THE ATTENUATION OF HEAVY METALS FROM LANDFILL LEACHATES BY BUNTER SANDSTONE AND CHALK

A thesis submitted for the degree of
Doctor of Philosophy

by

Patrick Malcolm Collison

at

The University of Aston in Birmingham

March, 1982

The University of Aston in Birmingham

The Attenuation of Heavy Metals from Landfill Leachates by Bunter Sandstone and Chalk

Patrick Malcolm Collison

Doctor of Philosophy 1982

Summary

Extensive quarrying in the Chalk and Triassic Sandstones, which are the two largest aquifers in the U.K., has produced a need for reclamation. Infilling these quarries with waste materials will create a potential pollution hazard to underground water supplies.

Laboratory experiments were set up to investigate the natural chemical processes by which the heavy metals and alkaline earth metals in landfill leachates may be attenuated by movement through these rocks. Results obtained indicate that carbonate precipitation is the most important mechanism in heavy metal uptake by the Bunter Sandstone, although cation exchange on clays and a possible two stage uptake by iron sesquioxides also play significant roles. Precipitation of the metals as carbonates was found to govern heavy metal mobility in Chalk groundwater.

Further experiments to compare heavy metal uptake by both rock types in the absence and presence of the other common constituents of leachate and under varying pH conditions were made. The leachate constituents tested were the alkaline earth metals, ammonium, chloride and short chain carboxylic acids. The results of those experiments showed that the initial solution pH has little importance due to the buffering capacity of the Bunter Sandstone. Neither alkaline earth metals nor chloride had any adverse effects on heavy metal uptake. Metal uptake is decreased in the presence of ammonium ions and by increasing concentrations of the carboxylic acids, with acetic acid having greatest effect.

The conclusions reached imply that heavy metals are unlikely to contribute seriously to groundwater contamination in either the Bunter Sandstone or Chalk provided that an adequate unsaturated zone is left beneath the fill to maintain aerobic conditions.

Key Words: leachates; heavy metals; cation exchange; precipitation; iron sesquioxides.

Acknowledgements

I would like to thank Dr. J.W. Gaskarth of the Department of Geological Sciences and Professor W.R. McWhinnie of the Department of Chemistry for their help and guidance throughout the project. My thanks are also extended to all the academic and technical staff of the Geology Department for their assistance and useful discussion. Much credit is owed to Mrs. Cathy Kennedy for her patience in typing the manuscript.

The co-operation and assistance of Leigh Interests Ltd., of Brownhills, and Stablex Ltd., of West Thurrock, is acknowledged for information on their landfill experiment.

Finally, the Natural Environment Research Council is gratefully acknowledged for the provision of a Training Award to finance this project.

List of Contents

List of Figures

Page

Chapter 1.

Chapter 2.

Chapter 3.

Chapter 4.

Chapter 5.

Chapter 6.

List of Tables

Page

Chapter 1

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 1. Introduction

1.1 Landfill Waste Disposal

Landfill is the oldest and most widely used method for the disposal of solid waste materials. In the broadest and historic senses of the word, landfill implies the depositing of waste on land, usually in a natural depression or worked out quarry, affording some, if only token, concealment from the community. With increased awareness of the need for hygiene, and the recognition of putrifying waste as a potential breeding ground for diseases and pests, it became common practice to cover waste with a layer of topsoil at regular intervals. This practice reduced access to the refuse by pests and went part of the way to containing those organisms associated with disease. It lead to the introduction of the term sanitary landfill. Present-day legislation in the U.K. governing the granting of site licences for operation of landfills (Deposit of Poisonous Wastes Act, 1972; Control of Pollution Act, 1974) requires, in most instances, a daily cover of topsoil, or inert waste material such as ash or builders rubble. This maintains sanitary conditions, prevents wind blown litter and reduces infiltration of rainwater by encouraging runoff.

As a means of waste disposal, landfill offers many advantages over other available methods. It requires no special facilities other than earth moving and compacting machinery and so requires less capital investment than other techniques, such as incineration and pyrolysis. Furthermore, landfill on a large scale does not suffer the limiting factors governed by plant capacity that are met using incineration, pyrolysis or composting (Anon, 1971). Direct landfilling without pre-treatment is less costly (Parker _et al_, 1974) and the bulk of the materials deposited leads to quicker land reclamation. There is a wide variety of waste materials which can safely be disposed of by this method, which includes bulky, inert materials unsuitable for incineration or pulverisation and many types of industrial wastes as well as domestic and other wastes.

In addition to the provision of a valuable means of disposal, landfilling is a suitable method for reclaiming land previously made derelict by mineral extraction. In any highly industrialised and densely populated country, mineral extraction is important to the economy. However, such surface excavations leave large areas of land unsuitable for agricultural or development purposes, either because of the loss of topsoil, or in particular, the extreme topography produced. Open cast coal mining and extraction of some metaliferous and non-metaliferous ores, quarrying of limestone, gravels, sands and some igneous and metamorphic rocks for aggregates all result in land requiring reclamation (Mundy and Gaskarth, 1979). The open cast mining of coal and, in some instances, metaliferous and non-metaliferous ores commonly produces spoil material which may be used in reclamation. Because little or no other material need be imported for the reclamation of these sites they are not considered to be an important category of waste disposal site, although locally they may be valuable. Where limestone or chalk is found in proximity with suitable clays, their extraction for cement manufacture has lead to very large areas requiring reclamation.

The need for aggregates, however, requires no such happy coincidence of rock types and the prime conditions are low extraction cost and proximity to the market. This has lead to the utilisation of local materials throughout the country, leaving quarries requiring reclamation close at hand to the aggregate users. The main markets are invariably centres of population, and these in turn are major waste producers.

Landfills as Sources of Pollution

After deposition and compaction, many wastes undergo some degradation. The moisture content of wastes such as animal and vegetable matter may be sufficiently high for decay. Movement of the breakdown products and of soluble constituents of the waste will not occur, however, until the field capacity has been exceeded (Langmuir, 1972), at which point a leachate will be produced. Achievement of field capacity depends on several factors, including infiltration by groundwater and precipitation, run-off and evapo-transpiration of surface waters. The latter parameters may lead to a seasonal variation in quality and quantity of leachate (Fungaroli, 1971; Rovers and Farquahar, 1973). Increased precipitation and decreased evapo-transpiration during winter leads to the removal of larger quantities of leachate, although its concentration will be lower. The Ministry of Housing and Local Government substantiated this (Anon, 1961) with experiments in which landfills above and below the water table were simulated. This work showed that larger volumes of polluting material was leached from the saturated fills than the unsaturated ones.

A time dependant change of leachate characteristics was also reported (Hughes and Cartwright, 1972) whilst other authors reported a change in temperature within the landfill with time (Golwer and Matthess, 1968; Fungaroli, 1971; D.O.E., 1978). Variations in temperature, with initial values reaching as high as 70°C (Stiff and Young, 1976) dropping over a period of months, and an increase in the mobility of pollutants following saturation are both related to the oxygen concentration of the waste. Initially within a landfill, near the tipping face, the oxygen content is similar to that of the atmosphere, around 21% by volume. Under these conditions, rapid aerobic decomposition occurs, leading to the production of simpler organic molecules from carbohydrates, carbon dioxide gas, water, nitrates, sulphates and phosphates, with most metals being precipitated as their oxides. Anaerobic conditions follow due to the depletion of the available oxygen by aerobic decomposition, by reduction of access to atmospheric oxygen because of covering with successive layers of waste and topsoil and by saturation with oxygen poor groundwater. Anaerobic decomposition, which is slower than aerobic activity, leading to a more long term pollution effect, utilises oxygen from the nitrates, sulphates and phosphates. The end products are larger quantities of gas than in aerobic conditions, including carbon dioxide, methane, hydrogen, hydrogen sulphide and ammonia, with intermediates such as short chain carboxylic acids (D.O.E., 1978; Robinson and Maris, 1979). These anaerobic conditions lead to a decrease in pH which in turn produces an increase in the solubility of most metal species. Anaerobic pathogens present in this leachate represent a biological threat to water quality.

The overall composition of a leachate depends on many factors, including waste composition, landfill environment and age and a summary of some reported leachate compositions are shown in Table 1.1.

Table 1.1. Reported range of concentrations of leachate parameters.

	Robinson & Maris (1979)[1]	Clark & Piskin (1977)[2]
pH	6.2 - 7.6	1.5 - 9.5
B.O.D.	2 - 8000	87 - 6200
C.O.D.	66 - 11600	63 - 70740
Carbohydrate	0.9 - 85	N.D.
Short-chain carboxylic acids		
Total	2 - 3672	N.D.
Acetic	1.0 - 1321	N.D.
iso butyric	0.0 - 152	N.D.
n butyric	0.0 - 562	N.D.
iso hexanoic	0.0 - 9.4	N.D.
n hexanoic	0.0 - 197	N.D.
propionic	0.0 - 1371	N.D.
iso valeric	0.0 - 144	N.D.
n valeric	0.0 - 302	N.D.
Phenols	N.D.	0.17 - 6.6
Organic N	0.0 - 155	N.D.
NH_3 - N	5 - 730	1.8 - 1250
NO_3 - N	0.5 - 85	0.0 - 1.8
NO_2 - N	0.02 - 1.84	N.D.
PO_4	0.02 - 4.43	0.0 - 52

Table 1.1 (Continued).

Cl^-	70 - 2777	31 - 4350
SO_4^{2-}	55 - 456	0.0 - 84000
CN^-	N.D.	0.0 - 0.8
Ca	130 - 1150	23 - 3050
K	20 - 650	2 - 1920
Mg	12 - 480	12 - 1102
Na	43 - 2500	15 - 8000
Fe	0.09 - 380	0.9 - 42000
Mn	0.19 - 26.5	0.0 - 678
Cd	0.03 - 0.13	0.0 - 1.16
Cr	0.005 - 0.14	0.0 - 22.5
Cu	0.009 - 0.15	0.0 - 1100
Ni	0.02 - 0.16	0.0 - 1.7
Pb	0.003 - 0.15	0.0 - 6.6
Zn	0.02 - 0.95	0.0 - 250

N.D. = not determined

1 analyses from domestic refuse sites only

2 analyses include industrial landfill leachates

All units µg/ml except pH

1.2 Attenuation Mechanisms

The identification of pollutants below and short distances from landfills at concentrations below that predicted or found in leachates has drawn attention to the mechanisms by which they may be attenuated. The term "attenuate" strictly means to lessen, or make thin, but for the purpose of this review "attenuation mechanism" will be taken as any process which reduces the concentration of a potential pollutant migrating through, or away from, a landfill site.

Fuller and Korte (1976) reviewed factors within soils affecting trace element mobilities and ranked attenuation mechanisms in order of importance. They grouped mechanisms together as being either considered important, unimportant or as having had little or no research into their importance. This last group contains several of those mechanisms defined in the previous two groups, which may be taken to suggest that their inclusion in those groups is uncertain. A more satisfactory summary which treats factors affecting the mobility of leachate constituents in a systematic way is given by Langmuir (1972) and subsequently by Mather (1977). This classification will be followed in this review, and is summarised here in Table 1.2.

Physical Processes

Dilution, the mixing of a leachate with volumes of relatively uncontaminated water, and dispersion, the distributing of fractions of a concentrated leachate throughout the medium into which it is introduced, will not play an important role in landfills below field capacity. In unsaturated zones, flow is vertically downwards, with little horizontal spreading. Vertical dispersion may be increased by the different rates of travel between pollutants and water (Bresler, 1973). Where permeable materials are saturated, greater dispersion

Table 1.2. Summary of factors affecting the mobility and concentration of leachate constituents (After Langmuir, 1972).

Physical Processes:-

- Dilution
- Dispersion
- Filtration
- Gas Movement

Biochemical Processes:-

- Decay
- Cell Synthesis

Chemical Processes:-

- Complexation and Ionic Strength
- Acid/Base Reactions
- Oxidation/Reduction
- Precipitation/Solution
- Adsorption/Desorption

will occur (Langmuir, 1972), with accelerated dispersion occurring at heterogeneity boundaries. This was shown by Skibitzke and Robinson (1963), using dyes to show the refraction of flow lines at the boundary between materials of contrasting permeability.

The physical characteristics of leachates, in particular density and miscibility, play a governing part in dispersion within the saturated zone (Theis, 1954; Brereton and Wilkinson, 1976). Completely miscible leachates with density and viscosity properties similar to the groundwater, will be diluted and dispersed both vertically and transversely, to an extent dependant upon the hydrological conditions. Where a leachate is miscible, but has a different density or viscosity, dilution by mixing will be less, and will depend on the occurrence of some vertical movement to mix the two fractions together. Where a pollutant is immiscible, such as an oil, it may float on top of the groundwater and its movement away from the site will not follow that of dissolved pollutants because of this.

Permeability of igneous and metamorphic rocks is secondary in that it is controlled by jointing and fissures. Fissure flow can also be important in sedimentary rocks. Flow within fissures speeds the movement of leachates to the water table and increases the velocity of movement away from the site. With increasing depth, however, both porosity and permeability decreases because the fissuring is less open (Davis, 1969). Monkhouse and Fleet (1975) concluded, from investigations of saline intrusions in the Chalk, that upper highly permeable horizons give way to horizons with low permeability due to fissuring at depth (between 100m and 140m). Edmunds et al (1973) showed that there is a difference in chemistry between interstitial water and fissure water in the Chalk. Edmunds (1976) suggested that diffusion between the two would lead to a reduction in concentration of pollutants migrating from a landfill with the movement of solutes from the higher concentration fissure water to the lower concentration interstitial water. Conversely, after the concentration of leachate produced had declined because of ageing and stabilisation of the landfill, the fissure water would have a lower concentration of solutes than the now polluted interstitial water, leading to a reversal of the concentration gradient and release of pollutants. Thus this mechanism acts only as a temporary fixing process although aiding in attenuation by dilution.

Fissured formations, with fissure width greatly in excess of the suspended particle diameter, will have little ability to filter out particles such as micro-organisms and clay sized metal oxide colloids. In non-fissured formations, interstitial filtration is most effective through fine-grained materials such as medium and fine-grained sands. Very fine-grained (clay size) materials have permeabilities which are too low to allow sufficient volumes of water to pass through for them to act as effective filters. The effectiveness of soils beneath a landfill as a filtering medium has been described by Apgar and Langmuir (1971). Hagerty and Pavoni (1973) gave a quantitative equation, although without its deravation, for filtration capacity (Fc) in terms of particle size:-

$$Fc = 10.0/\log (2.54\varnothing)$$

where the average particle diameter ($\varnothing$) is given in centimetres. Edmunds (1976) summarised, by use of a diagram, the principle size fractions of some mobile particles in relation to pore diameters in rocks of the major aquifers (Figure 1.1).

Biochemical Processes

Biochemical reactions are controlled by the composition of the waste and its temperature, water content and aeration. Micro-organisms decompose organic matter, relying on it as a source of carbon, consequently only wastes with an organic content will be

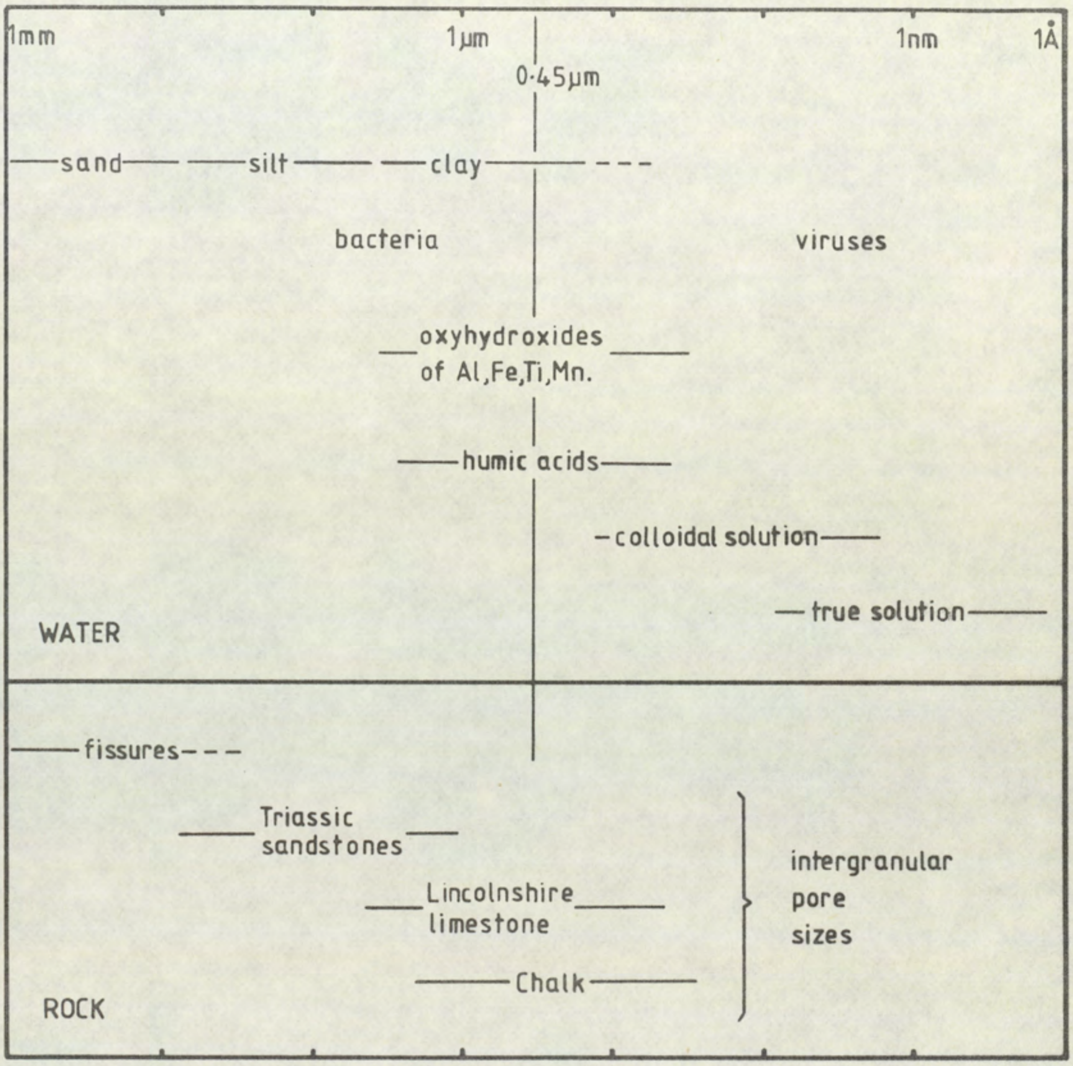


Figure 1.1. Principle size fractions of suspended particles in relation to pore diameters of the major aquifers. (From Edmunds 1976).

subject to biochemical degradation. Similarly water is required in biochemical reactions, and a temperature suitable for cell synthesis must be maintained. According to Langmuir (1972), little degradation will occur at temperatures below -6°C, the waste being mummified and no leachate produced with a moisture content below field capacity. Equally important, oxygen is required for biological metabolism to continue. For aerobic decomposition this oxygen comes from the atmosphere, and gas exchange between it and the gas content of the fill must occur or the oxygen content in the fill will become exhausted. Gas exchange with the atmosphere depends on the state of compaction, produced by site plant operations and natural settlement, associated with the depth of refuse and daily cover subsequently deposited. Under aerobic conditions, organic wastes are biochemically oxidised, leading to the formation of nitrates, sulphates and phosphates with the liberation of water and carbon dioxide from respiration. Acetates are formed as intermediates in these reactions (Stiff and Young, 1976).

In addition to the chemical products generated, energy is liberated in the form of heat. In studies of landfill sites, Golwer and Matthess (1968) and the Harwell/IGS research group (D.O.E., 1978) recorded temperatures in groundwater below sites of up to 25°C. This is some 15°C above ambient temperatures for Germany and the U.K. where the observations were made. In controlled experiments using a lysimeter, the same investigations (D.O.E. op.cit.) recorded temperatures of 18°C in unsaturated Greensand irrigated with a synthetic leachate. Rovers and Farquahar (1973), in Canada, reported temperatures within fill of 30°C, well above daily air temperatures. Although seasonal fluctuations were recorded, a peak temperature was determined shortly after emplacement, when aerobic conditions prevailed. Stiff and Young (op.cit.) stated that temperatures within a landfill can rise up to 60-70°C, while Golwer and Matthess (op.cit.) suggested they may reach 80°C.

When the oxygen is depleted by aerobic decomposition in the absence of significant gas exchange, anaerobic mechanisms take over. This leads to a zoning effect within and away from the landfill site. An outer oxidising zone is formed which may have anaerobic pockets within it (Rovers and Farquahar op.cit.) and this is followed by an anaerobic zone which extends from the centre of the fill to some distance below it. The extent of the anaerobic zone depends on the conditions prevailing below the site, but it is restricted to an area downgradient of the landfill. Golwer and Matthess (op.cit.) suggested that where groundwater flow was less than 1m/day, this anaerobic or reducing zone would be in the order of tens of metres wide and that it would decrease with increasing groundwater velocity. With increasing oxygen carried in the groundwater anaerobic conditions give way to a transition zone and finally to an aerobic, oxidising zone (Matthess, 1972).

Tittlebaum <u>et</u> <u>al</u> (1975) described anaerobic decay as occurring in two phases, beginning with the large organic molecules such as the carbohydrates, through intermediate short chain volatile fatty acids, produced by acid fermentation, to the ultimate gaseous products such as carbon dioxide and methane. Golwer <u>et</u> <u>al</u> (1970) characterised a similar reaction in the equation:-

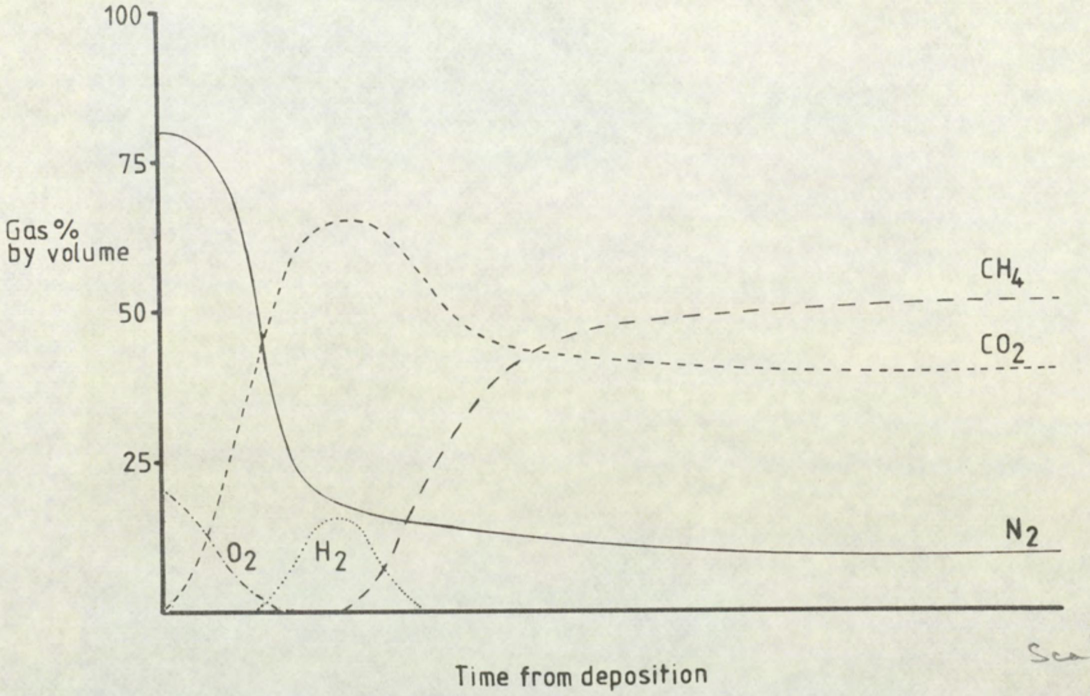
1.

$$2CH_2CHOH\ COOH + H_2SO_4 \rightarrow 2CH_3COOH + 2CO_2 + H_2S + 2H_2O$$

In this reaction, sulphate, a product of aerobic decomposition, is used as a source of oxygen, giving rise to elemental sulphur or hydrogen sulphide. Equally well nitrates may be reduced to liberate the oxygen with production of associated gaseous nitrogen or ammonia. Ammonia is highly soluble in water and presents a serious threat to water potability. Elemental sulphur is taken up by some bacterial species, while hydrogen sulphide may react with metal ions to form metal sulphides in the reducing zone. The second stage of anaerobic decomposition, the breakdown of fatty acids, occurs at a slow rate, accounting for their persistence in leachates (Stiff and Young op.cit.).

The transition from aerobic to anaerobic conditions is identified by the differing proportions of gases in the pore spaces in the fill. In Canada, Rovers and Farquahar (op.cit.), using cylindrical cells filled with domestic refuse, noted the continued presence of oxygen for up to 47 days from the start of the experiment where the cell had its surface open to the atmosphere. During the initial period, however, some methane was detected, suggesting the existence of pockets of anaerobic activity. Carbon dioxide present in the cell increased to 40% of the total gas volume at 350 days, with nitrogen falling from the normal atmospheric level (79%) to 50% over the same period. The proportion of methane in the pore gases dropped sharply during the spring thaw, when infiltration was high, with subsequent oxygen replenishment thus favouring aerobic decomposition. In another open cell, under natural precipitation conditions, but started during spring to avoid heavy rainfall infiltration, oxygen was depleted rapidly. Carbon dioxide rose until it reached a steady state at 70% of the total gas volume with nitrogen comprising the remainder and a complete lack of methane. In a cell closed to the atmosphere and artificially irrigated, oxygen depletion was complete in 9 days, with carbon dioxide reaching 90% by the 38th day. By the end of the study period, nitrogen had dropped to 10% and methane 2%. Figure 1.2 shows the relative proportions of gases and their production with time as shown by Hoeks (1976).

Elements are incorporated into the cell structure of micro-organisms during cell synthesis. Carbon, nitrogen, oxygen and hydrogen, along with phosphate, sulphate and potassium, are constituents of cellular material, and although water makes up the majority of its



Scale ?

Figure 1.2. Gas evolution from a domestic landfill. (From Hoeks 1976).

weight, the biomass may account for significant quantities of these elements. Trace quantities of other elements such as metals are also taken up, although they may not represent a significant removal from the leachate. Uptake by cell synthesis, however, will not represent a permanent removal from the system because the dead organisms release their constituents on decomposition, but at any one time it may play a significant part in stabilising potential pollutants. Bacterial slimes may aid in attenuation by physically reducing permeability and hence increasing filtration capacity; also chemically by providing adsorption sites.

Chemical Processes

Complexation and ion-pair formation lead to an increased mobility of multivalent ions such as metals, which would otherwise be restricted by processes such as oxidation, precipitation or adsorption (Langmuir, 1972). Ionic solution strength has a direct effect on equilibrium in that increases in ionic strength produce decreases in the activity coefficient, relating observed concentrations with the thermodynamic activities. The decrease in activity coefficient means equilibrium requires greater ionic concentrations (Edmunds, 1976). Calcium carbonate precipitates from a solution of calcium bicarbonate at 80 µg/ml Ca under conditions of pH 7 and a temperature of 25°C. Under the same conditions, but in the presence of 500 µg/ml sulphate, calcium carbonate will not precipitate until the calcium concentration reaches 160 µg/ml because a calcium sulphate ion-pair is formed (Langmuir, 1972). Stiff and Young (1976) gave the hydrous iron complex system Fe^{3+}, $FeOH^{2+}$ $Fe(OH)^{2+}$, $Fe(OH)_3$ as an example of solubility affected by hydroxyl complex formation. The solubility of iron (iii) is increased by increasing the concentrations of $FeOH^{2+}$ and $Fe(OH)_2{}^+$ from 5.6×10^{-14} µg/ml to

5.6 x 10^{-10} µg/ml at pH 7.

In the presence of organic acids, organo-metallic complexes have been demonstrated to increase metal mobility. For example, Leenheer et al (1976) showed in laboratory experiments that phthalic acid forms a soluble complex with iron(ii). In column experiments, Boreham et al (1975) found metal ions to be more mobile in the presence of short chain carboxylic acids.

Acid-base reactions contribute to the control of pollutant movement. At high pH, the mobility of many species decreases as precipitation occurs. With decreasing pH, there is a corresponding increase in solubility. In natural groundwaters, the carbon dioxide-carbonate system maintains the pH between 6.0 and 8.5 (Edmunds, op. cit.). Within and below landfills, biochemical reactions lead to a decrease in pH with the production of carbonic acids and organic acids, whereas with anaerobic reduction of nitrates and sulphates, an increase in pH occurs. Because common rock forming minerals are composed of salts of stronger bases than acids, acid wastes are most efficiently neutralised, while alkaline wastes are less likely to be neutralised and so more likely to create a pollution problem. Carbonate rocks have a greater neutralising capacity than the silicate rocks (Langmuir, op.cit.), and it has been suggested that concrete waste placed in the base of landfills would be advantageous in increasing pH and thus precipitation rates (Apgar and Langmuir, 1971).

Redox reactions in groundwater are largely controlled by the abundance of oxygen, which in turn is determined by the rate with which it is introduced into and taken out of the system. In unsaturated conditions, or shallow groundwater, oxygen is relatively abundant, with a positive Eh. Within a landfill, saturated conditions isolate the waste from the atmosphere, preventing oxygen replacement. Aerobic decomposition also leads to a decrease in oxygen until anaerobic conditions take over. Anaerobic conditions with negative Eh conditions persist until the leachate moves into an unsaturated aerobic aquifer, or reduced groundwater is mixed with aerated water.

Redox reactions will occur where electron transfer is possible (Edmunds, op.cit.). In natural waters, and leachates, the most important ionic species involved are of iron and related transition metals (Apgar and Langmuir, op.cit.; Langmuir, op.cit.; Edmunds, op.cit.). Under oxidising conditions, dissolved iron is commonly below 0.5 µg/ml, with most of the iron occurring as solid oxyhydroxides. Anaerobic bacteria lead to a partial reduction of oxyhydroxides, and as the Eh becomes less positive, this is reflected in the equilibrium between remaining solid oxyhydroxides and Fe^{2+}, which is increasingly soluble with negative Eh values. The reversible reaction is given as:-

$$Fe(OH)_3 + 3H^+ + e^- \leftrightharpoons Fe^{2+} + 3H_2O$$

The theoretical boundaries between the two phases have been shown in relation to Eh and pH values by Apgar and Langmuir (op.cit.) (Figure 1.3).

Although under anaerobic, negative Eh conditions, iron is expected to be more mobile, on reaching aerobic conditions it is again precipitated as oxyhydroxides. An oxyhydroxide slime was reported (D.O.E., 1978) in a drainage channel below the entry of an anaerobic leachate. Co-precipitation with oxyhydroxides is considered by many authors to be effective in the removal of some cation and anion species from leachate, among them the heavy metals, fluorides and phosphates (Matthess, 1972; D.O.E., op.cit.; Mather and Parker, 1978). In an acid leachate from a studied site, the I.G.S./Harwell Hazardous Wastes Studies Group (D.O.E., op.cit.) observed the precipitation of the complex hydrated iron and potassium sulphate, jarosite, $K\,Fe_3(SO_4)_2(OH)$, which adsorbed manganese, tin, chromium and nickel. An earlier report was cited by Mather and Bromley (1976), stating that jarosite from below a

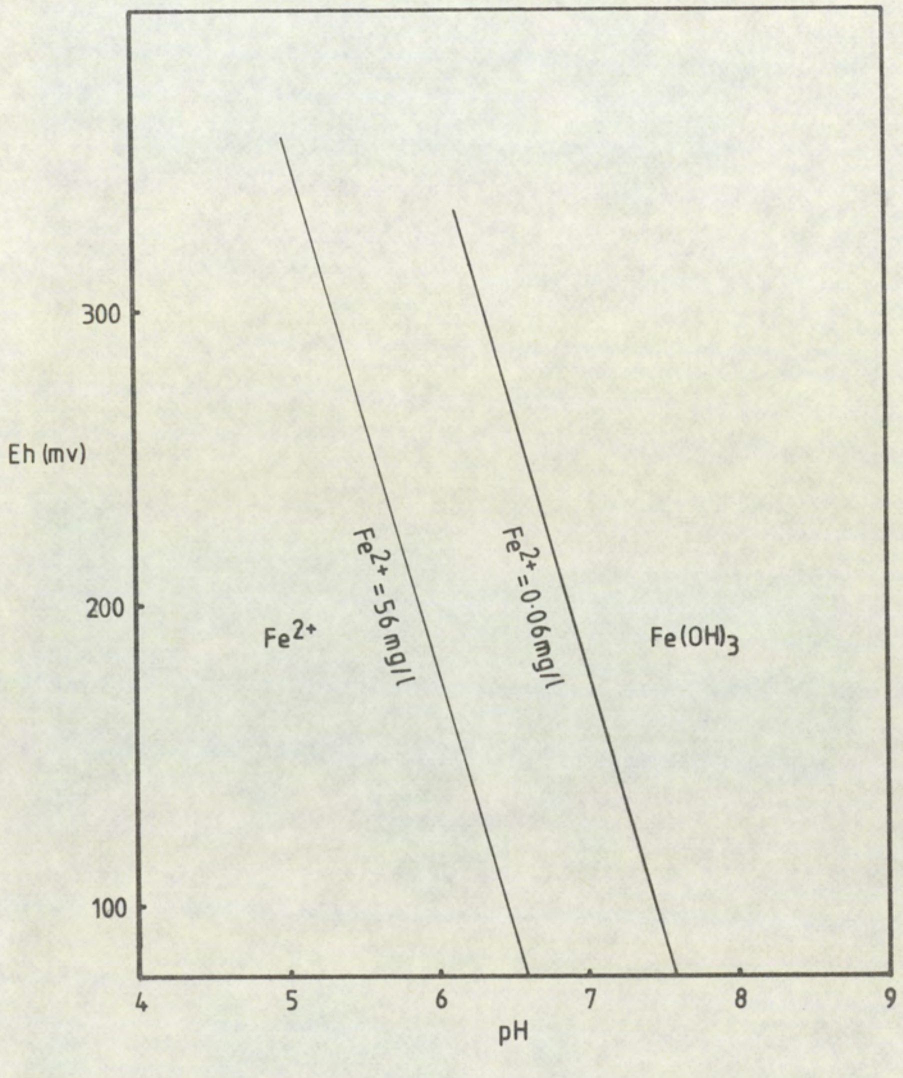


Figure 1.3. Eh-pH diagram showing equilibrium boundaries between Fe^{2+} and Fe(OH)$_3$ at 25°C for Fe^{2+} concentrations of 0.06 mg/l and 56 mg/l. (From Apgar and Langmuir, 1971).

site contained 6%. of metal impurities. Jarosite is, however, unstable at pH values greater than 4 and so its formation is likely to be of importance only in sites where acid wastes are tipped and where the substrate is predominantly silicate and hence unlikely to neutralise the leachate. Above pH 4, sulphate is released, and iron hydroxides precipitated (D.O.E., op.cit.). Heavy metals released from the jarosite in this way may either be co-precipitated or adsorbed with the hydroxides formed as the pH rises.

Beneath a site receiving industrial waste overlying chalk, Mather and Parker (op.cit.) found fissure surfaces with a thin coating of a dark deposit, with adjacent areas of lighter material. Emission spectrography showed the dark material to be rich in iron, nickel, barium, lead and manganese. X-ray diffraction was unsuccessful in identifying the material and the authors concluded that is was likely to be an amorphous mixed iron/manganese hydrated oxide, with the lighter areas containing more calcium.

The pH dependence of precipitation reactions is illustrated by Stiff and Young (1976) for metal sulphide formation. This is likely to occur in the reducing zone where sulphide is formed as a result of anaerobic reduction of sulphates. For lead sulphide formation,

$$Pb^{2+} + S^{2-} \leftrightharpoons PbS,$$

the solubility product is given in terms of $\left[Pb^{2+}\right] \left[S^{2+}\right]$ (the brackets indicating concentration). However, the proportions of H_2S and HS^- are both pH dependant and thus affect $\left[S^{2-}\right]$. The calculated solubility of lead in the presence of lead sulphide and with a sulphide concentration of 0.03 µg/ml changes over the pH range 6 - 8 from 2×10^{-8} µg/ml to 2×10^{-11} µg/ml. Griffin and Shrimp (1976a), using sand column experiments, found an increase in uptake of metals from solutions with initiation of insoluble hydroxide and carbonate precipitation at pH values between 5.5 and 7.5, depending on the element and its concentration.

Ion exchange refers to the process of substitution between solutions and surface ions in a stoichiometric exchange. For any material to enter exchange reactions there needs to be a charge imbalence (Edmunds, 1976). The most common minerals showing cation exchange are the clays, where the network of silica tetrahedra require a positive charge to impart neutrality (Adamson, 1976). The suppliers of this charge most commonly associated with the clays, in their order of abundance, are calcium, magnesium, hydrogen, potassium, ammonium and sodium (Grim, 1962). Other minerals, including impure carbonates and colloidal iron hydroxides, both with poorly ordered crystal structures, are known to have ion exchange properties (Edmunds, op.cit.).

The kinetic considerations of ion exchange are somewhat complicated, but have been regarded in terms of a parallel plate capacitor, the Gouy-Chapman model, with the Stern modification employing a layer of water molecules between the cations and a solid surface (Adamson, op.cit.; Ross, 1978). The Stern modification allows for the selectivity shown by some ions of equal valency by taking into account ionic radii. In mineralogical and chemical terms, ion exchange has been explained by the existence of several sites within and around the clay lattice (Grim, op.cit.). Firstly there are sites on the edges of silicon-aluminium tetrahedra having broken bonds giving rise to a charge imbalence. Secondly, substitutions may be made within the lattice itself, with divalent ions such as magnesium replacing trivalent aluminium, thus giving rise to a charge imbalence. The third method, which Grim casts some doubt upon, involves the replacement of the hydrogen groups on the edge tetrahedral sites. All these give rise to a stoichiometric exchange effect, but there is considerable evidence to suggest that all cation uptake by clays does not follow this pattern. A review of the evidence for this is given later (Section 1.3).

The co-precipitation of heavy metals with iron oxyhydroxides has already been discussed, and Nalovic et al (1976) showed that transition elements take up isomorphous positions in them. Earlier work by Subramanian (1973) largely supports this, but he gave evidence for a solid solution or occlusion effect after the hydroxide formation. The ability of natural oxyhydroxides of iron and manganese within soils and rocks to adsorb metals from aqueous solutions was discussed by Jenne (1968), who suggested that the oxyhydroxides act as a "sink". The mechanism of retention is, however, not clear. Gadde and Laitinen (1973), working on synthetic oxyhydroxides, suggested a mechanism whereby hydrogen ions are released in exchange for lead; however, their experimental ratio of moles of hydrogen per mole of lead taken up were less than one at all the pH values investigated. This is in agreement with Subramanian (op.cit.) who stated that manganese and iron hydroxides do not follow physical adsorption laws.

Some authors imply that oxyhydroxide coatings may prevent cation exchange reactions (Jenne, op.cit.; Suarez, 1976). Subramanian (op.cit.) suggested that provided the oxyhydroxides are stable, which they are likely to be with high transition metal content (Nalovic et al, op.cit.), they may act as an inert permeable membrane. It thus appears that the location of natural oxyhydroxides within rocks will have little effect on their adsorption capabilities. Suarez (op.cit.) suggested these oxyhydroxides are carried on the clay fraction whilst Gadde and Laitinen (op.cit.) reported them mainly on quartz grains. In a permeable sandstone, they are likely to cover all grains, and their importance in metal uptake means that the clay fraction, with greater surface area, will be of greatest importance.

The capacity for metal uptake by natural oxyhydroxide coatings for a given rock volume has a fixed value. However, even after this value has been reached, adsorption will continue to be important within a landfill because of constant addition by precipitation.

Langmuir (1972), considered that adsorption and cation exchange have been overrated in importance in leachate attenuation. Both adsorption and cation exchange have stimulated a good deal of research in the past, and because much of this work shows that heavy metal uptake may be due substantially to these mechanisms it is necessary to review this work.

1.3 Previous Work

Cation Exchange Mechanisms in Clays

The fact that different cations do not show the same exchange capacities on specific clays indicates that their uptake does not in all cases follow the stoichiometric effect expected for pure ion exchange. This suggests that either not all exchange sites are available to different cations or that there is more than one type of site selectively available to different cations. Similar conclusions can be drawn from the reversal of selectivity coefficients for calcium(ii) vs copper(ii) with pH and relative ionic concentration changes reported by Kishk and Hassan (1973) and from reversals with temperature changes (Singhal and Kumar, 1977). Maes and Cremers (1975) concluded that at least two different sites exist for montmorillonite, one of which does not follow simple ion exchange theory. They found that zinc could be totally displaced from montmorillonite by 1M $CaCl_2$ at pH 4 provided the clay was not treated with sufficient quantities of the metal to saturate sites proven by cation exchange capacities. At zinc values near saturation, a significant proportion of zinc was not displaced from the clay with subsequent treatment with 1M $CaCl_2$, unless the pH value was lowered. Holdridge (1969), investigating competition between cations for clay exchange sites, explained the low replacement of magnesium(ii) by manganese(ii) as an ionic size difference. However, he was forced to assume that the low replacement of calcium(ii) by iron(ii), with similar ionic radii, indicated some reaction other than pure ion exchange. Carter (1975) was forced to a similar conclusion after finding that cations given out did not balance with those taken up; however, she measured only the potassium and sodium given out and did not take any account of calcium despite working with a calcium-rich montmorillonite.

Hodgson (1960), working with montmorillonite, demonstrated that in addition to simple base exchange reactions, other specific reactions must occur. He ascribed one of these to the formation of chemical bonds on the edge of the crystal lattice. He discounted simple electrostatic attraction between the cations and negative OH^- and O^{2-} groups because no interference with cobalt uptake was determined when calcium was introduced into the system. He did, however, find this reaction to be reversible with other cations, and produced a displacement series, ranking cations on their ability to displace radio-active cobalt from montmorillonite. Steger (1973) assigned lattice hydroxyl groups at edge sites and crystal defects as the prime adsorption site for copper(ii) on bentonite. Swartzen-Allen et al (1973) and Farragh et al (1980) described the formation of $Al\text{-}OH_2^+$ groups by breaking of Al-O-Al linkages at crystal edges, giving rise to charged groups such as $Al\text{-}O^-$ and Al^+. Upon proton adsorption these give rise to $Al\text{-}OH_2^+$. The same authors implied that these sites are important on illite and are the prime site on kaolinite. They conflict with Steger (op.cit.), however, in that they state that these sites should be least effective on montmorillonite where they say the bulk of the exchange capacity is due to isomorphous substitution in the central aluminium octahedral layer. Harman and Fraulini (1940) observed a sharp increase in base saturation levels upon grinding kaolinite, and assigned this to the increase in number of O^{2-} and OH^- groups thus created.

Some uptake of metals by clay minerals appears to be by a non-exchange reaction. Hodgson (op.cit.) found a non-reversible uptake of cobalt(ii) on montmorillonite which took place at a slower rate than reversable reactions, but which continued after the equilibrium time for exchange reactions. Since neither subsequent treatment with stronger solutions of known competitive cations, nor leaching with 2.5% acetic acid would remove any of the cobalt taken up in this way, he concluded it had entered into the crystal lattice. McBride and Mortland (1974) found that whilst copper(ii) remained in a hydrated state, it remained on montmorillonite interlamellar surfaces, presumably at OH^- or O^{2-} sites. Upon heating until sufficient energy was provided to remove ligand H_2O, however, the copper ceased to be exchangeable and he concluded, like Hodgson (op.cit.), that penetration into the octahedral lattice must occur. Whilst McBride and Mortland (op.cit.) suggested this mechanism to be of little or no importance in soils (these conditions are only likely to prevail at depth), Reddy and Perkins (1974) found that metal ions could be bound irreversably by subjecting the clays to a wetting/drying sequence. This occurred equally well for non-expanding clays such as kaolinite and illite as for montmorillonite, and they too offered the inclusion into the lattice as an explanation.

