0.83	0.67
7	25-50000	11	8	58	21	1	0.43	0.74	0.86
8	50-100000	15	1	66	17	1	0.49	0.73	0.72
9	100-300000	23	7	59	10	1	0.41	0.70	0.82
10	>300000	26	7	58	8	1	0.46	0.78	0.65

a) Calculated from H/C elemental ratio Table 3.5 and previous column.

There were no systematic trends in the NMR data (Table 3.16) as were observed on analysis of other molecular weight fractionated humic acids (Sihombing *et al.*, 1996; Wilson *et al.*, 1999). A possible reason for these differences could be the severe oxidising conditions. To account for non systematic trends in f_a , it could be argued that some aliphatic material in each fraction is more stable than in others and therefore not as readily oxidised. However examination of the ^1H NMR data in more detail (Figure 3.22) shows another possible cause for variation, namely that each fraction can hold different numbers of discrete small molecular weight molecules. Normally humic materials show only broad resonances in ^1H NMR spectra due to the large number of environments for the protons in substances of such large molecular weight, however the spectra show discrete individual resonances. Discrete resonances might have been expected for material of molecular weight $<1.2\text{kD}$, but not in larger materials. However the results show that discrete resonances are seen in all fractions, not just in the lowest molecular weight fraction ($<1.2\text{kD}$). This shows that small molecules are present in all fractions. In effect, the membranes are not separating some small molecules into the lowest ($<1.2\text{kD}$) molecular weight fraction. We are convinced that the experimental work was done properly because the membranes properly separate other materials. Hence there must be some other explanation for this anomaly.

Figure 3.22 ^1H NMR spectra of Bayer Humic Materials (total spectrum). A) Pregnant liquor organics; B) Spent liquor organics; C) <1.2kD; D) 1.2-6kD; E) 6-12kD; F) 12-25kD; G) 25-50kD; H) 50-100kD; I) 100-300kD; J) >300kD. The resonance at 4.72ppm is from residual water.



In Figures 3.23 and 3.24, ^1H NMR spectra have been expanded to show detail. Discrete lines are made more visible by reducing the line broadening to 0.5 Hz. Table 3.17 lists the discrete resonances observed. Formate, lactate and other small molecular weight compounds previously identified in Bayer liquors are observed (Wilson *et al.*, 1988; Atkins and Grocott, 1988; Lever, 1978). It is difficult to assign the compounds present based on simple ^1H NMR evidence alone, however further analysis is possible with two-dimensional techniques (see below).

Several discrete resonances were observed in the aliphatic region (Figure 3.24) between 0.8 and 1.4 ppm. Some of the fractions displayed a triplet at 1.27 ppm, derived from methylene units in aliphatic chains with non-equivalent adjacent CH_2 units. A strong doublet at 1.36 ppm from protons on methyl groups on branched aliphatic chains, or methylene protons located β -to alkene double bonds, was also observed in several of the fractions. Alkane and unsaturated fatty acid aliphatic chains would produce these resonances.

The region of the spectra between 1.8-3.3 ppm is highly significant as it represents approximately 30% of the protons in each of the samples. This shows that many of the aliphatic protons are located near an electronegative group or are attached to functional groups located on an aromatic ring. Protons on carbons adjacent to carboxylic groups, or other oxygen containing groups, would produce resonances in this region. The discrete resonances seen in this region may therefore be derived from the fatty acid type compounds present in the fractions (identified in Section 3.10). Aliphatic substituents present on aromatic rings would also produce resonances in this region. Several strong resonances were present in the region between 1.9-2.2 ppm; these could be attributed to methylene groups located α to double bonds (Ellis *et al.*, 1999; Wilson, 1988).

The region between 3.3-4.2 ppm contains resonances from protons on carbon atoms that are directly attached to oxygen or nitrogen heteroatoms. The water resonance is observed in this region located at 4.72 ppm. Two distinct multiplet peaks were observed in several of the Bayer organic fractions, centred at 3.65 and 3.74 ppm resulting from ether linkages in the humic macromolecules or from furan type

molecules. The protons on tetrahydrofurans, which are formed in the Bayer process from the rearrangement of carbohydrates, would be seen in this region. Tetrahydrofuran-type compounds, which are possible poisons in the Bayer process (Wilson *et al.*, 1998) are significant components of the Bayer organic fractions as they were detected by pyrolysis GC/MS studies in large amounts (Section 3.7).

The aromatic region of the ^1H NMR spectra (Figure 3.23) extends from 6.0-8.8 ppm and was observed for each Bayer organic fractions as a broad hump with numerous sharp resonances superimposed. The resonances observed between 6.9-8.0 ppm result from unhindered aromatic protons. All fractions, except for the >300kD fraction, were seen to have several resolved resonances between 8.0-8.8 ppm resulting from sterically hindered aromatic protons, protons on N-heteroatoms, and formate. The aromatic region accounted for the highest proportion of protons for all fractions, with up to 52% of the protons being aromatic. This result supports findings by IR and ^{13}C NMR which indicated that the Bayer organic fractions were highly aromatic (Section 3.5).

The ^1H NMR spectrum of all fractions of molecular weight greater than 25kD showed few discrete resonances in the aromatic region. This is a result of these fractions containing very few small aromatic molecules in molecular aggregates. Instead these fractions form molecular aggregates with alkanes and aliphatic fatty acids. Discrete aromatic resonances were not seen for the >300kD fraction (Figure 3.23, Trace J), indicating that there were no small aromatic compounds in this fraction. Figure 3.24 (Trace J) and Table 3.17 (Column J) display that this fraction produces discrete resonances only in the aliphatic region of the spectrum due to the presence of small aliphatic compounds.

Figure 3.23 ^1H NMR spectrum of Bayer Humic Materials - aromatic region. A) Pregnant liquor organics; B) Spent liquor organics; C) <1.2kD; D) 1.2-6kD; E) 6-12kD; F) 12-25kD; G) 25-50kD; H) 50-100kD; I) 100-300kD; J) >300kD.

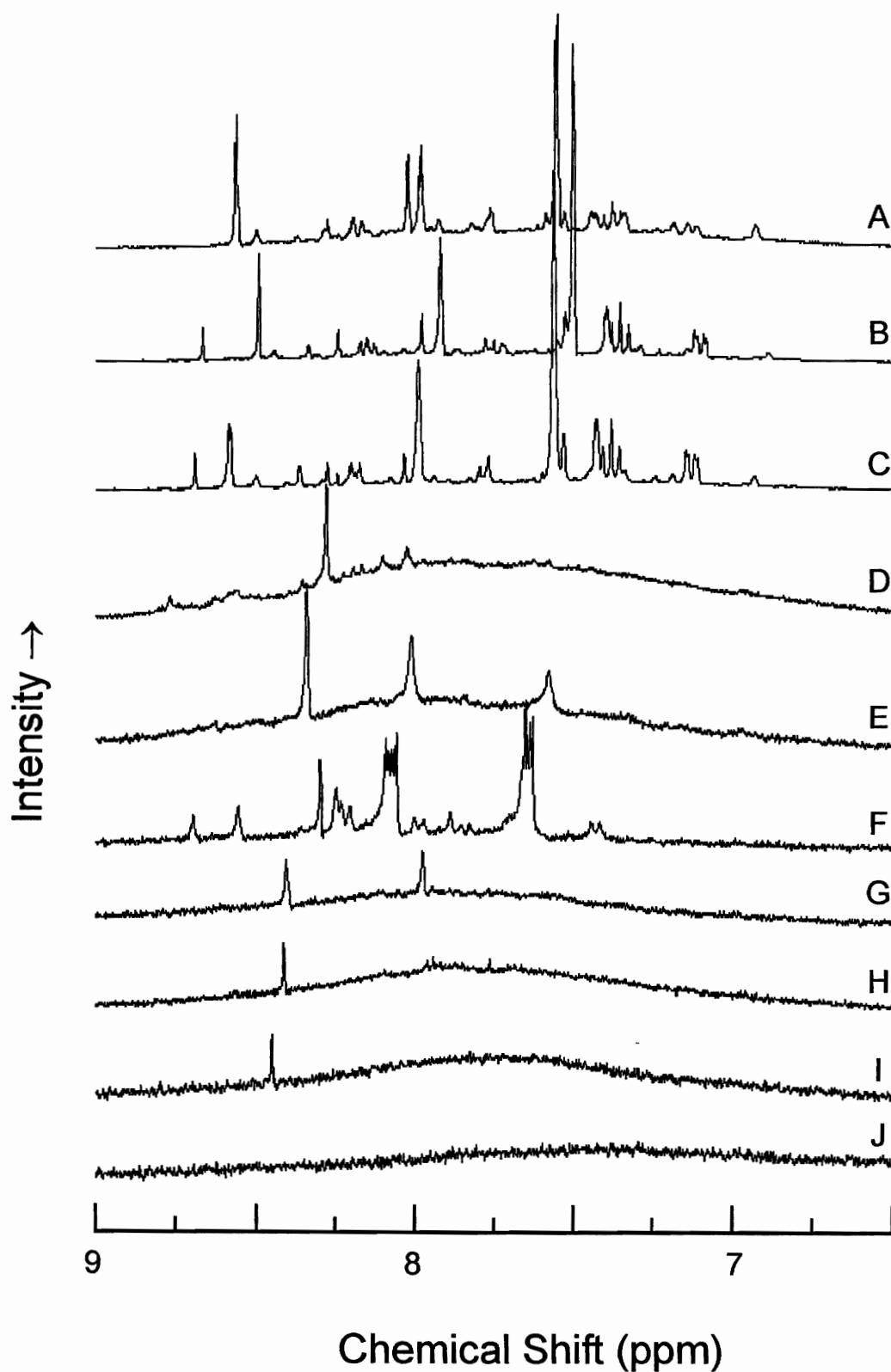


Figure 3.24 ^1H NMR spectrum of Bayer Humic Materials - aliphatic region. A) Pregnant liquor organics; B) Spent liquor organics; C) <1.2kD; D) 1.2-6kD; E) 6-12kD; F) 12-25kD; G) 25-50kD; H) 50-100kD; I) 100-300kD; J) >300kD.

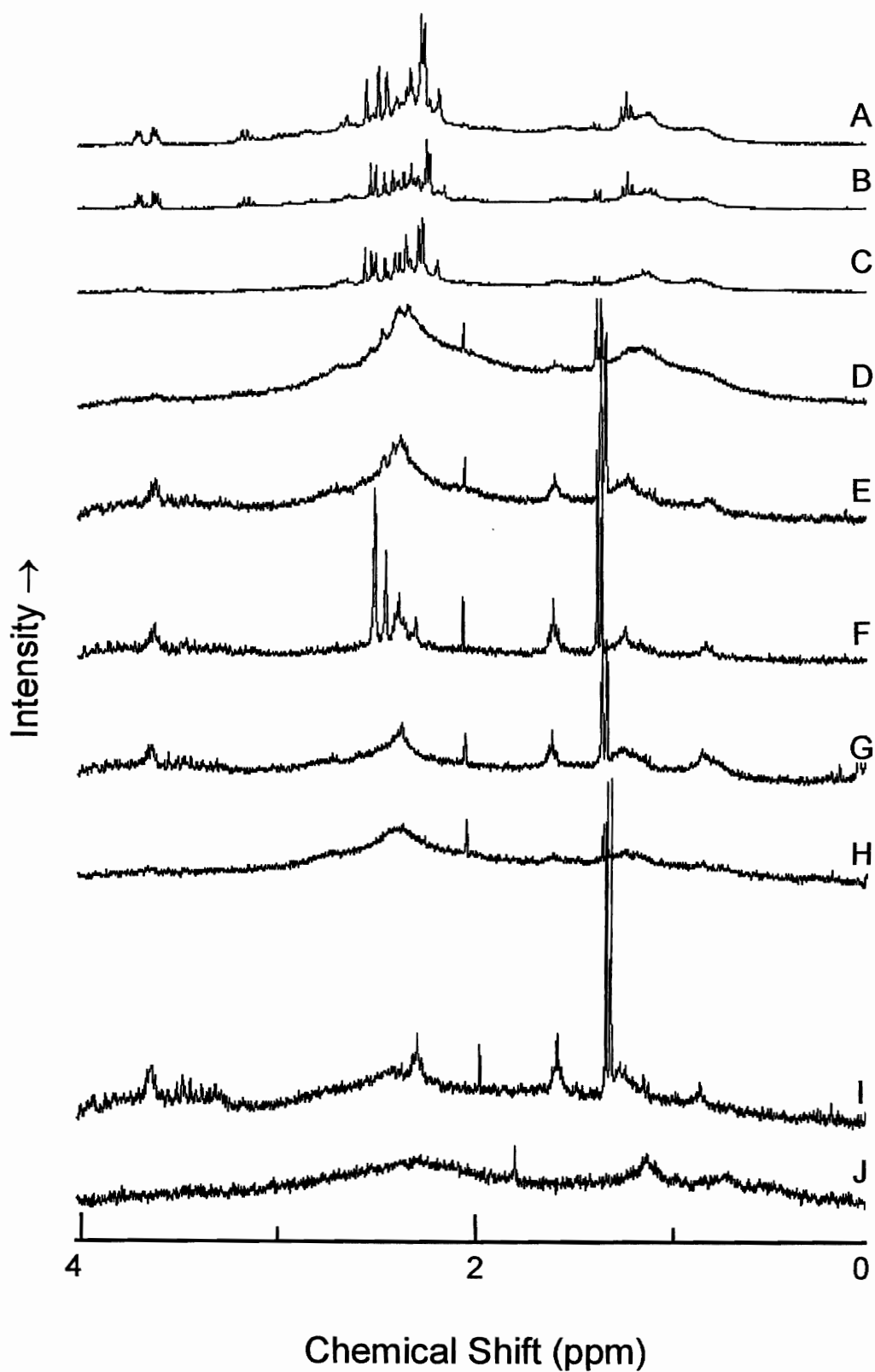


Table 3.17 Chemical shifts and assignments of individual resonances in molecular weight fractions of Bayer humic materials.

