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IDENTIFICATION OF ORGANICS IN BAYER LIQUOR

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The major organic compounds in Bayer liquor have been classified into the following three groups: (a) the humic matter, consisting of the coloured high molecular weight organics extracted from the bauxite and their initial degradation products; (b) the humic "building block" organic compounds which are mainly the benzene carboxylic acids and phenolic acids; and (c) the low molecular weight degradation products such as formic and oxalic acids. The organics in group (a) were characterized by measuring their molecular weight distributions by gel filtration chromatography and ultrafiltration. The organics in group (b) were extracted using organic solvents, methylated, separated by gas chromatography and identified by comparing their retention times and infrared spectra to those of known compounds. Group (c) compounds were already known to be present but their identification was confirmed by gas chromatography of their butyl esters.

Introduction

Bauxites usually contain from 0.1 to 0.3% organic carbon, but occasionally up to 0.6% is found when surface bauxites are mined. It is generally believed that the organic carbon is present in the form of humic substances. On digestion in the Bayer process, over 50% of the organic carbon is extracted into the liquor and its concentration gradually builds up to an equilibrium level with recycling of the liquor. The accumulated humic matter and its breakdown products are known to cause numerous process problems. An important example is the inhibiting effect of the organics on hydrate precipitation resulting in a decreased solution productivity. Also, the sodium oxalate concentration builds up to a critical supersaturated concentration, then precipitates giving rise to hydrate fines by interfering with agglomeration in the precipitation circuit and acting as nuclei for hydrate precipitation. The finely precipitated oxalate again interferes in the final decanting process of fine hydrate from the recirculated spent liquor, leading to the return of significant quantities of hydrate to the digestion circuit. Little is known, however, about the organic matter in Bayer liquor in terms of its identity and the mechanisms by which it causes the various process problems.

Other possible sources of organic carbon in Bayer liquor are the flocculants and antifoams used in the process. The contribution of these organics to the total organics present in the liquor is believed to be small and this presentation will therefore concentrate on the organic matter originating from the bauxite (1).

One of the earliest studies of the organics present in Bayer liquor was carried out in 1954 by Breuer, who estimated the concentration of eight organic compounds (2). Although his findings are important, many of the techniques used were long and involved and are of little relevance today. Another interesting investigation was that carried out by Jakab et al who detected over 30 phenolic compounds after hydrolysing a soil humic acid in 5N NaOH at 170°C (3). More recently Neyroud and Schnitzer subjected a humic acid to four successive hydrolyses in 2N NaOH at 170°C for 3 hours (4). Fatty acids, phenolics and benzene carboxylic acids were the major degradation products. Oxidation of the unhydrolysed humic matter with alkaline $KMnO_4$ gave high yields of benzene carboxylic acids. Soil chemists, in the last five to ten years, have applied powerful analytical techniques to the study of humic substances and a more meaningful picture of their structures is now emerging (5).

Because of the problems caused in the Bayer process by the organic matter, I have attempted to characterise the organics in order to study the effect of the individual compounds or fractions on different aspects of the process. The material has been classified into three groups:

(a) the humic matter, consisting of the freshly extracted high molecular weight material and its initial degradation products of molecular weight greater than 500,

(b) the intermediate degradation products which constitute the "building blocks" of the large humic molecules, e.g. benzene carboxylic acids and phenolic acids.

(c) The low molecular weight degradation products.

The two liquor samples investigated in this study were from Bayer plants processing Jamaican bauxites. One sample was from a low temperature (135°C) digestion plant and the other from a high temperature (240°C) digestion plant. The organic carbon content of the two liquors was 8.5 and 15.0 g.p.l. respectively.

It should be noted that although the organic acids are present as their sodium salts in Bayer liquor they will in this presentation often be referred to as the free acids.

Experimental Methods

Humic Matter

Molecular weight (M.W.) distributions were estimated using ultrafiltration and gel filtration chromatography.