Attenuation by Clay Materials

Prior to the introduction of legislation in both the U.K. and U.S.A. in the early 1970's, most work on clay/waste interreactions was concerned with radio-active wastes. Swartzen-Allen et al (1973) reviewed work concerning the relative uptake of metal cations by clays, and showed how different authors had reached conflicting orders of uptake. In the mid 1970's, no doubt reflecting the recognition of the pollution potential of landfills and as a result of legislation, material was published following research on clay/cation reactions with respect to landfill waste disposal.

Carter (1975) looked at montmorillonite and kaolinite reactions with industrial wastes, and found montmorillonite had a greater attenuating ability than kaolinite. The Environmental Geology

Laboratory at the Illinois State Geological Survey published results of their work in a series of papers on the reactions of montmorillonite, kaolinite and illite with landfill leachate (Griffin and Shrimp, 1976a; Griffin, Shrimp, Steel et al, 1976; Griffin, Cartwright et al, 1976). They showed that the order of attenuating ability of the clays was montmorillonite > illite > kaolinite, thus agreeing with Carter's findings (op.cit.). The ratios of qualitative uptake for the three clays was montmorillonite four times that of kaolinite, which corresponded closely to their measured cation exchange capacities (c.e.c.) and so it was concluded that attenuation was a function of the c.e.c. for each clay. The surface areas of the clays did not hold a similar relationship with uptake, excluding any other surface reaction.

Of the leachate parameters measured, the relative attenuation of each is given in Table 1.3 and from this they placed the elements into groups depending on their relative uptake. Lead, zinc, cadmium and mercury showed high attenuation; iron, potassium, magnesium, ammonia and silicon showed moderate attenuation; C.O.D., sodium and chloride had a low attenuation, while boron, manganese, and calcium were given out, or eluted, giving rise to concentrations greater than those put in. As can be seen from Table 1.3, for montmorillonite significantly more calcium was given out than from kaolinite or illite, and that significantly more potassium, magnesium, ammonia and slightly more sodium were taken up. This was taken as an indication of an exchange reaction between these ions and calcium and was confirmed when a mass balence between potassium, magnesium, sodium and ammonia uptake agreed closely with the amount of calcium given out. The fact that all the cation exchange could be accounted for by these species and that there was no significant difference between those metals which were highly attenuated for each clay, despite widely differing exchange

Table 1.3. Relative attenuation of leachate constituents by clays (From Griffin, Shrimp *et al.* 1976).

Leachate Parameter	Montmorillonite	Illite	Kaolinite	Ave
Pb	99.6	100.0	99.9	99.8
Zn	97.7	98.6	98.1	97.2
Cd	96.7	100.0	97.5	97.0
Hg	98.4	98.1	95.2	96.8
Fe	34.8	82.8	67.6	58.1
Si	39.2	81.6	71.2	54.7
K	58.9	31.0	23.2	38.2
NH_4	54.8	31.0	25.1	37.1
Mg	48.2	19.7	18.1	29.3
C.O.D.	24.6	23.2	16.2	21.3
Na	20.6	16.4	9.7	15.4
Cl	9.3	13.5	14.3	10.7
B	-16.1	-12.8	-11.5	-11.8
Mn	-73.2	-6.4	-266.2	-95.4
Ca	-885.5	233.2	-190.2	-656.7

Figures are relative attenuation numbers, expressed as a percentage.

capacities, and that they all had attenuation numbers close to 100 (complete removal), lead the authors to believe that precipitation rather than cation exchange was responsible. They went on to confirm this by conducting control experiments, passing the leachate through columns of pure sand, with no clay and hence no cation exchange capacity. These experiments showed that all the lead and significant quantities of cadmium, mercury and zinc were precipitated, presumably as carbonates, in the columns.

Unlike potassium, magnesium and ammonia, no linear regression of attenuation with cation exchange capacity or column clay percentage was found for boron, cadmium, C.O.D. iron,manganese or silicon. The observed elution of boron, the authors concluded, was due to its removal from the borosilicate glass used in the column construction and manganese release was due to the chemical reduction of manganese coatings on the clays to more soluble species. The larger quantities of manganese removed from kaolinite were not due to greater total content within the clay lattice, but correspond closely with surface manganese which is three times more abundant on kaolinite than montmorillonite. Iron, in the initial stages of the experiment, reacted in a similar manner to manganese, although over the duration of the experiment (six to ten months for each column) iron was actively attenuated (Table 1.3). The authors' conclusions were that iron was eluted by reduction from clay surfaces if conditions were anaerobic, but was precipitated in mildly anaerobic and aerobic conditions.

In a further series of experiments, Griffin and Shrimp (1976a) and Griffin _et al_ (1977), compared heavy metal uptake by clays from simple aqueous solutions with that from inorganic salt solutions similar in concentration to a leachate and with that from an actual landfill leachate. From the simple solutions at pH values less than 6, where precipitation is unlikely, they found that maximum uptake of lead from

$Pb(NO_3)_2$ on both kaolinite and montmorillonite reached values agreeing closely with the measured cation exchange capacities of the clays. In the presence of 0.1M NaCl, a reduction in lead uptake occurred, indicating either competition for exchange sites between the two cations or, more likely, Pb-Cl complex formation. When an actual leachate was used, the greater ionic strength and variety of competing ions was reflected in a decrease in uptake of between 70% and 80% (Griffin and Shrimp, 1976a). Furthermore, whereas from the simple $Pb(NO_3)_2$ solution five times more lead was taken up by montmorillonite than by kaolinite (reflecting c.e.c. differences), for an actual leachate, Griffin et al (1977) showed that montmorillonite took up less than twice as much lead as kaolinite, suggesting that not only does competition occur, but that competition for sites is specific for a given cation on different clays. This explanation does, however, take no account of anion influence. Complexation by NO_3^- will be weak, whereas the anion content of the real leachate, including Cl^-, will be more likely to complex with the metals.

Lagerwerf and Brower (1972 and 1973), studied the exchange and precipitation of cadmium and lead in clay soils treated with aluminium, calcium and sodium chlorides in order to study the competition between the cations. Cadmium uptake was greater in calcium treated soils than aluminium treated soils, with least uptake on sodium treated soils. This latter effect was thought to be the result of competition from other soil constituents following alkaline corrosion in the presence of NaCl. Lead was favourably taken up in the presence of calcium in soils, thus agreeing with Bittel and Miller's work (1974) on pure clays, but calcium was taken up in favour of cadmium, particularly with higher concentrations of calcium. Bittel and Miller (op.cit.) found cadmium and calcium to compete on an equal basis and they suggested that Lagerwerff and Browers (op.cit.) results were due to the low levels of cadmium, with regards to base saturation, used in their experiments. Confirmation that Bittel and Miller's (op.cit.) results followed an exchange reaction was made when they determined the selectivity coefficient for cadmium versus lead. Since calcium and cadmium competed equally, yet lead competed in favour of calcium, it was both expected, and found, that the Pb/Cd selectivity coefficient was similar in its favour towards lead as was Pb/Ca.

Carter (1975), using high concentrations of metals (up to 8000 µg/ml) simulating industrial effluent, found similar maximum uptakes for kaolinite and montmorillonite from single element solutions (Table 1.4). In competition experiments using four metals, the same author found a difference in percentage reduction for each metal compared to the single ion solution. Table 1.5 shows how the order differs for the two clay minerals. Although this indicates how selectivity varies between clays, it is difficult to draw any conclusions from Carter's data regarding preference for metals because the solutions were made to represent on industrial effluents and thus concentrations of each varied widely.

Farrah et al (1980) used mixtures of cations on illite, montmorillonite and kaolinite whilst maintaining a constant equilibrium pH and minimising concentration effects by retaining a constant total ionic concentration. Their comparative uptake affinity sequence is given in Table 1.6 and was completed by comparison of relative amounts taken up from binary solutions where concentrations of each competing ions were equal on a molar basis.

A further approach towards ionic competition on clays was adopted by Hodgson (1960) and subsequently by Farrah and Pickering (1977). Hodgson (op.cit.) treated calcium saturated montmorillonite with radioactive Co^{58} for three days, over which time equilibrium was reached. The Co^{58} - montmorillonite was then washed and treated with solutions

Table 1.4. Order of attenuation from maximum uptake data from single cation solutions (From Carter, 1975).

Montmorillonite	$Cr^{3+} \hat{=} Fe^{3+} > Zn^{3+} > Cu^{2+} = Ni^{2+} > Cd^{2+} > Pb^{2+}$
Kaolinite	$Cr^{3+} = Fe^{3+} > Zn^{2+} > Cu^{2+} > Ni^{2+} = Pb^{2+} > Cd^{2+}$

(The order for montmorillonite holds for all the concentrations applied (0 - 8000 μg/ml). The position of Cr, Fe and Zn alter with higher metal concentration for kaolinite).

Table 1.5. Order of percentage reduction in adsorption from a four element solution compared with the single element solution (From Carter, 1975).

Montmorillonite	$Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$
Kaolinite	$Cu^{2+} > Zn^{2+} > Cr^{3+} > Ni^{2+}$

decreasing % reduction ⟶

(Concentrations of metals in the four element solution not equal).

Table 1.6. Affinity sequence compiled from data from binary solutions with equal concentrations of each ion (From Farrah *et al*. 1980).

Montmorillonite	Pb^{2+}	Ca^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Mg^{2+}
Illite	Ca^{2+}	Zn^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Mg^{2+}
Kaolinite	Zn^{2+}	Cu^{2+}	Ca^{2+}	Pb^{2+}	Cd^{2+}	Mg^{2+}

Table 1.7. Displacement series for montmorillonite (ability of cations to displace another from an exchange site).

Hodgson (1960)

$$Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{3+} = Fe^{2+} = Ni^{2+} = Mn^{2+} > Mg^{2+} = NH_4^+$$

Farrah and Pickering (1977)

$$Ca^{2+} > Pb^{2+} > Cu^{2+} > Mg^{2+} > Zn^{2+}$$

of other cations. The amounts of Co^{58} released into solution was measured and taken to represent the relative efficiency of each ion to replace Co^{58}. The displacement series is given in Table 1.7. Farrah and Pickering (op.cit.) used a similar approach and found that with illite and kaolinite, the ion added first was taken up to near saturation values, and the ion added subsequently took up the remaining exchange sites. Only if the concentration of the second species added was greater or equal to the equilibrium concentration value of the first species did any displacement occur. Displacement of the first applied species occurred, however, at lower concentrations of the secondly introduced species on montmorillonite and from selectivity coefficients an order of preference was constructed (Table 1.7).

Comparison of the affinity sequences in Tables 1.6 and 1.7 show how differences can arise depending on the experimental procedure by which they are prepared, or indeed their method of calculation. Farrah et al (1980) stated that ranking orders have little relevance unless all are prepared in a similar manner owing to the many variables affecting the affinities of cations for any given clay type.

An increase in uptake with increasing pH is widely reported (Kishk and Hasson, 1973; Carter, 1975; Griffin and Shrimp, 1976b; Frost and Griffin, 1977; Farrah and Pickering, 1979). Most authors agree that the main cause for their increase is due to the decreasing competition from H^+ as pH increases. Carter (op.cit.) found an increase in uptake for most metals between pH 0 and 4 but little difference between pH 4 and 9. Griffin and Shrimp (1976a) implied precipitation to be important in their column experiments by running control experimental columns containing sand along which removed considerable amounts of metals in the absence of any significant cation exchange capacity. The same authors (1976b) identified a precipitate from a leachate with a pH greater than 6 as $PbCO_3$ which suggests the role of dissolved CO_2

may be critical.

The sharp increase in uptake at about pH 6 (varying slightly for different metals) has been shown to be associated with both the change from positive to negative sites on clays (Farrah and Pickering, 1979) and to the formation of hydrolysed species such as MOH, which have a greater affinity for negative sites than M^{2+} (James et al, 1975), or such species as $M(OH)_2$ which have a lower solubility than M^{2+} (Frost and Griffin, 1977).

From the evidence presented by previous workers it seems that a number of factors can be shown to influence metal uptake on clays. These include pH, the nature and concentration of cation, the nature of the substrate exhibiting cation exchange properties and its capacity, the concentration of anions present, the presence of organic materials, and the presence or absence of carbon dioxide.

Metal Uptake by Iron and Manganese Oxyhydroxides

Iron(iii) and manganese(ii) and (iv) oxides and hydroxides are commonly found as coatings on many sediment mineral grains and as concretionary deposits forming nodules in deep ocean environments. Although with regard to the attenuation of landfill leachate constituents the formation and behaviour of ferromanganese nodules may appear irrelevant, comparison of their unusually high concentrations of metals, including the heavy metals (Cronan, 1977), may bear some similarities with the ability of iron(iii) and manganese(ii) and (iv) oxides and hydroxides to take up metals from solutions. Further interest in various oxides was stimulated by their ability to act as exchange substrates for specific ions and the work in this field was reviewed by Zhabrova and Egorov (1961).

Goldberg (1954) showed that there were strong correlations between metals in deep sea nodules and iron and manganese content. He suggested, as did Krauskopf (1956), that adsorption onto iron and manganese hydrated oxides was responsible for their presence. Goldberg (op.cit.) went further, to say that the adsorption is a product of attraction of opposing charges, that is an electrostatic force, and that the rate of adsorption and the selectivity for ions are a function of the charge density. Zhabrova and Egorov (op.cit.) stated that most oxides are amphoteric and will show both cation and anion exchange depending on pH.

Morgan and Stumm (1964) suggested that manganese, as well as the other oxides, behave as hydrated solid electrolytes in which both cations and anions may be present in their lattices. As such, they could show a cation exchange capacity similar to that exhibited by the clays, which is strongly pH dependent. Dyck (1968), studying the uptake of silver on hydrous iron and manganese oxides, found the reactions followed Langmuir isotherms and was strongly pH dependent. He inferred either an exchange reaction for H^+ or a surface complex formation with the more hydrolysable metal ions being taken up to a greater extend than those weakly hydrolysed. McKenzie (1970), in an investigation of the sorption of cobalt onto synthetically produced manganese dioxide minerals, found that manganese was released into solution and he proposed that the high capacity of these minerals for cobalt resulted from the substitution of Co^{2+} for Mn^{2+}, the lower-valence manganese commonly occurring as a substitute for Mn^{4+} in all but one of the synthetic oxides used. This mineral, pyrolusite, showed a much lower replacement of manganese by cobalt than did the other four synthetic oxides.

Loganathan and Burau (1973), again using MnO_2 species, studied the ratios of H^+ released from 0.1g of the oxide minerals by 5.8 mmole of either sodium or zinc. Zinc released four times that released by sodium. To explain this, the authors proposed that zinc must have interchanged with H^+ sites not available to sodium. In further experiments, using cobalt as well as zinc, it was found that at pH 4 for each mole of either zinc or cobalt taken up, 2.1 moles of H^+ was given out in addition to small quantities of manganese. Cobalt was found to release four times as much manganese as zinc. Furthermore, it was noted that both cobalt and zinc deviated from Langmuir isotherms expected for exchange at a single site. Data for calcium and sodium, however, fitted these isotherms. The conclusions reached suggested that; calcium and sodium ions were taken up in exchange for H^+; zinc may have interchanged with Mn^{2+} in the lattice as well as surface H^+; and cobalt had interchanged with both Mn^{2+} and Mn^{3+} within the dissordered structure of the oxide lattice.

Anderson et al (1973) compared the uptake of silver by birnessite (manganous mangenite) with that of δMnO_2 and found the former to have a greater capacity at pH 7 (0.5M Ag/M MnO_2 for birnessite, 0.3M Ag/M MnO_2 for δMnO_2). Their results showed that the sorption maxima were not directly related to surface areas but that there was some correlation with the quantities of sodium and potassium impurities in the oxides. The authors presumed that the impurities occupied regular lattice positions or acted as "stuffing" cations balancing charge deficiences. Silver must show a preferance for those sites, accounting for the increased uptake in oxides with highest impurity content.

Gadde and Laitinen (1973) found that the H^+ released from hydrous ferric oxide did not correspond stoichiometrically with the amounts of lead taken up, thus agreeing with the observations of Morgan and Stumm (op.cit.) and Loganathan and Burau (op.cit.). As the pH decreased, the ratio of H^+/Pb taken up was found to be smaller than at higher pH's. They implied that this resulted from hydrolysis of Pb above pH 6, with complex formation on the oxide surface releasing varying quantities of H^+, depending on the complex formed, which in turn depended on the hydrolysis product.

Burns (1965) produced thermodynamic calculations to show that Co^{3+} and Fe^{3+} could constitute an isomorphous pair in the $FeOOH.nH_2O$ of manganese nodules, so implying that a solid solution series could occur. Subramanion (1973) produced experimental evidence for solid solution using I.R. and Mössbauer spectroscopy. He pointed out that solid solution with incorporation into the lattice could account for those cations taken up but not desorbed on subsequent leaching.

Hem (1978), in a review of interpretations of metal uptake on oxides, pointed out that a cation exchange mechanism requires a large surface area per unit weight of substrate. He suggested a co-precipitation mechanism by which the sorbed ion is included in the lattice. He then went on to show how manganese oxyhydroxides can disproportionate, facilitating an electron transfer process from the Mn species to other metal ions, decreasing their equilibrium solubilities and so precipitating them so that they are included in the lattice.

The application of the experimentally derived observations discussed above has been shown to have considerable bearing with respect to attenuation of landfill leachates. Suarez (1976) found that the order of abundance of heavy metals in manganese oxides in soils associated with landfills agreed with that of manganese nodules in oceanic environments. Ross (1978) showed in experiments on the Lower Greensand in the U.K. that the order of substitution in the amorphous iron oxide phase corresponded to the order of substitution arrived at by lattice considerations. Ku et al (1978) reported the association of chromium and cadmium with iron oxides coating the grains of a glacial gravel aquifer through which metal contaminated leachate was known to have passed.

Chapter 2. Aims

With the recognition of the pollution potential of landfills, most investigatory work has been concerned with site monitoring. Many such investigations have been conducted to delineate the extent of groundwater contamination following the identification of deteriation in groundwater quality adjacent to landfills (Hughes et al 1971; Nicholls, 1972; Weist and Pettijohn, 1975; Gray and Henton, 1975). These site investigations have provided information concerning either specific waste types or particular hydrogeological environments and as such are only useful in predicting the behaviour of landfills and their leachates where similar conditions prevail. Further work has recognised physical and chemical processes within the ground by which the impact of leachates may be lessened and their constituents attenuated (Baars, 1957; Matthess 1972; Myers 1974; Rovers and Farquahar, 1974; Stiff and Young, 1976).

Work on chemical processes of attenuation has resulted in the publication of much data on the uptake of the heavy metals by pure mineral phases such as the clays (Carter, 1975; Griffin and Shrimp, 1976a and b; Griffin et al, 1976) or pure synthetic materials such as iron and manganese oxyhydroxides (Dyck, 1968; Gadde and Laitinen, 1973; Loganathan and Buran, 1973; Subramarian, 1973). Only more recently has research been directed toward attenuation by specific rock types rather than single mineral phases (Boreham et al, 1975; Bromley et al, 1978; D.o.E., 1978). Research of this nature may be directed towards the prediction of the movement and behaviour of leachate constituents within a set of geological and hydrogeological conditions rather than merely identifying the ability of a mineral phase to take

Evaluation of the parameters influencing metal sorption enables prediction of most effective areas for future research. ~~to be work~~.

up metals from simple solutions.

The present work sets out to investigate the uptake of metals from aqueous solutions by two rock types, the Triassic Bunter Sandstones and the Cretaceous Chalk. In particular it aims to identify the processes by which that uptake is caused and where possible to quantify their relative importance. Having established this, the effects of other ~~leachate~~ G.W. constituents on the uptake of the metals are investigated so that their relative importance on R.N. migration may be assessed the results may thus be applied, not only in a specific geological setting, but also to different chemical conditions such as those governed by the nature of the waste (form) from which the leachate is derived.

The need for research on these rock types arises through their importance in terms of both landfill waste disposal and their water bearing properties. The Chalk and the Bunter Sandstone comprise the two major aquifers in the U.K., and crop out extensively in England (Figure 2.1). The Chalk is important economically in cement manufacturing, particularly in the south east, and the Bunter Sandstone is an important source of aggregate material for the construction industry. The worked out quarries are subsequently of value to the waste disposal industry and concern to local authorities who wish for their reclamation. Figure 2.1 also shows the location of waste disposal sites in England and Wales and comparison with the geology shows that large numbers of waste disposal sites are situated on either Bunter Sandstone or Chalk.

Inevitably the interests of Waste Disposal Authorities and contractors, and those of the Regional Water Authorities and water supply companies are seen to conflict. Whilst site operation and design can exercise some control over the generation and movement of

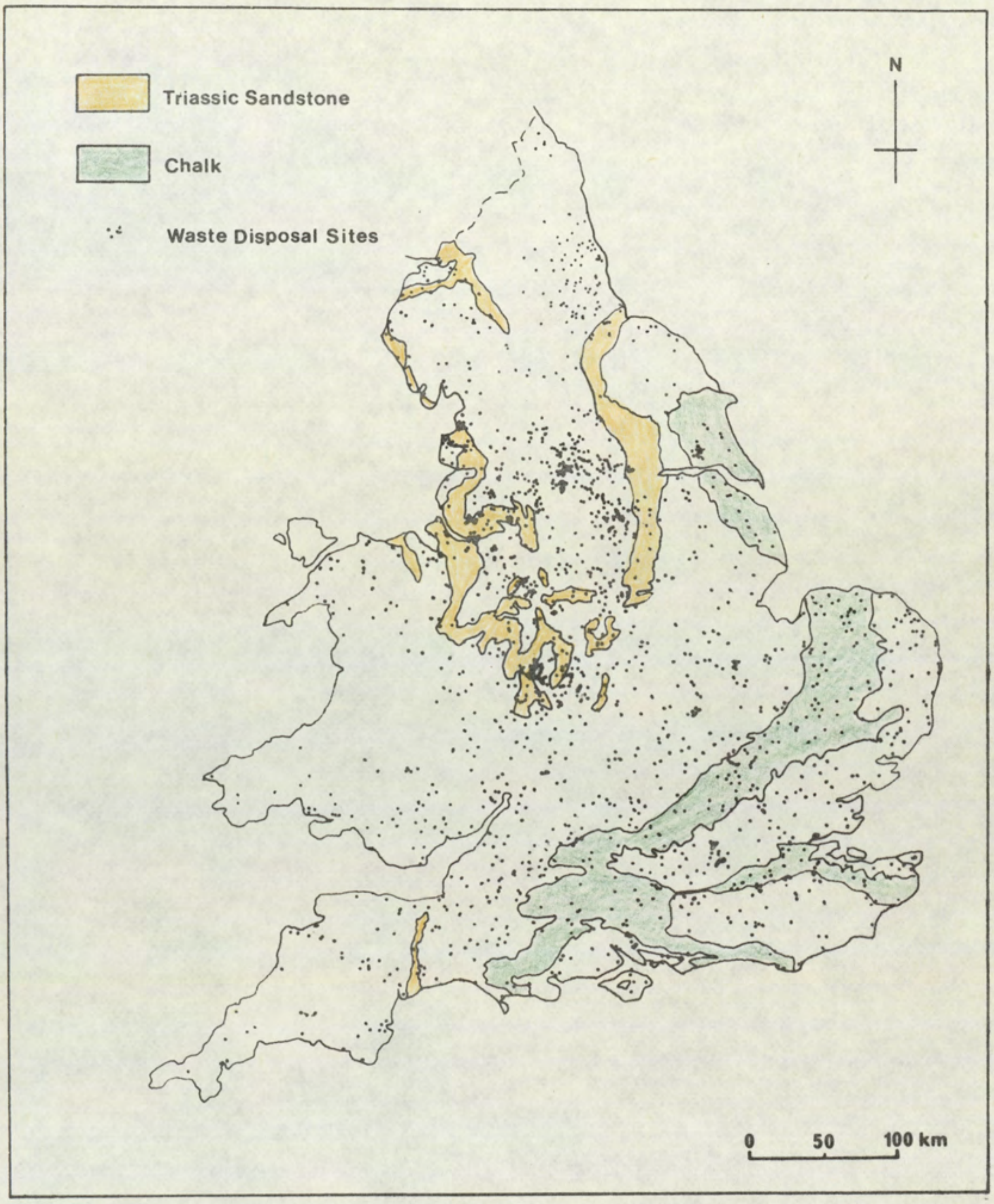


Figure 2.1. Chalk and Triassic Sandstone Outcrop in England and Wales and Waste Disposal Site Locations (Gray et al, 1974).

leachates there is a need to be able to predict the behaviour of leachate constituents within the rock matrix and groundwater. This would allow more accurate appraisals of potential waste disposal sites and would aid in designing monitoring procedures for use after waste emplacement.

Because of the recognition of the need for an aerobic zone to allow micro-organisms to breakdown complex organic compounds and the realisation that anaerobic conditions enhance the mobility of many leachate constituents it is now widely accepted that landfill design, for putrescible waste at least, should incorporate an unsaturated zone beneath the fill. The current work therefore investigates the uptake of heavy metals under aerobic conditions only. Anaerobic conditions will develop within and beneath landfill sites; however such conditions are localised and movement out of the site tends to be into aerobic environments.

Leachates vary in composition enormously (Table 1.1) and the uptake of metals and the effects of different leachate constituents on that uptake is subject to a great number of variables. Out of necessity, therefore, the solutions used in the experiments were much less complex than a landfill leachate. However, investigations were made using likely competitive species within concentration ranges likely to occur beneath landfill sites so that predictions might be made with regard to their importance on the mobility of the heavy metals.

Chapter 3. The Effects of pH on Heavy Metal Uptake by Bunter Sandstone

3.1. Experimental Materials and Procedures

Until recently the Bunter Sandstone was taken to form the lowest stage of the Trias in Great Britain and was subdivided into the Lower Mottled Sandstone, the Bunter Pebble Beds and the Upper Mottled Sandstone. The Lower Mottled Sandstones are fine-grained, contain well rounded quartz grains and are thought to be dune sands. The Bunter Pebble Beds are generally coarse sands commonly with abundant well-rounded pebbles. The Upper Mottled Sandstones are fine to medium sands and like the Pebble Beds were laid down in water. All three members of the series are soft, being poorly cemented, and have a strong red colouration.

Recent classification of British Triassic stratigraphy (Warrington et al, 1980), based upon lithological units, places the Bunter Sandstone units within the Sherwood Sandstone Group, along with arenaceous units at the base of the former Keuper stage. Although the Sherwood Sandstone group is placed within the Triassic nomenclature, the basal parts of the sequence may locally be Permian in age. Despite this recent classification, for convenience and to differentiate between experimental materials, the name Bunter is retained here when referring to the red sand used.

The material chosen for use in the experiments was from the Bunter Pebble Beds from Cheslyn Hay in Staffordshire (N.G.R. SJ 965071). It is poorly cemented so very little mechanical damage to individual grain surfaces was produced on dissaggregation. The rock contained a significant proportion of pebble-size material and this was considered unsuitable for adsorption experiments because of its low surface area to volume ratio. To remove the larger sizes the sand was sieved, after drying and dissaggregation, and the fraction over 2mm discarded. The mineralogy of the < 2mm fraction was determined by X-ray diffraction and was found to consist of quartz with small quantities of illite, kaolinite and chlorite. The X-ray traces showed other small peaks which were thought likely to be due to the presence of a very small quantity of a mixture of the silicate hydroxides osmulite, nacrite and tosalite. A thin section prepared from a more strongly cemented sample of a medium-coarse sand from the Pebble Beds in Nottinghamshire which gave a similar X-ray diffraction trace showed some 8 to 10% of heavily altered alkali feldspar. A grain-size analysis of the < 2mm fraction of the Cheslyn Hay sand is given in Table 3.1, along with the analyses of two samples from boreholes in the Nottingham area. Although this data shows the Cheslyn Hay Bunter sand to have a coarser grain size, it has similar proportions of finer material (< 125µm) and has a more even distribution amongst the coarser fractions than the two Nottingham samples.

For each experiment the procedure followed the same pattern. Metal ion solutions were prepared using their nitrates at a concentration of 100µg/ml of metal. Any pH adjustment or additions to the solution described later were made at this stage. For each experiment a measure of stock solution was transferred to a polyethylene bottle, which had a narrow neck with a screw top (close fitting, but not air tight). To each bottle a weighed quantity of air dried sand was added. An arbitrary 5:1 solution: solid ratio (volume: dry weight) was maintained throughout. 100ml or 200ml

Table 3.1. Grain size analysis of the <2000µm fraction of the Bunter sand from Cheslyn Hay, and of two sandstones from cores from the Nottingham area.

Grain size (µm)	Cheslyn (%)	Nottingham (%)	(%)
<2000 >1000	12.9	0.1	0.2
<1000 > 500	23.3	2.6	4.1
<500 > 250	28.8	47.6	47.9
<250 > 125	16.7	35.3	34.6
<125 > 63	9.7	7.9	7.5
<63 > 38	5.5	2.7	3.3
<38 (Pan fraction)	3.1	3.7	3.4

volumes were most commonly used, the governing factor being the amount of sand available (particularly in the experiments using the smaller grain-size fractions). It was considered undesirable to use less than 100ml in order that the solid:solution ratio was disturbed as little as possible through sampling and evaporation. Because of the narrow neck to the bottles, and the close fitting screw caps, loss due to evaporation was not considered to be unacceptable. A 200ml sample left for one week as a control lost less than 1% in volume through evaporation.

Sampling of the solution after different reaction times involved the removal of approximately 2ml of the liquid each time. This was done immediately after vigorously shaking the bottle. This ensured that an approximately proportionate amount of solid was removed each time, with the exception of the coarsest fraction only, again helping to maintain the solution:solid ratio over the experimental period.

Immediately after the addition of the sand to the solution the polythene bottles were placed, in replicates of three for each set of experimental conditions, on an orbital shaker set at a speed sufficient to agitate even the coarsest particles. Each sample was removed using an acid-washed Pasteur pipette and then transferred to a centrifuge tube and centrifuged until clear. The supernatant liquor was then transformed to a small (5ml) plastic sample vial which had a tight fitting screw cap. Analysis of samples was done by atomic absorption spectrophotometry (A.A.S.). The time interval between sampling and analysis varied, analyses being conducted when a convenient number of samples had been collected. In all instances the period never exceeded seven days. To see what affect keeping samples had on results, a number of samples were analysed only a few hours after collection and subsequently after seven days. The results showed no losses of metals from solution had occurred over that period. Percentage uptake of the metals was calculated from the original concentration which was also determined by A.A.S. Details of analytical conditions for A.A.S. are given in Appendix 1.

The results given are the average uptake from the three replicates for each set of conditions. The maximum variation in uptake either side of the mean is also given in each figure for that set of results.

3.2. pH Effects. Results.

The aim of these experiments was to investigate the effects of pH within the range common to domestic landfill leachates on the uptake of metals and to record pH changes during metal uptake. The pH adjustments were made in two ways. In the first, pH was adjusted only before mixing with the sand. In the second, pH was adjusted before mixing and maintained at that value throughout the duration of the experiments.

Figures 3.1 to 3.5 show the percentage uptake of the heavy metals cadmium(ii), copper(ii), nickel(ii), lead(ii) and zinc(ii) respectively. In each experiment the initial concentration of metal was 100μg/ml. The pH values chosen were 4, 6 and 8 in the case of cadmium(ii) and nickel(ii). For lead(ii) the upper value was 7.5 and for copper(ii) and zinc(ii) 6 since above these values rapid precipitation of the metals occurred before mixing with the sand, rendering any results invalid. The pH adjustments were made using small quantities of either 0.1M ammonium hydroxide or 5% nitric acid. Ammonium hydroxide was used in preference to sodium or potassium hydroxide in order not to interfere with the assessment of the quantities of any sodium or potassium given out during the uptake of the heavy metals.

The results given in the graphs show in each case that most uptake occurred within the first hour and that by 24 hours equilibrium was either complete or close to completion. The graphs for cadmium(ii), copper(ii), nickel(ii) and lead(ii) (Figures 3.1, 3.2, 3.3 and 3.4) show that at equilibrium there was no great difference in uptake for the initial pH values chosen. For zinc(ii), however, (Figure 3.5) the difference was quite marked, with the uptake from the pH 6 solution being nearly 8% greater than that from the pH 4 solution.

Figures 3.6 to 3.9 show the percentage uptake of the alkali metals calcium(ii), potassium(i), sodium(i) and magnesium(ii) respectively. Again, pH values of 4, 6 and 8 were chosen as were initial concentrations of 100µg/ml. The graph for potassium(i) uptake (Figure 3.7) shows a similar trend to the heavy metals with the uptake continuing until equilibrium after about 24 hours. The results for calcium(ii), sodium(i) and magnesium(ii) (Figures 3.6, 3.8 and 3.9) show a somewhat different trend. After a small initial uptake, calcium(ii) and sodium(i) were released, to the extent that there was a small overall increase in their concentrations with respect to the initial solution concentration. Magnesium(ii) showed an appreciable uptake initially, with the pH 4 and 8 solutions continuing to be taken up until 6 hours from the start. After this the pH 4 solution graph gradually falls again, while that of the pH 8 solution shows a situation approximating equilibrium. The solution at pH 6 showed an uptake considerably greater than either of the other two values after 1 hour, but fell back slightly until 6 hours, then regained its 1 hour uptake value after 24 hours and remained constant.

Tables 3.2, 3.3 and 3.4 give the quantities of calcium, iron, potassium, magnesium and sodium released during the uptake of lead(ii) for initial pH values of 4, 6 and 7.5. Results are given in meq/100g sand. Given alongside are quantities of the same elements released from the Bunter sand in blank solutions under similar conditions. The results show a very marked increase in the amounts of calcium, magnesium and sodium present in the lead(ii) solution after 48 hours compared to the blank. Potassium, and in particular iron, were released in greater quantities into the control blank than the lead(ii) solution. It is worth noting here that the blank solutions took a considerably longer centrifuging period to clear them of any colouration than for the metal solutions. Table 3.5 shows the uptake of lead(ii) from the same experiments expressed in meq/100g for comparison.

Changes in pH during the experiments using heavy metals are given in Tables 3.6 to 3.10. These are for experiments both with initial pH control and for those without any adjustment, where the initial pH value is governed by the metal ions themselves. For cadmium(ii), nickel(ii) and zinc(ii) (Tables 3.6, 3.8 and 3.10), the pH values after 48 hours agree closely despite a considerable initial pH range. The final pH values of the lead(ii) solutions do show some variation, with the pH 4 solution maintaining a degree of acidity whereas the equilibrium pH of the 7.5 and untreated solutions are alkaline and agree quite well. This occurs despite the untreated lead(ii) solution having a pH of 4.3, close to that of the acid adjusted solution. In all cases, a rapid change in pH occurs during the first hour in the pH adjusted solutions. In the unadjusted solutions the changes are more subtle, even though the initial pH of that solution is close to one of the pH adjusted solutions.

Figure 3.10 shows the variation in lead(ii) uptake with controlled pH throughout the experiment. The pH was altered initially to the pH values of 4 and 7.5 using 5% nitric acid and 0.1M sodium hydroxide. The pH was measured at 15 minute intervals during the first two hours after mixing the sand with the solution and subsequently at hourly intervals. After each measurement the pH was readjusted to its starting value. In this experiment sodium hydroxide was used in preference to ammonium hydroxide because it was thought that increasing ammonium concentrations arising from pH regulation might interfere in lead(ii) uptake during exchange reactions. The graphs show a clearly reduced uptake with the pH value maintained at 4. Both solutions with maintained pH values show a release of lead(ii) after the initial uptake, more so with the acid solution than the alkaline.

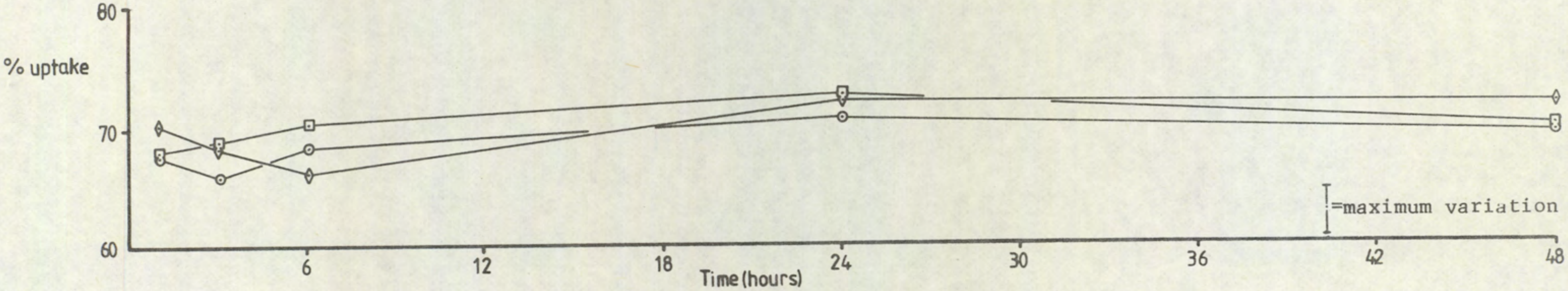


Figure 3.1. Uptake of cadmium(ii) by Bunter sand from solutions with different initial pH values.

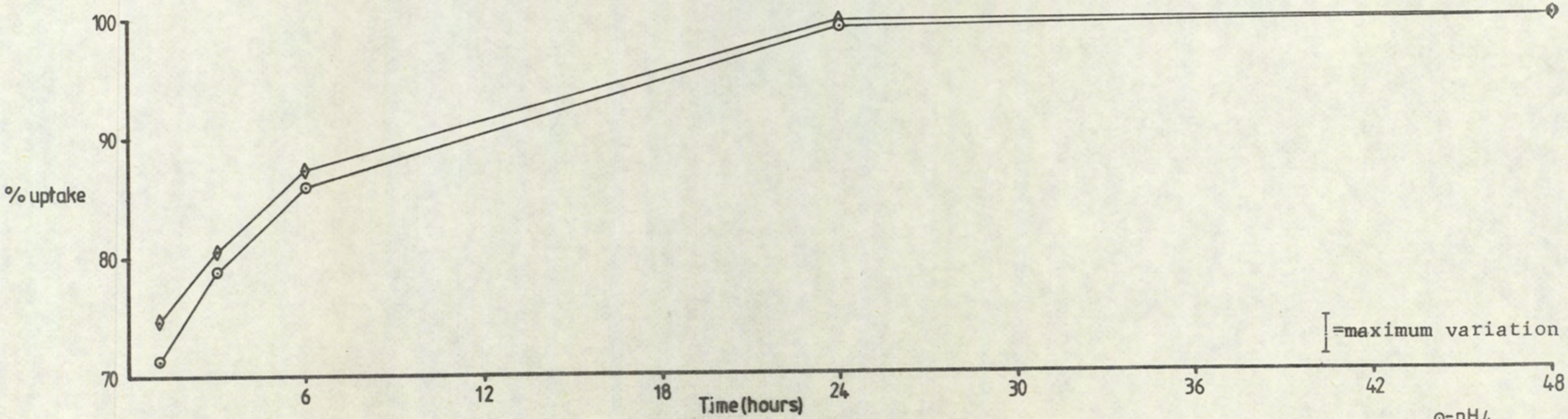


Figure 3.2. Uptake of copper(ii) by Bunter sand from solutions with different initial pH values.

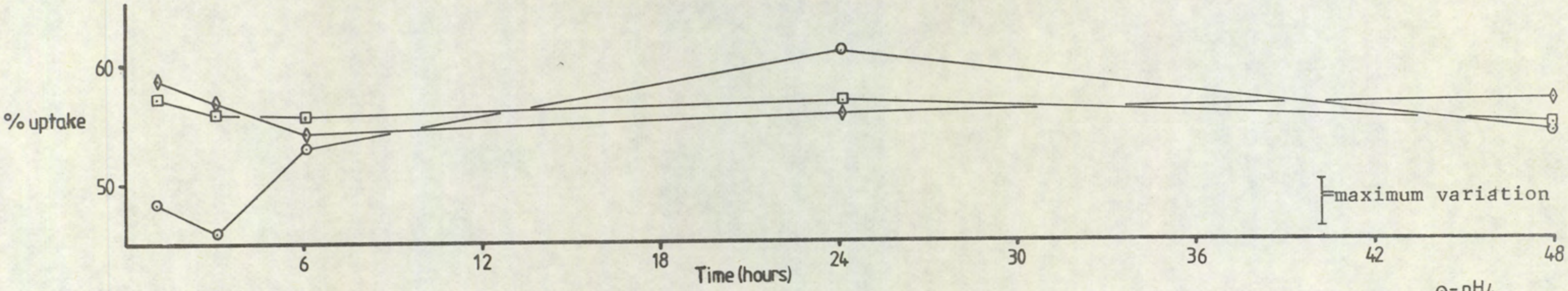


Figure 3.3. Uptake of nickel(ii) by Bunter sand from solutions with different initial pH values.

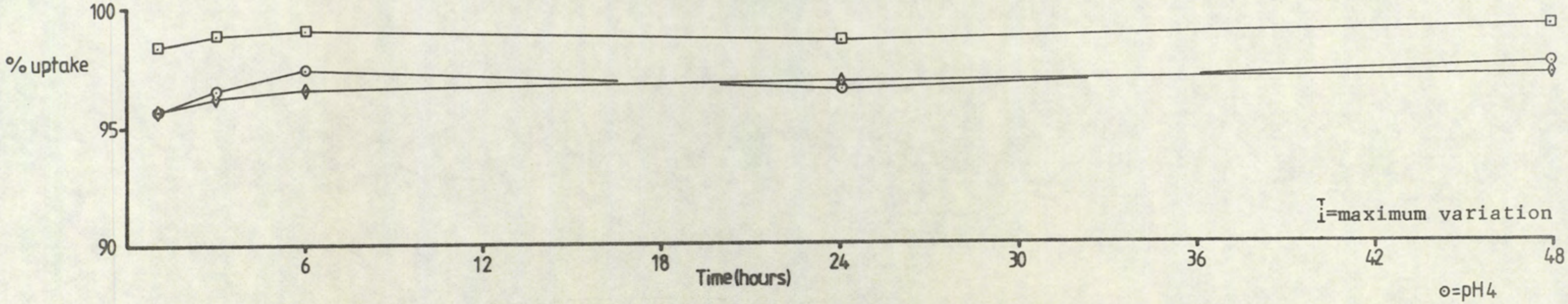


Figure 3.4. Uptake of lead(ii) by Bunter sand from solutions with different initial pH values.