Chemical shift (ppm)	Multiplicity (J Hz)	Assignment	Organic Fractions ^b									
			A	B	C	D	E	F	G	H	I	J
0.86		Terminal methyl		✓	✓			✓				
0.90				✓	✓							
0.92				✓	✓							
0.94			✓	✓	✓							
0.97				✓	✓							
1.18			✓	✓				✓				
1.20								✓				
1.27	t (7.4)	Methyl lactate in	✓	✓				✓			✓	
1.36	d (7.1)		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
1.59			✓	✓		✓	✓	✓	✓		✓	
1.99	s		✓	✓		✓	✓	✓			✓	
2.10	q(7.6)		✓	✓		✓	✓	✓	✓	✓		
2.20			✓	✓	✓							
2.26			✓	✓	✓			✓	✓			
2.28			✓	✓	✓							
2.29			✓	✓	✓			✓				
2.30	t (6.7)										✓	
2.31			✓	✓		✓	✓					
2.32			✓	✓	✓							
2.34			✓	✓	✓							
2.36			✓	✓		✓	✓					
2.38			✓	✓	✓					✓		
2.39			✓	✓	✓			✓				
2.40	t (6.8)		✓	✓	✓			✓	✓			
2.42			✓	✓								
2.43			✓	✓								
2.45			✓	✓								
2.49			✓	✓	✓	✓	✓	✓				
2.53			✓	✓	✓							
2.56			✓	✓	✓							
2.60								✓				
2.67	m		✓	✓	✓							
2.88	m		✓	✓	✓							
3.20	t (7.6)		✓	✓								
3.65	m		✓	✓	✓		✓	✓	✓		✓	✓
3.74	m		✓	✓	✓							
4.10								✓				
6.90			✓	✓	✓							
7.09	m		✓	✓	✓							
7.10			✓	✓	✓							
7.11			✓	✓	✓							
7.13			✓	✓	✓							
7.13			✓	✓	✓							
7.16			✓	✓	✓							
7.24			✓	✓	✓							
7.33			✓	✓	✓							
7.35			✓	✓	✓							
7.38			✓	✓	✓							
7.39			✓	✓	✓			✓				
7.40			✓	✓	✓							

Table 3.17 continued

Chemical shift (ppm)	Multiplicity	Assignment	Organic Fractions ^b									
			A	B	C	D	E	F	G	H	I	J
7.40			✓	✓	✓			✓				
7.41			✓	✓	✓							
7.45	d(8.0)							✓				
7.53			✓	✓	✓							
7.55	d(1.4)							✓				
7.56			✓	✓	✓	✓	✓					
7.60			✓	✓	✓			✓				
7.67	d(7.7)							✓				
7.75			✓	✓	✓					✓		
7.78			✓	✓	✓							
7.83			✓	✓	✓			✓				
7.86								✓				
7.92			✓	✓	✓	✓		✓		✓		
7.96								✓				
7.98	dd(8.0, 1.8)							✓				
7.99	s		✓	✓	✓	✓	✓	✓	✓			
8.03			✓	✓	✓	✓		✓				
8.08				✓	✓							
8.16	m		✓	✓	✓	✓		✓				
8.18	dd(7.7, 1.6)							✓				
8.24			✓	✓		✓	✓	✓				
8.24			✓		✓							
8.27			✓	✓	✓							
8.31				✓		✓						
8.32				✓		✓						
8.38	t(1.8)							✓				
8.35			✓	✓	✓							
8.41	s	formate							✓	✓		
8.45											✓	
8.46			✓	✓								
8.49	d(1.6)		✓	✓				✓				
8.57					✓							
8.62								✓				
8.58				✓	✓			✓				
8.62				✓	✓			✓				
8.74								✓				
8.76						✓						
8.82								✓				

^a s = singlet, d = doublet, dd = doublet showing secondary splitting, t = triplet, q = quintet

^b A = Pregnant liquor organics; B = Spent liquor organics; C = <1.2kD; D = 1.2-6kD; E = 6-12kD; F = 12-25kD; G = 25-50kD; H = 50-100kD; I = 100-300kD; J = >300kD.

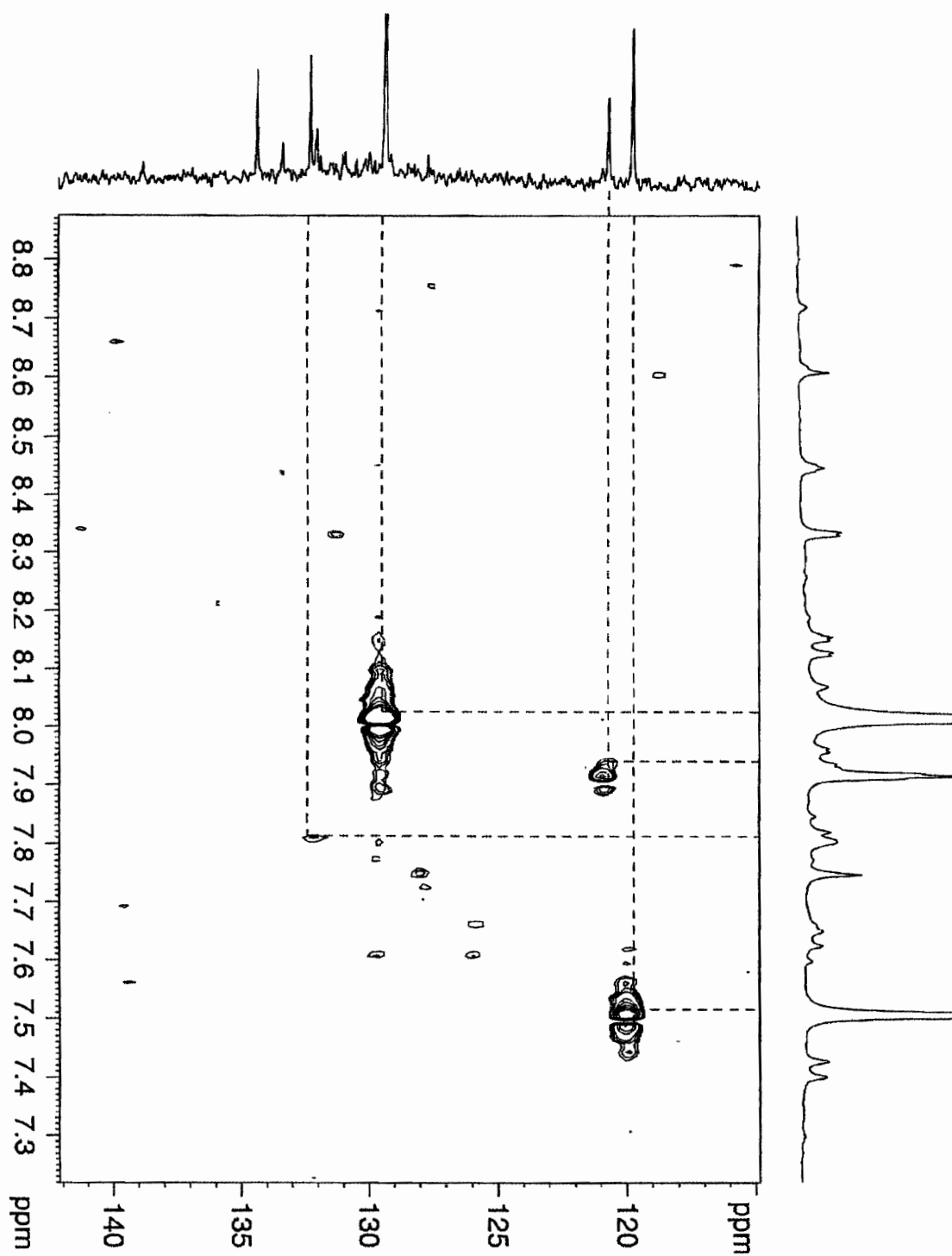
3.9.2 Results from HMQC (^1H - ^{13}C) 2-D experiments

HMQC and COSY analysis allowed some further information to be deduced on the fractions. This is illustrated by Figure 3.25 which displays the aromatic coupling of ^1H to ^{13}C in solution for the 12-25kD fraction dissolved in deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$). DMSO was used since this fraction is soluble in this solvent, it provides better resolution in the aromatic region and allows exchangeable protons to be observed. The results from the HMQC analysis show several strong couplings in the aromatic region of the spectrum (Figure 3.25). The ^{13}C resonance at 120.49 ppm was strongly coupled to the aromatic proton at 7.55 ppm, and the carbon at 121.39 ppm was coupled to the proton at 7.96 ppm. The ^1H and ^{13}C chemical shifts suggest the compound to be 5-methylbenzene-1,3-dicarboxylic acid. Coupling in the aromatic region was also observed between the carbon at 129.50 ppm with the proton at 8.08 ppm. The aromatic proton is located downfield suggesting it is located near an electron-withdrawing group. The COSY spectrum does not show any other coupling for this proton, suggesting that it is located on a symmetrically substituted benzene ring. The ^1H and ^{13}C chemical shifts suggest the compound to be benzene-1,4-dicarboxylic acid.

There are also a number of weaker correlations, the strongest being between 132.5 ppm and 7.86 ppm, see Figure 3.25.

Few distinct couplings were observed in the aliphatic region of the 2-D ^1H to ^{13}C spectrum due to the low intensity of the ^{13}C signal in this region and hence this spectrum is not shown. However aliphatic protons located at 2.55 ppm are coupled to a carbon located at 21 ppm. The absence of coupling of these protons in the COSY spectrum (see below) suggests it is an isolated methyl/methylene spin system. The position of this carbon is downfield at 21 ppm, indicating that the carbon bearing these protons is most likely attached to sp^2 carbon, such as an aromatic ring or an alkene group.

Figure 3.25 HMQC aromatic region spectrum of the 12-25kD fraction displaying the coupling of ^1H to ^{13}C in solution.



3.9.3 Results from COSY (^1H - ^1H) 2-D experiments

The COSY experiment revealed vicinal coupling in several areas of the spectrum of the 12-25kD fraction. The aliphatic region (Figure 3.26) displayed coupling between protons at 4.10 ppm from what appears to be a base unhydrolysable ester (or other strong electron withdrawing group) with a proton triplet resonating at 1.27 ppm from a methylene group. This coupling infers the presence of the group $\text{R}-\text{CH}_2-\text{CH}_2-\text{O}-\text{COR}$ in the molecules held in the structure of the 12-25kD fraction. A weak coupling was observed between the resonances at 0.86 ppm and 1.20 ppm. This coupling is between methylene protons and a terminal methyl group, from the structure $\text{R}-(\text{CH}_2)_n-\text{CH}_2-\text{CH}_3$.

Additional coupling was observed in the aliphatic region with the protons in the triplet at 3.20 ppm ($J = 7.6$ Hz) being coupled to the protons in a quintet at 2.10 ppm ($J = 7.6$ Hz). Integration, coupling and the location of the resonances indicate that the compound contains a three-carbon alkyl chain attached to highly electronegative functional groups at each end, with the two CH_2 groups adjacent to the electron withdrawing groups being equivalent. The ^1H NMR data is thus consistent with the compound 1,5-diphenylpentan-1,5-dione.

Two regions of coupling were observed between the aliphatic and aromatic region (Figure 3.27), with the resonances at 2.67 ppm and 7.83 ppm being coupled as well as the resonances at 2.60 ppm and 7.45 ppm. Protons at 2.60 ppm are of the aliphatic type located α to an electronegative group or directly attached to an aromatic ring. Methylene protons attached to aromatic rings, such as in $\text{Ar}-\text{CH}_2-\text{R}$, could produce these resonances. The resonances at 7.45 ppm and 7.83 ppm are from aromatic protons in different environments. Each of these aromatic protons would be located on aromatic rings containing different substituents or in a different positions (*o*, *m*, and *p*) relative to substituents on the rings.

Several couplings were observed between protons in the aromatic region (Figure 3.28). The proton at 7.96 ppm is coupled to the strong resonance at 7.55 ppm (unresolved doublet, $J = 1.4$ Hz). A J coupling of 1.4 Hz suggests *meta* coupling.

Hence the results indicate that the protons are located *meta* to one-another in different chemical environments on the same aromatic ring. The coupled protons located at 7.55 ppm and 7.96 ppm were the same protons observed in the ^1H - ^{13}C HMQC 2-D NMR spectrum. The integration results show that there are twice as many protons at 7.55 ppm as there are at 7.96 ppm. The small coupling constant, integration results, and the chemical shifts all suggest that 5-methylbenzene-1,3-dicarboxylic acid is present in the 12-25kD fraction.

Two examples of 1,3,4-trisubstituted benzene ring systems were observed. In the first a doublet at 7.45 ppm ($J = 8.0$ Hz) is coupled to another doublet at 7.98 ppm ($J = 8.0$ Hz) which is split again ($J = 1.8$ Hz). This coupling is to the proton at 8.38 ppm (unresolved triplet, $J = 1.8$ Hz). J coupling of 8.0 Hz suggests *ortho* coupling and as already noted the small coupling (here 1.8 Hz) indicates *meta* coupling. Hence the result indicates the presence of a 1,3,4-trisubstituted benzene ring, with two of the aromatic protons being deshielded due to the presence of adjacent electron withdrawing groups.

In the second example, the doublet at 8.18 ppm ($J = 7.7$ Hz) is also split again (1.6 Hz) and is coupled to resonances at 7.67 ppm ($J = 7.7$ Hz) and a broad peak at 8.49 ppm ($J = 1.6$ Hz). The splitting and coupling constants of these resonances indicate that all three of these protons are located on the same aromatic ring but in *ortho* and *meta* positions as above.

Intensities of the resonances at 7.83, 7.86, 8.31, 8.62, 8.74 and 8.82 ppm were either decreased or completely disappeared when D_2O was added to the DMSO solvent. Therefore it is likely that these resonances result from exchangeable protons such as those directly attached to nitrogen or oxygen, which exchange protons for deuterium with the addition of D_2O . Resonances between 5-6 ppm from phenolic protons and carboxylic protons between 10.0-10.3 ppm were also seen to disappear, or decreased in intensity on addition of D_2O .

In summary, the results from the 1-D and 2-D ^1H NMR analysis indicated that there were numerous small aliphatic and aromatic compounds present in each of the Bayer organic fractions. Several aliphatic resonances from saturated and unsaturated

aliphatic chains were detected particularly in the higher molecular weight fractions (>50kD). Discrete aromatic resonances were seen for all fractions excluding the >300kD fraction, indicating that there were no small aromatic compounds hydrogen bonded to the macromolecules in this fraction.

Figure 3.26 COSY (^1H - ^1H) 2-D experiments of the 12-25kD fraction - aliphatic region

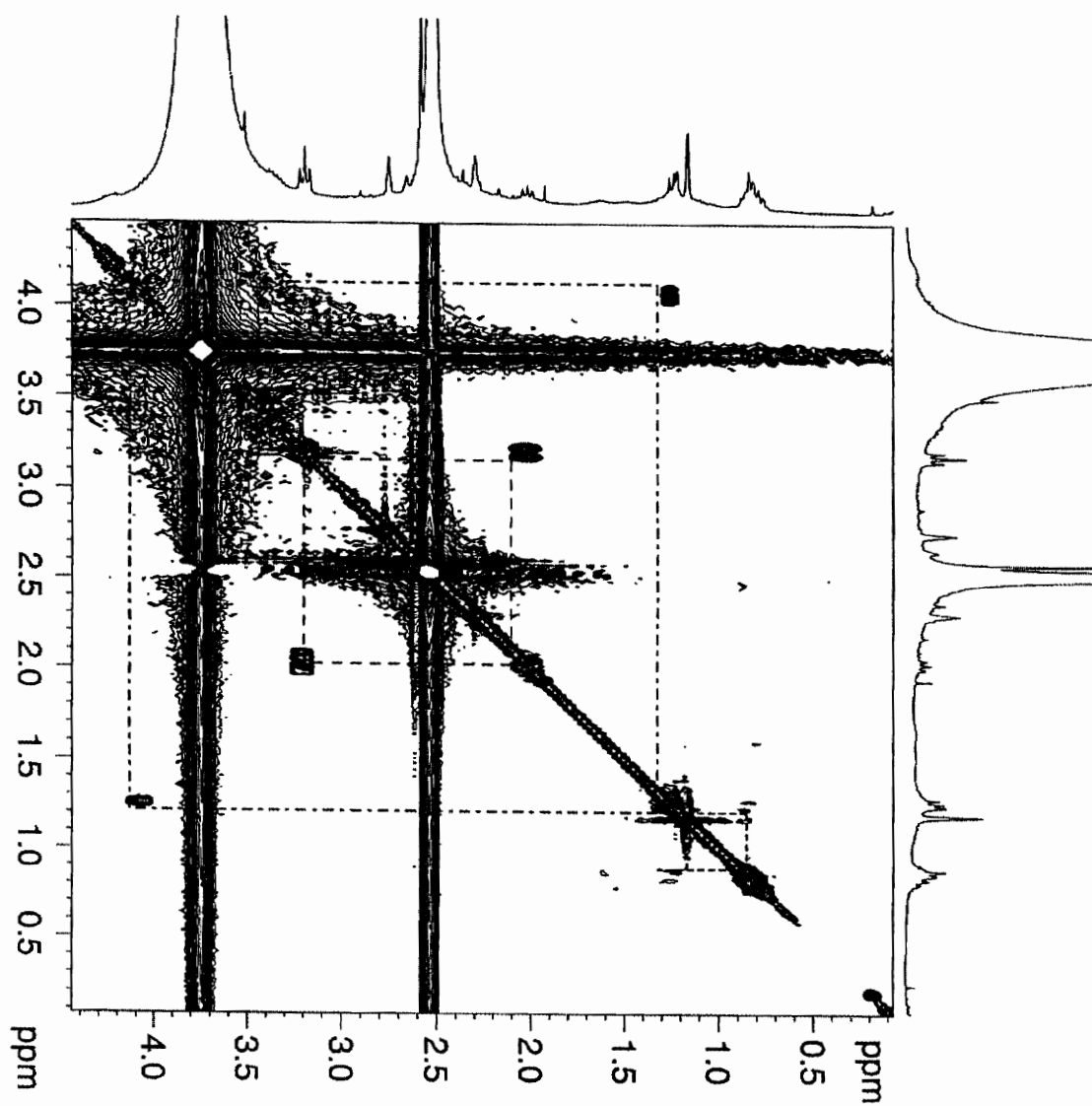


Figure 3.27 COSY (^1H - ^1H) 2-D experiments of the 12-25kD fraction – whole spectrum