Ultrafiltration. Fractionation of the humic matter by ultrafiltration was used to estimate its molecular weight distribution. An Amicon Model 402 stirred ultrafiltration cell of 400 ml volume and the following Amicon ultrafiltration membranes were used: UM05 (M.W. cut-off 500), UM2 (M.W. cut-off 1000), DM5 (M.W. cut-off 5000) and PM10 (M.W. cut-off 10,000). Each ultrafiltration membrane is characterised by its nominal M.W. cut-off as determined with protein (globular) molecules. Membrane preparation and operating pressures were as recommended by the manufacturer.

Because of the pH limitations of the stirred cell and membranes, it was necessary to pretreat the liquor prior to ultrafiltration. Of several methods investigated the following proved the simplest.

40 ml of Bayer liquor was placed in a separatory funnel and acidified with 7.2N hydrochloric acid to pH2. The sample was then extracted twice with 100 ml portions of n-butanol. The combined butanol extracts containing all of the humic matter was first washed with 150 ml of 1N NaOH to remove most of the hydrochloric acid that had extracted, then washed with 10 ml portions of 1N NaOH. The washings were discarded until the colour started to transfer into the aqueous phase. Small portions of the 1N NaOH were then added until all the coloured humic matter had extracted into the aqueous phase, which was then separated. The butanol was finally washed with water containing a small amount of NaOH to ensure the complete extraction of the humic substances. Using this method the humic substances could be extracted from the liquor almost salt-free. Removal of the final traces of salt was achieved by ultrafiltration through a UM05 membrane. Fractionation was then carried out by ultrafiltration, successively, through the PM10, DM5, UM2 and UM05 membranes. The fractions were gently evaporated to dryness at 90°C and weighed.

Gel Filtration Chromatography. An initial evaluation of two column packing materials, Spherosil porous silica beads and Biogel P, suggested the former had more promise. Porous glass beads had previously been used successfully for the analysis of water soluble polymers, containing carboxylate groups (6). Because humic substances are polymeric and have many carboxylate groups, it was thought that a similar type of packing would be suitable for our studies. Previous investigations with humic acid had shown that a high ionic strength eluant would be required to minimize ionic exclusion (7) (8). There was no visible sign of adsorption of the humic matter by the Spherosil packing.

The conditions used were as follows: two 50 cm x 0.7 cm internal diameter glass columns packed with Spherosil 100/200 micron porous silica beads of pore sizes 100 and 140 Å respectively. An aqueous solution of 0.4 M NaCl and 0.05 M borax of pH 8.5 was used as eluant. Flow rates of 0.5 to 1.0 ml/min. were used and controlled by applying pressure from a helium cylinder to the eluant reservoir. Sample volumes of 0.1 to 0.25 ml, and sample concentrations of 1 to 5% of humic substances dissolved in the eluant were used. A Beckman model B spectrophotometer set at 400 nm wavelength and fitted with a JP44G flow cell was used to monitor the column effluent. Modification of the spectrophotometer allowed the output to be displayed on a recorder.

Calibration of the instrument proved difficult due to the non-availability of suitable molecular weight standards. An attempt was made to calibrate the instrument using the fractions prepared by ultrafiltration. Because of the polydispersity of the fractions, calibration by this method could not be used for accurate molecular weight distribution measurements. However, the shape of the gel filtration curve was used as a fingerprint to characterise the humic material.

"Building Block" Organics

40 ml of spent Bayer liquor was carefully acidified to pH2 using 7.2N hydrochloric acid solution. The solution was then transferred to a Quickfit liquid/liquid extractor and extracted with 300 ml ether for 16 hours. The organic extract was then evaporated to dryness, the residue was dissolved in 25 ml of methanol and methylated using an ethereal solution of diazomethane, generated from Diazald, until all hydroxyl groups had reacted (9). After removing the solvents by evaporation, the residue was dissolved in methanol and transferred to a 5 ml volumetric flask.

The methylated sample was first examined by analytical gas chromatography using the following conditions: Perkin Elmer Model 3920 flame ionisation detector, 1.83 m x 3.18 mm O.D. stainless steel column containing 3% OV-17 on 80-100 mesh Gaschrom Q, programmed from 100° to 320°C at 8°C/min and nitrogen flow of 30 ml/min. An example of the type of chromatogram obtained is shown in Figure 1.