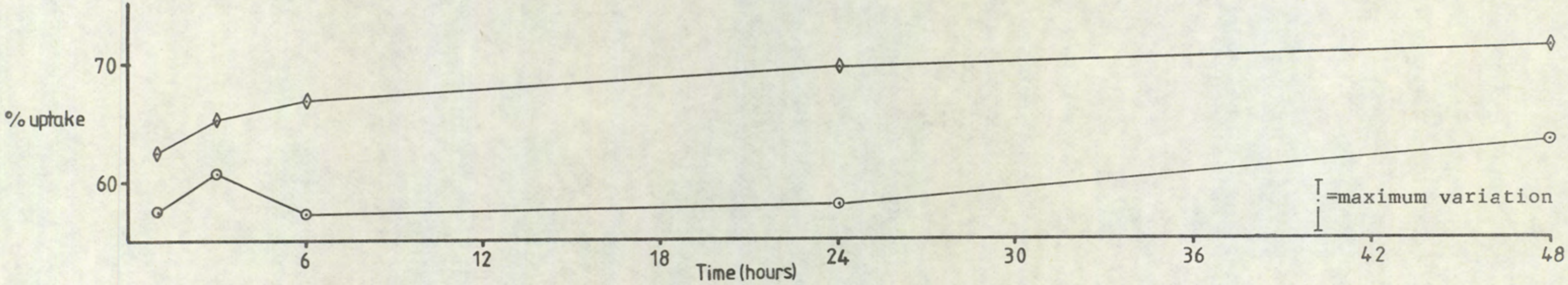


Figure 3.5. Uptake of zinc(ii) by Bunter sand from solutions with different initial pH values.

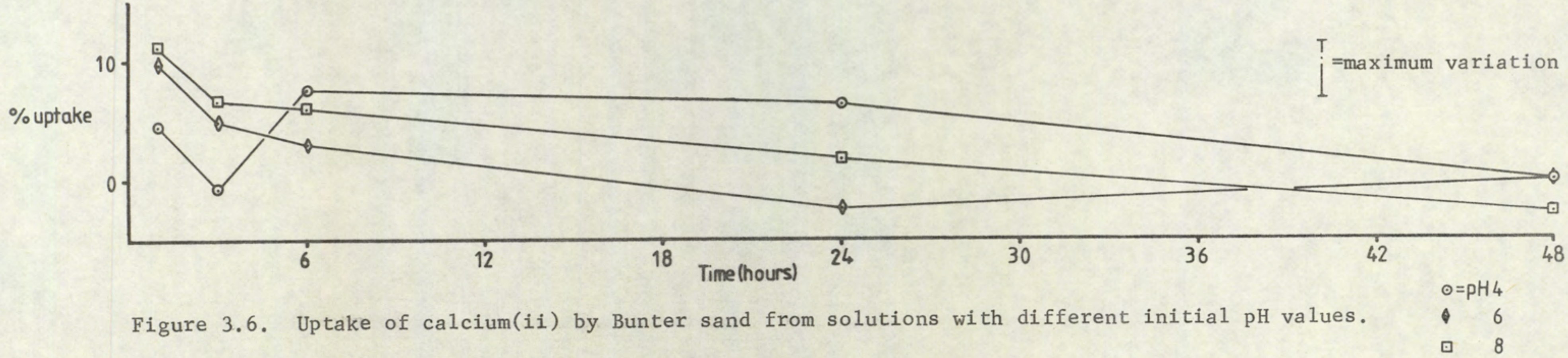


Figure 3.6. Uptake of calcium(ii) by Bunter sand from solutions with different initial pH values.

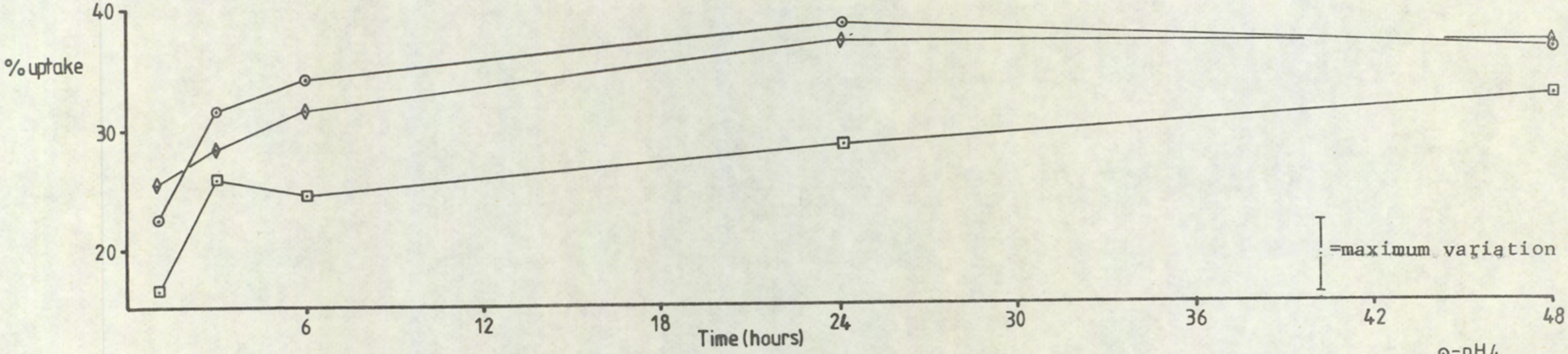


Figure 3.7. Uptake of potassium(i) by Bunter sand from solutions with different initial pH values.

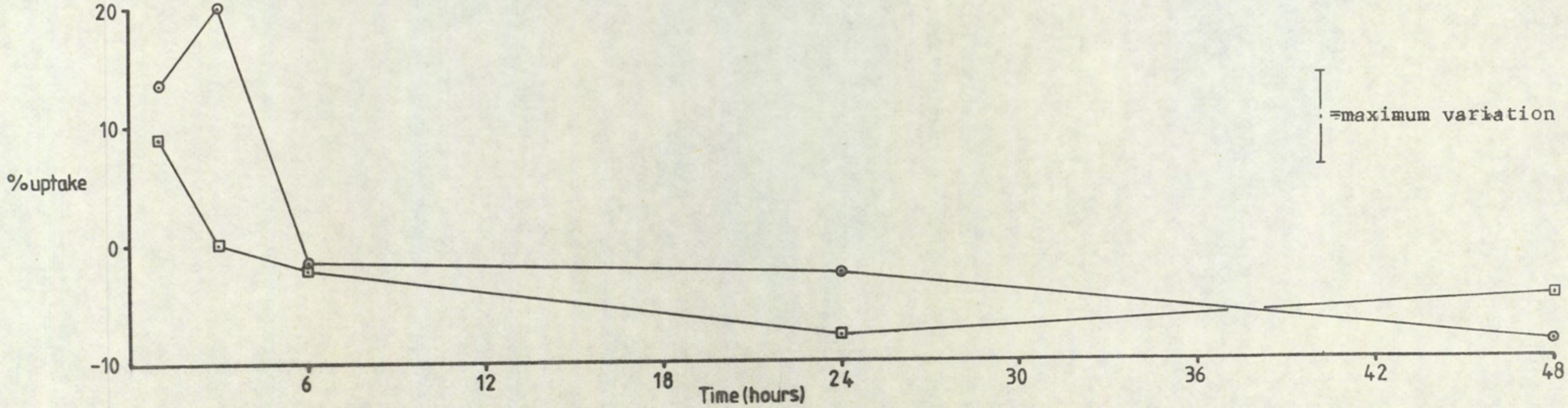


Figure 3.8. Uptake of sodium(i) by Bunter sand from solutions with different initial pH values.

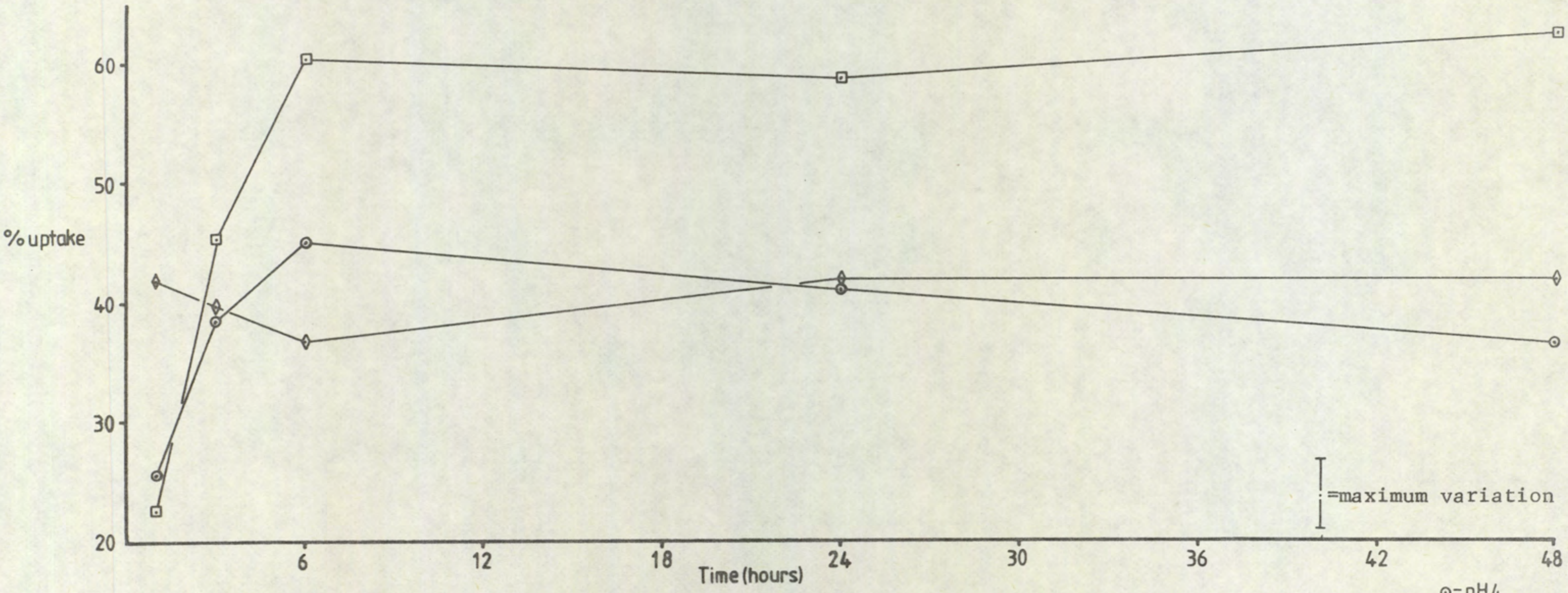


Figure 3.9. Uptake of magnesium(ii) by Bunter sand from solutions with different initial pH values.

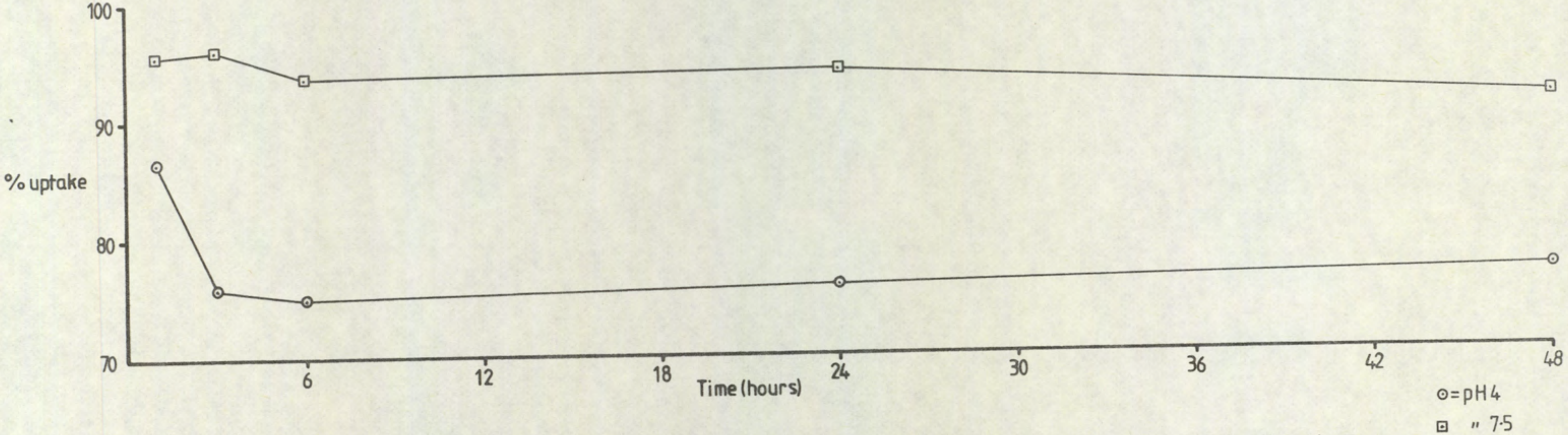


Figure 3.10. Uptake of lead(ii) by Bunter sand from solutions with different maintained pH values.

Table 3.2. Release of cations from Bunter sand by distilled water and a 100μg/ml lead(ii) solution at pH 4, after 48 hours.

Cation Released	Blank Solution (meq/100g)	Lead (11) Solution (meq/100g)
Ca	0.044	3.904
Fe	0.814	Trace
K	0.537	0.166
Mg	Trace	0.412
Na	0.089	0.406
Total	1.484	4.888

Table 3.3. Release of cations from Bunter sand by distilled water and a 100μg/ml lead(ii) solution at pH 6, after 48 hours.

Cation Released	Blank Solution (meq/100g)	Lead (11) Solution (meq/100g)
Ca	0.040	3.778
Fe	1.015	Trace
K	0.538	0.140
Mg	Trace	0.294
Na	0.066	0.343
Total	1.659	4.525

Table 3.4. Release of cations from Bunter sand by distilled water and a 100μg/ml lead(ii) solution at pH 7, after 48 hours.

Cation Released	Blank Solution (meq/100g)	Lead (11) Solution (meq/100g)
Ca	0.030	3.528
Fe	1.246	Trace
K	0.442	0.714
Mg	Trace	0.762
Na	0.074	0.311
Total	1.792	5.315

Table 3.5. Uptake of lead by Bunter sand from solutions of different initial pH values.`

pH 4 (meq/100g)	pH 6 (meq/100g)	pH 7.5 (meq/100g)
0.478	0.478	0.486

Table 3.6. pH changes with time for solutions of cadmium at different starting pH's after mixing with Bunter sand.

Before mixing	4.0	7.0	5.1 (unadjusted)
1 hour	5.8	5.9	5.2
3 hours	5.55	5.9	5.35
6 hours	5.6	5.9	5.4
24 hours	5.6	5.9	5.3
48 hours	5.7	5.8	5.7

Table 3.7. pH changes with time for solutions of copper at different starting pH's after mixing with Bunter sand.

Before mixing	4.0	6.0	4.3 (unadjusted)
1 hour	4.9	5.2	4.25
3 hours	4.5	4.8	4.5
6 hours	4.9	5.05	4.45
24 hours	4.8	4.95	4.55
48 hours	5.1	5.2	5.25

Table 3.8. pH changes with time for solutions of nickel at different starting pH's after mixing with Bunter sand.

Before mixing	4.0	8.0	5.3 (unadjusted)
1 hour	5.1	6.4	5.3
3 hours	5.1	6.4	5.7
6 hours	5.2	6.0	5.9
24 hours	5.6	6.1	6.2
48 hours	6.0	6.2	6.4

Table 3.9. pH changes with time for solutions of lead at different starting pH's after mixing with Bunter sand.

Before mixing	4.0	7.5	4.6 (unadjusted)
1 hour	4.4	6.0	4.55
3 hours	4.35	6.2	4.75
6 hours	5.05	6.4	5.0
24 hours	5.0	6.4	5.6
48 hours	5.0	6.4	6.2

Table 3.10. pH changes with time for solutions of zinc at different starting pH's after mixing with Bunter sand.

Before mixing	4.0	6.0	5.1 (unadjusted)
1 hour	5.0	4.9	5.2
3 hours	4.75	4.8	5.4
6 hours	4.65	4.75	5.6
24 hours	4.9	4.8	5.7
48 hours	4.8	4.8	5.9

3.3. Discussion

The effects of increasing pH on the uptake of heavy metals (Figures 3.1 to 3.5) are not consistent, for the most part, with those given by many authors working on pure clays or iron(iii) and manganese(iii) and (iv)oxides (Kinniburgh et al, 1976; Griffin and Shrimp, 1976b; Frost and Griffin, 1977; Farrah and Pickering, 1977). Whereas those authors showed a constant increase in metal uptake with increasing pH, here only lead(ii) and zinc(ii) demonstrated this effect significantly, although copper(ii) was taken up more slowly during the early stages of the experiment from an acid solution. pH values measured throughout the duration of the experiments show that at equilibrium the pH values of those solutions containing cadmium(ii), copper(ii), nickel(ii) and zinc(ii) were similar, independent of the initial pH. This illustrates that the sand has a buffering capacity which must reduce the importance of the pH of leachates coming into contact with it with regard to metal attenuation by exchange or adsorption mechanisms. A similar buffering capacity was shown for the Lower Greensand by Boreham et al (1975), who found that the pH of a solution with an initial pH of 1.75 was raised to 5 after passing through a column of Greensand.

The same authors found that the column of sand was capable of buffering several column volumes of the acid solution. Although no effort was made here to ascertain the volume of any solution at a given pH which may be buffered by an arbitrary weight of Bunter sand, the effect of maintaining an acid pH throughout the experiments duration does depress the uptake of lead(ii) (Figure 3.10). This suggests that the pH will play a more important role in metal uptake should the buffering ability of the sand be exceeded.

The occurrence of quantities of soluble alkaline earth metals, in particular calcium, indicated by their levels in the blank solution (Tables 3.2 to 3.4), leaves open the possibility of precipitation for removal of some of the heavy metals. In particular the carbonates of the heavy metals are likely to form at pH values between 5.5 and 7.5 (Griffin and Shrimp, 1976a). Precipitation of metal hydroxides is unlikely for any of those metals used, with the exception of lead, because the pH values measured throughout the experiments were below those for hydroxyl formation (Hahne and Kroonje, 1973). The increasing calcium levels with decreasing pH are consistent with increased solubility of phases such as carbonates. The reverse trend for potassium may result from either impurities in the ammonium hydroxide used in pH adjustment or from replacement in exchange sites by ammonium. Results given in Chapter 5 (Table 5.1) confirm that carbonate precipitation plays an important role, and is in fact responsible for the removal of more of the heavy metals than is cation exchange.

Comparisons of the total quantities of cations released into solution and the quantities of lead(ii) taken up with the cation exchange capacity given in Chapter 4 (Table 4.1) shows that whereas the totals of the cations eluted approach the exchange capacity, the levels of lead taken up do not. The latter observation is not remarkable in itself since insufficient lead(ii) was introduced to saturate available sites in a stoichiometric exchange process. What is remarkable is the large imbalance between those cations given out and those taken up. Even allowing for the soluble phases, there is a seven fold excess of calcium eluted alone. It seems likely that these cations must be exchanged for another species, the only available species being H^+ derived either from the HNO_3 or the NH_4^+ used in pH adjustment.

These results are in contrast with Carter (1975) who, although dismissing a stoichiometric exchange on montmorillonite, found heavy metal uptake exceeded those cations released. However, only sodium and potassium levels were monitored in her work making direct comparison impossible. Monsef-Mirzai (1980), continuing along the same lines found that a proportion of copper(ii) taken up remained labile and did not enter an exchange reaction, thus concurring with Carter (op.cit.).

The release of larger quantities of calcium than the other alkaline earth metals in the presence of lead(ii) suggests that it is either more easily displaced or that the Bunter sand is saturated with respect to calcium. The inability of the sand to take up more calcium (Figure 3.6) indicates the latter to be true.

Magnesium also shows a marked release into the lead(ii) solution whilst appearing in only trace quantities in the soluble phase. Its increase with increasing pH is consistent with an exchange reaction with lead(ii). The fact that magnesium(ii) is itself taken up by Bunter sand (Figure 3.9) indicates the sand is not saturated in this respect. The significantly elevated uptake from the pH 8 solution compared with the acid solutions suggests either exchange, precipitation or adsorption. Kinniburgh et al (1976) showed adsorption of Mg(ii) onto hydrous iron(iii) oxide at pH values above 6.5 and this could account for the greater uptake here, although a cation exchange cannot be discounted because no measurement of the other alkaline earth metals was made.

The uptake of potassium demonstrates a pH effect in reverse of that expected for an exchange reaction (Figure 3.7). Sodium, the ion most likely to be involved in an exchange reaction with potassium because of ionic radii and charge considerations, appears to be less readily exchangeable at higher pH values. This is shown by the values of sodium given out after lead(ii) uptake (Tables 3.2 to 3.4). These figures show that sodium is released in the presence of lead(ii), suggesting an exchange, even if not stoichiometric, occurs more readily at lower pH values. The fact that sodium is not actively taken up by Bunter sand (Figure 3.8) further indicates that it has a lower affinity for exchange sites than does potassium, thus agreeing with the attenuation sequence given by Griffin, Shrimp _et al_ (1976).

Several authors working with iron and manganese oxides have reported non-stoichiometric exchange reactions with imbalences similar to those found here. Loganathan and Burau (1973) measured an excess of released H^+ over the quantities of cadmium(ii) and zinc(ii) taken up by MnO_2 species. They concluded, after detecting small quantities of manganese eluted, that the heavy metals may enter into the disordered MnO_2 lattice as well as direct exchange for H^+, thus agreeing with Morgan and Stumm (1964). Anderson (1973), also working on MnO_2 species, found a correlation between the amounts of sodium and potassium impurities within the lattice, suggesting that the metal taken up, in this case silver, was preferentially taken into the sites previously held by the impurities. It is possible that some of the alkaline earth metals measured in solution here may be due to their replacement by lead(ii) and that part at least of the imbalance may be due to a non-stoichiometric exchange or interchange within the oxyhydroxides in the Bunter sand. The observation that the lead(ii) treated sand settled more quickly with centrifuging than the blank solution supports an association between the fine colloidal iron species and lead(ii), and is thought to be the result of flocculation of the fine particles with the addition of the heavy metal. The high levels of iron in the blank solution may possibly be accounted for by the presence of very fine suspended oxyhydroxides, even after centrifuging.

Chapter 4. The influence of grain size on metal uptake by Bunter Sandstone

4.1. Experimental Materials and Procedure

The purpose of these experiments was to establish relationships between grain size, hence surface area, and to some extent mineralogy, and the uptake of heavy metals. A further series of experiments was carried out using combinations of metal ions to determine their specificity for the different grain size fractions.

The sand used was the previously described < 2000µm fraction from Cheslyn Hay. The air-dryed sand was disaggregated completely by placing small quantities (5-10g) in a large mortar and gently pounding it with a rubber bung, following the method described by Folk (1974). A logarithmic grain size separation was chosen for convenience, with sieve sizes of 1000µm, 500µm, 250µm, 125µm, 63µm and 38µm. After crushing and sieving, a small sample from each pan was taken and viewed under a low power binocular microscope to determine if disaggregation was complete. Where this examination showed any degree of aggregation of grains, that fraction was subjected to further treatment by rubber bung and mortar and resieved. This procedure was continued until complete disaggregation was achieved. The residual pan fraction (< 38µm) was also collected and used in some experiments; however, because of the small quantities present in relation to the other fractions, it was not practicable to use it in all the experiments. X-ray diffraction charts from the pan and 38µm sieve fractions showed their mineralogy to be very similar with respect to peak heights, indicating that any differences in uptake in the experiments may be considered to result from surface area differences. The experiments were carried out under the same conditions described in Chapter 3, using a 5:1 solution: solid ratio and 100μg/ml metal solutions. No pH adjustments were made.

4.2. Results

The variations in uptake with grain size for cadmium(ii), copper(ii), nickel(ii), lead(ii) and zinc(ii) respectively are shown in Figures 4.1 to 4.5. The graphs for cadmium(ii) (Figure 4.1) show that for each sieve fraction most uptake occurred within the first hour and that subsequent changes were relatively small. Also apparent is the increase in uptake with decreasing grain size. Between the 63µm and 38µm this increase is markedly greater than between the coarser fractions.

Copper(ii) and zinc(ii) (Figures 4.2 and 4.5) show more even increases in uptake between the coarse fractions, but again show a marked increase between the 63µm and 38µm fractions. Nickel(ii) (Figure 4.3) shows the greatest increase between the 125µm and 63µm fractions, the latter showing the same degree of uptake after 48 hours as the 38µm sieve fraction. Lead(ii) has the greatest rise in uptake between 500µm and 250µm (Figure 4.4). As with nickel(ii), the 63µm fraction shows that at this solution concentration the uptake of lead(ii) is as high as that for the 38µm fraction.

The variation in uptake with grain size after 48 hours for all five metals is shown in Figure 4.6. It is obvious that, from a 100µg/ml solution, on a weight basis lead(ii) was taken up to a considerably greater degree. Of the other four metals, cadmium(ii) and copper(ii) were next most readily removed, with the coarser fractions taking up more cadmium(ii) and the finer fractions more copper(ii). Zinc(ii) was taken up to a greater degree than nickel(ii) by all grain sizes with the exception of the 63µm fraction. This is a reflection of the marked increase in nickel(ii) uptake between the 125µm and 63µm fractions as previously described.

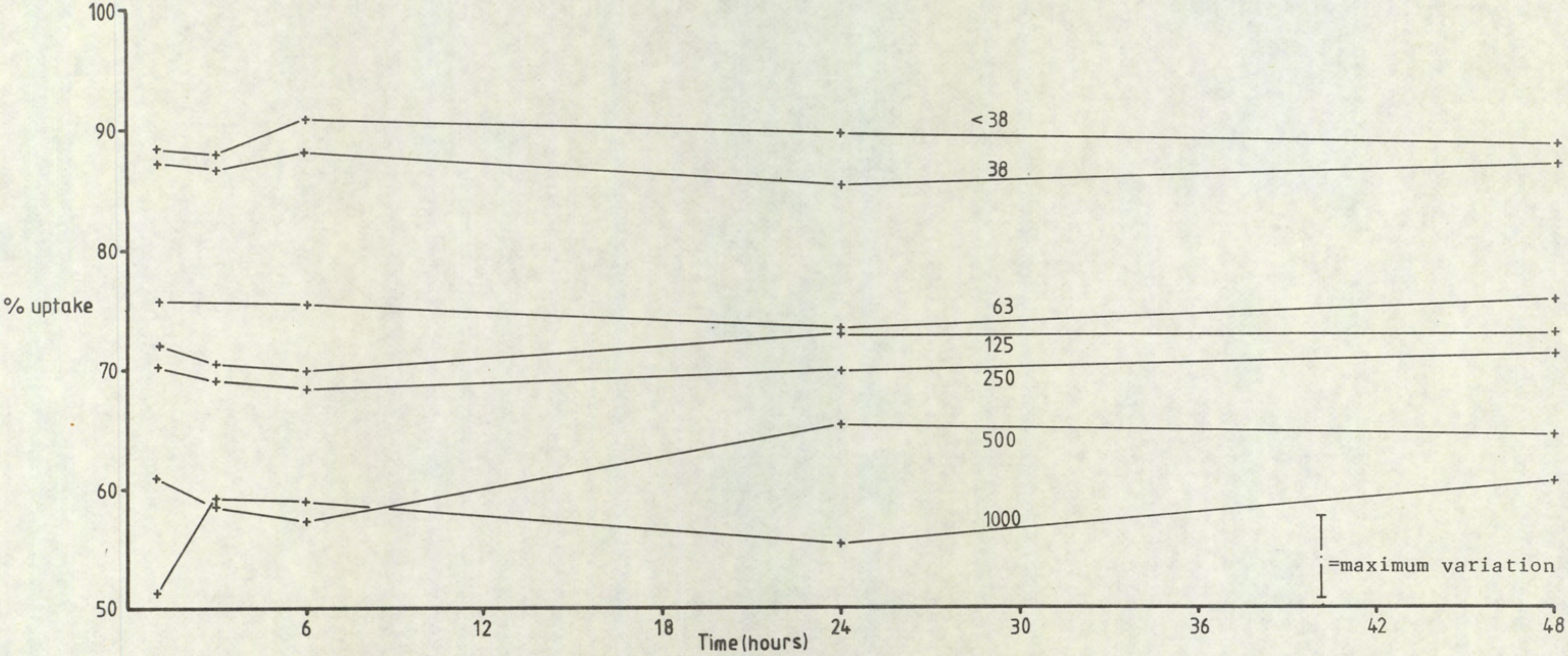


Figure 4.1. Uptake of cadmium(ii) by different grain size fractions of Bunter sand.

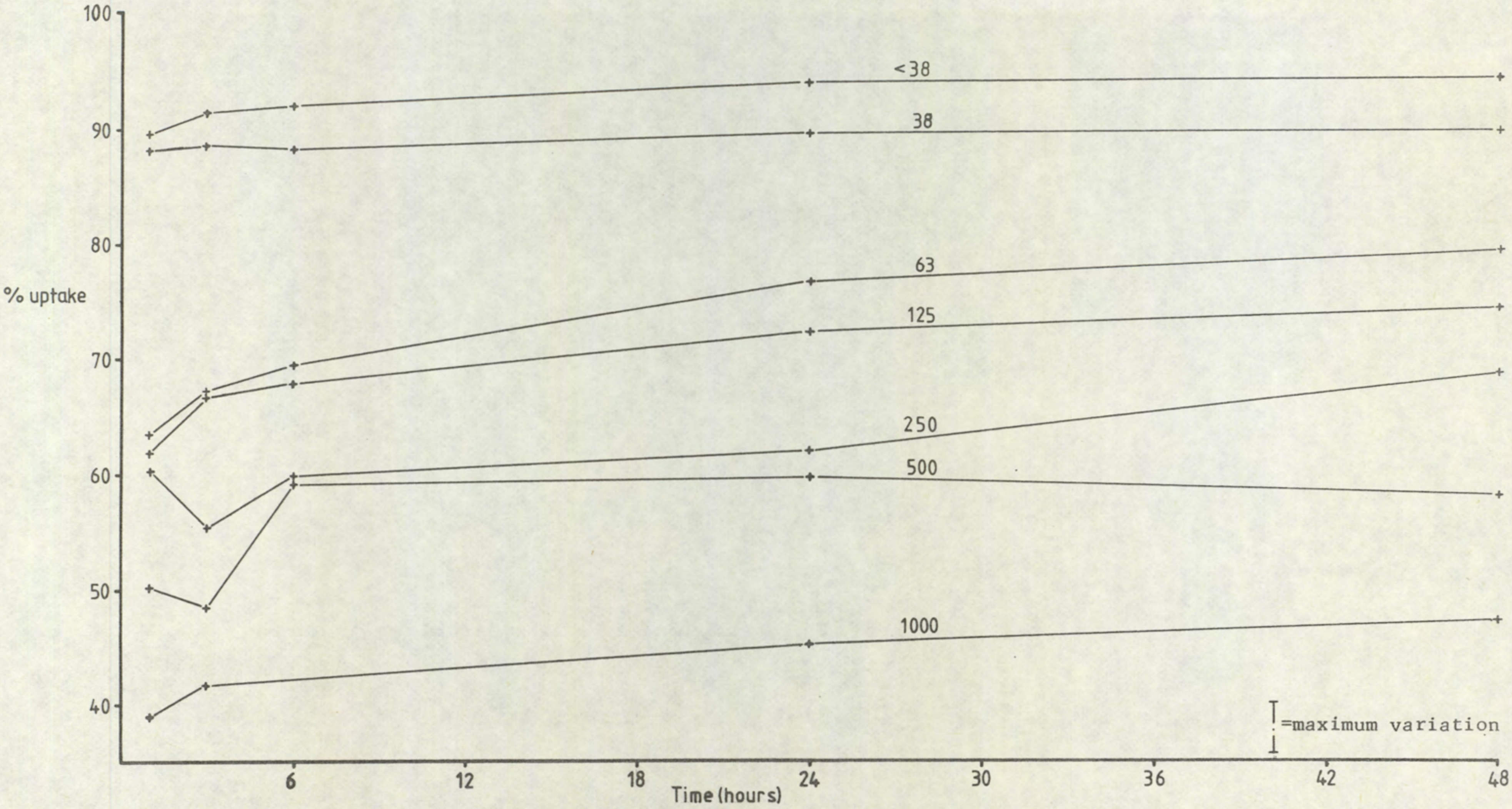


Figure 4.2. Uptake of copper(ii) by different grain size fractions of Bunter sand.

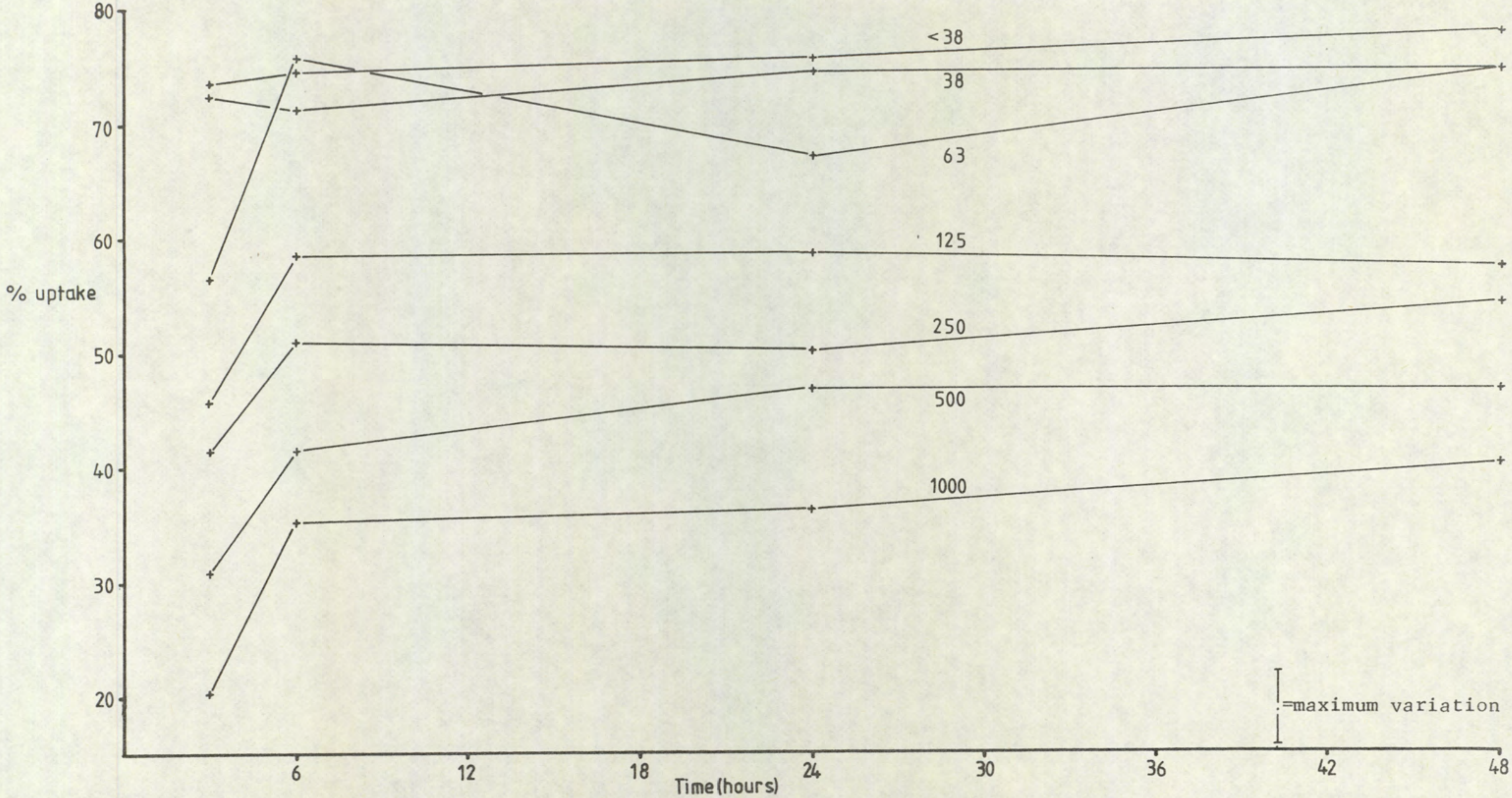


Figure 4.3. Uptake of nickel(ii) by different grain size fractions of Bunter sand.

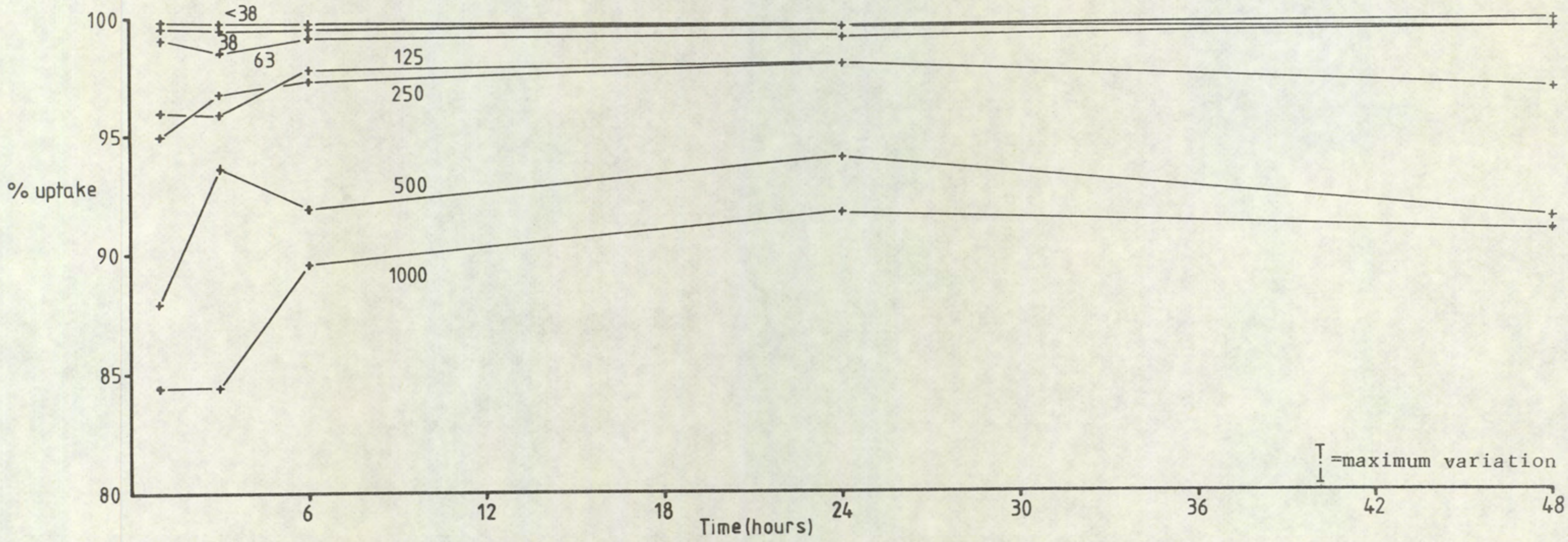


Figure 4.4. Uptake of lead(ii) by different grain size fractions of Bunter sand.

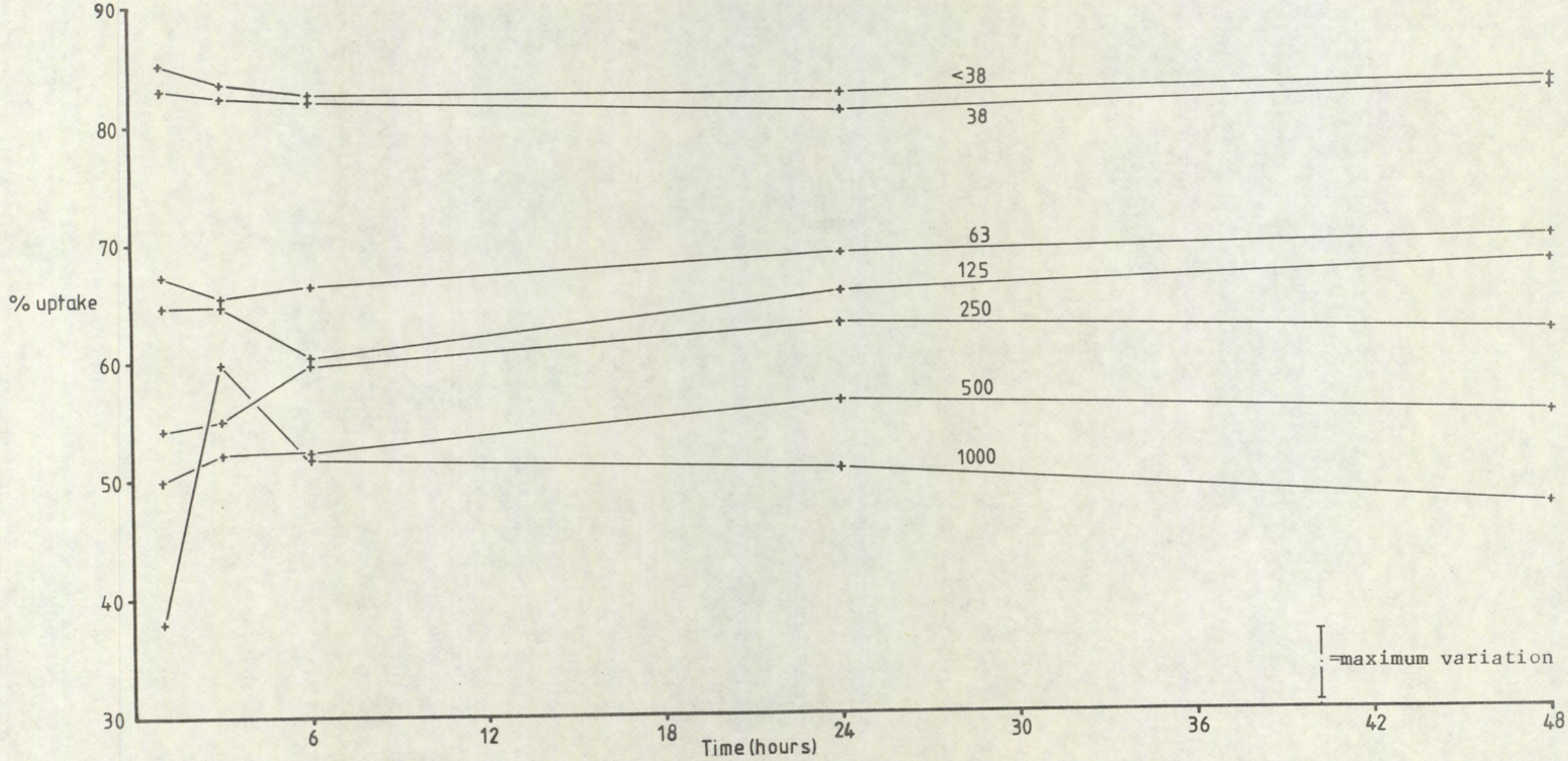


Figure 4.5. Uptake of zinc(ii) by different grain size fractions of Bunter sand.