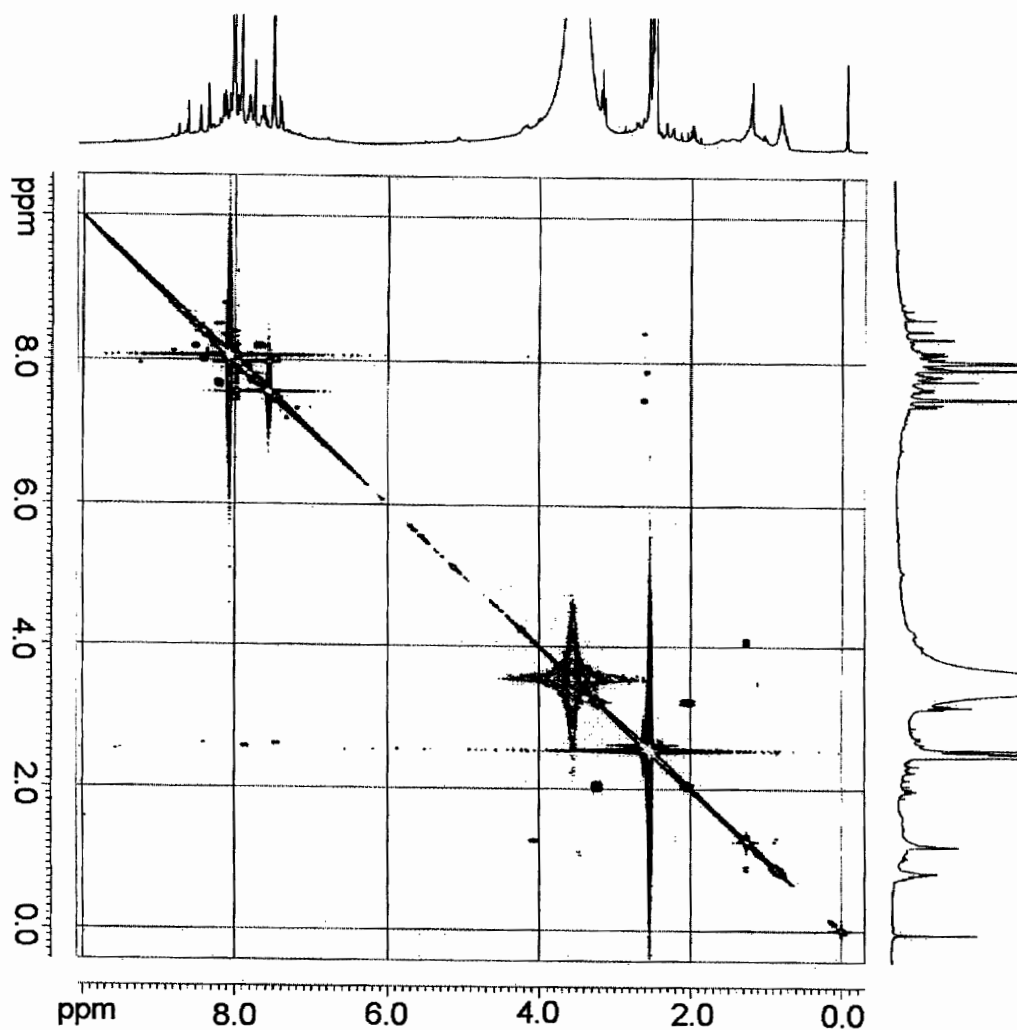
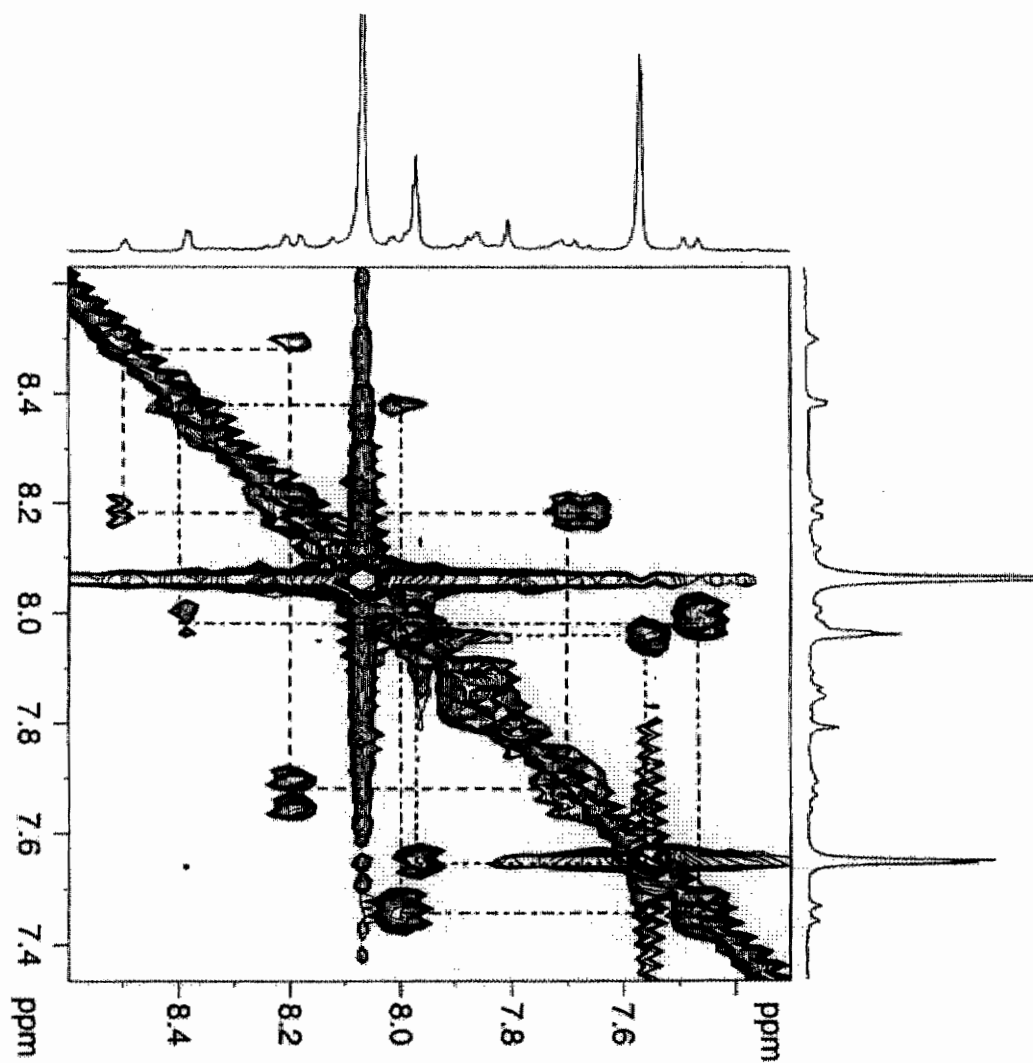


Figure 3.28 COSY (^1H - ^1H) 2-D experiments of the 12-25kD fraction - aromatic region



3.10 Methylation of Bayer organic fractions and analysis by gas chromatography – mass spectrometry (GC/MS)

Each of the Bayer organic fractions was methylated with tetramethylammonium hydroxide (TMAH) according to the method by Hatcher *et al.* (1995) (Experimental Section 2.3.9). On analysis of the fractions by GC/MS a wide variety of compounds were identified including the benzenecarboxylic acids mentioned above and others, and the suspected *n*-alkanes and fatty acids. These three families of compounds represented the majority of the compounds released by the fractions on methylation. Many of the compounds released from the Bayer organic fractions by methylation were identified as methyl ester derivatives, particularly the fatty acids and benzenecarboxylic acids. The compounds identified from the methylation of the Bayer organic fractions are detailed in Table 3.18.

Each of the fractions greater than 25kD released mainly aliphatic compounds including alkanes and fatty acids when methylated. Consistent with this is that each fraction produced very few, if any, discrete resonances in the aromatic region (6.0-8.8 ppm) of the ^1H NMR spectra (Section 3.9.1).

n-Alkanes were identified in the chromatograms with carbon chain lengths ranging from C_{11} to C_{29} . *n*-Alkanes are derived from algal, microbial and higher plant sources. In general those with carbon chain lengths from 12 through 22 are of algal or microbial origin, while compounds with longer carbon chains are derived from microbes or higher plants (Tissot and Welte, 1984; Hunt, 1979). The distribution of the alkane compounds also gives an indication of their origin. *n*-Alkanes of a microbial origin generally have a smooth distribution of carbon numbers while those derived from higher plants have a marked odd carbon number predominance, especially in the C_{25} , C_{27} and C_{29} compounds (Tissot and Welte, 1984; Hunt, 1979).

The *n*-alkanes in the Bayer organic fractions were observed to have a slight odd over even predominance, with a marked predominance observed for the C_{25} , C_{27} , and C_{29} alkyl chains. Alkane chains shorter than C_{20} made only small contributions to the

content of the Bayer organic fractions. The distribution of the *n*-alkanes in these fractions suggests that they were derived from the waxes of higher plants.

The longer chain *n*-alkanes (C₂₆ to C₂₉) were seen to make significant contributions to the larger molecular weight Bayer organic fractions (>50kD). These fractions with their larger macromolecules may have a higher ability to trap these molecules in larger voids, or by forming host-guest interactions. As already noted, these fractions were determined by ¹H NMR to contain few aromatic molecules, however methylene chains were clearly visible in their spectra. The aliphatic chains detected by ¹H NMR are sourced from the alkane and fatty acid compounds which are trapped or more likely hydrogen bonded to the structures of these larger molecular weight compounds.

As already noted, long chain aliphatic carboxylic acids were found to be one of the main chemical classes released by the methylation of the Bayer organic fractions. Aliphatic carboxylic acids with carbon chain lengths ranging from C₇ to C₂₂ were identified as products. Aliphatic carboxylic acids that were identified were found to have both monocarboxylic and dicarboxylic acids on their structures as well as unsaturations in several of the products. Numerous C₁₈ isomers were identified as products from the organic fractions (Table 3.18).

The distribution of fatty acids suggests that higher plants contributed to the Bayer organic fractions. The long chain lengths seen in many of the products (up to 22 carbons) and the strong even to odd predominance are indicative of a higher plant origin (Tissot and Welte, 1984; Hunt, 1979; Del Rio *et al.*, 1994).

Aliphatic carboxylic acids were detected in all of the organic fractions, however there were more varieties of these compounds identified in the larger molecular weight fractions, particularly those with molecular weight greater than 50kD.

Numerous substituted benzene mono and dicarboxylic acid compounds were identified as methylation products. As expected these compounds made the largest contribution to the <1.2kD fraction. These compounds probably originate in the larger humic molecules derived from lignin moieties. Repetitive digestions in the Bayer process liquor would chemically cleave many of the larger macromolecules to form

these small organic compounds which accumulate in the smallest molecular weight range.

Typical GC/MS chromatographs of the methylated Bayer organic fractions are shown in Figure 3.29. Figure 3.29A shows that without methylation small molecular weight compounds were not observed. Figure 3.29B shows the distribution of compounds released from a low molecular weight Bayer organic fraction (<1.2kD), which included numerous benzene carboxylic acids. Figure 3.29C shows the compounds released from a high molecular weight fraction (100-300kD) which included significant amounts of aliphatic carboxylic acids and *n*-alkanes. Methylation with TMAH acts to release small molecules trapped in the macromolecules by forming esters and ethers with carboxylic and phenolic groups respectively, thereby breaking the hydrogen bonding that holds the molecules in place. Without methylation the molecules are held tightly in the macromolecular matrix. As noted above, when the unmethylated fractions were analysed by GC/MS no small molecules were detected (Figure 3.29A), only the internal standard (C₂₀) was observed.

The compounds identified in Figure 3.29 include 3-methoxybenzoic acid methyl ester (1), 1,4-benzenedicarboxylic acid methyl ester (2), 1,4-benzenedicarboxylic acid dimethyl ester (3), 1,3-benzenedicarboxylic acid dimethyl ester (4), 4-hydroxy-2-methoxy-3,6,5-trimethylbenzoic acid methyl ester (5), hexadecenoic acid methyl ester (6), 7-octadecenoic acid methyl ester (7), 1-octadecenoic acid methyl ester (8), C₂₃ alkane (9), C₂₅ alkane (10), C₂₇ alkane (11), C₂₉ alkane (12). * C₂₀ internal standard.

Figure 3.29 GCMS spectra of molecular weight fractions A) before methylation B) after methylation of low molecular weight humic material (<1.2kD) and C) after methylation of high molecular weight humic material (100-300kD).

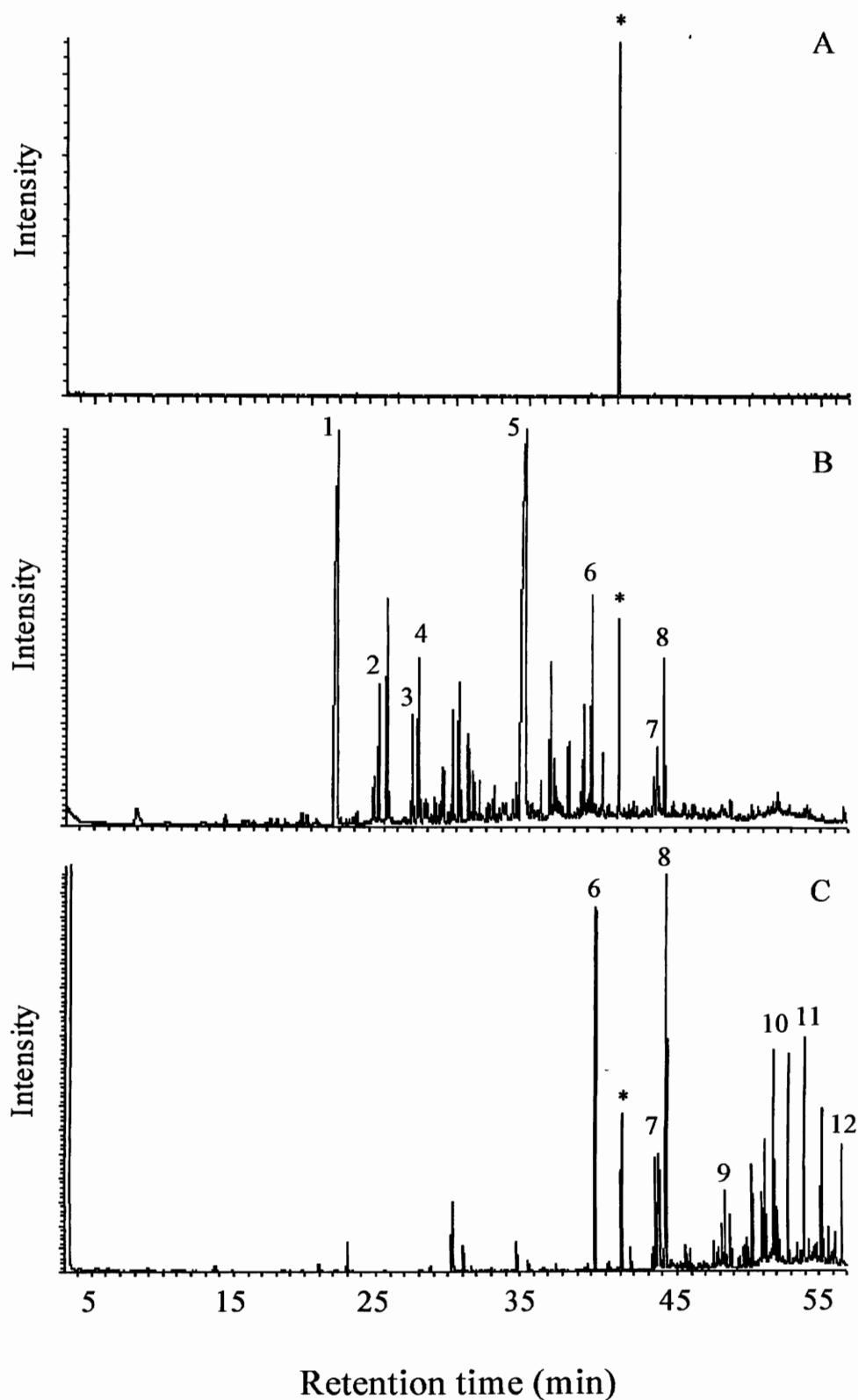


Table 3.18 Relative proportions (%) of identified compounds from methylation of humic fractions (relative to internal standard).

