To Mum and Dad, Othello, Makoushla and Sam

SOME ASPECTS OF THE GEOCHEMISTRY
OF LIQUID WASTE DISPOSAL

A THESIS

Submitted for the Degree of

Doctor of Philosophy

by

Marion Carter

at

The University of Aston in Birmingham

December 1975

ABSTRACT

Industrial waste liquids in volumes up to 29 million gallons are produced in the West Midlands. With the introduction of the Deposit of Poisonous Wastes Act and the pending Control of Pollution Act, information is necessary to allow planning of disposal of these wastes to conform with the law.

The industrial waste liquids containing copper, nickel, zinc, cadmium, iron, lead and chromium are commonly deposited in a variety of sites. Three such facilities known as Walsall Wood Mine, Mitco and Betton Abbotts are present in the West Midlands. Each site represents a different geological environment, a disused coal mine in Middle Coal Measures, a disused brick pit in the Etruria Marl Series, and a clay lined glacial kettle hole respectively.

Experiments were set up to determine whether the geological materials at the sites would react with wastes to remove the toxic materials. An attempt has been made to quantify the results, to determine the environmental pollution hazards produced by disposal at these sites. Solutions of the metals in acid were prepared and mixed with rocks from the sites, with montmorillonite, and with kaolinite. Samples of raw effluent were also used in a further set of experiments. The metal content of the liquids reacting with the rocks was determined prior to, and after reaction. The results show that reactions occur between the metal solutions, and the clay minerals to produce a decrease in the metal concentration of the solution. Similar results were obtained using raw effluent. Metals are adsorbed in varying quantities depending primarily on charge and on other secondary factors which are discussed. The quantity of metal adsorbed was found to depend on the clay mineral types eg montmorillonite adsorbs more metal than kaolinite. The pH of the medium is also a control in that adsorption for all metals increases by more than 50% between pH 0 and pH 4. From the results it is concluded that disposal to the ground under control of pH, and the type of material at particular sites, will not result in the production of environmental hazards arising from toxic metal contamination.

ACKNOWLEDGEMENTS

I wish to thank Professor W. R. McWhinnie and Dr. J. W. Gaskarth for advice and criticism during their supervision of this work.

Effluent Disposal Limited and Brasway Waste Disposal Limited kindly allowed the use of information and diagrams from unpublished reports produced by Dr. Gaskarth, provided samples of effluent, and allowed access to their sites. The Department of Geological Sciences, University of Aston in Birmingham is to be thanked for making laboratory and analytical facilities available, and Dr. Rice of Reading University for the use of an E.S.R. instrument. Thanks are also due to Miss H. Couper for help with the experimental work, Mrs T. Danby for typing, Mrs J. Montgomery for drafting, and Mr M. Husbands and Mr F. Frost for advice and suggestions. I wish to acknowledge the Science Research Council for the provision of a studentship, and Mr R. Holmes for allowing me time while in his employment to complete this thesis.

Thanks also to Juliette and Garth for moral support during the last three years.

CONTENTS

Page

Abstract (i)

Acknowledgments (iii)

Contents (iv)

Chapter 1. Introduction

- 1.1 The nature and Volume of Industrial Waste 1
- 1.2 Methods of Disposal 1
- 1.3 Legislation 3
- 1.4 Previous Work 4
- 1.5 Aims of the Present Work 10

Chapter 2. The Geology and Operation of Three Disposal Sites

- 2.1 Site Selection 12
- 2.2 Walsall Wood Site 13
- 2.3 Mitco Tip 21
- 2.4 Betton Abbotts Farm Site 27

Chapter 3. Introduction to Experimental Work

- 3.1 Clay Mineralogy 36
- 3.2 Past Work 43

Chapter 4. Analytical Techniques

- 4.1 Atomic Absorption Spectrophotometry 46
- 4.2 X Ray Diffraction 57
- 4.3 Infra Red Spectroscopy 58

Chapter 5. Adsorption Experiments; Methods and Results

- 5.1 Sampling of Materials 59
- 5.2 Experimental Design 61
- 5.3 Experiments and Results 63

Chapter 6. Analysis of the Rocks used for Adsorption Experiments

- 6.1 Clay Minerals 158
- 6.2 Coal Measures Rocks 158
- 6.3 Rocks from the Area of the Mitco Site 159
- 6.4 Betton Abbotts Site Rocks 160

Chapter 7. Discussion

- 7.1 Objectives 162
- 7.2 Adsorption Experiments 162
- 7.3 The Chemistry of the Adsorption of Metal Ions by Clay Minerals 171
- 7.4 Conclusions 182

Page

Chapter 8. Additional Work

8.1 Monitoring of the Mitco Borehole Liquid 187
8.2 To assess the change in pH of an acidic solution in contact with Coal Measures shale 191
8.3 Electron Spin Resonance 191
8.4 Mossbauer Spectrophotometry 192

Appendix 1. Mitco Site Borehole Logs 193

Appendix 2. Betton Abbotts Site Auger Borehole Logs 197

Appendix 3. Results of the experimental work on the adsorption of metal ions from solution by clay minerals 202

Appendix 4. The method for dissolving rock samples for analysis by atomic absorption spectrophotometry 254

Appendix 5. A.A. Analysis results for the rocks from the three disposal sites 255

References 256

List of Figures. 1 9a
2 14
3 16
4 18
5 22
6 23
7 25
8 29
9 30
10 31
11 33
12 37
13 38
14 38
15 39
16 41
17 47
18 50
19 50
20 53
21 65
22 75
23 85
24 91
25 104
26 116
27 127
28 145
29 154
30 169
31 172
32 174

List of Tables.

	Page
1.	34
2	54
3	56
4	100
5	124
6	144
7	152
8	153
9	164
10	176
11	188
12	191

CHAPTER 1. INTRODUCTION

1.1. The Nature and Volume of Industrial Waste

Industry disposes of between 10 and 20 million tonnes of waste per annum, of which 7% is potentially hazardous, including 4% acid or caustic waste.[1] In the West Midlands an estimated 29 million gallons (132 million litres) of waste is disposed of to one facility each year.[2]

Hazardous wastes include tar residues, organic solvents, alcohol wastes, chlorinated hydrocarbons, cyanide wastes, plating acids, and toxic metals.[1] The exact composition of wastes is rarely known and wastes from several processes are commonly mixed for transportation.

It is the spent acids resulting from plating processes, containing large quantities, up to 15%, of metal ions commonly iron, zinc, lead, copper, chromium, nickel and cadmium, which will be studied in this work.

1.2. Methods of Disposal

The majority of both solid and liquid wastes are disposed of by tipping onto the land surface. Surface tipping often utilises natural or man made depressions, known as land fill sites. Apparently more attractive alternative methods include incineration and recycling, but in most instances the cost of these processes is prohibitive.

The possibility of recycling zinc and hydrochloric acid based on figures supplied by a West Midland disposal company has been investigated.[2] However, the mixed metal content of the majority of waste acids makes recovery uneconomic as a costly purification system would be necessary to separate the metals.

Incineration may be the most suitable method of treating certain categories of waste. However, where both incineration or land fill methods are suitable, the latter will normally be used as the cost of incineration at approximately £20 per ton is far greater than that for land fill at approximately £3 per ton. Additionally there is the problem of complying with laws relating to pollution of the atmosphere, and the disposal of the resulting solid residue, generally less toxic than the original effluent, but still present.

Permanent safe storage in disused mines or other underground cavities is recommended in the Report on Disposal of Solid Toxic Wastes,[3] although the Institute of Chemical Engineers provisional code[4] states that "The working party feel a definite disquiet at the use of old mine workings and other underground cavities for the disposal of wastes. It is thought no one could be prepared to guarantee the geological structure as being safe." Few geologically safe sites of this type exist, although a facility using a vault in crystalline rock in America has been reported[5], and a West Midland company is at present using a disused mine shaft for disposal of liquid waste, into the old sub-surface workings. For a mine to be suitable for disposal it must be isolated from working collierys, have lateral and vertical seals to prevent movement of waste liquids from the mined area, be dry, ie there must not be water entering the workings from the overlying and surrounding strata, and there must be no possibility of the mine being reopened in the future. Ideally several seams should have been worked to allow the flow of wastes into the workings without a build up of air locks.

In America deep well injection methods have been developed, largely used for disposal of Oil Field Brines. The waste is pumped under pressure into fissured, permeable formations generally beneath ground water aquifer formations.[6,7,8.] This method, together with being very expensive, may lead to lubrication of underground fault systems, resulting in earth movements, and the build up of pressure sufficient to force the waste back up the disposal well.[9,10]

Deep sea disposal is used for a variety of wastes, including some radio active products. Again the cost of the method is high, and control is becoming stricter,[11] as the dangers of indiscriminate dumping in the sea become apparent.

From this consideration of other methods, the preference for surface disposal may be understood. The greatest danger in surface tipping of toxic wastes is the possibility of polluting water supplies, particularly underground water, by leakage of liquid waste or movement of soluble waste, from a tip.

1.3. Legislation

Until 1937 there was no legislation regarding the disposal of trade effluent, which was discharged to local authority sewers. The 1937 Public Health (Drainage of Trade Premises) Act gave industry and local government rights in the matter, and liquid effluent was brought under stricter control by Part V of the Public Health Act 1961, by which the trader was obliged to inform the local authority of his intention to discharge an effluent to the sewers, and the local authority could consent conditionally, unconditionally, or refuse. Rivers are protected by the 1951 and 1961 Rivers (Prevention of Pollution) Act, estuaries by the Clean Rivers (Estuaries and Tidal Waters) Act 1960 and discharges into an aquifer by well, borehole, or pipe by the Water Resources Act 1963, Section 72.

There was no equivalent legislation relating to solid toxic waste. The Public Health Act 1936 enables local authorities to take action to secure the abatement of "statutory nuisances" which includes "any accumulation or disposal which is prejudicial to health or a nuisance" eg a toxic waste tip. In addition the planning acts have to be satisfied before a tip can be established or extended.

In 1972, the Deposit of Poisonous Waste Act,[12] relating to both solid and liquid wastes was passed, which prohibits the depositing of poisonous and other dangerous waste on the land where it is liable to give rise to an environmental hazard. Since this act, all wastes have to be notified to the local authority and river authority in the area from which the waste is removed, and the area in which the waste is deposited, stating the volume, nature and chemical composition, and destination of the waste.

Contravention of the act can result in a fine of up to £400 or 5 years imprisonment.

The most recent legislation on the deposit of poisonous wastes is the Control of Pollution Act (1974), which, when it is implemented will repeal the Deposit of Poisonous Waste Act 1972. This is a more comprehensive Act to "make further provision with respect to waste disposal, water pollution, noise, atmospheric pollution, and public health; and for purposes connected with the matters aforesaid." Under the Act local authorities will be required to prepare and revise waste disposal plans in consultation with the water authority in the area, and all tips must be licensed with the agreement of both the local authority and river authority, unlicensed tips being prohibited. Companies must, as under the Deposit of Poisonous Waste Act, 1972, give notice of tipping to the river authority which may give its consent subject to very stringent conditions as to the rate of discharge, the temperature, monitoring and recording of these factors, and to the prevention of the discharge from polluting underground water.

The Act also gives the Secretary of State the right to prohibit or restrict importation of any substance which they consider will cause damage to persons, animals or plants, or pollution of air, water or land.

The Deposit of Poisonous Waste Act has improved the standard of tip operation and had led to more research into the suitability of sites as disposal facilities. Introduction of the Control of Pollution Act will further improve the standards, with the greater control that will be exercised over the suitability and operation of sites.

1.4. Previous Work

Until the publication of the government report by the Ministry of Housing and Local Government on "Disposal of Solid Toxic Wastes" in 1970, little research had been carried out, either privately or by government bodies, to evaluate the risks of toxic waste disposal sites, although some research has been carried out on the movement of contaminants from refuse disposal sites. In 1961 the Ministry of Housing and Local Government published a report on "Pollution of Water by Tipped Refuse" and during the 1960's several surveys were carried out in the United States into the movement of leachates from refuse disposal sites.[13,14,15]

The Report on the Disposal of Solid Toxic Wastes provides a fairly comprehensive study of the problems involved. The report reviews the various methods of disposal and concludes that tipping is the most economically favourable method, but concludes that safety must be paid for. The report states that the ideal condition of totally preventing drinking or river water from ever containing any waste extract is impractical, and suggests means of protecting water sources and a study of disposal by tipping, this method being the cheapest and most popular, and likely to go on for many years.

The reports recommendations for operating methods to reduce pollution include the consolidation and covering of waste by a clay umbrella to prevent percolation of rainfall through the waste, use of tips which have not caused pollution, such as household refuse tips, the reduction of volume of waste by reclamation, destruction of toxity before dumping, and dispersion, as long as there is no possibility of re-concentration.

The report recommends that specialist methods such as incineration, and permanent safe storage in deep underground caverns, should be reserved for the most toxic waste. To efficiently dispose of waste, it is suggested that all detailed decisions on the use of a site be left to a specialist, sufficiently concerned with other methods of disposal, to make use of these if tipping is not suitable.

The report summarises the travel of pollutants from tipping sites to groundwater sources and recommends ways of reducing the dangers, by reducing the volume of water which may pass through the waste, the amount of waste going into solution being dependent on the volume of water running through the waste. The siting of tips to allow slow movement of the waste through a maze of voids and small capillaries in a permeable rock, gives an opportunity for adsorption or destruction of toxic matter, which again reduces the danger to groundwater, while passage through fissured rock is rapid and allows no time for reaction. Dilution when the pollutant reaches an aquifer and further dilution at a pumping station, also reduce the potential danger of the waste.

With these considerations for improving the safe disposal by tipping, and accepting that tipping will continue as the most popular form of disposal, the report recommended a study of disposal by tipping, and its effects. A study of tips which have existed for a long time, and have been safe in the sense that water sources have not been affected by them, to determine whether such effects will occur in the future, is recommended, together with monitoring boreholes 10, 50, 250 and 1000 yards from the boundary of tips to give an early warning of pollution. The report states that information may show self purification during the early stages of tip operation indicating that the site is safer than expected and that its use could be extended.

Consequently, a survey of 2,494 tips in England and Wales was begun by the Institute of Geological Sciences in 1971. A desk study indicated that only 51 of the sites represent a serious pollution risk to major or minor aquifers. River authorities have classified[16] 80 sites as being unacceptable for future use, out of 714 locations they have examined. The Department of the Environment is at present financing a research programme into the movement of leachates from landfill sites, which will probably lead to recommendations on the selection of sites for disposal of various types of waste.

In March 1972, the Second Report of the Royal Commission on Environmental Pollution was published which states that "The Report on the Disposal of Solid Toxic Wastes" understated the problem, and predicts an absolute increase and greater diversity of wastes. Figures for tipping quoted 1,186 premises surveyed produce 202,000 tons per year of indisputably toxic waste, 429,000 tons per year of acid or toxic waste, and 129,000 tons per year of flammable waste of which 96%, 72% and 82% respectively are tipped.

In a paper by D. A. Gray, J. D. Mather and I. B. Harrison[16], guidlines for future selection of landfill sites were laid down. In selecting sites, the lithology of the strata, and the position and gradient of the water table, the level below which the rocks are saturated, are particularly studied. The greatest protection to groundwater is afforded by clays and shales which have a permeability of 10^{-6} to 10^{-8} mm sec $^{-1}$, the least protection by rocks through which water movement is by fissure flow or solution cavities, when permeability may be orders of magnitude higher than through intergranular formations. Slow movement of leachates through rocks gives an opportunity for decontamination by the biological, physical and chemical barriers, described in the "Deposit of Solid Toxic Waste" report. The biological barrier near the surface allows breakdown of organic matter, the physical barrier filters the water as it percolates slowly to the water table, and the chemical barrier of base exchange capacity holds back certain ions.

The presence and position of a water table determines whether the site is wet or dry (below or above the water table respectively), and the thickness of the unsaturated material underlying the site. The hydraulic gradient determines the direction and velocity of leachates when they have reached the water table.

A further consideration is the choice of policy; either "concentrate and contain" or "dilute and disperse". The authors of the paper favour the latter when recycling and recovery is not possible, and where permanently toxic checmicals are not involved. The ideal landfill site, they say, will allow leachates to move from the landfill site at such a rate that natural chemical and biological processes, adsorption and dilution, will render leachates innocuous by the time they reach groundwater abstraction zones.

With these considerations, the authors suggest a classification of wastes with specificationsfor sites suitable for each category of waste.

Category I wastes, with potential to cause groundwater pollution, including industrial liquids, sludges, soluble solids, and oily wastes, should be disposed of to a site underlain by at least 15m. of impermeable strata, and at least 2 km (1¼ miles) from a groundwater abstraction point using the water either directly or indirectly for domestic consumption or processing of food.

Category II wastes include those having the potential to cause groundwater pollution not because of any specific toxicity they possess but by increasing the concentration of organic or inorganic substances to a level sufficient to render groundwater non potable eg house and trade refuse. Leachate from these wastes degrade during passage through the rock strat by adsorption of inorganic components and biological degradation of organic components. Thus a dry site, or at least 15 m of strata with intergranular groundwater flow, and situated at least 0.8 km (½ mile) away from water supply sources is recommended eg excavations in poorly permeable silts and fine sand or sandstone.

Category III wastes are solid and inert, such as construction and demolition wastes which present no risk to groundwater, and may be tipped without any specific hydrogeological requirements for the site.

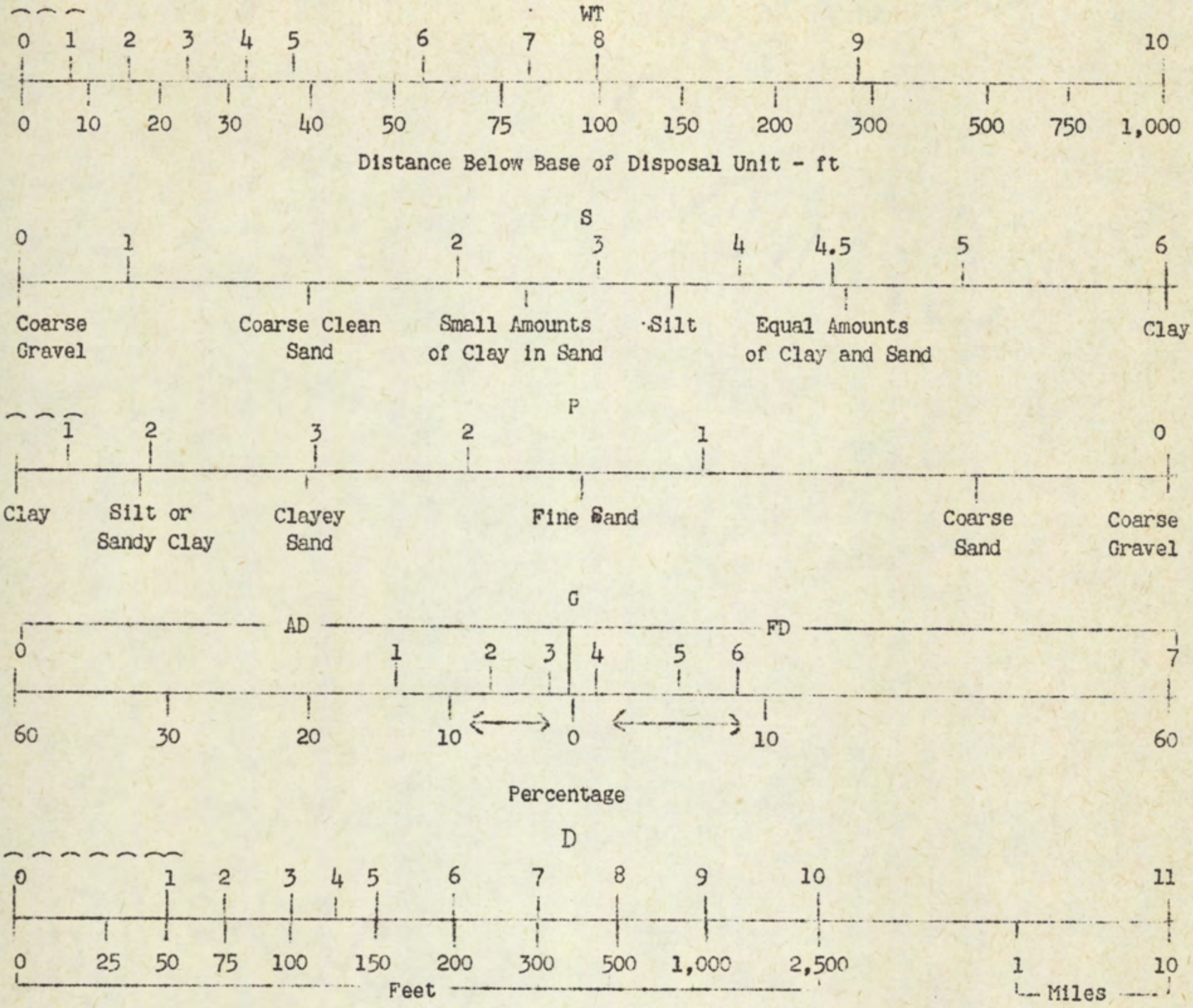
It is suggested by D. A. Gray et al[16], that Category I wastes, which includes the metal contaminated acids dealt with in this work, may be tipped in existing sites, if modified by lining with impermeable material such as clay, soil cement, plastic etc, and covering with clay when finished to prevent the formation of a leachate by percolation of rain water, although resettlement of the landfill may result in the breaking of the cover. Alternatively leachates could be collected from the base of a landfill, although these would still have to be finally disposed of. The authors also suggest that areas of limited water resources may be set aside for landfill, accepting that the groundwater would be polluted and excluded as a source of supply.

H. Le Grand[17] describes a quantitative system for evaluation of the contamination potential of waste disposal sites, for use with contaminants which attenuate or decrease in toxicity with time, or by oxidation, chemical or physical sorption, and dilution through dispersion. Numerical values from 1 to 10 are decided on for five factors; depth to the water table, sorption, permeability, water table gradient, and distance to a point of water abstraction. The values for the factors are totalled to give an indication of the suitability of the site, low values indicating a less suitable site and high values indicating a more suitable site. (Fig 1).

The cleaning of effluents during their passage through the ground has been observed and reported [18,19,20].

Biological explanations of this effect have been given, [20,21], together with more comprehensive views of the various reactions occurring during passage of effluent through the ground. [22,23,24] E. J. Mesu [22] gives five reasons for the lack of groundwater polution caused by waste tips; dilution in the groundwater disperaion and diffusion, filtration of solid components by soil, the adsorption, filtration of clay and humus, and precipitation, in the insoluble form, of the contaminating components.

Fig 1



RATING CHART FOR SITES IN LOOSE GRANULAR MATERIALS

The scales for the various factors are labelled as follows: WT, water table; S, sorption; P, permeability; G, gradient; and D, distance. On all scales the point values are indicated by the upper scale; the brackets indicate unacceptable ranges for any factor, except the two brackets on the gradient scale, one labelled AD, which is for an adverse direction of flow (toward point of water use), and one FD, which is for a favourable direction of flow. From H E LeGrand[17]

1.5 Aims of the Present Work

With the introduction of the Deposit of Poisonous Wastes Act 1972, waste producing companies were compelled to reconsider their disposal methods. When the Control of Pollution Act becomes law even more stringent controls will apply. Some companies are already financing research into the movement of contaminants from tipping sites, and it is likely that further investigations will take place to determine the most efficient way to utilise sites which comply with the new controls.

All disposal sites differ in their geological environment and the lithology of the rocks in the sites. As only a limited number of sites could be investigated during the work, laboratory experiments were devised, the results of which would be more generally applicable. Such experiments are possible as, although the sites are unique, some types of effluent are common to many sites.

Problems specific to the sites dealt with relate to the geoglogical environment, and determine the suitability of the site as a disposal facility.

More general results are obtained from the laboratory experiments which are concerned with the reactions of effluents with materials with which they come into contact. Although effluents vary greatly in composition, they have some common characteristics. Solids and oils in the effluent will generally be retained by the medium through which the effluent flows, in many cases the rocks around a disposal site, while the less viscous liquids with dissolved species will travel further. It is the dissolved species which are the greatest danger to groundwater sources as they may travel long distances to underground and surface water sources.

Thus, dissolved species were chosen for investigation, and metal ions selected as they are very common toxic components of effluents, and are readily detectable by atomic adsorption spectrophotometry.

The adsorption of metal ions by clay minerals in soils has been observed and it seemed likely that there would be a cleaning effect if metal ion contaminated liquids from disposal sites travelled through rocks containing clay minerals. This work was undertaken to determine whether adsorption effects could be observed under conditions likely to apply in a waste disposal situation. The conditions of all laboratory experiments were dictated by real situations, although simplifications were made to restrict the number of variables in early experiments.

CHAPTER 2.

THE GEOLOGY AND OPERATION OF THREE DISPOSAL SITES

2.1 Site Selection

Three sites, covering a range of geological environments and modes of operation, were investigated. The variation in geology of the sites allows comparison of the reactions of the effluents with a variety of materials. The range of geological environments, and disposal techniques, illustrate the degree of protection of the environment afforded by different situations.

The first site is a disused mineshaft at Walsall Wood, Staffordshire, into which liquid wastes are disposed under gravity. The facility is effectively sealed laterally and vertically by very low permeability material which prevents movement of the wastes from the area of the mine, which could result in contamination of ground or surface water. The rocks in contact with the effluents are carbonaceous shales and sandstones of the Middle Coal Measures. Wastes deposited comprise mainly acids with a pH of less than 1. These are predominantly sulphuric acid, with smaller quantities of nitric acid and hydrochloric acid. Some organic chemicals, mainly oil contaminated water, are also deposited at this site.