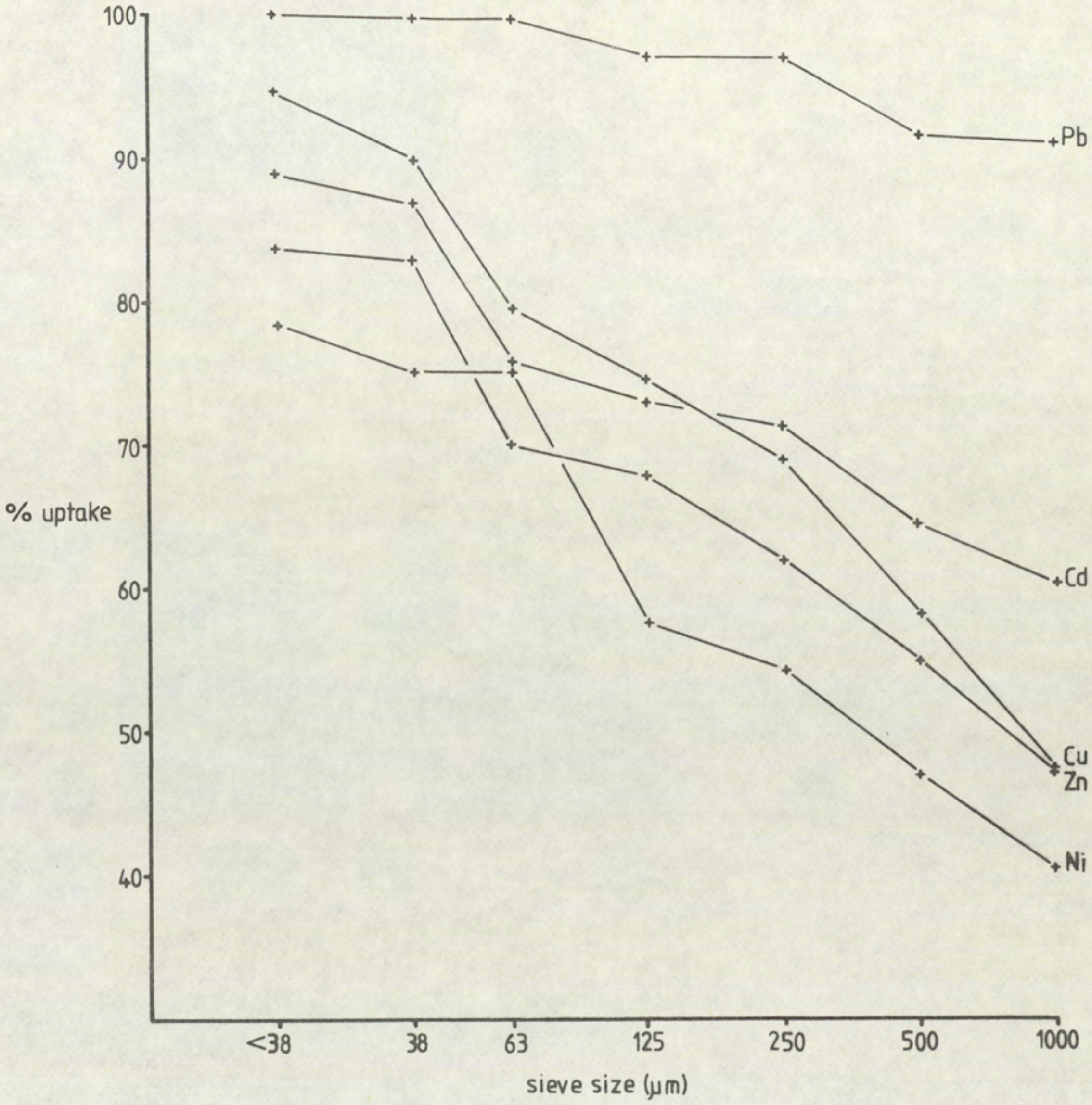


Figure 4.6. Variation in heavy metal uptake with grain size for Bunter sand (after 48 hours).

In order to show the effects that competing metals may have on each other and to see what specificity any metal may have, a series of experiments was carried out using combinations of the same five metals used previously and the different grain size fractions. As before, each of the metals used was in a concentration of 100µg/ml, and the pH was not adjusted. The combinations of metals were built up with the addition of one other metal, finally giving a five-metal solution. The order in which the metals were combined was that of their preferred uptake in weight as shown in Figure 4.6, i.e. lead(ii) plus copper(ii), then cadmium(ii), zinc(ii) and finally nickel(ii). The solutions, then, were: lead(ii) plus copper(ii); lead(ii) plus copper(ii) and cadmium(ii); lead(ii) plus copper(ii), cadmium(ii) and zinc(ii); and lead(ii), copper(ii), cadmium(ii), zinc(ii) and nickel(ii). As a comparison, to test if the apparently least well taken up metal had least effect on lead(ii) than those more strongly taken up, a lead(ii) plus nickel(ii) solution was also tested.

The results of these experiments are shown in Figures 4.7 and 4.8. These show the reduction in uptake of lead(ii) and copper(ii) respectively for each of the solutions of competing ions. The percentage reduction was calculated in each case by comparing the uptake from the single ion solutions with that from the multiple solution. The reduction in uptake of lead(ii) for the different solutions and for the different grain size fractions is shown in Figure 4.7. The results clearly show that the presence of competing metals had greatest effect on lead(ii) uptake in the coarser fractions and that there was only a limited effect at the fine end of the scale. The results for the two bi-metallic solutions, lead(ii) with copper(ii) and lead(ii) with nickel(ii), show that nickel(ii), which on a weight basis was taken up to the least extent of any of the metals chosen (Figure 4.6), had less effect on the lead(ii) uptake than did copper.

The reduction in uptake of copper(ii) for the same solutions is shown in Figure 4.8. Although the graphs are less even than those for lead(ii) (Figure 4.7), they show a similar trend, with the greatest percentage reduction occurring in the coarsest fractions. There was a much greater reduction in copper(ii) uptake for the finer fractions with each additional metal than demonstrated by lead(ii).

The results of these experiments, expressed in meq/100g, are shown in terms of the total uptake from the solutions in Figure 4.9, where the uptake of lead(ii) from its single solution; that of copper(ii) alone; and those of the increasingly complex solutions are shown. The shapes of the graphs show that, with the inclusion of extra metals, the total uptake increases from solution to solution. The greatest increase is in the finer grain sizes. The five-metal solution had little difference in total uptake compared to the four-metal solution for the finer fractions (63µm and less). For the coarser fractions (125µm and above) there was actually a slight decrease in total uptake with increasing metal content for the three, four and five metal solutions.

The cation exchange capacities for the different grain sizes, expressed in meq/100g are shown in Table 4.1. These capacities were determined using an ammonium acetate extraction according to the method described by Bascomb (1964). The variation in aluminium, iron and silicon content of the sand is shown in Figure 4.10 for each grain size. Each is expressed as a percentage and is calculated on the metal oxide. It is probable that the aluminium content represents the clay materials present. The iron content is thought to represent the oxide/hydroxide coatings on grains and the silicon content predominantly from quartz. Thus, while the proportions of clay materials increase significantly with decreasing grain size, the percentage of quartz decreases. Determination of these constituents was done using a lithium metaborate fusion, followed by atomic absorption spectrophotometric analysis as described by Van Loon and Parissis (1969). This technique is described in full and a more complete analysis given in Appendix 2.

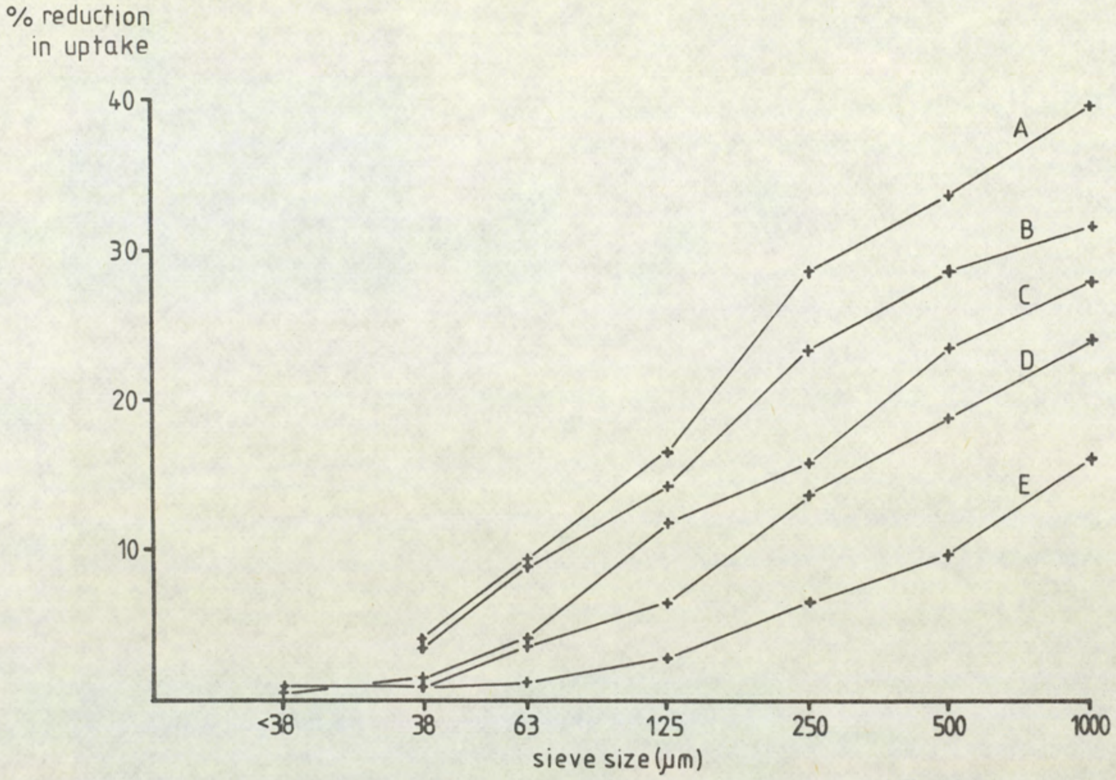


Figure 4.7. Reduction in lead(ii) uptake by competing metals for different grain size fractions of Bunter sand (after 48 hours).

A = Pb + Cd + Cu + Ni + Zn
B = Pb + Cd + Cu + Zn
C = Pb + Cd + Cu
D = Pb + Cu
E = Pb + Ni

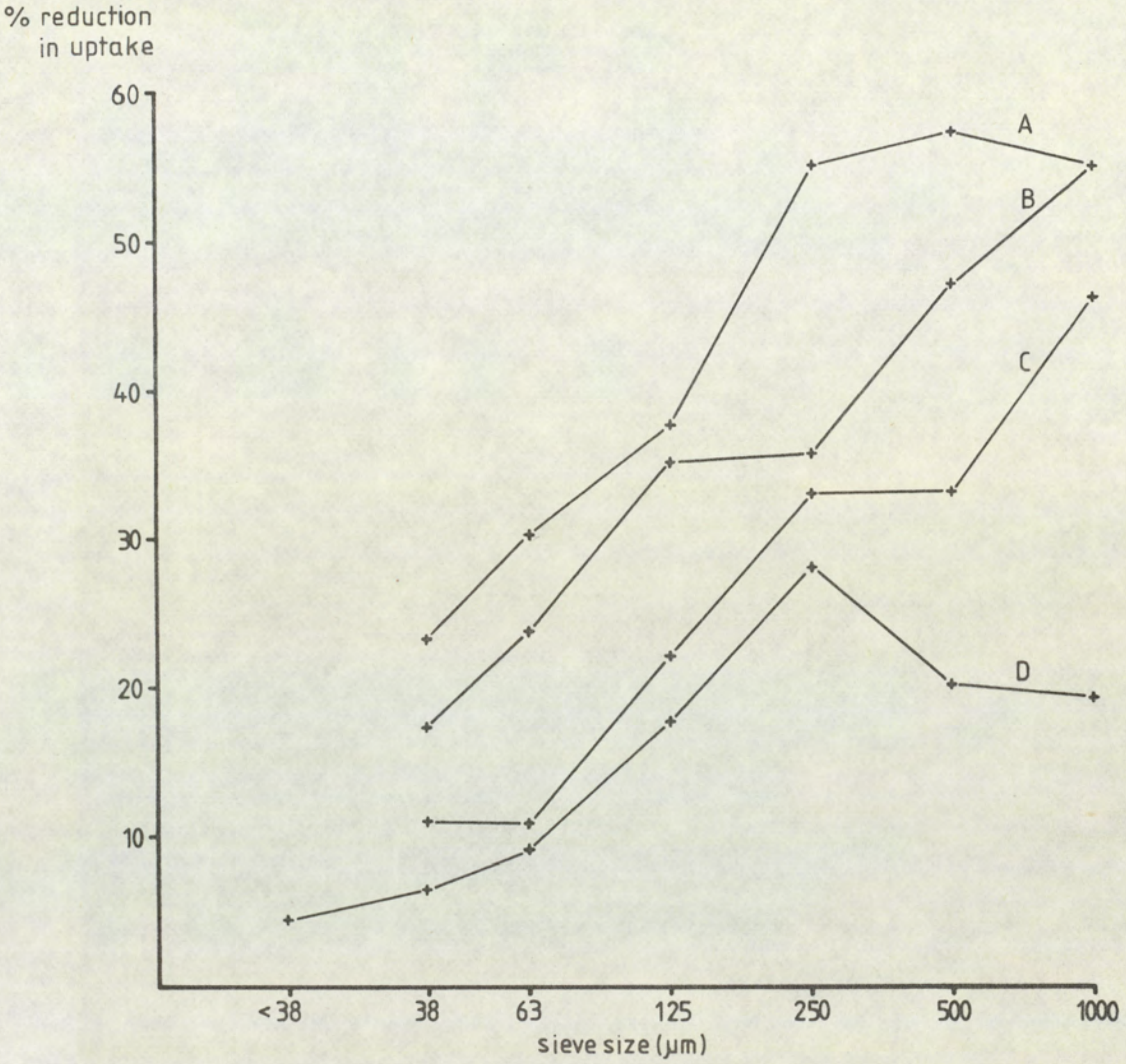


Figure 4.8. Reduction in copper(ii) uptake by competing metals for different grain size fractions of Bunter sand (after 48 hours).

A = Cu + Cd + Ni + Pb + Zn
B = Cu + Cd + Pb + Zn
C = Cu + Cd + Pb
D = Cu + Pb

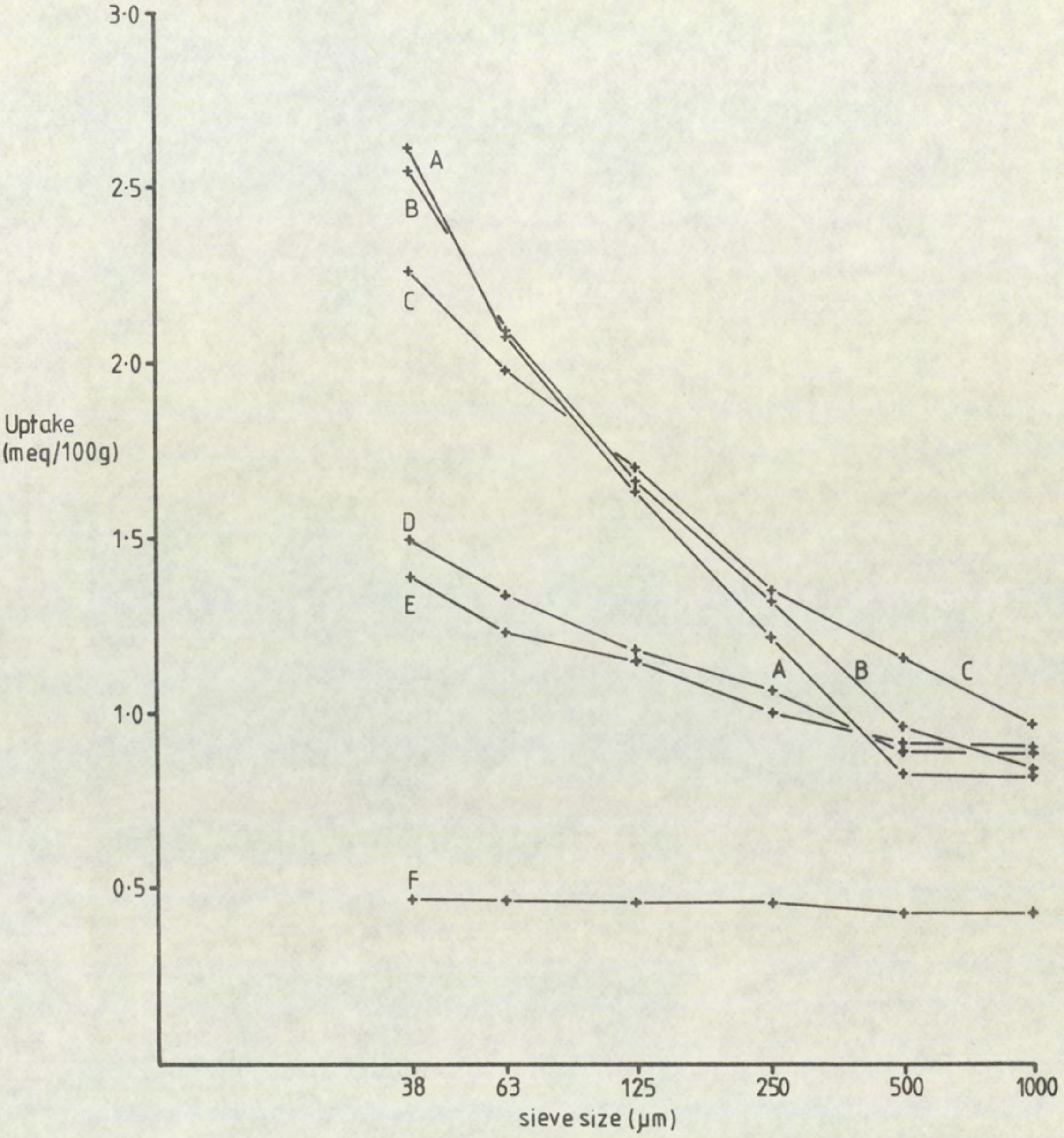


Figure 4.9. Variation in total metal uptake with grain size for Bunter sand.

A = Cd + Cu + Ni + Pb + Zn
B = Cd + Cu + Pb + Zn
C = Cd + Cu + Pb
D = Cu + Pb
E = Cu alone
F = Pb alone

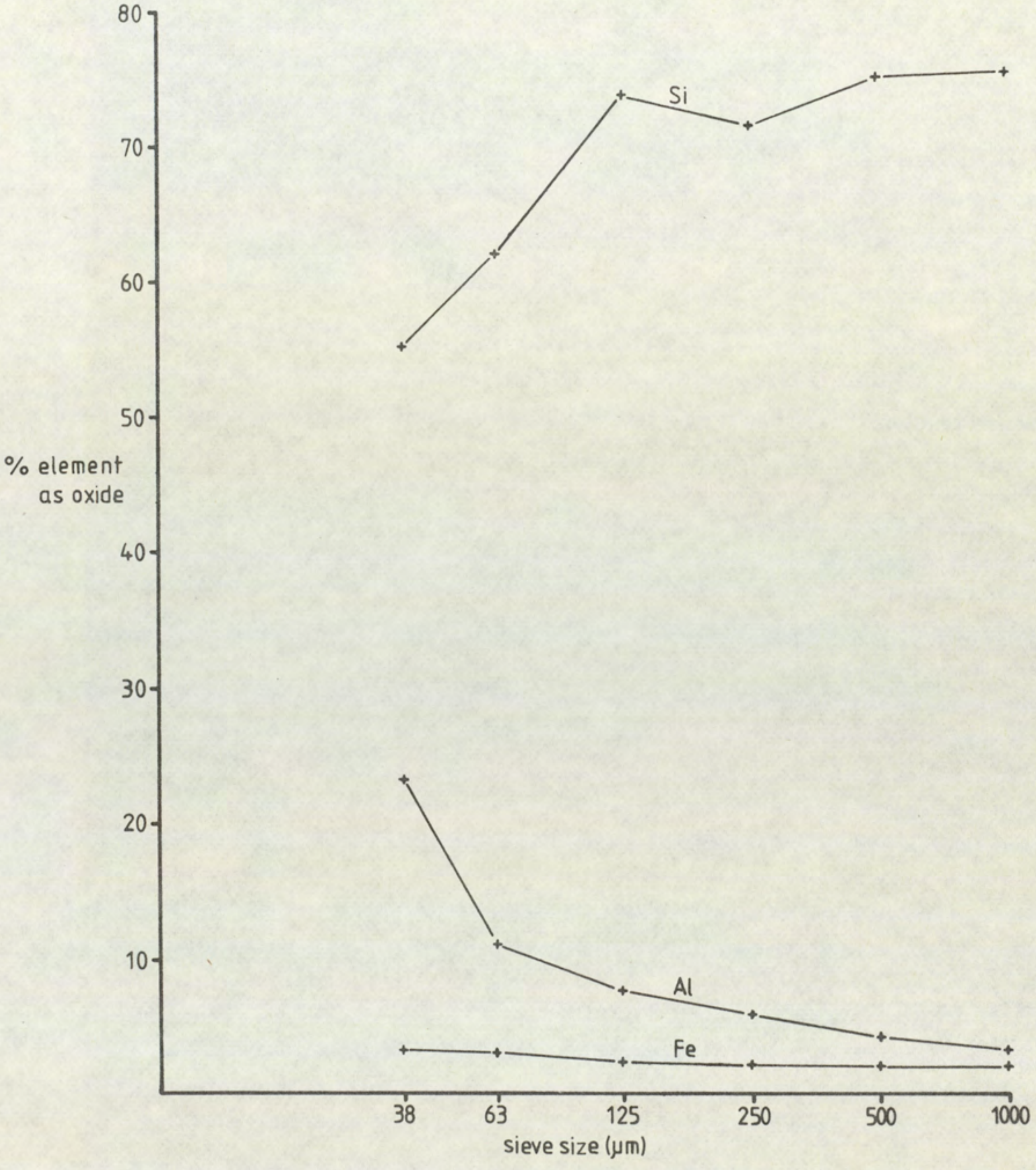


Figure 4.10. Variation in aluminium, silicon and iron content of Bunter sand with grain size.

Table 4.1. Variation in cation exchange capacity with grain size in the Cheslyn Hay Bunter sand.

Grain size (μm)	C.e.c. (meq/100g)
<2000 >1000	4.28
<1000 > 500	4.28
< 500 > 250	5.28
< 250 > 125	7.51
< 125 > 63	9.48
< 63 > 38	13.80
2000 bulk	6.00

4.3. Discussion

For each of the five heavy metals tested, there was an increased uptake by decreasing grain size fractions of the Bunter sand (Figures 4.1 to 4.5). These results are predictable when taking into account the increasing total surface area and the higher cation exchange capacities of the finer fractions (Table 4.1).

Since the cation exchange capacity of the > 1000µm fraction and the > 500µm fraction is the same, it might be assumed that any increase in metal uptake is attributable to the differences in surface area. There is, however, a slightly greater proportion of aluminium in the > 500µm fraction, with an associated lower proportion of silica, indicative of a slight increase in clay content in favour of quartz (Figure 4.10). Comparison of Figures 4.1 to 4.5 show that for all the metals but lead(ii) there was a significantly higher uptake by the > 500µm fraction than would be expected from the Al/Si changes. Since the sand grains are covered by iron sesquioxides it would seem likely that, due to the increase in surface area of the smaller fraction, the increased uptake is associated with the iron species. Figure 4.10 does not show an overall increase in iron content of the > 500µm fraction to support this.

Cadmium(ii), copper(ii) and zinc(ii) all show steadily increased uptake from the > 1000µm to the > 63µm fractions and a marked increase by the > 38µm fraction. Nickel(ii) shows a similarly large increase between the > 125µm and > 63µm fractions. Comparing these increases with cation exchange capacities, a larger increase would be expected between the > 500µm and the > 250µm fractions than between the > 1000µm and the > 500µm fractions.

Similarly a slightly greater increase between the < 250μm and < 125μm fractions would be expected than between the < 500μm and < 250μm. The marked increase in copper, cadmium and zinc by the <38μm fraction corresponds with the greatest increase in cation exchange capacity (Table 4.1) and clay content as shown by the aluminium percentage (Figure 4.10), whilst the increase in nickel uptake by the < 63μm fraction corresponds to the greatest increase in iron content.

The situation regarding the uptake of lead(ii) is less clear. The small difference in uptake between the two coarser fractions, together with a sharp rise for the < 250μm fraction, suggests that cation exchange is perhaps more important for lead than for the other metals. However, because the uptake by the finer fractions is so close to 100%, no picture of the relative importance of the clay and iron sesquioxide fractions can be made.

The competition experiments carried out with various combinations of the heavy metals also help to show the different mechanisms affecting the different metals for each grain size. Comparison of the % reduction in lead(ii) and copper(ii) from a solution containing both metals shows a consistent decrease in % reduction from the coarsest fraction, levelling off towards the finer fractions as the % reduction approaches zero (Figure 4.7). This suggests that lead competes for sites with copper on all grain sizes. The graph for copper, however, (Figure 4.8) does not show the same trend for the coarsest fractions. Rather than the % reduction in copper uptake continuing to rise with increasing grain size as would be expected if both metals competed for the same sites, the % reduction levels off at around 20% for the two coarser fractions (the increase for the < 250μm fraction appears anomalous and must be assumed to be experimental error). This suggests that copper(ii) competes with lead(ii) for cation exchange sites at all grain sizes, but that there is another mechanism by which copper is taken up preferentially to lead in the coarser fractions, masking the expected reduced uptake there.

The graphs for lead (Figure 4.7) show similar trends for each of the metal combinations, with decreasing lead uptake with the introduction of competing metals, as for the lead/copper solution. For copper(ii), rather than a leveling off of the % reduction as encountered for the lead/copper solution for the coarser fractions, the trend is similar to that for lead, with the % reduction increasing with grain size. This is consistent with the existence of a second mechanism, discussed previously for which lead does not compete as effectively as the other metals.

From the small reduction in lead uptake at the finer end of the grain size scale with competition from two, three and four other metals, compared with substantial % reduction in copper uptake, it seems that lead is taken up preferentially by the clay fraction under the conditions here. Several authors have produced selectivity series for metal uptake by clays (Lagerwerff and Bower, 1972; Bittel and Miller, 1973; Carter, 1975; Farrah and Pickering, 1977) but as Farrah and Pickering pointed out, ranking orders have little relevance unless they are all prepared in the same way and under the same conditions because of the many variables affecting the affinities of metals for cation exchange sites. In particular, when dealing with a mixture of mineral phases, as here, rather than a specific clay type, a ranking order can be given only to the bulk meterial. The results given here indicate that different mechanisms favour the uptake of different metals. This implies that ranking order could change with local mineralogical or grain size variations within a sequence such as the Permo-Triassic sandstones, although without affecting the overall attenuating ability of the rock.

Chapter 5. The Role of Iron Sesquioxides, Clay and Carbonate Phases in Metal Uptake by Bunter Sandstone

5.1. Aims

The aim of this series of experiments is to determine what part the iron sesquioxides, or oxyhydroxides, which exist as coating on the mineral grains, the clays and the carbonate fraction play in the uptake of metals by the Bunter sands. The experiments were divided into three parts. Firstly a series of wet chemical extractions were carried out which allowed the quantities of the metals removed from solution as carbonate or by cation exchange to be determined. Secondly, uptake experiments involving Bunter sand from which the iron species coating the grains had been chemically removed and a clean quartz beach sand were performed to try and identify the relative roles of the iron species and the clays. Finally, further uptake experiments were carried out using clean beach sand onto which goethite and haematite had been precipitated. In this way, the ability of each of the two iron species to take up the metals was assessed and compared with previous results to determine which of the two is most likely involved in the Bunter sand.

5.2. Cation Exchange and Carbonate Precipitation

Gupta and Chen (1975) described a series of wet-chemical extractions for determination of the partitioning of metals among geochemical phases within sediments. The phases involved include the soluble, exchangeable, carbonate, easily reducible oxide, organic and sulphide, moderately reducible oxide and the lithogenic fractions. The complete series of extractions is lengthy because of the requirement for drying and mixing of the sample between extractions and the small sample size used by necessity in some stages make duplication desirable. The time limitations alone are prohibitive to applying the techniques to a large number of samples. In addition, not all the reagents used are specific making it necessary to adhere rigidly to the extraction sequence. The extraction techniques used in the determination of the chemically easily reducible and moderately reducible phases infer a purely arbitrary distinction between the two, and for the purposes of this investigation can be considered to be the same. In any case both methods were found to be inadequate in reducing the iron sesquioxides (Section 5.3). Furthermore the technique for determining the metal content in exchange sites is not specific to the iron species or the clays.

However, as discussed in the previous two chapters, the possibility that carbonate precipitation plays an important role made a shortened series of extractions desirable, and the first three stages described by Gupta and Chen (op.cit.) were followed for samples of Bunter sand which had previously been treated with 100μg/ml concentration solutions of one of the heavy metals.

The soluble phase was determined by washing 20g of dryed metal-treated Bunter sand with 200ml of distilled water for 90 minutes, followed by centrifuging and analysis of the supernatant liquor by atomic absorption spectrophotometry. After drying and mixing, 10g of the washed sand was shaken with 50ml of 1M ammonium acetate for 90 minutes, centrifuged and the supernatant liquor analysed by atomic absorption spectroscopy to determine the exchangeable metal content. The residue from this stage was washed with distilled water, air dryed and thoroughly mixed. A 5g sample was shaken with 200ml of 1M acetic acid for 90 minutes, centrifuged and the supernatant liquor analysed for metals associated with the carbonate fraction. Each extraction was carried out in plastic laboratory ware.

The results, expressed in µg of metal per gramme dry weight of sand are given for each of the single-metal/Bunter sand combinations in Table 5.1. None of the metals was found in high concentrations in the soluble phase and all were found in greater concentrations as carbonate than as exchangeable cations. Cadmium(ii) and nickel(ii) showed the least difference between these two phases whilst the ratio of carbonate:exchangeable metal was greatest for zinc(ii).

A similar set of extractions as those described here was carried out on a sample of untreated Bunter sand and determinations for the heavy metals showed that none were present in either the soluble, exchangeable or carbonate forms.

Table 5.1. Concentrations of heavy metals associated with the soluble, exchangeable and carbonate fractions of Bunter sand after metal uptake.

	Metal Concentration (µg/g)				
	Cd	Cu	Ni	Pb	Zn
Soluble	11	5	6	2	9
Exchangeable	115	55	84	104	20
Carbonate	135	386	120	556	172

5.3. Iron Sesquioxide and Clay Fractions

The aim of this series of experiments was to determine what part the iron sesquioxide coatings and the clay fraction play in the uptake of metals. In order to do this it was first necessary to remove the sesquioxides from the sand. The experiments on metal uptake were conducted using the iron-free material and the results compared with those obtained with untreated sand.

Several methods of removing the iron sesquioxides have been developed for use in soil and clay analysis. Included among these methods are boiling in acid and the use of strong reducing agents such as hydroxylammonium chloride (Chao, 1972), acid ammonium oxalate and buffered sodium dithionite (McKeague et al, 1971). The acid digestion methods were considered to be unsuitable because of the likelyhood of damaging the clay minerals. The hydroxylammonium chloride and ammonium oxalate methods were both tried, but neither removed all the red colouration from all the grains. The extraction time given for the buffered dithionate/citrate method by McKeague et al (op.cit.) was not sufficient to remove the red colouration but an overnight extraction using reagent concentrations similar to those given by Holmgren (1967) was found to work well.

The procedure followed was to add 2g of sodium dithionite and 20g of sodium citrate to 5g of dry sand in a flask. To this, approximately 100ml of distilled water was added, a bung placed in the flask and the mixture stirred overnight using a magnetic stirrer. The sand was filtered using a Whatman No.1 filter in a Buchner funnel. The sand was then transferred to another flask, taking care to include all clay-size material stuck to the filter paper, and the material shaken for about one hour in approximately 100ml distilled water to remove excess reagents. The sand was filter again and a further 100ml of distilled water passed through as a final wash. The resulting clean quartz sand and pale pink to cream coloured fines were then air-dried on the filter paper and mixed thoroughly before use in the experiments. X-ray analysis showed no deteriation of the clay minerals. The metal uptake experiments were carried out as before, using a 5:1 solution : solid ratio and 100μg/ml solutions.

Any metals removed from solution by this material should represent uptake by the clay fraction and quartz grains and any precipitation by carbonate formation. To further assess the role played by the different fractions it was then required to determine the part played by the clay fraction alone. This could be achieved in two possible ways; firstly by determining uptake by clays alone, or secondly by measuring uptake by the quartz alone and subtracting this contribution from the iron sesquioxide-free results. The first method necessitates separating the clay fraction from the quartz fraction, which would be both difficult and require large quantities of the sesquioxide-free sand to yield sufficient quantities of clays for experimental work. Because of this, it was decided to use the second alternative and determine uptake by quartz alone. This could be achieved in three ways. Either the quartz could be separated from the fines from sesquioxide-free sand, which as mentioned earlier would be difficult to achieve to a satisfactory degree; or the clays could be physically or chemically degraded; or a clean quartz sand could be used. Both the latter two methods were tried and compared.

By heating clays to above 500°C, some clay minerals are denatured. This method is used in the analysis of clay minerals (Brindley, 1951). Kaolinite is one such clay, and so it was decided to heat-treat Bunter sand and see what effect this had on the uptake of metals. Samples of the sand were heated at 600°C for one hour in a furnace. The sand changed colour to a brighter red, but after cooling in the open it regained its dull brown shade, and to the naked eye resembled the untreated sand. X-ray analysis, however, showed no trace of the clay. Despite being amorphous to X-rays, subsequent experiments on heavy metal uptake showed no difference to the untreated material. Cation exchange capacity determination also showed no substantial change from the untreated material and the only change was in fact an increase rather than the expected decrease (Table 5.2). This suggests that the products of the fusion of the clays behave similarly to the untreated materials despite possessing an X-ray amorphous structure.

Since this method was obviously unsuitable and not going to show uptake by the quartz fractions alone, a clean quartz beach sand was used. X-ray analysis of this sand indicated its composition to be entirely of quartz and microscopic examination showed the grains to be well rounded and similar to those in the Bunter sand. Small carbonate shell fragments were also seen, although because no other mineral phase showed on the X-ray diffraction trace it was assumed that they constituted only a very minor part of the sand. A grain-size analysis of the beach sand (Table 5.3) shows it to be finer grained overall than the Bunter sand (Table 3.1) but with less fine material ($< 63\mu m$) as well as less in the $> 500\mu m$ range.

Table 5.2. Cation exchange capacities of untreated Bunter sand, iron oxide-free Bunter sand, heat treated Bunter sand and a clean quartz-sand.

	Untreated Bunter sand	Dithionite/ citrate reduced Bunter sand	600°C heated Bunter sand	Clean quartz sand
Cation exchange capacity (meq/100g)	6.00	5.97	6.28	1.46

Table 5.3. Grain size analysis of the clean beach sand.

Grain size (μm)	%
>1000	0.3
< 1000 > 500	2.2
< 500 > 250	22.2
< 250 > 125	63.2
< 125 > 63	10.1
< 63 > 38	1.7
38 (Pan fraction)	0.3

The metal uptake onto both the iron oxide-free Bunter sand and beach sand are given in Figures 5.1 to 5.8, along with that of untreated Bunter sand for comparison. Figure 5.1 shows the results for cadmium(ii). Initial uptake by the dithionite/citrate treated Bunter sand was in the same order as that of the untreated material, but with time it gave up some of the metal, until after 48 hours the uptake was only about 50% that of the untreated material. The beach sand showed a much smaller uptake, only about 25% of that of the untreated Bunter sand after 48 hours.

Figure 5.2 shows that the dithionite/citrate treated Bunter sand took up less copper(ii) than the untreated. The latter continued to remove the metal from solution whereas the iron oxide-free material did not. The graph for the beach sand shows a similar profile to that of the untreated Bunter sand, with increases in uptake between the first four samples, but at a lower overall uptake. The 48 hour uptake is 60% for the beach sand as opposed to nearly 100% for the untreated Bunter sand. The beach sand took up slightly more copper(ii) than the iron oxide-free Bunter sand after 48 hours.

The dithionite/citrate treated Bunter sand took up nearly 50% of the lead(ii) from solution after 1 hour (Figure 5.3), rising to 60% after 3 hours and remaining steady about there throughout the remainder of the experiment. The beach sand, however, after an initially smaller uptake, continued to remove lead from solution until after 24 hours nearly all the metal had been taken up. Nickel(ii), after being taken up by 65% by iron oxide-free Bunter sand, was brought back into solution to a small extent, whereas the untreated material continued to remove the metal (Figure 5.4). The uptake by beach sand rose between 1 hour and 24 hours after which it remained steady. The profiles of zinc(ii) uptake by untreated Bunter sand and beach sand are similar (Figure 5.5) with the most rapid uptake during the first 6 hours. The beach sand, however, removed only about half as much zinc(ii) as the Bunter sand. The dithionite/citrate treated material showed a similar initial uptake to that of the untreated, but remained at that value whereas the latter continued to take zinc(ii) from solution.

Figure 5.5 shows that all the iron(iii) from a 100µg/ml solution was removed by untreated Bunter sand. Uptake by the iron oxide-free Bunter sand and the beach sand was considerably less (only about 50% in each case). The profiles of the graphs of these two are very similar, with an increase in uptake between 1 and 3 hours, followed by a drop indicating a return to solution after 6 hours and remaining at equilibrium at around 50% uptake after that. Both calcium(ii) and magnesium(ii) were removed from solution to a greater extent by dithionite/citrate treated Bunter sand than by the untreated (Figures 5.7 and 5.8 respectively). Calcium(ii) shows the most marked contrast, with virtually all of it being removed by the dithionite/citrate reduced material compared with a slight release by the untreated Bunter sand. This probably represents an exchange reaction with sodium since the clays must be converted to their Na^+ form in the sodium dithionite treatment. The beach sand also gave out small quantities of calcium, presumably from the carbonate shell fragments which similarly must also be the source of the magnesium given out. Magnesium(ii) was not taken up to such a large extent as calcium(ii) by iron oxide-free Bunter sand (60% as opposed to 100%) and followed more closely the trend of the untreated red sand (50%).

To test whether or not the uptake by the beach sand represented an adsorption effect onto the quartz, or was due solely to precipitation of the metal carbonate (since the presence of shell fragments, albeit in small quantities, had been established) experiments using different grain sizes were carried out. Lead(ii) and nickel(ii) were chosen for these experiments because of their contrasting uptake by the unsieved beach sand (Figures 5.3 and 5.4). Figure 5.9 shows that there is no direct relationship between grain size and lead(ii) but that there is a strong grain size correlation for nickel(ii). Both nickel(ii) and lead(ii) had grain size relationships with untreated Bunter sand (Figure 4.6).