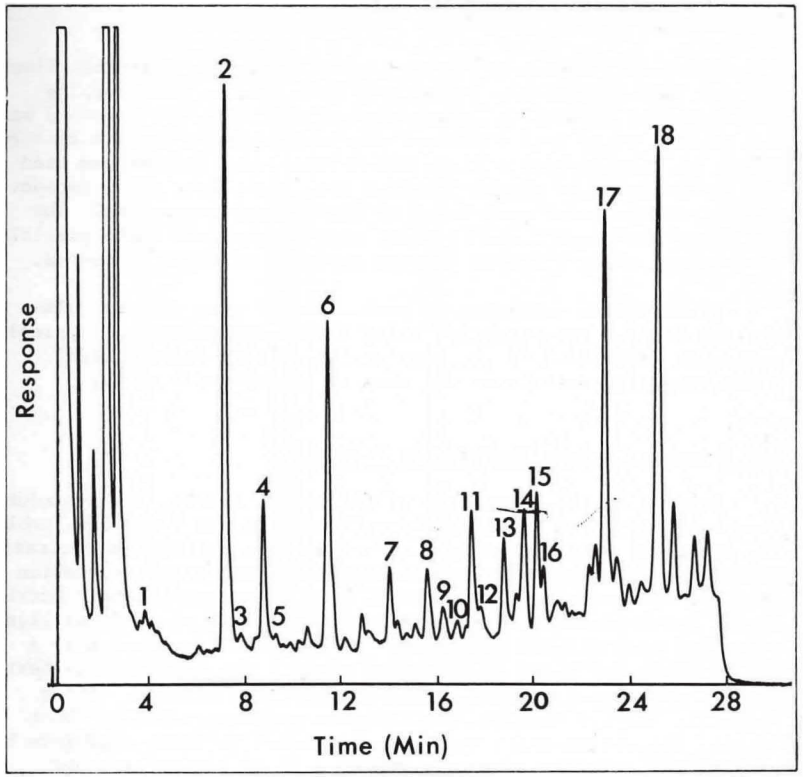


Fig. 1 - Gas Chromatogram of Methylated "Building Block" organics extracted from Bayer liquor.

Where possible the major compounds were tentatively identified by comparing their retention times to those of known compounds. As an initial guide, compounds that had been found in previous studies on humic acid degradation and that were readily available commercially, were tried (4).

Confirmation of the identity of the organics tentatively identified by their retention times was carried out using the following gas chromatography/micro-infrared spectrophotometry technique. A methylated sample was separated by preparative gas chromatography and the individual peaks were trapped, in glass capillary tubes containing several mg of potassium bromide as they eluted from the chromatographic column. It was necessary to use a column exit splitter which diverted about 95% of the eluant to the capillary tube. The chromatographic column was similar to the analytical column except for its size which was 1.83 m x 6.35 mm O.D. Gas chromatographic operating conditions were varied depending on the retention time of the eluting compound and the resolution required. After preparing a small pellet of the trapped material on potassium bromide, a micro-infrared analysis was carried out using a Beckman IR20 spectrophotometer equipped with a Barnes model 128 beam condenser. The identity of the compound was confirmed by matching its infrared spectra with those of known compounds.

Compounds that could not be identified by the retention time/infrared combination were identified as follows. The trapping procedure was repeated a second time, except that the compound was now trapped in an open capillary tube and analysed by mass spectrometry. A Hitachi-Perkin Elmer RMU-60 mass spectrometer was used for the analysis by Morgan Schaffer Inc., Montréal, P.Q., Canada. Several of the peaks were found to contain two components. The compounds were identified by their mass spectra and where possible by matching their infrared spectra to those of known compounds.

Quantitative estimates of each compound were made by calibrating the gas chromatograph using a standard mixture of typical compounds identified in the samples. A Hewlett Packard model 3390A computing integrator was used to measure peak areas.