The second site is a disused brick pit near Aldridge, Staffordshire. The rocks are mudstones, with some sand and pebble interlayers, of the Etruria Marl Series, Upper Coal Measures. Neutral metal-bearing liquids, together with solid household and industrial wastes are tipped at the site. Surface water and the nearby working brick pits have to be protected from contamination.

The third site, at Betton Abbotts Farm, near Shrewsbury, is a natural surface depression lined with clay-rich glacial materials, overlying glacially derived sands, which in turn overly a red sandstone bedrock. The site is to be used for the disposal of neutralised metal bearing sludges, dry factory wastes, and household refuse. Protection of the water in the sandstone bedrock, which may be exploited as a water source in the future, is afforded by the high clay content of the site lining and the presence of unsaturated sands above it.

2.2 Walsall Wood Site

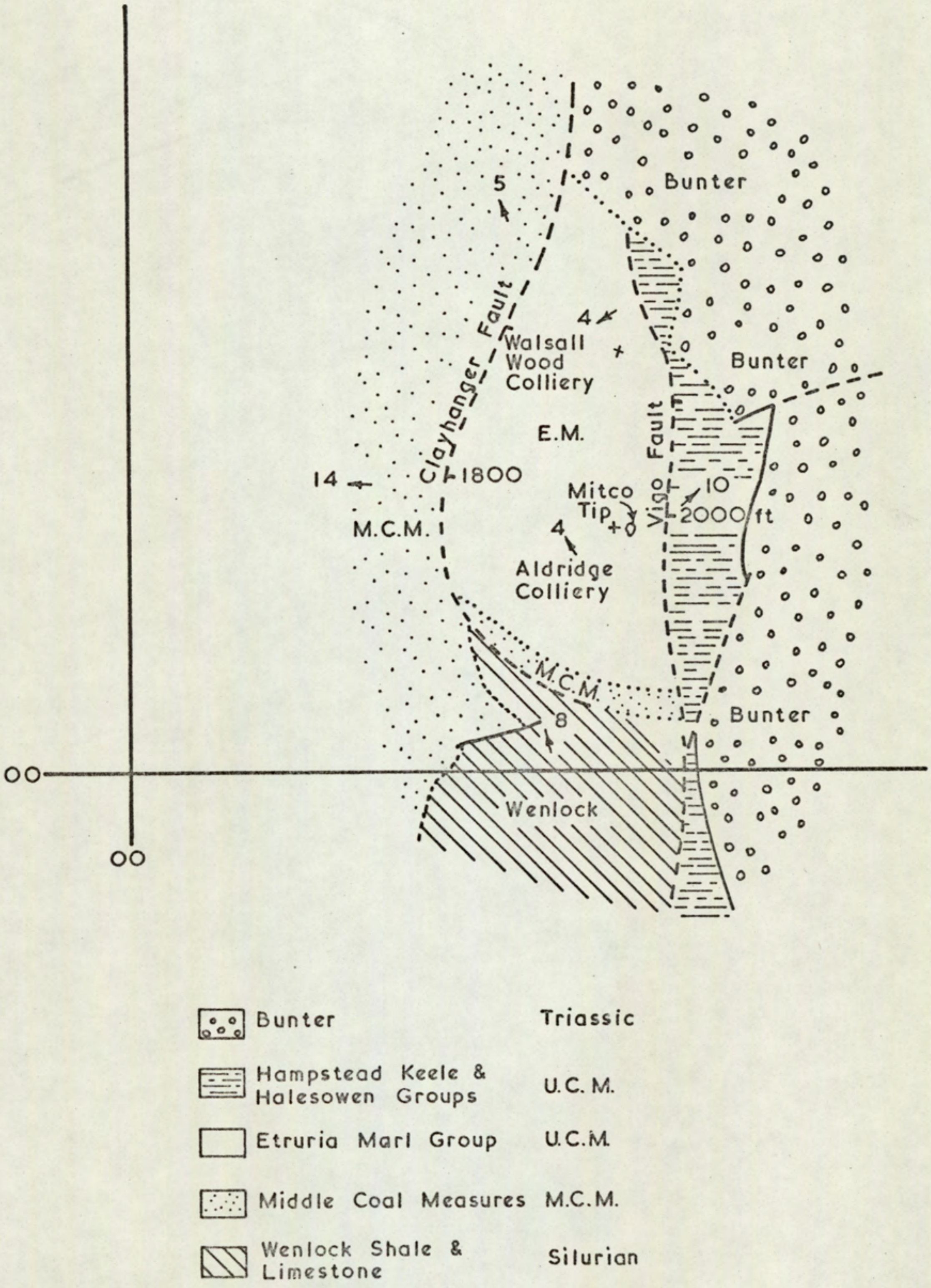
2.2.1. Description. The facility is located at Brownhills, Grid Reference 4050 3041, in the centre of the West Midlands industrial connurbation. The Walsall Wood mine is situated in a down faulted block of the South Staffordshire coal field (Fig 2). Mining ceased in 1964 and the No 1 shaft has been used as a disposal facility since 1965 under a consent issued by the Trent River Authority in accordance with Section 72 if the Water Resources Act 1963. Under the consent the workings may be filled to a depth of 500 ft (150 metres) below ordnance datum. The 1700 ft (500 metres) shaft has been reinforced with concrete to a depth of 200 ft (60 metres) and capped by an 8½ inch thick concrete slab over reinforced concrete beams. Originally the shaft was filled with colliery tailings to a depth of 650 ft (195 metres) below ordnance datum, in an attempt to make the effluent flow into the workings of the upper seams and percolate down to the other seams. After a short period of tipping this fill became unstable, due to saturation and slumped into the lower roadways.

2.2.2. Disposal Technique. Waste liquids are pumped from tankers to a discharge tunnel which opens into the No 1 shaft 15 ft (5 metres) below the surface. Effluent flows under gravity through polypropylene pipes down the inside of the shaft to a depth of 410 ft (125 metres). The liquid then falls under gravity to the bottom of the shaft, and drains northwards into the roadways and broken ground which has resulted from subsidence after mining.

Void space is available in the mined seams which varied in thickness from 3 ft (0.9 metres) to 8 ft (2.55 metres). Access to the void space

FIG. 2

GENERAL GEOLOGY OF THE WALSALL WOOD AREA

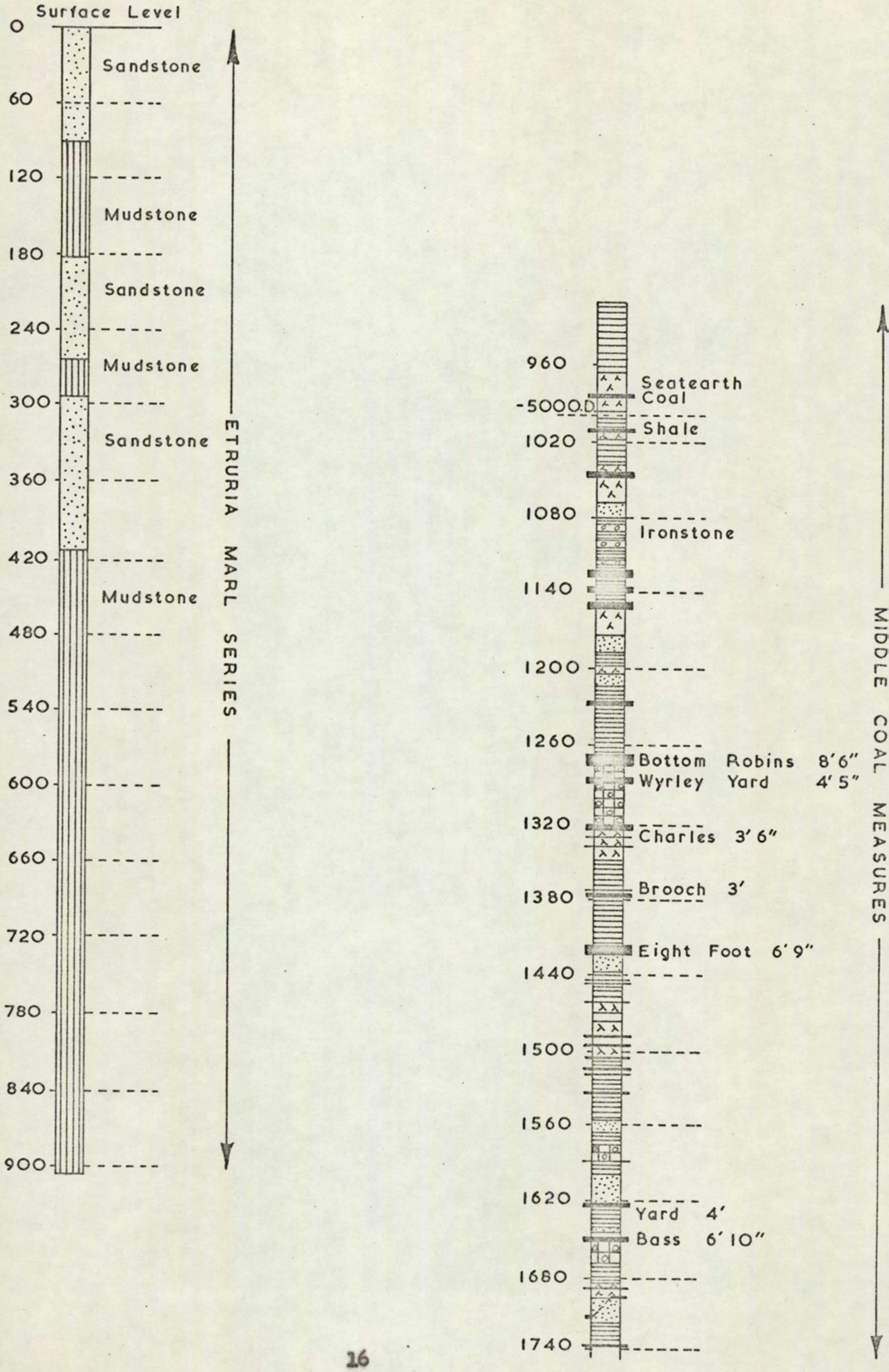


in the workings is via the shaft and roadways, and it is presumed that the liquids will move from one seam to another gradually filling the whole facility. It is difficult to estimate the volume of void space available for the effluent and a value of 10% of the volume removed by mining is taken as the void space, though this may not all be available. This volume could contain approximately 350 to 375 x 10^6 gallons (1.6 to 1.7 x 10^6 metres^3) in the mined area, and an additional 10 x 10^6 gallons (4.5 x 10^4 metres^3) in the roadways. Relatively rapid access to this void space would be available as long as the roadways remained open, after which access would be slower, and dependent on movement through broken and collapsed materials.

The worked areas of the Walsall Wood Colliery are connected with those of the disused Aldridge Colliery to the south, through the Bottom Robins and Shallow seams (Fig 3). This additional space is not available for use as it is up dip from Walsall Wood, and the majority of the Aldridge workings are above the level permitted by the disposal consent. At the end of the life of the mine as a disposal facility the consent requires that the shaft is sealed at the -500 O.D. level, and filled to the top with shale and rock wastes. The majority of wastes disposed are acids, with a pH less than 1, heavily contaminated with metal ions. Approximately 70% of the acids are sulphuric, with nitric and hydrochloric acids making up the rest, though small quantities of hydrofluoric acid are also accepted. The metals include iron, copper, zinc, chromium, nickel, lead, and cadmium, in varying quantities and combinations. Iron may constitute up to 15%, zinc up to 8% and chromium up to 5% of some loads. Cadmium is present in smaller quantities, rarely exceeding 50 ppm. Organic wastes, containing up to 300 ppm phenols, and oily wastes are also disposed, but solvents with low flash points are not accepted as they present an explosion hazard.

FIG. 3

WALSALL WOOD No.2 SHAFT SECTION



The approximate volume of liquid waste entering the mine is $1.35 \times 10^5 m^3$ per annum, which gives an estimated life of 13 years for the disposal facility if the total void space can be filled.

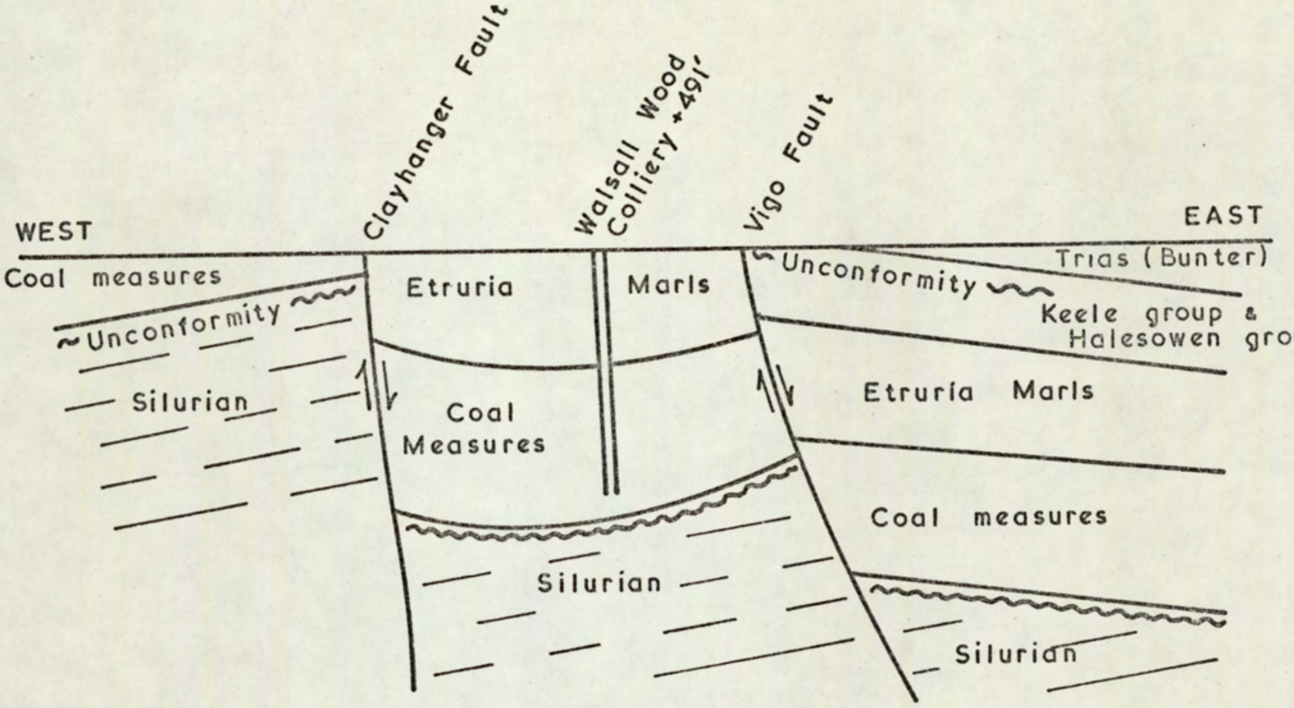
2.2.3. Geology. The down faulted block in which the mine is situated is separated from the main part of the South Staffordshire Coalfield by two major Pre-Triassic Faults (Figs 2 & 4). The Clayhanger Fault in the west has a downthrow of approximately 1800 ft (540 metres) to the east, and the eastern fault (Vigo) has a downthrow of more than 2,000 ft (600 metres) to the west. The geological succession in the fault block is illustrated by the section for the No 1 shaft given in Figure 3.

The rocks of the Middle Coal Measures in this area consist of approximately 70% black carbonaceous shales, some of which contain ironstone nodules, 20% seatearths (fossilised plant root and soil material) and coal, and 10% lighter-coloured medium grained sandstone. The rocks form a shallow synclinal structure with a northerly trending axis. Two series of smaller faults cross the area, one series with a northerly trend and the other with a north easterly trend. The location of these faults is shown on the 1:10560 scale Geological Survey Maps SK 00 SW and SK 00 SE.

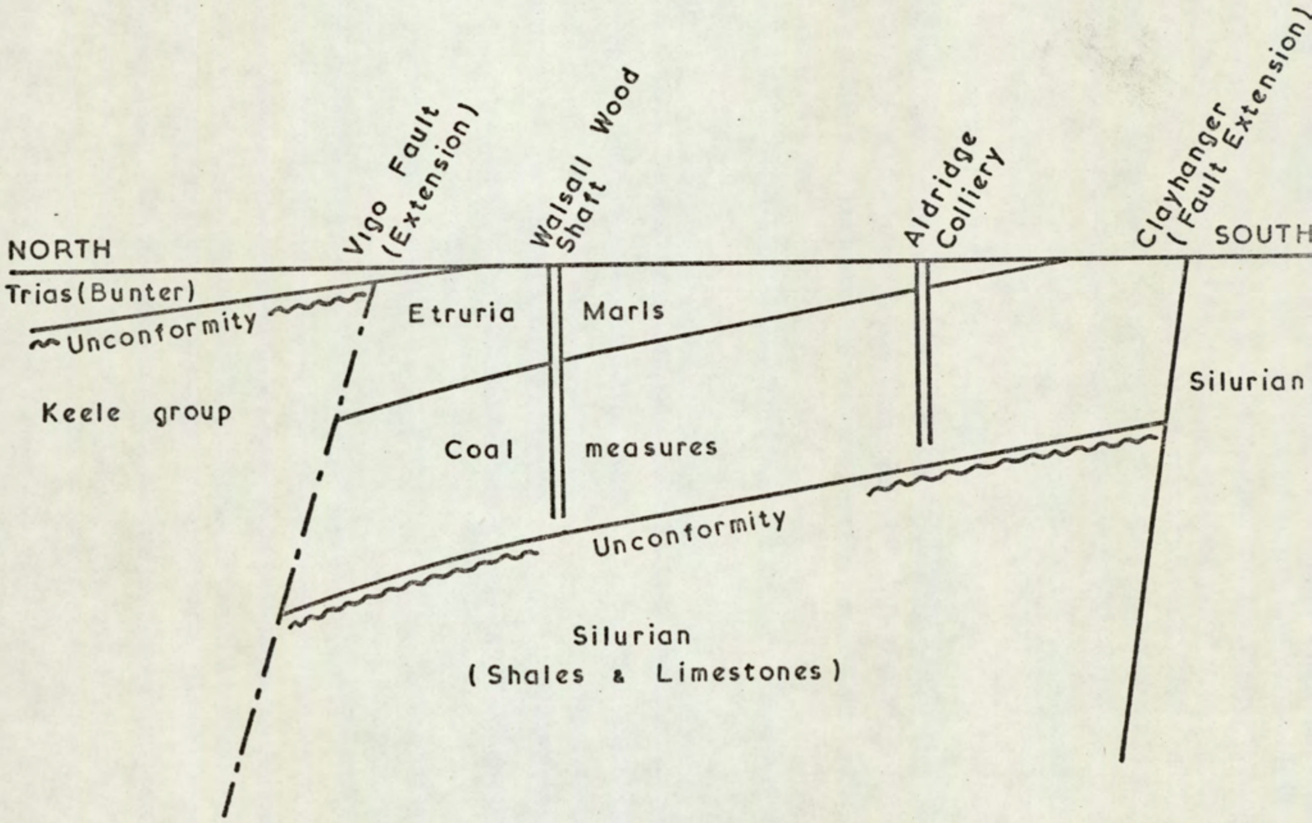
Nine coal seams were worked at the colliery shown on the shaft section (Fig 3) and below.

	Depth ft (metres)	Thickness ft (metres)
Bottom Robins Seam	1270 (381)	8.5 (2.55)
Wyreley Yard Seam	1285 (385)	4.5 (1.35)
Charles Seam	1320 (396)	3.5 (1.05)
Brooch Seams	1375 (412)	3.0 (0.9)
Eight Foot Seam	1425 (427)	3.75 (2.03)
Yard Seam	1625 (487)	4.0 (1.2)

FIG. 4



DIAGRAMMATIC E-W CROSS-SECTION TO INDICATE THE GEOLOGY OF THE DOWNFAULTED BLOCK (Not to Scale)



DIAGRAMMATIC N-S CROSS-SECTION ACROSS THE DOWNFAULTED BLOCK (Not to Scale)

	Depth ft (metres)	Thickness ft (metres)
Bass Seam	1650 (495)	6.75 (2.05)
Shallow Seam	1698 (509)	5 (1.5)
Deep Seam	1753 (523)	6.75 (2.05)

The small coal seams, shown on the section, were not worked. Below the Deep Seam are a further approximately 200 ft (60 metres) of Middle Coal Measures rocks which unconformably overly Silurian limestones and shales at a depth of 1,920 ft (576 metres) in the No 1 shaft. Rocks of the Etruria Marl Series of the Upper Coal Measures overly the coal bearing strata. They consist of an alternating sequence of red mudstones and sandstones (Fig 3). Mudstone constitutes about 70% of this sequence, and one 500 ft (150 metres) thick mudstone layer directly overlies the Middle Coal Measures rocks.

2.2.4. Environmental Protection. The main requirements for a safe disposal site are the protection of ground and surface waters, and the prevention of injury to animals and people.

The site at Walsall Wood is considered to exceptionally safe because the down faulted block, containing the workings into which the effluent drains, is a sealed unit. Lateral seals are provided by the two faults which contain a considerable thickness of low permeability, clay-rich, material. An exploratory tunnel, from the Shallow Coal Seam in the Walsall Wood Colliery, into the Vigo fault zone revealed a zone of shattered shale and clay material 250 yards (225 metres) wide. A tunnel from the Deep Seam, in the Aldridge Colliery, located south of, and interconnecting with Walsall Wood Colliery, revealed a zone of disturbance of at least 1,200 yards (1080 metres) across the fault.[24]

Vertical sealing is provided by the Middle Coal Measures sequence of black shales and sandstone which has a low permeability and is present both above and below the mined areas. The thick mudstones of the Etruria Marl Series provide a further protective seal.

The possibility of contamination of water sources is considered to be minimal because the mine workings containing the effluent, are well below any water sources and the zone of groundwater circulation.

2.2.5. Discussion. The main problem in operating the mine as a disposal facility is the possibility of blockages forming in the workings, slowing or preventing drainage of the effluent.

During its working life the mine was subject to floor heave, ie the clay rich layers moved plastically when the confining pressure was removed, causing the floors of the roadways to contort. This movement of the rocks made constant maintenance of the roadways necessary during the working life of the mine, and may contribute to the blocking of the roadways. Access to the void space would then depend on intergranular and fissure flow in broken rock material. The roadways in the bottom seam are probably largely blocked by the slumped mine tailings which were used to fill the shaft prior to commencement of disposal.

Intergranular flow, in well cemented fine grained rocks of the Middle Coal Measures type, is likely to be very low, and will be further reduced by swelling of clay minerals due to saturation by the liquid effluent. Fissure flow will be hampered by deposition of solids from the effluents in the intergranular spaces and openings between fragments in the collapsed material. Movement of the effluent is helped by the number of seams worked, as interconnecting passageways between the seams will help to prevent the build up of air locks in the system.

Coal mines commonly make water from the enclosing strata, consequently, when mining ceases and the shafts are filled, the workings tend to fill with water. At Wallsall Wood very little water entered the mine workings from the Middle Coal Measures. The only water entering the mine originated from gravelly layers in the drift and sandstones in the upper part of the Etruria Marl Series. This water was piped to a pumping station and returned to the surface, and the system is being continued to prevent the water taking up space in the workings.

2.3 Mitco Tip

2.3.1. Description. This site is an old brick pit in the Etruria Marl Series of the Upper Coal Measures. It is situated south of Walsall Wood in the down dropped fault block of the South Staffordshire Coalfield (Fig 2).

The quarry is one of nine in the area (Fig 5); three are still worked; two are flooded, two are overgrown and the other one is used as a solid refuse tip. The site, close to the filled shafts of the old Aldridge Colliery, is used for disposal of both solid and liquid wastes.

2.3.2. Disposal Technique. The site is a lagoon into which both liquid and solid wastes are disposed. Solid wastes are tipped at the southern end of the site, and liquid wastes are also discharged there from tankers.

The liquids discharged are most commonly, neutral to alkaline in nature, and contain small quantities of metal ions. The majority of the metal ions precipitate as the metal hydroxides as the pH of the liquid in the site is constantly above 6. The solids tipped are generally inert wastes which serve to soak up some of the liquids. Liquids are removed, at the northern end of the site, and are discharged into the mine shaft at Walsall Wood to prevent the liquid level from rising too high.

2.3.3. Geology. The Etruria Marl Series has a thickness of approximately 150 metres in this area. These rocks consist predominantly of red to purple mudstones with thin, sheetwash, sandstones which commonly grade laterally into gravelly, conglomeratic rocks with a clay matrix known as "espleys". A typical sequence is exposed in the quarry face at Aldridge Brixancole No 2 quarry (Fig 6).