Compound	A	B	C	D	E	F	G	H	I	J
2-Ethylhexanol								<1		
Undecane								<1		
Benzoic acid methyl ester	<1	9								
2-Methylbenzoic acid methyl ester	<1	3								
2-Hydroxybenzonitrile		<1								
3-Methylbenzoic acid methyl ester	<1									
Benzothiazole				<1				21		
Benzoic acid methyl ester derivative		2								
Dodecane								7		
2-Ethylbenzoic acid methyl ester		1								
3-Methylhexanedioic acid dimethyl ester			<1							
4-Ethylbenzoic acid methyl ester		2								
2,5-Dimethylbenzoic acid methyl ester		1								
C13-Alkane								<1		
3-Methoxybenzoic acid methyl ester	5	172	4863							
2,4,6-Trimethylbenzoic acid methyl ester	<1								24	
3-Methoxybenzeneacetic acid methyl ester		2	118							
3,5-Dimethylbenzoic acid methyl ester	12									
1,4-Benzenedicarboxylic acid dimethyl ester	8	21	370					<1		
1,3-Benzenedicarboxylic acid dimethyl ester	9	36	701							
Dodecenoic acid methyl ester								<1	<1	<1
Nonenedioic acid dimethyl ester			92					<1		
4-Methyl-1,2-benzenedicarboxylic acid dimethyl ester			126							
2-(Methylthio)-benzothiazole								39	21	8
4-Methyl-1,3-benzenedicarboxylic acid dimethyl ester	8	19	360		<1				<1	
5-Methyl-1,3-benzenedicarboxylic acid dimethyl ester	5	24	472							
Undecenoic acid methyl ester										8
Nonenoic acid methyl ester								28		
2-Nonylphenol				12						
4-Nonylphenol				8						
Tetradecenoic acid methyl ester	<1		107		1	1			17	
9H-Fluorene-2-carbonitrile			165							
3-Nonylphenol				5						

Table 3.18 continued

Compound	A	B	C	D	E	F	G	H	I	J
4-Hydroxy-2-methoxy-3,6,5-trimethylbenzoic acid methyl ester	41	249	3328					15	<1	
5-Methyl-2-phenyl-1H-indole	<1	<1	660							
Pentadecenoic acid methyl ester								<1	<1	
C19-Alkane				3						
1,3,5-Trimethylbenzoic acid trimethyl ester	15	17	378		1				<1	
Hexadecenoic acid methyl ester	14	13	735	5	8	22	17	305	287	121
1,2-Benzenedicarboxylic acid, butyl-2-methylpropyl ester ?	6	8	183	6		11			<1	<1
C20-Alkane (internal standard)	100	100	100	100	100	100	100	100	100	100
Heptadecenoic acid methyl ester								16	20	6
C21-Alkane				16		4	31	16	18	<1
9-Octadecenoic acid methyl ester		6	184		1					
7-Octadecenoic acid methyl ester	13		361		9	12	45	152	81	29
15-Octadecenoic acid methyl ester						3		50	83	18
6-Octadecenoic acid methyl ester	9				2	5		161	87	25
14-Methylheptadecenoic acid methyl ester				7						
1-Octadecenoic acid methyl ester	6	11	430		8	31		327	380	162
9,12-Octadienoic acid		9				3				
2-Hydroxy-cyclopentadecanone		9				7				
11,14-Octadecadienoic acid methyl ester				32		5		<1		
7,10-Octadecadienoic acid methyl ester								<1		
Octadecenoic acid						14				
8,11-Octadecadienoic acid methyl ester						6		17	23	<1
6,9-Octadecadienoic acid methyl ester				<1					17	
C22-Alkane				28						
n-Alkane						5		92	20	7
2,3,-Dihydro-2-methyl-7-phenyl-benzofuran	<1									
C23-Alkane				46				32	24	
n-Alkane			<1	<1		3			33	
Eicosenoic acid methyl ester			31			3		39	35	30
1,2,3,4,4a,9,10,10a-Octahydro-1,4a-dimethyl,1-7-(4-methylethyl)-1-phenanthrenecarboxylic acid methyl ester	11		<1	3				19	13	<1
C23-Alkane							158			<1
9,12-Octadecadienoic acid						3		15		2
C24-Alkane			<1	56	7	6		23	62	<1
N,N-Dimethyl-9-octadecanamide		4		7		5				
13-Octadecenoic acid methyl ester						2	8	15	84	44
C25-Alkane		2	48	65	2	7	139	75	97	15
Nonadecenoic acid methyl ester						4			26	
11-Eicosenoic acid methyl ester								53		30
Docosenoic acid methyl ester									53	11
C26-Alkane	3		<1	63					93	4
C27-Alkane	6			8					104	10
C28-Alkane	5			36					90	8
C29-Alkane	4			6					72	9

A = Pregnant liquor organics, B = Spent liquor organics, C = <1.2kD, D = 1.2-6kD, E = 6-12kD, F = 12-25kD, G = 25-50kD, H = 50-100kD, I = 100-300kD, J = >300kD.

1,5-diphenypentan-1,5-dione was not detected possibly because it is unstable under these conditions

3.11.1 Host guest theory

There are several interpretations of the results obtained from several of the techniques mentioned above, particularly the results from ^1H NMR, methylation GC/MS, and thermal analysis. Each of these techniques indicated the presence of small volatile compounds in the structures of much larger macromolecules. It might be assumed from these results that dialysis was not working properly, however, it appears that identical bags are capable of discriminating molecular weight fractions of other humic materials (Wilson *et al.*, 1999). Thus this conclusion is discarded. Second, it is possible that the discrete molecular weight signals are from impurities. However blanks showed no introduced material and this also seems unlikely because each of the fractions contain different small molecular weight entities. Clearly from the results of this study, small molecules are prevented from diffusing out of the dialysis bags. That is they must be held in some way in some supramolecular structure by the larger molecules (host-guest complexes) or they are complexed together.

The host-guest complexes formed by these highly oxidised humic molecules are unlikely to exist in the caustic environment of the Bayer process. In Bayer liquor the carboxylic groups located on the aliphatic carboxylic acids and in the humic macromolecules would be deprotonated, as will phenolic and other acidic groups. The deprotonated groups would not form strong hydrogen bonds under these conditions due to repulsion forces of similarly charged species. During precipitation however, intramolecular hydrogen and intermolecular hydrogen bonding may occur. In the large molecules, voids may also form which could occlude other molecules. It may well be true that some of these occluded molecules hydrogen bond to larger macromolecules but the presence of alkanes shows that for some molecules this is not always the case.

3.11.2 Existence of host-guest structures in other humic materials

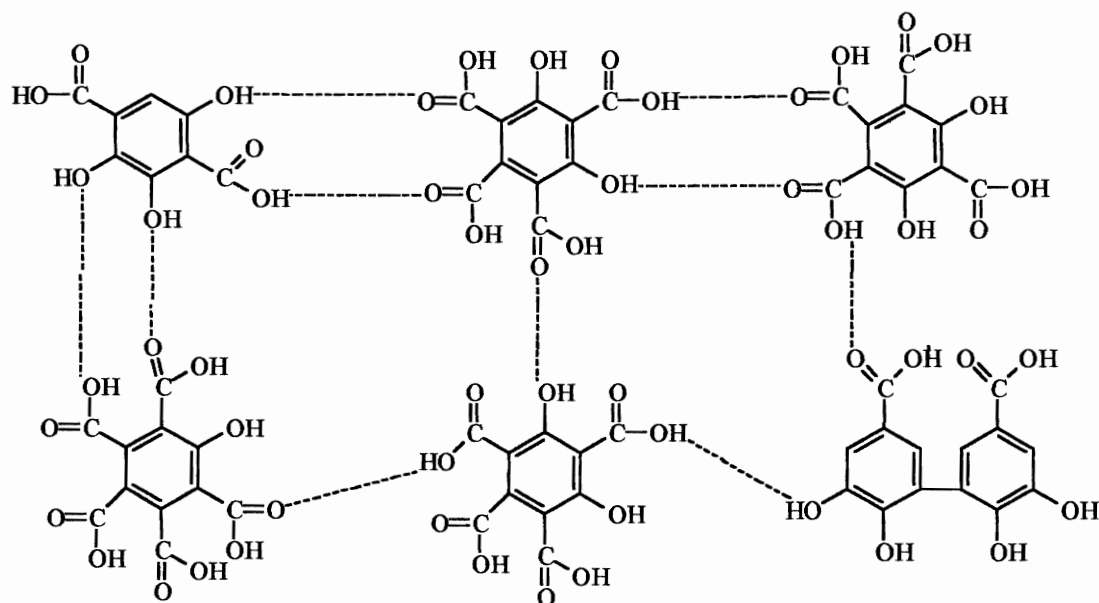
These host-guest interactions discovered in the structures of high temperature Bayer humic materials are likely to occur in other humic macromolecular compounds in the environment. It is also possible that the formation of these host-guest interactions through hydrogen bonding, or physical entrapment, trap other molecules including organic pollutants. While chelation of metal ions by humic materials is important (Ong and Bisque, 1968; MacCarthy and Rice, 1985), metal ions may also be responsible for breaking intra or intermolecular hydrogen bonding interactions that create voids. The destruction of host-guest complexes might be expected to be achieved more readily than the breaking of covalent bonds. Indeed it has been demonstrated that UV radiation can degrade humic substances (Allard *et al.*, 1994; Backlund, 1992; Dahlen *et al.*, 1996; Frimmel, 1998; Schmitt-Kopplin *et al.*, 1998), as can the presence of oxygen during the extraction of humic substances (Wershaw and Pinckney, 1977). These reactions could be through oxidation of phenols to quinones, breaking intermolecular hydrogen bonding resulting in the subsequent release of small molecular weight guests.

An early fulvic acid model proposed by Gamble and Schnitzer (1974) (Figure 3.30) suggested that fulvic acids consist of a polymeric network of phenolic compounds and benzenecarboxylic acids held together by hydrogen bonding to produce a stable structure. This early model indicated that the carboxylic acid groups were important for intermolecular hydrogen bonding. Although this early model does not suggest the presence of host-guest complexes, it indicates the importance of hydrogen bonding in aggregating small molecular weight compounds.

Host-guest complexes were first discovered during the study of the macromolecular structure of coals (Jurkiewicz *et al.*, 1982; Jurkiewicz *et al.*, 1987; Marzec *et al.*, 1983; Barton *et al.*, 1984; Given *et al.*, 1986). Each of these studies examined the changes in coal structure during contact with various solvents, including pyridine. It was discovered that 'donor-acceptor' interactions occur in coals (which are similar in

theory to our host-guest interactions), and that these interactions are disrupted by certain solvents allowing the detachment of small molecules from the rigid macromolecular part of the coal structure.

Figure 3.30 Hypothetical model of fulvic acid (from Gamble and Schnitzer, 1974).

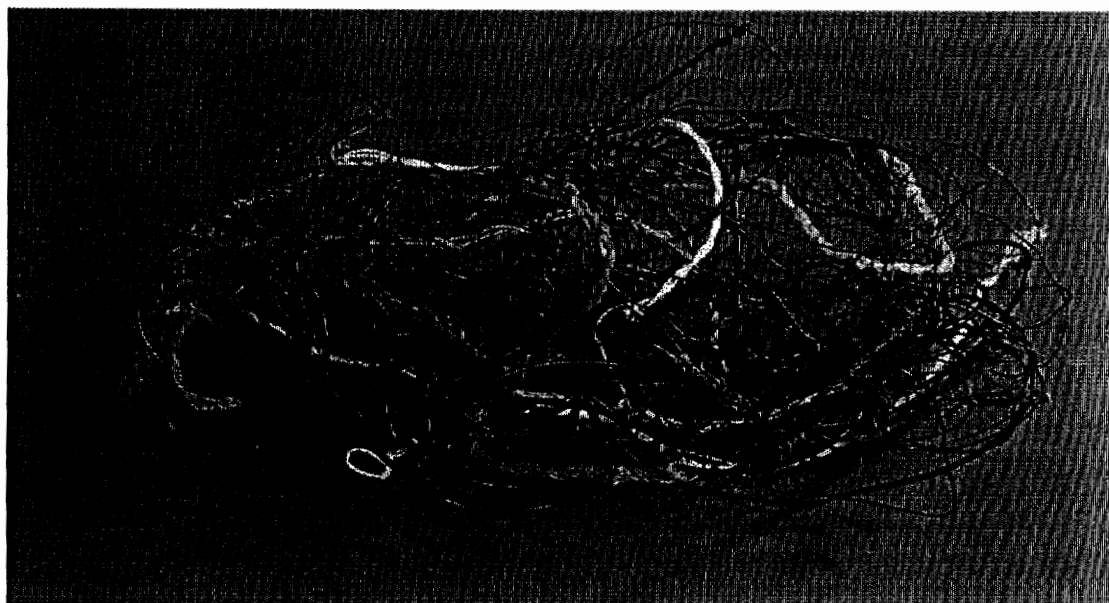


No other study on humic substances has previously identified host-guest complexes, however several recent studies support our proposal (Fetsch and Havel, 1998; Fetsch *et al.*, 1998; Havel *et al.*, 1998; Conte and Piccolo, 1999; Piccolo *et al.*, 1999) in that supramolecular aggregates have been observed in some humic materials by electrophoresis. The aggregation model proposed by these workers is likely to coexist with the host-guest behavior observed here. In addition, Zang *et al.* (2000) discovered that protein structures are preserved during humification by encapsulation in macromolecular hydrophobic domains. The study suggests that the protein molecules are held by physical entrapment in voids created by aliphatic macromolecules, protecting the proteins from chemical and microbial attack. The encapsulation of these protein molecules is similar to the host-guest complexes identified in our study, however the results of our study suggest that the small guest molecules are held in host-guest complexes by hydrogen bonding as well as physical entrapment.

Combining the results from the above study (Zang *et al.*, 2000) and our present study, it is reasonable to suggest that host-guest complexes can form from very different macromolecules. Non-polar aliphatic macromolecules can form aggregates by physical entrapment, and the highly polar aromatic macromolecules studied here can form host-guest complexes through physical entrapment of non-polar compounds, such as alkanes, and by hydrogen bonding to polar molecules.

