Cobalt and iodine complexes in groundwater and sodium humate solution

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COBALT AND IODINE COMPLEXES IN GROUNDWATER AND SODIUM HUMATE SOLUTION

by

ALI IBRAHEM KHALEEL

A thesis submitted in partial fulfilment of the requirements for the award of

MASTER OF PHILOSOPHY
of
Loughborough University of Technology

January 1989

Research supervisor: Dr P. WARWICK
Department of Chemistry

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DEDICATION

To,

My beloved parents
ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr P. Warwick for his brilliant suggestions and excellent assistance. His guidance and constructive criticism throughout the writing of my thesis has enabled me to successfully complete it.

I would like to thank Mr. Philip Shaw and Ms. Wendy Alderton for their wonderful friendship and invaluable assistance.

Thanks are also due to all members of nuclear chemistry section and to all members of the technical staff in the department especially Mrs. Linda Sands for their help.

I am grateful to G. Williams, D. Haigh, J. Higgo and P. Hooker from British Geological Survey (Keyworth) for advice throughout this work.

My thanks are also due to the Ministry of Higher Education and Scientific Research (IRAQ) for financial support.
ABSTRACT

This work is a comparative study between groundwater and sodium humate solution for cobalt and iodine interaction. The weak cationic adsorption properties of Sephadex gel (G-10) have been utilized to separate free cobalt from uncomplexed cobalt. Iodine species were separated by using the separation according to the difference in molecular size.

The kinetics of the association of cobalt with groundwater has been shown to be slow whereas that with sodium humate solution is fast. This association has been shown to be influenced by pH, cobalt concentration and the concentration of groundwater and sodium humate solution. The interaction of cobalt with sodium humate solution, in contrast to groundwater, has been found not to be affected by temperature. In contrast to groundwater, the percentage complexation of cobalt with unfiltered sodium humate solution has been shown to be higher than that of 0.45μm filtered sodium humate solution.

Iodide has been shown not to complex with groundwater whereas 10% of iodide appeared as a "complex" in sodium humate solution. The effect of reducing and oxidizing agents were investigated.

Gamma radiation has been shown to increase the groundwater's ability to complex with cobalt and to decrease the complexing ability of sodium humate solution. The pH and $E_4/E_6$ ratio of groundwater and sodium humate solution have been shown to decrease during irradiation. The effects of radiation on the kinetics of the interaction of cobalt with groundwater and sodium humate solution were studied. The effects of low doses (34 grays/hour) and high doses (61 grays/hour) of radiation on the association of cobalt with groundwater were investigated.

The effects of radiation on the iodine association with groundwater and sodium humate solution have been investigated. The change in pH values of both solutions was also investigated.
### CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dedication</td>
<td>i</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>ii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Contents</td>
<td>v</td>
</tr>
</tbody>
</table>

Chapter one: Introduction

1-1 Radioactive waste disposal and management                           | 1    |
1-2 Groundwater: general view                                          | 4    |
1-3 Organics in groundwater                                             | 5    |
   1-3.1 Definition                                                     | 5    |
   1-3.2 Origin                                                         | 5    |
   1-3.3 Classification                                                 | 5    |
   1-3.4 Some properties                                                | 6    |
   1-3.5 Chemical structure                                             | 6    |
   1-3.6 Analysis                                                       | 7    |
      1-3.6.A Functional groups                                         | 7    |
      1-3.6.B Elemental analysis                                         | 11   |
1-4 Spectroscopic studies on humics                                    | 14   |
   1-4.1 IR spectroscopy                                               | 14   |
   1-4.2 NMR spectroscopy                                              | 15   |
   1-4.3 U.V and visible spectroscopy                                  | 17   |
   1-4.4 Fluorescence                                                  | 18   |
1-5 Metal interactions with humic materials                            | 20   |
   1-5.1 General                                                       | 20   |
   1-5.2 Nature of interaction                                          | 21   |
1-6 Techniques used in the study of speciation equilibria              | 25   |
1-7 Objectives of the present work                                     | 27   |
Chapter two: Experimental

2-1 Technique and general remarks 28
2-2 Groundwater (G.W) 31
2-3 Sodium humate (NaHu) and chemicals 32
2-4 Comparison of Sodium humate solution and groundwater for cobalt complexation

2-4.A Sodium humate solution (NaHu) 33
  2-4.A.1 Kinetics
    Co complexation with fresh, unfiltered NaHu
    Co complexation with fresh 100ppm and 200ppm 0.45μm filtered NaHu
  2-4.A.2 Effect of temperature 34
  2-4.A.3 Effect of cobalt concentration 34
  2-4.A.4 Effect of pH 35

2-4.B Groundwater solution (G.W) 35
  2-4.B.1 Effect of groundwater concentration 35
  2-4.B.2 Effect of temperature 35
  2-4.B.3 Effects of pH 35
  2-4.B.4 Effect of cobalt concentration 36
  2-4.B.5 Molecular size effects 36
  2-4.B.6 Effects of adding EDTA 37
    Separation procedure 37
    Experimental 37

2-5 The effect of radiation on cobalt complexation with groundwater and with sodium humate

  2-5.1 Preliminary experiments 38
    Cobalt complexation 38
    E₄/E₆ ratio and pH investigations 39
  2-5.2 Reproducibility 39
  2-5.3 Cobalt-58 and distilled water 39
2-5.4 The effect of radiation on the kinetics of Co-5 with x10 concentrated groundwater x10 G.W solution irradiated before Co added x10 G.W solution equilibrated with Co then irradiated

2-5.5 200 ppm NaHu solution equilibrated with Co-58 then irradiated

2-5.6 Low dose delivered

2-5.7 Gel permeation chromatography of groundwater

2-6 Iodide complexation with groundwater and sodium humate solution

Non radiolytic investigations
Radiolysis investigations

Chapter three: Results and discussion

3-1 Technique
3-2 Some equilibrium studies of cobalt
3-3 pH effects
3-4 Effects of cobalt concentration
3-5 Molecular size effects
3-6 Effects of addition of EDTA
3-7 Radiolysis of cobalt solutions
3-8 Gel permeation of groundwater solution
3-9 Iodide interaction with NaHu and G.W
3-10 Irradiating iodide mixtures with Co-60 gamma photons
3-11 Investigation of iodine species
3-12 Statistics
3-13 Conclusions
3-14 Suggestions for further work
References
CHAPTER ONE
INTRODUCTION

1-1 Radioactive waste disposal and management

The behaviour of radionuclides in the geosphere in connection with the disposal of radioactive waste has become of major importance in recent years. Radioactive waste may be solid, liquid or gaseous wastes resulting from the production or use of radioactive substances. There are three main sources of radioactive waste:

1. Nuclear reactors and chemical processing plant;
2. Industrial establishments such as Amersham International, Amersham;
3. Other users, e.g.: hospitals, research institutions, universities, industries and military nuclear activities.

Radioactive waste can be divided into three levels, high level waste (HLW), intermediate level waste (ILW) and low level waste (LLW). However, a clear-cut distinction cannot be made between these three levels of radioactive wastes.

Following the House of Commons' Environment Committee recommendations, low level waste should contain only short lived radionuclides and should not contain alpha emitters.

HLW originates from spent fuel and reprocessing of spent fuel (4,5,6,7). HLW contains high activity materials such as precipitates and concentrates (3,4), and high concentrations of fission products and actinides.

HLW emits a considerable amount of heat and this must be taken into consideration when considering the design of storage or disposal facilities. Because of heat generation, borosilicate glass was chosen for high level disposal (4) because it resists heat and radiation, does not return the activity to the biosphere and can accommodate the radionuclides present in the concentrated solutions arising from the first cycle of solvent extraction. However, dissolution of the glass is likely to take place on a timescale of few thousand years.
The activity of ILW is 1000 times less radioactive than that of HLW and exceeds that of LLW. There are no heating problems to be considered in the design of storage or disposal facilities for ILW. This category of waste contains fuel cladding, used reactor and plant components, sludges, resins and filters. The radionuclides in ILW include $^{137}$Cs, $^{90}$Sr, and $^3$H whose half-lives are thirty years or less, and actinides such as U, Pu, Am and Np and other long-lived radionuclides such as $^{14}$C, $^{59}$Ni, and $^{99}$Tc. The activity of LLW is typically 1000 times less radioactive than ILW. LLW activity should not exceed 4 GBq/te with respect to alpha-activity or 12 GBq/te with respect to beta/gamma-activity. LLW contains laboratory or plant waste such as protective clothing, glassware, low concentrations of fission products and very low concentrations of actinides.

As well as the above three levels of classification, the U.K Department of the Environment classified another level, as very low level waste. This level can be defined as radioactive waste which contains such a low level of activity that it can be safely disposed of with household refuse. Up to 0.1 m$^3$ of materials of less than 400 KBq activity may be included in this level.

In general, radioactive waste may also be classified as into waste containing short lived or long lived radionuclides. It is desirable to store short lived (i.e. short half-life) material until its activity is low enough for it to be safely disposed of. For long lived wastes it is advisable to dispose of the waste as soon as possible.

Long-lived wastes require deep disposal, but disposal at shallower depth may be acceptable for shorter-lived wastes. A general requirement for the disposal of any waste is to ensure that the disposal location is remote from man's environment and thus the two methods which have been historically chosen are burial on the land or dumping in the sea.

Waste management includes the policy and practices which define the classification, control, movement, conditioning.
storage and disposal of wastes. The aim is to ensure that there is no significant exposure of the public to radiation at any time (5). For the disposal of any material, there are two options. Keeping it as long as necessary, "concentrate and confine", or allow it to mobilize and disperse harmlessly, "dilute and disperse". There are problems in adapting either of the two options. The first option is difficult to ensure for a long time. For "dilute and disperse" it is necessary to ensure that any eventual releases of radioactivity are within an acceptable level (5). In spite of the problems associated with both options, short-lived radionuclidic waste is usually contained until a sufficient number of half-lives have passed so that their concentration in the waste is extremely low. Long-lived radionuclide containment for any equivalent number of half-lives is impossible, thus their disposal is by the second option (5).

There are four main systems for disposal (5): shallow burial, deep injection of liquid wastes into porous strata, deep burial in a purpose-built or existing mine "repository" and deep burial in boreholes drilled from the surface. Irrespective of all other types of waste disposal, LLW material can be packed in bags or drums (7) and put into trenches of up to 10m depth (5). An example of the disposal of low activity solid radioactive waste at or near the surface (shallow ground burial) is the burial of large volumes of waste material at Drigg, on the Cumberland coast in the U.K (8).

Worthy of note is that the repository barriers can be broken into two zones, the near field and far field (5). The near field is the zone which has been significantly altered by the presence of the repository and it controls radionuclide releases from the repository. The far field is the unaltered natural geological zone which controls the rate at which water can enter the near field and also retard the transport of radionuclides from the near field. Near field barriers include; the insolubility of the solidified waste, corrosion resistant canister and the backfill material (7). The low local groundwater flow rate, adsorption on the rock and dilution in the biosphere are far field barriers.
Many factors participate in enhancing the mobilizing and release of radionuclides from the disposal region. The slow movement of the groundwater through the rock(5) or even static groundwater(7) will result in the leaching of radionuclides from the repository. The composition (Eh, pH, chemistry) and the quantity of groundwater are important factors which influence the release of radionuclides into the environment. Enhanced solubility of radionuclides in near field waters may occur due to complexation by humic and fulvic acids(9) and inorganic ions present in groundwater.

It is quite clear that an extensive investigation of the proposed disposal ground is of paramount importance when considering an area as a potential radioactive waste repository site. The behaviour of groundwater in the rock is a very important factor in the selection of a disposal site. From the foregoing introduction, it is clear that the study of groundwater movement, groundwater composition and complexation of radionuclides in groundwater is essential to assess the safety of a proposed radionuclide waste repository site.

1-2 **Groundwater: General view**

As this research is concerned with groundwater and the ability of materials present in groundwater to complex with radionuclides a general view of environmental waters follows and some useful definitions are proposed. Undergroundwater can be defined as all water below the surface of the ground including the water in the saturated zone, the unsaturated zone called "the vadose zone ", and the groundwater table itself(10). The saturated zone is that part of rock which resides below the water table or pressure surface. All voids in the saturated zone are filled with water. The unsaturated zone extends from the base of the soil to the water table which forms the upper surface of the unsaturated zone(11).
Pinly wrote "water takes on the properties of the rocks through which it has passed" (11). Accordingly, one can expect that the water of different regions may be different in its chemistry. It is thus obvious that research concerned with groundwater must take into account the chemistry of the groundwater. The analysis of the groundwater used in this research is shown in chapter two.

1-3 ORGANICS IN GROUNDWATER
1-3.1 DEFINITION

Organic matters, termed humic substances (or humus) can be described as heterogeneous, naturally occurring organic substances of yellow to black in colour and of high molecular weight. These organics are known not to correspond to a unique chemical identity(12,17).

1-3.2 ORIGIN

In general, humic substances originate from lignified tissues of plant residues or they are formed from sugar(17). Thurman(13) has proposed two hypotheses for the origin of humic substances present in groundwater. First, that humic material originates in the overlying soils. Second, that humic substances are leached from kerogen, the organic matter deposited with the sediment of the aquifer.

1-3.3 CLASSIFICATION

According to their solubilities(12,14), humic substances can be classed as follows: humic substances that are insoluble at pH 2, but soluble at pH 2 are humic acids, and any fraction soluble at all pH's are fulvic acids and any fraction insoluble within all pH's are humin. The alcohol-soluble fraction of the humic acid is hymatamelanic acid(15,16). It is believed that fulvic acids are similar in structure to humic acids but of lower molecular weight distribution and that they have a higher percentage oxygen content(14,22). Humins are thought to be
humic acids that are bound by mineral constituents of soils (9). Terrestrial humins contain more paraffinic structure, whereas humic acids contain more aromatic structures. Terrestrial fulvic acids, in contrast to humic acids and humins, contain significant amounts of polysaccharide-like substances (23).