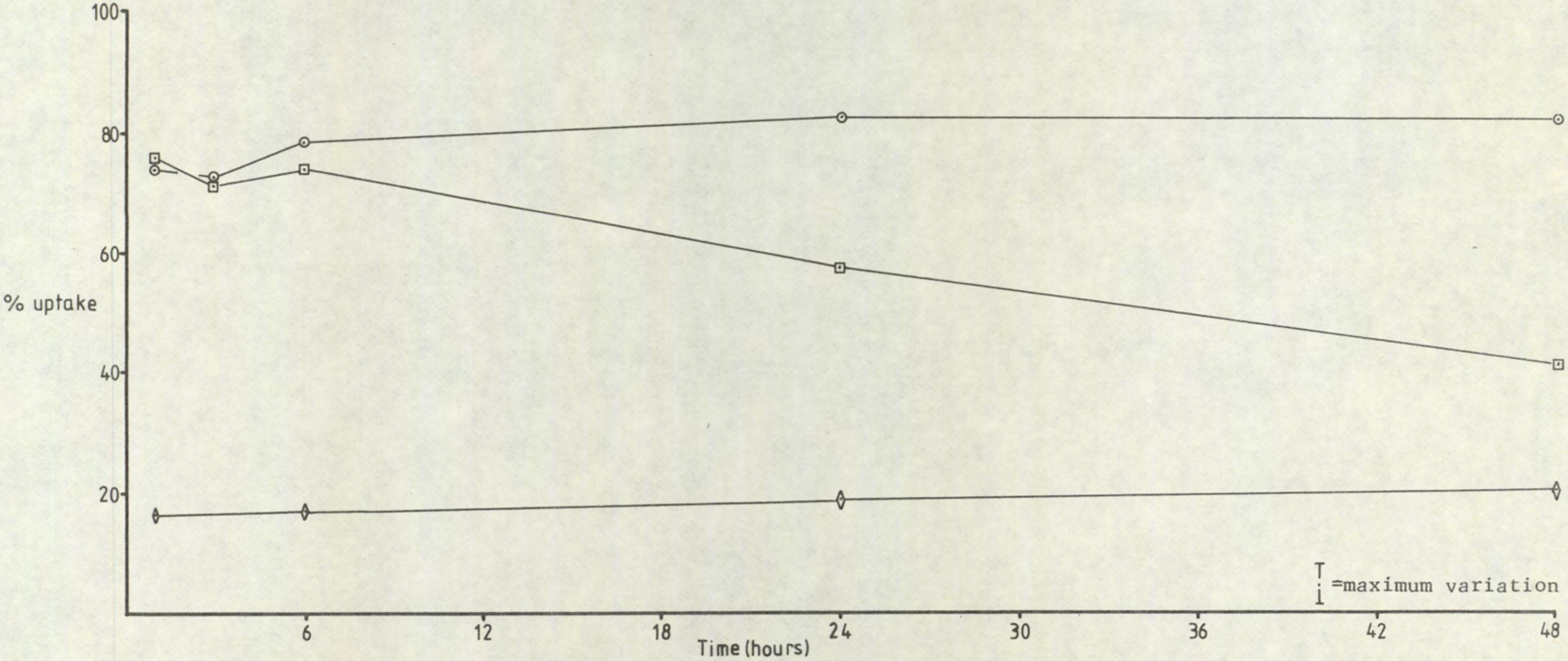


Figure 5.1. Uptake of cadmium(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

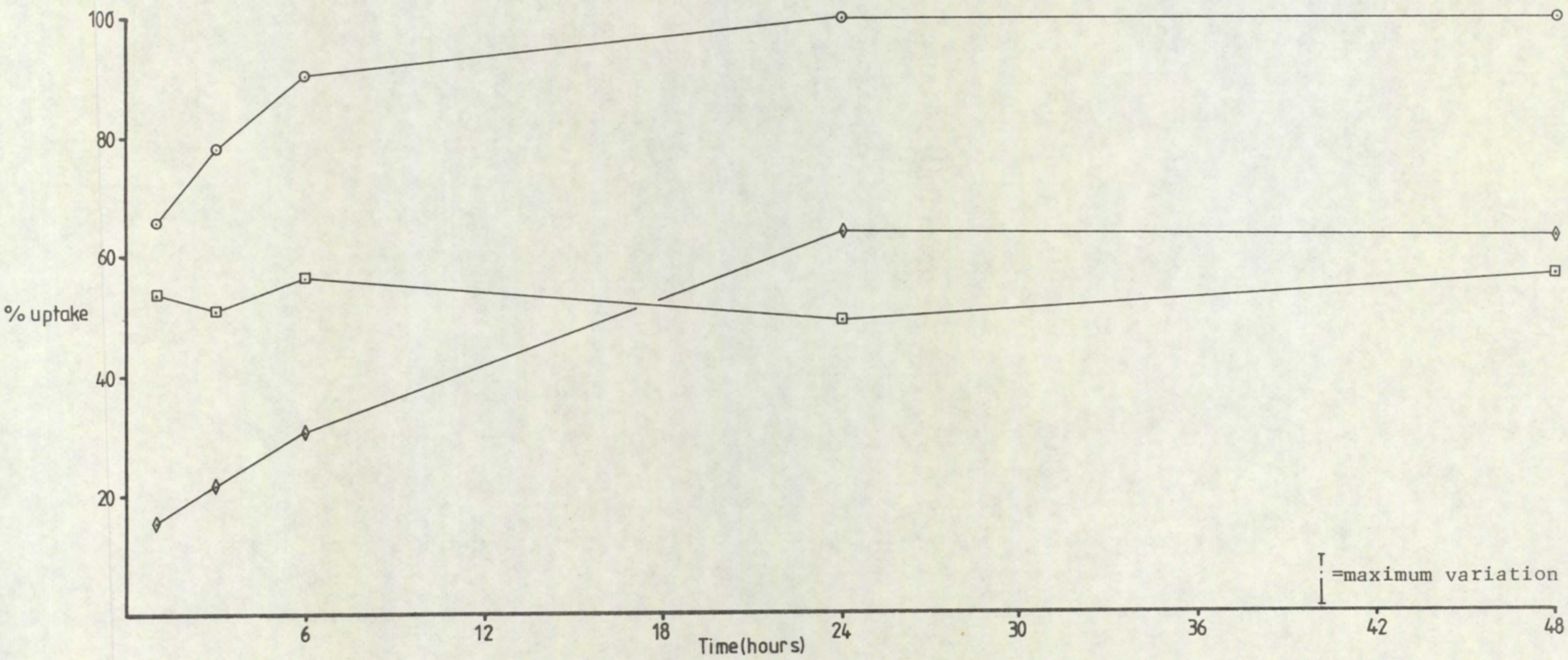


Figure 5.2. Uptake of copper(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

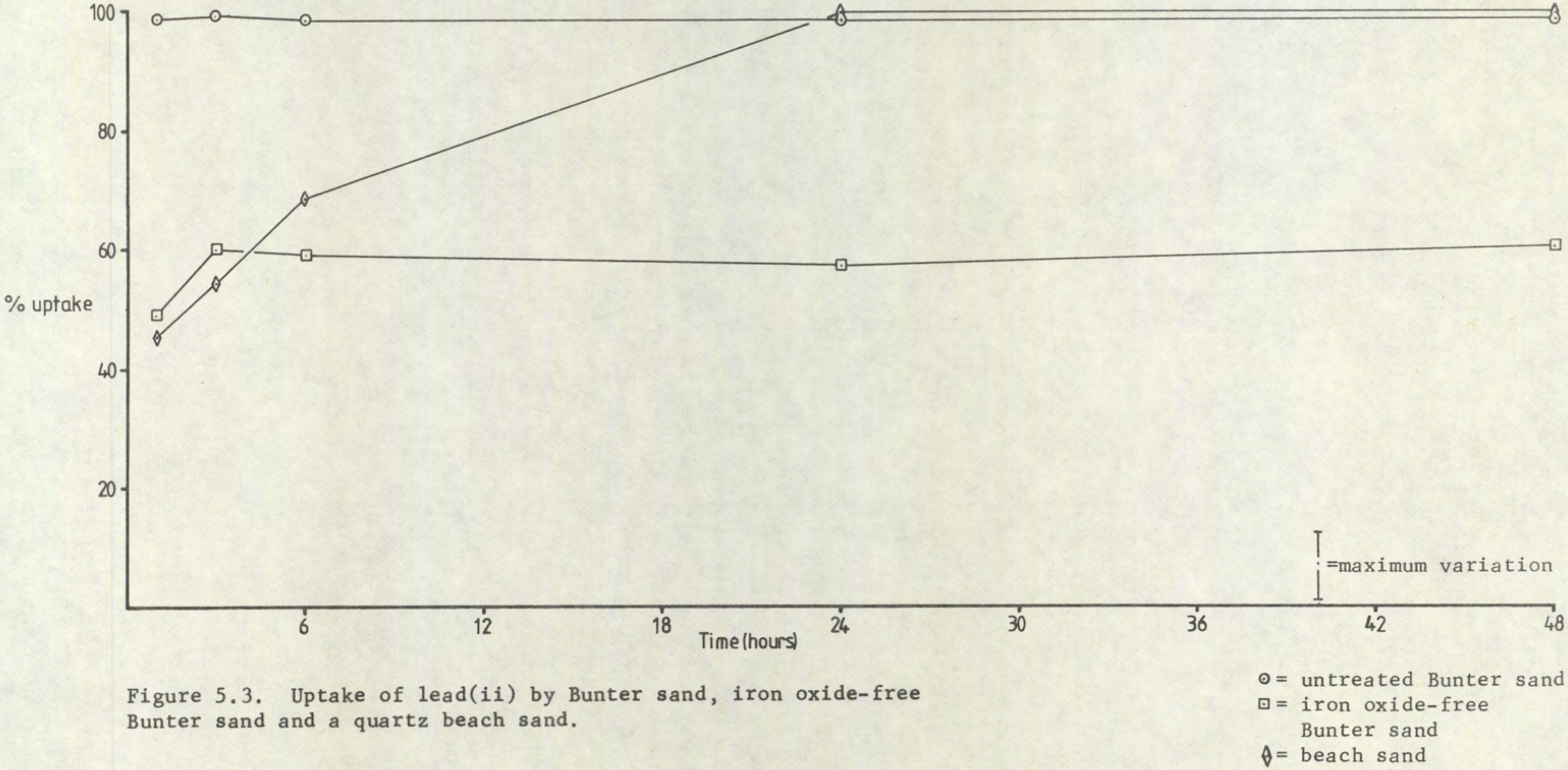


Figure 5.3. Uptake of lead(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

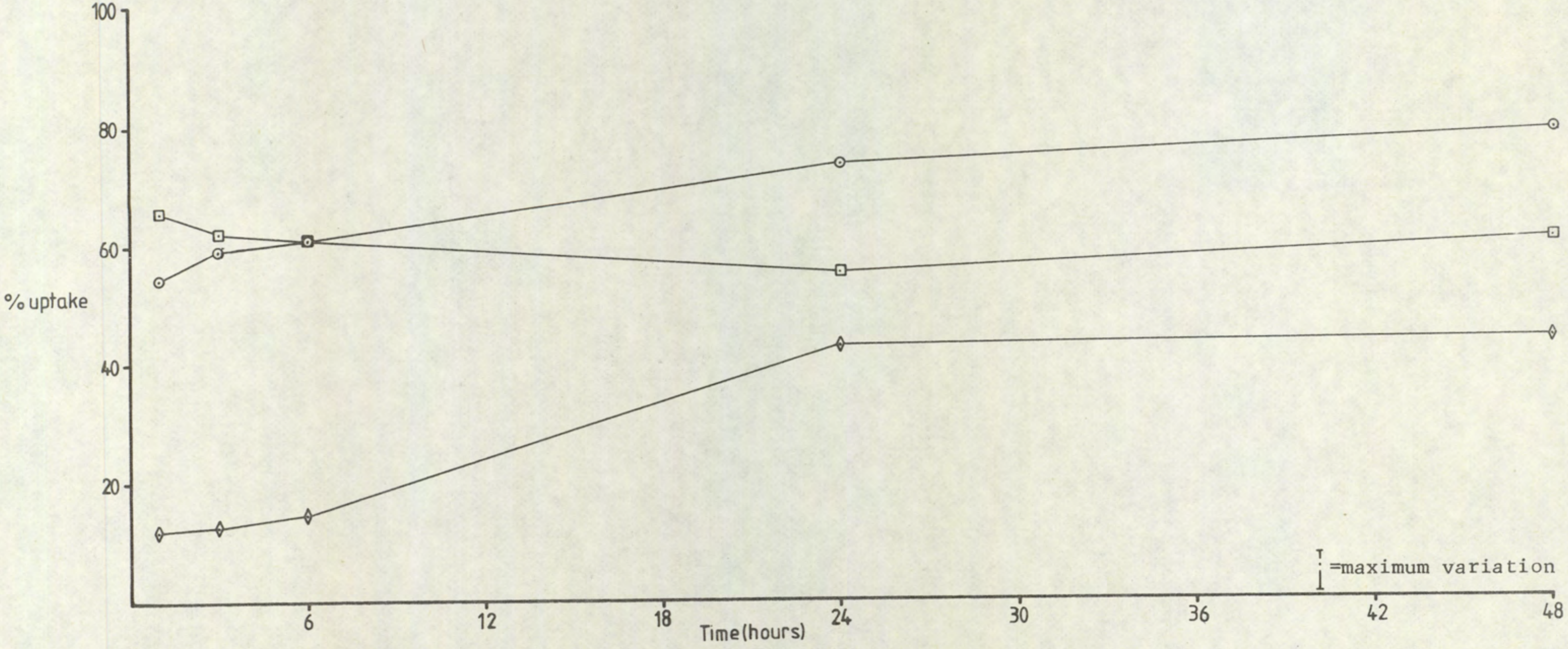


Figure 5.4. Uptake of nickel(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

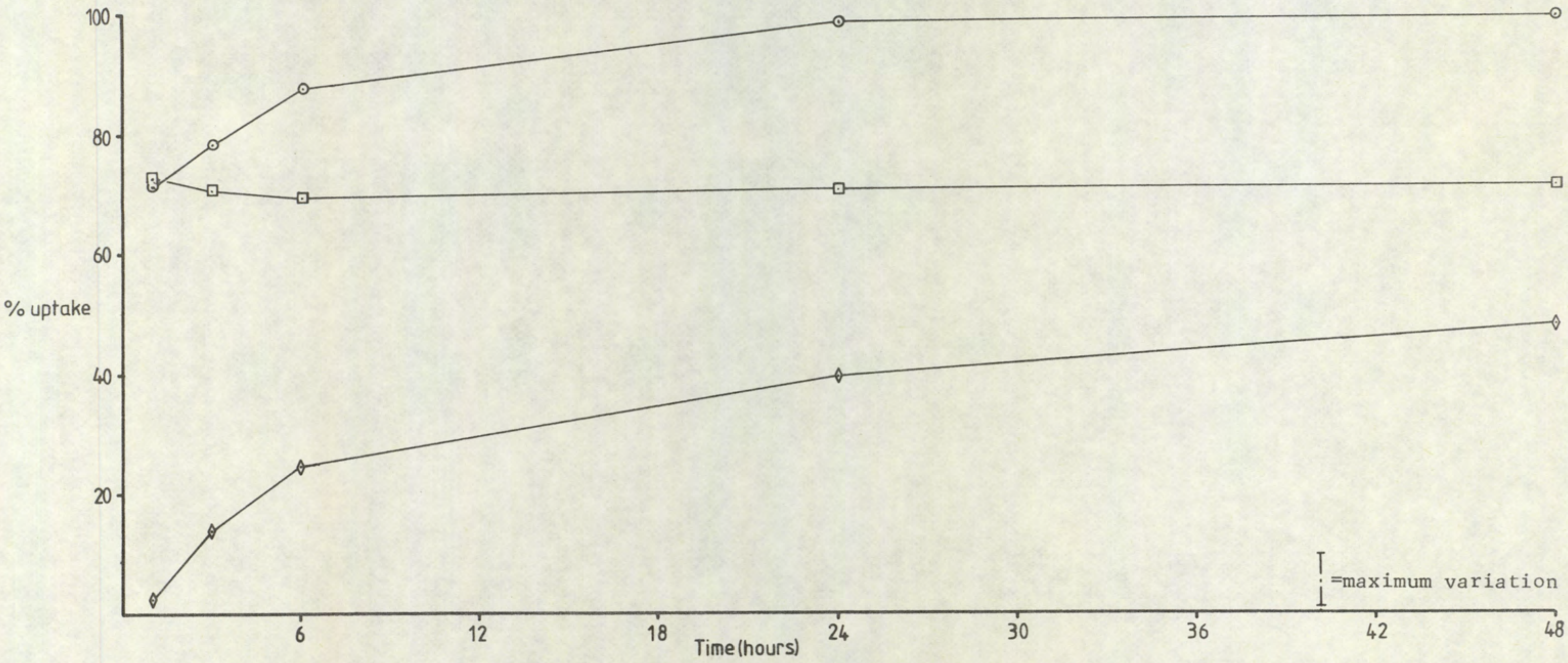


Figure 5.5. Uptake of zinc(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

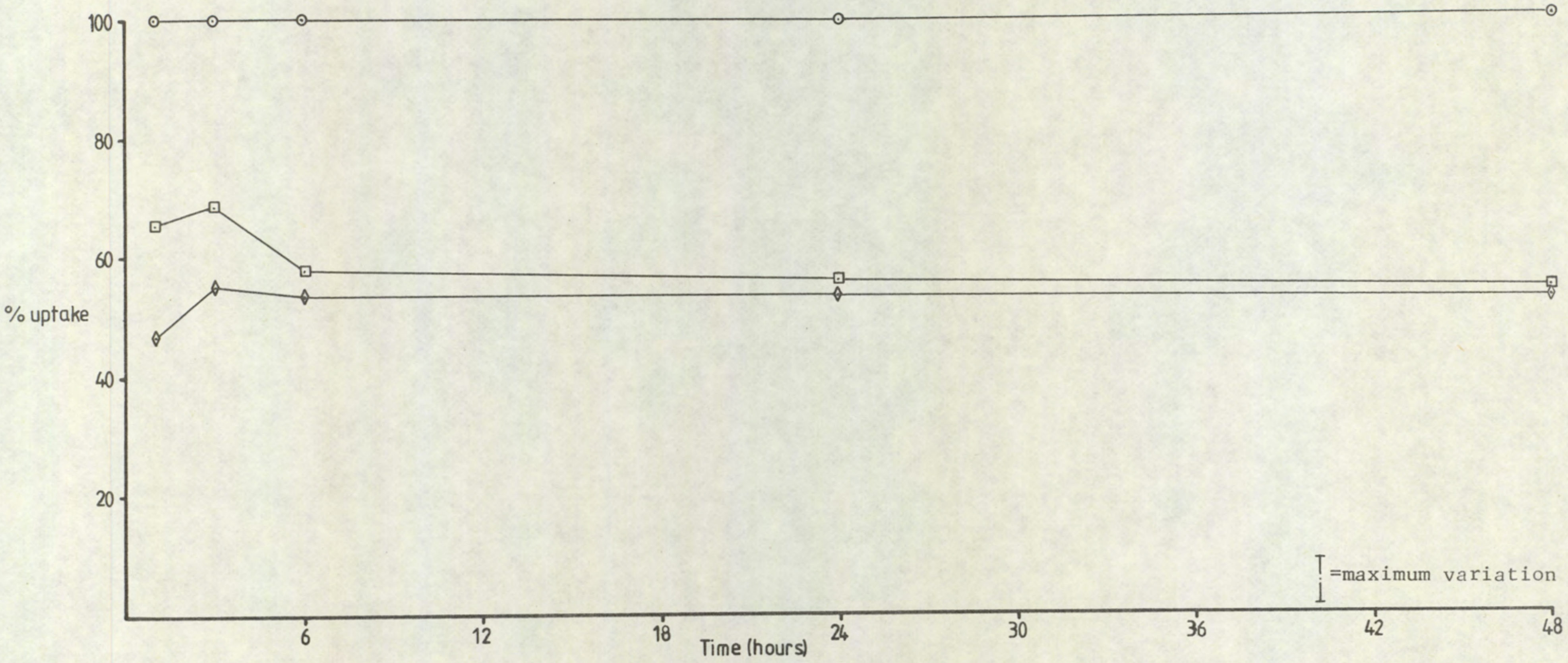


Figure 5.6. Uptake of iron(iii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

⊙ = untreated Bunter sand
⊡ = iron oxide-free Bunter sand
◊ = beach sand

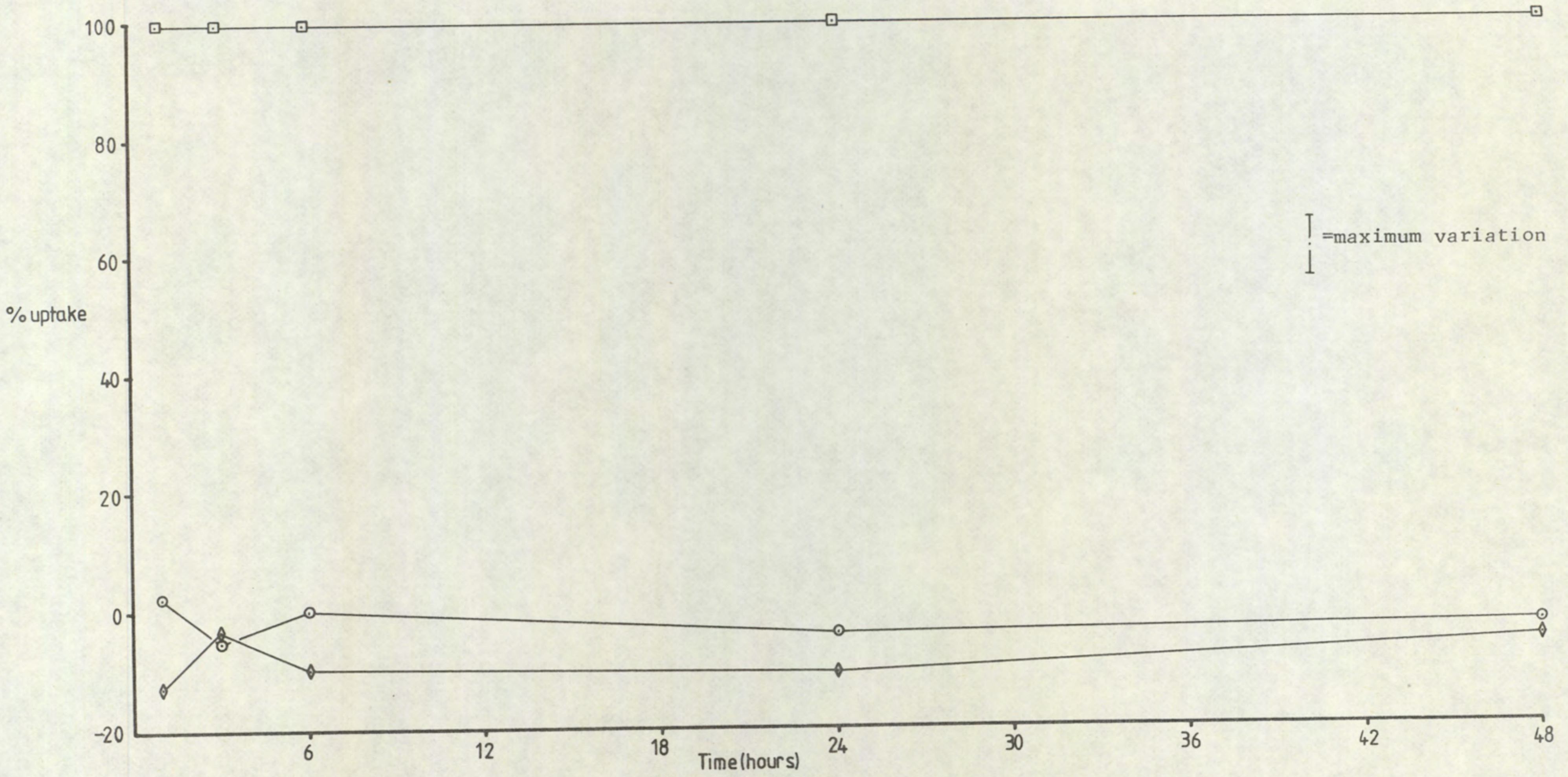


Figure 5.7. Uptake of calcium(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

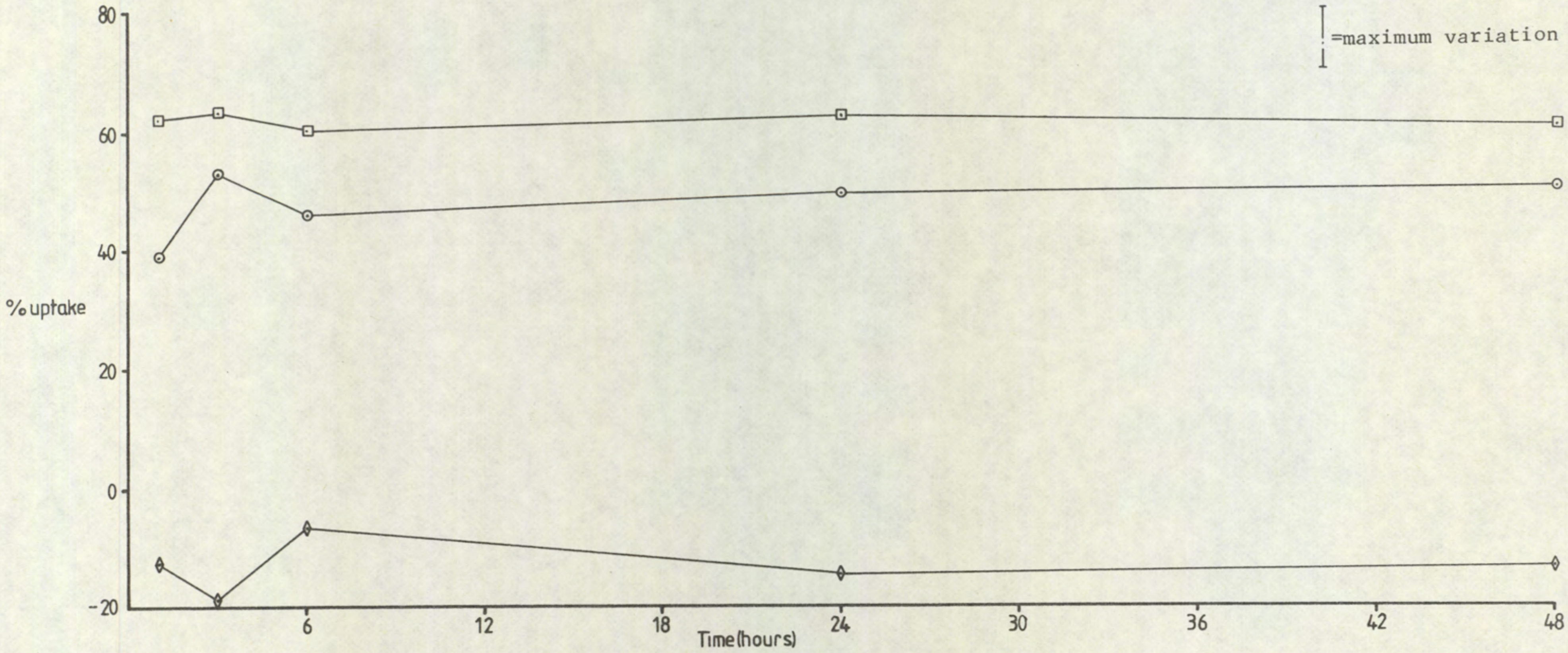


Figure 5.8. Uptake of magnesium(ii) by Bunter sand, iron oxide-free Bunter sand and a quartz beach sand.

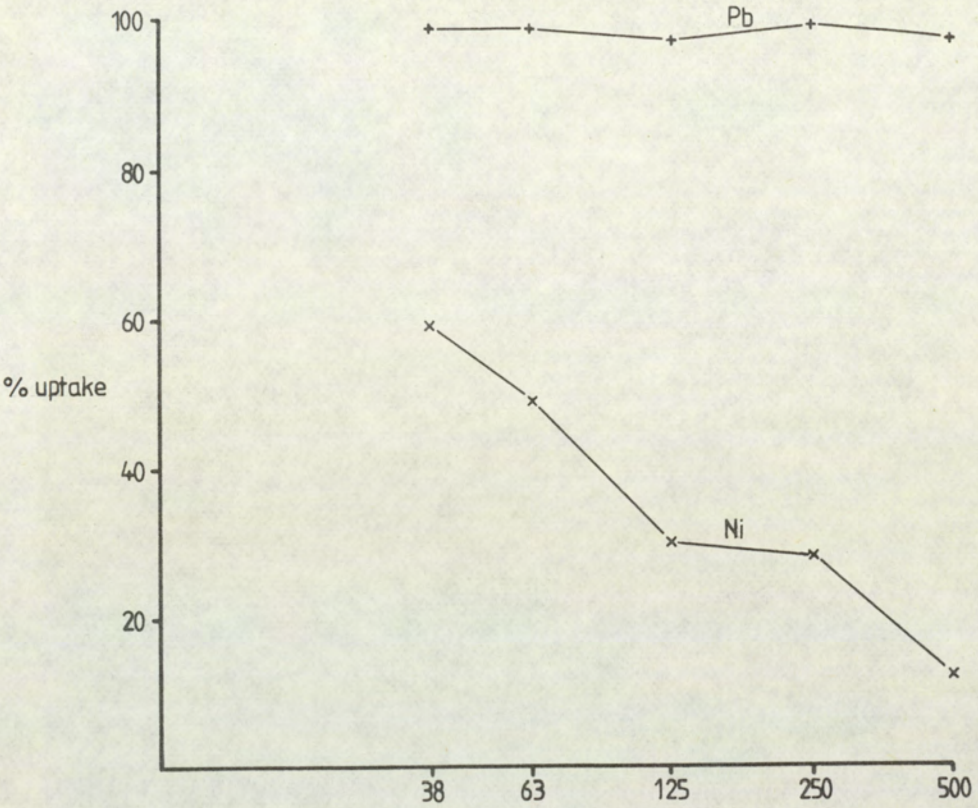


Figure 5.9. Variation in uptake of lead(ii) and nickel(ii) with grain size for a quartz beach sand.

5.4. Iron Oxides and Hydroxides

Because of the amorphous nature of the iron "oxide" coatings on red sands, it is not easy to determine their exact composition, hence the term sesquioxide has been used, inferring mixed hydrated oxides and hydroxides. In order to further assess the role played by the sesquioxides in metal uptake and to find if iron oxides and hydroxides are equally capable of removing metals from solution, two species were precipitated onto the previously described clean quartz beach sand. Rayleigh (1946) described the formation of both red and yellow sands from chalybeate water ($Fe(HCO_3)_2$). He described how the red sand is formed where the solution is close to the atmosphere with the yellow forming beneath. Hofer and Weller (1947) identified the two precipitates as lepidocrocite ($\alpha Fe_2O_3.H_2O$) and goethite. According to these authors, both precipitates are normally yellow but the lepidocrocite decomposes to haematite on drying to give the characteristic red-brown colour. Because of this it was decided to use goethite (which may also be expressed as $\gamma Fe\ OOH$) and haematite in the experiments.

Preparation of the chalybeate solution using Rayleigh's method of bubbling carbon dioxide through clean iron filings in distilled water gives very little control on the actual quantities of iron in solution. Consequently it was decided to use the method described by Fripiat and Gastuche (1952). In this method the chalybeate solution is prepared by mixing sodium carbonate and iron(ii) sulphate as given by the reaction

$$2H_2O + 2Na_2CO_3 + FeSO_4 \longrightarrow Fe(HCO_3)_2 + Na_2SO_4 + 2NaOH$$

In this way, the quantity of iron in solution could be directly controlled by the quantities of iron sulphate used. The iron content was adjusted so that when all had been precipitated it would amount to about 2.5% of the sand by weight (calculated as iron(iii) oxide) which compares closely with the $< 2000\mu m$ fraction of the Bunter sand (Appendix 2). To precipitate the iron, Fripiat and Gastuche (op.cit.) bubbled oxygen through the solution:

$$\tfrac{1}{2}O_2 + Fe(HCO_3)_2 \longrightarrow 2CO_2 + H_2O + FeOOH$$

It was found, however, that rather than passing oxygen through the solution,merely agitating the sand and solution in an open plastic bottle overnight on a rotary shaker provided sufficient oxygen for the reaction, at the same time ensuring an even precipitation over the quartz grains. A slight loss of iron resulted because of the formation of a thin layer of the precipitate on the sides of the bottle around the solution/air interface.

Haematite was precipitated directly from iron(iii) nitrate by the addition of small quantities of ammonium hydroxide. Continual stirring ensured an even coating on the quartz grains. An iron content of 2.5% as oxide was again aimed for. The sands prepared by both methods were filtered, using a Whatman No.1 filter and Buchner funnel, then washed, re-filtered and air-dried before use in the metal uptake experiments.

As in all the other experiments, the sand was mixed with 100μg/ml solutions of metals at a solution : solid ratio of 5:1. Four metals were chosen: lead(ii) because it showed nearly 100% uptake by the untreated Bunter sand and the beach sand; copper(ii) because it showed nearly 100% uptake by Bunter sand but only a moderate uptake by beach sand; cadmium(ii) because it showed a moderate uptake by Bunter sand but a low uptake by beach sand; and magnesium(ii) which showed only a 50% uptake by Bunter sand and an overall release by the beach sand. Thus these four metals afforded a wide range of uptake values in previous experiments.

The results for these experiments are given in Figures 5.10, 5.11 and 5.12 for cadmium(ii), copper(ii) and magnesium(ii) respectively. Lead(ii) showed 100% uptake after the first sample (1 hour) and did not re-release any throughout the experiments with goethite and haematite covered sands. The results for cadmium(ii) show the uptake by both the oxide and hydroxide coated material was greatly enhanced compared to the clean beach sand and greater even than the untreated Bunter sand. The haematite showed a slightly better uptake of cadmium(ii) than did goethite. For copper(ii), the uptake by haematite fell between that for the clean beach sand and untreated Bunter sand (Figure 5.11). Goethite, after an initial uptake greater than that for the clean sand, re-released some copper(ii) and eventually showed an uptake less than half that of the clean beach sand and one third that of the haematite. The iron oxide and hydroxide coated beach sands showed a slight uptake of magnesium(ii) (Figure 5.12) compared with the slight release by the clean beach sand. The two iron species took up the metal in similar quantities but considerably less than that by the untreated Bunter sand (17% compared with 50%).

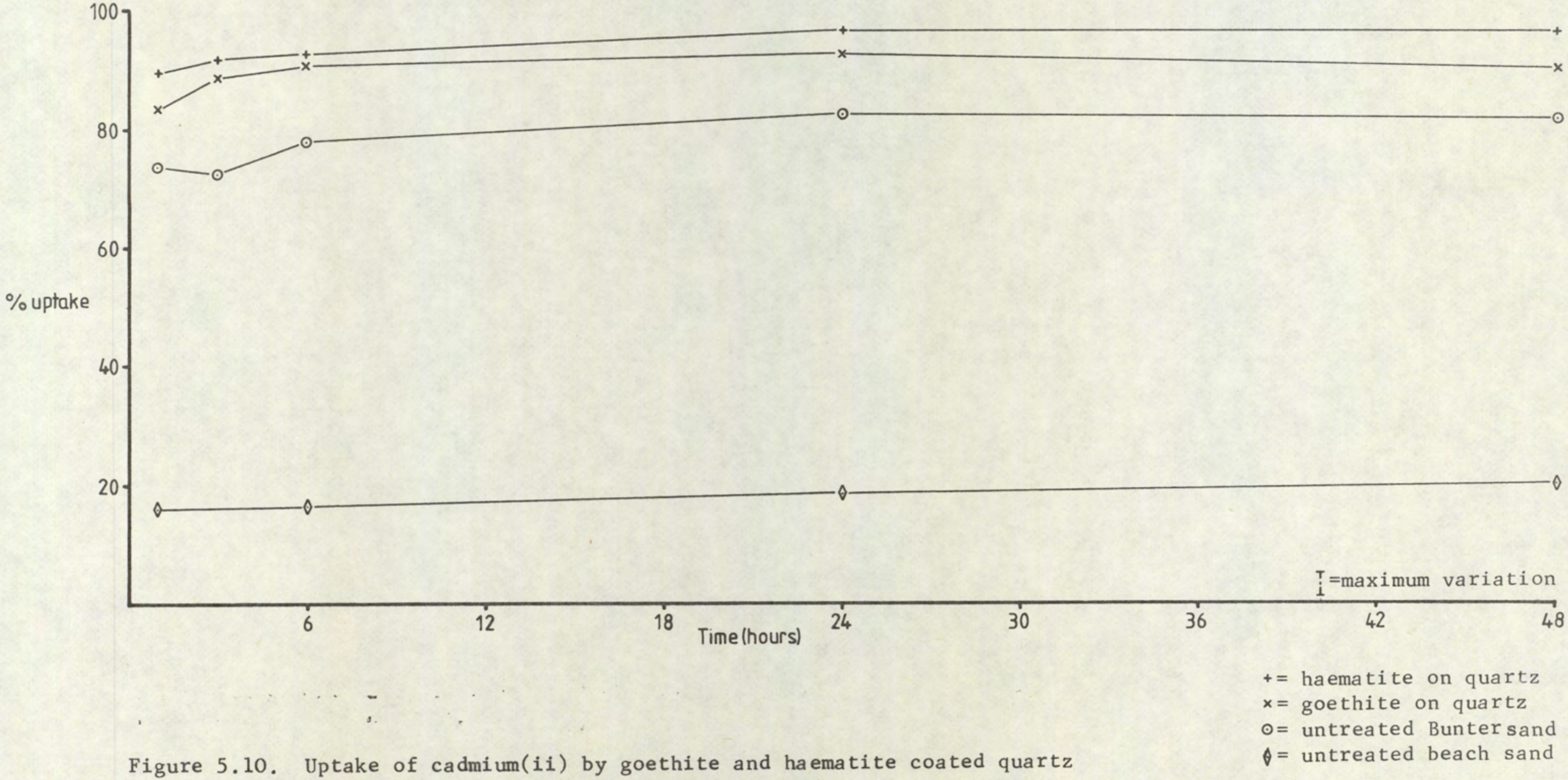


Figure 5.10. Uptake of cadmium(ii) by goethite and haematite coated quartz sand compared with untreated Bunter sand and beach sand.

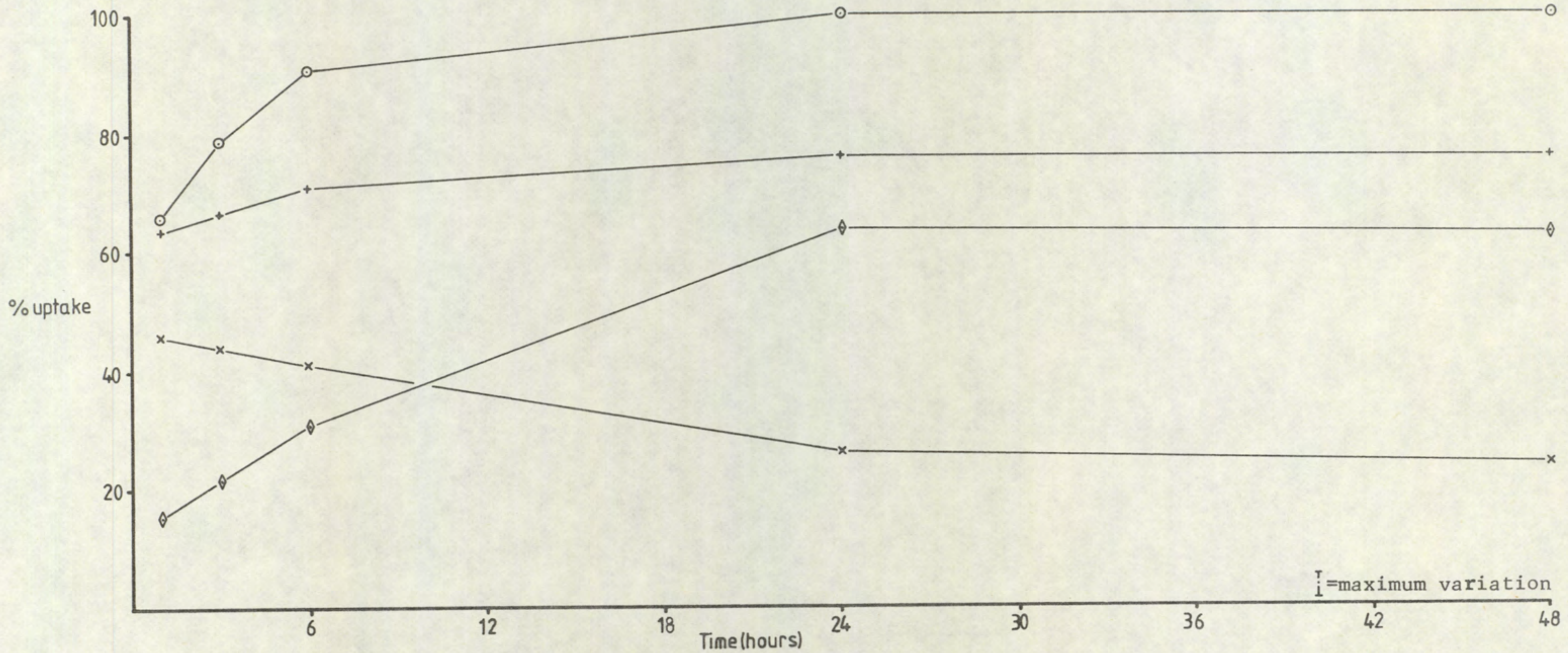


Figure 5.11. Uptake of copper(ii) by goethite and haematite coated quartz sand compared with untreated Bunter sand and beach sand.

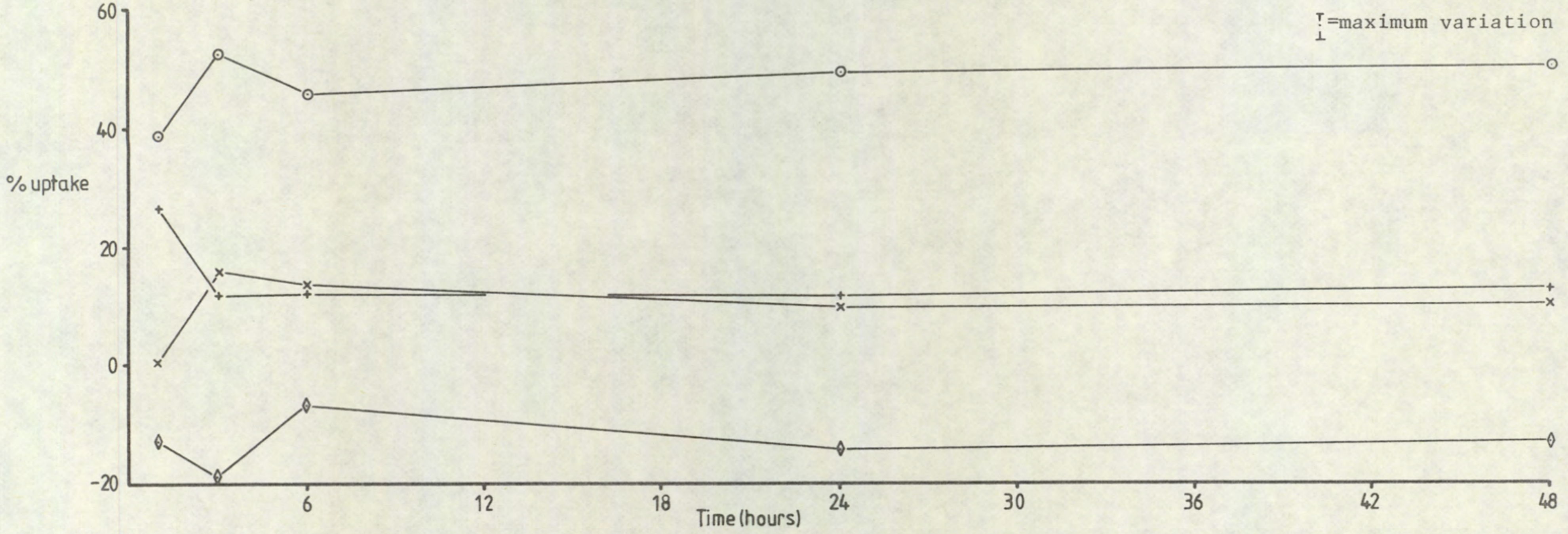


Figure 5.12. Uptake of magnesium(ii) by goethite and haematite coated quartz sand compared with untreated Bunter sand and beach sand.

5.5. Discussion

Cation Exchange and Carbonate Precipitation

The results of the chemical extractions performed on the metal treated Bunter sand (Table 5.1) show that only small quantities of each metal remain in a soluble form after equilibriating with the sand. These results are in general agreement with Ross (1978 and 1980), although she found greater quantities of copper and lead in the uppermost part of the metal leachate irrigated Greensand column. Taken over the whole depth of the lysimeter, however, the amounts of soluble metals reported by Ross (op.cit.) are similar to those found for the disturbed Bunter sand samples used here.

McWhinnie *et al* (1981), investigating the uptake of metals on montmorillonite suggested that at least part of the metal taken up by the clay may be labile and as such may be remobilised by subsequent irrigation by uncontaminated water. Ross (1980), however, indicated that the metals remaining in the soluble phase clearly parallel the exchange phase distribution. This is interpreted to mean that, with increasing depth below a leachate source, ~~on~~ as the concentrations of metals in the sand decreases so too will the soluble metal. Since the Bunter sand mineralogically more closely resembles the Lower Greensand than a pure clay it may be assumed that remobilisation of metals will not cause serious problems.

The quantities of metals occupying exchangeable cation sites are considerably higher than those for the Lower Greensand (Ross, op.cit.) as are the values for the carbonate fraction. The results given in Table 5.1 show that carbonate precipitation plays a greater role in removal of all the metals than does cation exchange. This is in agreement with Ross's results for all but nickel and cadmium, although it can be seen that here the difference in relative importance for these two phases is less than for the other metals.

The large imbalence in favour of precipitation over cation exchange agrees with the results of Griffin et al (1977) who worked on metal uptake by clay columns. They showed that there was no significant difference in attenuation of heavy metals by three clays from a landfill leachate despite differences in cation exchange capacities. By running the same leachate through a column of sand with no cation exchange capacity and still finding significant reductions in heavy metal concentrations (100% removal in the case of lead) they attributed the uptake to precipitation either as carbonate associated with the high bicarbonate value of the leachate or to hydroxide formation due to high pH (6.9-7.2). Hydroxide formation is unlikely to be important for the removal of the metals here because of the low equilibrium pH values (Tables 3.6 to 3.10) (Hahne and Kroontje, 1973; Sylva and Brown, 1980).

The solutions used here are not likely to have a high bicarbonate content unlike the leachate described by Griffin et al, nor is there any microbial action releasing CO_2 to the solution (Ross op.cit.), which implies the source of carbonate must lie within the sand itself. Whereas the Lower Greensand contains some 8% calcite and minor aragonite (Ross op.cit.) the Bunter Sandstone has no significant crystalline calcite as shown by X-ray diffraction. However, the small quantities of calcium eluted from the untreated sand, in particular with lower pH (Tables 3.2 to 3.4) are most likely due to dissolution of minor quantities of calcite. Edmunds and Morgan-Jones (1976) report groundwaters from Bunter Pebble Beds with

Ca and HCO_3 as the predominant ions despite being undersaturated with respect to calcite and dolomite.

The accuracy of the results given here must be questioned. The total weight of lead(ii) per gramme of sand given in Table 5.1 is 662µg whereas the maximum possible, assuming 100% uptake by the three phases included here, from 100ml of a 100µg/ml solution is only 500µg/g for the 20g samples used. In particular any inacuracies are compounded for the carbonate analyses, where the sample size is small (5g) in relation to reagent volume (200ml), such that the lead concentration falls close to the lowest value within the linear range for flame atomic absorbtion spectroscopy (Appendix 1). A further constraint on the interpretation of these results is the assumption that all the metals taken up in exchange reactions are released by excess ammonium concentrations. A non-reversible uptake by clays, even in the presence of stronger solutions of cations known to be competitive has been described by Hodgson (1960) who also showed that Co(ii) would exchange with other transition metals but not with ammonium.

It does appear, however, that whilst experimental error must be accepted to be significant, carbonate precipitation is more important than cation exchange, which is itself a major factor in metal uptake. The method described in Section 5.2, however, does not differentiate between exchange reactions on the clays and iron sesquioxides.

Effects of Deferrification

In chemically removing the iron oxides from the Bunter sand it should be possible, by comparing the uptake of heavy metals by iron oxide-free and untreated sand, to determine the role played by the surface iron species. However, the effect of the chemical removal on the deferrified residue must first be taken into account before any comparison can be made.

Aquilera and Jackson (1953) found that the removal of haematite and goethite, using a sodium dithionite/citrate method with a chelating agent, caused a decrease in the exchange capacity of iron containing layered silicates but increased the exchange capacity of kaolinitic soils. Summer (1962, 1963) compared the properties of china clay and a kaolinitic soil after deferrification by sodium dithionite according to the method described by Mitchell and Mackenzie (1954). He recorded an increase in negative change attributable to the freeing of exchange positions previously covered by the iron oxides. He concluded that the observed change in cation exchange capacity is dependent on the pH at which the determination is carried out and that the surface properties of the clays were not altered. Shuman (1976) found that the adsorption of zinc by soil clays was directly related to their cation exchange capacity and the amounts of zinc taken up after deferrification using the buffered sodium dithionite/citrate method of Mehra and Jackson (1960) were generally greater than for untreated clays.