The mudstones occur as massive units, up to 8 metres thick, with some coarser beds forming 5% of the rock. The coarser beds are poorly sorted, and consist mainly of clay sized materials, with some round quartz grains up to 0.5 mm in diameter. The espleys are poorly sorted,

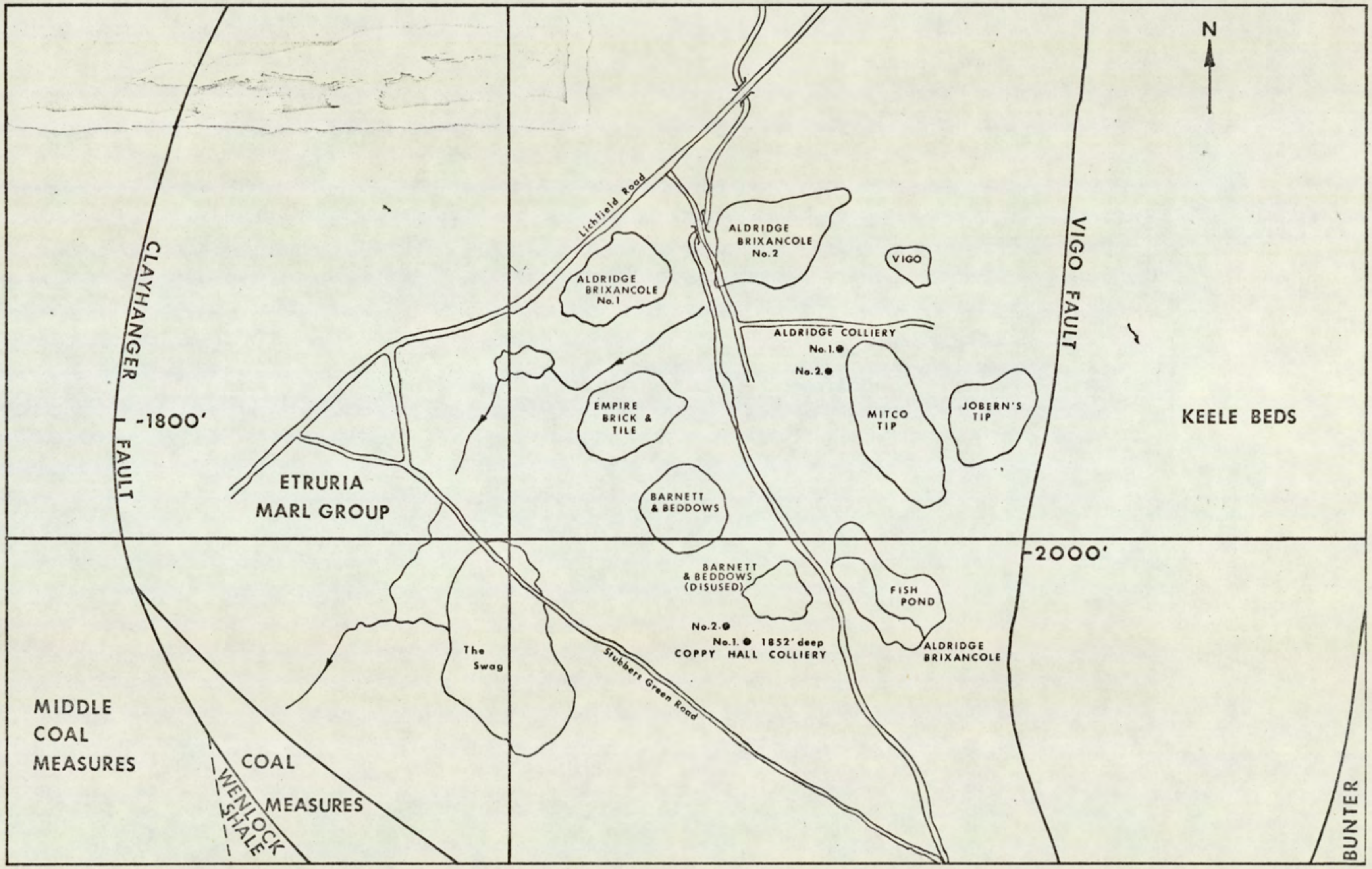
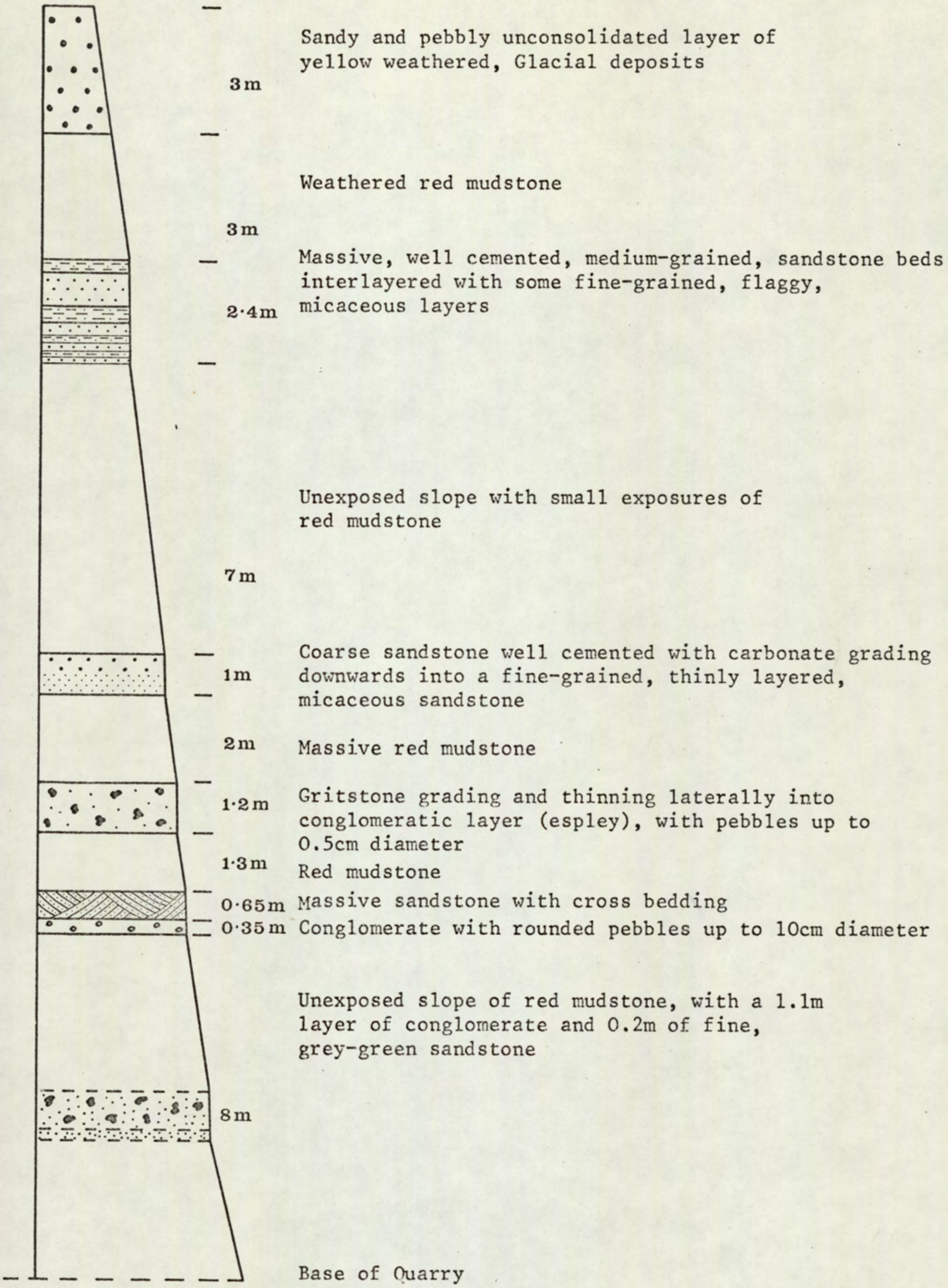


FIG. 5 SKETCH MAP TO SHOW THE LOCATION OF THE MITCO TIP AND OTHER QUARRIES IN THE AREA

SCALE :- 10,560

FIG. 6



Stratigraphic sequence in the north face of Aldridge Brixancole

Quarry No. 2

with fragments ranging from clay size to subangular pebbles over 10 cm in diameter. They are well cemented with carbonate though a clay mineral cement is also common. The esley units vary in thickness up to 1 metre, and have no evident bedding. The fine grained sandstones, with fragments less than 0.2 mm in diameter, are made up of thinly bedded layers (1 to 2 mm thick) with a clay matrix, combined to form lithological units up to 50 cm thick. The sandstone units and conglomerate (espley) units comprise between 40 and 60% of the sequence. Fissuring in the form of small faults and joints, is common in the more competent sandstones, though the fissures are widely spaced and are commonly clay filled.

Cores from two boreholes, only 300 metres apart (Appendix 1 Fig 7) allow no ready correlation which indicates that the sandstone and conglomerate layers have a lensoid nature.

Overlying the Etruria Marl Series are between 3 and 10 metres of superficial deposits of glacial sands and gravels, containing clay minerals.

2.3.4. Environmental Protection. There are two major problems with sites of the Mitco type. Firstly the physical nature of the site, in that it is a lagoon, is an environmental hazard. Secondly, the geological environment gives rise to a sealed basin from which liquids tipped cannot escape. The site is not isolated, as in the case of the mine shaft facility, and, although there are no groundwater sources in the area, the surrounding brick pits must be protected from pollution as water collecting in them is pumped directly into the surface water system. The nine quarries in the area were surveyed to determine the source of water in each one, and to detect any flow between them. In all cases, water was found to be from surface run off, leakage from the nearby canal (Fig 5), and flow through the glacial drift.

Any possible movement of liquids from this site will be by intergranular flow in the more coarsly grained sandstone and conglomerate

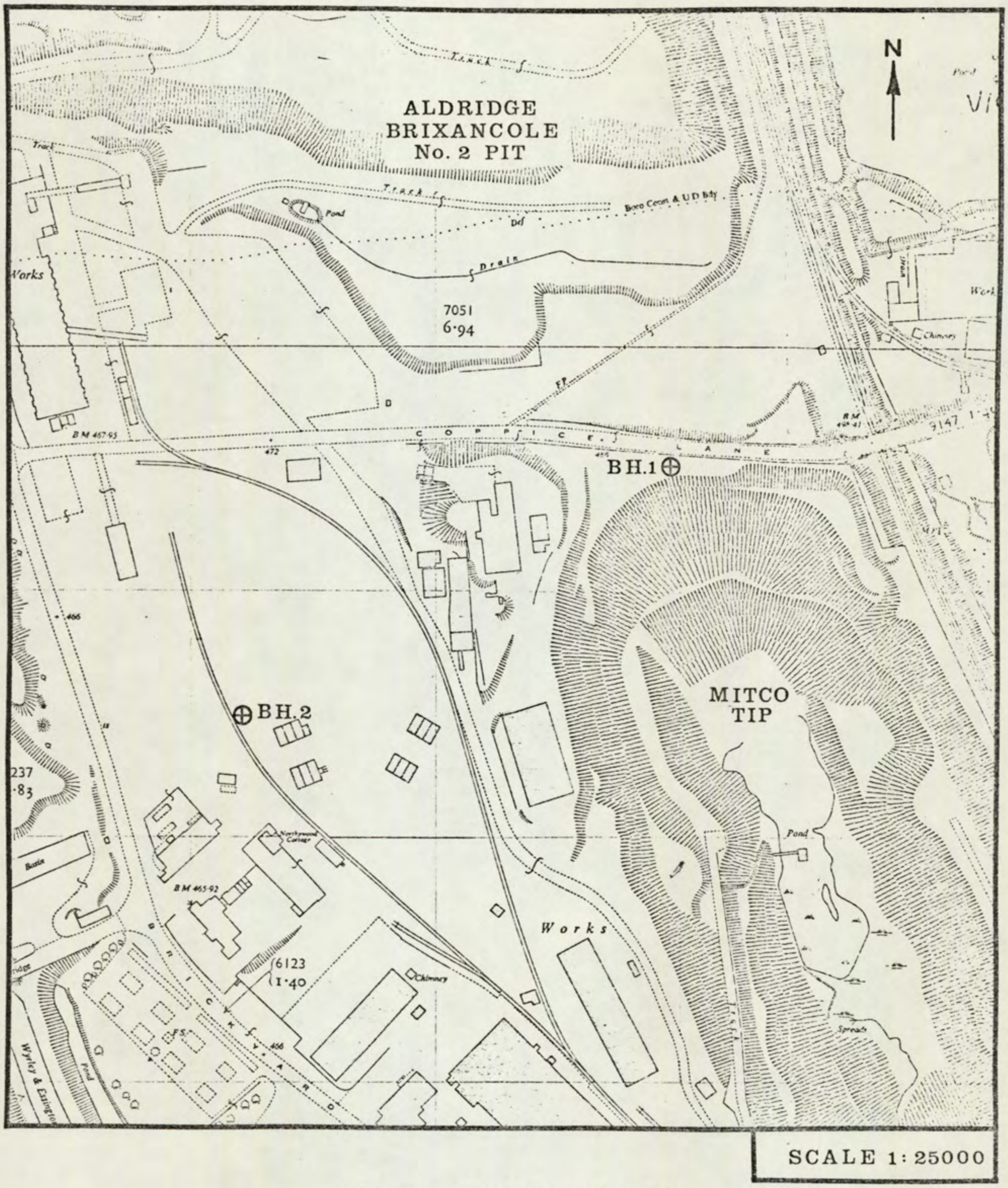


FIG.7 SITE PLAN

units, or through fissures in these rocks. Permeability tests on the rocks, carried out during drilling of the monitoring boreholes round the site, indicate a permeability of approximately 10^{-4} mm sec^{-1}. Horizontal flow over large areas is inhibited by the lenticular nature of the coarse grained units, and intergranular flow will be reduced by the large quantities of clay and carbonate cement. Joint planes in the sandstone units, seen in the borehole cores, are covered with clay grade materials which will probably inhibit flow.

The underlying rocks were probably fractured by mining subsidence, but such fractures are likely to have resealed with clay materials. The only water movement evident in these units is along the bedding planes of some of the coarser units.

Protection of the more permeable lithological units is afforded by degraded mudstone which covers the faces of Mitco Tip preventing direct contact of the rock units with the liquid in the site.

2.3.5. Discussion. The surrounding brick pits are largely protected from contamination from Mitco tip by the degraded mudstone cover and the lithology of the enclosing rocks.

However, quarrying in the Aldridge Brixancole No 2 pit could cause stress relief on the north face of Mitco Tip, which may result in fracturing of the bedrock beneath Coppice Lane (Fig 5). Care must be taken to prevent the water table in these rocks rising as they dip in a northerly direction and any instability may result in movement of the rocks towards the brick pit.

At the end of the working life of the tip all liquids should ideally be removed, by soaking up with solid waste, removal to another site, or by treatment to make them suitable for disposal to the local sewers. The site should then be clay capped and landscaped to prevent run off water moving into the saturated tipped materials and forcing contaminants out into the surface water system.

2.4. Betton Abbotts Farm Site

2.4.1. The site is a natural, clay lined, depression situated in a rural area south east of Shrewsbury, Grid Ref 541082. Prior to development as a waste disposal site it was a peat bog with no agricultural value. The site covers approximately 10 acres, with a minimum depth of 20 m and steep sides, except at the eastern end where the ground slopes more gradually.

2.4.2. Disposal Technique. To increase the space available, the site is to be drained and the peat deposits removed. Run off water from the surrounding area will be collected in drainage trenches constructed around the perimeter and pumped, or diverted, into the surface drainage system.

To facilitate immediate use of the site it is being divided into four areas (Fig 8) which are to be dewatered, and have the peat removed in turn. The first part to be developed is at the western end of the site. To separate this area a bund wall of clay was constructed anchored into the clay lining which is close to the surface at the eastern end of the area (Fig 8). Metal bearing sludges are being disposed of in this area. The technique used is to allow liquids to seep through three beds of sand in turn, in order to remove the heavy metals by reaction with clay minerals leaving a liquid suitable for disposal to the surface drains. When the sand becomes heavily contaminated, and is no longer an effective filter, it is to be excavated and encapsulated in one of the clay lined areas of the site. Fresh sand from pits on the north side of the site will be used to replace it and the system restarted.

Before use, the other areas will be drained, and the peat removed, in order to prove the extent of the clay lining and to increase the volume available for tipping.

As each area is filled it will be covered with a 2 metre thick layer of clay, overlapping the sides, and landscaped to prevent run off water entering the tipped materials. Water in boreholes around the site (Fig 8) will be monitored during the life of the facility, and for some years afterwards, to detect any movement of contaminants from the site. It is proposed to sink pipes in the middle of the site to sample the leachate and determine changes in the chemical nature of the liquids present.

2.4.3. Geology. The site is a glacial kettle hole, containing peat deposits up to 10 metres, in glacial drift deposits overlying red sandstone Details of the site geology were revealed by 19 auger holes, drilled to a depth of 10 metres, in and around the site (Fig 10).

The site is lined by strutureless plastic grey-green clay of variable thickness which is over 2 metres thick near the centre of the site. The clay dips beneath grey, sandy material, up to 10 metres thick, at the eastern and western ends of the site. The grey sandy material contains considerable quantities of clay with some organic material (Fig 9). From the numerous excavations and auger holes around the site, the base of the depression was found to be very irregular and complex in shape (Appendix 2, Fig 10).

Underlying the grey clays and sands are heterogeneous deposits of red till. These vary in thickness from approximately 2 metres on the northern edge of the site to well over 10 metres on the southern side. At the western edge of the site the grey sandy clays directly overly the red till deposits indicating that the grey clay does not extend to that edge of the site.

Underlying the red till are uncemented red sands, in places containing glacially derived gravels. These sands are probably glacially derived, and are thought to represent reworked material from the underlying red sandstone bedrock.

The bedrock consists of well-sorted, red fine-grained, quartz sandstones of probably Triassic, and possibly Bunter Age. The nature of the sandstone was determined from cores produced from the three monitoring boreholes drilled around the site (Fig 8).

FIG. 8

SKETCH MAP OF THE PROPOSED SITE AT BETTON ABBOTTS

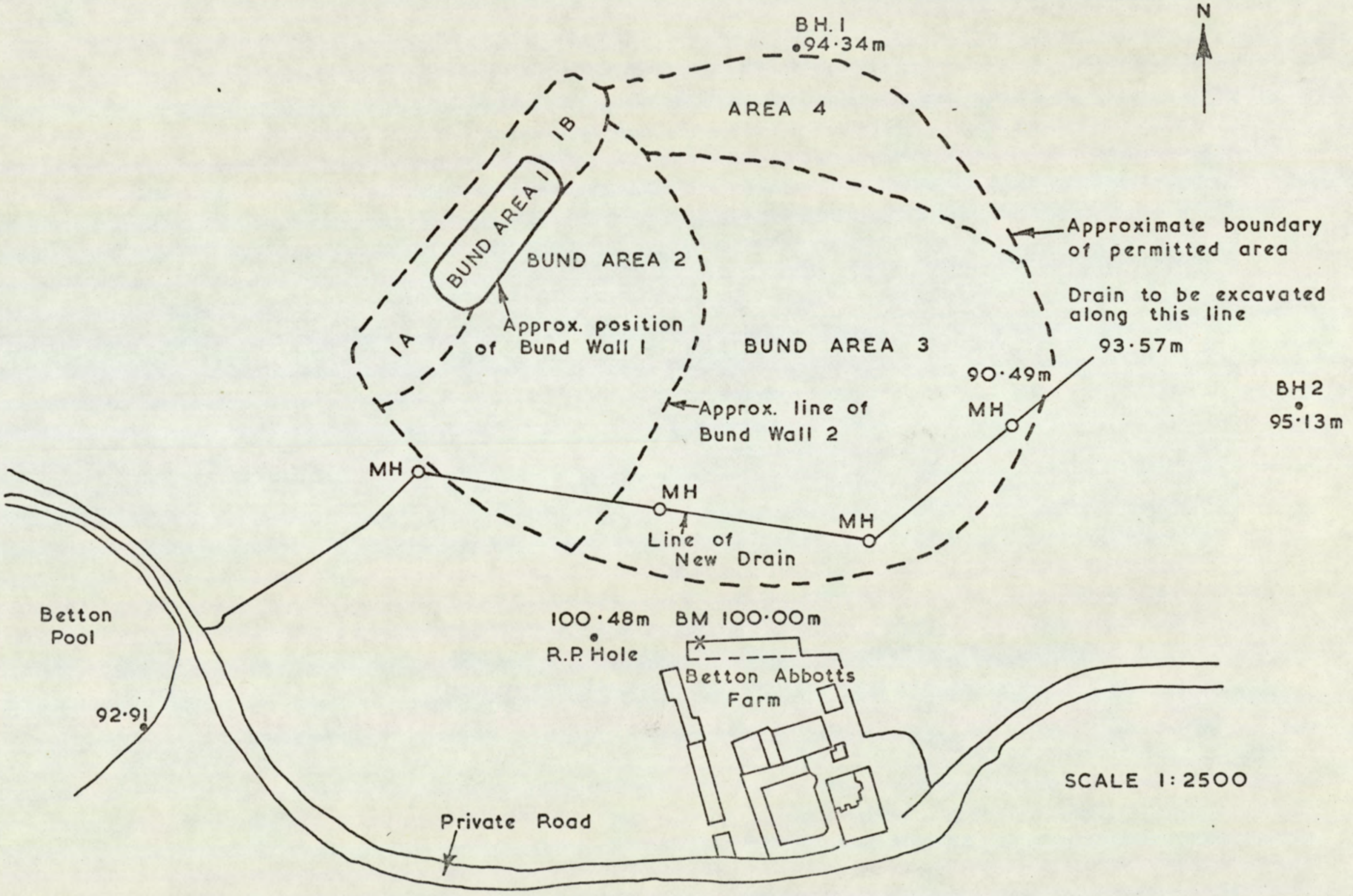


FIG. 9

SKETCH SECTIONS THROUGH E. END OF PROPOSED TIP AREA TO INDICATE INTERPRETATION OF AUGER BOREHOLE RESULTS AND TO SHOW PROBABLE RELATIONSHIPS OF SANDS TO BOULDER CLAY.

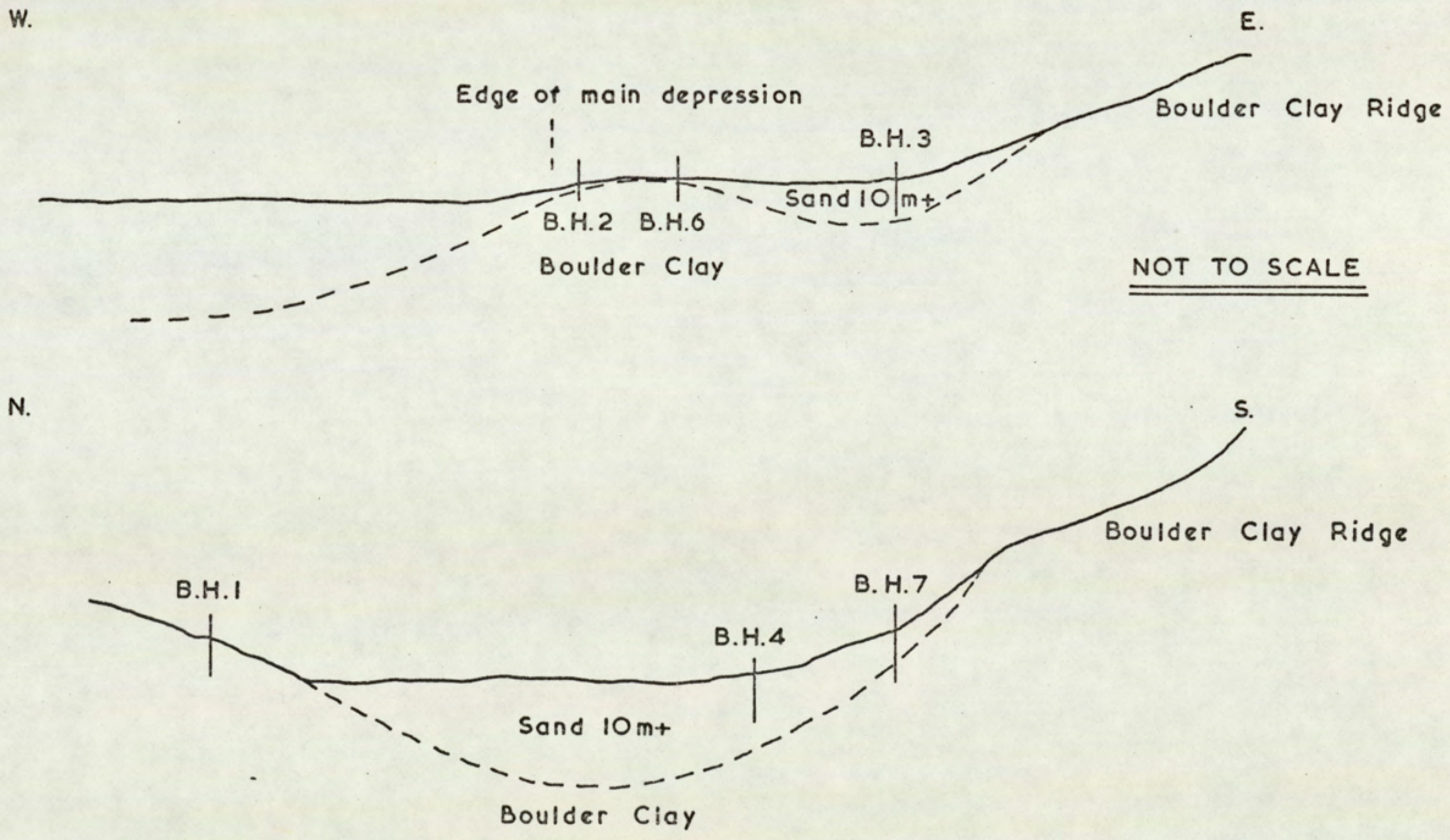
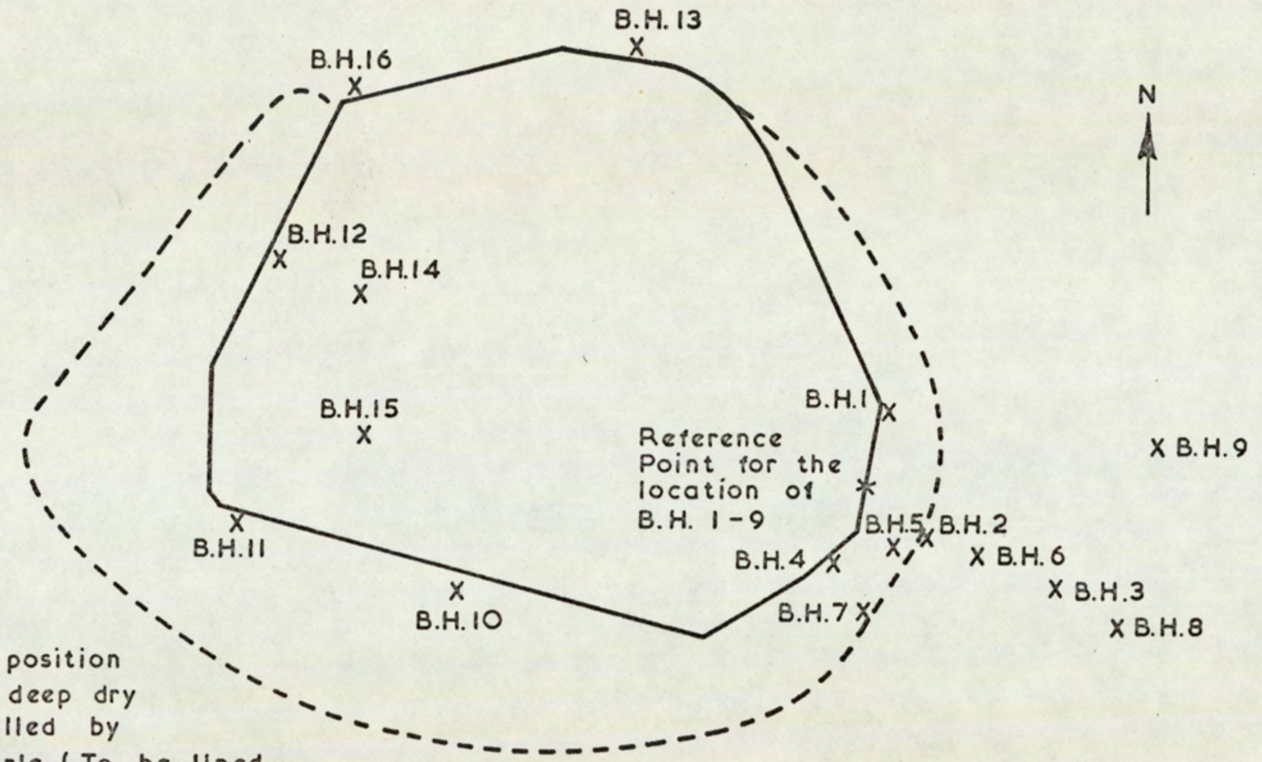


FIG. 10

SKETCH MAP TO SHOW APPROXIMATE POSITIONS OF AUGER BOREHOLES 1-16



X Approximate position of 35-40m deep dry borehole drilled by Redland - Purle (To be lined and kept as a monitoring-hole)

SCALE 1:2500

2.4.4. Environmental Protection. The major considerations for this site are the protection of surface and groundwater. The Bunter Sandstone, although undeveloped as an aquifer in this area, is a major aquifer elsewhere, and could be developed in this area in the future. However, water is taken from other strata in the area, the nearest abstraction point being only 1348 metres away from the site, (Fig 11, Table 1) giving a relatively short time for dilution or breakdown of long lived contaminants should they escape through the base of the site.