Low Molecular Weight Degradation Products

Because of the volatility of the methyl esters, the procedure used to analyse the "building block" organics was found unsuitable for the lower molecular weight compounds. The following quantitative method was developed whereby the organic acids, after separation from the liquor using ion exchange, were converted to their butyl esters and determined by gas chromatography. 10 ml of Bayer liquor which had been diluted by a factor of ten, was transferred to a 100 ml flask and 30 ml of hot water added. The solution was heated to 80°C and gassed with CO_2 to precipitate the alumina. After filtering off the alumina, the filtrate was evaporated to about 30 ml. The sodium salts were then converted to their acid form by passing the solution through a 200 mm x 16 mm cation exchange column containing Amberlite IR-120 resin. Care had to be exercised due to the vigorous evolution of CO_2 from the solution. The sample was eluted with eight 10 ml portions of water into a 250 ml Erlenmeyer flask. A reflux condenser was added and the eluate boiled for 5 minutes to remove any dissolved CO_2. After cooling to room temperature, the solution was neutralized with 0.1N NaOH using a phenolphthalein indicator. The solution was evaporated to dryness and after dissolving in a small volume of water, transferred quantitatively to a one ml Pierce Reactivial and evaporated to dryness a second time using a Pierce Reactitherm heating module at 90°C. After cooling, the sample was butylated as follows. Two drops of 7.2N hydrochloric acid and 400 µl of an internal standard solution, containing 500 mg of nonanoic acid per 100 ml of butanol were added and the solids dissolved. A magnetic stirrer was added, the vial closed, and heated at 110°C for 40 minutes. After cooling, the excess acid was carefully neutralized by adding sodium bicarbonate. The supernatant liquid was then analysed by gas chromatography under the following conditions: Perkin Elmer model 3920, flame ionisation detector, 1.53 m x 3.18 mm O.D. stainless steel column packed with 5% Carbowax 20M on 80-100 mesh, Gaschrom Q, programmed 2 minutes at 50°C then at 16°C/min. to 210°C and nitrogen flow of 30 ml/min. An example of the type of chromatogram is shown in Figure 2. The concentrations of the individual

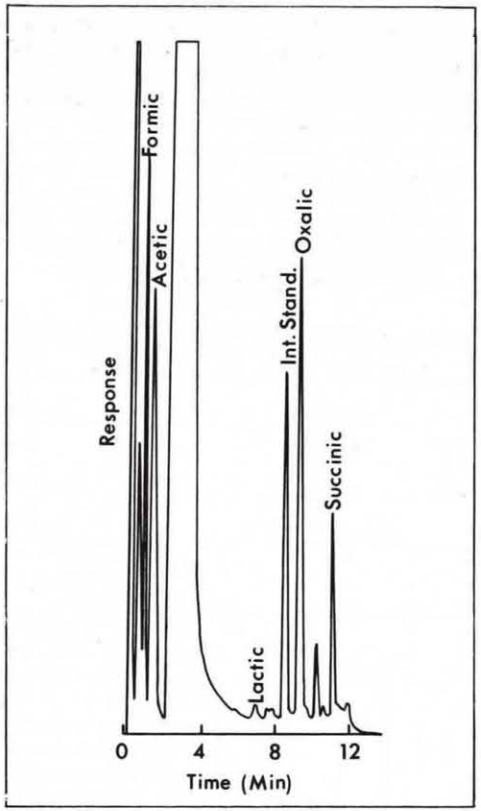


Fig. 2 - Chromatogram of Low Molecular Weight Degradation Product.

low molecular weight acids were measured by comparing to a known standard solution using the internal standard method.

Results

Humic Matter

The percentage of the total humic matter retained by each ultrafiltration membrane is listed in Table I. From the results it can be seen that the apparent molecular weight distributions as determined by ultrafiltration fractionation are very similar for the two samples, with most of the humic matter having an apparent molecular weight of between 1,000 and 5,000. The organic carbon content of the humic matter corresponded to 2.1 g.p.l. for the low temperature liquor and 3.6 g.p.l. for the high temperature liquor, or approximately 25% of the total organic carbon present in each liquor.