Table 5.2 shows that the sodium dithionite/citrate treated Bunter sand shows a very slightly reduced cation exchange capacity which gives no reason to suspect that the reagent strength and reaction time used here had any adverse effect on the properties of the residue. One aspect of using these reagents to be considered is that the monovalent sodium is likely to saturate any exchange sites due to its high concentration in solution. On subsequent treatment, divalent ions are likely to enter exchange reactions more easily than they would with the untreated Bunter sand because of the greater affinity for divalent ions for exchange sites than the monovalent sodium.

Iron Sesquioxide and Clay Fractions

Figure 5.1 shows an initial uptake of cadmium(ii) by the iron oxide-free Bunter sand equal to that by the untreated red sand, with a subsequent release of the metal three hours into the experiment. The cause of the subsequent re-release of the metal is unclear. One possible explanation is that following an initial uptake of cadmium(ii) by the clays by ion exchange onto weak negative sites such as at the broken edges of the clay lattice, the metal is incorporated into the iron sesquioxide lattice, possibly by isomorphous substitution (Nalovic et al, 1976). In the absence of the iron species the cadmium equilibriates with displaced sodium or H^+ causing its release into solution. McWhinnie et al (1981) report a release of copper after reaching an initial equilibrium after 24 hours on montmorillonite. They suggest that at least part of the metal remains labile after being taken up.

The difference in uptake between that by the beach sand and that of the deferrified and untreated Bunter sands shows the importance of the iron oxide and clay fractions. The uptake by the beach sand represents either adsorption onto negatively charged sites on broken edges of the quartz grains or, more likely, carbonate precipitation. Since carbonates are present in only small quantities in the beach sand (shell fragments are apparent under microscopic examination, but X-ray diffraction does not confirm their presence) an analogy with the Bunter sands is not unreasonable. Table 5.1 shows that the uptake of cadmium(ii) by untreated Bunter sand by ion exchange and carbonate precipitation is quite similar. It is possible that given more time the cadmium equilibrium for the deferrified Bunter sand would more closely resemble that of the beach sand.

The trends for copper(ii) uptake differ from those for cadmium(ii) for each of the three sands (Figure 5.2). The uptake of copper(ii) by the untreated Bunter sand is not as rapid as that for cadmium(ii), with equilibrium attained only after 6-24 hours as opposed to the first 3 hours. The deferrified Bunter sand does not elute copper after its initial uptake, nor does that uptake equal the untreated sand. The beach sand differs in that it shows a higher uptake of copper(ii) than cadmium(ii) and does not equilibriate until between 6 and 24 hours.

If it is assumed that the uptake of copper(ii) by the iron oxide-free Bunter sand is due to cation exchange and precipitation (suggested by the initial cadmium uptake) then the extra uptake by the untreated Bunter sand represents that due to the iron oxides. This implies that the removal of the metal ion from solution by the iron species is not as rapid as by clay ion exchange and supports the previous suggestion for cadmium(ii) that metal are taken up more slowly by the iron sesquioxides. In the case of cadmium(ii), the graph (Figure 5.1) remains level as the uptake of the metal by the iron species balances its elution from the clay fraction.

An alternative explanation assumes that any carbonate present in the original Bunter sand is dissolved during the sodium dithionite/citrate treatment and that the subsequent uptake is due to cation exchange alone. By combining the uptake of the iron oxide-free Bunter sand with the beach sand, the resultant graph would look similar to that for the uptake by the untreated Bunter sand (although it would actually total more than 100% uptake after 24 hours). A similar situation applied for zinc(ii) (Figure 5.5), as the profiles for its uptake are very similar to that of copper(ii). This analogy would suggest that the iron sesquioxides play no part in the uptake of copper(ii). The experimental uptake of copper(ii) by Fe_2O_3 precipitated on the beach sand shows a very similar profile to that for the untreated Bunter sand (Figure 5.11) which is taken to indicate that this is not the case.

The profiles of the graphs for uptake by the beach sand of copper(ii), lead(ii), nickel(ii) and zinc(ii) are all similar, although the total uptake for lead is significantly higher than that for copper (100% and 60%) which is in turn greater than that for nickel and zinc (40% in each case). These data confirm the results of the selective leaching tests (Section 5.2) which showed the association of metals with the carbonate phase in the order:

$$Pb > Cu > Zn > Cd > Ni .$$

This order corresponds closely with the order of retention of the metals by Lower Greensand reported by Boreham et al (1975) who noted that the order of elution from their sand columns followed the order of the metal carbonate solubilities. The small cation exchange capacity measured for the beach sand (Table 5.2) and the grain size dependent uptake of nickel(ii) (Figure 5.9) do suggest that adsorption onto the quartz grains may contribute to a proportion of the uptake by the beach sand.

Comparison of the uptake profiles for the deferrified Bunter sand (Figures 5.1 to 5.5) with the exchangeable metals (Table 5.1) does not provide as good a match as that for the carbonate phase.

Cadmium(ii) shows a slightly higher uptake by the deferrified Bunter sand than the other metals, in the initial stage at least, which agrees with results from the ammonium acetate extraction. Cadmium is shown to be released from exchange sites (Figure 5.1), so it would not therefore be expected that at equilibrium the level of cadmium in clay exchange sites would be less than that for the other metals. As pointed out previously the procedure adopted to measure exchangeable cations does not differentiate between sites on clays and iron sesquioxides. If the uptake by the iron species is an exchange reaction, albeit slower than that of the clay fraction, the result could hold true. Furthermore, the ammonium acetate method assumes that all the metals taken up are displaced by ammonium, which Hodgson (op.cit.) found not to be the case. Thus whereas zinc(ii) uptake by the dithionite/citrate treated sand is greater than that for either copper(ii), lead(ii) and nickel(ii) the ammonium citrate method suggests that zinc(ii) is taken up least of all the metals by an exchange reaction.

The uptake of iron(iii) is greatly reduced by the removal of the iron sesquioxides (100% to 60%, Figure 5.6). This shows their strong tendency to adsorp or precipitate Fe^{3+} ions. The similarity in both profile and magnitude of the graphs for the deferrified Bunter sand and the beach sand implies that precipitation is the only mechanism responsible for removal and that iron(iii) does not enter into exchange reactions with the clays present in Bunter sands.

The complete removal of calcium(ii) from solution by the dithionite/citrate treated sand compared to the slight elution from the untreated Bunter sand must be a function of the ease with which Ca^{2+} replaces Na^{+} on exchange sites. The inability of the untreated

Bunter sand to remove any calcium(ii) is evidence that all the exchange sites in the untreated material are saturated with respect to calcium. The uptake by the deferrified material must represent ion exchange alone since the beach sand shows no calcium(ii) removal. Because no other metal demonstrates a 100% uptake by cation exchange on the dithionite/citrate treated material it appears that calcium(ii) has the greatest affinity of all the metals on a weight basis for exchange sites.

The graphs for magnesium(ii) do not contradict this as Figure 5.8 shows only 60% magnesium removal by the clay fraction. Again, as none of the metal is removed by the beach sand it can be assumed that no precipitation or adsorption onto quartz grains took place.

Iron Oxides and Hydroxides

The association between heavy metals and iron and manganese oxides was first recognised in deep sea nodules (Goldberg, 1954). Research with hydrous ferric oxide established heavy metal adsorption and the strong pH dependence similar to that for cation exchange on clays (Morgan and Stumm, 1964; Dyck, 1968; Gadde and Laitiner, 1973; Kinniburgh et al, 1976). The brief series of experiments described in Section 5.4 was not designed to add significantly to that work, but to confirm the implication from the preceeding experiments (Section 5.3) that the iron sesquioxides may play a significant part in metal uptake by Bunter sand. Such an association has been established in a glacial gravel aquifer (Ku et al) and the Lower Greensand (Ross, 1978) influenced by landfill leachates.

That lead(ii) was completely removed by haematite and goethite covered beach sand in less than 1 hour confirms a rapid adsorption by the iron species since the untreated beach sand took 24h to achieve 100% lead(ii) uptake (Figure 5.3). Cadmium(ii) was removed equally efficiently (c. 90%) by both the goethite and haematite covered sand which is substantially greater than the removal by the untreated sand (Figure 5.10). The initial rapid uptake (< 1 hour) is followed by a slow increased uptake until apparent equilibrium after 24 hours. This conforms with the suggestion of two mechanisms active in metal uptake. A similar reaction occurs for copper(ii) uptake on haematite but not on goethite (Figure 5.10). The trend is similar to that demonstrated by the untreated Bunter sand but not to that of the deferrified Bunter sand (Figures 5.1 and 5.2). Hodgson (1960) reported a two-fold uptake of heavy metals on montmorillonite, with an initial, reversible, exchange reaction followed by a non-reversible uptake, possibly an incorporation into the crystal lattice. Ross (1978) demonstrated that the order of substitution of heavy metals into the crystalline iron oxide phase of the Lower Greensand can be shown to be a function the lattice energy contributions of the metal ions. The lower uptake of magnesium(ii) without the slower secondary uptake suggests that it enters into an exchange reaction only.

Chapter 6. The Effects of Other Leachate Constituents on Metal Uptake by Bunter Sandstone

6.1. Experimental Procedure and Results

Leachates are complex solutions and have a wide variety of inorganic and organic constituents (Table 1.1). Some constituents may compete with the heavy metals for adsorption or exchange sites or affect their uptake in other ways. In order to assess the effects of some of the commoner constituents of domestic landfill leachates on heavy metal uptake a series of experiments was conducted along the same lines as those already described, but introducing other inorganic and organic species into the solutions. Because of the large range of combinations of heavy metals and leachate constituents, it was necessary to limit them in number. Lead(ii) was used because it is the most readily taken up heavy metal of those investigated, on a weight basis at least, and any noticeable effects on this metal should occur among the other heavy metals. To substantiate this and to provide further results where lead(ii) showed little or no significant changes from the single metal solution, other heavy metals were used when needed.

The experiments were carried out using the same procedure as outlined previously, using solutions of 100μg/ml lead(ii) as nitrate. In the first instance a series of cations was chosen to compete with lead, each at a concentration of 100μg/ml. In each case the competing cation was added to the solution as its nitrate before mixing with the sand. The solution : solid ratio was 5:1 as in all previous experiments and the sand used was the <2000μm fraction of the disaggregated Bunter sand from Cheslyn Hay.

The Alkaline Earth Metals

The alkaline earth metals were used in the experiments because they are common in leachates (Table 1.1) and are species likely to fill clay cation sites (Grim, 1962). The experimental results (Table 6.1) show that there was no appreciable reduction in lead(ii) uptake from solutions containing either calcium(ii), magnesium(ii), potassium(i) or sodium(i). Indeed, with the exception of sodium(i), there was a slight increase in lead(ii) uptake from each solution. This increase is unlikely to be of any significance because the levels of lead remaining in solution were too close to the detection limits of flame A.A.S. to be reliably accurate.

The Heavy Metals

Copper(ii), iron(iii) and nickel(ii) were selected for these experiments. From the results of the previous experiments, copper(ii) and iron(iii) might be expected to have most effect on lead(ii) uptake because they are both strongly taken up from their respective single-metal solutions. Nickel(ii), being less strongly taken up, should perhaps show less effect on lead(ii) uptake.

After 48 hours only copper(ii) and nickel(ii) caused a reduction in lead(ii) uptake (Table 6.1), with 100µg/ml copper causing an 11% reduction compared with 7% for 100µg/ml nickel. However, in the early stages of the experiment, iron(iii) had a considerable effect (Figure 6.1), the lead uptake being only 71% after one hour compared with 99% for the lead-only solution. By 24 hours into the experiment, the lead uptake from the lead(ii)/ iron(iii) solution had reached that of the lead-only solution, in fact surpassing it slightly. The graphs for lead uptake from the lead(ii)/copper(ii) solution are also given in Figure 6.1.

The effects of lead(ii) on the uptake of those metals it was competing against are given in Table 6.2 for copper(ii), nickel(ii) and iron(iii) and in Figures 6.2 to 6.5 for calcium(ii), magnesium(ii), potassium(i) and sodium(i) respectively. Comparison of Table 6.2 with Table 6.1 shows that, on an equal weight basis, lead(ii) caused a greater decrease in the uptake of copper(ii) and nickel(ii) than the reciprocal effect of those two metals on lead(ii) uptake. The presence of lead(ii) had no appreciable effect on iron(iii) uptake.

Ammonium Ion

The effects of lead(ii) and ammonium ions on the uptake or release of the alkaline earth metals is shown in Figures 6.2 to 6.5 and for comparison their uptake from single metal solutions. In each experiment, the alkaline earth metal was present at an initial concentration of 100μg/ml, as were the lead(ii) and ammonium in their respective mixed solutions. There was no net uptake or release of calcium(ii) from its single-metal solution (Figure 6.2) but in the presence of lead(ii) and even more so ammonium, there was a net release, as represented by a negative value for the % uptake. Both lead(ii) and ammonium produced a decrease in magnesium(ii) uptake (Figure 6.3). For potassium (Figure 6.4) there was approximately 35% uptake from the single-metal solution but in the presence of lead(ii) and to a lesser extent ammonium there was an increase in uptake after 48 hours. However, in the early stages of the experiment ammonium caused a release of potassium(i) into solution, an effect also shown for magnesium(ii).

45% of sodium(i) was removed from its single-metal solution but less than half that amount was taken up in the presence of ammonium (Figure 6.5). In competition with lead(ii), there was a steady release of sodium for the first 6 hours of the experiment, after which the level remained constant at about 15% release.

The effects of ammonium in competition with the heavy metals is shown in Table 6.3. For copper(ii) and iron(iii) there was no discernible change in uptake. Lead(ii) showed a slight increase in uptake from 99% to 100% but it is not possible to assign any relevence to this because the actual quantities of lead(ii) remaining in solution were too close to the flame A.A.S. limits of sensitivity. Cadmium(ii) and to a lesser extent zinc(ii), however, both showed decreases. Cadmium(ii) uptake was reduced by 12.2% and zinc(ii) by 2.0%. Nickel(ii) appears anomalous among the heavy metals tested in that it showed a percentage increase of 5.1 in the presence of ammonia.

Chloride

The chloride ion is a very common anionic species in both groundwater and leachates (Table 1.1), and although unlikely to compete for adsorption sites, its presence was tested for interference on lead(ii) uptake to see if it might act in other ways. The chloride content of the solutions used was varied, using 10, 100 and 1000µg/ml concentrations. These were prepared using sodium chloride because it had already been shown that sodium(i) had no appreciable effect on lead(ii) uptake (Table 6.1). The results show that there is very little difference in lead(ii) uptake (Table 6.4).

Table 6.1. Effect of competing cations on lead(ii) uptake by Bunter sand.

	Competing cation *	% uptake lead(ii) (48 hours)	% reduction in lead(ii) uptake
	-	90	-
Alkaline Earth Metals	Ca^{2+}	100	nil
	Mg^{2+}	100	nil
	K^+	100	nil
	Na^+	99	nil
Ammonium	NH_4^+	100	nil
Base Metals	Fe^{3+}	100	nil
	$Fe^{3+} + NH_4^+$	100	nil
	Cu^{2+}	88	11
	Ni^{2+}	92	7

(* Each at 100µg/ml)

Table 6.2. Competition effects of lead(ii) on the uptake of other metals by Bunter sand.

Metal	% uptake (48 hours) single solution	% uptake (48 hours) vs. Pb(ii)	% reduction in uptake
Cu(ii)	100	56	44
Ni(ii)	79	42	47
Fe(iii)	100	100	nil
Fe(iii)*	100	100	nil

* In competition with Pb(ii) and NH_4^+, each at 100µg/ml

Table 6.3. Effect of ammonium on metal uptake by Bunter sand.

Metal	% uptake (48 hours)		% difference
	single solution	vs. NH_4^+	
Cd(ii)	82	72	-12.2
Cu(ii)	100	100	nil
Fe(ii)	100	100	nil
Ni(ii)	79	83	+ 5.1
Pb(ii)	99	100	+ 1.0
Zn(ii)	100	98	- 2.0

Table 6.4. Effect of chloride concentration on lead(ii) uptake by Bunter sand.

Chloride Concentration (ug/ml)	% uptake Pb(ii) (48 hours)	% difference in Pb(ii) uptake
0	99	-
10	99	nil
100	99	nil
1000	100	+1.0

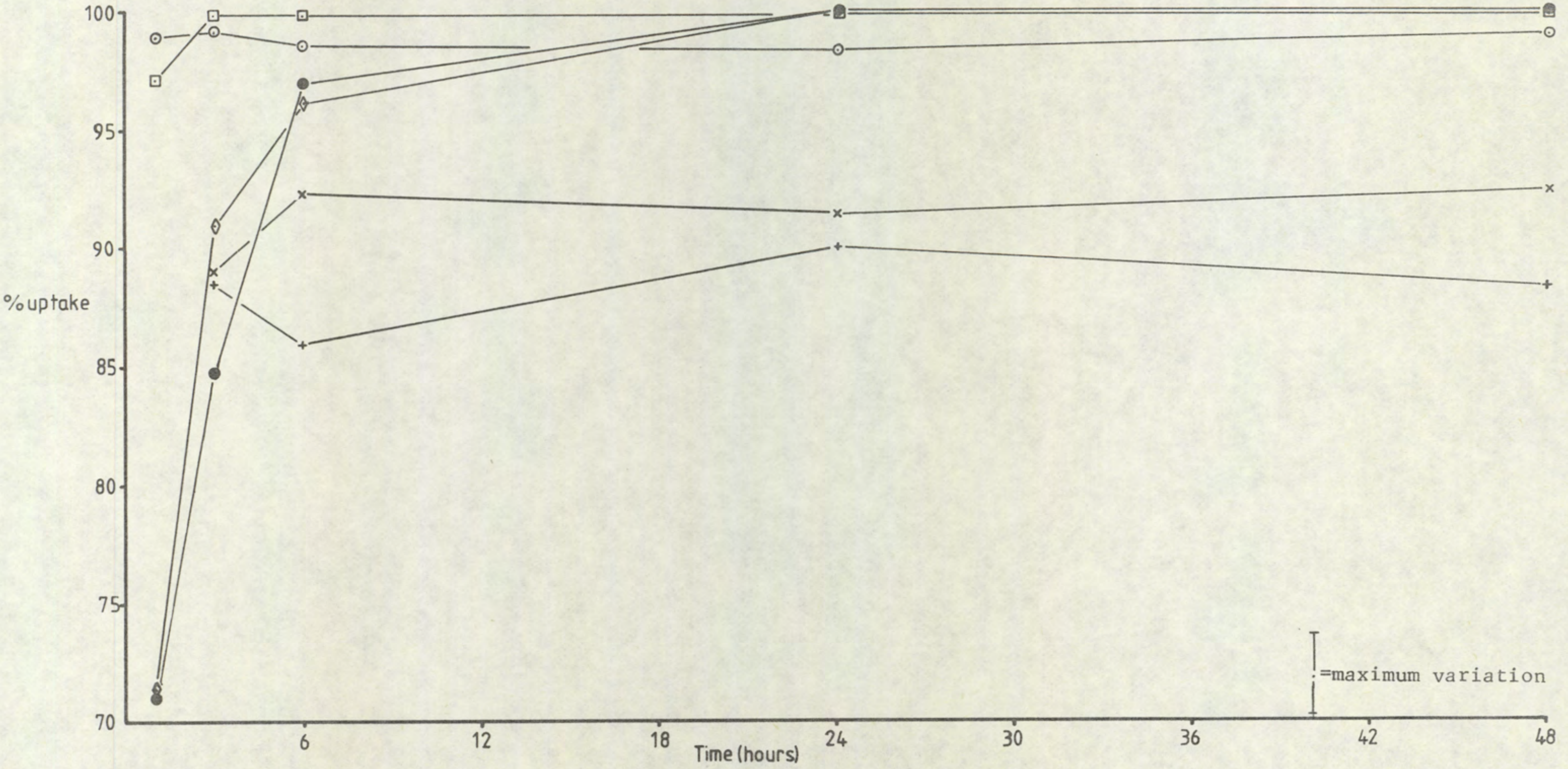


Figure 6.1. The effect of competing cation species on the uptake of lead(ii) by Bunter sand.

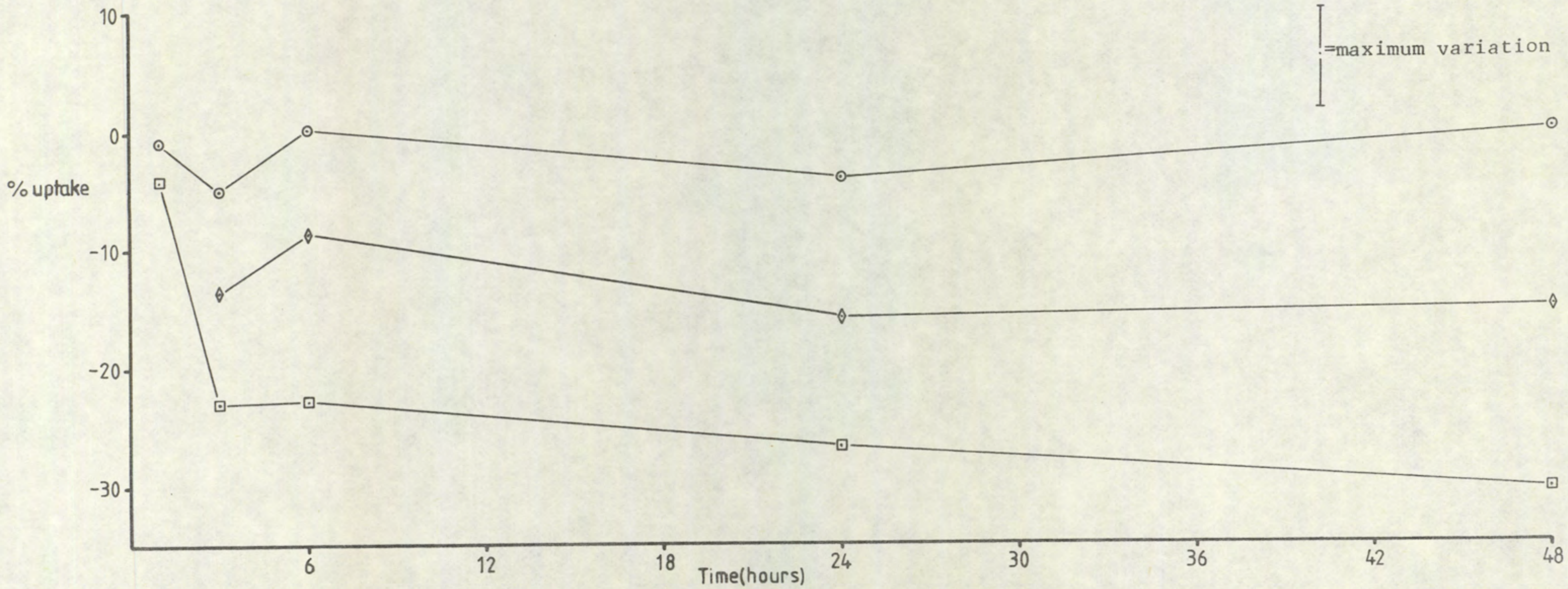


Figure 6.2. The uptake of calcium by Bunter sand and the effects of lead(ii) and ammonium in competition with calcium.

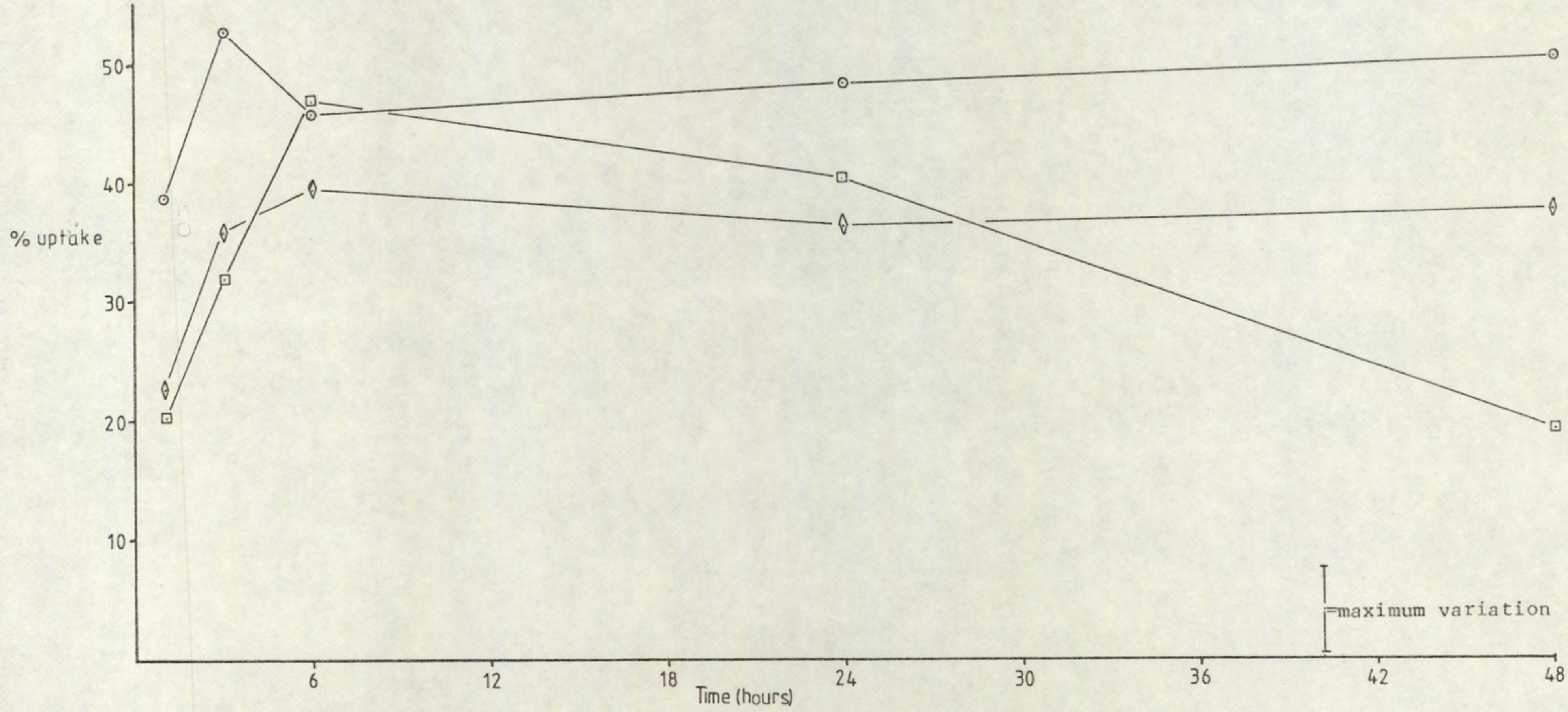


Figure 6.3. The effects of lead(ii) and ammonium on magnesium(ii) uptake by Bunter sand.

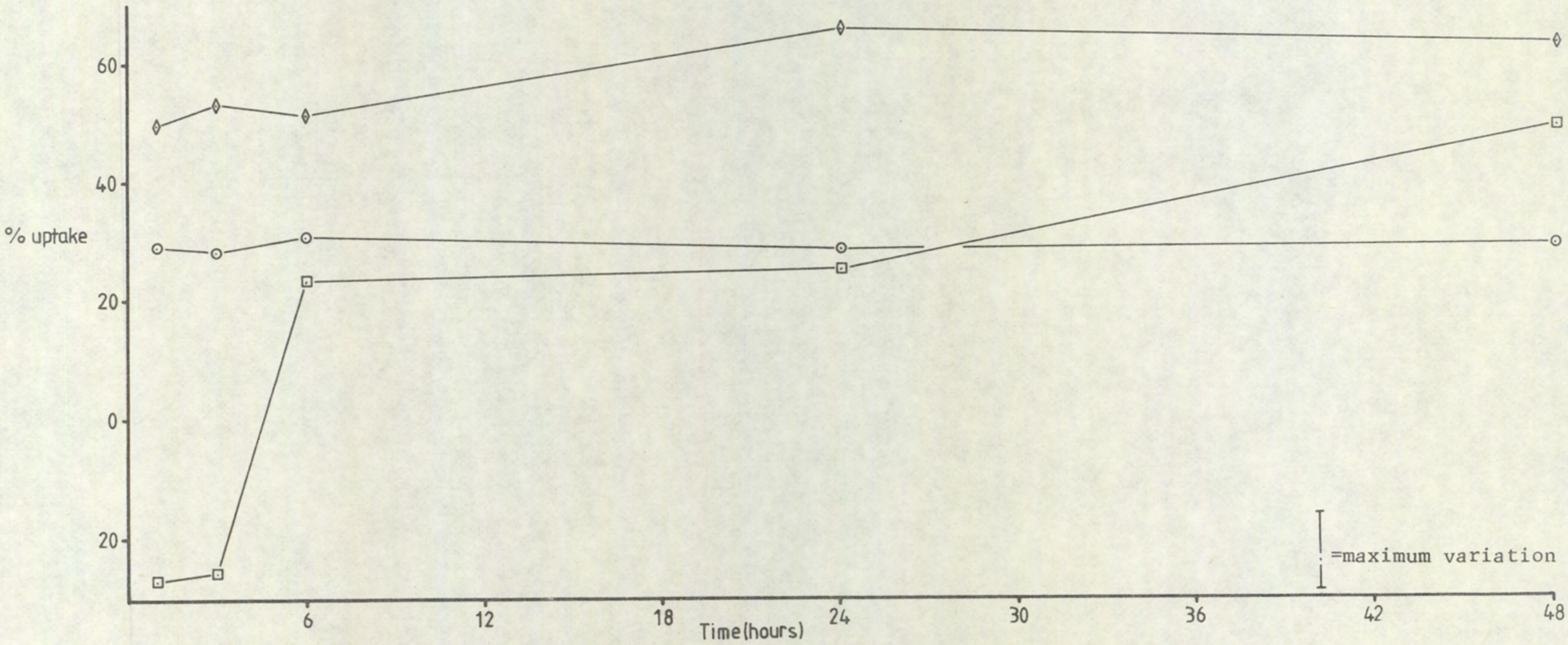


Figure 6.4. The effects of lead(ii) and ammonium on potassium uptake by Bunter sand.

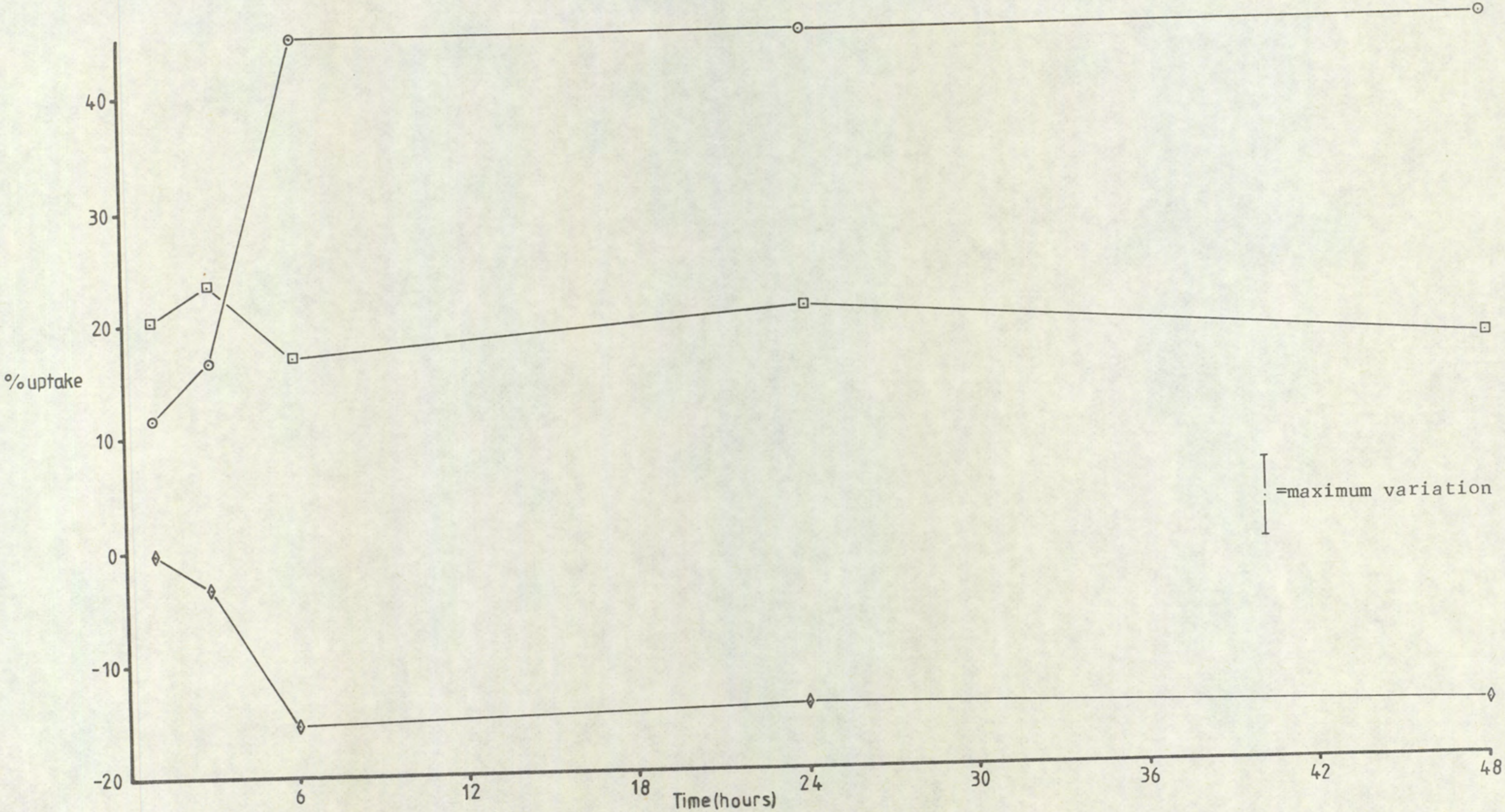


Figure 6.5. The uptake of sodium by Bunter sand and the effects of lead(ii) and ammonium in competition with sodium.

As before, with such minor changes it is difficult to draw any conclusions from the slight increase in lead(ii) uptake in the presence of the highest chloride content because of the low levels of residual lead in solution.

Organic Acids

In their analysis of domestic waste landfill leachates, Robinson and Maris (1979) reported the occurrence of widely varying but commonly considerable quantities of carboxylic acids. Because of the wide range of concentrations found (Table 1.1) it was decided that the effects on metal uptake of varying acid levels should be determined.

Lead(ii) was chosen for these experiments in the first instance, with a shortened series of experiments on iron(iii) and zinc(ii) for comparison. Because the analyses given by Robinson and Maris (op.cit.) included both iso and n isomers of some acids, one series of experiments was conducted using both. The results obtained from these experiments were very compatable (within 1% for most determinations), indicating both isomers had a very similar effect. Consequently all other experiments were conducted with an equal mixture of the two isomers.

The metal solutions were used, as in all previous experiments, at concentrations of 100µg/ml in their nitrate form and the organic acids were added to give concentrations of either 10, 100 or 1000µg/ml. No attempt was made to buffer the solutions because to do so would have introduced more chemical species and hence more variables into the system. Also, pH dependency of metal uptake had already been determined using mineral acids as described in Chapter 3.

The results for lead(ii) with each organic acid are given in Figures 6.6 to 6.10 and include acetic, butyric, hexanoic, propionic and valeric acids respectively. The graphs of lead(ii) uptake against time for acetic acid show a very substantial decrease in lead(ii) uptake for the highest acid content compared with that for the 100μg/ml acid solution which showed only a slightly reduced uptake during the first 6 hours after which there remained only a trace of the metal in solution (Figure 6.6). 10μg/ml of acetic acid appeared to have no effect on the removal of lead(ii) from solution, the graph showing the uptake remaining fairly steady at about 99% throughout the experiment.

A very similar picture appears for butyric acid, although the reduction in uptake at the highest acid content was less marked than for the same concentration of acetic acid (around 95% uptake compared with 81%). Again, the 10μg/ml acid solution exerted no appreciable effect on lead(ii) removal and once more 100μg/ml of acid caused a depressed uptake during the first 6 hours only, after which only a trace of the metal remained in solution.

Hexanoic, propionic and valeric acids all showed the same trends for the 10 and 100μg/ml acid solutions (Figures 6.8, 6.9 and 6.10 respectively). In each case, however, the effects of the acids at 1000μg/ml were much less apparent after 48 hours than for the acetic or butyric acids. Indeed for propionic and valeric acids (Figures 6.9 and 6.10) the uptake was virtually identical to that from the 10μg/ml solutions.

The quantities of calcium, potassium and sodium released into solution were measured in order to assess what effect the organic acids had on the Bunter sand (Table 6.5). The results are given for a distilled water/Bunter sand control (blank), the 100µg/ml lead(ii) solution with sand and for the lead(ii)/1000µg/ml acid combinations. The results show that the sodium values differ very little for any of the organic acids compared with the acid-free lead(ii) solution. The calcium and magnesium values for acetic and, to a lesser extent, propionic acids are notably higher than for the other organic acids and for the acid-free solution. The same two acid solutions (acetic and propionic) have higher potassium levels than the other acids, again with acetic the highest, with potassium values close to that of the acid-free solution.

Two further series of experiments were carried out on metal/carboxylic acid combinations; the first using zinc(ii) and the second iron(iii). These experiments used only 100µg/ml concentrations of the acids. Zinc(ii) was chosen because it has a similarly high uptake to lead(ii) after 48 hours from the metal-only solutions but with a slower initial uptake. Iron(iii) was chosen because in earlier experiments it had acted differently to the heavy metals which might indicate that it is taken up by a different mechanism. Any variation in its behaviour discovered here would help confirm the likely mechanism difference.

The graphs of results for zinc(ii) are shown in Figure 6.11 and include those for the acid-free zinc(ii) solution for comparison. The values for butyric, hexanoic and propionic acids were virtually identical and only the graph for propionic is given. The reduction in uptake after 48 hours was small for all the acids, except acetic although the graphs do show a distinct depression during the first 24 hours. Acetic acid had a much more marked effect. The initial uptake of zinc(ii) (after 1 hour) from the acid/zinc(ii) combination was much lower than from the acid-free solution (46% against 71%) and was followed by a re-release of the metal after 3 hours. This follows the trend found for lead(ii) with 1000μg/ml acetic acid (Figure 6.6). After 6 hours a sharp but steady increase in zinc(ii) uptake occurred until after 48 hours 91% of the metal had been removed from solution.

The percentage uptake of iron(iii) after 1 hour, 24 hours and 48 hours is shown in Table 6.6 where no significant reduction in uptake is seen with 100μg/ml carboxylic acids, even during the early stages of the experiment. The lowest uptake after 1 hour was 99% for acetic acid, a drop of only 1% from the metal-only solution, the uptake values for which are given in Table 6.6 for comparison.

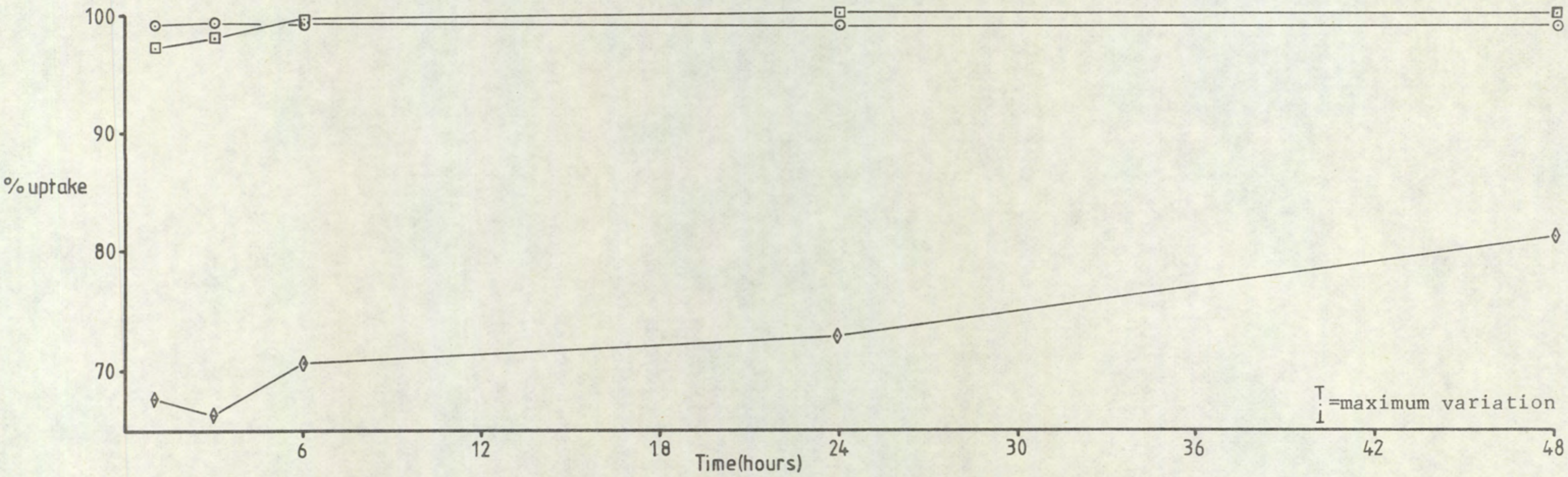


Figure 6.6. The effects of increasing concentrations of acetic acid on lead(ii) uptake by Bunter sand.

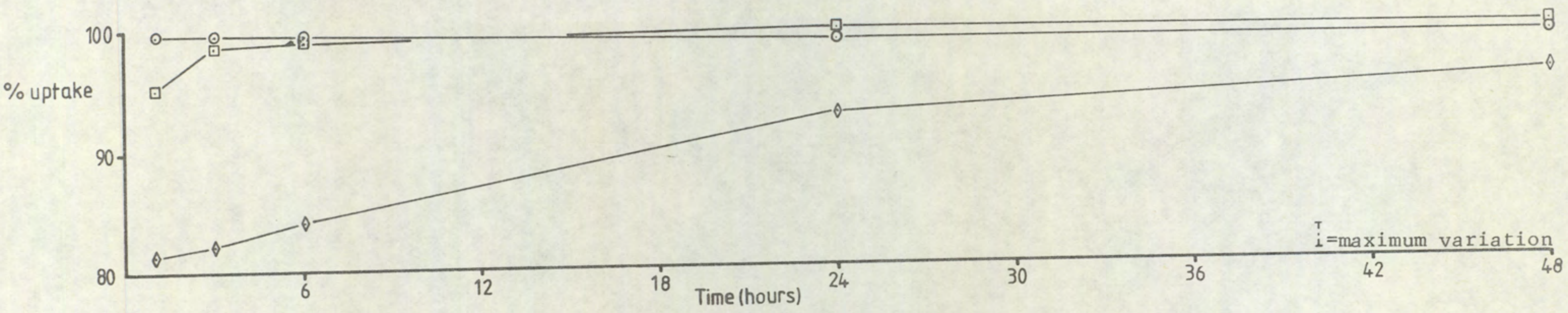


Figure 6.7. The effects of increasing concentrations of butyric acid on lead(ii) uptake by Bunter sand.