1-3.4 SOME PROPERTIES

Natural organic matter results from the biodegradation or oxidation of plants (17,18). Since they are a heterogeneous mixture of many molecules (12,22,19,18,14) their characterization is difficult. The aromatic (19,20) and polyelectrolyte character of these substances (13,19,24,25,18) has been strongly emphasized.

1-3.5 CHEMICAL STRUCTURE

Many workers have presented models for humic substances and some of these are presented below. Wershaw et al (14) considered humic acid as being made up of a hierarchy of structural elements. The lowest level in this hierarchy consists of simple quinoid and benzene carboxylic acid groups. These groups are linked together covalently into small particles. Groups of similar particles are in turn linked by weak covalent and noncovalent bonds into aggregates. As stated previously Kononava (18) assumed that humic acids are heterogeneous mixtures of high molecular weight polymers, but Wershaw and Pinckney (26) showed that this hypothesis is not the case, and that humic acids are mixtures of a limited number of more or less chemically distinct fractions of relatively low molecular weight that form aggregates in solution. The aforementioned models are different from that of Haworth (27), in which polysaccharides, proteins, simple phenols and metals are attached to an aromatic core. The model proposed by Schnitzer and Khan (21) is a molecular sieve to which phenolic and benzene carboxylic acids are joined by hydrogen bonds, with voids able to trap low molecular organic as
well as inorganic compounds. The latest models are more adaptable to fulvic acid, whereas the other models reflect humic acid.

Gamble and Schnitzer (19) described fulvic acid as aromatic rings which form an open structure in a two- or three dimensional array, held together partly by hydrogen bonds between the functional groups.

Buffel's model structure of fulvic acid (17) contains aromatic and aliphatic components. Both Schnitzer and Buffel structures show an abundance of -COOH groups, as well as the aromatic character of the molecule (see page 8).

The composition of humic acid is somewhat different from that of fulvic acid. Fulvic acids are generally less cross-linked and polymerized, have lower molecular weights and contain more oxygen than humic acids. The hydroxyl and carboxyl contents of fulvic acids are higher than that found in humic acids. Both humic and fulvic acids show an abundance of aromatic rings. Some proposed structures for humic and fulvic acids are shown on page 8. Structure C and D (17) of humic acid show an abundance of the aromatic and the aliphatic components whereas structure E (9) shows the aromatic character as the main component.

1-3.6 ANALYSIS
1.3.6.A FUNCTIONAL GROUPS

A variety of functional groups are present in humic and fulvic acids, these being generally attached to an aromatic core-system. These functional groups include mainly hydroxyl-, carbonyl-, and carboxylic acid moieties. Many different functional groups and simple organic molecules have been identified in fulvic acid (29).

Table 1 shown on page 9 is a list of these molecules and functional groups.
A: FA STRUCTURE AS PROPOSED BY GAMBLE AND SCHNITZER.
B: FA STRUCTURE AS PROPOSED BY BUFFEL.
C, D AND E: SOME HA STRUCTURES.
TABLE 1
MOLECULES AND FUNCTIONAL GROUPS FOUND IN HUMICS

<table>
<thead>
<tr>
<th>CH₃(CH₂)₃CO₂CH₃</th>
<th>CH₂-CO₂CH₃</th>
<th>CH₂-CO₂-C₆H₁₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 n = 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 n = 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 n = 14</td>
<td></td>
<td>CH₂-CO₂-C₆H₁₇</td>
</tr>
<tr>
<td>19 n = 16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 R₁ = CO₂CH₃; R₂ = OCH₃; R₃ = R₄ = R₅ = H
2 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
3 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
4 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
5 R₁ = CO₂CH₃; R₂ = R₃ = OCH₃; R₄ = R₅ = H
6 R₁ = CO₂CH₃; R₂ = R₃ = OCH₃; R₄ = R₅ = H
7 R₁ = CO₂CH₃; R₂ = R₃ = OCH₃; R₄ = R₅ = H
8 R₁ = CO₂CH₃; R₂ = R₃ = OCH₃; R₄ = R₅ = H
9 R₁ = CH₂CO₂CH₃; R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
10 R₁ = CH₂CO₂CH₃; R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
11 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
12 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
13 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
14 R₁ = R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
15 R₁ = CH₂CO₂CH₃; R₂ = CO₂CH₃; R₃ = R₄ = R₅ = H
16 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = R₅ = H
17 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = R₅ = H
18 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = R₅ = H
19 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = R₅ = H
20 R₁ = CH₂CO₂CH₃; R₂ = R₃ = CO₂CH₃; R₄ = R₅ = H
21 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
22 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
23 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
24 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
25 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
26 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
27 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
28 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
29 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
30 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
31 R₁ = R₂ = R₃ = CO₂CH₃; R₄ = OCH₃; R₅ = H
32 R₁ = CH₂CO₂CH₃; R₂ = R₃ = R₄ = R₅ = CO₂CH₃

X : O, S, NH, C(O)O
Y : O, S, NH
Z : OH, SH, NH₂, alkyl/aryl
Many workers have presented the equivalent of these functional
groups as meq/g or meq/100g. Tables 2 and 3 summarise some
functional group equivalents of fulvic and humic acids of different
origin.

**TABLE 2**

**FUNCTIONAL GROUP EQUIVALENT OF HUMIC ACIDS meq/g**

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>Total acidity</th>
<th>COOH</th>
<th>Phenolic OH</th>
<th>Alcoholic OH</th>
<th>Quinone C=O</th>
<th>Ketonic C=O</th>
<th>Carbon xyl</th>
<th>Hydroxyl</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Florida mucks</td>
<td>4–8.6</td>
<td>2.8–6.8</td>
<td>0.0–2.9</td>
<td>0.0–5.5</td>
<td>0.6–7.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>Soil</td>
<td>7.2</td>
<td>3.1</td>
<td>4.2</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>Lake Celyn</td>
<td>8.9</td>
<td>5.9</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>Ogeechee stream</td>
<td>4.7 and 6.8</td>
<td>3.0</td>
<td>1.9 and 3.9</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>Lake Sediment</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>Soil</td>
<td>-</td>
<td>3.9</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>Aldrich free acid</td>
<td>6.86</td>
<td>3.32</td>
<td>3.54</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td>Aldrich Sodium salt</td>
<td>6.67</td>
<td>3.19</td>
<td>3.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td>Loamy Sand</td>
<td>5.84</td>
<td>3.14</td>
<td>2.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36</td>
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<tr>
<td>HA-model</td>
<td>6.7</td>
<td>3.6</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>37,38</td>
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</table>
### TABLE 3

**FUNCTIONAL GROUP EQUIVALENT OF FULVIC ACIDS meq/g**

<table>
<thead>
<tr>
<th>Source</th>
<th>Total acidity</th>
<th>-COOH</th>
<th>Phenol-lic OH</th>
<th>Alcohol-lic OH</th>
<th>Carbon-yl</th>
<th>Hydrox-yl</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>8.6</td>
<td>4.0</td>
<td>4.6</td>
<td>0.6</td>
<td>4.3</td>
<td>---</td>
<td>31</td>
</tr>
<tr>
<td>Lake celyn</td>
<td>11.0</td>
<td>8.9</td>
<td>2.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>32</td>
</tr>
<tr>
<td>Ogeechee stream</td>
<td>6.4 and 6.8</td>
<td>1.7</td>
<td>1.6 and 2.1</td>
<td>5.1</td>
<td>---</td>
<td>---</td>
<td>33</td>
</tr>
<tr>
<td>Soil</td>
<td>---</td>
<td>9.1</td>
<td>3.3</td>
<td>3.6</td>
<td>3.1</td>
<td>---</td>
<td>39</td>
</tr>
<tr>
<td>FA-Model</td>
<td>10.3</td>
<td>8.2</td>
<td>3.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>37</td>
</tr>
<tr>
<td>Suwannee river</td>
<td>---</td>
<td>6.0-6.2</td>
<td>1.7-3.6</td>
<td>---</td>
<td>1.7</td>
<td>5.4-8.6</td>
<td>20</td>
</tr>
</tbody>
</table>

Where two values are shown, the first value is determined by titration and the second value determined by NMR. The values shown for Suwannee river are in mmol./g.

### 1-3.6.B ELEMENTAL ANALYSIS

The elemental composition of humic substances is an essential characteristic of the substance. Elemental analysis for fulvic and humin are rare in comparison to those of humic acid. The carbon content of fulvic acid is lower than that of humic acid while nitrogen displays the opposite trend. Analysis of a number of humic and fulvic acids extracted from various sources is shown in table 4 and 5.
<table>
<thead>
<tr>
<th>Source</th>
<th>%C</th>
<th>%H</th>
<th>%O</th>
<th>%N</th>
<th>% S</th>
<th>% Ash</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Different aquifer</td>
<td>58.3</td>
<td>3.4</td>
<td>23.5</td>
<td>3.2</td>
<td>---</td>
<td>5.1</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>-62.1</td>
<td>-4.9</td>
<td>-30.1</td>
<td>-5.8</td>
<td>---</td>
<td>-10.4</td>
<td></td>
</tr>
<tr>
<td>Sava river</td>
<td>53.0</td>
<td>5.0</td>
<td>---</td>
<td>3.7</td>
<td>1.7</td>
<td>---</td>
<td>44</td>
</tr>
<tr>
<td>HA-Model</td>
<td>56.2</td>
<td>4.7</td>
<td>35.5</td>
<td>3.2</td>
<td>0.8</td>
<td>---</td>
<td>37</td>
</tr>
<tr>
<td>Aldrich</td>
<td>56.5</td>
<td>4.82</td>
<td>34.3</td>
<td>0.5</td>
<td>3.84</td>
<td>9.16</td>
<td>36</td>
</tr>
<tr>
<td>Free acid</td>
<td>46.66</td>
<td>5.12</td>
<td>44.5</td>
<td>0.45</td>
<td>3.27</td>
<td>---</td>
<td>36</td>
</tr>
<tr>
<td>Sodium form</td>
<td>53.3</td>
<td>5.6</td>
<td>35.8</td>
<td>4.0</td>
<td>1.5</td>
<td>---</td>
<td>42</td>
</tr>
<tr>
<td>Sackville Peats</td>
<td>49.6</td>
<td>5.2</td>
<td>41.1</td>
<td>3.4</td>
<td>0.8</td>
<td>---</td>
<td>42</td>
</tr>
<tr>
<td>Sackville Mucks</td>
<td>50.2</td>
<td>3.1</td>
<td>44.8</td>
<td>1.9</td>
<td>---</td>
<td>---</td>
<td>40</td>
</tr>
<tr>
<td>Lake Celyn</td>
<td>52.05</td>
<td>5.65</td>
<td>36.55</td>
<td>5.63</td>
<td>---</td>
<td>---</td>
<td>41</td>
</tr>
<tr>
<td>Lake Sediment</td>
<td>55.94</td>
<td>4.13</td>
<td>36.52</td>
<td>1.27</td>
<td>0.93</td>
<td>1.13</td>
<td>33</td>
</tr>
<tr>
<td>Ogeechee Stream</td>
<td>57</td>
<td>4.5</td>
<td>34.8</td>
<td>3.3</td>
<td>0.4</td>
<td>---</td>
<td>31</td>
</tr>
<tr>
<td>Florida Mucks</td>
<td>56.5</td>
<td>5.9</td>
<td>32.7</td>
<td>3.9</td>
<td>1.0</td>
<td>---</td>
<td>30</td>
</tr>
<tr>
<td>Gōtō river</td>
<td>51.9</td>
<td>4.32</td>
<td>37.3</td>
<td>1.04</td>
<td>0.7</td>
<td>0.02</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>-56.0</td>
<td>-4.76</td>
<td>-39.8</td>
<td>-1.36</td>
<td>-3.05</td>
<td>-1.02</td>
<td></td>
</tr>
<tr>
<td>Finnsjön Lake</td>
<td>55</td>
<td>4.30</td>
<td>---</td>
<td>2.10</td>
<td>0.8</td>
<td>---</td>
<td>45</td>
</tr>
</tbody>
</table>
# TABLE 5

**ELEMENTAL COMPOSITION OF DIFFERENT FULVIC ACIDS**

<table>
<thead>
<tr>
<th>Source</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>% N</th>
<th>% S</th>
<th>% Ash</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Celyn</td>
<td>43.5</td>
<td>2.7</td>
<td>51.6</td>
<td>2.2</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Lake Sediment</td>
<td>44.98</td>
<td>5.12</td>
<td>42.27</td>
<td>7.63</td>
<td></td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Ogeechee Stream</td>
<td>54.56</td>
<td>4.97</td>
<td>38.2</td>
<td>0.87</td>
<td>0.74</td>
<td>0.86</td>
<td>33</td>
</tr>
<tr>
<td>Florida Mucks</td>
<td>54.5</td>
<td>5.3</td>
<td>37.6</td>
<td>1.9</td>
<td>0.8</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Sackville Peat</td>
<td>44.7</td>
<td>6.7</td>
<td>44.2</td>
<td>3.4</td>
<td>1.2</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Sargasso Sea</td>
<td>50.0</td>
<td>6.8</td>
<td>38.9</td>
<td>6.4</td>
<td></td>
<td>3.37</td>
<td>43</td>
</tr>
<tr>
<td>Sackville Mucks</td>
<td>42.6</td>
<td>6.8</td>
<td>46.3</td>
<td>3.3</td>
<td>1.2</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Soil of Bh horizon of Padzol</td>
<td>46.7</td>
<td>4.5</td>
<td>44.3</td>
<td>0.5</td>
<td></td>
<td>2.35</td>
<td>43</td>
</tr>
<tr>
<td>Different Aquifers</td>
<td>55.4</td>
<td>4.2</td>
<td>29.1</td>
<td>0.4</td>
<td></td>
<td>0.4</td>
<td>13</td>
</tr>
<tr>
<td>Suwannee river</td>
<td>51.3</td>
<td>4.32</td>
<td>42.9</td>
<td>0.56</td>
<td>&lt; 0.2</td>
<td>&lt; 0.05</td>
<td>20</td>
</tr>
<tr>
<td>FA- Model</td>
<td>45.7</td>
<td>5.4</td>
<td>44.8</td>
<td>2.1</td>
<td>1.9</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>Göto river</td>
<td>51.96</td>
<td>4.32</td>
<td>37.25</td>
<td>1.04</td>
<td>0.72</td>
<td>0.02</td>
<td>45</td>
</tr>
<tr>
<td>Finnsjön Lake</td>
<td>51.47</td>
<td>4.51</td>
<td>40.78</td>
<td>1.63</td>
<td>1.14</td>
<td>0.34</td>
<td>45</td>
</tr>
</tbody>
</table>

13
SPECTROSCOPIC STUDIES ON HUMICS

1-4.1 IR SPECTROSCOPY

The IR spectrum of humic substances consists of a number of very broad bands. This is in agreement with the fact that humic materials are considered to be complex mixtures. The IR spectra of fulvic and humic acids are rather similar (45), except for the carboxyl bands at 1740 cm\(^{-1}\) for fulvic acid and at 1720 cm\(^{-1}\) for humic acid (46,47). However, the absorption spectra of fulvic acid extracted from the same sediment are not necessarily the same. The following conclusions were made after studying materials using IR spectroscopy:

1- For marine sediment the aliphatic content of fulvic acids is less than that observed for humic acids, and the shape of aliphatic bands indicates that fulvic acids contain mainly -CH groups (48);

2- The wave number of the OH absorption in humic substances is greater than that in many simple carboxylic acids, and the OH absorption band is not considerably broad when compared with pure compounds (49);

3- The major difference in the IR spectra of humic substances from groundwater and humic substances from surface water is the increased absorption at 2960 cm\(^{-1}\) probably caused by greater aliphatic carbon (17).