Figure 3.31 is a schematic representation of the host-guest complexes discovered in this study, the purpose of this figure is to provide a simple visualization of how these complexes are likely to exist. The black backbone of the model represents the aggregated humic macromolecular structure, or host structure, while the coloured materials represent the guest molecules. Many of the host-guest complexes were found to have very large molecular weights of up to and exceeding 300 000 Daltons with the trapped guests having relatively small molecular weights of up to 1000 Daltons.

Figure 3.31 Pictorial representation of host-guest complexes



3.12 Conclusions on Host-Guest interactions in humic materials

The humic materials isolated from a high temperature (250-255°C) alumina refinery were found to have unusual dialysis properties. It was shown that many small molecules become entangled with larger molecules and could not be separated by dialysis. The structures of these small molecules were shown to consist of *n*-alkanes, aliphatic fatty acids and benzenecarboxylic acids by gas chromatography mass spectrometry and solution NMR techniques.

Methylation with tetramethylammonium hydroxide released the small molecules trapped in the macromolecules by forming esters and ethers with carboxylic and phenolic groups respectively; thereby breaking the hydrogen bonding that holds the molecules in place. Without methylation the molecules were held tightly in the macromolecular matrix. Since some of the guests are alkanes it suggests that they were not held by hydrogen bonding, instead they had become trapped in molecular voids.

These host-guest interactions are likely to occur in other humic macromolecular compounds in the environment, where they may complex with other organic molecules such as organic pollutants.

PART D

***Poisoning of the precipitation
of aluminium hydroxide by
molecular weight fractions of
Bayer humic substances***

This section of the thesis examines the effects of the organic materials isolated from the Bayer process liquor on the precipitation dynamics of aluminium hydroxide and sodium oxalate from synthetic Bayer liquor. These tests were performed so that more could be known on which fractions of organic matter are particularly detrimental to the operation of the Bayer process, so that methods could be developed to negate their influence.

3.13 Results from precipitation testing

Details of the experimental procedures for the precipitation experiments are detailed in Section 2.4 of Chapter 2.

The chemical compositions of the organic molecular weight fractions are detailed earlier in this thesis (Sections 3.3-3.12). Table 3.5 reveals that the smallest molecular weight fraction, the <1.2kD fraction, accounts for 87% of the recovered organic material. Structurally the <1.2kD fraction contains mainly hydroxybenzene carboxylic acids. The 12-25kD and 25-50kD fractions appear to resemble material more akin to kerogen, while the higher molecular weight organic material behaves as a soluble char (Sections 3.3-3.12; and Smeulders *et al.*, 2000, 2001).

Table 3.5 (repeated here for convenience), shows that the acidities of the organic fractions are highly variable. The two whole organic fractions, from the pregnant and spent liquors, as well as the <1.2kD fraction are the most acidic. The pH of each fraction generally increases with increasing molecular weight, however the 12-25kD fraction is an exception. Acidity of the fractions is an important factor during precipitation testing as this effects local ionic strength of the Bayer solutions which has an impact on oxalate stability and precipitation yields.

Table 3.5 (repeated) Yields, acidity and elemental analysis of the Bayer humic substance fractions (dry ash free basis)

Fraction No.	Molecular weight fraction (kD)	%C	%H	%N	%S	%O Difference	O/C	H/C	N/C	S/C	pH at 5g/litre in water	Mass yield (%) ^a
PL ^b	<1.2 to >300	56	3.7	0.41	0.21	39	0.53	0.78	0.0055	0.0015	2.4	100
SL ^b	<1.2 to >300	53	3.6	0.11	0.11	43	0.61	0.80	0.0018	0.00078	2.4	100
1	<1.2	50	4.2	0.56	0.17	44	0.65	0.99	0.0095	0.0013	2.5	87
2	1.2-6	48	3.8	1.9	0.32	46	0.71	0.93	0.033	0.0025	2.9	3.3
3	6-12	54	4.2	3.2	0.60	38	0.52	0.93	0.051	0.0041	3.4	0.6
4	12-25	54	3.7	1.4	0.44	41	0.57	0.81	0.022	0.0031	2.9	1.6
5	25-50	56	5.4	3.7	0.42	35	0.47	1.2	0.057	0.0028	3.8	1.0
6	50-100	49	4.1	4.9	0.68	42	0.64	0.99	0.086	0.0052	4.0	3.8
7	100-300	49	4.9	5.9	0.99	39	0.60	1.2	0.10	0.0075	4.6	0.7
8	>300	55	3.8	2.1	0.42	39	0.54	0.83	0.032	0.0029	4.4	2.0

a) The weight of fraction over total weight of material recovered. b) PL = pregnant liquors, SL = spent liquors

Table 3.19 Results from dose rate experiments with humic molecular weight fractions under pseudo-Bayer plant conditions (Group A experiments) on aluminium hydroxide precipitation using caustic-washed seed

Organic fraction	Organic dose (g/L)	Difference in yield of alumina (g) relative to blank	% Change in product with surface area <20 μm^2 relative to blank	% Change in surface area of product relative to blank	% Change in oxalate concentration relative to blank
<1.2kD	2.48	0.86 (2.5%)	+0.79	-0.82	+11.20
1.2-6kD	0.095	0.12 (0.34%)	+0.66	+4.06	-8.86
6-12kD	0.018	-0.05 (-0.1%)	+0.57	+3.25	-12.68
12-25kD	0.046	-0.43 (-1.2%)	+0.05	+9.76	-12.73
25-50kD	0.018	0.08 (0.2%)	+0.32	-6.50	-6.69
50-100kD	0.108	-0.01 (-0.03%)	+0.14	-2.80	+11.10
100-300kD	0.020	0.56 (1.6%)	+0.16	-0.82	+15.00
>300kD	0.065	0.54 (1.5%)	+0.23	-0.82	+8.60
Pregnant liquor	5.26	1.50 (4.3%)	+0.20	-2.80	+33.37
Spent liquor	5.10	1.49 (4.3%)	+0.14	-1.87	+23.60

The results for Group A experiments (Table 3.19) conducted with the organic fractions at the concentrations recovered from the Bayer process liquor showed few negative impacts from the presence of the organic fractions. Figure 3.32 shows little inhibition of the precipitation of aluminium hydroxide, with the yields of aluminium hydroxide for samples containing organic species being almost identical to the blank sample. In some cases the yield was higher than the blank possibly as a result of the humic acids decreasing the concentration of the sodium hydroxide by protonation of hydroxide ion proximate to aluminate species or its derivative, thereby providing a greater driving force for precipitation and therefore higher precipitation yields. Indeed increases in yield as high as 1.50g and 1.49g were observed for the pregnant and spent liquor organics. The highest increases in yield were observed for the three most acidic samples (Tables 3.5 and 3.19). The largest decrease in yield was observed for the 12-25kD fraction (-0.43g) which appears to have different properties to the other fractions (see Sections 3.3-3.8).

Figure 3.33 shows that there appears to be no correlation between surface area of crystals and yield. However the greatest change in surface area was exhibited by the 12-25kD fraction which also inhibited yield the most. The 12-25kD fraction produced an increase in surface area. These results do not translate directly to particle size because of agglomeration and microcavities. All fractions increased the percentage of very fine crystals with surface areas less than $20\mu\text{m}^2$ (Figure 3.34) with the largest increase seen for the <1.2kD fraction. This fraction produced a 0.79% increase in the amount of fine material. Interestingly the 12-25kD fraction, which reduced yield and increased surface area, produced the smallest change in particle size. Thus the role of these organics is complex and is not simply one of inhibiting growth of crystals. Rather they also effect nucleation and agglomeration as well as growth in rather subtle ways. All three effects appear to be at least partly independent of each other.

Figure 3.32 Difference in alumina yield due to the presence of each molecular weight fraction in Group A experiments (caustic washed seed).

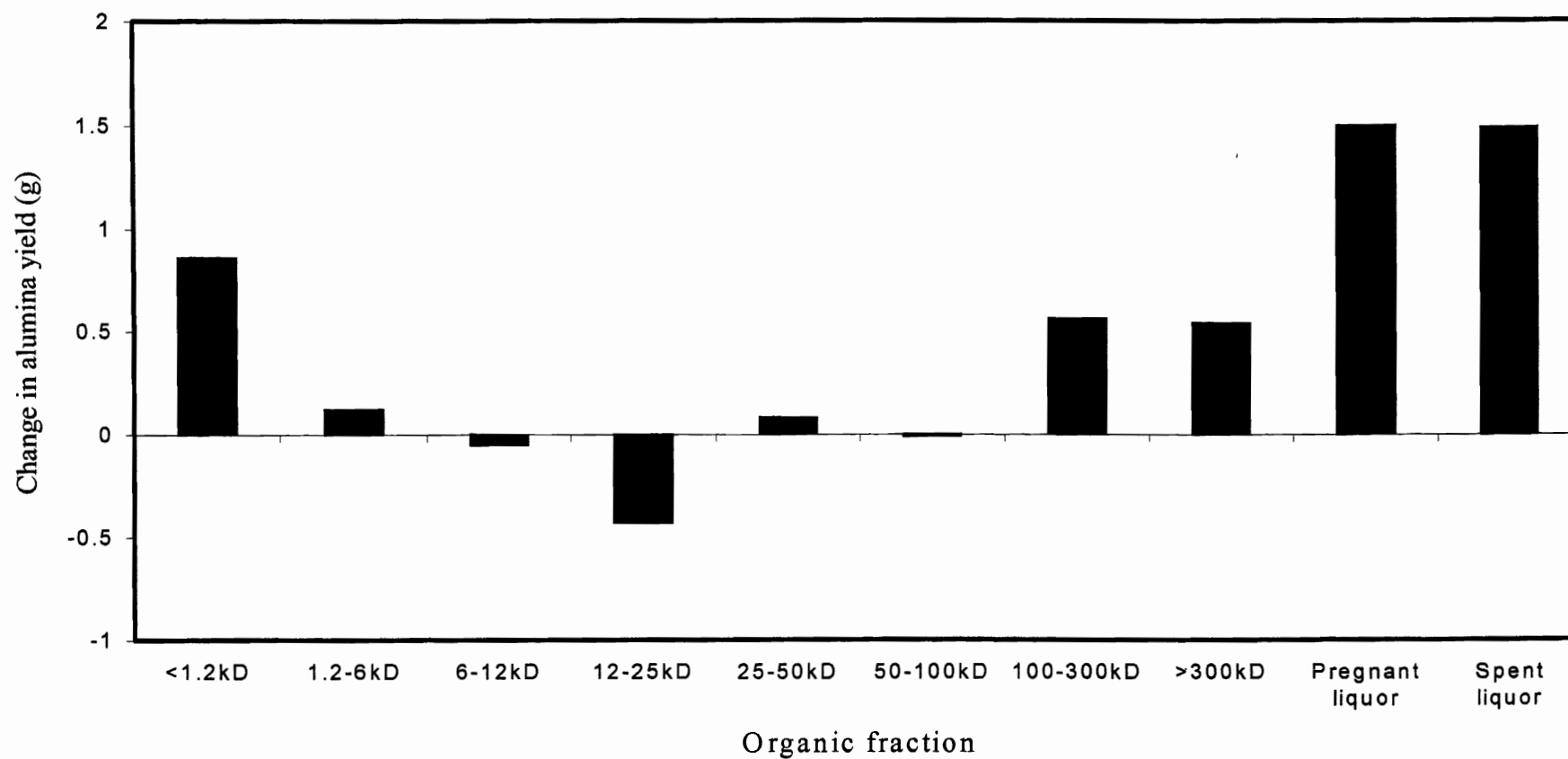


Figure 3.33 Percentage change in product crystal surface areas for Group A experiments.

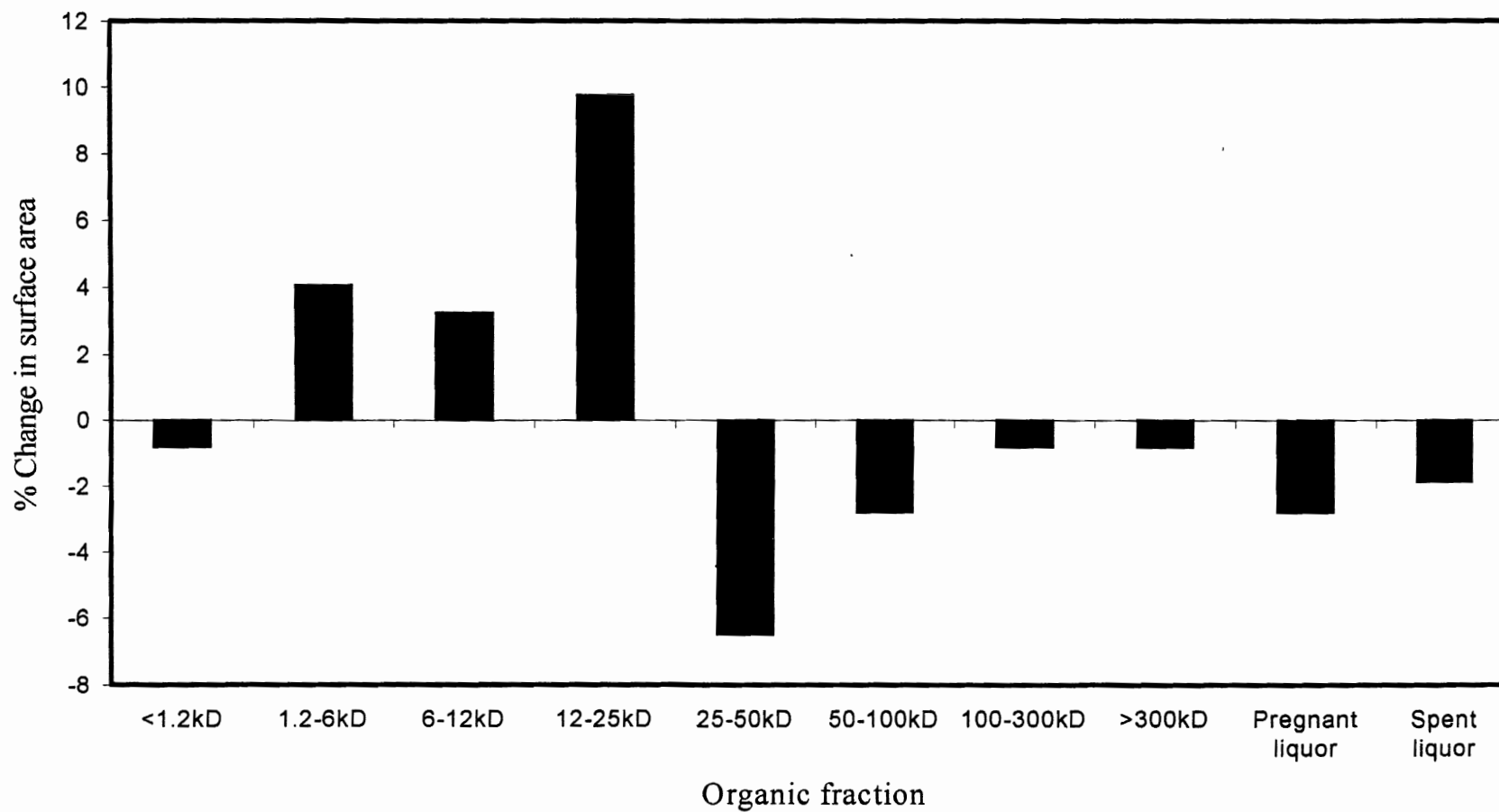
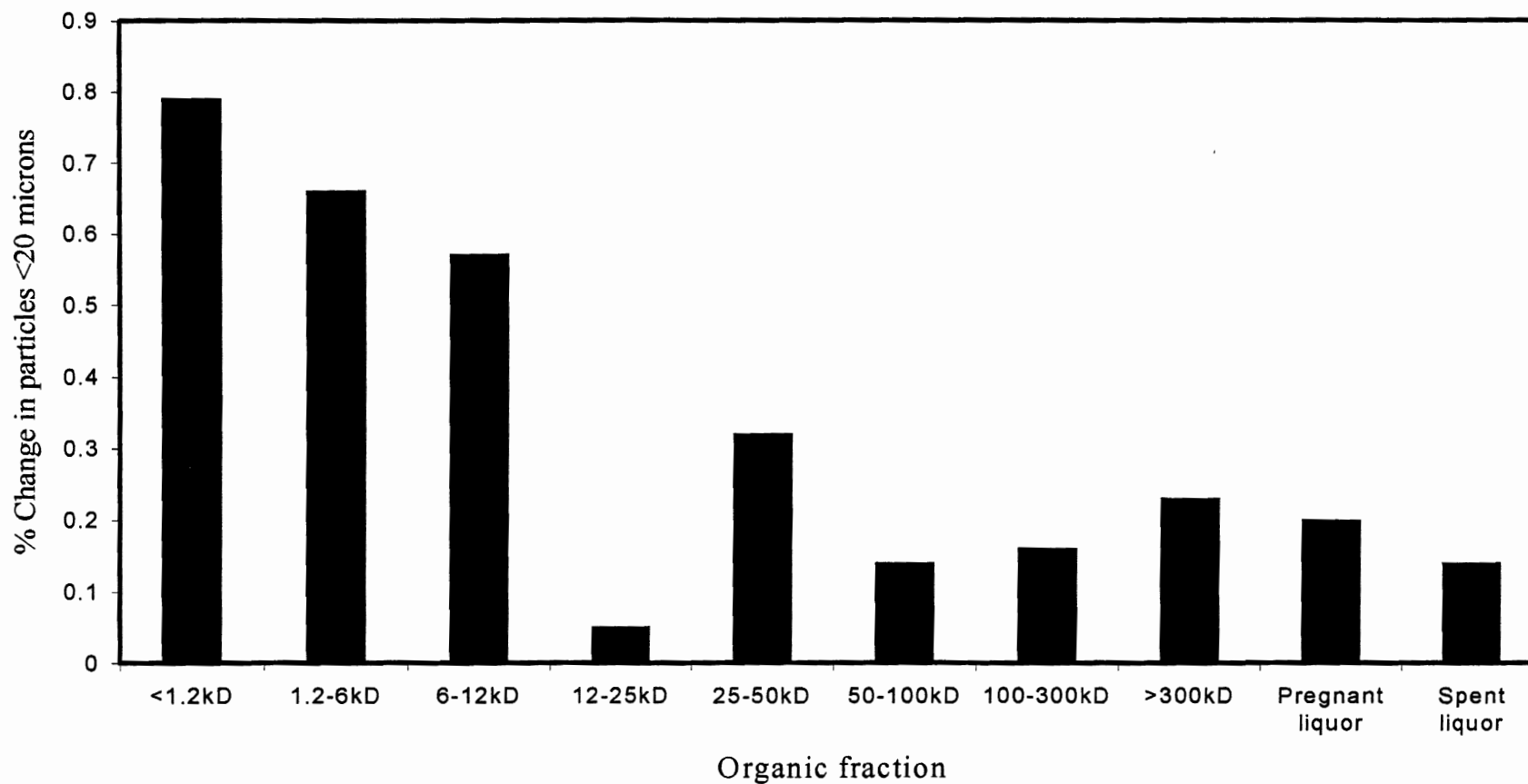