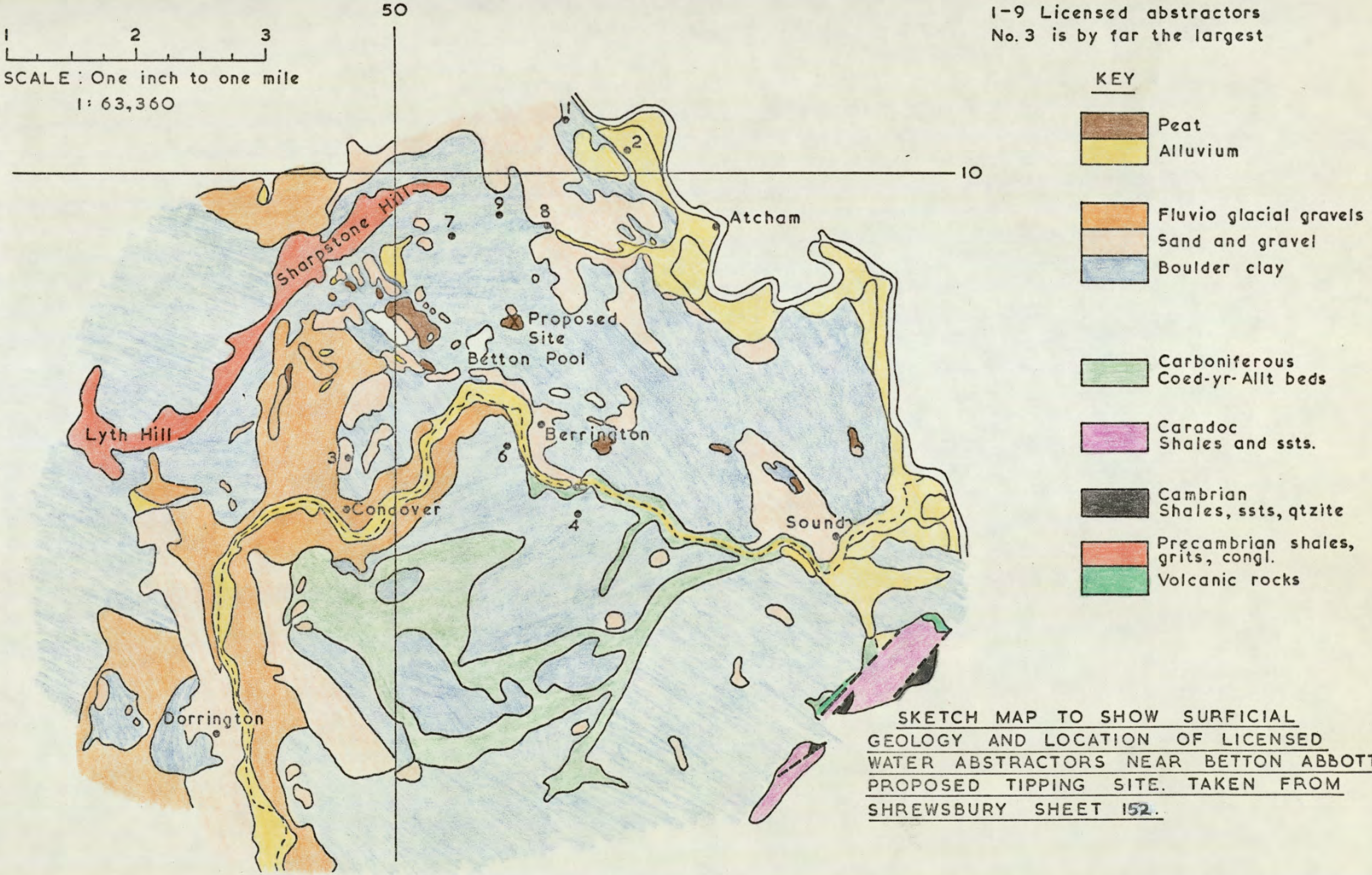
Protection of the aquifer is afforded by two geological factors; the clay lining of the site, and an aerated zone below the site and above the aquifer. The aerated zone was found to be at least 15 metres thick, and suggests that the water in the site is perched, and has no contact with the aquifer in the underlying bedrock.

Two 40 metre boreholes have been completed and a third is in progress. A further borehole previously drilled by another company and indicated as RP (Fig 8), was redrilled to a depth of 42 metres, to prove the water table. The presence of the main water table is at a depth of approximately 30 metres. The water table is almost horizontal though a northerly dip is indicated from survey data. Monitoring of the water table in the boreholes showed that the level varied with barometric pressure suggesting that some of the sandstone layers above the water table are acting as aquitards.

Thus, the water in the site is confined, presumably by the grey plastic clay lining, although this lining is thin compared with the recommended 15 metres quoted by Gray et al [16] for disposal of wastes of extreme toxicity.

Further evidence that the water is confined is afforded by the relationship between the site and Betton Pool (Fig 8). The latter is a water filled depression lying west of the site, with a surface level 3 metres above that of the water in the site. There is no movement of the

FIG. 11



1-9 Licensed abstractors
No. 3 is by far the largest

SKETCH MAP TO SHOW SURFICIAL GEOLOGY AND LOCATION OF LICENSED WATER ABSTRACTORS NEAR BETTON ABBOTT PROPOSED TIPPING SITE. TAKEN FROM SHREWSBURY SHEET 152.

TABLE 1

LIST OF LICENSED ABSTRACTIONS NEAR THE PROPOSED TIPPING SITE

		Gallons x 1000 Per Day	Gallons x 1000 Per Year	N.G.R.	Distance
1.	Well 15'	0.3	110	SJ 521106 Agriculture	2605m NNE
2.	Well 18'	0.05	18	SJ 52771029 Agriculture	2560m NE
3.	2 Bores 133' 6" & 135'	920.0	275000	SJ 494065 W/U	2673m SW
4.	Bore 90'	2	600	SJ 522058 Dom & Agric	2468m SSE
5.	Bore 47'	1.5	250	SJ 522061 Agriculture	2102m SSE
6.	Bore 160'	3	1095	SJ 51280659 Agriculture	1554m S
7.	Bore 140'	4.8	1217	SJ 506092 W/U	1440m NW
8.	Bore 130'	3.2	1168	SJ 519093 Agriculture	1348m NNE
9.	Bore 170'	2	730	SJ 51260945 Agriculture	1348m N

water from the pool, down the hydraulic gradient to the Betton Abbotts site suggesting that the two depressions are separated by a waterproof barrier.

Liquids entering the site are, therefore, likely to be confined by the grey clays and clay rich sands which affords protection for the underlying aquifer. Although some movement of liquids through the lining may occur, this will be very slow and in small quantities. Such leakage would be diluted and probably cleaned by reaction with the clay minerals in the rocks and glacial materials through which it would pass. Final covering of the site with a clay umbrella, landscaped to direct run off away from the site, would complete the seal and ensure that there was no movement of waste liquids or leachates into the surrounding rocks or water courses.

CHAPTER 3

INTRODUCTION TO EXPERIMENTAL WORK

3.1 Clay Mineralogy

To investigate the reactions likely to occur in disposal sites, the properties of the rocks composing the site must be understood. In the particular case of the removal of metal ions, it is the properties of the clay minerals in the rocks which are important.

Clay minerals commonly found in sedimentary rocks include kaolinite, illite, chlorite, montmorillonite, and mixed layer clays. Montmorillonite and kaolinite are used in this work as they were readily available in large quantities in their pure form.

Each clay mineral is composed of two basic units which may extend indefinitely in two dimensions, and have a finite thickness in the third dimension, to form the tetrahedral or silica sheet, and the octahedral or alumina sheet. (Fig 12). Kaolinite is a two layer clay mineral consisting of one tetrahedral sheet and one octahedral sheet. (Fig 13). The mineral is not expansible as the sheets are firmly held together by the electrostatic attraction of the oxygen atoms between them. Montmorillonite is a three layer clay mineral consisting of an octahedral layer between two tetrahedral layers (Fig 14). Bonds between the sheets are weak, allowing polar molecules to enter and expand the structure. Substitution of Al^{3+} for Si^{4+} in the tetrahedral layer, and of Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral layer gives rise to a charge deficiency compensated by the presence of inorganic cations, Na^{+}, Ca^{2+} and Mg^{2+}, known as exchangeable cations on the surface. Illite is also a three layer clay mineral, but the charge deficiency in the tetrahedral layer is compensated by potassium ions which lie between the unit layers binding them together and preventing expansion (Fig 15). Chlorite consists of alternate illite layers (2 tetrahedral sheets + 1 octahedral sheet)

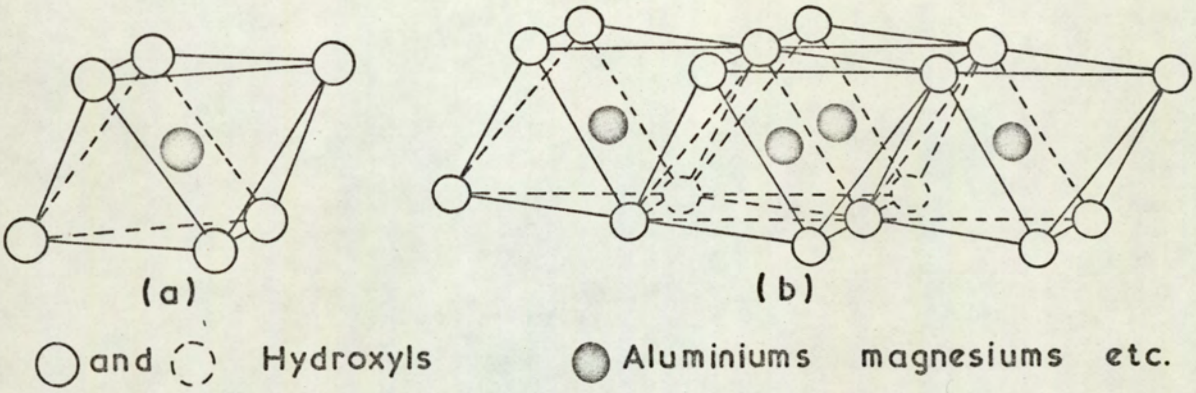


FIG. 12 A. Diagrammatic sketch showing (a) single octahedral unit and (b) sheet structure of the octahedral units

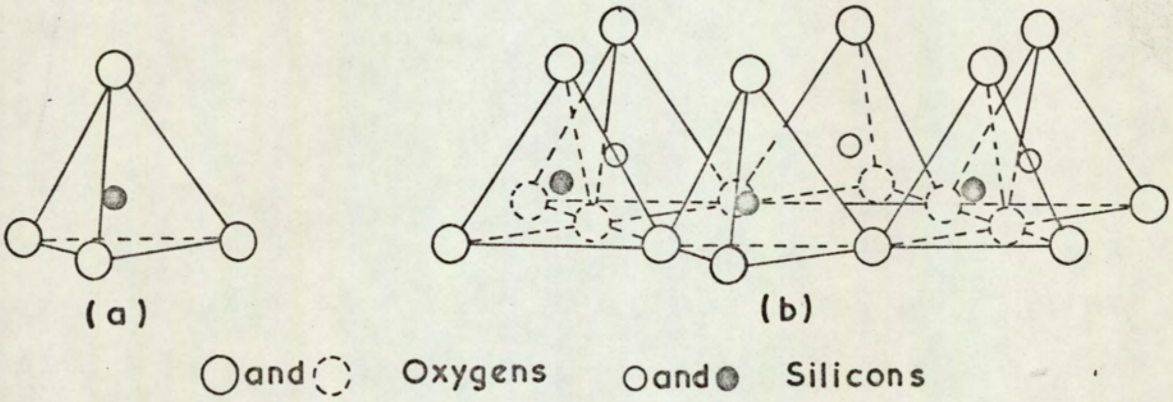


FIG. 12 B. Diagrammatic sketch showing (a) single silica tetrahedron and (b) sheet structure of silica tetrahedrons arranged in an hexagonal network (After Grim, 1962)

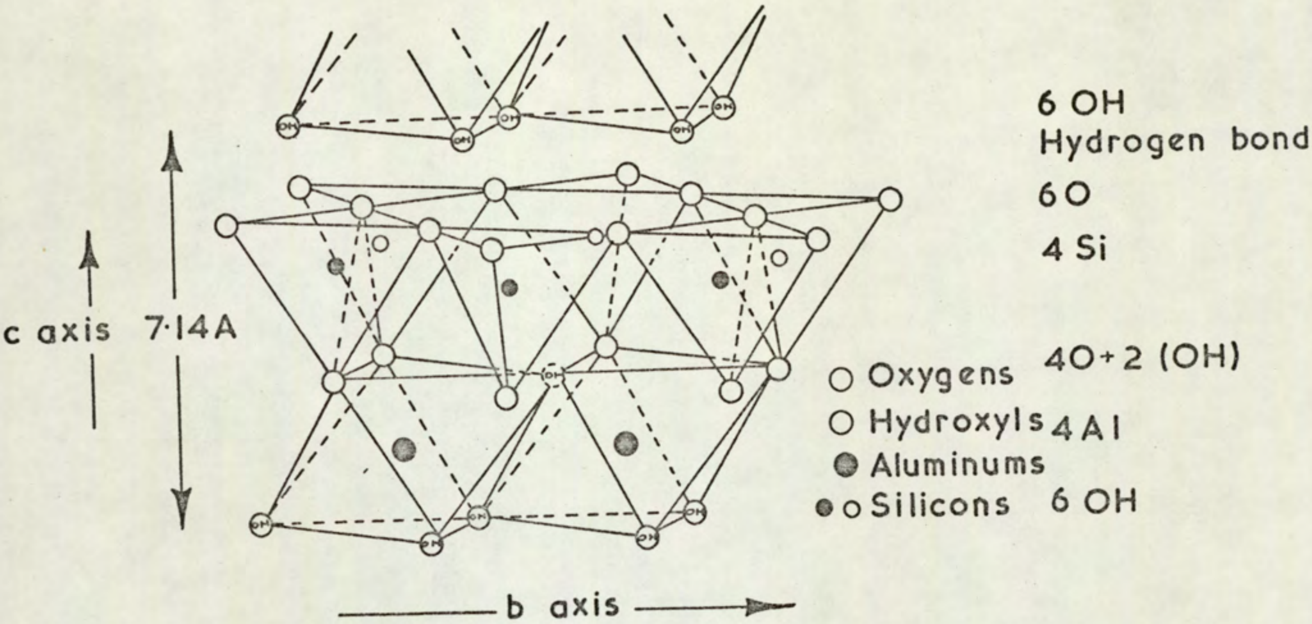


FIG. 13. Diagrammatic sketch of the structure of Kaolinite (After Grim, 1962).

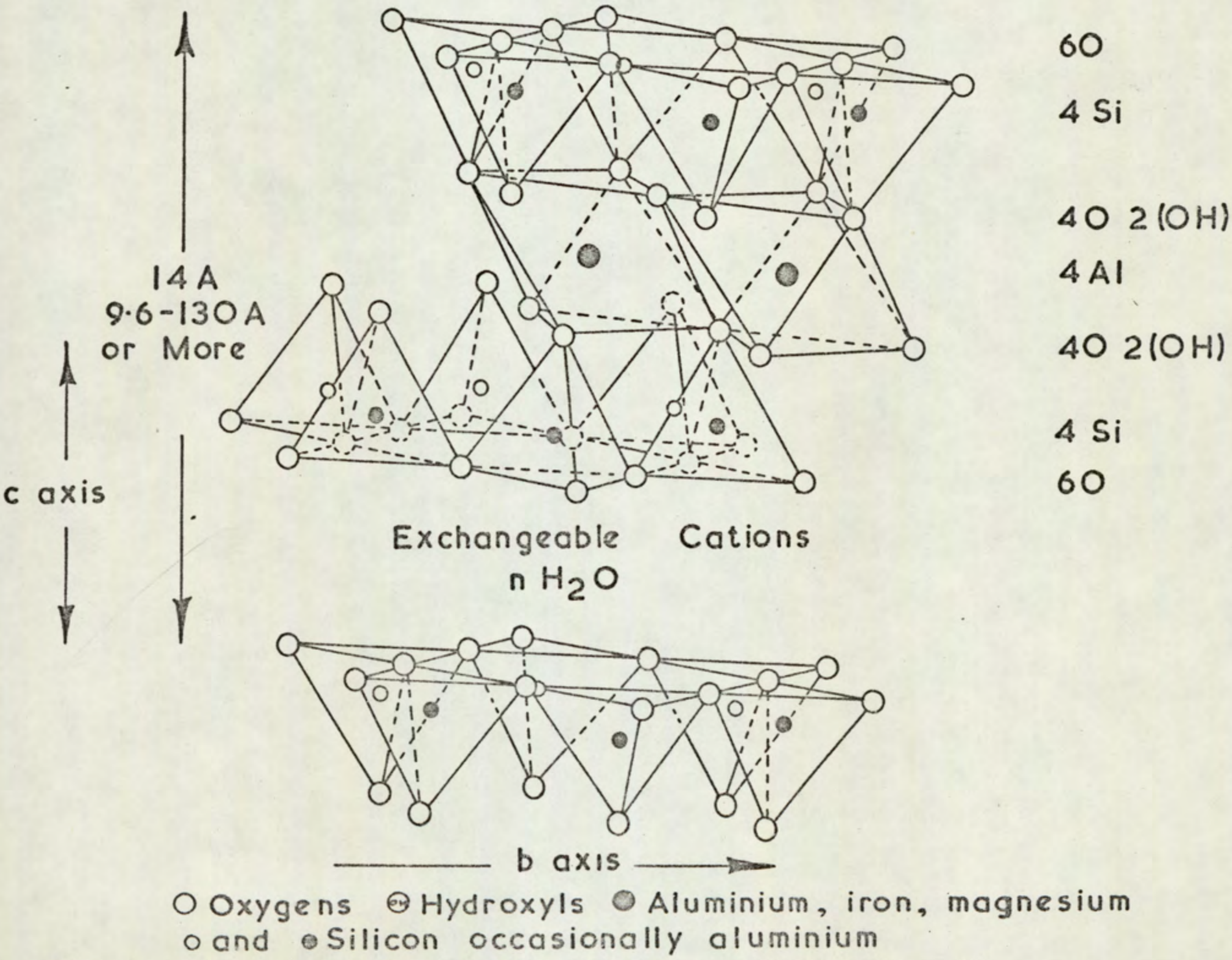


FIG. 14 Diagrammatic sketch of the structure of Montmorillonite (After Grim, 1962)

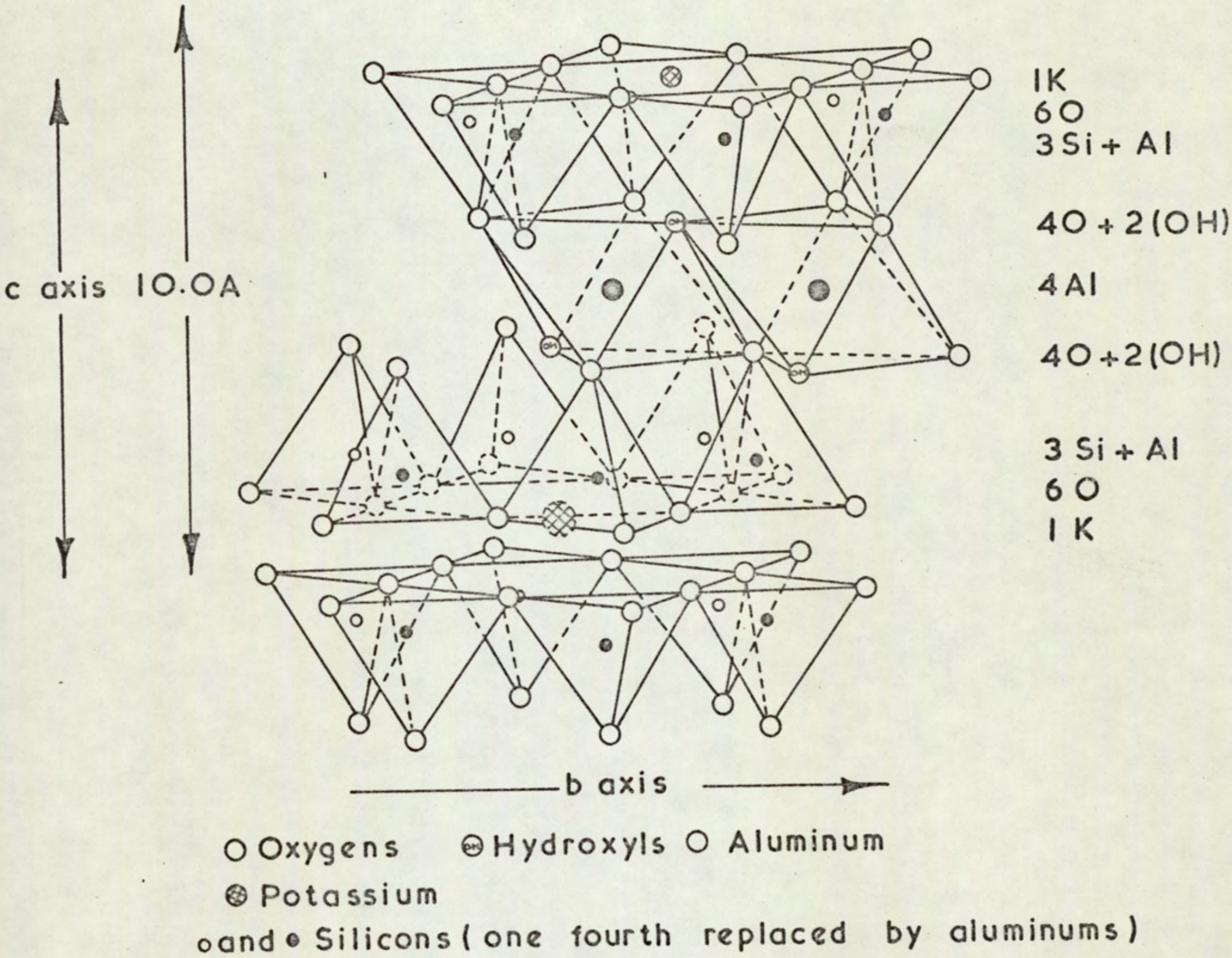


FIG. 15
Diagrammatic sketch of the Structure of Muscovite (after Grim 1962)

and brucite layers (Fig 16). The 'brucite' layer may consist of either magnesium, aluminium or iron hydroxides, or a combination of all three. Mixed layer minerals consist of montmorillonite units alternating with illite or chlorite units, not necessarily in a 1:1 ratio. The properties of the mixed layer clay mineral will resemble most closely those of the predominant clay unit.