4- All humic substances show a band at 3400 cm\(^{-1}\) which is related to -OH groups (22);

5- The 2920 cm\(^{-1}\) and 2860 cm\(^{-1}\) bands are more pronounced in humic acids than in fulvic acids (49);

6- The absorption at 2960 cm\(^{-1}\) is consistent with the increased H/C ratio of humic material of groundwater (17).

7- OH\(^{-}\) and -COOH groups participate in the binding of heavy metal ions Cu > Pb > Ca (53).
**TABLE 6**

IR CHEMICAL SHIFTS OF HUMIC SUBSTANCES

<table>
<thead>
<tr>
<th>WAVELENGTH cm(^{-1})</th>
<th>ASSIGNMENT</th>
<th>REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>-OH groups</td>
<td>17</td>
</tr>
<tr>
<td>2960</td>
<td>Aliphatic C-H</td>
<td>17</td>
</tr>
<tr>
<td>1725</td>
<td>-COOH groups</td>
<td>17</td>
</tr>
<tr>
<td>1385</td>
<td>C-H deformation</td>
<td>17</td>
</tr>
<tr>
<td>1400</td>
<td>-OH bending vibrations of alcohols</td>
<td>49</td>
</tr>
<tr>
<td>1720</td>
<td>-COOH groups</td>
<td>50</td>
</tr>
<tr>
<td>1600-1650</td>
<td>aromatic C=C conjugated with C=O</td>
<td>51</td>
</tr>
<tr>
<td>1510</td>
<td>stretching vibration of aromatic C=C</td>
<td>52</td>
</tr>
<tr>
<td>1540</td>
<td>bending vibration of aliphatic C-H groups</td>
<td>52</td>
</tr>
<tr>
<td>1220</td>
<td>C-O stretching vibration and OH bending deformation due mainly -COOH groups</td>
<td>52</td>
</tr>
<tr>
<td>3400 (band)</td>
<td>-OH stretching</td>
<td>45</td>
</tr>
<tr>
<td>2600 (inflection)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2990 and 2970</td>
<td>C-H stretching</td>
<td>45</td>
</tr>
<tr>
<td>1725</td>
<td>unconjugated C=O</td>
<td>45</td>
</tr>
<tr>
<td>1620</td>
<td>conjugated C=O</td>
<td>45</td>
</tr>
<tr>
<td>1510</td>
<td>aromatic nucleus</td>
<td>45</td>
</tr>
<tr>
<td>1250</td>
<td>C-O stretching of phenol and alcohol and O-H deformation in carboxyl groups</td>
<td>45</td>
</tr>
</tbody>
</table>

---

1-4.2 NMR SPECTROSCOPY

Nuclear magnetic resonance is the spectroscopic technique most used in the characterization of humic substances, especially for determining functional group concentrations. The hydroxyl, carboxyl, carbonyl, and aromatic content of humic substances have been determined by the use of NMR...
spectroscopy (20). The following conclusions were made after studying humic materials by NMR spectroscopy:

1- Lignin was presumed to be the source of the aromatic component of terrestrial humic substances, aromatic structure is a major component in aquatic sedimentary (23);

2-a- Humic acids appear to have higher carbohydrate content than fulvic acids and fulvic acids have more highly substituted aromatic rings than humic acids;

b- There are three groups of hydroxy functionality: carboxy, phenolic and carbohydrate moieties (55);

3- The concentration of aromatic protons in Sargasso sea fulvic acid is much lower than that detected by others in terrestrial (soil) fulvic acids (43);

4- The amount of carbohydrate hydroxyl acids and uronic acids in fulvic acids is a function of the way that the material was isolated (20).

5- The humic acids of Huruna and Kizaki lakes are aliphatic in character (presence of a large peak in 1.0-1.4 ppm) with no aromatic protons (absence of a peak in 6.0-8.0 ppm). However, this apparent absence may be due to the very low concentration of aromatic rings (56).

6- Humic acids divided into two groups one with strong aliphatic hydrocarbons and the other without strong aliphatic hydrocarbons. All humic acids have strong H-NMR signal in the range of 3.0-6.2 ppm and strong absorption in the range 100-160 for $^{13}$C-NMR spectra (57).

Table 7 shows the $^{13}$C and $^1$H NMR chemical shifts of some humic materials.
**TABLE 7**

<table>
<thead>
<tr>
<th>CHEMICAL SHIFT</th>
<th>ASSIGNMENT</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0-1.7 ppm</td>
<td>aliphatic protons</td>
<td>43</td>
</tr>
<tr>
<td>1.7-2.7 ppm</td>
<td>protons on C atoms adjacent to functional groups</td>
<td>43</td>
</tr>
<tr>
<td>7.3-7.9 ppm</td>
<td>aromatic protons</td>
<td>43</td>
</tr>
<tr>
<td>190-200 ppm</td>
<td>carbon in aldehyde, ketones and C=S groups</td>
<td>32</td>
</tr>
<tr>
<td>160-190 ppm</td>
<td>carboxyl group carbons in carboxyl, ester and amide</td>
<td>32</td>
</tr>
<tr>
<td>110-160 ppm</td>
<td>aromatic carbons and olefinic carbons</td>
<td>32</td>
</tr>
<tr>
<td>90-110 ppm</td>
<td>acetal carbons</td>
<td>32</td>
</tr>
<tr>
<td>50-70 ppm</td>
<td>C=O carbons -alcohols esters, ethers carbohydrate, amines</td>
<td>32</td>
</tr>
<tr>
<td>0-50 ppm</td>
<td>alkyl carbons</td>
<td>32</td>
</tr>
<tr>
<td>sigma&lt;7</td>
<td>hydroxyl protons</td>
<td>45</td>
</tr>
<tr>
<td>sigma=7</td>
<td>aromatic protons</td>
<td>45</td>
</tr>
<tr>
<td>sigma&lt;3</td>
<td>alkyl groups</td>
<td>45</td>
</tr>
<tr>
<td>sigma3.71</td>
<td>methoxy groups</td>
<td>45</td>
</tr>
<tr>
<td>sigma4.03</td>
<td>CH-O and -CH&lt;sub&gt;2&lt;/sub&gt;-O</td>
<td>45</td>
</tr>
<tr>
<td>sigma170</td>
<td>methoxy groups</td>
<td>45</td>
</tr>
<tr>
<td>sigma120</td>
<td>aromatic carbons</td>
<td>45</td>
</tr>
<tr>
<td>sigma56.1</td>
<td>-OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>45</td>
</tr>
<tr>
<td>sigma51.6</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-O</td>
<td>45</td>
</tr>
<tr>
<td>sigma=30</td>
<td>alkyl groups</td>
<td>45</td>
</tr>
<tr>
<td>10-50 ppm 13C</td>
<td>aliphatic component</td>
<td>54</td>
</tr>
<tr>
<td>78 ppm</td>
<td>alcohol and ethers carbons</td>
<td>54</td>
</tr>
<tr>
<td>125-150 ppm</td>
<td>protonated aromatic carbon</td>
<td>54</td>
</tr>
<tr>
<td>183 ppm</td>
<td>carboxy, amide, ester carbons</td>
<td>54</td>
</tr>
<tr>
<td>0-50 ppm</td>
<td>parafinic carbons</td>
<td>23</td>
</tr>
<tr>
<td>50-110 ppm</td>
<td>alcohols C-OH, amines(C-NH&lt;sub&gt;2&lt;/sub&gt;, C-NHR, C-NR&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>23</td>
</tr>
<tr>
<td>110-160 ppm</td>
<td>Olefinic-C, aromatic-C</td>
<td>23</td>
</tr>
<tr>
<td>190-220 ppm</td>
<td>aldehyde, ketone</td>
<td>23</td>
</tr>
</tbody>
</table>

**1.4.3 U.V AND VISIBLE SPECTROSCOPY**

All references to u.v.-visible spectra of humic substances note that the spectra are featureless with absorptivities
increasing with decreasing wavelengths of the incident light. The u.v-visible spectra of humic substances result from the overlap of the absorbances of various chromophores (58). Thus, the u.v.-visible spectra can not be used for the determination of functional groups in humic substances. However, the literature suggests that these spectra have useful applications, such as the estimation of the degree of humification using the $E_4/E_6$ ratio (59) or for studying the interaction of metal ions with fulvic acid (21). Humic substances from groundwater are less coloured (i.e. less chromophores) than humic substances from surfacewater so the absorption at 465 nm for humic substances in groundwater is 3-10 times less than that of surfacewater (13).

The u.v.-visible absorbivities of humic substances do vary with pH (60, 61) and the difference in absorbances between pH 12.4 and pH 7 suggests that the absorbance of humic acids at 600 nm does not depend on the phenolic content but on the extent of the conjugate systems in humic acids.

1-4.4 FLUORESCENCE

Humic substances are known to fluoresce both under irradiation from U.V and visible light and it has been suggested that fulvic acid and humic acid solutions show fluorescence due to their humic matter properties i.e not due to contaminating substances (62,63). Datla et.al.(62) reported that the electronic absorptions of these materials are non-specific and decrease monotonously with wavelength. However, they reported that sodium humate and fulvate show maximum fluorescence at 470 nm in aqueous solution which was unaltered after hydrolysis with 6M HCl but was wavelength shifted by different solvents. The optimal concentration for fluorescence of humic compounds has been suggested to be between 10 and 40 ppm (64) or between 16-70 ppm (65). Studies on fluorescence spectroscopy have suggested
the following:

1- The intensity of fluorescence of humic matter from aquatic origin is higher at shorter wavelengths, than soil humic compounds (65);

2- The maximum intensity of fluorescence appears only when the solutions of humic materials are extremely dilute suggesting that the molar absorptivity of the fluorescing species is very high (62);

3- Humic and fulvic acids exhibit nearly a similar, green, weak fluorescence with a more or less flat maximum in the region of 500-540 nm (66);

4- Fluorimetric methods can be used for the determination of lignin, sulphonates and humic substances in seawater (67);

5- According to the similarity of their emission spectra, the suggestion has been made that fulvic and humic acids are not dissimilar groups of compounds, but may be represented as polymers (66);

6- Two major excitation bands for humic matter, one at 334 ± 7 nm and the other at 415 ± 20 nm exist, which may be correlated to their phenolic content (65);

7- Dissolved organic matter of terrestrial origin had a single emission peak at 410 nm, whilst fluorescence observed from samples taken from saline lakes shows a peak at 426 nm (68);

8- The intensity of the excitation peak increases with an increase in pH and a decrease in temperature (65);

9- The stability spectra depend on the origin and kind of humic substances (69); and the fluorophore is suggested to be aromatic in nature (70);

10- A great part of the fluorescence originates from macromolecular substances (65,71).
1-5 METAL INTERACTIONS WITH HUMIC MATERIALS

1-5.1 GENERAL

Organic matter in soil(12), natural water(21,72) and groundwater(73) is known to complex with metal ions. Actinides are the most studied ions. Trivalent actinides form strong complexes with humic acids as indicated from studies carried out on Eu$^{3+}$ and Am$^{3+}$ (25). For Th$^{4+}$ strong complexes have been observed both for humic and fulvic materials (74) and at least four (75) or seven(76) types of complexing sites are involved in the binding of thorium to humic acids. By using the ultrafiltration technique, Caceci(77) found that two types of coordination sites are involved in the complexation of Eu$^{3+}$ with humic acid. The complexation capacity increased with pH. U$^{4+}$ and U$^{5+}$ complexation with humic and fulvic acids was studied by Li et al(78). They found that two types of binding sites are involved. By reviewing actinide complexation with humic and fulvic acids, Carlsen(36) concluded that humic- and fulvic complexes of the actinides in their tetra and hexa valent states are stable enough to compete with other complexing species in groundwater, such as -CO$_3^{2-}$ and OH$^-$ ions. This also applies to divalent ions. Hence, as stated previously, it is expected that the reaction between humic- and fulvic acids and metal ions in groundwater may play an important role in determining the migration behaviour of metal ions through the environment.

Complexation of Cs, Sr, Co and Ni with humic materials has also been studied(36, 79, 80, 81). Cobalt, Sr and Ni(79, 80, 81) interact with humic- and fulvic acids to form fairly stable complexes at pH 4. At lower values of pH, a decrease in the stability is observed. Carlsen(36) reported that Cs ions interact only weakly with humic acids in solution and attributed this to the generalization that mono- valent alkali metal ions form very weak complexes with chelating agents.