The shapes of the gel filtration elution curves were also found to be similar. The curve for the low temperature digestion liquor is shown in Figure 3. Normally the system would be calibrated by measuring the elution volumes of standards of known molecular weight but this was not possible.

Table I

Percentage of Total Humic Matter Retained by Each Ultrafiltration Membrane

Membrane	M.W. Cut-off	Liquor Digestion Temp. 135°C	240°C
PM 10	10,000	2	0
DM 5	5,000	14	12
UM 2	1,000	75	76
UM 05	500	9	12

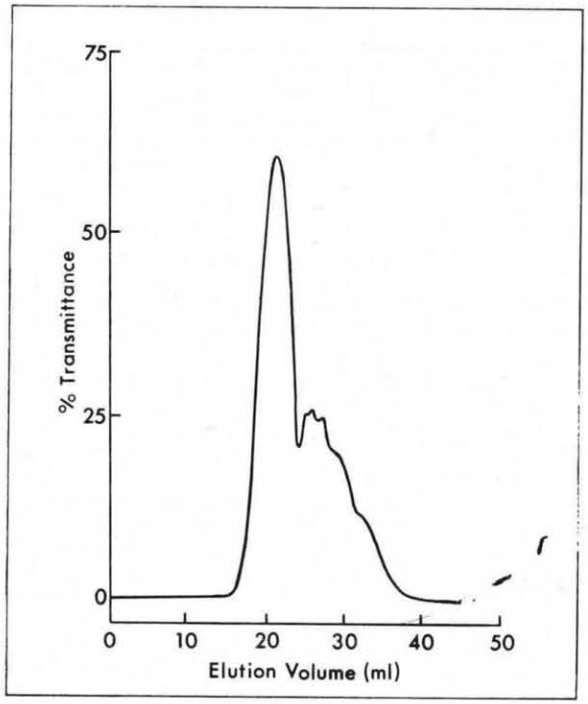


Fig. 3 - Gel Filtration Elution Curve for Humic Matter Extracted from a Low Temperature Digestion Bayer Liquor.

"Building Block" Organics

The major and certain minor compounds identified in a low temperature digestion liquor and a high temperature digestion liquor are listed in Table II. Estimates of the concentrations of the individual compounds are also given. From the computing integrator surface area measurements, it was estimated that 81% of the low temperature liquor "building blocks" and 93% of the high temperature liquor "building blocks" were identified.

Table II

"Building Block" Compounds (mg/l) Identified in Bayer Liquors

No.	Compound	Liquor Digestion Temperature 135°C	240°C
1	Glutaric acid	10	20
2	Pentanedicarboxylic acid	540	100
3	2-Hydroxy benzoic	10	70
4	Hexanedicarboxylic acid	150	250
5	Dihydroxybenzoic acid	10	10
6	Pentanetricarboxylic acid*	340	10
7	Hydroxybenzenedicarboxylic acid	70	470
8	1,2,4-benzenetricarboxylic acid	70	260
9	1,3,5-benzenetricarboxylic acid	50	410
10	Methyl-benzenetricarboxylic acid	25	250
11	Ethyl-benzenetricarboxylic acid	150	360
12	Dihydroxybenzenedicarboxylic acid		
13	Hydroxybenzenetricarboxylic acid	100	10
14	1,2,4,5-benzenetetracarboxylic acid	140	490
15	1,2,3,5-benzenetetracarboxylic acid	120	990
16	Methyl-benzenetetracarboxylic acid	40	200
17	Benzenepentacarboxylic acid	460	1580
18	Benzenehexacarboxylic acid	640	570
	* Tentatively Identified		
	Identified	2925	6050
	Total from integrator count	3600	6500
	% of compounds identified	81	93

Table III classifies the identified organics according to the type of compound. Examples of the structures of the three types of compounds identified in the "building block" organics are shown in Table IV. The total organic carbon present in the "building block" organics was estimated at about 1.8 g.p.l. for the low temperature liquor and 3.3 g.p.l. for the high temperature liquor, or about 22% of the organic carbon present in each liquor.