For the purpose of this work, the significant property of clay minerals is their ability to absorb ions. The property arises from unbalanced forces at the surface of the mineral which gives rise to an electrical double layer, the counter ions of which are exchangeable forother species of the same sign. The degree of adsorption is evaluated as the cation or anion exchange capacity, expressed in milliequivalents per hundred grams of clay, and is dependent on the magnitude of the surface energy. The charge on clay particles is positive on the edges and negative on the faces, with a resultant negative charge.

The charge defect on the clays arise from three sources; isomorphous replacement, broken bonds, and hydroxyl radicals exposed at the surface. Isomorphous substitution of Al^{3+} for Si^{4+} in the lattice of the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer is responsible for 80% of the exchange capacity in montmorillonite.[26] Broken bonds occur at the edges of octahedral and tetrahedral units:

```
Octahedral Layer    Al - O - Al - O  - ive :   Al
                    Al - O - Al - O - Al :+ ive ¦   O
                                                ¦
Tetrahedral Layer   Si - O - Si - O  - ive :
                    Si - O - Si - O - Si ;+ ive ¦   O
                                                ¦
```

As the number of broken bonds depends on the particle size, the cation exchange capacity will increase with a decrease in particle size. Broken bonds are thought to be the major factor responsible for the exchange capacity of kaolinite, but for only 20% of the capacity of montmorillonite. The hydrogen of hydroxyl

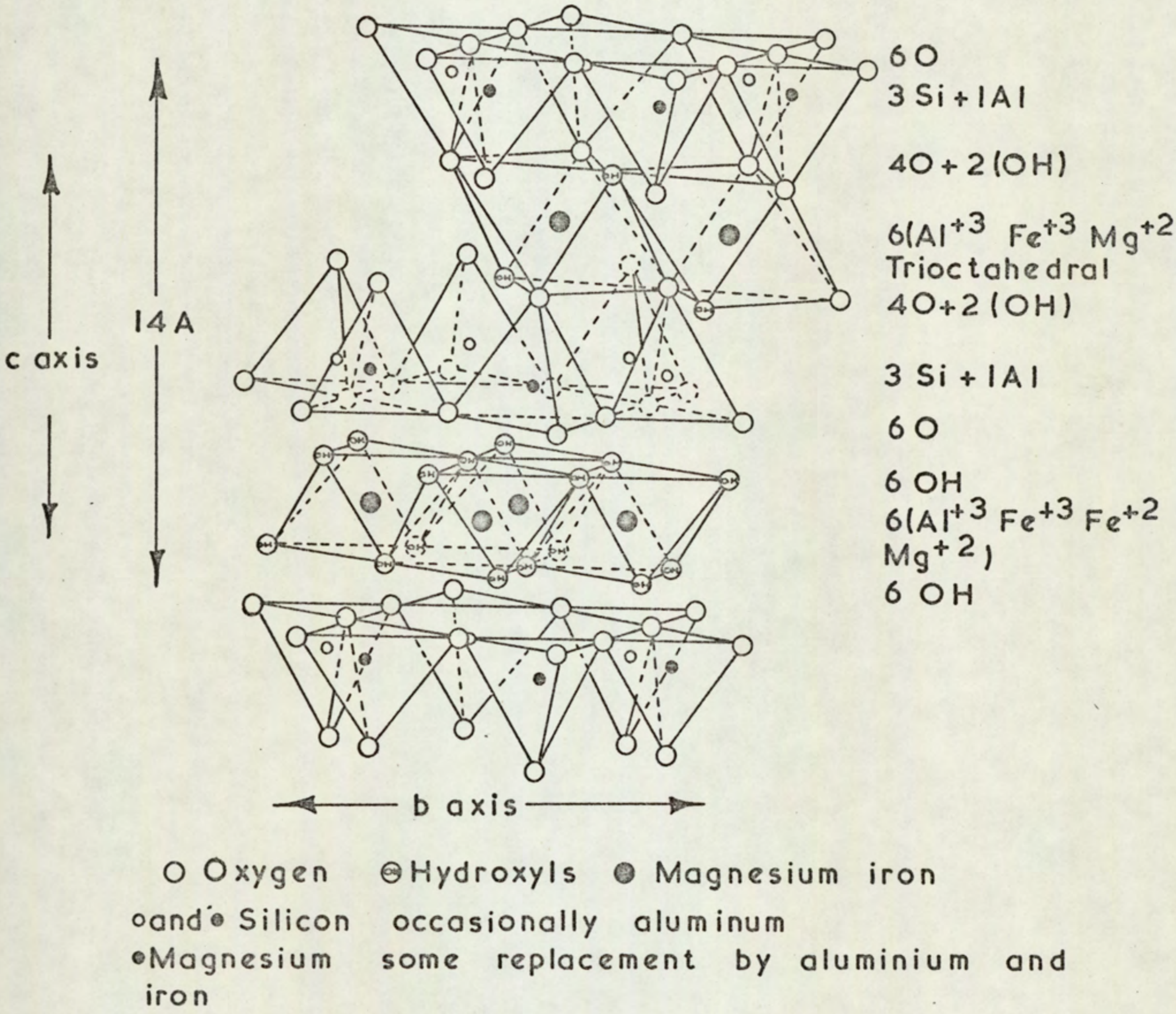


FIG. 16 Diagrammatic sketch of the Structure of Chlorite (after Grim 1962)

radicals exposed at the surface is available for exchange and contributes to the charge deficit.

The Adsorption of metal ions by clay minerals is dependent on the nature of the adsorbing ion, the nature of the clay mineral, and the environment. The relevant properties of the adsorbed ions are the hydrated ion radius, the ion size, the oxidation state and the charge: size ratio. The simple assumption is that an ion with greater electrostatic charge, would be more strongly adsorbed and for ions of the same charge, the smaller ion would be more strongly held by its closer approach to the clay mineral. However, when the hydrated ion radius is considered, the smaller ion will be more strongly solvated and therefore have a greater hydrated ion radius. Ions with the same hydrated ion radius as holes in the clay structure will be difficult to replace. There is disagreement over the importance of the hydrated ion radius,[27,28] and it has been suggested that the hydration energy is the important factor in cation selectivity[29]. In general, a high charge size ratio will give maximum adsorption, and the series of ionic replacement will be $M^{3+} > M^{2+} > M^{+}$.

The cation exchange capacity depends on the nature of the clay mineral, which therefore affects adsorption.

Montmorillonite Meq/100 gm	Illite Meq/100 gm	Kaolinite Meq/100 gm	Chlorite Meq/100 gm	
80-150	10-40	3-15		26
80-100	14-20	3-15		28
80-150	10-14	3-15	5.30	30
85-165		1.5 - 20.2 (most values between 3 and 10)		31

The low values for Kaolinite are due to the high charge density on the surface which limits the freedom of movement of ions. The capacity for kaolinite increases with surface area[32] as the majority of exchange occurs at broken bond sites on the surface of the mineral.

The rate of reaction is also influenced by the nature of the clay mineral. For kaolinite, the exchange is virtually instantaneous as it takes place at the surface of the particles. Montmorillonite and illite react more slowly as the rate determining step for three layer clays is the movement of ions into interlamellar spaces, which does not occur for kaolinite. The clay mineral type may also affect the relative adsorption of different cations as the nature of the sites will favour different cations.

The pH of the environment has an effect on the ion exchange phenomena. Where H^+ and OH^- ions occupy sites on the clay mineral, the acidic or basic nature of the sites will depend on the pH of the environment. The charge of hydrated ion and hydrated alumina varies with pH, hence their presence on clay minerals will alter the charge with pH changes in the environment. The zero point of charge (where the charge reverses from positive to negative) lies between pH 2.2 and 5.6 for hydrated alumina and 6.7 to 8.5 for hydrated ion. The zero point of charge for kaolinite and montmorillonite are given as 4, and below 3 respectively [27]. In acidic solutions, clays will be positively charged giving rise to positive sites which will undergo anionic exchange. At pH 3 and above the clays will be negatively charged and undergo cationic exchange. The presence of organic ions in the environment may also affect the cation exchange capacity with respect to metal ions as the exchange sites may be occupied by the organic ions [33].

3.2 Past Work

Although the reactions of metal ions with clay minerals have been studied, the work has not been directed towards an understanding of real situations.

Wentink and Etzel [34] have studied the effects of allowing solutions of metal ions to percolate through columns of soil.

Chromium, copper and zinc sulphates were used in concentrations from 1 to 300 mg/litre, at neutral pH. It was found that copper and chromium were completely removed from the solution during percolation through the columns. Copper was removed after 7 days, and chromium immediately. Although zinc was never fully removed, the efficiency of removal was always greater than 99.7%. Adsorption was found to increase when larger quantities of the metal ions were applied. Leaching with water removed small quantities of zinc (up to 0.2% of the quantity originally adsorbed), but no copper or chromium. Although figures are given to indicate that metal ion removal is achieved by ion exchange reaction with clay minerals in the soils, insufficient information is given to evaluate this assumption. The authors conclude that zinc is most loosely held on the clay minerals, with copper more strongly held and chromium the most strongly held.

Ion exchange reactions have been studied with respect to the treatment of wastes [35] and particularly for the treatment of radioactive wastes [36,37]. The adsorption of caesium and rubidium has been documented in detail [37,38,39,40,41, 42]. Series of relative adsorption of ions have been given [4 ,4], but in most instances the transition metals have not been included. Swartzen-Allen and Matjevic [44] have suggested an order of preference for montmorillonite and kaolnite for transition metals:

$$Mn^{2+} \simeq Ni^{2+} \simeq Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$$

Investigation of the availability of potassium for exchange in soils has given information on the mechanism of exchange reactions, [45,46,47], but the results cannot be used to predict the type of reaction likely to occur in disposal sites. The ionic species studied are rarely those commonly found in effluents, and the concentrations studied are in general lower than those found in disposal situations.

Past work has been carried out at neutral pH, compared to an acidic environment in most disposal sites. The conditions present in a disposal situation therefore make it impossible to predict the reactions likely to occur, from the results of past work.

CHAPTER 4

ANALYTICAL TECHNIQUES

4.1 Atomic Absorption Spectrophotometry

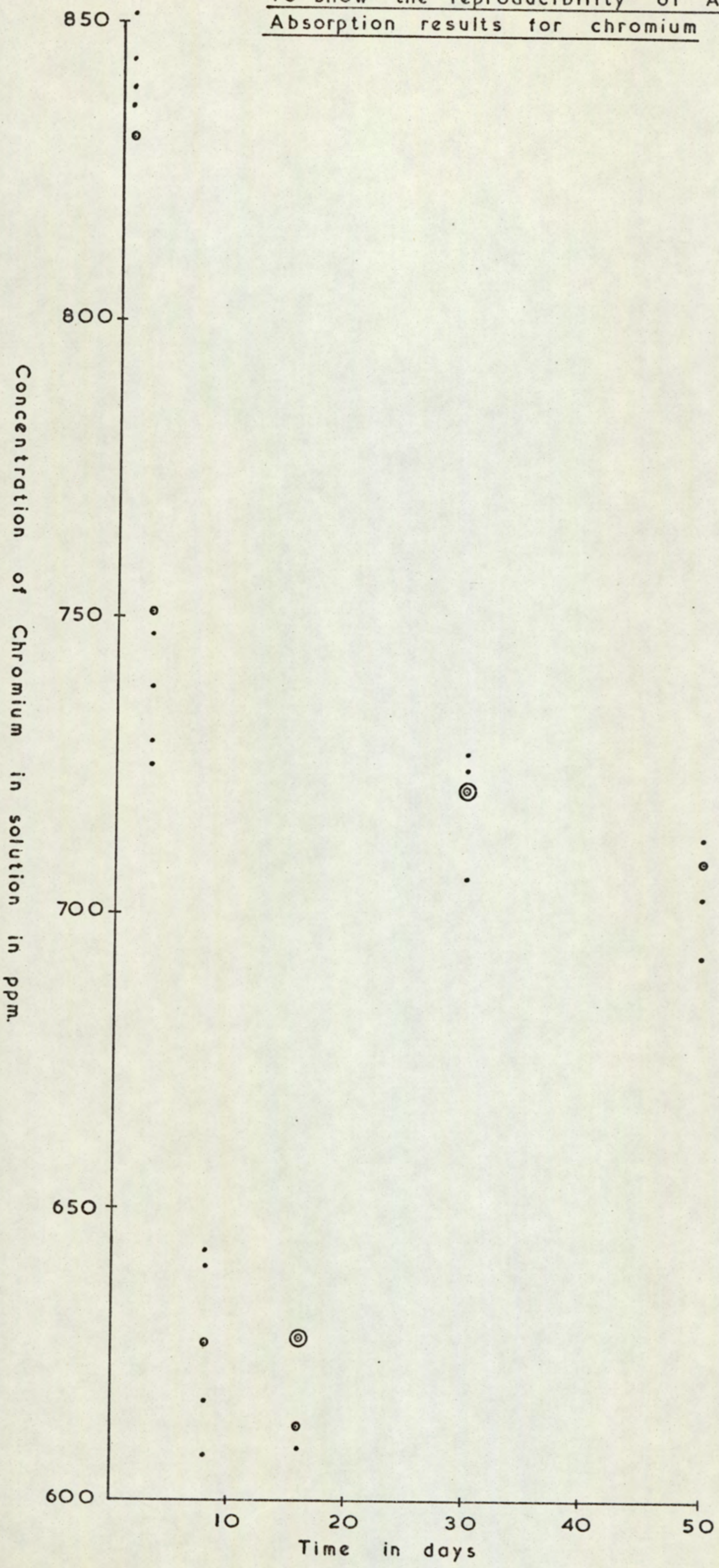
4.1.1. Flame Method. The determination of metal ion concentrations was carried out by flame atomic absorption techniques. The instrument used was a Perkin Elmer Model 303 Absorption Spectrophotometer. Standard solutions were prepared from 1000 mg/l solutions, supplied from B.D.H. Chemicals Ltd, by dilution with distilled water. Absorbance of the solutions was automatically recorded and was converted to parts per million of metal ion in solution by a computer programme.[48]

The reproducibility of the results was assessed for each metal by the following method. Beakers were prepared containing 30 grams of montmorillonite to which was added a solution containing a single metal species (100 mls). The solution was analysed for metal content at least four times at intervals of two days. The experiment was replicated six times for each metal. For each analysis, the mean value for the six samples was found, and the greatest percentage difference calculated. The average value of these percentages was taken as the degree of reproducibility of the results. This test reflects not only the reproducibility of the atomic absorption technique, but also the experimental technique. Figure 17 shows the variation in the readings for the chromium experiment over a period of fifty days. The values of reproducibility found are as follows: chromium ± 2%, cadmium ± 3%, nickel ± 1%, zinc ± 3%, iron ± 5%, copper ± 4%, and lead ± 10%. When plotting values of the concentration of metal ions in solution, bar representations are used to indicate the possible variation in the position of the points.

Dilution of the solutions was necessary in the majority of cases as the concentration of metal ions required for the experiments

FIG. 17

To show the reproducibility of Atomic Absorption results for chromium



was higher than the working range of the instrument. A Hooke and Tucker variable auto diluter was used. The reproducibility of dilution was checked every month and a standard deviation of between 0.01 and 0.4% of the mean value was found.

When using flame atomic absorption as a method of analysis for solutions containing more than one element, interference effects have to be considered,[49,50.] Known interference effects of relevance to this work are; depression of the iron signal by silicate, and enhancement by sulphuric and hydrochloric acids; enhancement of cadmium by hydrochloric acid; cadmium, chromium and potassium are affected by the presence of iron. Copper, sodium and zinc are not subject to interference effects and lead is little affected. When analysing effluent samples, interference affects will occur due to the presence of organic components. In the presence of more volatile solvents the rate of aspiration of the solution medium will increase with a resultant enhancement of the signal. An attempt was made to overcome this difficulty by using the heated graphite atomiser attachment for flameless atomic absorption analysis.

4.1.2 The Heated Graphite Atomiser. The advantage of this equipment for analysing complex solutions is the ability to select a programme for thermal destruction of the matrix before atomisation of the metal to be analysed. With this stage in the process the interference effects of the many components of the effluent may be eliminated. Other features of the flameless method are the detection limits, which may be as low as 10^{-13} grams, and the use of small quantities of sample, in the nanolitre range. The use of small quantities of sample was of little importance in this work, and the low detection limits were a disadvantage as the effluent samples had to be diluted to fall within the working range of the instrument. To overcome this difficulty a less sensitive wavelength was used for zinc but this was not possible for the other elements.

A Perkin Elmer Model HGA 74, heated graphite atomiser was installed in the atomic absorption spectrophotometer in place of the burner system. Atomisation of the sample solution is achieved by the action of a resistance heated graphite tube, operating on a preset programme, selected by temperature and time controls for each of the stages of the process. The first stage of the programme is drying of the sample, followed by thermal destruction of the matrix, and finally atomisation. A fourth stage, heating out, may be operated after atomisation during which the graphite tube reaches a very high temperature to burn off any traces of sample which may be left (Fig 18). During thermal destruction of the matrix, mixtures with strongly differing thermal properties can be destroyed at the same time by employing the temperature programme, which involves a gradual increase in the temperature of the stage at a preset rate (Fig 19).

Twenty microlitre samples were used for the analysis, injected into the graphite tube by means of a micropipette with disposable plastic tips. The tip of the pipette was changed for every sample, and great care was taken with the sample injection as reproducibility is dependent on the accuracy of the sample dosing.

When the work was carried out, no information on the conditions of analysis were available from Perkin Elmer, consequently the conditions for each element were established by a trial and error process. The conditions were obtained by using only the drying, atomisation and heating out stages. As water standards were used for setting up the conditions the drying stage was kept at 100°C. The thermal destruction stage was unnecessary as there was no matrix to be removed. A random temperature was set for atomisation, taking into consideration the degree of volatility of the element, and a

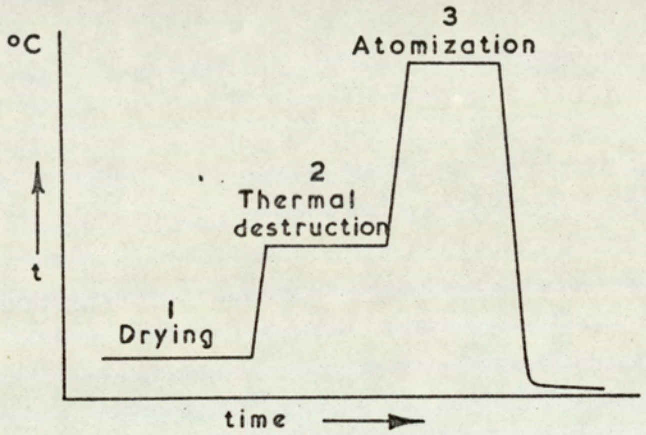


FIG. 18 A

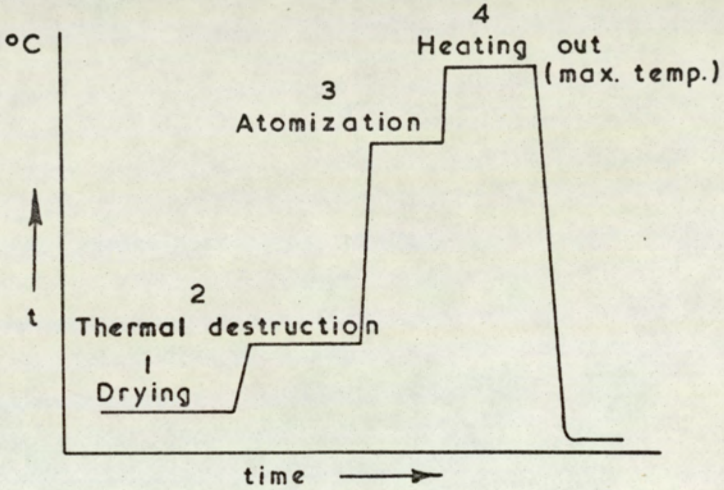


FIG. 18 B

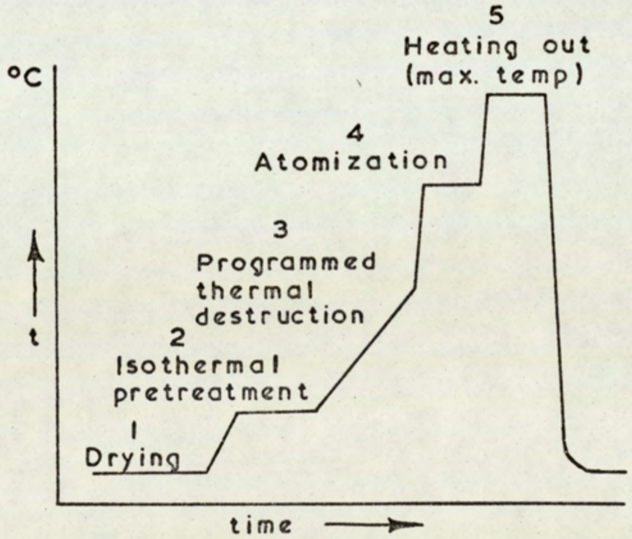


FIG. 19

slightly higher temperature set for heating out. The programme was run, and if a second peak was obtained during the heating out stage it was concluded that the atomisation temperature was too low, and some of the element was left to atomise during heating out. In this case the atomisation temperature was increased gradually until the second peak was eliminated. If at the original temperature no second peak was obtained, the temperature of atomisation was taken to be too high and was reduced gradually until a second peak appeared. This set the minimum temperature at which atomisation could be achieved. The temperature at which the second stage, for matrix removal, could be set was then determined. This stage was set at a temperature below that of atomisation and a standard solution run through the programme. If the height of the peak for atomisation was equivalent to that when the second stage was absent, then it was assumed that no atomisation was occuring at the matrix removal temperature. The temperature setting was increased until the peak height at atomisation was reduced. This set the maximum temperature for the second stage. The time settingswere established again by trial and error. For the drying stage the time allowed was 1½ seconds for each microlitre of sample. For the atomisation stage sufficient time was allowed for the chart recorder to reach the maximum peak height and return to the base line. The heating out stage, if used, was only programmed to last a fraction of a second as the tube cleans quickly at this temperature, and prolonged heating reduces the life of the graphite tube.

Chromium presented great difficulties during the initial stages. When the deuterium arc background corrector was switched on it was found that an energy reading could not be obtained even when the intensity was increased to a maximum. This problem was overcome by moving the chromium lamp to reduce the intensity of the beam by putting it out of focus. The intensity of the deuterium lamp beam was then sufficient to balance the chromium lamp beam.

Having determined the conditions for water solutions of the elements, a sample of effluent from the Walsall Wood Site was analysed, and the conditions checked by varying the temperature settings to ensure that the maximum peak height was obtained at atomisation.

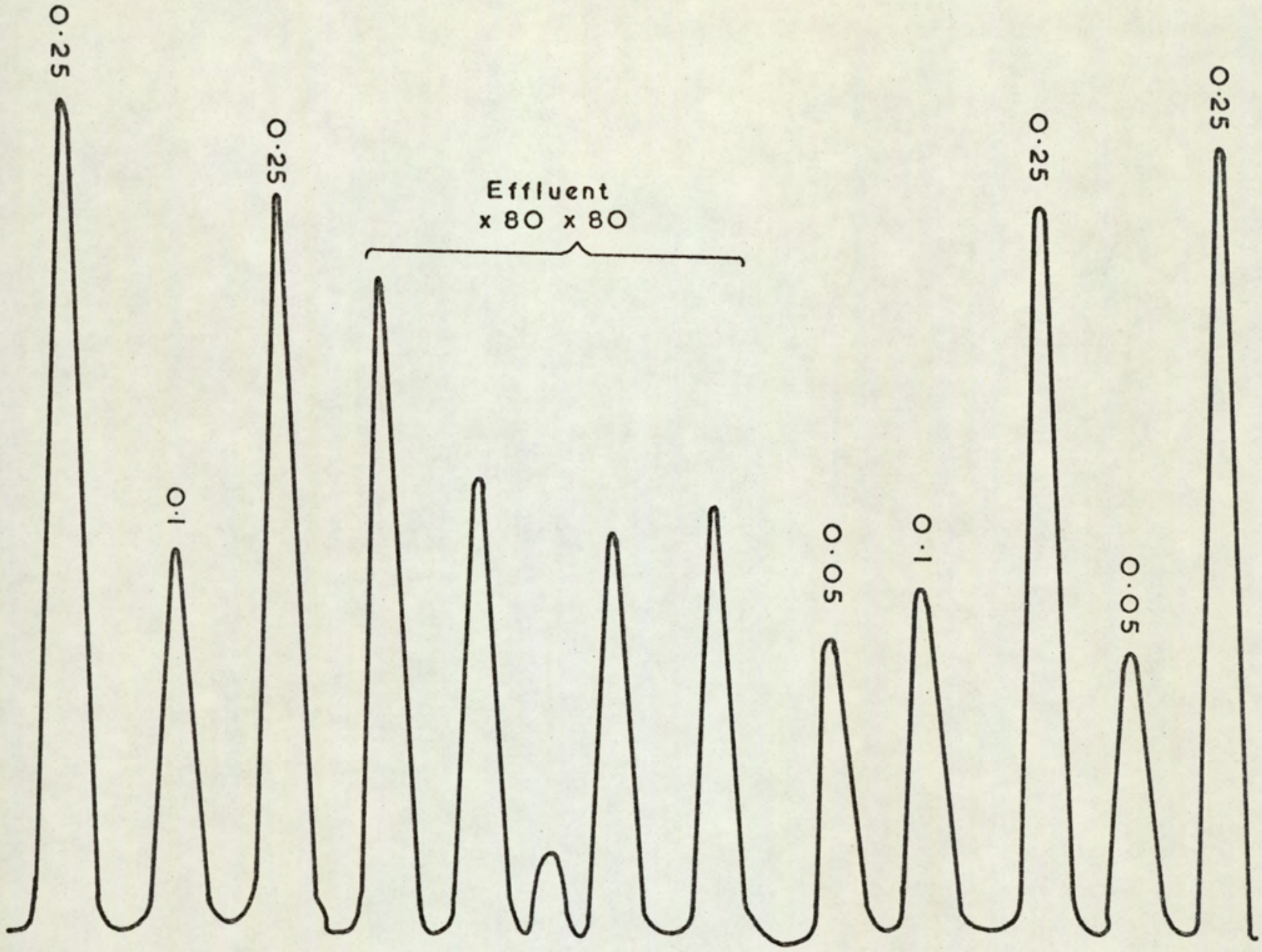
Recently Perkin Elmer published a set of recommended conditions for analysis of elements by the H.G.A. 74. The recommended conditions were similar to, but less precise than, the conditions established during this work (Table 2).