The interaction of Ca, Zn, Fe, Mn, Al, Cu and Cd with humic
materials has also been studied (82, 83, 84, 85, 86, 87). Dkhar et al (83) reported that the metal retaining capacity of humic substances depends upon the nature of the cations. The capacity follows the order Cu>Zn>Fe>Mn. This finding is in agreement with Kango’s results for Fe and Zn, in which Zn showed great affinity for humic acids. Cadmium complexation with humic material increased as the pH increased (87) whereas that of Al within the pH range of 3-5, showed little variation (84). For Fe, the binding constant at pH 1.0 is slightly larger than that at pH 1.5 and pH 2.5 (86). Langford explained these observations by considering the Fe species present. In the most strongly acidic solutions Fe$^{3+}$ is predominant and decreases towards higher pH values. Reactions of Ca with fractions of fulvic acid (fractionated by desorption from nonionic resin, XAD-7, at different pH's) is different. The pH-dependence of the reaction was considerable for the fractions extracted at pH 4 and negligible for the fulvic acid fraction extracted at pH 10. Calcium complexation with fulvic acid is independent of fulvic acid concentration (84).

Whatever the differences in the binding capacity and the number of binding sites are, the intensity (i.e. the relative amounts of certain metals bound to ligand) of metal-humic acid interactions has been determined. Takamatsu et al (88) found the intensity to be Cu >Hg >Pb >Ni >Zn >Cd =Co >Mn. Kerndorff and Schnitzer have grouped the studied metal ions into three categories of complexation strength with humic acid:

- strong: Fe, Hg
- intermediate: Cu, Pb, Al
- weak: Ni, Cr, Zn, Mn, Co, Cd

Takamatsu et al (88) have also reported that Hg is likely to be bound to humic acid more tightly than Cu.

1-5.2 Nature of interaction

The interaction strength of humic materials with metal ions varies with the nature of the ion, pH, ionic strength and
with the concentration of humic materials present during the interaction. Furthermore, stability constants for metal interactions vary considerably from one study to another. It is clear that the measurable properties of any interaction with humic material are unique to the particular humics under study. Accordingly properties will be discussed which one expects to be valid to all humic substances. Before presenting the interaction mechanisms, it is worth noting that the predominant interactions between metal ions and humic materials are considered to be chelation type interactions (89,85,90). Langford et al (28) described the reaction as "pseudo-chelation". It is "pseudo" because the donor atoms come from two molecules, and it is "chelate-like" behaviour suspecting that H-bonding and/or hydrophobic interactions between the ligand parts render the ligand in the aggregate chelate-like. From ESR investigations (91) McBride concluded that humic acid does not form highly covalent metal organic bonds with Cu nor with Mn. He believes that a single electrostatic bond is formed which appears to put some doubt on chelation as the predominant mechanism. However, the interaction between metal ions and humic and fulvic acids can be divided into homogeneous and heterogeneous reactions. The first takes place in solution between the metal ions and the dissolved humic- or fulvic acids, whereas the second type consist of reactions between metal ions and solid humic- or fulvic acids. Before presenting the possible proposed mechanisms it is necessary to define inner and outer sphere complexes. In the former, ligand functional groups may enter into coordination positions and displace strongly coordinated $\text{H}_2\text{O}$ molecules. The latter type is where the ion is bound electrostatically to the polyanion (such as humic acid) with displacement of water of coordination from the ion by negatively charged functional groups.

As stated previously (page 9) there are many types of ligand in
humic materials though Schnitzer and coworkers (89,91) proposed two types of interaction with metals:

\[
\text{Humic acid} + M^{2+} \rightleftharpoons \text{Metal complex} + n^+ \quad (1)
\]

\[
\text{Humic acid} + M^{2+} \rightleftharpoons \text{Metal complex} + n^+ \quad (2)
\]

Schnitzer and Skinner (92) have reported that phenolic and carboxylic groups are important in metal ion interactions with humic materials. Reaction (1) as shown above, is assumed to be the correct description for the Cu$^{2+}$—fulvic acid chelation reaction. Mannvug and Ramamoorthy (93) disagree with this statement, reporting that Cu$^{+2}$ is likely to bind to fulvate via a phthalate rather than via salicylate (reaction 2). Gamble and Schnitzer (19) considered unneutralised phenolic groups, carboxyl groups ortho to the phenolic -OH groups and carboxylic groups meta to the phenolic -OH groups may influence any metal ion fulvic acid interaction.
Carlsen(36) has suggested that the following reactions are important:

1. Chelation:
   \[ ZXY + M^{n+} \rightleftharpoons ZXY^{(n-1)+} + H^+ \]
   - Outer-sphere weak hydrogen bonding.
   - Inner-sphere carboxylate reactions.

2. Chelation:
   \[ ZXY + M(H_2O)_x^{n+} \rightleftharpoons ZXY^{n+} \]
   - Outer-sphere weak hydrogen bonding.
   - Inner-sphere carboxylate reactions.
Techniques used in the study of speciation equilibria

The aqueous reaction between metal ions and organics can be represented (simplified by omitting charges and stoichiometry) as:

\[ M_i + L \rightleftharpoons M_iL \]  \hspace{1cm} (3)

The equilibrium constant is given by:

\[ K_i = \frac{[M_iL]}{[M_i][L]} \]  \hspace{1cm} (4)

where \([M_iL]\) is the metal-organic complex concentration;
\([M_i]\) is the free metal concentration;
\([L]\) is the uncomplexed ligand concentration.

Speciation can be defined as the elucidation of the individual physical and chemical forms of nuclides in a sample. Speciation may include the determination of oxidation states, charges, complexation, polymerisation and particle size distribution of each nuclide.

To assess the possible transport of radionuclides from the repository into the environment it is necessary to know the extent of complexation of radionuclides with naturally occurring organics. To know the degree of complexation and to obtain a numerical value to describe equation 4, techniques must measure the complexed metal concentration and/or free metal concentration and ligand concentration.

Many techniques have been used in the study of soluble metal ion-humic/fulvic acids concentration. All techniques disturb the existing equilibria, i.e., all techniques will be invasive to some extent and all have advantages and disadvantages. However, ion exchange equilibria have been used to separate complexed from free metal ions. Potentiometric titration and liquid-liquid partition have also been used. Ion selective...
Electrodes (ISE) have been used to determine the free metal concentration by titrating a solution of organics with free metal ions (87, 99) or by direct measurement of free metal (100) or by combining ISE with spectrophotometric monitoring of visible absorption spectra to measure free and complexed metal ion concentration (101). Cathodic stripping voltammetry (102, 103, 104, 105) has also been used to measure free and complexed metal by stripping metal-complexes from the cathode.

Anodic stripping voltammetry (ASV) has been used to study the effect of the organics on ASV signals (106).

Dialysis and ultrafiltration have also been used to study the interaction between metal ions and humic substances (36, 107, 108, 109). The above two methods give information on the important molecular sizes of organics in metal interaction and on the complexing capacity of humic substances. The use of gel permeation chromatography (size exclusion principle) allows a separation of complexed from free species. This technique also gives information on molecular size distributions of the complexed molecules (72, 110, 111, 112).

All the methods discussed above have disadvantages and advantages associated with them. Ion selective electrodes would be preferred due to non-ambiguity of the species being measured but low sensitivity limits their use. Ion-exchange followed by voltammetric measurement can suffer from adsorption of the complexes or ligands and can be adversely affected by slow kinetics. However, these two techniques are the most popular. Voltammetric techniques are popular for their sensitivity and specificity and the ease of analysis whereas the popularity of ion-exchange methods is because of the versatile techniques that can be employed to measure the metal remaining in solution. The disadvantages of dialysis and ultrafiltration are the high cut-off of the available membranes which result in passing any complexes below the cut-off value and problems associated with size calibration. The limitation of gel filtration
techniques is the fact that small metal chelate complexes will be retained and thus not separated from the free metal. This could be important when inorganic complexing agents are dominant. Irrespective of these disadvantages, gel filtration (in contrast to dialysis and ultrafiltration) fractionate down to very low molecular size e.g: Sephadex G-10 has a range of 0-700 daltons for dextrans.

For equilibrium studies, the concentration of ligand or available sites have also been measured by different means. Some functional groups have been analysed and taken as a ligand concentration(95,113). Ligand concentration has also been considered as total organic carbon(TOC) dissolved in solution(101,114).

1-7 OBJECTIVES OF THE PRESENT WORK

All of the studies on humic materials cited in the introduction to this work have employed humic or fulvic material which has been extracted from soil or water before being used in investigations. Extraction of humics from soil solutions or groundwaters is accomplished by the use of DEAE cellulose or XAD resins. Humics are recovered from these materials by treating the extractant with an aqueous solution of sodium hydroxide. The extraction procedure must inevitably change the physical and chemical characteristics of humic materials. The first objective of this work was to compare the reactions of cobalt and iodide with aqueous solutions of sodium humate and with groundwater taken from the waste repository at Drigg.

The second objective of this work was to investigate reactions of cobalt and iodide with aqueous solutions of sodium humate and with groundwater that had been subjected to gamma photons from a $^{60}$Co source.

Aspects of the interaction of cobalt with groundwater were studied by Shaw as part of his research leading to a PhD. Some of his work was repeated in this investigation in order to compare the interaction of cobalt in groundwater with that of sodium humate solutions.
CHAPTER TWO
EXPERIMENTAL

2-1 TECHNIQUE AND GENERAL REMARKS

In the following chapters, the term "complex" will be used to refer to cobalt that is present in solution, but is not present as "free" hexaaquo cobalt cation. From the introduction to this work, it is evident that radionuclides can interact with a number of different species present in groundwater such as naturally occurring organics, anthropogenic organics, inorganic ions, organic and inorganic colloids and microorganisms. In this work, no attempt is made to define the species that associate with cobalt, thus forming the so called cobalt complex. Similar considerations should be given to the so called iodine complex. Except for the EDTA experiments in which IR-120 (Na) cation exchange resin was used, and the gel permeation chromatography experiments in which sephadex G-15 gel was used, all separations of complexed from uncomplexed species were achieved by using a system which loaded samples onto a column (15 cm G-10 gel bed height, 1 cm i.d.) from a 0.6 ml sample loop, constructed using two Pharmacia SRV-4 valves (115). Fig.1, shown below, gives details of the experimental system. The eluent flow-rate was controlled by a peristaltic pump (Pharmacia P-1) and passed from the column through a 1mm i.d. coil seated in the well of a sodium iodide crystal gamma detector. The output of the gamma detector was fed to a Nuclear Enterprises SR-5 Scaler -ratemeter. The analogue output from the ratemeter was connected to a potentiometric recorder. As the aim of any separation is to minimize the invasiveness caused by the technique used, 0.45μm filtered groundwater was employed as a mobile phase.
Separation of components within a mixture is achieved in gel permeation chromatography by differences in molecular size. Separation of free iodide from complexed iodine used the gel permeation technique, as did some of the work carried out...
during the investigation of the effect of radiation on cobalt complexation. However, most of the separations of free from complexed cobalt were achieved by using the weak cationic sorption properties of Sephadex G-10 gel. Although the cationic properties of Sephadex gel have been reported by many workers (116,117), this property of the gel is normally eliminated by the use of high ionic strength buffers. However, Warwick et al (118) used this property to separate complexed cobalt from free cobalt and this method was used throughout this study. A mobile phase flow rate of 0.546 ml/min (unless otherwise stated in the experimental) was used to separate complexed from free cobalt. The method developed by Warwick et al (118) showed good reproducibility for percentage complexed cobalt with a standard deviation of ± 5.27%. However, the background counts of the detector were found to rise with time and this may be due to the sorption of a certain species onto the inside wall of the coil in the well crystal which subsequently may have affected the accuracy of the measurement. Consequently, after a period of 3–4 weeks the coil was replaced and decontaminated by Decon.

Another problem associated with the use of Sephadex gel was that the gel became contaminated with activity which was probably caused by algae growing in the gel. Algae was removed by passing sodium azide (0.02%) solution through the column, in most cases the gel was replaced.

In contrast to cobalt, iodide was separated by Sephadex gel utilizing the size exclusion principle only. During these separations, a slow flow rate of 0.073 ml/min was used.

During the separation of free cobalt from complexed cobalt and free iodide from complexed iodine, two gamma active peaks were observed. The activity associated with each peak was determined either by integrating the counts in each peak by using the scaler of the SR-5 scaler/ratemeter or by fraction collecting the mobile phase and counting each fraction on a Philips PW4800 gamma counter. Improved counting statistics were achieved by the latter method.
The groundwater was obtained from the Drigg LLW repository site in Cumbria which has a sandy aquifer at a depth of 6 metres (119). The organic carbon concentration of the groundwater is low (less than 10 ppm) (13), and in order to achieve sufficient complexation, the concentration of the organics in the groundwater must be increased. Concentration by mild rotary evaporator was chosen because it was believed that this method would cause little change in the groundwater apart from concentration.

A concentrated groundwater was prepared by rotary evaporating a sample of 0.45μm filtered groundwater at 35 °C (to avoid decomposition and chemical reaction within the sample) until 30 times or 10 times concentrated groundwater was obtained. Times 5 concentrated groundwater was obtained by diluting a sample of times 10 groundwater. The concentrate was 0.45μm filtered again to remove any particulate matter.

As the chemical analysis of groundwater used in this study is important, (as stated in page 4 ), the chemical analysis of a typical groundwater (bore-hole 1 at Drigg) was carried out by BGS (Keyworth). Total organic carbon (TOC) was analysed by a Shimadzu TOC 500. Cation concentrations were measured by inductively coupled plasma atomic emission spectroscopy on a Perkin-Elmer Plasma 2. Anion concentrations were analysed on a Dionex 2000. pH and Eh were measured with an Orion 401 meter with Orion combination pH and platinum Eh electrodes. The analysis of the groundwater used in this research is shown in table 8.
apart from pH and Eh all results are expressed in mg/l
< denotes the detection limit for that element.