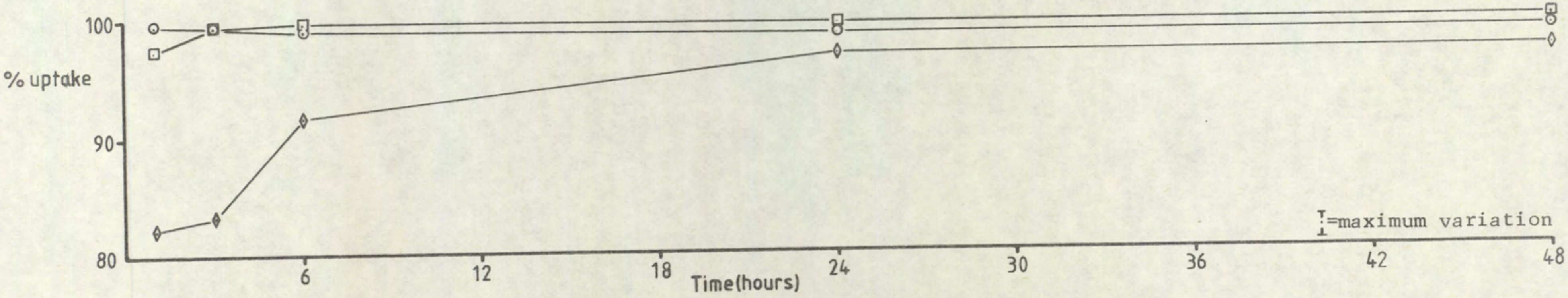


Figure 6.8. The effects of increasing concentrations of hexanoic acid on lead(ii) uptake by Bunter sand.

⊙ = 10 ug/ml organic acid
⊡ = 100 " " "
◊ = 1000 " " "

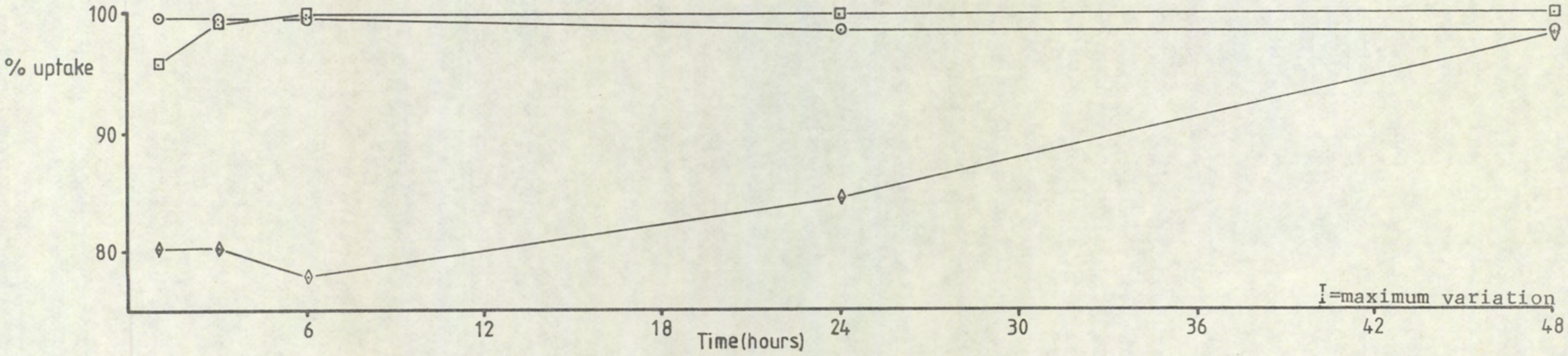


Figure 6.9. The effects of increasing concentrations of propionic acid on lead(ii) uptake by Bunter sand.

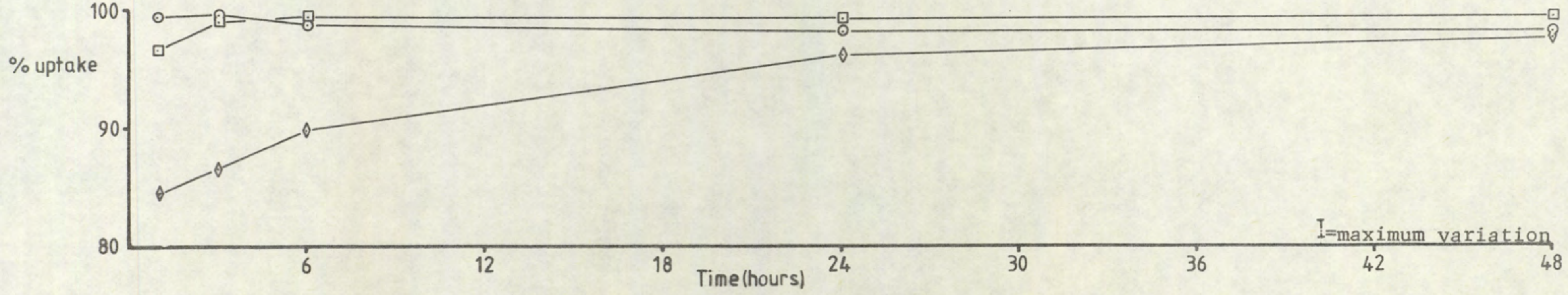


Figure 6.10. The effects of increasing concentrations of valeric acid on lead(ii) uptake by Bunter sand.

⊙ = 10 ug/ml organic acid
⊡ = 100 " " "
◊ = 1000 " " "

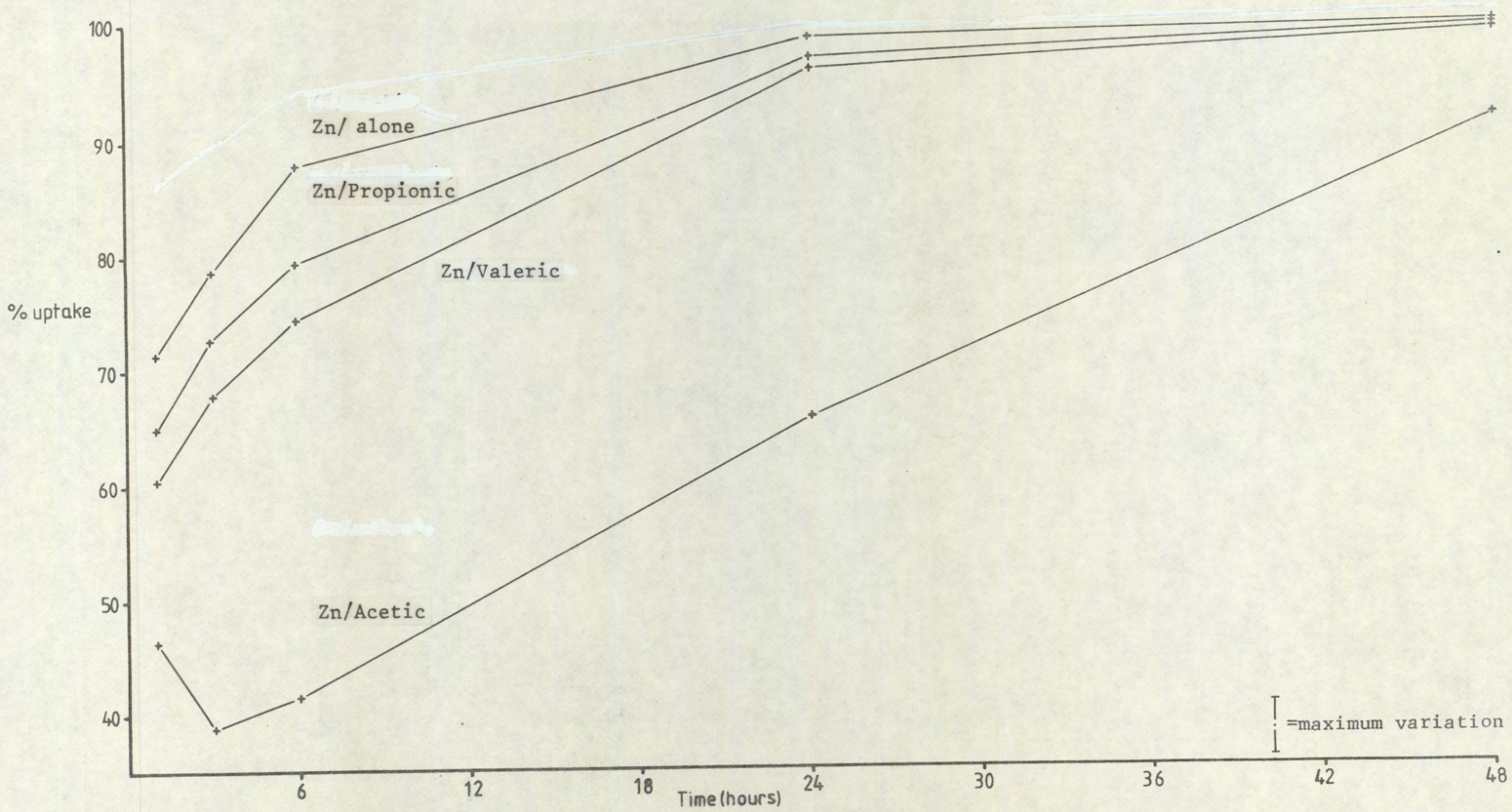


Figure 6.11. The effects of organic acids on zinc(ii) uptake by Bunter sand.

Table 6.5. Quantities of cations released from Bunter sand during lead uptake and in the presence of organic acid at 1000μg/ml.

Solution	Cations released (μg/g) after 48 hours			
	Ca	K	Mg	Na
Blank	8.0	210.5	Trace	15.0
Pb only	895.0	279.5	56.5	32.5
Pb/acetic acid	1112.0	288.5	88.5	27.0
Pb/butyric acid	843.5	183.5	66.0	20.5
Pb/hexanoic acid	664.5	99.5	50.0	32.0
Pb/propionic acid	961.0	208.0	77.5	19.0
Pb/valeric acid	576.0	189.0	68.5	28.0

Table 6.6. Uptake of iron(iii) by Bunter sand from solutions containing 100µg/ml of organic acid.

	% uptake of Fe^{3+} from solutions of:-					
	Fe(iii)alone	Fe(iii)/acetic acid	Fe(iii)/butyric acid	Fe(iii)/hexanoic acid	Fe(iii)/propionic acid	Fe(iii)/valeric acid
1 hour	100	99	100	100	99	100
24 hours	99	100	99	100	100	100
48 hours	100	98	98	99	99	99

6.2. Discussion

The Alkaline Earth Metals

The failure of sodium(i) and potassium(i) to reduce lead(ii) uptake is not surprising since divalent cations must have a greater affinity for negatively charged sites such as clay lattice edges than will monovalent cations competing in similar concentrations. The experiments on the effects of chloride where sodium concentrations of up to 600µg/ml were used also showed no effect on lead(ii) uptake. Calcium(ii) and magnesium(ii) might be expected to compete more equally on charge considerations. The uptake of calcium by the iron oxide free Bunter sand was greater than that for lead (100% and 60% respectively, Figure 5.7) suggesting that calcium(ii) has a greater affinity than lead(ii) for sodium saturated clay sites. This conflicts with the results of Lagerwerff and Brower (1973) and Bittel and Miller (1974) who found lead(ii) was favoured over calcium on montmorillonite, kaolinite and illite. Farrah et al (1980) using the sodium form of the same clays showed that the affinity sequence, based on the amounts of metals taken up from solutions of equal concentrations, favoured calcium over lead for kaolinite and illite (Table 1.6) with which the results given in Chapter 5 agree. However, as the untreated Bunter sand is saturated with respect to calcium, and lead(ii) shows a strong affinity for iron oxides as well as precipitating as carbonate, it appears that the presence of similar concentrations of calcium has no overall effect on lead(ii) removal. Similarly, Figure 5.12 showed that magnesium(ii) is taken up only poorly by the iron oxides ($< 20\%$) whereas lead(ii) was removed completely from a 100µg/ml solution.

The Heavy Metals

The effects of other heavy metals on lead(ii) uptake has already been discussed briefly for the different grain size fractions (Chapter 4). The results presented here confirm those results for the bulk untreated Bunter sand, with copper(ii) having a greater effect on lead uptake than does nickel(ii) (Table 6.1). This apparently greater competition by copper than nickel follows the uptake results from the 100µg/ml mono-metalic solutions from which copper(ii) is removed completely compared with only 79% removal of nickel(ii). Figures 5.2, 5.3 and 5.4 showed the uptake of copper(ii), lead(ii) and nickel(ii) respectively by untreated and deferrified Bunter sand and comparison shows that uptake by the iron oxide free sand is similar for all the metals (c.60%). As discussed in the previous chapter this uptake probably represents an ion exchange on clay sites and possibly precipitation by carbonate formation. The difference between the uptake and that by untreated Bunter sand represents that by the iron species. Comparison of the uptake by the untreated sand (100% for copper(ii) and lead(ii), 79% for nickel(ii)) with that by deferrified sand (around 60% for each) indicates that the iron species play a greater part in copper(ii) and lead(ii) removal than for nickel(ii). This in turn suggests that the reduction in lead uptake by the other metals is due to competition for sites on or within the iron species rather than clay cation exchange sites. Further evidence for this is given by comparison of Figure 4.9 and Table 4.1 which shows that metal uptake does not equal cation exchange capacity, even for the five metal solution, for any of the grain size fractions, and as such ion exchange is not the limiting factor on metal uptake. This casts some doubts as to the validity of assessing the attenuation ability of rocks on their cation exchange capacity alone.

Iron(iii) was removed completely by untreated Bunter sand from the 100μg/ml solution but by only 60% by the deferrified sand (Figure 5.6), as were nickel(ii), copper(ii) and lead(ii). It might therefore be expected that its effect on lead(ii) uptake would be similar to that of copper(ii). However, as Figure 6.1 shows, the depression of lead uptake was evident only during the first 24 hours of the experiment by which time all the lead was removed from the solution. Since the deferrified Bunter sand removed similar amounts of iron(iii) and lead(ii) it must be assumed that the reduced uptake is due to competition for sites on the iron sesquioxides. This competition seems to be reduced with time since the lead is completely removed within 24 hours. This suggests that either the iron(iii) is initially preferentially taken up onto sites on the iron sesquioxides, after which they are incorporated into the lattice and the surface charge balance is restored, or that the iron precipitates as hydroxide onto the sesquioxides blocking potential exchange sites, but upon ageing the precipitate takes on properties similar to the original iron oxide surface.

Co-precipitation of lead(ii) with iron(iii) must be ruled out since the lead is not removed at the same rate as the iron. Ross (1978) showed by lattice energy considerations that lead is unlikely to be incorporated into crystalline oxides, whilst the amorphous oxides play a significant role in lead attenuation by the Lower Greensand. It seems likely that metals compete with lead(ii) for surface adsorption sites on iron oxides and clays, whilst they may be incorporated into the oxide lattice. This is substantiated by the uptake profiles for the heavy metals (excluding lead) by untreated Bunter sand, which show a gradual uptake on top of the rapid initial removal. McKenzie (1970) described a two stage uptake of cobalt by manganese oxide, the first rapid stage comprising a surface exchange reaction followed by a slower substitution into the crystal lattice.

That the untreated Bunter sand does not take up any calcium(ii) has already been discussed to indicate that the sand is saturated with respect to the alkaline earth metal. The apparent failure of calcium(ii) to reduce lead(ii) uptake has also been discussed. The deferrified Bunter sand showed that calcium(ii) has a greater affinity for sodium saturated cation exchange sites than lead(ii) but Figure 6.2 shows that the heavy metal displaces calcium into solution from the untreated sand, even in the presence of an excess of the alkaline earth metal. However, the 15% elution after 48 hours is equivalent to 0.375 meq/100g sand, which is only one tenth of that given out in the presence of lead(ii) alone (Tables 3.2 to 3.4). This indicates that calcium may indeed compete favourably with lead(ii) for exchange sites, but that the abundance of alternative sites available to the heavy metal is such that it is still efficiently removed by the sand.

The uptake of magnesium(ii) dropped from 51% from its monometallic solution to 30% in the presence of lead(ii) (Figure 6.3). This represents a reduction of 0.535 meq/100g which falls in the middle of the range of magnesium levels found given into solution by the lead(ii) single metal solution (Tables 3.2 to 3.4). Similarly, the 15% elution of sodium in the presence of lead(ii) and sodium(i) (Figure 6.5) is equal to 0.326 meq/100g, again agreeing closely with the values given out by the Bunter sand treated with lead(ii).

These observations confirm the previous discussion that neither of these alkaline earth metals offer any competition to lead(ii) uptake when present in quantities similar to those used here. Indeed from the experiments using NaCl (discussed later with respect to chloride), where there was no reduction in lead(ii) uptake even with sodium concentrations in excess of 600μg/ml (when: Cl^- = 1000μg/ml), it would appear that considerable quantities of sodium(i) have no effect on lead(ii) uptake.

The increase in uptake of potassium(i) in the presence of lead(ii) compared to the monometallic solution equals 0.326 meq/100g sand, which is less than that found in the blank solution (Tables 3.2 - 3.4) and shows the same order of decrease found in the presence of lead(ii) for initial pH values of 4 and 6. This implies that the presence of lead(ii) increases the uptake of potassium, although there is no evidence to indicate by what mechanism this occurs.

Ammonium Ion

At a concentration of 100μg/ml, ammonium ions had no effect on the uptake of either copper(ii) or lead(ii) (Table 6.3), despite its known affinity for cation exchange sites (hence its use in cation exchange capacity determinations). This may be indicative that the low ammonium concentrations are insufficient to compete with or displace these metals from cation exchange sites. Alternatively, if as discussed in Chapter 5, lead and copper are incorporated into the lattice of iron sesquioxides, and the capacity of that phase is sufficient to allow uptake of any heavy metal not taken up by clay exchange sites, then the effect of ammonium competition would not be revealed simply by determining the quantity of the metal left in solution.

Cadmium(ii) showed the greatest reduction due to the presence of ammonium (72% uptake compared with 82%). That this is due to competition for clay cation exchange sites substantiates the evidence from the experiments using deferrified sand (Chapter 5) suggesting that cadmium is held only weakly on exchange sites. From binary solutions using equal concentrations of each ion, Farrah and Pickering (1980) showed cadmium has a lower affinity for clays than does lead, copper and zinc (Table 1.6).

It is not possible to assign any emphasis to the slight increase in nickel(ii) uptake, nor the slight decrease in zinc(ii) uptake because the measured differences in metal concentrations remaining in solution were small, and any inaccuracies due to dilutions or sensitivity during atomic absorption spectrophotometry could have produced these results. Accordingly, it appears that the presence of 100μg/ml ammonium makes little or no difference to the uptake of these metals, either because it does not compete with the divalent ions for cation exchange sites, or due to the availability of other sites, such as the iron oxides, to zinc and nickel. The latter explanation seems unlikely here, since neither nickel(ii) or zinc(ii) were totally removed from either their monometallic solutions suggesting that the capacity of the sand for these metals was reached.

In competition with ammonium in equal concentrations, calcium(ii), magnesium(ii) and potassium(i) all showed a net elution from the Bunter sand during the first hour after mixing (Figures 6.2 to 6.4). Magnesium and potassium were subsequently taken out of solution implying that the ammonium is preferentially absorbed after which the alkaline earth metals occupy any remaining available sites. In both cases uptake reached a level similar to that from their ammonium free solutions within 6 hours, but magnesium was given back into solution during the remaining experimental period, suggesting that it is only weakly held and remains labile to some extent. Calcium was eluted to a greater extent in the presence of ammonium than lead(ii), but this probably reflects the greater ionic strength of the NH_4^+ solution (5.88meq/l NH_4^+ compared to 0.97meq/l Pb^{2+}).

Sodium was not eluted from the sand under the influence of ammonium (Figure 6.5) although its uptake was greatly reduced throughout (20% compared to 45%) which suggests that sodium(i) competes more equally with NH_4^+ than the other alkaline earth metals.

Chloride

Farrah and Pickering (1977), whilst investigating the effects of high sodium concentrations on heavy metal uptake by illite and kaolinite found similar results using both nitrate and chloride compounds and dismissed chloro-complexes as the cause of any reduction in metal uptake. The results given in Table 6.4 support that conclusion in that chloride concentrations up to 100μg/ml have no effect in reducing lead(ii) uptake by Bunter sand.

Monsef-Mirzai (1980) provided evidence to suggest that whilst their formation may not reduce initial uptake by clays, chloro-complexes may increase the proportion of labile metal. For chloride concentrations greater than three molar, all copper(ii) previously taken up by montmorillonite was subsequently remobilised by washing with distilled water compared with only one fifth of that taken up from a $Cu(NO_3)_2$ solution in the absence of chloride ions. Since no leaching tests were carried out on the lead(ii)/NaCl treated Bunter sand, this effect cannot be discounted here.

Organic Acids

The graphs of lead(ii) uptake with time show that in each case there is little or no reduction in uptake at concentrations of up to 100µg/ml organic acid (Figures 6.6 to 6.10). In all cases, however, there were marked reductions at an acid concentration of 1000µg/ml over the first 24 hours. Only acetic and butyric acids showed any significant reduction after 48 hours (the actual range of values are given for the butyric acid solution after 48 hours as well as the maximum range throughout the experiment, showing that there is a reproducable difference between the 100µg/ml and 1000µg/ml solutions). However, the trend of lead(ii) uptake from both the acetic acid and butyric acid solutions indicates continuing removal and it may well be that given sufficient time all the metal may be removed from solution.

Boreham et al (1975) found increased mobility of several heavy metals with higher organic acid concentrations passed through Lower Greensand columns. Although these authors detected no lead, even after several column volumes of artificial leachate had been passed through the column, it seems likely that the effect shown here by lead(ii) is analogous to that demonstrated by the other heavy metals in the Greensand columns. Any increase in mobility is likely to be exagerated in these experiments compared to the columns due to the greater solution to solid ratio and hence lower surface area of sand to remove the metal from solution.

The cause of an increase in the mobility of iron(ii) in the presence of organic acid was shown by Leenheer et al (1976) to be due to the formation of metal-complexes, and Ross 1980 attributed increased heavy metal mobility in Lower Greensand to the same cause.

In Chapter 3 the ability of the Bunter sand to buffer acid and alkaline solutions, to pH values dependent of the metal ion present, was clearly shown (Tables 3.6 to 3.10). It was for this reason, and in order not to complicate the situation by introducing further quantities of anionic species, that no artificial buffering was carried out. This does, however, mean that at least part of the shown effects may be due to the pH dependence of attenuating mechanisms.

Since the effects of 1000μg/ml organic acid had a much more pronounced effect on lead(ii) uptake than did adjusting the initial solution pH to 4 (Figure 3.4), it seems likely that other factors other than pH are involved. However, because the effects are not permanent, indicated by the continuing metal uptake, it seems that the sand is able to counter the effect in a similar way to the buffering type reaction discussed previously, or that any metal complexing only reduces the rate of either ion exchange/adsorption or precipitation rather than preventing it totally. Unpublished data by Park (pers.comm.) indicates that acetic acid shows an affinity for Fe(iii) and thus may modify the surface of the sesquioxides with respect to metal uptake. The lead(ii) may therefore be taken up by less available sites at a lower rate.

Table 6.5 shows that the acetic acid/lead(ii) solution released

20% more calcium and over 50% more magnesium into solution than did the lead(ii) on its own, whilst Figure 6.6 shows a 20% reduction in uptake. From this it is evident that the calcium and magnesium are not due to cation exchange for lead(ii), and supports the suggestion made in Chapter 3 that some acid soluble calcium and magnesium compounds, possibly carbonate, are present in the Bunter sand. The propionic acid/lead(ii) solutions show similar trends, although less dramatically than the acetic acid solution.

Potassium and sodium levels for the acetic acid/lead(ii) solution are similar to those of the metal-only solution whilst those for the propionic acid solution are close to the blank suggesting a reduction in cations given out in exchange reactions. Similar conclusions may be drawn from the levels of sodium given out into the butyric, hexanoic and valeric acid solutions, which fall between those of the organic free lead solution and the blank, and from the depressed calcium levels in the hexanoic and valeric acid solutions.

The effects of the organic acids on zinc(ii) uptake are similar to those for lead(ii), in that there is a depression in the rate of metal removal, and that the effect is most noticeable with acetic acid (Figure 6.11). However, these experiments with zinc(ii) were conducted with only 100μg/ml organic acid and thus the results clearly show that zinc is much more mobile in the presence of organic acids than lead(ii). This agrees with Boreham et al (op.cit.) who showed zinc(ii) passed through Greensand columns in leachates containing organic acids whereas lead(ii) did not, even after several column volumes of solution.

The opposite seems to be true for iron(iii) (Table 6.6) which shows no signfiicant drop at all in uptake with 100μg/ml organic acid during any part of the experiments duration, unlike lead which exhibited a decreased rate of uptake. This may indicate that iron(iii) does not form metal complexes as readily on either lead(ii) or zinc(ii) (Leenheer et al (op.cit.) worked with iron(ii) in connection with deep well disposal of industrial waste), or that precipitation of iron(iii) occurs despite an affinity of the carboxylates for the sesquioxides (Park op.cit.). Whichever the case, it seems that organic acids are unlikely to increase the mobility of iron in aerobic conditions below and away from landfill sites, whereas there is a potential risk of heavy metal movement dependent upon hydrogeological conditions.

Chapter 7. Heavy Metal Uptake by Chalk

7.1. Experimental Materials and Procedures

The Chalk represents the largest aquifer in the U.K. It consists of a series of limestones which show some lithological changes, and is divided stratigraphically into the Lower, Middle and Upper Chalk. The Lower Chalk has at its base the Glauconitic Marl, a highly calcareous clay, and above this the Totternhoe Stone, a very compact and hard chalk. Similar beds are locally developed and occur in both the Chalk Marl or higher in the sequence than the Totternhoe Stone, which itself dies out in the west in Berkshire. The remainder of the Lower Chalk is mostly typical chalk without flints, but commonly with marcasite nodules. A shaly marl, the Belemnite Marl, is found at the top of the Lower Chalk which varies in thickness but reaches up to 75m in Berkshire.

The Middle Chalk has a hard, generally nodular chalk, the Melbourn Rock, at its base. The remainder is largely unremarkable chalk with few flints. Like the Lower Chalk, its thickness varies but reaches up to 70m in Buckinghamshire. The Upper Chalk has at its base a series of harder bands, the Chalk Rock, composed of hard creamy limestones each about 30cm thick. The rest of the series is generally softer than the Middle and Lower Chalk and flints are common. It reaches over 100m in thickness in Berkshire.

The average chalk lithology, excluding flints or marl, is a very low magnesium limestone (< 0.15% MgO) with a calcium carbonate content of around 98% and not less than 96% (Hancock, 1975). The only other notable contents are silica and clay minerals. Montmorillonite, kaolinite and illite have been identified in very small quantities as expected from the low Al_2O_3 content which is generally less than 1% (Hancock, op.cit.).

The porosity of the Chalk is high, varying between 35% and 47% (Carter and Mallard, 1974). Despite this it has a low interstitial permeability, averaging around 8m/day. The high permeability associated with the Chalk is due to fissure flow. Hancock (op.cit.) cites examples of flows measured in excess of 2km/day flow a swallow hole, whereas in open chalk Downs percolation through the unsaturated zone has been measured at only a few metres per year.

The material used in all the experiments described here was taken from the chalk quarries at Grays-Thurrock in Essex (N.G.R. TQ 577 788) which were excavated for cement manufacture. In common with the Upper Chalk throughout the London Basin, the chalk here is soft with abundant flints, both in nodular form and in tabular layers. X-ray diffraction patterns produced for this chalk showed no mineral phase other than calcium carbonate.

All experiments were carried out as for the Bunter Sandstone, using a 5:1 ratio of solution to solid. The solutions were prepared at 100µg/ml of the metal as nitrate. The chalk was added as a powder, prepared by crushing in a Tema mill for 3 seconds after drying. Each metal/chalk combination was tested in triplicate. All results given are the average of those three determinations.

7.2. Metal Uptake. Results

Because of the carbonate nature of chalk it was not relevant to conduct any pH adjusted experiments since any acid solution will be rapidly neutralised. The uptake results for five of the heavy metals and the alkaline earth metals are given in Table 7.1. Of the heavy metals, cadmium(ii), copper(ii) and lead(ii) were effectively removed from the 100µg/ml solutions. Zinc(ii) showed a slightly less complete removal, at 97%, with only a slight increase from the first determination (96% after 1 hour). Nickel(ii) showed only a 75% removal after 48 hours, having climbed from 64% removal after the first hour. All 100µg/ml of iron(iii) was taken from solution within the first hour.

Of the alkaline earth metals, calcium(ii) was released into solution rather than being taken up, while magnesium(ii) levels showed small variations between minimal uptake and release. Sodium(i) showed an initial substantial release into solution after 1 hour but after that a small uptake. Potassium(i) showed very little uptake (1% after 48 hours).

Table 7.1. Uptake of metals by chalk from single-metal solutions*.

Metal	% uptake after:-			
	1 hour	6 hours	24 hours	48 hours
Cd(ii)	100	100	100	100
Cu(ii)	100	100	100	100
Ni(ii)	64	70	73	75
Pb(ii)	100	100	100	100
Zn(ii)	96	97	97	97
Fe(iii)	100	100	100	100
Ca(ii)	-62	-47	-78	-51
Mg(ii)	1	-1	2	-6
K(i)	1	-1	3	1
Na(i)	-32	2	6	7

* Initial concentrations of 100 µg/ml for each metal

7.3. Effects of Other Leachate Constituents

Heavy Metals

The effect of the presence of the other heavy metals was assessed for each of the five metals previously tested. The metals were added on or equal weight basis (100μg/ml) in binary solutions. The % reduction in uptake for each metal in competition with the others is shown in Table 7.2. Neither cadmium(ii), copper(ii), nor lead(ii) showed any decrease in uptake in the presence of any of the other metals. Nickel(ii) showed a slight decrease with lead(ii) (5.5%), a slightly greater decrease with zinc(ii) (15.5%) and cadmium(ii) (18.9%) and a considerable decrease with copper(ii) (31.9). Zinc(ii) showed only very slight percentage decreases with copper(ii) and nickel(ii), a marginal increase in uptake with lead(ii), and a considerable decrease with cadmium(ii) (50.2% reduction).

Ammonium Ion

Ammonium nitrate was added to the metal solutions at a concentration of 100μg/ml NH_4^+ before mixing with the chalk. Of the alkaline earth metals, calcium(ii) was given out to a lesser extent in the presence of ammonium than from the single solution. Magnesium(ii) was taken up to a small degree from the ammonium containing solution compared with a small release. Both potassium(i) and sodium(i) were released to a considerable degree in the presence of ammonium. Of the base metals, iron(iii) was unaffected by the presence of ammonium, as were cadmium(ii) and lead(ii). Only nickel(ii) showed any remarkable reduction in uptake (42.6% reduction) after 48 hours. Zinc(ii) showed a small reduction (2.0%) and copper(ii) an even smaller decrease (1%) (Table 7.3).

Table 7.2. Reduction in uptake of the heavy metals by chalk when in competition with each other*.

Metal	% reduction in uptake in competition with:-				
	Cd(ii)	Cu(ii)	Ni(ii)	Pb(ii)	Zn(ii)
Cd(ii)	-	nil	nil	nil	nil
Cu(ii)	nil	-	nil	nil	nil
Ni(ii)	-18.9	-31.9	-	-5.5	15.5
Pb(ii)	nil	nil	nil	-	nil
Zn(ii)	-50.2	-1.3	-2.7	+0.9	-

* Initial concentrations of 100 µg/ml for each metal

Table 7.3. Effects of ammonium ions on metal uptake by chalk.

Metal*	% uptake (48 hours)		% in uptake
	single solution	vs NH_4^+	
Cd(ii)	100	100	nil
Cu(ii)	100	99	1.0
Ni(ii)	75	43	42.6
Pb(ii)	100	100	nil
Zn(ii)	98	96	2.0
Fe(iii)	100	100	nil
Ca(ii)	-51	-38	
Mg(ii)	-6	7	
K(i)	1	-31	
Na(i)	7	-16	

* Initial concentrations of 100µg/ml for each metal.

Chloride

Chloride is commonly found in significant concentrations in chalk groundwaters near the coast where saline water is drawn into the aquifer by abstraction inland (Monkhouse and Fleet, 1975) and as a result of contamination by mine drainage from the Kent coalfield (Headworth et al, 1980). The effects of chloride on metal uptake by chalk were carried out at concentrations of 100µg/ml and 1000µg/ml.

Sodium chloride was added to the 100µg/ml metal solutions to the chosen chloride concentration before mixing with the chalk. No significant decrease in uptake was found for any of the heavy metals chosen with chloride levels up to 1000µg/ml (Table 7.4).

Organic Acids

The effects of organic acids on uptake was tested on three metals, copper(ii), iron(iii) and zinc(ii). Copper(ii) and iron(iii) were chosen because they were taken up rapidly and almost entirely from their single-metal solutions (Table 7.1). Zinc(ii) was taken up to a slightly lesser extent from its single solution. The organic acids were added at a maximum concentration of 1000µg/ml for each metal and an additional series of experiments at 100µg/ml was done for copper(ii).

The results show that even 1000µg/ml of all the carboxylic acids tried had very little effect on copper(ii) and zinc(ii), though iron(iii) showed slightly greater percentage decreases, the largest being that in the presence of acetic acid (2.3%, Table 7.5). Copper(ii) and zinc(ii) showed only slight variations in uptake with time, but again iron(iii) showed a greater variation (Table 7.6). In these experiments there was a steady increase from the initial uptake at around 93% after 1 hour to the final reading approaching complete removal after 48 hours.

Table 7.4. Effects of chloride concentration on metal uptake by chalk after 48 hours.

Chloride concentration	% decrease in uptake of:-				
(µg/ml)	Cd(ii)	Cu(ii)	Ni(ii)	Pb(ii)	Zn(ii)
100	nil	0.1	nil	nil	0.1
1000	nil	nil	0.1	nil	nil

Table 7.5. Reduction in copper(ii), iron(iii) and zinc(ii) uptake by chalk in the presence of organic acids (after 48 hours)

Organic acid concentration (µg/ml)	% reduction in uptake of:- Cu(ii)	Fe(iii)	Zn(ii)
Acetic			
100	nil		
1000	0.8	2.3	0.7
Butyric			
100	nil		
1000	0.3	0.6	0.4
Hexanoic			
100	nil		
1000	nil	2.1	0.5
Propionic			
100	0.3		
1000	0.3	1.0	0.5
Valeric			
100	nil		
1000	0.3	0.9	0.5

Table 7.6. Uptake of iron(iii) by chalk from solutions containing 1000µg/ml of organic acid*.

	% uptake of Fe(iii) from solutions of:-					
	Fe(iii)alone	Fe(iii)/acetic acid	Fe(iii)/butyric acid	Fe(iii)/hexanoic acid	Fe(iii)/propionic acid	Fe(iii)/valeric acid
1 hour	100	94	95	95	93	93
24 hours	100	96	98	97	96	98
48 hours	100	98	99	98	99	99

* Initial concentration of iron(iii) of 100µg/ml in each solution.

7.4. Chalk Landfill Experiments, West Thurrock, Essex

As stated earlier, the cement manufacturing industry has left large areas of chalk quarries requiring reclamation. In south-east Essex, one of the centres of the U.K. Portland cement industry, there is a large demand for disposal sites to accommodate both domestic and industrial waste from east London. However, in many cases chalk has been extracted down to or below the water table and such sites have not previously been considered suitable for reclamation because of the dangers of serious groundwater pollution.

In association with a commercial disposal company, Stablex Ltd., a series of laboratory and in situ experiments were designed to examine the behaviour of treated industrial wastes, in the form of "Stablex", in chalk quarries. "Stablex" polymer was developed by Leigh Interests Ltd. of Brownhills and is a process designed to combine liquid and solid industrial wastes into a neutral, inert solid. Since "Stablex" production is unlikely to be sufficiently large for rapid reclamation of large chalk quarries the possibility of incorporating domestic waste with the polymer is being considered. With this in mind a series of in situ landfill experiments have been designed to assess the control different combinations of the polymer and domestic waste have on the volume and chemical constitution of leachate in saturated and unsaturated conditions in chalk pits. The site for these experiments at West Thurrock in Essex has been prepared and their design is described in Appendix 3.

7.5. "Stablex" Laboratory Experiments

These experiments consisted of a series of simple leaching tests to determine which, if any, of the waste constituents incorporated into the polymer were likely to be leached out under field conditions. After setting and hardening the polymer was ground to a powder and then leached using four agents; distilled water; chalk groundwater; domestic refuse leachate from the G.L.C. tip at Aveley, Essex; and a synthetic domestic refuse leachate. Full analyses of these leaching agents and the polymer used are given in Table 7.7 (Gaskarth, Chappell and Todd, 1980).

For each of the leaching experiments, 100g of the ground polymer was mixed with 500ml of the solution in polypropylene laboratory ware and stirred using a magnetic stirrer for a period of 1 hour. The solutions were then filtered through a Whatman No.2 filter paper and analysed for the major cation and anion constituents of the polymer, plus pH and C.O.D. The results are given in Table 7.8.

The distilled water and chalk groundwater had similar leaching characteristics. There was little leaching of heavy metals, the greatest being chromium (0.7µg/ml for distilled water, 1.0µg/ml for the groundwater). Mercury was leached less by the groundwater than by the distilled water, although in both cases only very small quantities were found. Calcium, potassium and sodium were leached to a greater extent, as were chloride, sulphate and nitrate. The increases in C.O.D. after leaching the polymer was similar for both leaching agents.

The leaching of heavy metals by the Aveley landfill leachate was again small, with the exception of copper, which was considerably greater than for both the distilled water and groundwater results. Leaching with synthetic leachate also produced an increase in copper concentrations, although not as great as that for the Aveley landfill leachate. Mercury was leached to a lesser extent by both the landfill and synthetic leachates than by distilled water.

The level of iron in both the synthetic and Aveley landfill leachates was reduced after mixing with the polymer to values similar to that produced by distilled water leaching of the polymer. Manganese was also reduced to similar levels for the landfill leachate, but was leached by synthetic leachate, again bringing it to a similarly low value to that found in the distilled and groundwater leachates. Sodium and potassium were found in considerably higher concentrations in the landfill and synthetic leachates but comparison with Table 7.7 shows that for the Aveley landfill leachate at least, the actual increase after leaching the polymer was no greater than that for distilled water.

Chalk Attenuation Experiments

Following on from the leaching tests, the solutions produced were reacted with Upper Chalk from Thurrock to determine its attenuating properties. In four experiments 20g of ground chalk were mixed with 100ml of one of the resultant leachates in polypropylene laboratory ware. The chalk/leachate mix was stirred for 1 hour using a magnetic stirrer. The solution was then filtered using a Whatman No.2 filter and analysed for the same parameters determined in the leaching experiments. The results are given in Table 7.9.

Comparison of Tables 7.8 and 7.9 shows that most parameters were not attenuated. Of the heavy metals, mercury showed a slight decrease from the distilled water, groundwater and landfill leachates, bringing them down to very low levels. The copper level of the Aveley landfill leachate/polymer liquor was lowered slightly.

Cyanide levels were reduced slightly for the groundwater, landfill and synthetic leachates, while sulphate levels increased for all the leachates. Chloride values remained around the same levels as those after mixing with the polymer.

Table 7.7. Analyses of the "Stablex" polymer and leaching agents used in laboratory experiments.

	Polymer	Distilled Water	Chalk Groundwater	Refuse Leachate	Synthetic Leachate
pH	12.0	6.7	8.0	7.7	6.5
C.O.D.	N.D.	nil	10	1240	6900
Total Dry Matter	47.4	nil	nil	nil	nil
Propionic Acid	N.D.	N.D.	N.D.	N.D.	3000
NH_3-N	110	nil	6	960	660
NO_3-N	1470	nil	15	730	nil
Cl^-	15600	nil	2100	2300	1100
SO_4^-	33600	nil	420	30	890
CN^-	10.5	nil	0.02	0.7	nil
Ca	32000	nil	110	38	180
Mg	N.D.	nil	N.D.	N.D.	156
K	3500	nil	280	940	720
Na	21000	nil	1000	2700	940
Fe	5000	nil	0.3	7.0	34
Mn	210	nil	nil	0.3	nil
As	125	nil	nil	0.19	nil
Cd	80	nil	nil	0.05	nil
Co	7	nil	nil	0.1	nil
Cr	300	nil	0.1	0.1	nil
Cu	410	nil	0.1	0.1	nil
Hg	20	nil	nil	0.001	nil
Ni	170	nil	0.1	0.4	nil
Pb	380	nil	0.1	0.2	nil
Zn	1100	nil	0.02	0.2	nil

All results in µg/ml except pH (units) and T.D.M. (% w/w)

Table 7.8. Analyses of leaching solutions after stirring with "Stablex" polymer for 1 hour.

	Distilled Water	Chalk Groundwater	Refuse Leachate	Synthetic Leachate
pH	9.6	7.9	8.2	8.8
C.O.D.	170	120	1310	6400
NH_3-N	11	15	790	490
NO_3-N	91	73	610	120
Cl^-	4300	5000	5300	3900
SO_4^-	1800	2300	2800	1800
CN^-	0.44	0.43	0.68	0.62
Ca	40	220	52	280
Mg	N.D.	N.D.	N.D.	N.D.
K	680	780	2400	2000
Na	1500	1806	5600	4900
Fe	1.4	0.9	0.6	1.3
Mn	0.05	0.05	0.1	0.05
As	0.04	0.04	0.04	0.04
Cd	0.05	0.05	0.05	0.05
Co	0.1	0.1	0.2	0.2
Cr	0.7	1.0	0.6	0.5
Cu	0.1	0.1	3.6	0.5
Hg	0.016	0.010	0.006	0.007
Ni	0.1	0.1	0.5	0.2
Pb	0.1	0.1	0.1	0.2
Zn	0.02	0.02	0.2	0.02

All results in µg/ml except pH (units)
N.D. = not determined

Table 7.9. Analysis of chalk treated leachates.

	Distilled Water	Chalk Groundwater	Refuse Leachate	Synthetic Leachate
pH	8.2	8.2	7.9	8.0
C.O.D.	120	80	1600	6100
NH_3-N	9.9	23	760	400
NO_3-N	80	37	580	100
Cl^-	3900	5000	5700	3900
SO_4^{-}	2100	2400	3300	2000
CN^-	0.44	0.38	0.48	0.55
Ca	70	28	200	310
Mg	N.D.	N.D.	N.D.	N.D.
K	620	760	2200	1900
Na	1500	1800	5600	5000
Fe	1.6	1.1	0.6	1.3
Mn	0.05	0.05	0.1	0.05
As	0.04	0.04	0.04	0.04
Cd	0.05	0.05	0.05	0.05
Co	0.1	0.1	0.2	0.2
Cr	0.7	0.6	0.7	0.4
Cu	0.1	0.1	3.0	0.3
Hg	0.012	0.008	0.003	0.008
Ni	0.2	0.1	0.6	0.2
Pb	0.1	0.1	0.2	0.1
Zn	0.02	0.02	0.1	0.02

All results in µg/ml except pH (units)
N.D. = not determined

7.6. Discussion

Because of the predominantly carbonate mineralogy of the Upper Chalk (Hancock, 1975) carbonate precipitation of the heavy metals is the most likely mechanism responsible for their removal from solution and the data in Table 7.1 agrees with this in that the order of uptake inversely agrees with their relative carbonate solubilities. Any small quantities of the clay minerals are likely to remove some of the metals, but their importance in relation to precipitation is likely to be small with perhaps the exception of nickel(ii) which showed a marked reduction in uptake in the presence of ammonium (Table 7.3).

Mather and Parker (1978) found dark coatings on chalk fissure surfaces in a borehole adjacent to a landfill containing industrial and domestic wastes and concluded that the material was a mixed manganese/iron hydrated oxide. Thus it is possible that the iron(iii) is removed from the solutions in these experiments in a similar way.