Much time was spent with the instrument, but no satisfactory results were obtained. The main difficulty was in obtaining reproducible results, with copper presenting most problems in this respect. Although the greatest care was taken in sample injection, the peak heights varied even for standard solutions. The variation itself was inconsistant, with reproducible results on some days, and inexplicable variation in results on other occasions (Fig 20). Steps were taken when the discrepancy occurred to ensure that the temperature settings were correct and it was concluded that the observations could only be explained by a fault in the instrument. A further problem was the presence of a secondary peak during the heating out stage. Although this was usually remedied by changing the temperature and time of the atomisation stage, in some cases it was impossible to eliminate the second peak entirely. Additional peaks appeared when the graphite tube was nearing the end of its life, but these were easily eliminated by changing the tube.

FIG. 20

Flameless atomic absorption results

a) Results for copper on the 6th March 1974 showing the difference in peak height for a sample & effluent analysis



b) Results for iron on the 6th. March 1974 showing the second peak after atomisation and good reproducibility of results

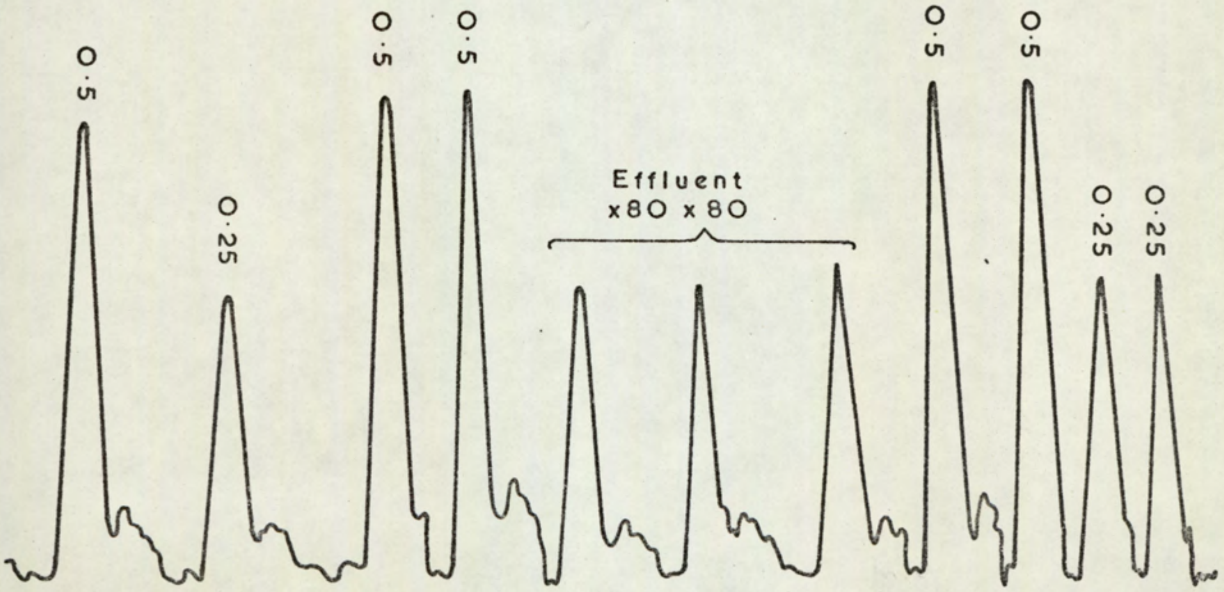


TABLE 2

Comparison of the conditions established for use of the H.G.A. with those recommended by Perkin Elmer.

Element	Programme Stage	Conditions Established		Conditions Recommended	
		Time (Sec)	Temp (° C)	Time (Sec)	Temp (° C)
Copper	1. Drying	30	100	20-60	100
	2. Thermal Destruction	30	490	20-30	900
	3. Atomisation	15	2600	10-20	2550
	4. Heating out				
Chromium	1.	30	100	20-60	100
	2.	15	700	20-30	1200
	3.	15	2660	20	2660-2700
	4.				
Cadmium	1.	30	100	20-60	100
	2.	30	140	20-30	300
	3.	10	1800	10-20	1900
	4.				
Iron	1.	30	100	20-60	100
	2.	30	700	20-30	1200
	3.	10	2590	10-20	2500
	4.				
Lead	1.	30	100	20-60	100
	2.	30	140	20-30	700
	3.	15	2040	10-20	2100
	4.				
Nickel	1.	30	100	20-60	100
	2.	10	485	20-30	1200
	3.	10	2620	20	2660-2700
	4.				
Zinc	1.	30	100	Not given	
	2.	30	450		
	3.	10	1685		
	4.	0.5	2330		

After running samples containing a high concentration of iron through the instrument, when analysing for other elements, it was found that the carbon rod had to be changed for iron analyses, as it appeared to be saturated with iron which could not be removed by heating out. This effect could be caused by the formation of iron carbide by reaction of iron in the sample, with the graphite tube during analysis of other elements. The component would decompose releasing iron in large quantities during the analysis for iron, resulting in a greatly enhanced signal. After correcting the effect several times by changing the tube, this remedy became ineffective and it was concluded that the graphite sleeves holding the tube must have become contaminated. Iron was being released when the carbon rod reached the atomisation temperature for iron.

Attempts were made to use the flameless atomic absorption technique for analysing solutions from experiments, but the reproducibility was so poor that no conclusions could be drawn. A comparison of results obtained for flame and flameless analysis of an effluent sample from the Walsall Wood Site is given in Table 3. The results for nickel, iron and zinc are comparable, while those for copper, chromium and lead are inconsistant and not comparable. The results for cadmium may be explained by the dilution factor, which is 800 times greater for the graphite atomiser analysis, which at these low values could account for the discrepancy.

In view of the difficulties in the operation of the heated graphite atomiser, the method was abandoned for the purpose of this work. The inconsistency of the results made it impossible to guarantee that the instrument would give reproducible results on the days when analyses were necessary. The experiments with effluent samples were carried out with analyses for metals performed by the flame method.

TABLE 3

Comparison of the results of an analysis carried out on a sample of effluent, by flame atomic absorption, and flameless atomic absorption.

Element	Flame ppm	H.G.A. + D_2 arc ppm
Zinc	4464	4313
Iron	37500	37201
Chromium	1042	1181
repeated	627	1065
"	798	1370
Lead	50	83
repeated	42	74
"	42	75
Copper	935	682
repeated	850	596
"	734	820
Nickel	107	108
Cadmium	7	14

The repeated results will not be directly comparable to the original results due to changes which may occur in the effluent during the standing time.

Since the completion of the work, the graphite furnace has been fitted with new sleeves to hold the graphite tube. Since this treatment the results from the instrument have been consistently reproducible, confirming that the difficulties encountered were due to an instrumental defect. The fault was not corrected in time to make the instrument available for this work, but it will enable useful results to be obtained in the future.

4.2. X Ray Diffraction

This technique was used to identify the clay minerals present in rock samples from the disposal sites. A Phillips 1130 X Ray generator with broad focus Cu tube was used. The identification of peaks was carried out using the 2Θ (Cu) table for common minerals by G.Y. Chaos [51].

Slides were prepared representing a range of particle sizes for the rock materials. The rocks were first crushed by pestle and mortar to a size less than 600µ. From this sample a slurry was prepared in water, and placed on a slide. A 100 gram sample was used to obtain sub 20µ, sub 10µ, and sub 2µ samples by sedimentation [52]. Analyses were carried out at 1° per minute with a chart speed of 10 mm per minute.

To aid clay mineral identification, the sub 2µ slide was glycolated by placing the slide in a desiccator containing a beaker of ethylene glycol at 60° C for 4 hours. The organic molecules will penetrate the sheets of the three layer clays, increasing the d spacing, which will be reflected in a movement of the peaks for these minerals to a lower 2Θ angle. Expansible three layer clays can be distinguished from the non expanding types by this method.

4.3. Infra Red Spectroscopy

Infra red spectra of the rocks were obtained, using a Perkin Elmer model 225 instrument. The rocks were prepared as K Br discs. Only the Coal Measures rocks were analysed by this method as the information gained was more readily seen by XRD analysis. Interpretation of the spectra was aided by a summary of the main infra red absorption bands to be found in layersilicates [53].

CHAPTER 5

ADSORPTION EXPERIMENTS: METHOD AND RESULTS

5.1 Sampling of Materials

The choice of material used for the experimental work was governed by the conditions in the disposal sites being investigated. Representative rock types from the Coal Measures were obtained from borehole cores from Cannock No. 5 Colliery, situated in the main South Stafforshire Coalfield, Although rocks from Walsall Wood were unobtainable as the colliery has been closed for several year, the rocks used are very similar. Both sandstone and shale were collected and used for the early experiments, although later experiments were carried out only on the shale. Four rock types were selected to represent the lithologies found at the Betton Abbotts disposal site; grey clay from the centre of the site below the peat, red boulder clay from the glacial deposits, grey sand from the western end of the site and red sandstone from the borehole core. Red mudstone from the Mitco site completed the collection of rock samples from the sites.

To promote rapid results from the experiments undertaken, the surface area of the rocks was increased by crushing to a grain size of less than 600μ. The Coal Measures rocks were crushed by Tema Mill, and the other rocks by pestle and mortar. A representative sample of each rock type was obtained after the initial crushing. The total rock sample was divided into four equal parts. Opposite quarters were taken, mixed and again divided into four. The process was repeated until a representative sample of approximately thirty grams was obtained for use in the analytical work.

The pure minerals montmorillonite and kaolinite were obtained from Berk Limited, and English China Clays Sales Co Ltd., respectively. Analyses supplied by the companies gave the following specifications for the clays.

CHEMICAL ANALYSIS	MONTMORILLONITE %	KAOLINITE %
SiO_2	52.2	46.2
Al_2O_3	12.8	38.7
Fe_2O_3	10.2	0.56
TiO_2	0.6	0.09
MgO	2.5	0.2
CaO	2.2	0.2
K_2O	0.4	1.01
Na_2O	0.1	0.07
H_2O (- 105° C)	12.3	
H_2O (+ 105° C)	6.6	
Loss on ignition		13.14
pH	6.5 - 7	5.0 ± 0.5
CATION EXCHANGE CAPACITY	80-85	
PARTICLE SIZE		
% below 53	87	99.99
% below 0	88	99.8
% below 2	84	80 ± 3

Sampling of the effluent was difficult due to the seasonal variations in the volume and nature of loads discharged to the Walsall Wood Mine Shaft, and the uncertainty as to the effluent types which would be tipped at Betton Abbotts site. Samples were taken from tanker loads discharged to the mine over a period of four months, and mixed to obtain a representative sample. Analyses of effluent discharged to the mine over a one month period were used to calculate the concentration of metal ions in typical loads, from which the concentrations for the pure acid solutions were selected. The solutions of more than one element represented typical combinations of metals found in effluent loads, eg many elements in small concentrations, many elements in small quantities with one dominant element, and small numbers of metal species in high concentrations. In general, the concentrations of nickel and iron are high, in the region of tens of thousands of ppm with zinc, chromium and copper in thousands, lead in hundreds and cadmium in tens of parts per million. Three samples of waste representative of that to be disposed at Betton Abbotts were mixed to obtain an effluent sample for use with the rocks from the site. Chemical analyses of wastes handled by the company were used to calculate an average value of the metal content of the wastes. These values were used when preparing the solutions of pure metal salts in acid for use with the Betton Abbotts Shrewsbury rocks. Iron was present either in quantities of about 600 ppm or in very high quantities (tens of thousands of ppm), copper and zinc in hundreds of ppm and thousands of ppm, nickel in thousands of ppm, chromium and lead in hundreds of ppm and cadmium in tens of ppm. A sample of liquid from the Mitco site was obtained at the abstraction point at the northern end of the site. Solutions made up with pure acids and metal salts for use with the Mitco site rock were similar to those used for the Betton Abbotts rocks as the effluent type disposed at the two sites are similar.

Thus, for each site there was a representative sample of effluent, and prepared solutions containing metal ions in proportions representative of the effluent loads disposed at each site. Details of the concentrations of the solutions used are given in the results section for each experiment.

5.2 Experimental Design

The experiments on the adsorption of metal ions by clay minerals were conveniently carried out in 250 ml beakers, using approximately 30 gms of rock material and 100 mls of liquid. The volume of the liquid had to be large enough to allow removal of small quantities for analysis without varying the quantity of metal ions present to any great extent. For each analysis approximately two millilitres of liquid were removed, giving an overall reduction of approximately 16% over the experimental period as the analyses were performed on average about eight times. However, the majority of the reaction was found to occur during the first week, when only three analyses were carried out giving a reduction of only 6% in the volume of the liquid. Sufficient quantities of rock material were used to allow for the large percentage of inert silica present compared to the amount of material with active exchange sites. The possibility of replacing the liquid withdrawn was considered, but a suitable convenient method which would reduce the inaccuracies could not be found. Hence it was considered reasonable to allow the losses as further inaccuracies would occur in trying to rectify the error.

The beakers were weighed without and with the rock sample to obtain the weight of the rock material used. The solutions of metal ions were prepared using the nitrates of the metals concerned. On adding the prepared solutions to the rock material the mixture was stirred, and covered with a polythene square secured by an elastic band. The liquid was analysed for metal ions at intervals of one, three, seven and fifteen days after preparation of the beakers, and every fortnight until the concentration became stable. The solutions were sampled with disposable pipettes, and the samples placed in disposable glass sample bottles. Samples were taken on the day when the analyses were carried out to reduce the possibility of removal of the metal ions by adsorption onto the surface of the glass sample bottles. After sampling, the mixtures were stirred and the polythene tops replaced.

The problem of evaporation of liquid from the beakers, although reduced by the polythene tops, was not completely solved. Where the adsorption of the metal ions is very efficient evaporation will have little effect on the result, but where adsorption is very inefficient, reductions in the concentration of metal ions in the solution caused by adsoprtion could be compensated by evaporation of the liquid, and in some cases the concentration of metal ion appeared to increase due to a reduction in the volume of the liquid. For example, a solution containing originally 2000 parts per million of metal ion in 100 mls of solution will contain 2 x 10^5 milligrams of metal. If the volume of the liquid is reduced by 10% by evaporation the concentration will become 2222 parts per million, adsorption of 200 ppm of metal from this solution could therefore be masked if a 10% evaporation occurs. However, if the original concentration is reduced by adsorption to only 20 ppm, a reduction in the volume of liquid of 10% will alter the concentration by 2% to 22 ppm.

As the majority of adsorption occurs during the first week of the experiment the problem of evaporation was overcome by using analyses from the first seven days during which evaporation is minimal.

5.3 Experiments and Results

Where removal of metal ions from the solution is observed the phenomena is referred to as adsorption. There will be a discussion of the mechanism of the removal in Chapter 8.

5.3.1. The reaction of Coal Measures rocks at pH0. The first set of experiments were carried out using Coal Measures Sandstone and Shale rock types with solutions of a single metal species in a single acid. Perchloric acid, nitric acid and hydrochloric acid were chosen for the experiments at pH 0 representing the pH of the majority of the acid effluents disposed of at the Walsall Wood facility. The metal ions, Fe III, Pb II, Zn II, Cu II, Cr III, Ni II and Cd II were used in concentrations representative of those found in typical effluents. Control experiments were prepared containing the rock material and acid with no metal salt added. The metal ion solutions were analysed to determine any contamination by other metal ions which may be present in the nitrate salts used for preparation of the solutions. Each combination of rock type, acid and metal was prepared in triplicate to examine the reproducibility of the experiments. The combination of lead in hydrochloric acid is missing as the lead precipitates as lead chloride.

The results are presented in the form of graphs showing the reduction in concentration of the metal ions in the acid solutions over a period of time. Bar representations of the points are used to indicate the variation due to experimental error, and limits of reproducibility of the atomic absorption results (Section 4.1).

Fig 21. Graphs of the reduction in the concentration of metal in solution against time when the solution is in contact with

a. Coal Measures Sandstone

b. Coal Measures Shale

Fig 21. 1 Chromium in Perchloric acid

Fig 21. 2 Chromium in hydrochloric acid and nitric acid

Fig 21. 3 Zinc

Fig 21. 4 Cadmium

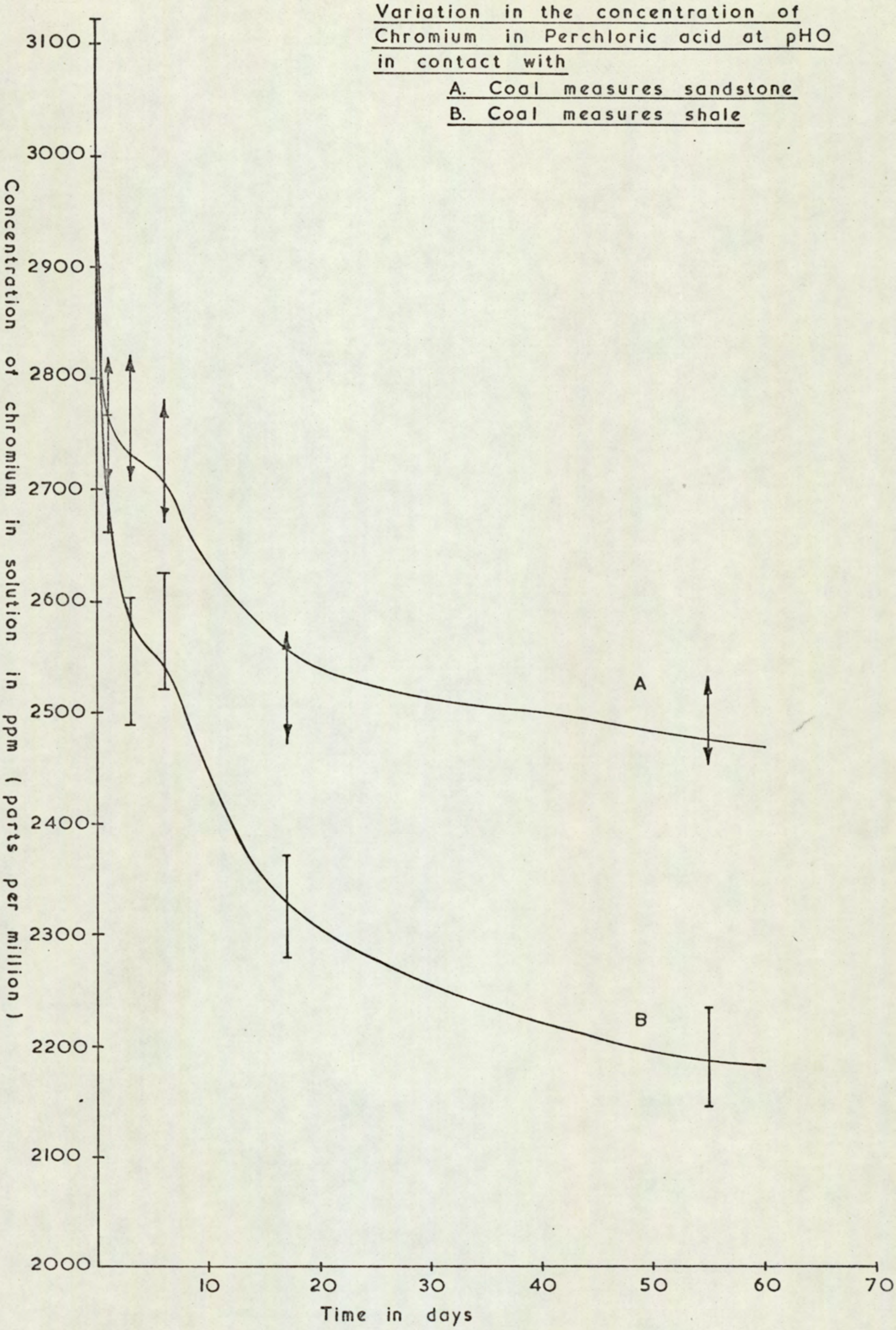
Fig 21. 5 Lead

Fig 21. 6 Copper

Fig 21. 7 Nickel

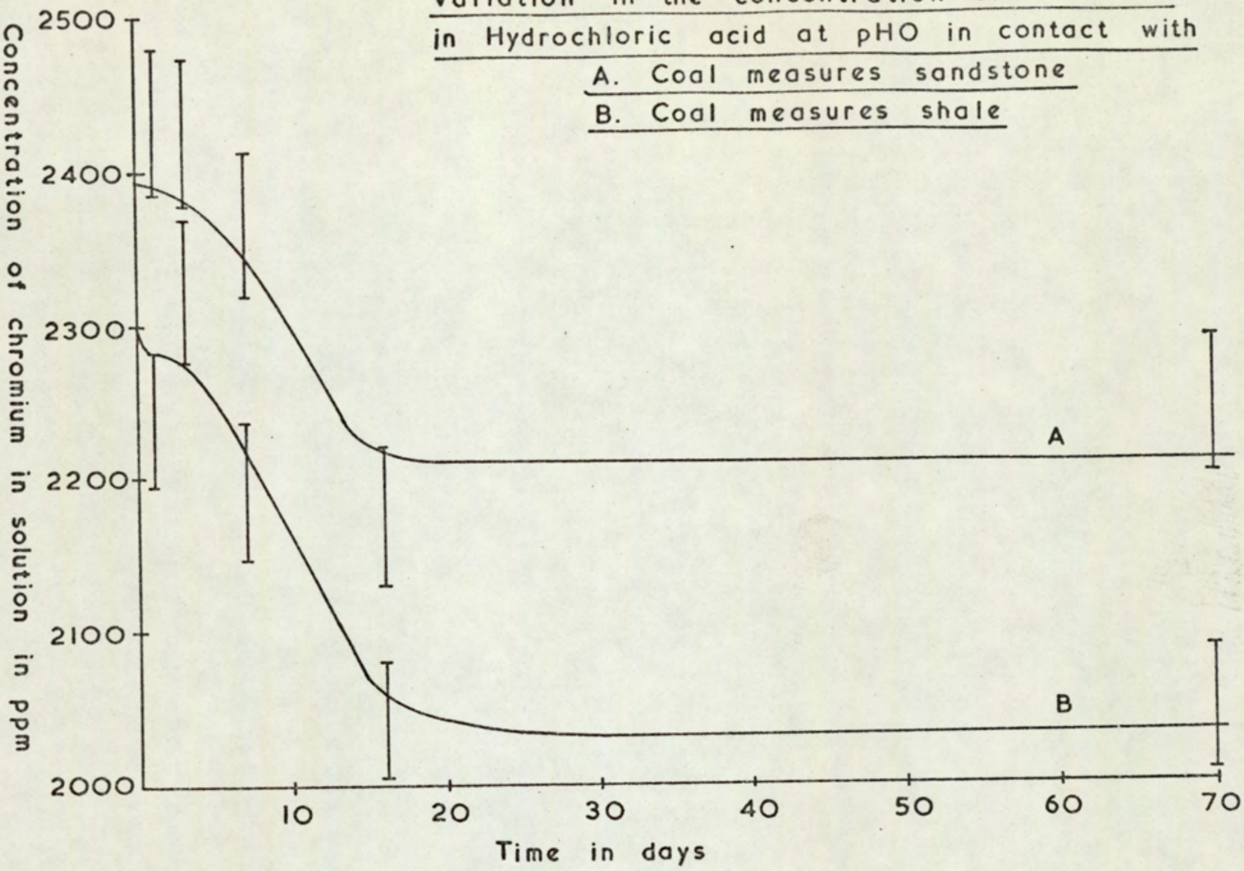
Fig 21. 8 Iron

FIG. 21.1

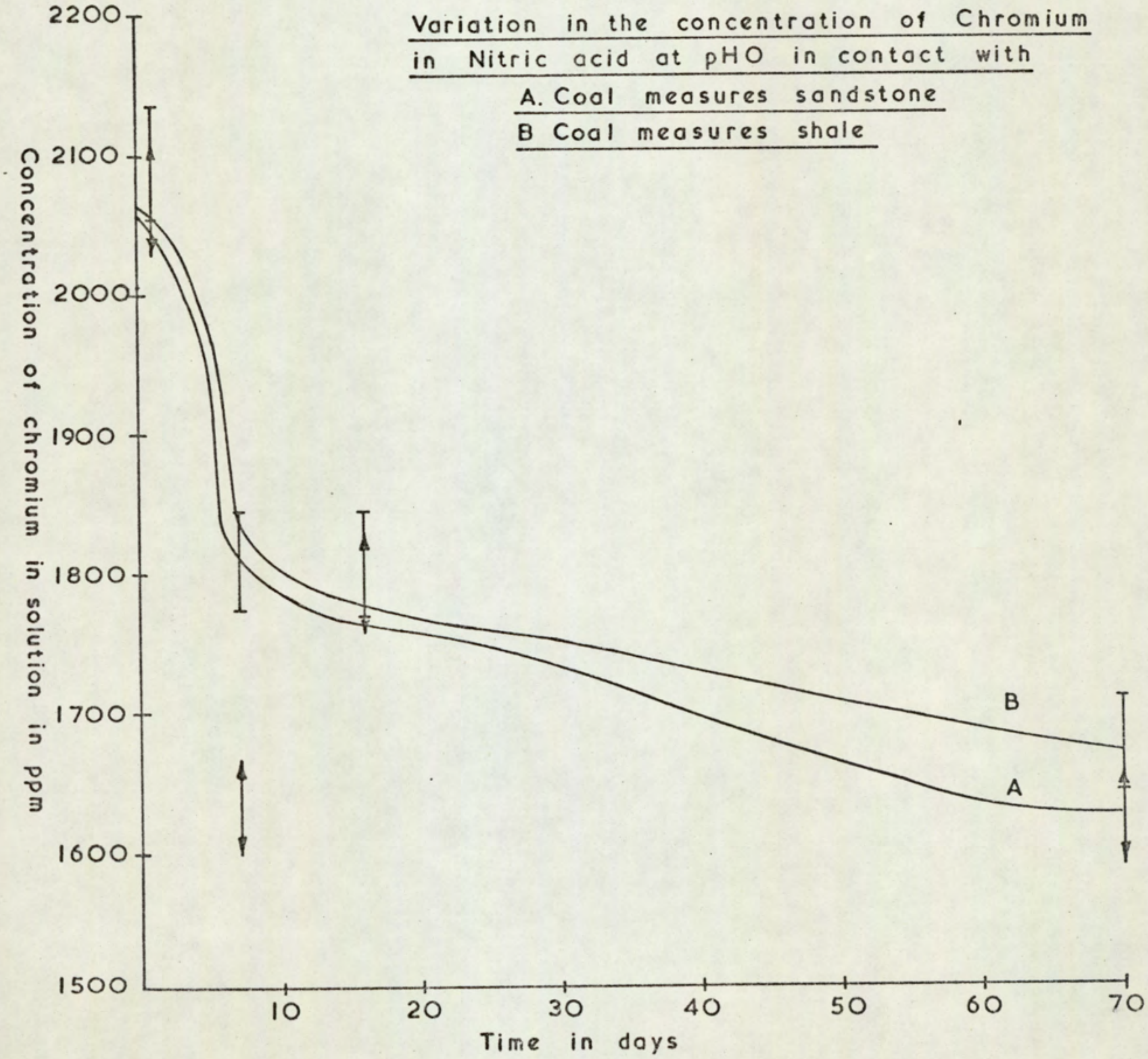


Variation in the concentration of Chromium in Perchloric acid at pHO in contact with
A. Coal measures sandstone
B. Coal measures shale