### 2-3 SODIUM HUMATE (NaHu) AND CHEMICALS

The sodium humate used in this study was purchased from Aldrich Co. LTD. and is the subject of an interlaboratory comparison study. A number of laboratories situated in Europe are analysing this material by various techniques in order to determine the most suitable and reproducible methods for the analysis of humic materials. Table 9 shows the elemental analysis of a 200 ppm solution of sodium humate in distilled water used in this research.

Sodium metabisulphite S.L.R grade (Na₂S₂O₅) and Sodium azide were purchased from Fisons Scientific Apparatus. Chloramine-T (CH₃C₆H₄SO₂N(Cl)Na·XH₂O) and EDTA(Analar) were purchased from Aldrich Chemical Co. LTD. ⁵⁸Co and ¹²⁵I solutions were purchased from Amersham International PLC. The cobalt solution was purchased as Cobalt (11) Chloride in 0.1 M HCl. Iodide solution was purchased as Sodium Iodide in dilute Sodium

---

### TABLE 8

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>VALUE</th>
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<tbody>
<tr>
<td>TOC</td>
<td>6.9</td>
</tr>
<tr>
<td>Na</td>
<td>19.0</td>
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<tr>
<td>K</td>
<td>1.22</td>
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<tr>
<td>Ca</td>
<td>22.1</td>
</tr>
<tr>
<td>Mg</td>
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</tr>
<tr>
<td>Fe</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.03</td>
</tr>
<tr>
<td>Ba</td>
<td>0.055</td>
</tr>
<tr>
<td>Sr</td>
<td>0.094</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.035</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.06</td>
</tr>
</tbody>
</table>

Zn <0.1 Pb <0.3 Cu <0.04 Si 2.28 Cl 32.8 Br 0.21 NO₃ 0.22 SO₄ 17.1 pH 7.3 Eh(mV) 380
Hydroxide. Amberlite IR-120 (H) was purchased from BDH Chemicals LTD. Sephadex gel was purchased from Pharmacia Fine Chemicals.

**TABLE 9**

**ELEMENTAL ANALYSIS OF 200 ppm SODIUM HUMATE**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.61</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0015</td>
</tr>
<tr>
<td>Ca</td>
<td>2.415</td>
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<tr>
<td>Na</td>
<td>19.4</td>
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<tr>
<td>Cu</td>
<td>0.069</td>
</tr>
<tr>
<td>Si</td>
<td>1.847</td>
</tr>
<tr>
<td>Fe</td>
<td>1.8</td>
</tr>
<tr>
<td>Sr</td>
<td>0.027</td>
</tr>
<tr>
<td>K</td>
<td>&lt;1.0</td>
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<tr>
<td>S</td>
<td>4.893</td>
</tr>
<tr>
<td>Mg</td>
<td>0.19</td>
</tr>
<tr>
<td>Zn</td>
<td>0.231</td>
</tr>
</tbody>
</table>

All results are expressed in mg/l, < denotes the detection limit.

2-4 **COMPARISON OF SODIUM HUMATE SOLUTION (NaHu) AND GROUNDWATER FOR COBALT COMPLEXATION**

2-4.A **SODIUM HUMATE SOLUTION (NaHu)**

2-4.A.1 **KINETICS**

i) **COBALT COMPLEXATION WITH FRESH, UNFILTERED (NaHu)**

7 mls. of a mixture of 200 ppm fresh, unfiltered (NaHu) and $^{58}$Co (131.7 kBq) were prepared. A 0.6 ml. aliquot of the mixture was separated at zero time incubation in order to obtain the percentage of complexed cobalt. The remainder of the solution was maintained at 10 °C. After known periods of time, 0.6 ml. aliquot of the mixture was introduced into the gel column (G-10) and the percentage complexation determined.

ii) **COBALT COMPLEXATION WITH FRESH 100 ppm AND 200 ppm, 0.45μm FILTERED (NaHu)**

50 ml. of freshly prepared solutions of 200 ppm and 100 ppm (NaHu) were filtered through a 0.45 μm filter. 70 μl of $^{58}$Co
of total activity 784 kBq were added to each solution. A 0.6 ml.
 aliquot of each solution was separated at zero incubation time in
 order to obtain the percentage of complexed cobalt. The
 remaining solutions were incubated at 10 °C. After known
 periods of time, a 0.6 ml. aliquot of each solution was introduced
 into the gel column (G-10) and the percentage cobalt
 complexation determined.

2-4.A.2 EFFECT OF TEMPERATURE

A mixture of 2x7 ml. solutions of 200 ppm fresh, 0.45
μm filtered (NaHu) and 58Co (131.7 kBq) were prepared. 0.6 ml.
of each was separated by Sephadex G-10 in order to obtain a
value for cobalt complexation at zero reaction time. One solution
was maintained at 10 °C and the other at 25 °C. Periodically, 0.6
ml. amounts of these two solutions were separated on the G-10
column and the percentage cobalt complexation determined in
each separation.

2-4.A.3 EFFECTS OF COBALT CONCENTRATION

A solution of inactive cobalt was prepared by dissolving
59.5 mg of CoCl$_2$.6H$_2$O in 10 ml. of ultrapure water. A solution
(A) containing 138 μl of 58Co (3427 kBq), 100 μl of CoCl$_2$.6H$_2$O
solution and 12 μl of ultrapure water was prepared. Two other
solutions (B) and (C) were also prepared. Solution (B) was
prepared by mixing 30 μl of (A) with 270 μl of ultrapure water.
Solution (C) was prepared by mixing 20 μl of (B) with 180 μl of
ultrapure water. Known amounts of A, B, or C were added to vials
containing 1 ml of 100 ppm (NaHu). To keep the volume in each
vial constant, known amounts of ultrapure water were added. All
samples were allowed to reach equilibrium at 10 °C. The flow
rate of the mobile phase through the column was kept at 0.433
ml/min. 0.6 ml aliquots of the samples were separated and
fraction collected in vials of 1.5 ml each and counted on a
Philips PW 4800 automatic gamma counter.
2-4.A.4 EFFECTS OF pH

20 ml of 200 ppm, 0.45 μm filtered (NaH₂U) were adjusted to different pH's by adding various amounts of 0.2 μm filtered 5M, 1M and 0.2M HCl. After each adjustment, 2 ml were taken and 10 μl of ^58Co were added to produce a solution of specific activity 19 kBq/ml. The solutions were allowed to reach equilibrium at 10°C before a 0.6 ml aliquot of each sample was separated and the percentage cobalt complexation determined.

2-4.B GROUNDWATER SOLUTION (G.W)

2-4.B.1 EFFECTS OF GROUNDWATER CONCENTRATION

5 ml of x10 concentrated groundwater was diluted to x5 concentration with 0.45 μm filtered groundwater. Two samples of 10 ml each of either x10 or x5 concentrated groundwater were spiked with ^58Co (190 kBq) and maintained at 10°C. Periodically, 0.6 ml aliquots of the two solutions were separated and fraction collected in vials of 1.5 ml each and counted on a Philips PW4800. The percentage of cobalt complexation was determined in each solution.

2-4.B.2 EFFECTS OF TEMPERATURE

A mixture of 20 ml of x10 groundwater and ^58Co (380 kBq) was prepared. A 0.6 ml aliquot of the mixture was separated for zero time cobalt complexation. The remainder of the solution was then split into two equal volumes. One volume was incubated in a water bath maintained at 10°C and the other at 25°C. After known periods of time, 0.6 ml aliquots of the solutions were separated and fraction collected in vials of 1.5 ml each and counted as in (2-4.B.1). The percentage of cobalt complexation was determined in each solution.

2-4.B.3 EFFECTS OF pH

15 ml of x10 concentrated groundwater was adjusted to different pH values by adding various volumes of 0.2 μm filtered
5M HCl. One ml. was taken after each adjustment and 5 µl of $^{58}$Co were added to produce a solution of specific activity 19 kBq/ml. All samples were allowed to reach equilibrium in a waterbath which was maintained at 10 °C. After equilibrium was reached all samples were separated and the percentage cobalt complexation was determined in each solution.

2-2.B.4 EFFECTS OF COBALT CONCENTRATION

A solution of inactive cobalt was prepared by dissolving 59.5 mg of CoCl$_2$.6H$_2$O in 10 ml. of ultrapure water. A solution (A) containing 100 µl of CoCl$_2$.6H$_2$O solution, 70 µl of $^{58}$Co (2430 kBq) and 80 µl of ultrapure water was prepared. Two other solutions (B) and (C) were also prepared. Solution (B) was prepared by mixing 30 µl of (A) with 270 µl of ultrapure water. Solution (C) was prepared by mixing 20 µl of (B) with 180 µl of ultrapure water. Known amounts of (A), (B), or (C) were added to vials containing 1 ml of x30 concentrated groundwater. To keep the volume in each vial constant, known amounts of ultrapure water were added, all samples were allowed to reach equilibrium at 10 °C. The flow rate of the mobile phase passing through the column was adjusted to 0.433 ml/min. 0.6 aliquots of the samples were separated and fraction collected in vials of 1.5 ml each and counted on a Philips PW4800 automatic gamma counter.

2-4.B.5 MOLECULAR SIZE EFFECTS

A solution of x10 unfiltered groundwater was filtered through six filtration papers of different ranges of molecular size cut-off. The unfiltered groundwater and the six different filtrates were analysed for concentrations of Ca, Mg by inductively coupled plasma emission analysis and HCO$_3^-$ by Dionex HPLC. The pH and the absorption at 465 nm($E_4$) were also measured. To 10 ml. of each solution, 50 µl of $^{58}$Co were added to produce solutions of final specific activity equivalent to 19 kBq/ml. All solutions were
incubated in a water bath maintained at 10 °C. After 40 days incubation, 0.6 ml. aliquot of each solution was separated on a column of sephadex gel (G-10) and fraction collected in vials of 1.5 ml. fractions and counted as in (2-4.B.4). The percentage of cobalt complexation in each solution was determined.

2-4.B.6 EFFECTS OF ADDING EDTA

1) SEPARATION PROCEDURE

Separation of complexed cobalt from free cobalt was achieved using Amberlite IR-120 cation exchange resin in the sodium form. 1ml of EDTA-groundwater solution was counted for cobalt activity then introduced onto the top of 3 cm long column of resin held in a 1 cm diameter glass tube. Complexed cobalt was eluted from the resin by adding distilled water to the column. The uncomplexed cobalt was retained on the resin. The activity of the complexed cobalt was determined by counting the distilled water washings on a Philips PW 4800 automatic gamma counter. The percentage of complexed cobalt was calculated from the following formula:

\[
\% \text{ of complexed Co} = \frac{\text{activity of complexed Co} - \text{background}}{\text{total activity added to the resin} - \text{background}} \times 100
\]

2) EXPERIMENTAL

1 ml of 10 ppm EDTA (Sodium form, Analar grade) and 1 ml of 14C labeled EDTA solution (specific activity 1.85 x 10^4 Bq/ml) was added to 3 ml of 0.45 μm filtered groundwater and allowed to incubate at 10°C for seven days. After this time, 5 ml of 58Co in 0.45 μm filtered groundwater were added to the EDTA solution producing a final specific activity of 36 Bq/ml with respect to 58Co and incubated for a further 10 days at 10 °C. The experiment was repeated with 50, 100, 200, 300, 400, and 500 ppm solutions of inactive EDTA.

In order to show the effect of adding EDTA after incubation of
groundwater with cobalt, 5 ml of the $^{58}$Co solution used previously was incubated for seven days at 10 °C. After this time, 1 ml of 10ppm EDTA solution, 1 ml of $^{14}$C labelled EDTA and 3 ml of 0.45 μm filtered groundwater were added to the mixture and incubated at 10 °C for a further 10 days. The experiment was repeated with 50, 100, 200, 300, 400, and 500 ppm solutions of EDTA. Separation of complexed cobalt from free cobalt was achieved as described in the separation procedure (see 2-4.B.6). The purpose of using $^{14}$C labelled EDTA is discussed in chapter 3. The kinetics of the reaction of cobalt in groundwater with 1ppm EDTA solution was also investigated.

2-5 THE EFFECT OF RADIATION ON COBALT COMPLEXATION
WITH GROUNDWATER (G.W) AND WITH (NaHu)

2-5.1 PRELIMINARY EXPERIMENTS

1) COBALT COMPLEXATION

To investigate the effect of gamma radiation on the complexation of cobalt with groundwater and NaHu solution, a series of experiments were carried out. The general procedure adopted was to add $^{58}$Co to either natural groundwater that had been concentrated by a factor of times 10 or to 200 ppm NaHu solution to produce solutions of final specific activity equivalent to 18 to 20 kBq/ml. The solutions were then allowed to equilibrate for a minimum of 10 days in a water bath held at 10 °C. Half of the volume of the resulting solutions were then introduced into a $^{60}$Co gamma field (Gammacell 200) which delivered a dose rate of 61 grays/hour as measured by a Fricke solution. The other half of the solutions were not introduced into the gamma field but were maintained at the same temperature and for the same time as those placed in the gamma field. After irradiation for five days, complexed cobalt from free cobalt was separated in both sets of solution by sephadex gel (G-10). The percentages of complexed cobalt were then calculated in each solution.
Experiments in which concentrated groundwater or 200 ppm NaHu was irradiated first (for five days) and then $^{58}$Co added were also carried out.

11) $E_4 / E_6$ RATIO AND pH INVESTIGATION

10 ml solutions of either times 10 groundwater or 200 ppm NaHu solution were introduced into the gamma field. Before and after irradiation (five days), the absorbances at 465 nm and 665 nm ($E_4/E_6$ ratio) and pH's of both sets of solutions were measured.

2-5.2 REPRODUCIBILITY

The reproducibility of the effect of radiation on complexed cobalt formation was checked by adding 3 µl of $^{58}$Co (22 kBq) to five separate samples of times 10 concentrated groundwater which had already been irradiated in the gamma field for five days. All solutions were allowed to equilibrate for 10 days in a water bath maintained at 10 °C after which the percentages of complexed cobalt in each sample was determined by using a Sephadex (G-10) column.