Figure 3.34 Percentage change in the amount of product crystals with surface areas of $<20\mu\text{m}^2$ for Group A experiments.



Group B experiments used hot water washed seed crystals to promote crystallisation, with the organic fractions added at equal dosage rates of 0.1g/L. Like Group A experiments sodium oxalate was also included to simulate plant like conditions, although the results should not be extrapolated directly since the precipitation environment is different. Group B experiments showed clear effects of humic materials as precipitation poisons. Each fraction clearly had an effect on yield (Figure 3.35 and Table 3.20). The most poisonous fraction was the >300kD fraction and the least the <1.2kD fraction. The differences observed in the Group A experiments may result from the use of caustic washed seed in those experiments, which may negate many of the detrimental impacts of the poisoning organic species.

Figure 3.36 shows that the larger molecular weight fractions (1.2-6kD, 12-25kD, 50-100kD and >300kD) produced aluminium hydroxide crystals with a slight increase in surface area, however the <1.2kD fraction decreased the surface area of the alumina. Figure 3.37 shows that for these experiments, the changes in surface area are related to particle size. The <1.2kD fraction produced the smallest sized crystals.

Table 3.20 Results from constant dose rate experiments with humic molecular weight fractions at 0.1g/L (Group B experiments) on aluminium hydroxide precipitation using hot water washed seed

Organic fraction	Organic dose (g/L)	Difference in yield of alumina (g) relative to blank	% Change in product with surface area <20 μm^2 relative to blank	% Change in surface area of product relative to blank	% Change in oxalate concentration relative to blank
Pregnant liquor	0.1	-0.82 (-2.3%)	-2.97	+30.39	-2.80
Spent liquor	0.1	-0.86 (-2.5%)	-2.58	+26.39	0
<1.2kD	0.1	-0.11 (-0.32%)	+3.16	-16.65	0
1.2-6kD	0.1	-0.31 (-0.89%)	-2.68	+27.30	+0.40
12-25kD	0.1	-0.75 (-2.2%)	-2.91	+28.87	+3.66
50-100kD	0.1	-0.71 (-2.0%)	-2.87	+28.63	+9.40
>300kD	0.1	-1.68 (-4.8%)	-1.70	+20.46	+16.60

Figure 3.35 Difference in alumina yield due to the presence of each molecular weight fraction in Group B experiments (hot water washed seed).

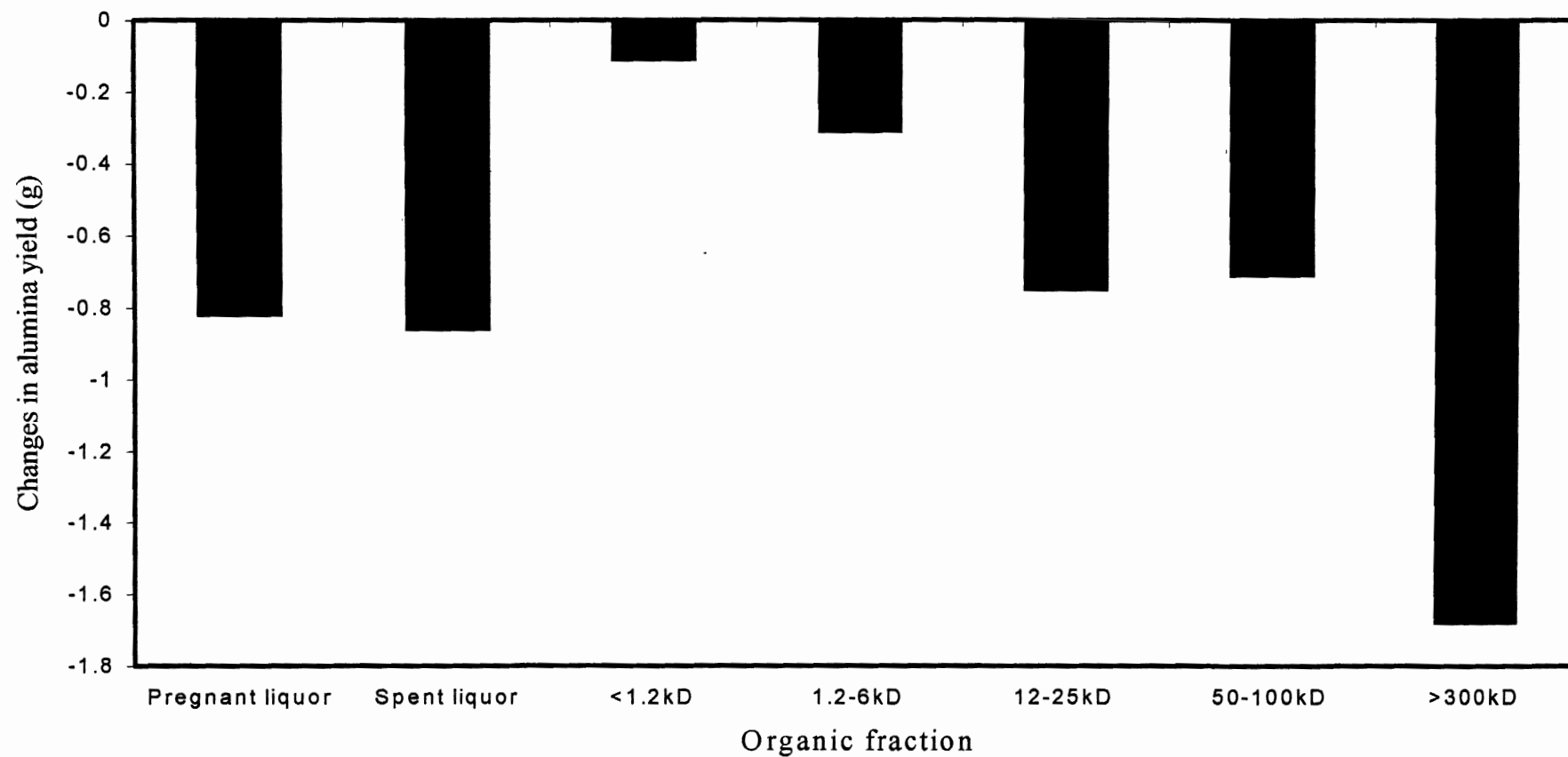


Figure 3.36 Percentage change in product crystal surface areas for Group B experiments with each fraction at a concentration of 0.1g/L.

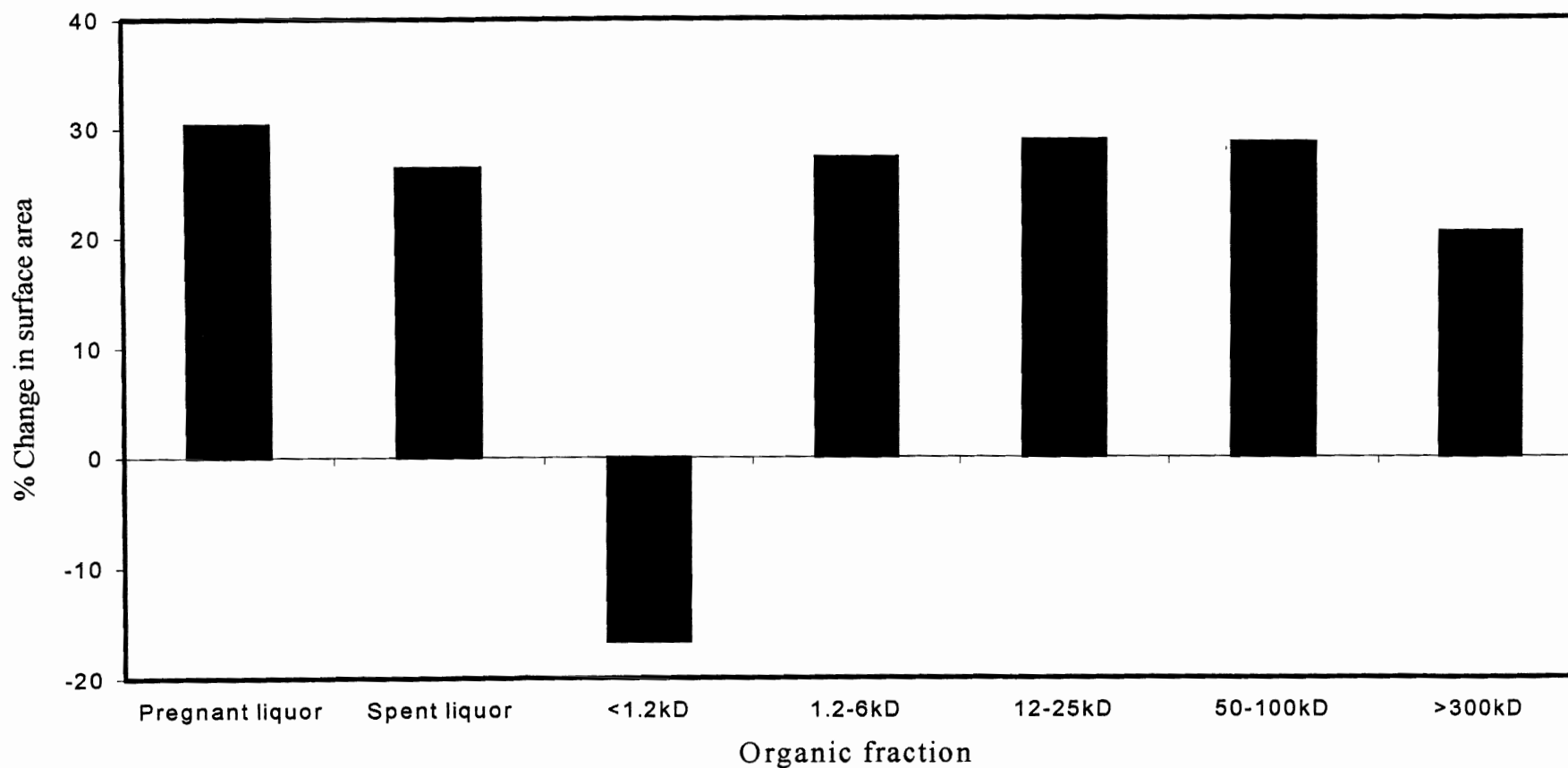
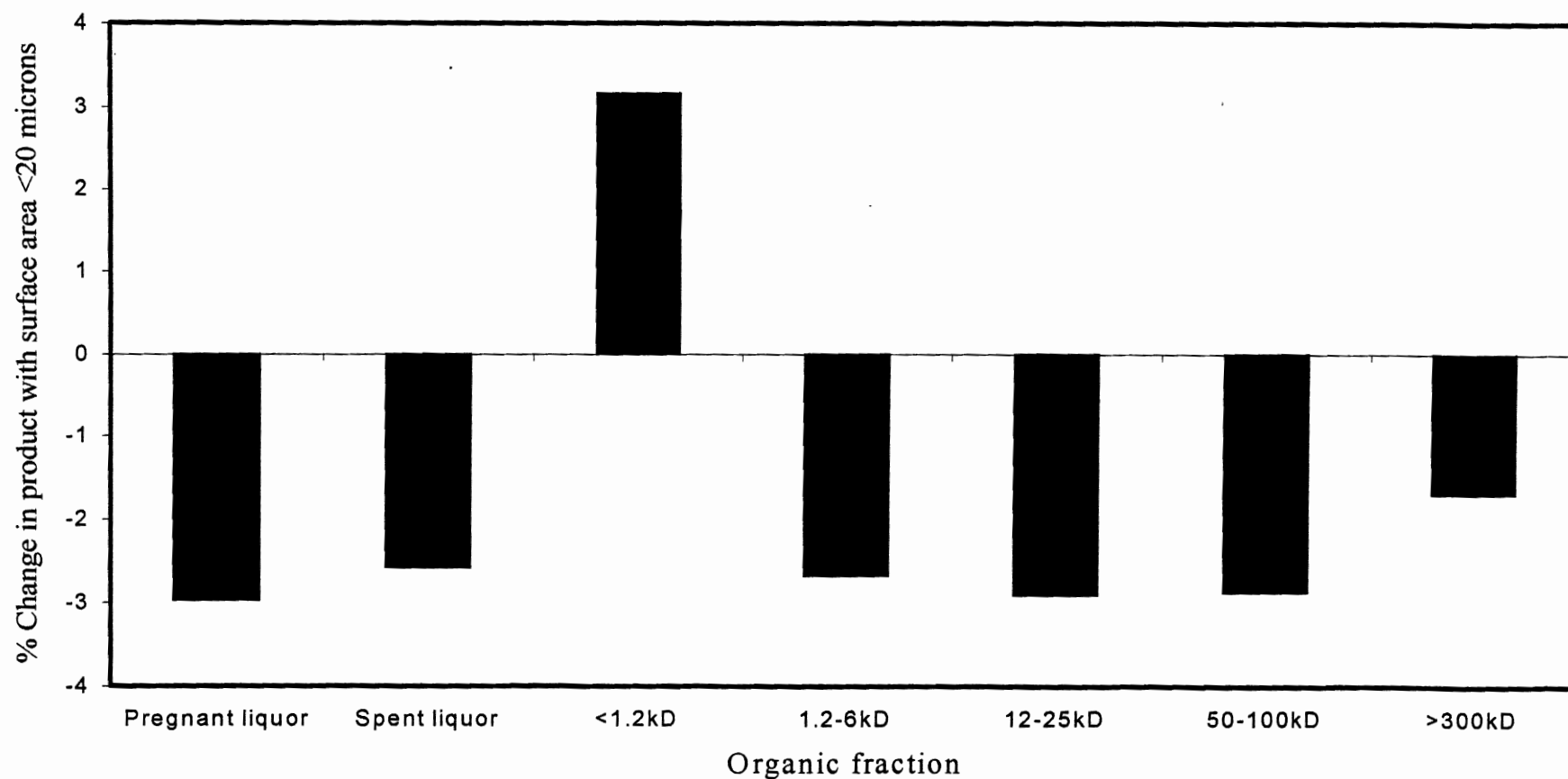


Figure 3.37 Percentage change in the amount of product crystals with surface areas of $<20\mu\text{m}^2$ for Group B experiments with each fraction at a concentration of 0.1g/L.