FIG. 21. 2



Variation in the concentration of Chromium in Hydrochloric acid at pHO in contact with
A. Coal measures sandstone
B. Coal measures shale



Variation in the concentration of Chromium in Nitric acid at pHO in contact with
A. Coal measures sandstone
B Coal measures shale

FIG. 21.3

Variation in the concentration of zinc in 3 acids at pHO over 70 days on
A. Coal measures sandstone
B. Coal measures shale

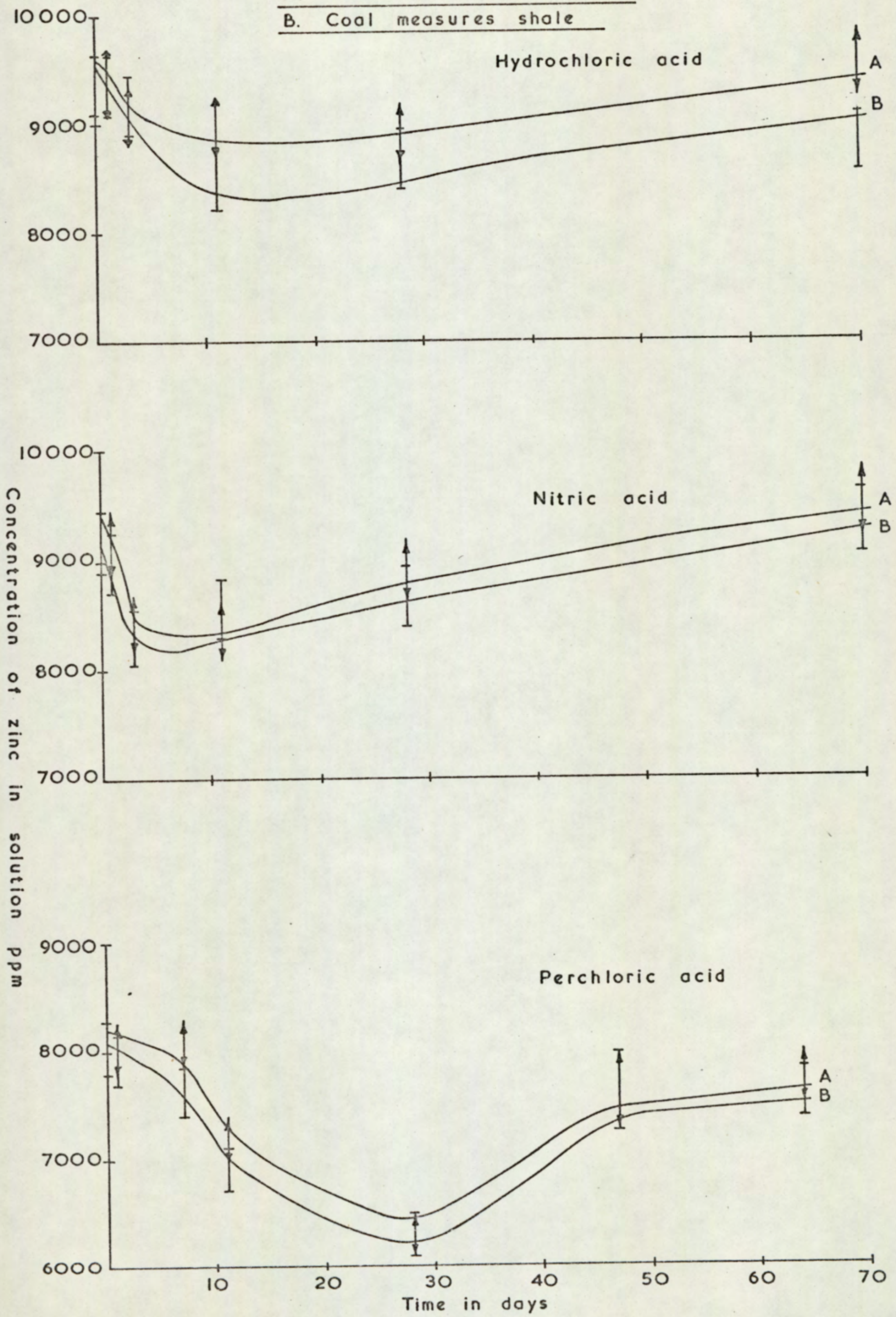


FIG. 21. 4

Variation in the concentration of Cadmium in 3 acids at pHO over 70 days on
A. Coal measures sandstone
B. Coal measures shale

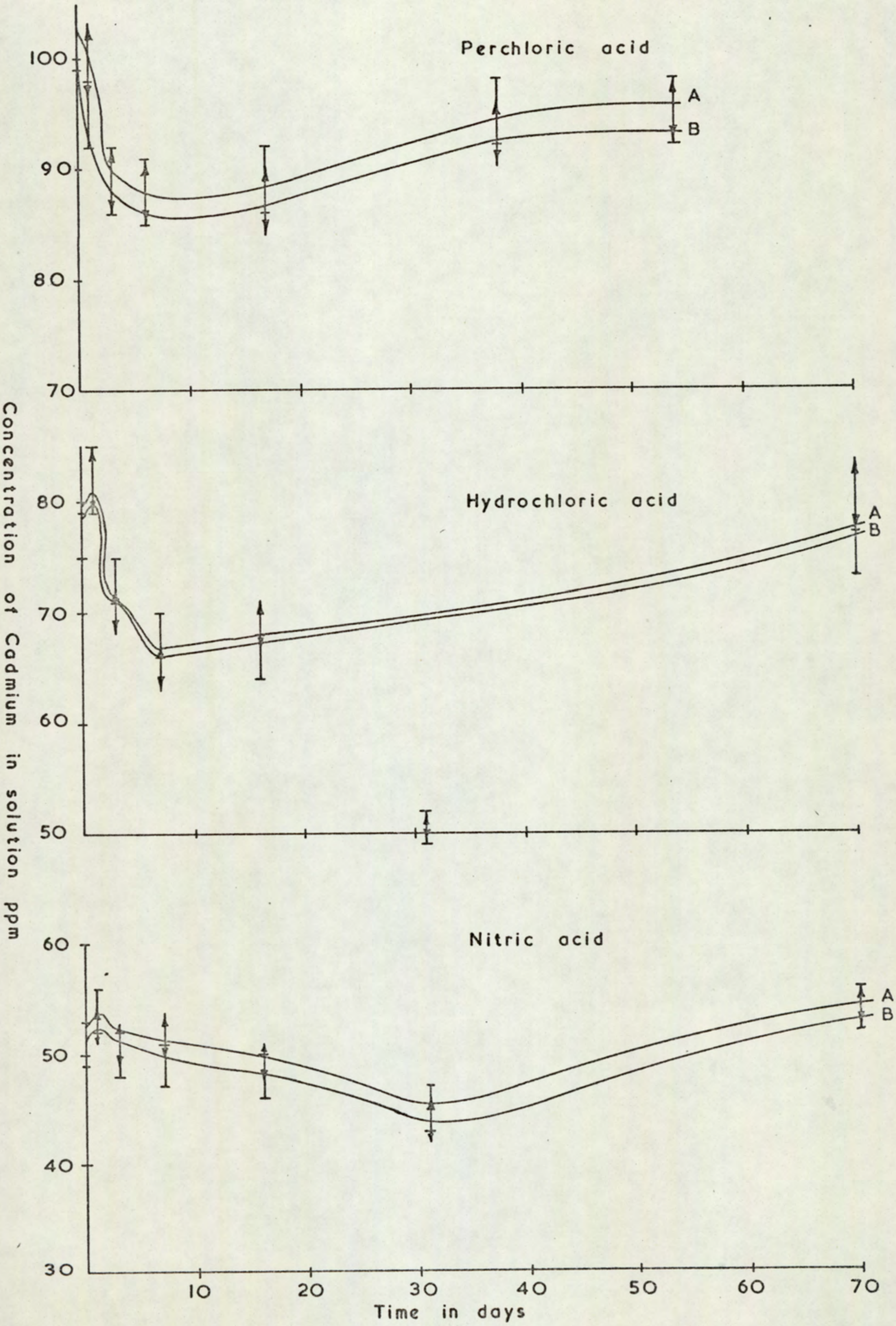


FIG. 21.5

Variation in the concentration of lead in 2 acids at pHO over 70 days on

A. Coal measures sandstone

B. Coal measures shale

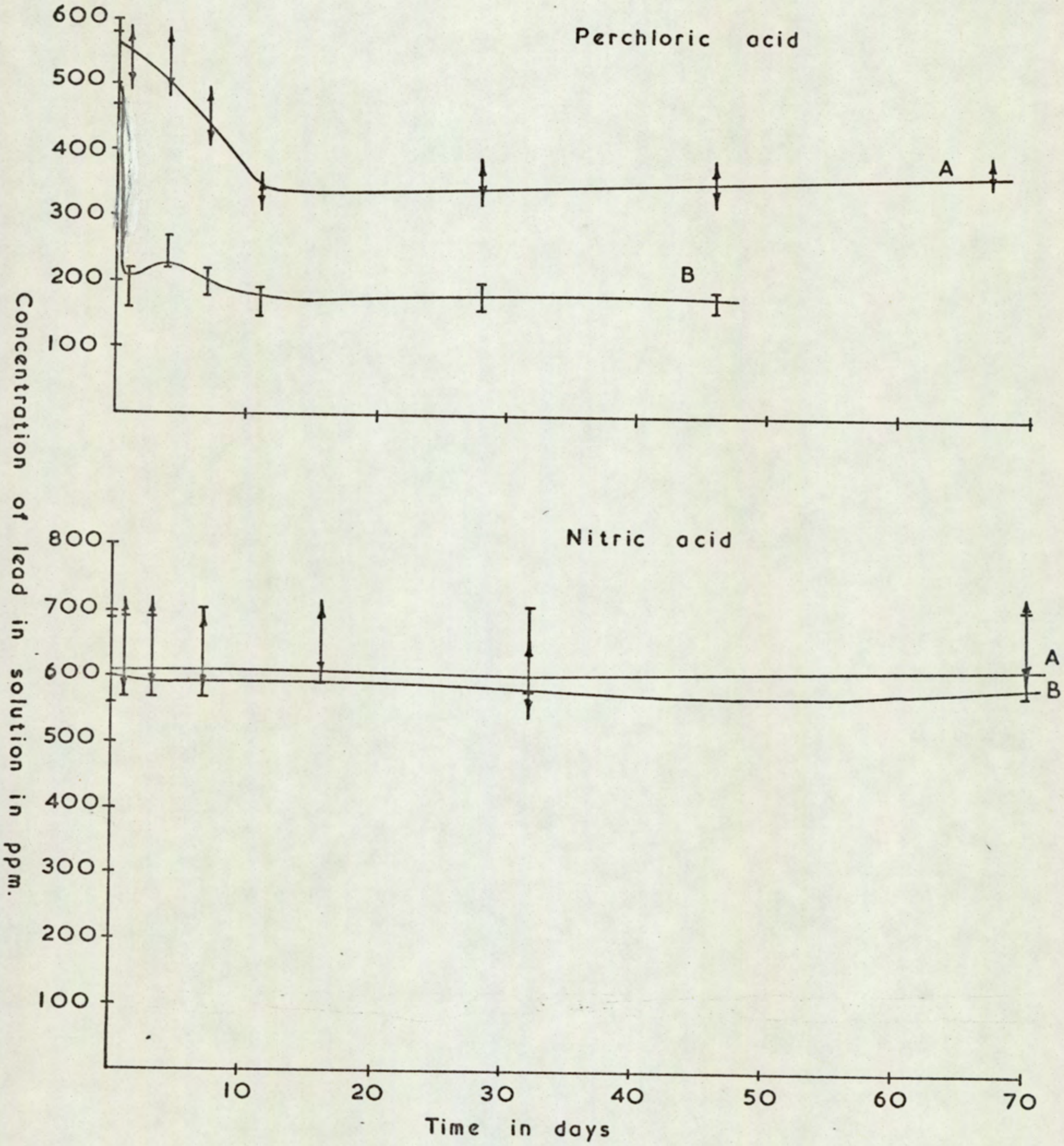


FIG. 21.6

Variations in the concentration of copper in 3 acids at pH0 over 70 days on
A. Coal measures sandstone
B. Coal measures shales

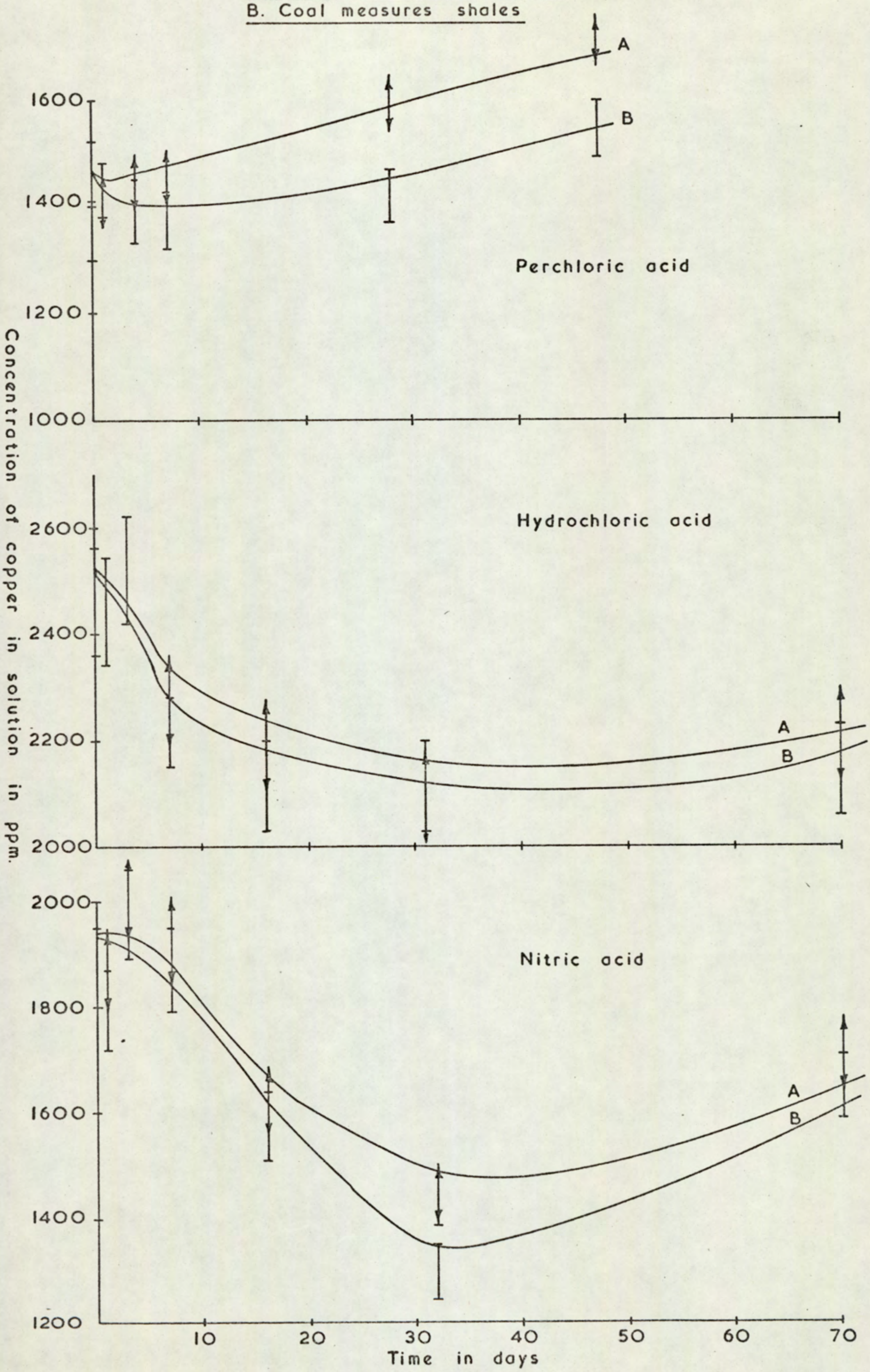


FIG. 21. 7

Variation in the concentration of Nickel in 3 acids at pHO over 70 days on

A. Coal measures sandstone

B. Coal measures shale

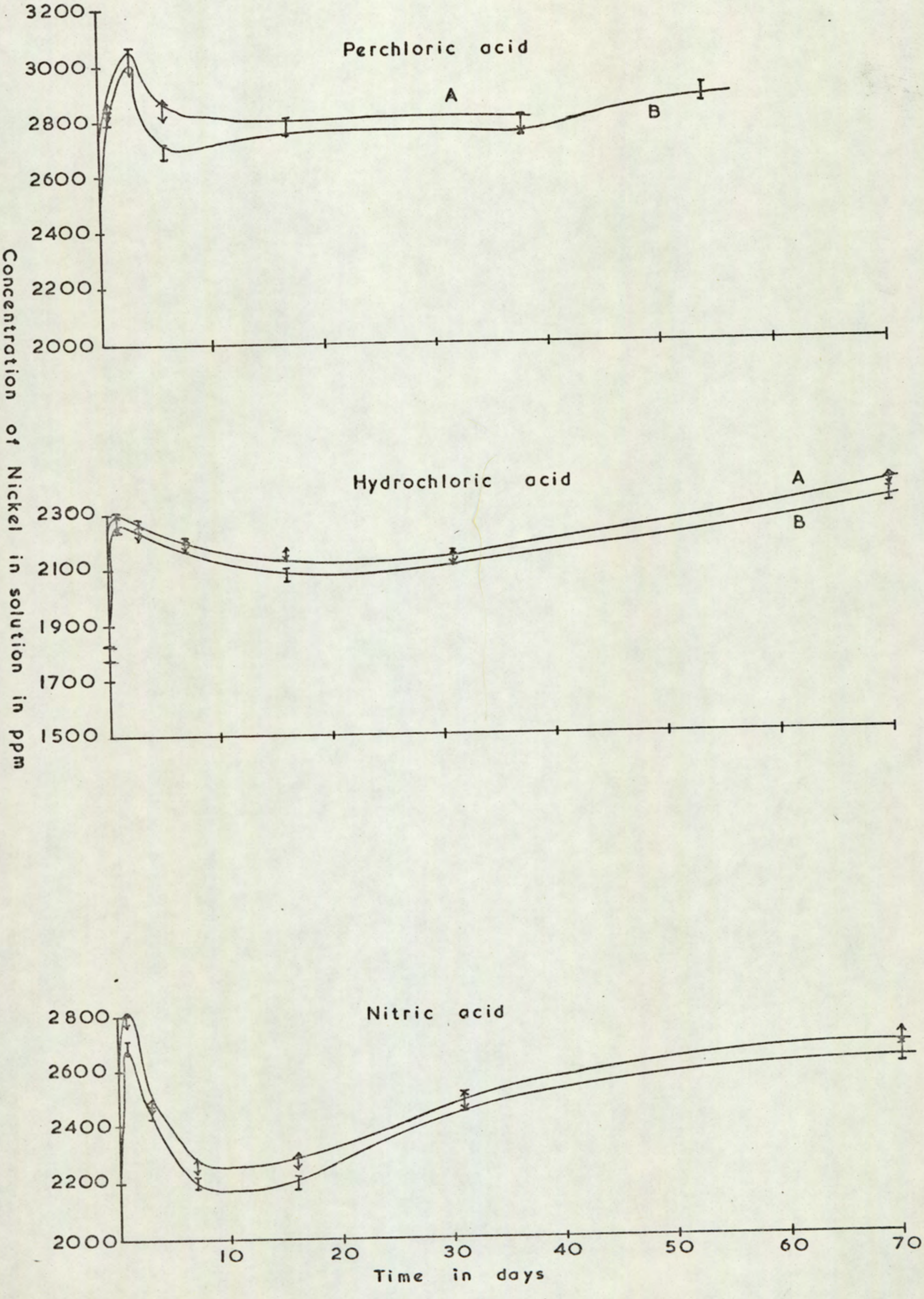
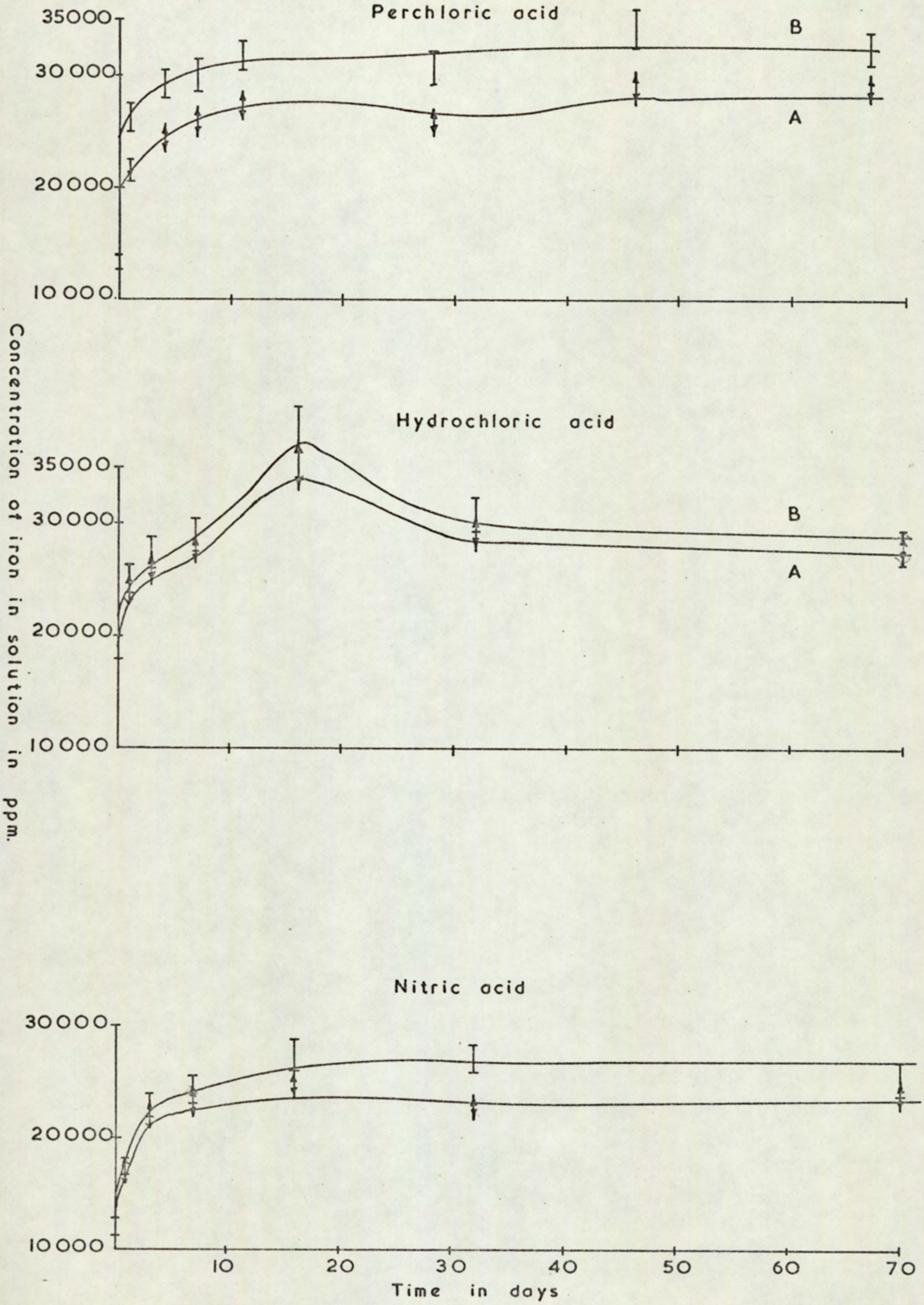


FIG. 21. 8

Variation in the concentration of Iron in 3 acids at pHO over 70 days on

A. Coal measures sandstone

B. Coal measures shale



5.3.2 Experiments with Montmorillonite and Kaoline in contact with solutions of metal ions at a series of pH values

Having established that little adsorption occurs at pH 0, the next series of experiments were carried out at different pH values, using pure clay minerals to eliminate the effects of the large quantities of iron present in the Coal Measures rocks.