2-5.3 COBALT-58 AND DISTILLED WATER

To 7 ml of distilled water, 20 µl of $^{58}$Co were added to produce a solution of final specific activity equivalent to 20.8 kBq/ml. The solution was incubated for five days at 10 °C before introducing it into the gamma field. After five days of irradiation, a 0.6 ml aliquot of the solution was separated by Sephadex gel (G-10) and the percentage cobalt complexation determined. The retention time of complexed and uncomplexed cobalt was noted.
2-5.4 THE EFFECT OF RADIATION ON THE KINETICS OF COBALT-58 WITH X10 CONCENTRATED GROUNDWATER

1) X10 GROUNDWATER SOLUTION IRRADIATED BEFORE Co ADDED

A solution of 10 ml of x10 concentrated groundwater was introduced into the $^{60}$Co gamma field. After irradiation for five days, 50 µl of $^{58}$Co were added to produce a solution of final specific activity of 19 kBq/ml. A 0.6 ml aliquot of the solution was separated at zero time in order to determine the percentage cobalt complexation. The remainder of the solution was incubated in a water bath maintained at 10 $^\circ$C. After known periods of time, a 0.6 ml aliquot of the solution was separated and the percentage of cobalt complexation determined. The kinetics of the reaction of unirradiated x10 concentrated groundwater with $^{58}$Co (final specific activity 19 kBq/ml) was also investigated.

2) X10 GROUNDWATER SOLUTION EQUILIBRATED WITH COBALT-58 THEN IRRADIATED

To 10 ml of x10 concentrated groundwater solution, 50 µl of $^{58}$Co were added to produce a solution of final specific activity of 19 kBq/ml. The solution was incubated in a water bath maintained at 10 $^\circ$C. After incubation for ten days, a 0.6 ml aliquot of the solution was separated to enable the percentage cobalt complexation to be measured at zero time of irradiation. The remainder of the solution was introduced into the $^{60}$Co gamma field. After known doses of irradiation, the pH of the solution was measured and a 0.6 ml aliquot of it was separated and the percentage of cobalt complexed determined.

To investigate the effect of a short time of irradiation on the kinetics of cobalt complexation, a solution of x10 G.W and $^{58}$CO (19 kBq/ml) was equilibrated at 10 $^\circ$C for 10 days. When the mixture had reached equilibrium, a 0.6 ml aliquot of the solution was separated and the percentage cobalt complexation...
determined. The same solution was then irradiated for 1h (61 grays/h), after which a 0.6 ml aliquot was separated and the percentage cobalt complexation determined. Periodically, a 0.6 ml aliquot of the solution was separated and the percentage of cobalt complexation in the mixture determined.

2-5.5 200 ppm NaHu SOLUTION EQUILIBRATED WITH COBALT-58 THEN IRRADIATED

The same procedure as that used for the x10 groundwater (see 2-5.4i) investigation was adopted except that the final specific activity of the 200 ppm 0.45 μm filtered NaHu solution was 17 kBq/ml.

2-5.6 LOW DOSE DELIVERED

The aim of this experiment was to investigate the effect that the amount of radiation delivered had on the formation of the complex. Following the method described by Arnikar(120), the dose delivered by a 60Co gamma source (61 grays/hour) was reduced to 34 grays hr⁻¹ (as measured by a Fricke solution) by inserting the sample (x10 groundwater in a glass vial) in a thick lead canister.

A solution of 10 ml. of x10 groundwater containing 190 kBq of 58Co was prepared. The solution was incubated in a water bath maintained at 10 °C. After 10 days a 0.6 ml aliquot of the solution was separated for zero time irradiation. The vial containing the remainder of the solution was inserted into a thick lead canister then introduced into the 60Co gamma field. The dose delivered to the solution was attenuated to 34 grays hr⁻¹. Periodically, 0.6 ml. aliquots of the solution were separated and fraction collected in vials of 1.5 ml. each and counted on a Philips PW4800. The percentage of cobalt complexation in each solution was calculated.

The kinetics of the association of cobalt in x10 G.W was investigated after irradiating the solution for 1 hour. These results are shown in figure 20 (page 66).
2-5.7 GEL PERMEATION CHROMATOGRAPHY OF GROUNDWATER

Two solutions of 2 ml each of x10 concentrated groundwater and \(^{58}\)Co of final specific activity equivalent to 18.3 kBq/ml were prepared. The two solutions were allowed to equilibrate for 15 days in a water bath maintained at 10 °C. After equilibrium was reached, one of these solutions was introduced into a \(^{60}\)Co gamma field (for 3 days). The other solution was not introduced into the gamma field but was maintained at the same temperature and for the same time as the solution placed in the gamma field.

A 0.6 ml aliquot of each solution was separated on a column of sephadex (G-15) gel (45 cm gel bed height, 1.5 cm i.d) using a flow rate of 7.3 ml/hour. At this flow rate, it was expected that separation by size was the predominant mode of separation. The U.V of the eluent was monitored continuously by a PYE UNICAM PU 4021 multichannel detector linked to a Linseis pen recorder. The complexed peak was fraction collected (5 min. fractions) and counted on a Philips PW 4800 automatic gamma counter, the activity of the fractions was plotted along with U.V trace as a function of elution time.

2-6 IODIDE COMPLEXATION WITH GROUNDWATER AND SODIUM HUMATE SOLUTION

i) NON RADIOLYTIC INVESTIGATIONS

A mixture of 18 ml of ultrapure water and \(^{125}\)I (180 kBq) was prepared. A 0.6 ml aliquot of the mixture was separated for zero time iodide complexation. The remainder of the solution was incubated in a water bath maintained at 10 °C. After known periods of time, a 0.6 ml aliquot of the solution was separated by sephadex gel (G-10) and fraction collected in vials of 0.2 ml each and counted on a Philips PW4800 gamma counter. The percentage of complexed iodide in each solution was determined.

Similarly, mixtures of either x10 concentrated groundwater or
200 ppm 0.45 μm filtered NaHu with $^{125}$I (180 kBq) were prepared and separated.
To investigate the effect of an oxidizing and a reducing agent on iodide species in ultrapure water, 100 μl of either 0.1M chloramine-T (oxidant) or 1M of Na$_2$S$_2$O$_5$ were added to 18 ml of ultrapure water containing 180 kBq of $^{125}$I. A 0.6 ml aliquot of each mixture was separated as above. The oxidation and reduction experiments described above were repeated with x10 groundwater.

[II] RADIOLYSIS INVESTIGATIONS

A mixture of 18 ml of ultrapure water and $^{125}$I (180 kBq) was prepared. After 40 hour incubation at 10°C, a 0.6 ml aliquot of the mixture was separated for zero time irradiation. The remainder of the solution was introduced into the $^{60}$Co gamma field. After known doses of irradiation were delivered to the solution, a 0.6 ml aliquot of the solution was separated and counted as above (see 2-6j).
The same procedure as above was adopted for x10 groundwater and 200 ppm 0.45 μm filtered NaHu except that the pH's were measured after each period of irradiation.
CHAPTER THREE
RESULTS AND DISCUSSION

3-1 TECHNIQUE

Fig. 2 shows a typical chromatogram of cobalt and iodide separated by Sephadex gel (G-10).

FIGURE 2

Typical chromatogram of cobalt and iodide separation.

With flow rates noted in chapter two (0.546 ml/min for cobalt and 0.073 ml/min for iodide), the complexed cobalt eluted in 15-20 minutes and the free cobalt eluted in 100-120 minutes. For iodide, the apparently complexed iodide eluted in 135 to 145 minutes and the free iodide eluted in 245 to 255 minutes.
Figure 3 shows the kinetics of the reaction of cobalt with x10 groundwater when the mixtures were held at 10 °C and at 25 °C. Approximately 35% and 47% complexed cobalt was found after holding the solution for 265 and 168 hours at 10 °C and 25 °C respectively thus indicating that the forward reaction of cobalt with groundwater is endothermic. The kinetics of the association of cobalt with x10 groundwater were slow at both temperatures (10 °C and 25 °C). It is possible that the solution held at 10 °C had not reached equilibrium and therefore the value of 35% cobalt complexation obtained after 265 hours is lower than the true equilibrium value.

**FIGURE 3**

![Graph showing the effect of temperature on Co interaction with x10 G.W](image)

**Effect of temperature on Co interaction with x10 G.W**

By applying the data of the interaction of cobalt with groundwater at 25 °C to the equations relevant to first and second order reaction kinetics, curves were obtained in both cases, as shown in figures 4 and 5.
FIGURE 4

Equation for first order kinetics

FIGURE 5

Equation for second order kinetics
This suggests that the kinetics of cobalt interaction with species present in groundwater is complex and does not follow simple first or second order kinetics.

Fig. 6 shows the kinetics of the reaction of cobalt with 200 ppm 0.45 μm filtered NaHu at 10 °C and 25 °C. Approximately 15 % complexed cobalt was observed at equilibrium at both temperatures. In contrast to the groundwater, the position of equilibrium of the reaction of cobalt with NaHu solution did not alter with a change in temperature.

**FIGURE 6**

![Graph showing effect of temperature on Co interaction with 200ppm NaHu](image)

**Effect of temperature on Co interaction with 200ppm NaHu**

Figure 13 (page 55) shows the effect of cobalt concentration on bound cobalt activity. For 100 ppm NaHu solution the maximum cobalt complexation occurs at approximately 75 μmolar with respect to added cobalt. The results shown in figure 6 were obtained from solutions containing 2.64 x 10⁻¹⁰ M of added cobalt and therefore the amount of cobalt used in the solutions of figure 4 are much lower than the amount required to saturate the binding sites of the sodium humate. The consistency in the position of equilibrium as the temperature changes is therefore
not due to saturation of the binding sites. The change in the equilibrium constant brought about by a change in temperature is given by:

\[
\ln K(T) = \ln K(T^*) - \left[ \frac{\Delta H^\circ(T^*)}{R} \right] \left[ \frac{1}{T} - \frac{1}{T^*} \right]
\]

If the equilibrium constant remains the same after a change of 15 °C \(\Delta H\) must be small or equal to zero. This might suggest that a chemical reaction, in which bonds are broken and reformed is not taking place when cobalt reacts with an aqueous solution of sodium humate but that physical sorption is the mechanism of the interaction between cobalt and sodium humate.

Figures 7 and 8 show that the concentration of groundwater and sodium humate affects the position of the equilibrium of the reaction with cobalt at 10 °C. From figures 7 and 8, it can be seen that in x5 and x10 groundwater approximately 21% (for x5) and 47% (for x10) of cobalt is complexed. Although 47% complexed cobalt was observed in x10 groundwater held at 25 °C (figure 3) and 10 °C (Figure 7) the samples of groundwater were taken from the Drigg site at different times during the year. This explains the anomaly in the results. For 0.45µm filtered NaHu solutions, the percentages of complexed cobalt were approximately 7% for 100ppm and 15% for 200ppm concentrations.
FIGURE 7

Effect of groundwater concentration on Co interaction

FIGURE 8

Effect of NaHu concentration on Co interaction

It is worth noting that the concentration of organic substances in groundwater changes seasonally, hence the complexation...
capacity of groundwaters sampled at different times will subsequently be different. Consequently, in an assessment of metal–organic complexes in a groundwater system, the complete analysis of groundwater composition is essential.

Rossotti and Rossotti (121) have shown that if the number of protons associated with a ligand is independent of the concentration of the ligand when the concentration of ligand is not negligible, then the interaction must be mononuclear with respect to the ligand. Accordingly, if the interaction of metal with organics is dependent on the concentration of organics this indicates that the reaction is polynuclear. The reaction of cobalt with NaHu and groundwater can be considered as a polynuclear where the multiple-ligand interaction is more likely to occur than the chelation interaction (the binding sites are on the same molecule). However, considering the size of the organic polyelectrolyte anions (i.e. humic substances) and the number of binding sites per molecules, chelation reactions may also be of importance.

3.3 pH EFFECTS

In humic substances, no two molecules are identical and each molecule can be expected to contain a diversity of carboxyl and phenolic hydroxyl functional groups. Table 1 (page 8) showed the typical ligands found in humic substances. Most of these ligands would be expected to be either fully protonated, partially protonated or unprotonated at certain pH values. Fig. 9 shows the effect of pH on the complexation of cobalt with NaHu and with x10 groundwater solution.
For both solutions, no complexation was observed at a pH of 5 and less. Assuming a ligand type reaction, this suggests that the ligands (complexing species) in both solution are fully protonated at pH 5. At pH values higher than 5 the percentage cobalt complexation of both solutions increased with increasing pH. The drop in cobalt interaction within three pH units suggests that the interaction is a result of deprotonation of various ligands at pH values characteristic for each ligand.

Choppin et al (122) have considered carboxylic and phenolic groups to be important in metal complexation. They found that when titrating solutions of fulvic and humic acids with base, curves with gradual pH changes and poorly defined inflection points were obtained which can be associated with neutralization of the carboxylic and the phenolic groups. Calculation of the acidity constant, $pK_a$, of these groups at different points in the titration vary with the degree of ionization of these functional groups. At 50% ionization of the carboxylate groups, the $pK_a$ value was found to be $3.6 \pm 0.1$ for different fulvic acids. For humic acids this value is about $4.8 \pm 0.2$. For lake humic acid the $pK_a$ at
50% ionization was found to be $9.7 \pm 0.2$ (123). For molecular weight of 200,000 at pH values of 6 and above, the predominant binding sites was reported to be phthalate group (124). Gamble et al (89) have suggested that reaction of salicylic and phthalic ligand types are important in reaction of metals with humic material. Considering these ligands, the effects of pH are shown below. For phthalic acid;

\[
\begin{align*}
\text{P1} & \quad \text{pK}_a = 2.95 \\
\text{P2} & \quad \text{pK}_a = 5.41 \\
\text{P3} &
\end{align*}
\]

At pH 2.95 P1 and P2 are equally predominant. At pH between 2.95 and 5.45 P2 is the predominant species. P3 species are predominant species at pH >5.45.