It is noteworthy that yield, particle size and surface area of alumina from the spent liquor does not add up to the weighted sum of the respective yields, particle sizes and surfaces area from the individual molecular weight fractions. This is illustrated by the data in Figure 3.36 where the <1.2kD fraction gives quite different behavior to the spent liquor, yet it is the major constituent in the liquor. Thus the humic materials must interact with each other in producing precipitation effects or interact in tandem with the surface. Research on natural systems suggests that the poisoning mechanism of humic material is a sequential one (Ochs *et al.*, 1994). Binding sites exist for both newly settling alumina carrying species and humic material, and these species compete for the binding site. Initially ligand exchange of water occurs at the surface followed by a fast process where small molecular weight species occupy binding sites. These molecules are then displaced by irreversibly adsorbing large macromolecular organic species. This would suggest that all the molecular weight fractions play a role in the poisoning process, with the largest molecular weight material having a later role. Thus the data in Figure 3.36 can be explained if the <1.2kD fraction binds to the surface and stops the larger humic materials from enveloping growing surfaces thereby producing smaller surfaces. Similar arguments follow on yield. The spent and pregnant liquors have higher yields than the <300kD fraction but lower yields than the <1.2kD fraction. The presence of the <1.2kD fraction prevents the <300kD fraction from undertaking its activity by occupying binding sites.

These concepts are supported by comparative experiments on seed. Group A experiments (using caustic washed seed) showed a much greater tolerance to humic material, this suggests that caustic washing increases the number of sites at which new alumina carrying species or humic materials can bind. Thus if humic materials bind, there are still plenty of sites left to grow alumina. Indeed Group A experiments showed much less variation in the surface area of the product crystals. Group A experiments showed a maximum change in the surface area of the product crystals of $\pm 10\%$, with many organic fractions producing a change of less than 4% (Figure 3.33). From these results it appears that changes in surface area can be minimised through the use of caustic washed seed.

3.14 Sodium oxalate

Sodium oxalate plays an important role in the sodium content of alumina, as well as in determining crystal size and quality (Armstrong, 1993; Grocott and Rosenberg, 1988). The presence of organic matter in the Bayer liquor is thought to stabilise the sodium oxalate in solution preventing its precipitation. This results in 'oxalate showers' during the precipitation of aluminium hydroxide, where oxalate crystal nuclei form in solution onto which the aluminium hydroxide precipitates, leading to poor quality alumina high in sodium (Armstrong, 1993; Grocott and Rosenberg, 1988).

Figure 3.38 shows results from the oxalate concentrations in the Group A experiments (caustic washed seed). They reveal that the small molecular weight organic species (<50kD) decreased oxalate stability by up to 13%, with the exception being the <1.2kD fraction, this fraction showed a slight increase in oxalate stability (11%). These experiments were performed with the organic fractions at the concentrations recovered from the process liquor. The larger molecular weight organic species (>50kD), although added at low concentrations, were each seen to increase oxalate stability by between 8-15%, including the 100-300kD fraction (15%) which was not tested in Group B experiments due to insufficient sample quantity. The materials from the pregnant and spent liquor also increased oxalate stability, with the pregnant material increasing stability by 33% and the spent material by 23%.

Figure 3.39 shows the oxalate concentration in solution in the presence of each organic fraction at a concentration of 0.1g/L in the Group B experiments (hot water washed seed). Oxalate stability was significantly increased by the 12-25kD, 50-100kD and >300kD organic fractions with the oxalate concentration being increased by more than 16% by the largest molecular weight fraction (>300kD). The oxalate concentration in solution was largely unaffected by the spent fraction (0% change) and pregnant fraction (-2.8% change) when they were added at low concentrations (0.1g/L). The smallest molecular weight fraction (<1.2kD) when added at this concentration also produced no effect on the oxalate concentration. These effects however are very concentration dependent (Table 3.21, Figures 3.39 and 3.40).

Figure 3.39 suggest that there is some relationship between humic molecular weight and capacity to stabilise oxalate in solution. The sodium oxalate may aggregate with the large organic macromolecules via hydrogen bonding, forming host-guest complexes in much the same way as small molecular weight Bayer organics were observed to do (Sections 3.9-3.12). The formation of such complexes prevents the oxalate from agglomerating into a form where it can be precipitated from solution, leading to increased concentrations of the oxalate in solution (i.e stabilisation).

Table 3.21 Results from experiments with humic molecular weight fractions showing concentration affects (Group B experiments) on aluminium hydroxide precipitation using hot water washed seed

Organic fraction	Organic dose (g/L)	Difference in yield of alumina (g) relative to blank	% Change in product with surface area <20 μm^2 relative to blank	% Change in surface area of product relative to blank	% Change in oxalate concentration relative to blank
Pregnant liquor	5	0.31	+6.40	-43.52	+48.60
Spent liquor	5	1.87	+18.54	-60.40	+28.00
<1.2kD	5	-0.79	-2.10	+21.73	+6.63
Pregnant liquor	0.1	-0.82	-2.97	+30.39	-2.80
Spent liquor	0.1	-0.86	-2.58	+26.39	0
<1.2kD	0.1	-0.11	+3.16	-16.65	0

Figure 3.38 Percentage change in oxalate concentration for Group A experiments.

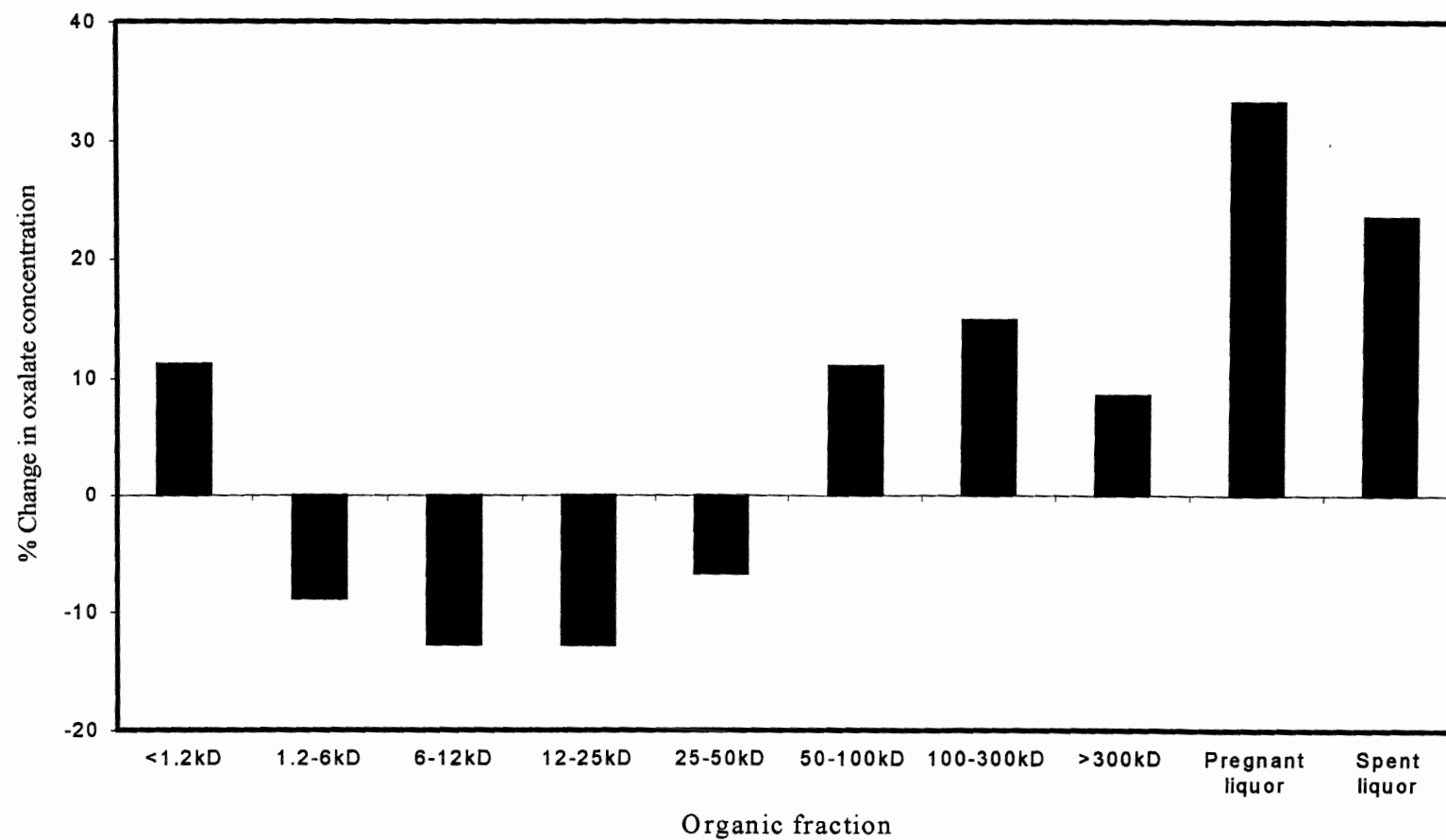


Figure 3.39 Percentage change in oxalate concentration for Group B experiments with organic fractions at concentrations of 0.1g/L.

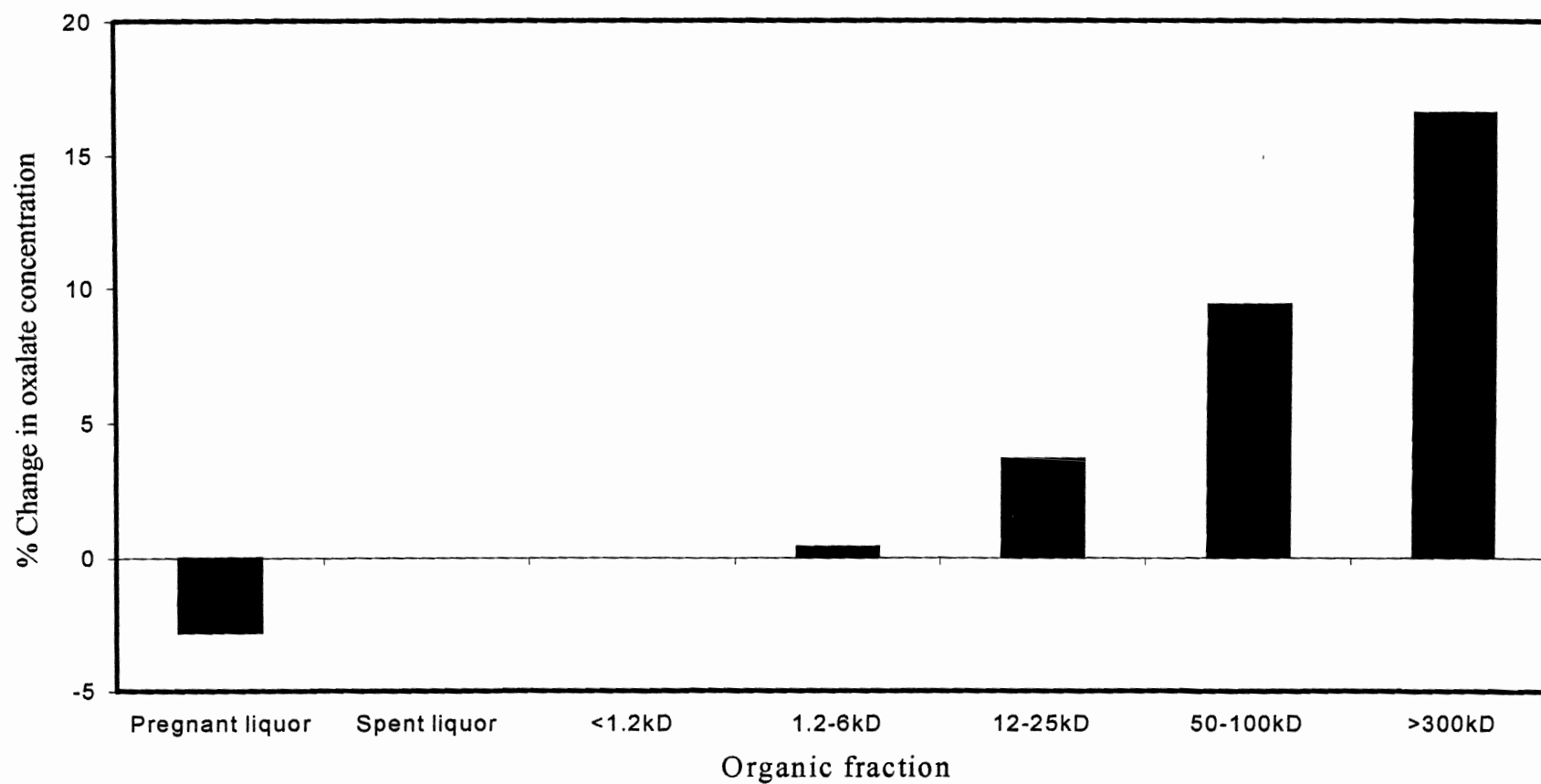
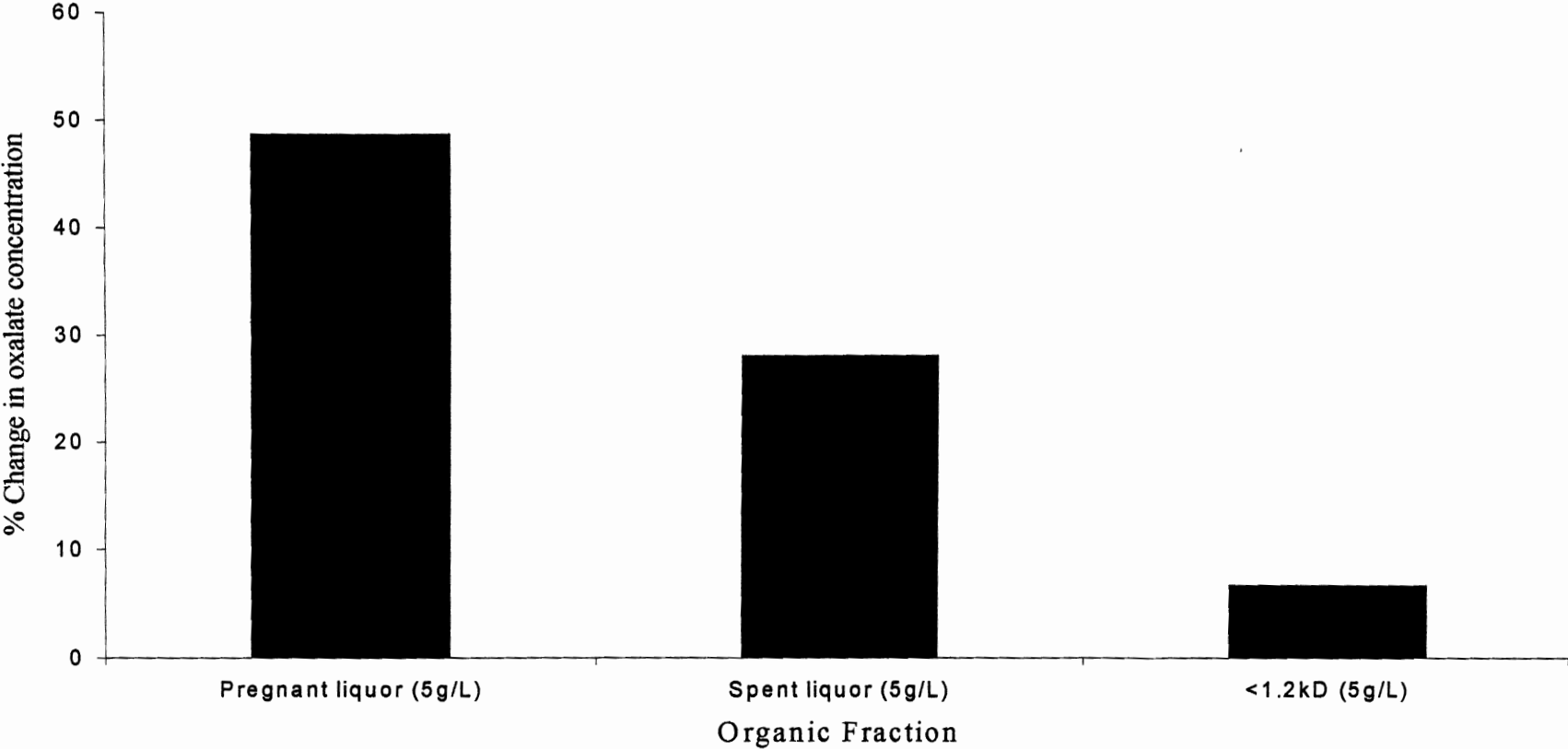