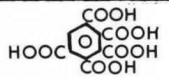
Table III

Percentage of Each Type of Compound Present in the Identified "Building Block" Organics

Type of Compound	Liquor Digestion Temperature 135°C	240°C
Benzenecarboxylic acids	55	81
Phenolic acids	9	12
Aliphatic acids	36	7
Ratio of benzenecarboxylics to phenolics	6.1	6.8

Table IV

Examples of the Structures of the Three Types of Compound Identified in the "Building Block" Organics

Type of Compound	Example	Structure
Benzenecarboxylic acid	Benzenepentacarboxylic acid	
Phenolic acid	2-hydroxy benzoic acid	
Aliphatic acid	Pentane dicarboxylic acid	$HOOC(CH_2)_5COOH$

Low Molecular Weight Degradation Products

Although the identity of these compounds was already known, their presence was confirmed by gas chromatography of their butyl esters. Table V lists the concentrations of five of the major low molecular weight acids present in a low temperature digestion liquor.

Table V

Low Molecular Weight Degradation Products Present in Low Temperature Digestion Bayer Liquor

Compound	Concentration (mg/l)
Formic acid	2290
Acetic acid	4440
Lactic acid	180
Oxalic acid	2530
Succinic acid	1420

The organic carbon content of the low molecular weight degradation products corresponds to 3.73 g.p.l., or 44% of the organic carbon present in the low temperature digestion liquor.

Discussion

The results reported in this study show that the organic matter in Bayer liquor is present as a complex mixture of humic matter and its intermediate and low molecular weight degradation products. Compounds with molecular weights ranging from 50 up to about 10,000 are present. Approximately half of the organic carbon in Bayer liquor is present as low molecular weight organic acids, with the rest about equally divided between the humic matter and the "building block" organics.

Of the fractions investigated, the humic matter proved the most difficult to characterise because of its complex nature. The molecular weight distribution techniques used were not entirely satisfactory due to the lack of a suitable calibration procedure. However, the results have provided a useful estimate of the molecular weight distribution of the humic matter. Further studies are underway in our laboratory to better characterise this fraction.

The percentage of the total organic carbon present in the humic matter and the "building block" organics was surprisingly similar for the two liquors. Major differences were, however, found in the "building block" organics, suggesting different degradation mechanisms of the humic matter at the two digestion temperatures. Further research is necessary before any conclusions can be arrived at concerning the similarities and differences of the organic substances in the two samples.

The results of the study support the structure proposed by Schnitzer for humic substances as being made up of benzene carboxylic acids and phenolic acids joined by hydrogen bonding to form a stable polymeric structure (10). Breakdown of the structure leads to the release of the benzene carboxylic acid and phenolic acid "building blocks".

Soil chemists have shown that the ratio of benzene carboxylic acids to phenolic acids varies between 0.2 and 3.5 depending on how drastically the humic matter has been oxidised (11). In the case of Bayer liquor the relatively high ratio can be explained by the fact that we have found the rate of oxidation of the phenolic acids is much higher than that of the benzene carboxylic acids, resulting in an accumulation of the latter and thus a higher ratio in the liquor at equilibrium.

There are several possible explanations for the presence of the aliphatic acids in the "building block" organics. The most likely is that they are esterified to the phenolic OH groups present in the original humic matter, probably acting as bridges between the benzene carboxylic acids-phenolic acids structures. On hydrolysis in the Bayer process the aliphatic acids are liberated. It is also possible, especially with regard to the lower polybasic aliphatic acids, that they are formed by opening of the aromatic rings of the phenolic acids during digestion.

From this study, the organic matter extracted from the bauxite, can be visualised as being continuously hydrolysed and slowly oxidised through the intermediate "building blocks" to the low molecular weight acids and eventually to carbonate. Also, sufficient data has now been generated to commence meaningful studies on the effect of the organic matter on the different aspects of the Bayer process.

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