For salicylic acid;

\[
\begin{align*}
\text{S1} & \quad \text{pK}_a = 2.89 \\
\text{S2} &
\end{align*}
\]

At pH 2.89 $[\text{S1}] = [\text{S2}]$. At pH >2.89 the predominant species is S2.

According to Gamble Cu$^{2+}$ reacts with phthalic and with salicylic acid (page 23) via P2 and S2 species respectively. P2 should be the predominant phthalic acid species between pHs of 2.95 and 5.41 and S2 should be the predominant species at pHs above 2.89. These observation, together with these results shown in figure 9 suggest that the P2 ion shown above may not play a significant part in the complexation of cobalt. The S2 and P3 ion may be of importance in cobalt complexation.
The most perplexing chemical equilibrium problem is the thermodynamic description of the binding of metal ions to a complex mixture such as humic substances. Any study with these humic substances will inevitably be complicated. For instance, the titration curves for such a complex mixture of ligands with metal ions would be expected to be complex and featureless, with no sharply defined equivalent points (125). The chemical models that have been proposed to describe metal binding by humic substances have considered the complexity of these substances. A Scatchard plot (126) was first used to determine the number of binding sites in proteins (such as albumin) by reacting the proteins with NaCl and NaI. Scatchard plots were then used by researchers to study the binding of protons and metal ions by humic substances. A Scatchard type plot (127, 128) as shown in figures 10 and 11 may indicate by its curvature fit that either the interaction of cobalt with NaHu and with groundwater occurs with a mixture of site types or there is interaction between sites, or that both statements are true. Figures 10 and 11 indicate that the interaction of cobalt with material in groundwater and with sodium humate solution occurs by reaction of cobalt with a mixture of site types.
Scatchard type plot of Co with $x30$ G.W

Scatchard type plot of Co with 100 ppm NaHu

Scatchard plots can also provide a numerical value for the binding capacity of the organics under study. From figures 12 and 13 it can be seen that the maximum values for cobalt complexation were within the range 70-90μmolar cobalt for $x30$
G.W and 75-95μmolar cobalt for 100 ppm of 0.45μm filtered NaHu solution.

**FIGURE 12**

Saturated point of Co with x30 G.W

**FIGURE 13**

Saturated point of Co with 100 ppm NaHu

55
Figure 13 also shows that an increase in added cobalt beyond 100 μmolar cobalt reduces the activity associated with the bound cobalt. This reduction in activity possibly results from precipitation of the complex due to metal loading of the humic material. The metal loading may cause a change from hydrophilicity to hydrophobicity in the humic molecules. Adding metal ions reduces the electrostatic repulsion by the anionic groups in humic substances and also releases solvation water resulting in configurational change in the molecules to more hydrophobic structures. Beyond 200 μmolar of added cobalt a gradual increase in the activity of the bound cobalt is also evident. This increase in the activity of bound cobalt may due to heavy loading of cobalt (19).

By knowing the binding capacity (after Scatchard plots) of organic matter with elements in the waste repository site, and the distribution of the associated radionuclide between the aqueous and the aquifer phase, the amount of these elements that migrate over a certain period of time, can be assessed.

3-5 MOLECULAR SIZE EFFECTS

Colloids and particles are known to play an important role in the transport of radionuclides in waste waters from nuclear power plants (129,130). Some of the UK clay formations contain significant amounts of organic materials which could give rise to groundwater containing 1 to 10 mg/l of dissolved organic carbon. These organics are high molecular weight acids, some of which could be regarded as colloids(130). These molecules have the ability to complex with some radionuclides which could enhance their solubility and hence mobility. Because of the large size of these complexes, lack of filtration into the pore structure of the clay in the near field may result in enhancement in the transport of radionuclides. It has been reported that polyvalent cations can serve as bridges as they bind simultaneously to the anionic silicates sites of a clay and anionic carboxylate sites of
humic and fulvic molecules (131). In this study, the percentage complexation of cobalt with 200 ppm NaHu solution reduced from 22% to 14% after filtering the solution through 0.45 μm filter (Fig. 14).

**FIGURE 14**

![Graph showing the percentage complexation of cobalt with NaHu](image)

**Particulate effect on Co interaction with NaHu**

In contrast to NaHu solution, 0.45μm filtered x10 groundwater appeared to have a similar percentage cobalt complexation as that of unfiltered x10 groundwater (Table 10). From table 10 it is obvious that the organics of molecular weight >1000 are the important complexing species. The dramatic reduction in complexation value after filtering the groundwater through a YM2 filter is in a good agreement with the change in E₄ value suggesting that the species which absorb at 465 nm are the species which are responsible for cobalt complexation. In this study no attempt was made to determine the colloids concentration in groundwater. However, in a study (132), > 96% of Am³⁺ was found to associate with the colloidal humic after 6 months equilibration. In another study (133) humic acids were
found to enhance the adsorption of $\text{Np}^{5+}$, $\text{Am}^{3+}$, and $\text{Th}^{4+}$ on $\text{Al}_2\text{O}_3$ relatively low pH values, while a lower actinide adsorption occurs at high pH. The results of the investigation on the effects of pH on cobalt complexation with groundwater shows an increase in the percentage of complexed cobalt as the pH increased above 5. If the complex or complexes are adsorbed on Drigg sand, sorption will result in a reduction of cobalt concentration in groundwater thus a reduction in the migration of cobalt via groundwater. However, Warwick (134) has performed sorption experiments which showed that the cobalt complex in groundwater passed through a column packed with Drigg sand and was not retained by the column. 100% of the complex was recovered from the column.

**TABLE 10**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>pH</th>
<th>TOC</th>
<th>$E_4$</th>
<th>Ca</th>
<th>Mg</th>
<th>$\text{HCO}_3^-$</th>
<th>% complexed</th>
</tr>
</thead>
<tbody>
<tr>
<td>unfiltered</td>
<td>8.43</td>
<td>56</td>
<td>0.021</td>
<td>111</td>
<td>105</td>
<td>498</td>
<td>45.0</td>
</tr>
<tr>
<td>0.45$\mu$m filtered</td>
<td>8.45</td>
<td>54</td>
<td>0.019</td>
<td>115</td>
<td>103</td>
<td>552</td>
<td>52.4</td>
</tr>
<tr>
<td>0.2$\mu$m filtered</td>
<td>8.51</td>
<td>--</td>
<td>0.021</td>
<td>116</td>
<td>103</td>
<td>550</td>
<td>52.4</td>
</tr>
<tr>
<td>0.1$\mu$m filtered</td>
<td>8.33</td>
<td>55</td>
<td>0.021</td>
<td>115</td>
<td>105</td>
<td>547</td>
<td>44.2</td>
</tr>
<tr>
<td>YM5 (&gt;5000) filtered</td>
<td>8.64</td>
<td>59</td>
<td>0.019</td>
<td>110</td>
<td>100</td>
<td>505</td>
<td>47.3</td>
</tr>
<tr>
<td>YM2 (&gt;1000) filtered</td>
<td>8.46</td>
<td>--</td>
<td>0.013</td>
<td>119</td>
<td>105</td>
<td>514</td>
<td>8.20</td>
</tr>
<tr>
<td>YCO5 (&gt;500) filtered</td>
<td>8.43</td>
<td>61</td>
<td>0.006</td>
<td>84</td>
<td>77</td>
<td>482</td>
<td>6.10</td>
</tr>
</tbody>
</table>

All the above concentrations of anions and cations are in mg/l

3-6 **EFFECTS OF ADDITION OF EDTA**

Natural organic and anthropogenic organics present in the near field clay and groundwater may complex with radionuclides. Allard and Presson (135) have considered EDTA to be a very strong complexing agent for actinides. In this study,
EDTA was found to complex strongly with $^{58}\text{Co}$ when EDTA was introduced into groundwater. Figure 15 shows about 90% of the cobalt was complexed with EDTA. The same percentage complexation was found whether EDTA was introduced into groundwater before cobalt or when cobalt was introduced into the groundwater before the addition of EDTA. This may not be the same with very low concentrations of EDTA especially in groundwaters containing cations of stability constants higher than that of cobalt.

**FIGURE 15**

![Graph showing EDTA effect on Co interaction in G.W]

**EDTA effect on Co interaction in G.W**

The kinetics of the reaction of cobalt with EDTA in groundwater was found to be very fast when cobalt was added to 1ppm of EDTA solution. To determine the EDTA ($^{14}\text{C}$-labelled) contribution to the complexation of cobalt in groundwater, ion exchange (cation and anion) was used. The results of this investigation showed that Co-EDTA complex was exchanged with the exchangeable ion on anionic resin. Using Drigg sand, sorption experiments were carried out with
the Co-EDTA complex which showed that all $^{14}$C-EDTA activity remained in solution (i.e. $K_d=0$ with respect to EDTA) and very little of the cobalt activity was adsorbed onto the sand (136). Cationic cobalt (free species) was shown to sorb strongly onto the Drigg sand.

3-7 RADIOLYSIS OF COBALT SOLUTIONS

The radiation chemistry of pure water is well understood(137). During the radiolysis of water the following radicals, ions or molecules are formed.

$$H_2O \rightarrow e^{-}_{aq}, OH^-, H^+, H_2O_2, H_2, H^+$$

In the presence of dissolved oxygen, radicals like $O_2^*$ and $HO_2^*$ can be produced additionally. The passage of a gamma photon through water produces regions of high concentration of radical pairs, which are spaced along the track of the gamma photon at relatively large intervals. Combination of the radicals in the spurs produces $H_2, H_2O_2$ and $H_2O$. When the concentration of a solute is less than a few percent by weight it is unnecessary to consider the direct interaction of the gamma photon on the solute. However, species which react with $OH^-$ (e.g $Cl^-, Br^-$) lower the molecular yield of $H_2O_2$ as their concentration is increased.

Oxidizing (e.g $H_2O_2$) and reducing species (e.g $e^{-}_{aq}$) are produced during the passage of ionizing radiation through water and aqueous solutions and are therefore expected to enter into oxidation and reduction reaction.

Considering the radiolysis of groundwater containing small amounts of iodine or cobalt, attention has to be paid to possible changes in materials present in groundwater and to possible changes in iodine and cobalt. In the near field of a waste repository site, radiolytic effects will inevitably be present which may affect the groundwater’s ability
to form complexes with radionuclides. In considering the effect of radiolysis on materials, other than radionuclides, present in groundwater, changes in natural organic materials present in the groundwater must be taken into account. Few studies have been conducted on the effect of radiation on the interaction of radionuclides with material present in groundwater. Studies on the UV degradation of lake water have shown that the complexation capacity for inorganic iron ($^{59}$Fe) by high and low molecular weight organic fraction, separated from lake water, was increased significantly after exposure to UV light (138). Sunlight (139) and high intensity UV light (139,140) were found to cause alterations in the spectral characteristics of dissolved humic materials. Using sephadex gel (G-50) Storme and Miller showed that the proportion of large molecules in a humic sample was reduced after high intensity UV irradiation. In peat, humic acids were found to decompose less rapidly than cellulose (141). Temperature and gamma irradiation were found to enhance the release of radioactive species from the solid matrices into the leaching aqueous media(142).

The objective of this study was to investigate the effect of radiation on the complexation capacity of groundwater and sodium humate solution with cobalt.

Table 11 shows the results from preliminary experiments. These results show that Co complexation is dramatically increased in x10 groundwater after irradiation, but complexation is almost eliminated in 200 ppm of 0.45μm filtered NaHu solution. Chen et al (143) have shown that the $E_4/E_6$ ratio of a solution containing humic and fulvic material is governed primarily by the particle size and that the $E_4/E_6$ ratio decreases as the particle size of the organics increases. Particle size also changes with the pH of the solution, the particle size increasing as the pH of the solution decreases.
TABLE 11 Results of the preliminary experiments

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% Co COMPLEXED</th>
<th>E₄/E₆</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>16.2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>5.2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>7.28</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>8.55</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>4.92</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>G.W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1, 4, 6 UNIRRADIATED</td>
<td>40.5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>2 EQUILIBRATED THEN IRRADIATED</td>
<td>81.6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>5, 7 IRRADIATED</td>
<td>82.6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>3 IRRADIATED THEN EQUILIBRATED</td>
<td>9.50</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7.95</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>7.35</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

The ratio of the absorbances measured at 465 nm (E₄) and 665 nm (E₆) (143) for groundwater and sodium humate decreases after five days irradiation (by 3.78 units for NaHu, and by 1.5 units for x10 groundwater). After five days irradiation the pH of x10 G.W was decreased by 0.6 of a pH unit while the pH of NaHu solution was decreased by 3.63 pH units. The decrease in the E₄/E₆ ratio and pH when sodium humate solution is irradiated suggests that a redistribution of particle size occurs to larger values. The small change in pH value of x10 G.W (only 0.6 of pH unit) must be due to the inherent buffering capacity of groundwater. The small decrease in E₄/E₆ ratio (1.5 units) after irradiation indicates that a small redistribution in particle size occurs during irradiation.

The complexation abilities of both solutions are the same whether the solutions are equilibrated with cobalt then irradiated or irradiated first and then equilibrated with cobalt suggesting that the irradiation caused changes in the groundwater but not in the cobalt. This fact is also evident from the radiolysis of Co present in distilled water which showed only 1% of the cobalt appeared as a complexed cobalt. The remaining active cobalt eluted from the column at the same retention time as that expected from free cobalt.
Table 12 shows the results of the reproducibility experiments showing an average of the percentage complexed cobalt of 88% with a standard deviation of ± 1.5% (1 sigma).

TABLE 12
REPRODUCIBILITY RESULTS

<table>
<thead>
<tr>
<th>RUN NUMBER</th>
<th>%-complexed Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85.8</td>
</tr>
<tr>
<td>2</td>
<td>89.4</td>
</tr>
<tr>
<td>3</td>
<td>89.3</td>
</tr>
<tr>
<td>4</td>
<td>88.3</td>
</tr>
<tr>
<td>5</td>
<td>87.3</td>
</tr>
</tbody>
</table>

Fig.16 and Fig.17 show the effect of gamma dose on the complexing ability and pH of x10 G.W and 200 ppm 0.45 μm filtered NaHu solution.