Figure 3.40 Percentage change in oxalate concentration for Group B experiments with organic fractions at concentrations of 5g/L.



3.15 Relationship between poisoning and chemical composition

Studies with model compounds have shown that many small hydroxy-organic compounds act as poisons to the Bayer process (Armstrong, 1993; Coyne *et al.*, 1994; Alamdari *et al.*, 1993; The, 1980; Watling *et al.*, 1996). Model hydroxybenzene carboxylic acid compounds, similar in structure to the compounds isolated in the smallest molecular weight fraction of the Bayer humic substances (Sections 3.3-3.8), were found to be effective aluminium hydroxide precipitation poisons (Armstrong, 1993). The present study supports the findings of the tests with model compounds, revealing that the small molecular weight compounds do effect precipitation yields, as do the larger molecular weight materials. Studies with model compounds have determined that hydroxy-organic compounds produce decreases in particle size of product crystals (Alamdari *et al.*, 1993; The, 1980; Watling *et al.*, 1996). These findings were supported by the results obtained here, as the small molecular weight material isolated from the Bayer process had very strong adverse effects on product sizing, leading to the generation of excessive amounts of fine aluminium hydroxide crystals. However such effects are only seen when there is a deficiency of sites for newly settling alumina carrying species and humic material to bind. Caustic washed seed (Group A experiments) was found to minimise the decreases in yield caused by the poisoning of the precipitation of aluminium hydroxide by the Bayer organic fractions. The reductions in yield when caustic washed seed was used were much smaller than those obtained using hot water washed seed (Group B experiments), even when the organic fractions were present in roughly equivalent concentrations (1.2-6kD, 12-25kD, 50-100kD and >300kD). Caustic washed seed also minimised the changes in crystal size due to the presence of organic compounds, producing crystals of a similar size to the crystals produced with no organics present.

Hot water washed seed (Group B experiments) would already contain significant amounts of bound organics on the crystal surfaces reducing the number of potential sites for aluminate ions to precipitate from solution. Moreover the presence of additional organic compounds in solution would bind with the remaining free precipitation sites on the hot water washed seed effectively preventing further aluminium hydroxide precipitation, thus resulting in a decrease in precipitation yields.

The caustic washed seed (Group A experiments) acts to decrease the inhibition caused by process organics by providing more free sites to precipitate aluminate ions. Caustic washing removes the outer crystal surfaces and bound organics from the seed crystals, thus providing additional aluminate ion precipitation sites that were previously occupied by the process organics.

3.16 Conclusions on the poisoning effects of molecular weight fractions of Bayer humic materials

All molecular weight fractions (from <1.2kD to >300kD) of Bayer humic substances effect the precipitation yields, particle sizes and surface areas of product aluminium hydroxide, however the effects only occur when there is competition for the number of sites at which new alumina carrying species or humic material can bind. The preparation of seed crystal is therefore very important, and because of competition for binding sites the poisoning effects are also concentration dependent.

The higher molecular weight fractions (>50kD) were found to be the most detrimental to the precipitation of aluminium hydroxide from Bayer process liquors, decreasing product yields significantly. The >300kD fraction had the largest effect.

Yield, particle size and surface area of aluminium hydroxide from the spent liquor do not add up to the weighted sum of the respective yields, particle sizes and surface areas from the individual molecular weight fractions. Thus the humic materials must interact with each other in producing precipitation effects, or the organics interact in tandem with the surface. It is probable that initially ligand exchange of water occurs at the surface followed by a fast process where small molecular weight species occupy binding sites. These molecules are then displaced by irreversibly adsorbing large macromolecular organic species. This would suggest that all the molecular weight fractions play a role in the poisoning process, with the largest molecular weight material having a later role.

Oxalate stabilisation in solution is promoted by higher molecular weight organic fractions, especially under conditions in which the system is deficient in binding sites. The highest molecular weight fraction ($>300\text{kD}$) is the most effective, increasing oxalate stability in synthetic Bayer liquor by up to 20%. These results support a model in which humic material can capture oxalate and make it unavailable for precipitation by forming host-guest complexes.

CHAPTER FOUR

CONCLUSIONS

Prior to the commencement of this project, the alumina industry had a significant knowledge of the structures of the thousands of simple organic compounds present in Bayer liquors and which of these compounds actively retard the precipitation of aluminium hydroxide and sodium oxalate. However little was known about the larger molecules collectively known as humic substances, these are compounds of molecular weight greater than 500 Dalton and they are not simple oxidation products such as benzene carboxylic acids.

This thesis focused on characterising the organic materials present in a high temperature (250-255°C) Bayer alumina refinery (The Queensland Alumina Limited refinery, Gladstone, Australia). During the processing of bauxite in the alumina refinery, both soluble and insoluble organic materials are formed. The insoluble organic materials accumulate in certain areas of the refinery including the waste solid material termed "red mud", in the shell-side of the heat exchangers, on sodium oxalate crystals, on aluminium hydroxide "gibbsite" precipitated crystals, in precipitation tank scale, and on oxalate-gibbsite co-precipitation fines.

Analysis of the insoluble organic materials from the Bayer alumina refinery by ^{13}C NMR and pyrolysis GC/MS with in-situ methylation allowed the following conclusions to be drawn:

1. The pyrolysis products for bauxite and red mud were found to differ considerably, with the red mud pyrolysates consisting mainly of aromatic polycyclics. Iron oxide was found to have catalytic effects during pyrolysis leading to the production of simple aromatic compounds, but the materials are intrinsically different.
2. The organic material recovered from the heat exchanger units was found to have characteristics similar to those of a light pitch or tar.
3. Sodium oxalate and aluminium hydroxide produced several common pyrolysis products including alkanes, alkenes, and long chain aliphatic carboxylic acids, predominantly with C_{14} to C_{16} carbon chain lengths, as well as short chain (C_4 - C_7)

aliphatic mono- and di-carboxylic acids. Nitrogen containing compounds seem to favour the oxalate surface.

4. Organic material on the precipitation tank scale was similar in composition to soluble Bayer humic substances. However differences in the concentrations of styrene, methoxybenzene, 4-ethyl-1,2-dimethylbenzene, indene, 1-methylindene, 1-methylfluorene, pyrene, methyl benzoate, and 4-methylquinoline, were observed in the pyrolysates.
5. The oxalate-gibbsite co-precipitation fines surprisingly produced very different pyrolysis products to those from the sodium oxalate and aluminium hydroxide.

The sodium hydroxide soluble organic materials, known as Bayer humic substances, were obtained from the Bayer process liquor, then separated into molecular weight fractions by dialysis. The subsequent characterisation of these materials by various instrumental techniques allowed the following conclusions to be made:

1. The organic material in Bayer liquors from a refinery operating at 250-255°C differs from that in a refinery operating at 150°C. Not unexpectedly, the material has a lower average molecular weight because many of the larger molecules are degraded to smaller molecular weight material by the high temperature processing. The <1.2kD fraction yields mainly hydroxybenzene carboxylic acids on pyrolysis and structurally resembles the highly oxidised humic acids that are found in podsols.
2. The 12-25kD and 25-50kD fractions appear to resemble material more akin to oxidised kerogen while material of higher molecular weight behaves as a soluble char.
3. Novel findings from pyrolysis of the molecular weight fractions were: Pyrolysis of the 6-12kD fraction at 400°C produced the most aromatic hydrocarbons and heteroaromatic hydrocarbons as well as significant amounts of the less toxic materials such as aromatic carboxylic acids, alcohols and aldehydes and ketones.

The less toxic materials were also produced by the fractions of lower molecular weight than this, but the higher molecular weight material is less volatile and produces little identifiable material at this temperature. At 425°C all fractions start yielding significant amounts of aldehydes and ketones, and the <1.2kD fraction produces large amounts of hydroxybenzoic acids. As the temperature is raised further to 450°C, volatiles from the 25-50kD fraction become important, particularly alcohols and aliphatic hydrocarbons. By 500°C all fractions contain significant quantities of aromatic hydrocarbons, phenols, carboxylic acids, alcohols, nitriles, aldehydes and ketones.

A novel finding from the analysis of the soluble organic material present in the high temperature Bayer process liquor was that this material formed host-guest complexes. Host-guest complexes had not been previously identified in humic materials, and the existence of such complexes may have ramifications in explaining the behaviour of humic substances in other environments. Evidence from several instrumental techniques including one and two dimensional nuclear magnetic resonance spectroscopy, methylation with GC/MS, as well as thermal analysis showed the existence of these complexes. The following conclusions could be drawn from this work:

1. The Bayer humic material isolated from the high temperature (250-255°C) alumina refinery had unusual dialysis properties. Many small molecules become entangled with larger molecules and could not be separated by dialysis. The structure of these small molecules was shown to consist of *n*-alkanes, fatty acids and benzenecarboxylic acids.
2. Methylation with tetramethylammonium hydroxide acts to release small molecules trapped in the macromolecules by forming esters and ethers with carboxylic and phenolic groups respectively, thereby breaking the hydrogen bonding that holds the molecules in place. Without methylation, the molecules are held tightly in the macromolecular matrix. Since some of the guests are alkanes it suggests that not all guests are held by hydrogen bonding, that they may also become trapped in molecular voids.

The final section of this thesis examined the effects of the molecular weight fractions on the precipitation dynamics of the Bayer process. Prior to this study it was not known which mass ranges of organic material were most detrimental to the process, or how the poisoning actions could be overcome, as little was known about the structures of the organic materials. In addition, many of the published studies looking at the poisoning of the precipitation of aluminium hydroxide from Bayer liquors used model compounds to draw conclusions about this problem area. Unfortunately, model compounds do not simulate actual conditions encountered during precipitation from Bayer process liquors. It is for these reasons that performing precipitation tests in the presence of fractionated Bayer organic materials is both novel and highly useful. The results from these precipitation tests allowed the following conclusions to be drawn:

1. All molecular weight fractions from <1.2kD to >300kD of Bayer organic material effect precipitation yields, particle sizes and surface areas of product alumina, however the effects only occur when there is competition for the number of sites at which new alumina carrying species or humic material can bind. The preparation of seed crystal is therefore very important and because of competition the effects are concentration dependent.
2. Higher molecular weight fractions (>50kD) were found to be the most detrimental to the precipitation of aluminium hydroxide from Bayer process liquor, decreasing product yields significantly. The >300kD fraction had the largest effect. The higher molecular weight organic fractions were also seen to have the largest impact on oxalate stability, increasing oxalate stability in synthetic Bayer liquor by up to 20%.
3. Yield, particle size and surface area of alumina from the spent liquor do not add up to the weighted sum of the respective yields, particle sizes and surface areas from the individual molecular weight fractions. Thus the humic materials must interact with each other in producing precipitation effects or interact in tandem with the surface. It is probable that initially ligand exchange of water occurs at the surface followed by a fast process where small molecular weight species occupy binding sites. These molecules are then displaced by irreversibly adsorbing large

macromolecular organic species. This would suggest that all the molecular weight fractions play a role in the poisoning process, with the largest molecular weight material having a later role.

4. Oxalate stabilisation in solution is promoted by higher molecular weight fractions, especially under conditions in which the system is deficient in binding sites. The highest molecular weight fraction ($>300\text{kD}$) is the most effective. These results support a model in which humic material can capture oxalate and make it unavailable to the precipitation pool by forming host-guest complexes.

As a result of this thesis the structures of the organic material from a high temperature alumina refinery are now known, including both soluble and insoluble materials. The poisoning effects of the soluble materials on the precipitation of aluminium hydroxide and sodium oxalate have also been determined. In addition a new host-guest theory for humic materials has been proposed.

Recommendations

I recommend that the alumina industry further investigate seed crystal preparation and the effects on the Bayer process. Caustic washing of seed crystals was identified as one area that significantly altered the precipitation process.

Now that the chemistry of the Bayer process organics is largely known, methods for negating the effects of these organics need to be developed. The macrovegetation entering the Bayer process also needs to be characterized as part of future work. Research on the chemistry of the macrovegetation is currently being performed at UTS.

CHAPTER FIVE

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Appendix A

Published Manuscripts

The following manuscripts were written, submitted and accepted during the course of this thesis.

Smeulders D.E., Wilson M.A., Patney H.K. and Armstrong L. Structure of molecular weight fractions of Bayer humic substances. II Pyrolysis behaviour of high temperature products. *Industrial and Engineering Chemistry Research*, **2000**, 39, 3631-3639.

Wilson M.A., Kannangara G.S.K. and Smeulders D.E. Funeral arrangements for plants: An essay in organic geochemistry. *Journal and Proceedings of the Royal Society of New South Wales*, **2000**, 133, 71-85.

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Smeulders D.E, Wilson M.A. and Kannangara G.S.K. Host-guest interactions in humic materials. *Submitted to Organic Geochemistry*, **2000**.

Smeulders D.E., Wilson M.A., and Armstrong L. Insoluble organic compounds in the Bayer process. *Submitted to Industrial and Engineering Chemistry Research*, **2000**.

Smeulders D.E., Wilson M.A., and Armstrong L. Poisoning of the precipitation of aluminium hydroxide by molecular weight fractions of Bayer humic substances. *Submitted to Industrial and Engineering Chemistry Research*, **2000**.

Structure of Molecular Weight Fractions of Bayer Humic Substances. 2. Pyrolysis Behavior of High-Temperature Products

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Reprinted from
Volume 39, Number 10, Pages 3631–3639