The elution of calcium is not remarkable considering the $CaCO_3$ nature of chalk, which although only sparingly soluble does release some calcium into solution under natural conditions (as shown by the analysis of the chalk groundwater in Table 7.8). The initially high concentration of sodium is probably caused by the presence of sodium in the groundwater in this area due to saline intrusion (Table 7.7).

The results of competing heavy metals (Table 7.2) shows that the metals with the most soluble carbonates (nickel(ii) and zinc(ii) are most affected by the presence of other heavy metals. In a landfill situation, however, this is unlikely to be of any serious consequence for any great distance from a site because after rapid precipitation of cadmium, copper and lead, nickel and zinc precipitation will occur. In addition any iron or manganese oxides formed (Mather and Parker, op.cit.) will act as a substrate for heavy metal adsorption.

Ammonium had no significant effect on the uptake of either cadmium(ii), copper(ii), lead(ii) or zinc(ii) (Table 7.3), which is to be expected if carbonate precipitation is the predominant mechanism of their removal from solution. The dramatic reduction in nickel(ii) uptake suggests that ammonium competes with it for uptake sites, or that nickel mobility is increased by the formation of ammine complexes. Although no measurements were taken of ammonium levels, nor of any cations likely to be present in clay exchange sites, it seems likely that cation exchange, or the small quantities of clay assumed to be present, may be important in nickel(ii) uptake. Similarly it would appear that ammonium displaces monovalent potassium and sodium from exchange sites leading to their elution rather than a small uptake after 48 hours.

From the experimental results of metal uptake in the presence of up to 1000ug/ml chloride (Table 7.4) it appears that chloro-complexing is not likely to be of significant consequence in increasing metal mobility. Had the reverse been true, this may have been of particular relevance in assessing waste disposal sites in coastal effected parts of the chalk aquifer, where saline intrusion leads to high chloride in the groundwater (Table 7.7).

The presence of organic acids had only very limited effect on copper(ii) and zinc(ii) after 48 hours, and only marginally reduced iron(iii) uptake (Table 7.5). However comparison of Table

7.6 with Table 7.1 shows that the rate of iron(iii) removal was slowed down. This probably reflects a reduction in the rate of precipitation as either carbonate or hydroxide due to the depressed initial pH caused by the carboxylic acids. The possibility of complex formation is considered unlikely (see Chapter 6).

Comparison of Tables 7.7 and 7.8 brings to light several factors which would require consideration before large scale tipping of the Stablex polymer in chalk pits close to or above the water table. Firstly the extreme alkalinity of the polymer is sufficient to buffer the slightly acid synthetic leachate and distilled water to pH values greater than that of the chalk groundwater. This has possible advantages in reducing heavy metal mobility, and this is borne out in the results given here, with the exception of copper, which show concentrations equal to or only slightly above those of the natural groundwater. Table 7.5 showed that copper(ii) is slightly more mobile in the presence of organic acids, and this may be the cause of the higher copper levels in the leachates after mixing with the polymer. However it was also shown that zinc(ii) mobility is increased with organic acids and from the quantities of the two metals in the polymer it would be expected that more zinc than copper would be leached from the polymer by the organic acid bearing solutions.

The second point of note is the substantial release of anions from the polymer. Cyanide, although in terms of health is potentially the most harmful, is unlikely to be of consequence after dilution with unaffected groundwater is taken into account, and unlikely to rise significantly above background concentrations. Nitrate levels were substantially higher in each solution except the Aveley leachate, and well above the World Health Organization recommended limit for drinking water (11.3µg/ml NO_3 as N) and this in an area where nitrates must already cause some problems in terms of supply due to the background groundwater nitrate level (15µg/ml). Furthermore the chloride and sulphate levels were increased dramatically, for all the leaching solutions, to levels likely to be unacceptable for either potable or industrial supply. Again, the chloride concentrations compound an existing problem in that that found in the natural groundwater is already high, presumably due to an ingression of saline water.

The third main observation is that of the increase in the alkaline earth metals (magnesium was not measured, but it seems likely that it follows a similar trend). The occurrence of these species coupled with the high pH could lead to an unacceptable increase in hardness, again where this parameter is already likely to be a serious constraint on groundwater use. Thus in an area where there is significant groundwater abstraction for industrial purposes, serious and costly groundwater problems could occur. Since dilution is the only mechanism by which these parameters are lessened, careful consideration of hydrogeological conditions would need to be taken in selecting sites for depositing the polymer.

Treatment with chalk from the site showed little change in the concentrations of the leachate parameters (Table 7.9). The copper levels which were unusually high were reduced slightly as may be expected from the work described in Section 7.2. No other parameters showed any sign of attenuation, as indeed none was expected. The alkaline earth metals were shown previously (Section 7.2) not to be removed from solution by chalk. Perhaps the only change of significance was not one of attenuation, but that of an increase in sulphate, presumably as a result of soluble sulphates in the chalk (the natural chalk groundwater has 420μg/ml SO_4; Table 7.7).

Chapter 8. Conclusions

The small scale laboratory shaking tests undertaken have demonstrated that, under aerobic conditions, heavy metal attenuation occurs due to chemical interaction with mineral phases in the Bunter Sandstone and Chalk. Whilst hydrogeological and chemical conditions affecting the mobility of leachate constituents will vary between individual waste disposal sites, the following conclusions are drawn from the laboratory experiments:

1) The order of retention of the heavy metals by the Bunter Sandstone expressed on a weight basis is:

$$Pb > Cu > Zn > Cd > Ni$$

This order relates to the material as a whole, but since more than one mechanism is responsible for metal uptake, with each mechanism showing varying affinities for metal species, the ranking order could change within the stratigraphic sequence without significantly altering the overall ability of the rock to attenuate heavy metals.

2) Three mechanisms of heavy metal uptake were identified in the Bunter Sandstone:

i) Precipitation as carbonates is responsible for the greatest part of heavy metal removal and the overall order of retention is a reflection of the association between the heavy metal and the carbonate phase. In the presence of bicarbonate ions derived from a landfill leachate, precipitation would restrict heavy metal migration further provided that the buffering capacity of the sand is not exceeded allowing acid conditions to prevail

ii) Cation exchange of the heavy metals by alkaline earth metals, particularly calcium, increases in importance with decreasing grain size and increasing clay content. The order of association, expressed on a weight basis, between the heavy metals and cation exchange sites is:

Cd > Pb > Ni > Cu > Zn

Local increase in clay content of the rocks could alter the affinity sequence of metal uptake whilst at the same time increasing the overall capacity. Further elution of calcium occurs due to exchange with excess hydrogen ions

iii) Exchange/adsorption onto iron sesquioxides occurs by two mechanisms. There is a rapid, possibly reversible, cation exchange or adsorption reaction followed by a slower uptake, which may be due to the incorporation of the metal into the crystal lattice. The most likely iron species involved in these reactions is haematite (Fe_2O_3).

Iron(iii) precipitates from solution onto the sesquioxides. In an aerobic zone down hydraulic gradient from a landfill, precipitation of iron(iii) from a leachate would give rise to a continuous replenishment of substrate for heavy metal uptake.

3) The Bunter Sandstone shows a strong capacity to buffer both acid and alkaline solutions to values close to neutrality. This factor must be beneficial to heavy metal attenuation from acid leachates by precipitation and cation exchange, both of which are inhibited by acid conditions.

Alkaline earth metals released by dissolution of soluble phases, particularly by acid solutions, and as a result of cation exchange will add to the levels found in any leachate. Since the Bunter sand is saturated with respect to calcium, which therefore is not chemically attenuated, a local increase in hardness (a hardness "halo") is inevitable around tipsites on Bunter Sandstone.

4) The presence of alkaline earth metals in leachates is not likely to affect the uptake of heavy metals by the Bunter Sandstone, despite calcium(ii) showing a stronger affinity for cation exchange sites than the heavy metals. The heavy metals show a strong affinity for the iron sesquioxides, whereas the alkaline earths show very little, and the heavy metals are more likely to precipitate as carbonates.

5) Competition between the heavy metals may reduce the amount of any one metal taken up by the Bunter Sandstone, but increasing total metal concentration increases the overall uptake. Quantities of heavy metals in most landfill leachates are unlikely to exceed the uptake capacity of the Bunter Sandstone for any great distance where the leachate passes through the rock by intergranular flow.

6) High ammonium ion concentrations in leachates may increase the mobility of the heavy metals, and in particular cadmium, passing through the Bunter Sandstones. This reflects the tendency of ammonium to compete more successfully with cadmium(ii) than with other ions for available exchange sites.

Calcium is eluted from the Bunter sands due to its replacement by ammonium ions.

7) Chloride ion concentrations up to 1000µg/ml have no effect on metal uptake although the possibility that chloro-complex formation may increase the proportions of metals remaining labile cannot be ruled out.

8) The reduction is heavy metal uptake by the Bunter Sandstone in the presence of up to 1000µg/ml of short chain carboxylic acids appears to be temporary. This may be the result of the affinity of the organic molecules for iron(iii) which alters the kinetics of metal uptake by the sesquioxides. Acetic acid shows the greatest affect on metal uptake and due to its abundance in landfill leachates is most likely to affect metal mobility.

The organic acids increase the dissolution of soluble calcium and magnesium phases, which will add to the production of a hardness halo.

9) Precipitation of the heavy metals as carbonates is responsible for their effective uptake by chalk, although exchange reactions on minor quantities of clays found in the Upper Chalk may also remove a small percentage of the heavy metals from solution. Competition between the heavy metals is unlikely to be important in promoting metal mobility, whilst precipitation of iron and manganese hydroxides will increase the removal of these metals from solution.

10) High concentrations of ammonium ions increases the mobility of nickel(ii) and to a lesser extent zinc(ii) and is thought to be due either complex formation or their

displacement by the ammonium from cation exchange sites.

11) Chloride, which is commonly found in high concentrations is coastally affected chalk groundwater, as well as landfill leachates, has no effect on heavy metal uptake by chalk.

12) Only a high concentration ($> 1000\mu g/ml$) of carboxylic acids has any significant effect on heavy metal uptake, although the rate at which iron(iii) precipitates is reduced. Locally reduced pH values due to carboxylic acid is likely to lead to solution of the chalk with a subsequent release of calcium. This is unlikely to be widespread because of rapid neutralisation.

13) The industrial waste treatment polymer, "Stablex" behaves well in retaining heavy metals when in contact with either chalk groundwater and landfill leachates. There is, however, a significant release of anions such as sulphate, nitrate and chloride which are not chemically attenuated by chalk. High dilution of these anions by groundwater flow in fissured chalk must be considered in assessing the suitability of the polymer for chalk pit reclamation.

All the experiments were carried out under aerobic conditions and as such any conclusions drawn regarding the attenuation ability of Triassic Sandstones and Chalk should only be applied to similar conditions. Anaerobic conditions are inevitable under site conditions where there is mechanical compaction of the waste and cover applied. Under these conditions, bacterial action will deplete available oxygen giving rise to anaerobic conditions. Metal mobility may then be increased, in particular iron which is more mobile in its divalent state.

The results discussed in this work underline the potential for heavy metal attenuation under aerobic conditions and support the current requirement of most statutory bodies concerned with groundwater pollution prevention in seeking an unsaturated zone beneath landfills.

The importance of iron sesquioxides, clays and carbonates in metal uptake may be applicable to sites other than Triassic Sandstones. All red sandstones and glacial sands and gravels contain varying proportions of sesquioxides and clays. It is reasonable to assume that similar processes to those found in the Bunter Sandstone will occur in them. Thus it may be desirable to place a layer of glacial overburden or washings from sand and gravel production where available over any aquifer bedrock prior to tipping to produce an aerobic unsaturated zone to maximise toxic metal attenuation.

References

ADAMSON, A.W. 1976. Physical chemistry of surfaces, 3rd Edition. Wiley, New York.

AGEMIAN, H. & CHAU, A. SY. 1976. Evaluation of extraction techniques for the determination of metals in aquatic sediments. Analyst. 101, 761-767.

AGUILERA, N.H. & JACKSON, M.C. 1953. Iron oxide removal from soils and clays. Soil Sci. Soc. Amer. Proc. 17, 359-364.

ANDERSON, B.J., JENNE, E.A. & CHAO, T.T. 1973. The sorption of silver by poorly crystallised manganese oxides. Geochim. Cosmochim. Acta 37, 611-622.

ANON. 1961. Pollution of water by tipped refuse. Report of the Technical Committee on the Experimental Disposal of House Refuse in Wet and Dry Pits. Ministry of Housing and Local Government, HMSO, London, 141pp.

ANON. 1971. Refuse disposal. Report of the Working Party on Waste Disposal. Dept. of the Environment, HMSO, London, 198pp.

APGAR, M.A., LANGMUIR, D. 1971. Groundwater pollution potential of a landfill above the water table. Groundwater 9, 76-96.

BAARS, S. 1957. Travel of pollution and purification en route in sandy soil. Bull. World Health Organisation 16, 727-747.

BASCOMB, C.L. 1964. Rapid method for the determination of cation-exchange capacity of calcareous and non-calcareous soils. J. Sci. Fd. Agric. 15, 821-823.

BITTEL, J.E. & MILLER, R.J. 1974. Lead, cadmium and calcium selectivity coefficients on a montmorillonite, illite and kaolinite. J. Env. Quality 3, 250-253.

BOREHAM, D., PARKER, A. & WRIGHT, S.J. 1975. The retention by sand of cations present in synthetic landfill leachates. Waste and Landfill Research Tech. note 21, Dept. of the Environment, London.

BRERETON, N.R. & WILKINSON, W.B. 1976. Flow mechanisms governing the movement of a pollutant in a groundwater system. Groundwater quality, measurement, prediction and protection Paper 4. Water Resource Centre Conference, University of Reading, September 6-8.

BRESLER, E. 1973. Simultaneous transport of solutes and water under transient unsaturated flow conditions. Water Resources Research 9 (4), 975-986.

BRINDLEY, G.W. (ed). 1951. The X-ray identification and crystal structure of clay minerals. Mineralogical Society, London.

BROMLEY, J. & BOREHAM, D. 1978. A comparison of data on the movement of metal ions through sands and clays from the Lower Greensand formation. Waste and Landfill Research Tech. note 58, Dept. of the Environment, London.

BURNS, R.G. 1965. Formation of cobalt(iii) in the amorphous $FeOOH.nH_2O$ phase of manganese nodules. Nature 205, 999.

CARTER, M. 1975. Some aspects of the geochemistry of liquid waste disposal. Ph.D. Thesis. University of Aston in Birmingham, 261pp.

CARTER, P.G. & MALLAR, D.J. 1974. A study of the strength, compressibility and density trends within the Chalk of south east England. Q. J. eng. Geol. 7, 43-55.

CHAO, T.T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Amer. Proc. 36, 764-768.

CLARK, T.P. & PISKIN, R. 1977. Chemical quality and indicator parameters for monitoring landfill leachate in Illinois. Environ. Geol. 1 (6), 329-339.

CRONAN, D.S. 1977. Deep sea nodules : distribution and geochemistry. In: GLASBY, G.P. (ed). Marine Manganese Deposits. Elsevier, New York.

DAVIS, S.N. 1969. Porosity and permeability of natural materials. In: De WEIST, R.J. (ed). Flow Through Porous Media. Academic Press, New York & London.

DEPARTMENT OF THE ENVIRONMENT. 1978. Cooperative programme of research on the behaviour of hazardous waste in landfill sites. Final report of the Policy Review Committee. HMSO, London, 184pp.

DYCK, W. 1968. Adsorption and coprecipitation of Ag on hydrous ferric oxide. Can. J. Chemistry 46, 1441-1444.

EDMUNDS, W.M. 1976. Groundwater geochemistry - controls and processes. Groundwater quality, measurement prediction and protection, Paper 6. Water Research Centre Conference, University of Reading, September 6-8.

EDMUNDS, W.M., LOVELOCK, P.E.R. & GRAY, D.A. 1973. Interstitial water chemistry and aquifer properties of the Upper and Middle Chalk of Berkshire, England. J. Hydrol. 19, 21-31.

EDMUNDS, W.M. & MORGAN-JONES, M. 1976. Geochemistry of groundwater in British Triassic sandstones : the Wolverhampton-east Shropshire area. Q. J. eng. Geol. 9, 73-101.

EDWORTHY, K.J. & BROWN, S.L. 1976. An in-situ groundwater sampling device. Internal Laboratory Report, Water Research Centre, Medmenham, Bucks.

FARRAH, H., HATTON, D. & PICKERING, W.F. 1980. The affinity of metal ions for clay minerals. Chem. Geol. 28, 55-68.

FARRAH, H. & PICKERING, W.F. 1977. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water, Air Soil Pollution 8, 189-197.

FARRAH, H. & PICKERING, W.F. 1979. pH effects in the adsorption of heavy metal ions by clays. Chem. Geol. 25, 317-326.

FOLK, R.L. 1974. Petrology of Sedimentary Rocks. Hamphill, Texas.

FRIPIAT, J.J. & GASTUCHE, M.C. 1952. Etude physico-chimique des surfaces des argiles. Publication de l'Institute National Pour l'Etude Agronomique Du Congo Belge (INEAC) Ser. Sci. (54).

FROST, R.R. & GRIFFIN, R.A. 1977. Effect of pH on adsorption of copper, zinc and cadmium from landfill leachate by clay minerals. J. Env. Sci. & Health A12 (4-5), 139-156.

FULLER, W.H., KORTE, N. 1976. Attenuation mechanisms of pollutants through soils. In: GENETTELLI, J. & CIRELLO, J. (ed). Gas and leachate from landfills : formation, collection and treatment. US EPA 600/9-76-004, 111-121.

FUNGAROLI, A.A. 1971. Pollution of subsurface water by sanitary landfills. US EPA SW-12RG pp.131.

GADDE, R.R. & LAITINEN, H.A. 1973. Study of the sorption of lead by hydrous ferric oxide. Environ. Lett. 5, 223-235.

GASKARTH, J.W., CHAPPELL, C.L. & TODD, D.W.R. 1980. The use of poisonous, noxious and polluting wastes in land reclamation. 1st International Environment and Safety Exhibition, Wembley, September 1-4.

GOLDBERG, E.D. 1954. Marine geochemistry. 1. Chemical scavengers of the sea. J. Geol. 62, 249-265.

GOLWER, A. & MATTHESS, G. 1968. Research on groundwater contaminated by deposits of solid waste. Int. Assoc. Sci. Hydrol. 78, 129-133.

GOLWER, A., MATTHESS, G. & SCHNEIDER, W. 1970. Selbstreinigungsvorgange im aeroben und anaeroben grundwasserbereich. Vom Wassen, Weinheim/Bergstrasse, 81-90.

GRAY, D.A., MATHER, J.D. & HARRISON, I.B. 1974. Review of groundwater pollution from waste disposal sites in England and Wales, with provisional guidelines for future site selection. Q. J. eng. Geol. 7, 181-196.

GRAY, R. & HENTON, M.P. 1975. An investigation into the contamination of groundwater at an industrial tipping site. Solid Wastes 65, 153-170.

GRIFFIN, R.A., CARTWRIGHT, K., SHRIMP, N.F., STEELE, J.D., RUCH, R.R., WHITE, W.A., HUGHES, G.M. & GILKESON, R.H. 1976. Attenuation of pollutants in municipal landfill leachate by clay minerals. Part 1 - Column leaching and field verification. Illinois State Geol. Survey Environmental Geol. note 78, 34pp.

GRIFFIN, R.A., FROST, R.R., AU, A.K. & ROBINSON, G.D. 1977. Attenuation of pollutants in municipal landfill leachate by clay minerals. Part 2 - Heavy metal adsorption. Illinois State Geol. Survey Environmental Geol. note 79, 47pp.

GRIFFIN, R.A. & SHRIMP, N.F. 1976a. Leachate migration through selected clays. In: GENETELLI, J. & CIRELLO, J. (ed). Gas and leachate from landfills : formation, collection and treatment. US EPA 600/9-76-004, 111-121.

GRIFFIN, R.A. & SHRIMP, N.F. 1976b. Effect of pH on exchange-adsorption or precipitation of lead from landfill leachates by clay minerals. Environ. Sci. Technol. 10 (13), 1256-1261.

GRIFFIN, R.A., SHRIMP, N.F., STEELE, J.D., RUCH, R.R., WHITE, W.A. & HUGHES, G.M. 1976. Attenuation of pollutants in municipal landfill leachates by passage through clays. Environ. Sci. Technol. 10 (13), 1262-1268.

GRIM, R.E. 1962. Clay Mineralogy. McGraw-Hill, New York.

GUPTA, S.K. & CHEN, K.Y. 1975. Partitioning of trace metals in selective chemical fractions of nearshore sediments. Environ. Lett. 10, 129-158.

HAGERTY, D.J. & PAVONI, J.L. 1973. Geologic aspects of landfill waste disposal. Eng. Geol. 7, 219-229.

HAHNE, H.C.H. & KROONTJE, W. 1973. Significance of pH and chloride concentration on behaviour of metal pollutants mercury(ii), cadmium(ii), zinc(ii) and lead(ii). J. Environ. Qual. 2, 444-450.

HAINS, B.A. & HORTON, A. 1969. British Regional Geology : Central England (3rd Edition). HMSO, London.

HANCOCK, J.M. 1975. The petrology of the Chalk. Proc. Geol. Assoc. 86 (4), 499-535.

HARMAN, C.G. & FRAULINI, F. 1940. The properties of kaolinite as a function of its particle size. J. Amer. Ceramic Soc. 23, 252-259.

HEADWORTH, H.G., PURI, S. & RAMPLING, B.H. 1980. Contamination of a chalk aquifer by mine drainage at Tilmanstone, east Kent, U.K. Q. J. eng. Geol. 13 (2), 105-117.

HEADWORTH, H.G. & WILKINSON, W.B. 1976. Measures for the protection and rehabilitation of aquifers in the U.K. Groundwater Quality, Measurement, prediction and protection, Paper 21. Water Research Centre Conference, University of Reading, September 6-8.

HEM, J.D. 1978. Redox processes at surfaces of manganese oxides and their effects on aqueous metal ions. Chem. Geol. 21, 199-218.

HODGSON, J.F. 1960. Cobalt reactions with montmorillonite. Soil Sci. Soc. Amer. Proc. 24, 164-168.

HOEKS, J. 1976. Pollution of soil and groundwater from land disposal of solid wastes. Institute for land and Waste Management Research Tech. Bull. 96, 70-86. Wageningen, Netherlands.

HOFER, L.J.E. & WELLER, S.O.L. 1947. The nature of the iron compounds in red and yellow sandstone. Science 106, 470.

HOLDRIDGE, D.A. 1969. The sorption of heavy metal cations by ball clay. Proc. Int. Clay Conf. Israel, 341-349.

HOLMGREN, G.S. 1967. A rapid citrate-dithionite extractable iron procedure. Soil Sci. Soc. Amer. Proc. 31, 210-211.

HUGHES, G.M. & CARTWRIGHT, K. 1972. Scientific and administrative criteria for shallow waste disposal. J. Amer. Soc. Civ. Eng. 42, 70-73.

HUGHES, G.M., LANDON, R.A. & FARVOLDEN, R.N. 1971. Summary of findings on solid waste disposal sites in northeastern Illinois. Environ. Geol. Notes 45, 25pp.

JAMES, R.O., STIGLICH, P.J. & HEALY, T.W. 1976. Analysis of models of adsorption of metal ions at oxide-water interfaces. Faraday Discuss. Chem. Soc. 59, 142-156.

JENNE, E.A. 1968. Controls on Mn, Fe, Ni, Cu and Zn concentrations in soils and water in the significant role of hydrous and Fe oxides. In: GOULD, R.F. (ed)., Trace Inorganics in Water, Adv. Chem. Ser. 73, 337-387.

KINNIBURGH, D.G., JACKSON, M.L. & SYERS, J.K. 1976. Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminium. Soil Sci. Soc. Amer. Proc. 40, 796-799.

KISHK, F.M. & HASSAN, M.N. 1973. Sorption and desorption of copper by and from clay minerals. Plant Soil 39, 497-505.

KRAUSKOPF, K.B. 1956. Factors controlling the concentration of thirteen rare metals in sea water. Geochim. Cosmochim. Acta 9, 1-32.

KU, F.H., KATZ, B.G., SULAM, D.J. & KRULIKAS, R.K. 1978. Scavenging of chromium and cadmium by aquifer material - South Farmingdale - Massapequa area Long Island, New York. Groundwater 16 (2), 112-118.

LAGERWERFF, J.V. & BROWER, D.L. 1972. Exchange adsorption of trace quantities of cadmium in soils treated with chlorides of aluminium, calcium and sodium. Soil Sci. Soc. Amer. Proc. 36, 734-737.

LAGERWERFF, J.V. & BROWER, D.L. 1973. Exchange adsorption or precipitation of lead in soils treated with chlorides of aluminium, calcium and sodium. Soil Sci. Soc. Amer. Proc. 37, 11-13.

LANGMUIR, D. 1972. Controls on the amounts of pollutants in sub-surface waters. Earth and Min. Sci. Bull. 42 (2), 9-13.

LEENHEER, J.A., MALCOLM, R.C. & WHITE, W.R. 1976. Investigation of the reactivity and fate of certain organic components of an industrial waste after deep well injection. Environ. Sci. Technol. 10, 445-451.

LOGANATHAN, P. & BURAU, R.G. 1973. Sorption of heavy metal ions by hydrous manganese oxide. Geochim. Cosmochim. Acta. 37, 1277-1293.

MAES, R.G. & CREMERS, A. 1975. Cation-exchange hysteresis in montmorillonite - a pH dependent effect. Soil Sci. 119, 198-202.

MATHER, J.D. 1977. Attenuation and control of landfill leachates. Inst. Solid Waste Management, 79th Ann. Conf., 14pp.

MATHER, J.D. & BROMLEY, J. 1976. Research into leachate generation and attenuation at landfill sites. Land Reclamation Conf. Paper 25, Thurrock, Essex.

MATHER, J.D. & PARKER, A. 1978. The disposal of industrial and domestic waste to a landfill overlying Lower Chalk. AERE-R9097, HMSO, London.

MATTHESS, G. 1972. Hydrogeological criteria for the self-purification of polluted groundwater. Proc. 24th Int. Geol. Congress, Montreal, Section 11, 296-304.

McBRIDE, M.B. & MORTLAND, M.M. 1974. Copper(ii) interactions with montmorillonite-evidence from physical methods. Soil Sci. Soc. Amer. Proc. 38, 408-415.

McKEAGUE, J.A., BRYDON, J.E. & MILES, N.M. 1971. Differentiation of forms of extractable iron and aluminium in soils. Soil Sci. Soc. Amer. Proc. 35, 33-38.

McKENZIE, R.M. 1970. The reaction of cobalt with manganese dioxide minerals. Aust. J. Soil Res. 8, 97-106.

MEHRA, O.P. & JACKSON, M.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Min. 7, 317-327.

McWHINNIE, W.R., MONSEF-MIRZAI, P. & GASKARTH, J.W. 1981. Clay Chemistry and toxic waste disposal. 2nd International Environment and Safety Exhibition, Wembley, September 2-4.

MONSEF-MIRSAI, P. 1980. Geochemical aspects of waste disposal. Ph.D. Thesis. University of Aston in Birmingham, 171pp.

MILLBANK, P. 1978. Promising future of chalk needs D.O.E. investigation. Surveyor 151 (4467), 14, 17.

MITCHELL, B.D. & MACKENZIE, R.C. 1954. Removal of free iron oxide from clays. Soil Sci. 77, 173-184.

MONKHOUSE, R.A. & FLEET, M. 1975. A geophysical investigation of saline water in the Chalk of the south coast of England. Q. J. eng. Geol. 8, 291-302.

MORGAN, J.J. & STUMM, W. 1964. Colloid chemical properties of manganese dioxide. J. Colloid Sci. 19, 347-359.

MUNDY, M.J. & GASKARTH, J.W. 1979. Practical considerations of waste landfill operations. Proc. Symp. Midland Geotech. Soc., Birmingham University.

MYERS, R. 1974. Soil influence on landfill leachates. Ph.D. Thesis. Drexel University, 305pp.

NALOVIC, L.J., PEDRO, G. & JANOT, C. 1976. Demonstration by Mössbauer spectroscopy of the role played by transitional trace elements in the crystalogenesis of iron hydroxides(iii). Proc. Int. Clay Conf. 1975, Applied Publishers Ltd., Wilmette, Illinois, 601-610.

NICHOLLS, G.D. 1972. Pollution affecting wells in the Bunter Sandstone. Proc. Water Research Association Conf. 1, 187-196.

PARK, A. 1981. Personal communication. (Department of Chemistry, University of Aston in Birmingham).

PARKER, C. & PORTLOCK, P. 1974. Waste disposal planning. Local Government Operational Research Unit. Report, T51.

RAYLEIGH, LORD. 1946. Experimental production of red and yellow sandstone from chalybeate water. Proc. Roy. Soc. London, Series A 186, 411-422.

REDDY, M.R. & PERKINS, H.F. 1974. Fixation of zinc by clay soils. Soil Sci. Soc. Amer. Proc. 38, 229-231.

ROBINSON, H.D. & MARIS, P.J. 1979. Leachate from domestic waste : generation, composition and treatment. A review. Water Research Centre Tech. Report 108.

ROSS, C.A.M. 1978. Extractive characterization of heavy metal distribution in contaminated Lower Greensand. Waste and Landfill Research Tech. note 61, Dept. of the Environment, London.

ROSS, C.A.M. 1980. Experimental assessment of pollutant migration in the unsaturated zone of the Lower Greensand. Q. J. eng. Geol. 13, 177-187.

ROVERS, F.A. & FARQUAHAR, C.J. 1973. Infiltration and landfill behaviour. J. Env. Eng. Div., Amer. Soc. Civ. Eng. 99 (EES), 671-690.

ROVERS, F.A. & FARQUAHAR, G.J. 1974. Evaluating contaminant attenuation in the soil to improve landfill selection and design. Proc. Int. Conf. Land for Waste Management, Ottawa, 1973, 161-173.

SHERLOCK, R.L. 1947. British Regional Geology : London and the Thames Valley (3rd Edition). HMSO, London.

SHUMAN, L.M. 1976. Zinc adsorption isotherms for soil clays with and without iron oxides removed. J. Soil Sci. Soc. Amer. 40, 349-352.

SINGHAL, J.P. & KAMUR, D. 1977. Thermodynamics of exchange of zinc with Mg-bentonite and Mg-illite. Geoderma 17, 253-258.

SKIBITZKE, H.E. & ROBINSON, G.M. 1963. Dispersion in groundwater flowing through hetergeneous materials. U.S. Geol. Surv. Prof. Paper 386-B.

STEGER, H.F. 1973. Mechanisms of the adsorption of trace copper by bentonite. Clays Clay Min. 21, 429-436.

STIFF, M.J. & YOUNG, C.P. 1976. Factors affecting the transport of pollutants within and away from landfill sites. Groundwater quality, measurement, prediction and protection, Paper 13. Water Research Centre Conference, University of Reading, September 6-8.

SUAREZ, D. 1976. Heavy metals in waters and soil associated with several Pennsylvania landfills. Ph.D. Thesis. University of Pennsylvania.

SUBRAMANIAN, U. 1973. Mechanisms of fixation of the trace metals manganese and nickel by ferric hydroxide. Ph.D. Thesis, Northwestern University, 121pp.

SUMNER, M.E. 1962. The effect of sodium dithionite on the surface properties of clays. Agrochimica 6, 183-189.

SUMNER, M.E. 1963. Effect of iron oxides on positive and negative changes in clays and soils. Clays and Clay. Min. 5, 218-226.

SWARTZEN-ALLEN, S. & MATIJAVIC, C. 1973. Surface and colloid chemistry of clays. Chem. Reviews 74, 385-399.

SYLVA, R.N. & BROWN, P.L. 1980. The hydrolysis of metal ions. Part 3, lead(ii). J. Chem. Soc. (Dalton) 9, 1577-1581.

THEIS, C.V. 1954. Geologic and hydrologic factors in ground disposal of waste. Sanitary Engineering Conf., Baltimore. U.S. Geol. Survey, WASH 275, 261-283.

TITTLEBAUM, M.E., PAVONI, J.L. & HAGERTY, D.J. 1975. Investigation of leachate heavy metal and organic carbon content stabilisation. 5th Ann. Environmental Engineering and Science Conf., Louisville Kentucky, 61-67.

van LOON, J.C. & PARISSIS, C.M. 1969. Scheme of silicate analysis based on the lithium metaborate fusion followed by atomic absorption spectrophotometry. Analyst 94, 1057-1062.

WARRINGTON, G., AUDLEY-CHARLES, M.G., ELLIOT, R.E., EVANS, W.B., IVIMEY-COOK, H.C., KENT, P., ROBINSON, P.L., SHOTTON, W. & TAYLOR, F.M. 1980. A correlation of Triassic rocks in the British Isles. Geol. Soc. Lond. Special Report No.13, 78pp.

WEIST, W.J.Jr. & PETTIJOHN, R.A. 1975. Investigating groundwater pollution from Indianapolis landfills - the lesson learned. Groundwater 13, 191-196.

ZHABROVA, G.M. & EGOROV, E.V. 1961. Sorption and ion exchange as amphoteric oxides and hydroxides. Russ. Chem. Rev. 30, 338-346.

Appendix 1. Atomic Absorption Spectrophotometry standard conditions for analysis*

Model: Perkin Elmer 460

Element	Source	Wavelength (nm)	Slit Setting (nm)	Flame	Sensitivity (ug/ml)
Al	Hollow cathode lamp	309.3	0.7	Nitrous oxide/ acetylene	1
Ca	"	422.7	0.7	Air/acetylene	0.08
Cd	"	228.8	0.7	"	0.025
Cu	"	324.8	0.7	"	0.09
Fe	"	248.3	0.2	"	0.12
K	"	766.5	2.0	"	0.04
Mg	"	285.2	0.7	"	0.007
Na	"	589.0	0.7	"	0.015
Ni	"	232.0	0.2	"	0.15
Pb	"	283.3	0.7	"	0.5
Si	"	251.6	0.2	Nitrous oxide/ acetylene	1.8
Zn	"	213.9	0.7	Air/acetylene	0.018

* From "Analytical Methods for Atomic Absorption Spectrophotometry", Perkin-Elmer, September 1976

Standards prepared from B.D.H. stock solutions for A.A.S.

Appendix 2

Chemical Analysis of the Bunter Sandstone

Method. (Van Loon and Parissis, 1956).

Clean graphite crucibles were ignited at 950°C for 30 minutes and allowed to cool (with care taken not to disturb the powdery inside surface). 0.200g of powdered rock sample (crushed by Tema mill) was mixed with 1.400g of lithium metaborate in a porcelain crucible and transfered to the pre-ignited graphite crucible. The samples were then fused at 900°C for 15 minutes and the melt poured into 100ml of 1 + 24 nitric acid in a plastic beaker. The sample was then dissolved using a teflon coated stirrer.

Analysis.

In order to overcome interference between elements in atomic absorption spectroscopy the following procedures of standard preparation and analysis were used.

Si, Fe, Na, K and Mn standards were prepared using stock solutions and nitric acid (1 + 24) with the addition of lithium metaborate to give a concentration of 0.56% $LiBO_2$.

Al, Ca and Mg solutions were prepared in a similar fashion but with the addition of lanthanum to give 1% La.

Mn was determined by direct aspiration into an air/ acetylene flame.

Fe was determined by diluting on aloquot of the sample with nitric acid (1 + 24) plus sufficient lithium metaborate to give 0.56% $LiBO_2$.

Ca and Mg were treated as for Fe, but with the addition of lanthium to give 1% Li.

All determinations were done by Perkin Elmer model 460 atomic absorbtion spectrophotometer under standard conditions described in Appendix 1.

Results (expressed as % as oxide)

	grain size (μm)						
	Bulk	1000	500	250	125	63	38	Blank
Al	4.53	3.20	4.18	5.79	7.71	10.68	23.13	0.00
Ca	0.04	0.01	0.01	0.01	0.01	0.02	0.03	0.75
Fe	2.40	1.95	2.11	2.10	2.28	3.05	3.14	0.03
K	2.48	1.89	2.13	2.54	2.85	3.12	3.49	0.00
Mg	0.06	0.04	0.05	0.05	0.05	0.08	0.15	0.00
Mn	0.25	0.09	0.06	0.04	0.06	0.06	0.04	0.02
Na	0.12	0.09	0.10	0.12	0.14	0.12	0.11	0.10
S	73.90	75.62	75.36	71.68	73.80	62.07	55.08	0.00

Appendix 3

In situ Landfill Experiments

As part of the programme of research into the behaviour of "Stablex" polymer in worked out chalk pits and combined with domestic refuse, a series of in situ landfill experiments were designed. The experiments were divided into three parts, each consisting of several cells. Construction of the experiments was started during the summer of 1978 in Tunnel No.4 quarry at West Thurrock (N.G.R. T.Q.577788).

Part 1 was designed with four large cells ($2 \times 10^4 m^3$), each with a different combination of domestic refuse and/or polymer, to determine the suitability of each fill for large scale commercial disposal and land reclamation. These cells were constructed in the northern limb of the quarry and separated by chalk bunds, initially about 3m thick and 2m high, to be raised as filling progressed. The four fills to be used are:-

Cell 1 : "Stablex" alone

Cell 2 : "Stablex" mixed with pulverised domestic refuse

Cell 3 : A "Stablex" base with interlayered high density baled domestic refuse

Cell 4 : A "Stablex" base, walls and top escapsulating baled domestic refuse

The layout of the cells is shown in Figure (i).

The cell floors are approximately 2m above the pumped water table recorded in the winter months. A series of 150mm diameter percussion drilled boreholes were sunk to depths of 5m and 10m below the site base to act as groundwater sampling points. These boreholes should penetrate the water table, even during the summer

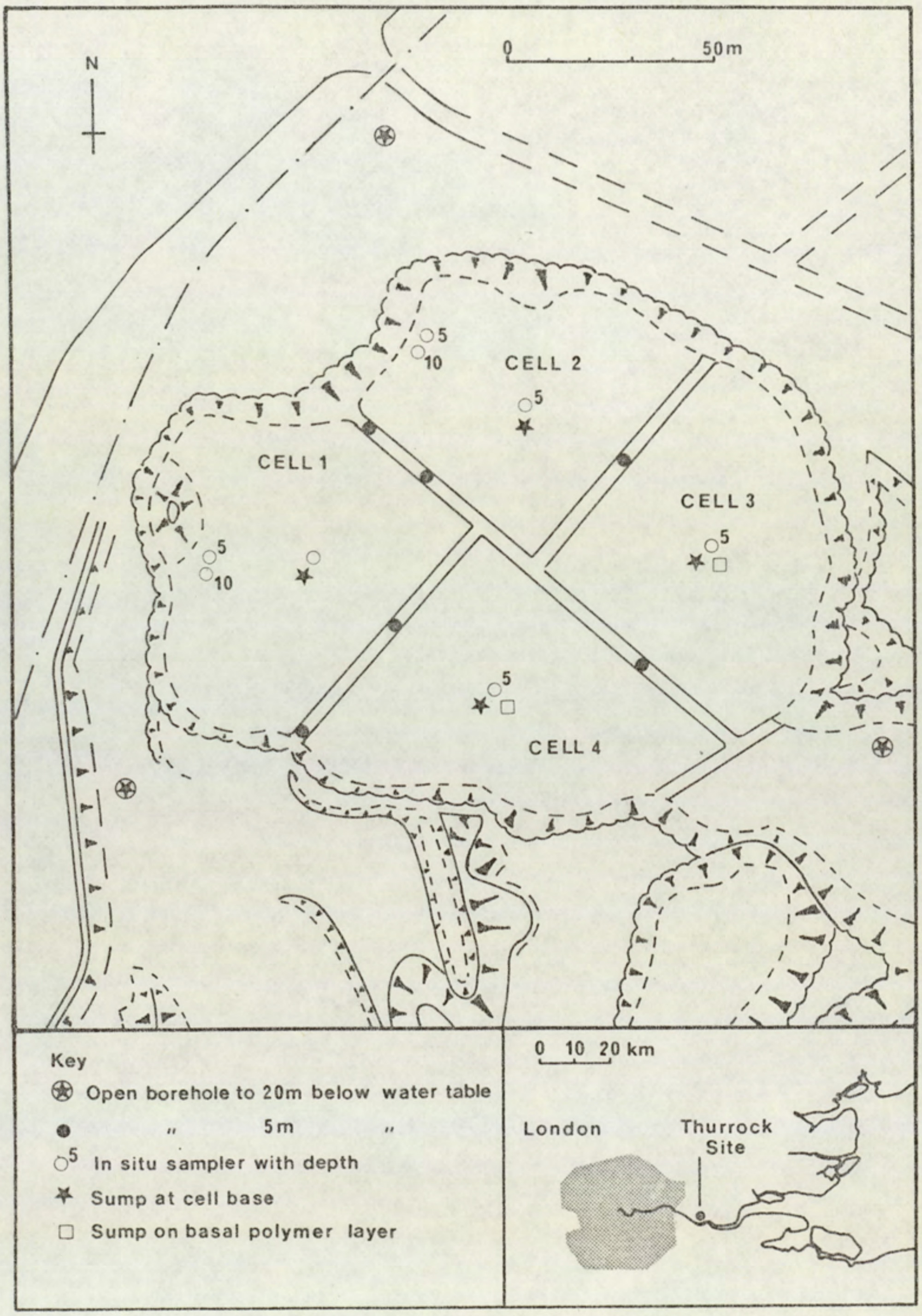


Figure (i). Experimental landfill site at Thurrock, Essex, showing groundwater monitoring network.

months. Four in situ water samplers similar to those described by Edworthy and Brown (1976) were placed in 5m deep holes in the centre of each of the cells. Two other samplers were placed at the foot of the west face in cell 1 and a further two at the north west face of cell 2, in each case one at 5m and one at 10m (Figure (i)). All the in situ samplers were backfilled with bentonite to ensure that the samples they deliver are representative of the water for the depth at which they are situated.

In addition to these samplers, each cell will have a sump, in the centre beneath the fill, fed by a polythene sheet and sampled via a standpipe. Cells 3 and 4 will have an additional sump with standpipe on top of the basal layer of polymer to sample leachate generated within the cell. To ensure maximum information about movement of any contaminants and to allow detection of leachate from each or any cell, six open stand pipe sampling points were drilled within the bund walls to a depth of 5m below the quarry floor and lined with slotted plastic pipe.

Part 2 of the experiment consists of five small cells, each 125m^3 and 10m above the pumped winter water table. The cells will be filled with similar combinations of "Stablex" polymer and domestic refuse to those in Part 1 with an additional cell filled with domestic refuse alone. The floor of each cell has a polythene liner and slopes to a central sump with a standpipe to allow sampling. After filling these cells are to be irrigated to enhanse leachate production. The leachates will be collected and analysed to give information on their volumes and composition for extrapolation to predict the behaviour of the Part 1 cells.

Part 3 of the experiment consists of three cells, similar in size to those in Part 2, but excavated below the summer water table, providing a saturated state at all times. Four percussion drilled boreholes have been sunk for each cell, one on each side, 10m away and 5m beneath the summer water table. This part of the experiment is designed to provide information on attenuation of any leachate constituents and by extrapolation predict the situation which might occur should the large (Part 1) cells become flooded due to discontinuation of pumping. No direct contact between groundwater and domestic refuse is to be allowed to minimise the risk of contamination of the aquifer. The first cell has been filled with polymer alone. The other two will be filled with homogenised domestic refuse and polymer and polymer escapsulated baled domestic refuse.