FIGURE 16

Effect of radiation on pH and Co interaction with x10 G.W
Fig. 16 shows that after 19 hours of irradiation 93% of the cobalt was complexed. After 68 hours of irradiation the percentage of complexed cobalt started to decrease. The pH of x10 G.W was decreased from 8.15 to 6.90 after 190 hours irradiation. Fig. 17 shows that the complexation ability of 200 ppm NaHu solution was decreased from 15% complexed cobalt to 2.7% after 144h of gamma irradiation. The pH of the solution decreased from 6.71 to 4.5.

FIGURE 17

**Effect of radiation on pH and Co interaction with NaHu**

When x10 G.W was irradiated for five days and cobalt then added an increase in the rate of production of the complex was observed. For comparison Fig. 18 shows the slow kinetics of unirradiated x10 G.W.
Kinetics of irradiated and unirradiated $x_{10}$ G.W.

Fig.19 shows the effect of low dose (34 grays/h) and high dose (61 grays/h) of gamma radiation on the complexation ability of $x_{10}$ G.W. It is clear from fig.19, that within the range of doses used there is no difference in the complexation ability of $x_{10}$ G.W.

Effect of dose rate on Co interaction with $x_{10}$ G.W.
In Fig. 16 the percentage of complexed cobalt was determined immediately after removal of the irradiated solution from the gamma field. There is therefore uncertainty as to whether the increase in cobalt complexation is a function of dose delivered or whether the increase is a consequence of the kinetics of complexation. Fig. 20 shows the kinetics of x10 G.W which was equilibrated with cobalt and then irradiated for one hour (61 grays/h). At equilibrium the percentage of complexed cobalt was 41%. It is evident that low doses of radiation caused this increase in the percentage of cobalt complexation. This factor may have a major influence on cobalt migration even in conditions of very high flow rate of groundwater.

**FIGURE 20**

The kinetics of irradiated (one hour) solution of cobalt equilibrated with groundwater

After irradiating a mixture of x10 groundwater and $^{58}$Co for 24 hours, the percentage of complexed cobalt was the same as that observed in a similar mixture which was irradiated for one hour and equilibrated at 10 °C. This is also an indication that the
increase in cobalt complexation is a result of an increase in the speed of cobalt interaction with species formed during irradiation.

3-8 GEL PERMEATION OF GROUNDWATER SOLUTION

Fig. 21 shows the gel permeation separation (G-15) of a mixture of $\times 10$ G.W after equilibration with $^{58}$Co. Figure 20 shows the separation of the same mixture after irradiation for three days with gamma rays. Figure 21 shows that cobalt was associated with two different sets of complexing species. It can also be seen that other than the first two peaks, no cobalt is associated with any U.V absorbing peaks. After irradiating the groundwater (Fig. 22) the cobalt activity associated with the group of molecules of larger size is eliminated and a redistribution of size of these molecules occurs. Protonation of large molecules may also occur producing a species which is less U.V absorbing and eliminating the complexation ability of these species. In considering the mobility of associated cobalt after radiolysis, the charge and the size of the complexes formed should be investigated. In situ experiments, taking the charge of species and the pore structure of clay in the near field into account, are also needed.
FIGURE 21

Gel permeation of unirradiated x10 G.W equilibrated with Co

FIGURE 22

Gel permeation of irradiated x10 G.W equilibrated with Co
IODIDE INTERACTION WITH NaHu AND G.W

The difficulty of predicting the movement of iodine in the environment arises from its complex chemistry. However, Whitehead and Truesdale (144) have shown that iodine can enter groundwater from the atmosphere via deposition in rainfall. Iodine may be adsorbed by plants and soil, then immobilized by soil organic matter before being leached through the soil by groundwater. In marine environments, iodine was found to associate with organic fractions and particularly with humic substances (145). Iodate was found not to react with humic substances unless it was reduced to iodine (145,146).

In this study, the interaction of $^{125}$I interaction with G.W and with NaHu solution was investigated. When iodide was added to ultrapure water an apparently "complexed" iodine ($28\% \pm 3\%$) was eluted from the sephadex column at the retention time expected of the iodide complex. The same value of "complexation" was found when iodide was added into x10 G.W. This suggests that groundwater does not complex with iodide. Fig.23 shows that about 40% iodide appeared as "complexed" iodine species when iodide was added to 200 ppm 0.45 µm filtered NaHu.

FIGURE 23

Kinetics of iodide with NaHu and G.W
IRRADIATING IODIDE MIXTURES WITH COBALT-60 GAMMA PHOTONS

After irradiation mixtures of iodide and sodium humate or x10 groundwater, the production of "complexed" iodine was increased in both solutions. The pH of both solutions decreased during irradiation. Fig. 24 shows that after 50 hours of irradiation the percentage of "complexed" iodine was increased to 75% for x10 groundwater. Figure 25 shows that iodine "complexation" increased to 69% before decreasing to a final value of 48% after 102 hours of irradiation. Deprotonation of functional groups may also occurred resulting in reduction in pH value.

FIGURE 24

Effect of radiation on iodide interaction with X10 G.W
Effect of radiation on iodide interaction with 200 ppm NaHu

3-11 INVESTIGATION OF IODINE SPECIES

In an aqueous solution containing I\(^-\), reactions of oxidation, reduction and disproportionation of I\(_2\), which occur during irradiation, give rise in a closed system to I\(^-\), I\(_2\)\(^-\), I\(_3\)\(^-\), I\(_2\), HOI, HOI\(_2\)\(^-\), IO\(^-\), IO\(_2\)\(^-\), IO\(_3\)\(^-\), IO\(_4\)\(^-\) (147,148). Within the pH range 7-8.5 the probable species are I\(^-\), I\(_3\)\(^-\), IO\(_3\)\(^-\) and IO\(_4\)\(^-\) (144). The oxidation yield G(I) in dilute slightly alkaline and neutral iodine solution is about 1-3 or less and increases with increasing H\(^+\) and I\(^-\) concentration up to 7-10. The reduction yield of iodine G(-I\(_2\)) is much lower at about 0.3 and almost independent of pH(147).

When a nonradiolized solution of iodide and ultrapure water was separated by Sephadex (G-10) two distinct broad peaks (A and B) appeared. This might be due to the presence of different species of iodine. When the solution of iodide in ultrapure water was irradiated, peak (A) became larger and less broad and a split in peak (B) occurred. The apparent value of peak (A) remained at 28 \(\pm\) 3 % of the total iodide activity after irradiation for 40 hours.
To investigate whether oxidation or reduction of iodide occurred during irradiation, the oxidant Chloramine-T and the reductant Na$_2$S$_2$O$_5$ were used. After oxidation of an unirradiated solution of I$^-$ in ultrapurewater by Chloramine-T, peak (A) was dramatically increased while peak (B) disappeared. After the addition of Na$_2$S$_2$O$_5$ to an unirradiated solution of I$^-$ in ultrapurewater, peak (B) increased and a dramatic reduction in peak (A) occurred. The above investigations show that during irradiation oxidation of iodide occurred. It is possible that small iodide species were oxidised to large species which were excluded by Sephadex (G-10).

Three peaks (A medium, B shoulder, C large) eluted from the column when a mixture of iodide and groundwater was separated. When Chloramine-T was added, peak (A) was increased and a decrease in peak (C) was observed. Shoulder (B) was unaffected. The same trend was observed for all three peaks when the solution of iodide and groundwater was irradiated. When Na$_2$S$_2$O$_5$ was added to a fresh mixture the opposite trend was observed. Peak (C) increased while peak (A) and peak (B) almost disappeared. It can therefore be said that during radiolysis oxidation of the iodide species occurred probably by the ·OH radical produced by radiolysis of water.

After irradiation of the mixture of iodide and groundwater, peak (A) eluted with the same retention time as that observed for an unirradiated mixture of iodide and groundwater. This suggests that during irradiation oxidation of the iodide species and/or complexation with small molecules in groundwater occurred.
FIGURE 26

Typical chromatograms of iodide in ultrapure water.
1- $^{125}$I in ultrapure water (40 hours at 10 °C).
2- $^{125}$I in ultrapure water, Chloramine-T added (17 hours at 10°C)
3- $^{125}$I in ultrapure water (equilibrated), 23.5 hours irradiation.
4- $^{125}$I in ultrapure water, Na$_2$S$_2$O$_5$ added (zero time incubation)
FIGURE 27

Typical chromatograms of iodide in groundwater

1- $^{125}$I in x10 G.W (44 hours at 10 °C).
2- $^{125}$I in x10 G.W, Chloramine-T added, (5 hours at 10 °C).
3- $^{125}$I in x10 G.W (equilibrated) 23.5 hours irradiation.
4- $^{125}$I in x10 G.W, Na$_2$S$_2$O$_5$ added, (zero time incubation).
3-12 STATISTICS

The absence of errors in the calculations of percentage of radionuclidic complexation and in the graphs of experimental results does not signify that the author underestimates the importance of such calculations. To rectify the absence of estimated errors, an example calculation is shown below:

\[
\text{activity of complexed - background} \\
\% \text{ of complexed radionuclide} = \frac{\text{activity of complexed - background}}{\text{total activity - background}} \times 100
\]

Where total activity = Activity of free radionuclide + Activity of complexed radionuclide

The error in this calculation is given by:

\[
\frac{A}{B} \pm \left( \frac{A^2 + B^2}{B^2} \right)^{1/2}
\]

Where \( A_c \) = total activity of complexed radionuclide;

\( B_{d1} \) = background count of complexed radionuclide;

\( A_f \) = total activity of free radionuclide;

\( B_{d2} \) = background count of free radionuclide;

\[
A = (A_c - B_{d1}) \\
B = (A_c - B_{d1}) + (A_f - B_{d2}) \\
a = (A_c + B_{d1})^{1/2}, \text{ the error in } A \\
b = (A_c + B_{d1})^{1/2} + (A_f - B_{d2})^{1/2}, \text{ the error in } B
\]

A typical example of a calculation of an equilibrated sample of x10 concentrated groundwater with \(^{58}\)Co (final specific activity of 19 kBq/ml) furnishes the following:

\( A_c = 88326 \text{ cpm} \quad B_{d1} = 5150 \text{ cpm} \quad A_f = 147242 \text{ cpm} \quad \text{and} \quad B_{d2} = 18165 \text{ cpm} \).

After calculating the values of A, B, a and b and substituting them
into equation (1) a value of 39.1% ± 0.13% was obtained.

By following the above calculations, a sample of \( x_{10} \) concentrated groundwater which was equilibrated with \(^{58}\text{Co} \) (specific activity 19 kBq/ml) then irradiated for one hour, gave the value of 55.9% ± 0.18%

From the above calculations it is clear that the error involved in the calculation of the percentage complexation value is low. Considering the results shown for 216 hours in figure 3 (page 45), for \( x_5 \) G.W the percentage of complexed cobalt was calculated to be 20.6% and for \( x_{10} \) G.W was calculated to be 49%. The difference of 28.4% is significant and real as can be shown by calculating the error associated with both measurements.

Other than the small error involved in the above calculations, errors can be caused by other sources. As stated in chapter two, the activity of free and complexed species was calculated by the integration of counts under peaks. The greatest errors were obtained when the ratio of complexed to free was very large or very small. In these cases, the counts measured above the background count were low and the error involved in the background subtraction became significant.

A rotary evaporator was used to concentrate groundwater samples. The samples were not necessarily concentrated to the same extent in all experiments, thus introducing a possible error. In the experiments where many samples were prepared (e.g. the effect of cobalt concentration on cobalt complexation) an error resulting from the measurement of volumes of groundwater and radionuclidic containing solution was also possible.

3-13 CONCLUSIONS

The use of Sephadex gel for the separation of free from complexed species has been shown to be a reliable and reproducible technique. The kinetics of the interaction of cobalt with groundwater have been shown to be slow, whereas the interaction of cobalt with NaHu solution appears to be fast. The
interaction of cobalt with NaHu solution, in contrast to groundwater, has been shown to be unaffected by temperature.
The interaction of cobalt with NaHu solution and with groundwater increases as the pH of the solutions increase (for pH values higher than 5) and also as the concentration of the solution increases. The effect of particulates on the complexation of cobalt is more pronounced in NaHu solution than in groundwater. When EDTA was added to groundwater, the interaction of cobalt with groundwater was shown to increase dramatically.
Irradiation of groundwater increased the cobalt association capacity of the groundwater but decreased the association capacity of NaHu solution.
The kinetics of cobalt association in an irradiated groundwater, in contrast to unirradiated groundwater, was shown to increase.
The pH of groundwater was only marginally affected by radiation due to its inherent buffering capacity, but the pH of NaHu solution was reduced significantly during irradiation.
Irradiation of NaHu solution considerably decreased the $E_4/E_6$ ratio whereas only a slight decrease was observed for groundwater. Low and high doses of radiation were shown to have the same effect on cobalt association in groundwater.
Irradiation increased the capacity of groundwater and, initially, of NaHu solution, to associate with iodine. Prolonged irradiation of NaHu solution however decreased the solution's ability to associate with iodine. Radiation may cause oxidation to iodide species and/or complexation with the small molecules.

3-14 SUGGESTIONS FOR FURTHER WORK

In the present work, iodine and cobalt association with groundwater and sodium humate solution was investigated. An effort should be made to investigate other radionuclides present in the environment such as those used entering the environment from medicinal and scientific research.
The migration of radionuclides through groundwater and aquifers to the biosphere is highly influenced by the charge on the radionuclide or radionuclidic complex. Thus an investigation of the overall charge must be carried out. Since the size of these complexes also plays an important role in the transport of radionuclides an investigation of the size of these complexes should also be carried out.

In the near field radiation may cause a change in the charge and size of radionuclide complexes. The effects of radiation on these properties of the complexes needs to be studied. The pH in the near field may be high and thus the effect of radiation on solutions of high pH should be investigated.

The effect of radiation on the association of radiologically important nuclides other than iodine and cobalt needs to be studied.
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