Hence solutions of each of the seven metals were prepared in perchloric, nitric and hydrochloric acid at pH values 1, 2, 3 and 4. The pH 9 solutions were prepared with sodium hydroxide. Each solution was mixed with both montmorillonite and kaolinite.

The results are plotted as graphs of the reduction of metal in solution against time. The results for the three acid types are similar, hence only the results for perchloric acid have been presented as graphs.

Fig. 22. Graphs of the reduction in concentrations of metal in solution against time for seven metals in perchloric acid at pH 1, 2, 3 and 4, and in sodium hydroxide at pH9, in contact with montmorillonite and kaolinite.

Fig 22. 1 Chromium, Montmorillonite

Fig 22. 2 Chromium, Kaolinite

Fig 22. 3 Zinc

Fig 22. 4 Nickel

Fig 22. 5 Cadmium

Fig 22. 6 Copper

Fig 22. 7 Iron

Fig 22. 8 Lead

FIG. 22. I

Variation in concentration of Chromium on Montmorillonite at pH 1, 2, 3, 4, 9 over a period of 70 days

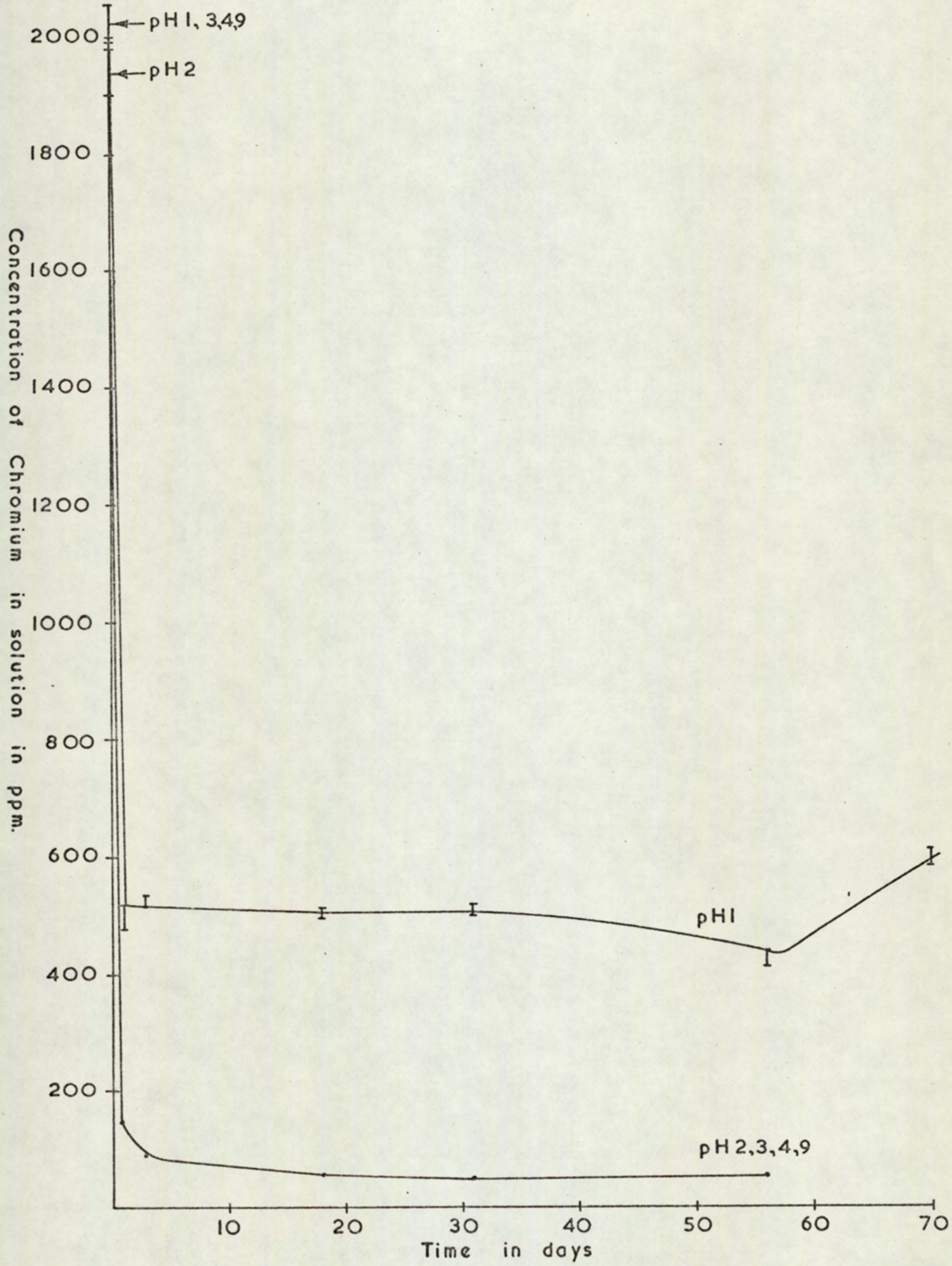


FIG. 22. 2

Variation in the concentration of Chromium on Kaolinite at pH 1,2,3,4,9 over 70 days

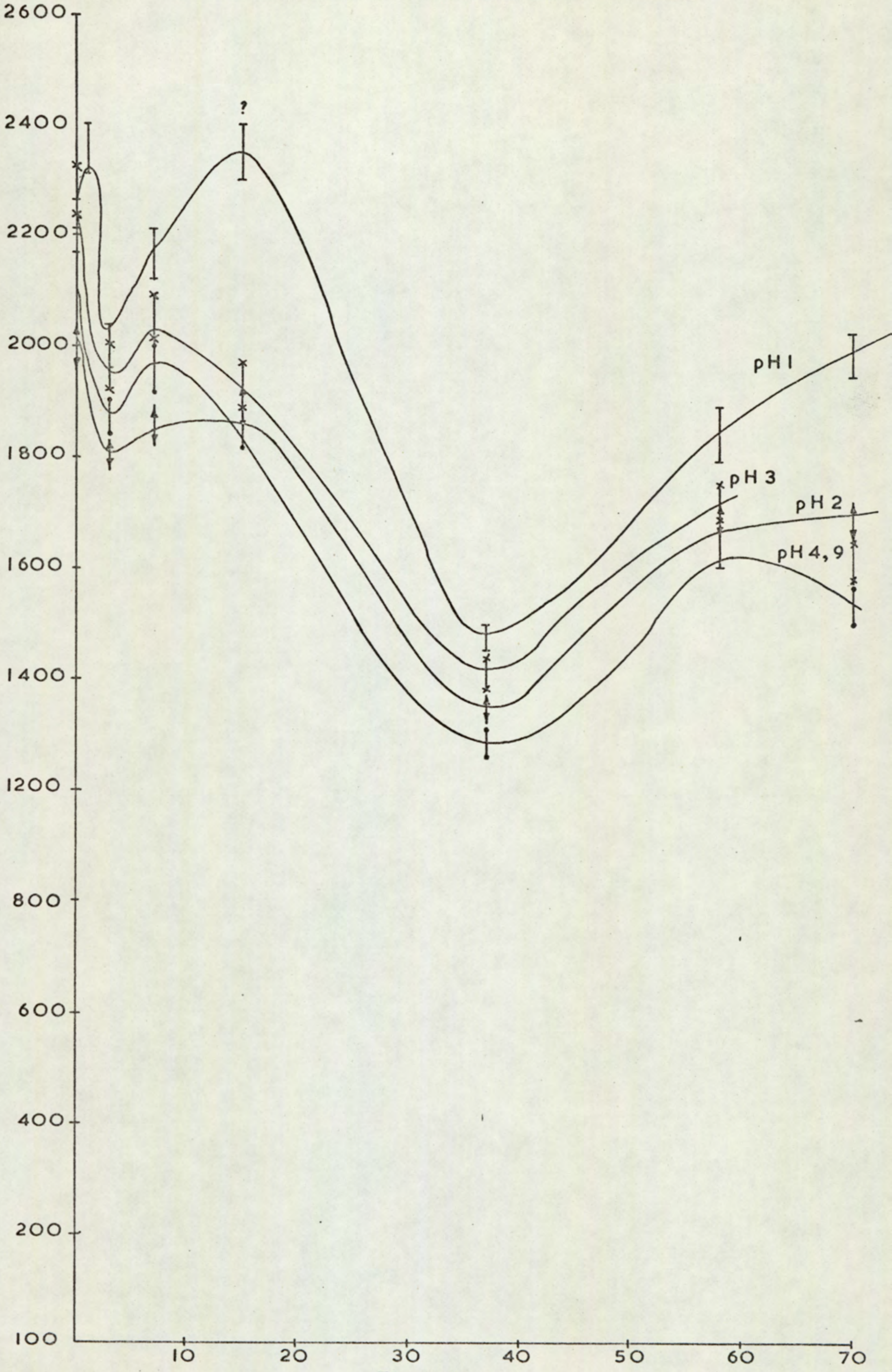
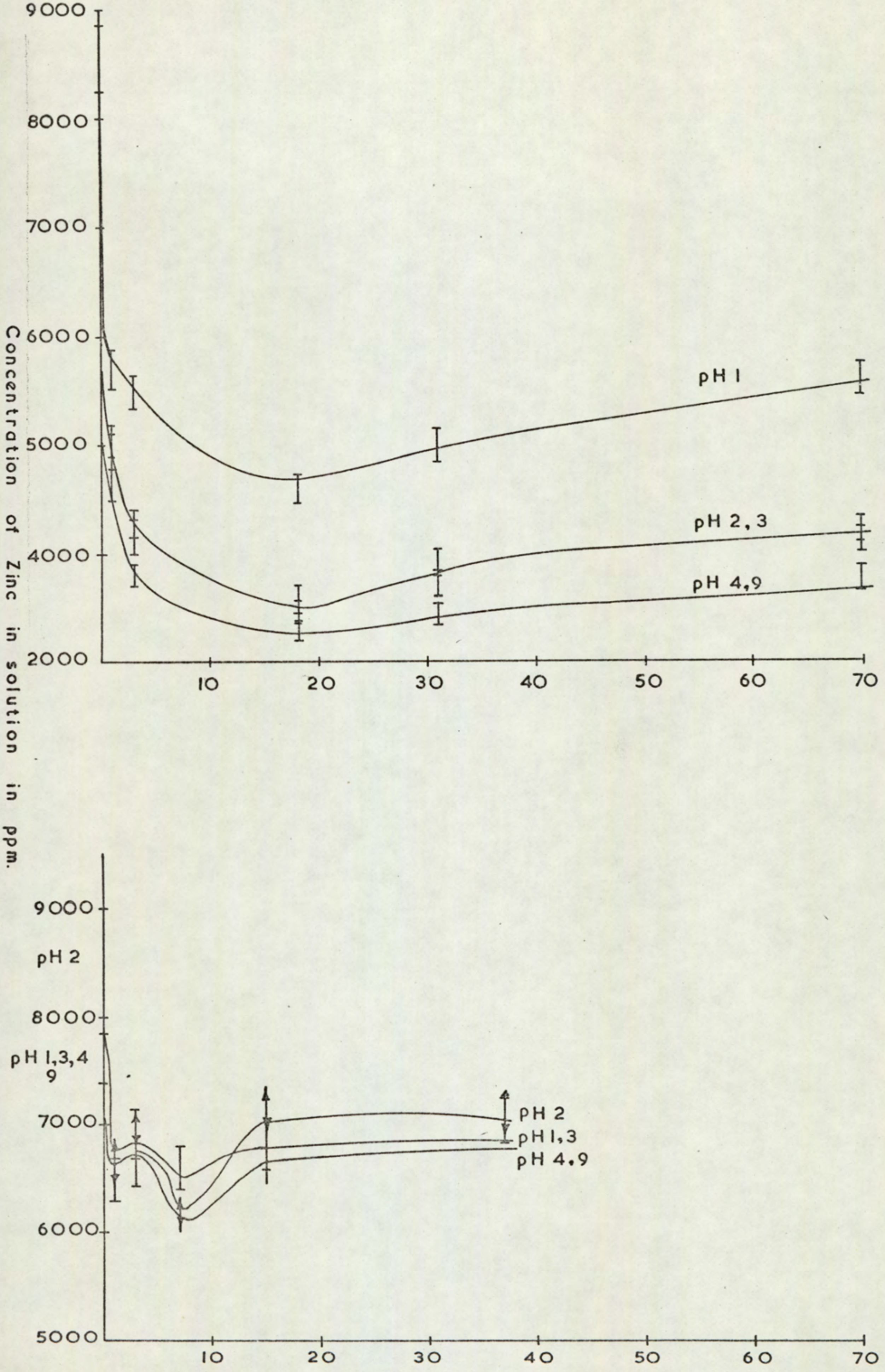


FIG. 22. 3



Concentration of Zinc in solution in ppm.
9000
8000
7000
6000
5000
4000
2000
10
20
30
40
50
60
70
pH I
pH 2, 3
pH 4, 9
9000
pH 2
8000
pH I,3,4
9
7000
6000
5000
10
20
30
40
50
60
70
pH 2
pH I,3
pH 4.9
Time in days

FIG. 22.4

Variation in concentration of Nickel on Montmorillonite and Kaolinite at pH 1,2,3,4,9

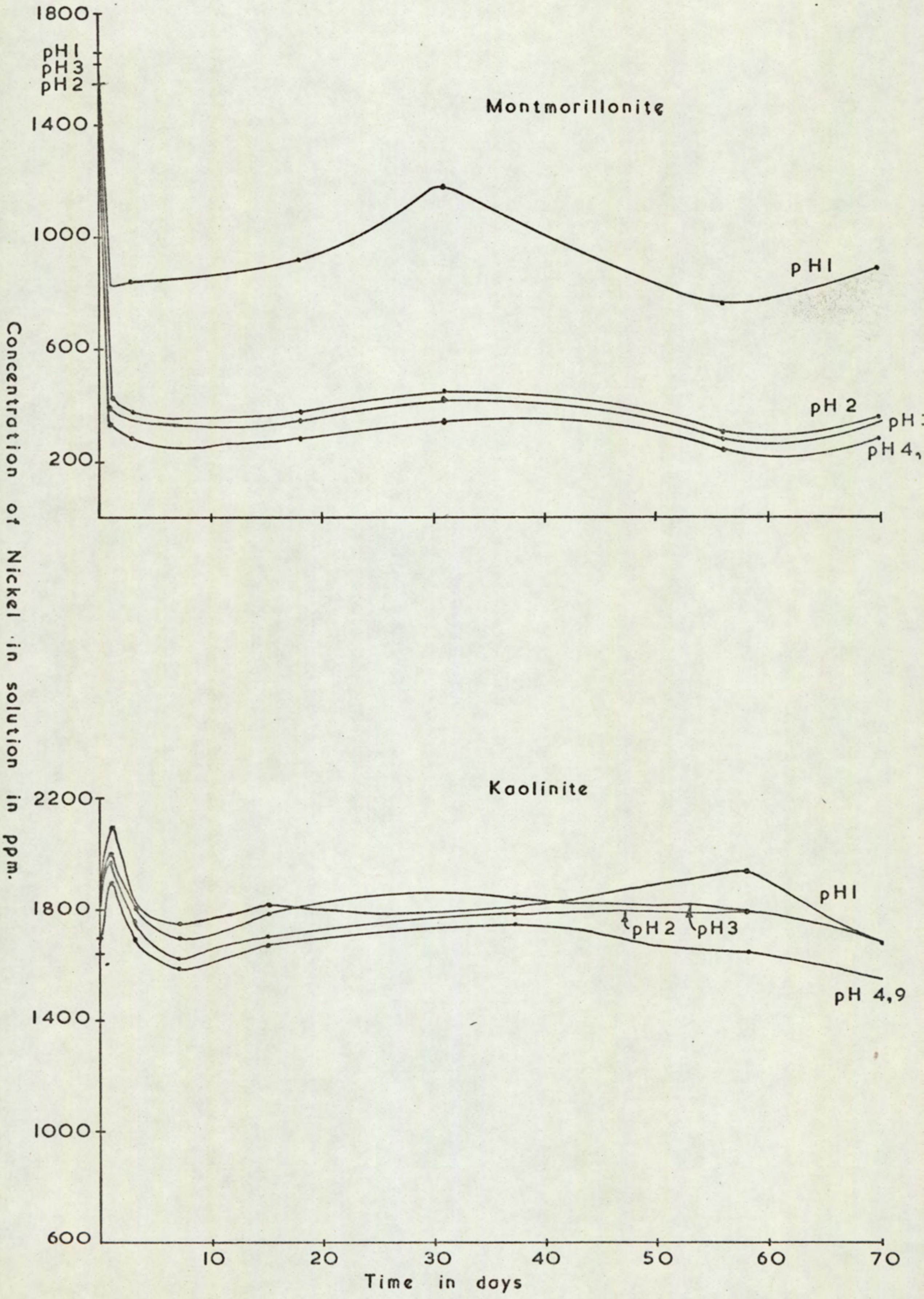


FIG. 22.5

Variation in concentration of Cadmium on Montmorillonite and Kaolinite at pH 1,2,3,4,9 over 70 days

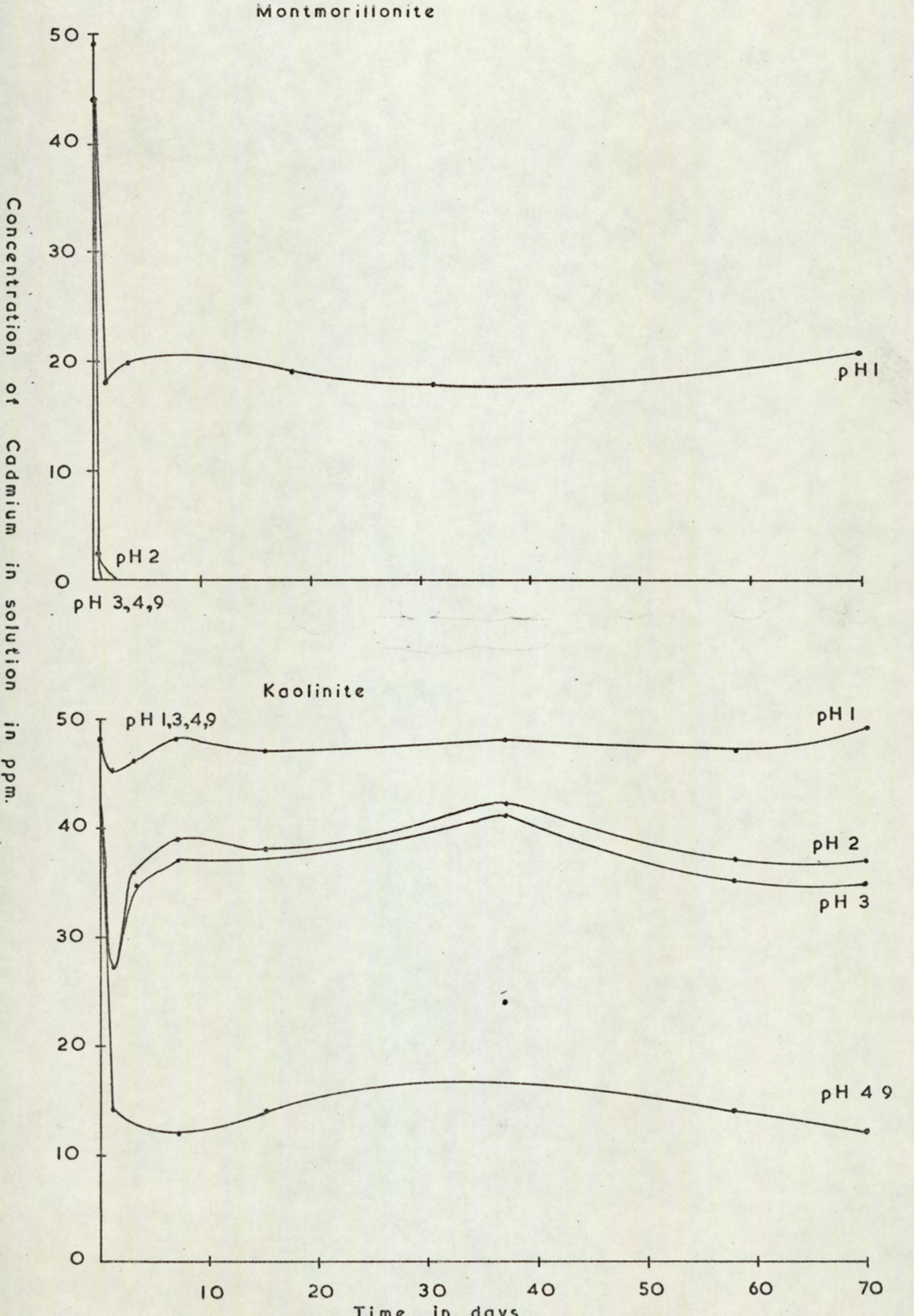


FIG. 22.6

Variation in concentration of Copper on Montmorillonite and Kaolinite at pH 1 2 3 4 9 over 70 days

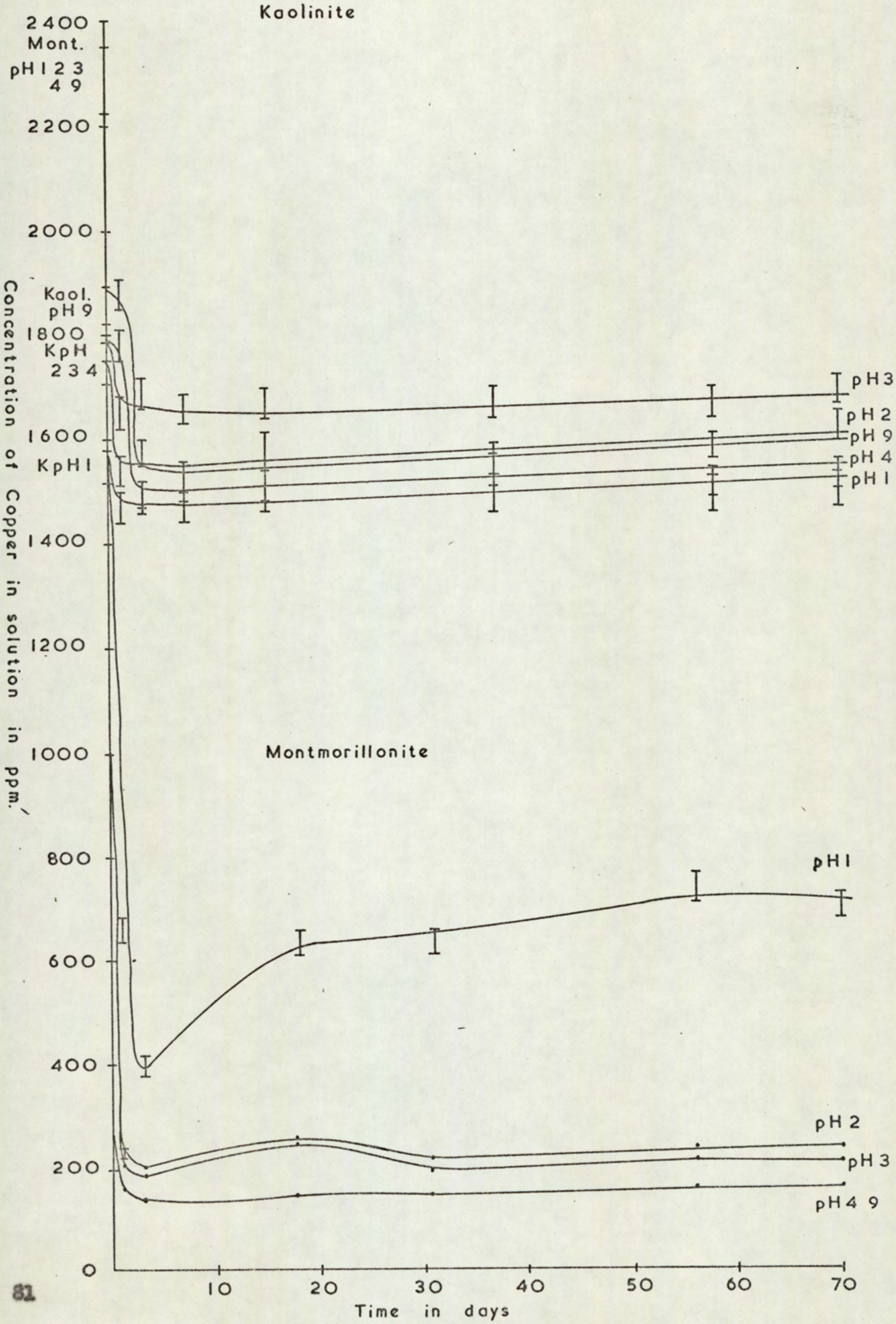


FIG. 22.7

Variation in concentration of iron on Montmorillonite and Kaolinite at pH 1 2 3 4 9 over 70 days

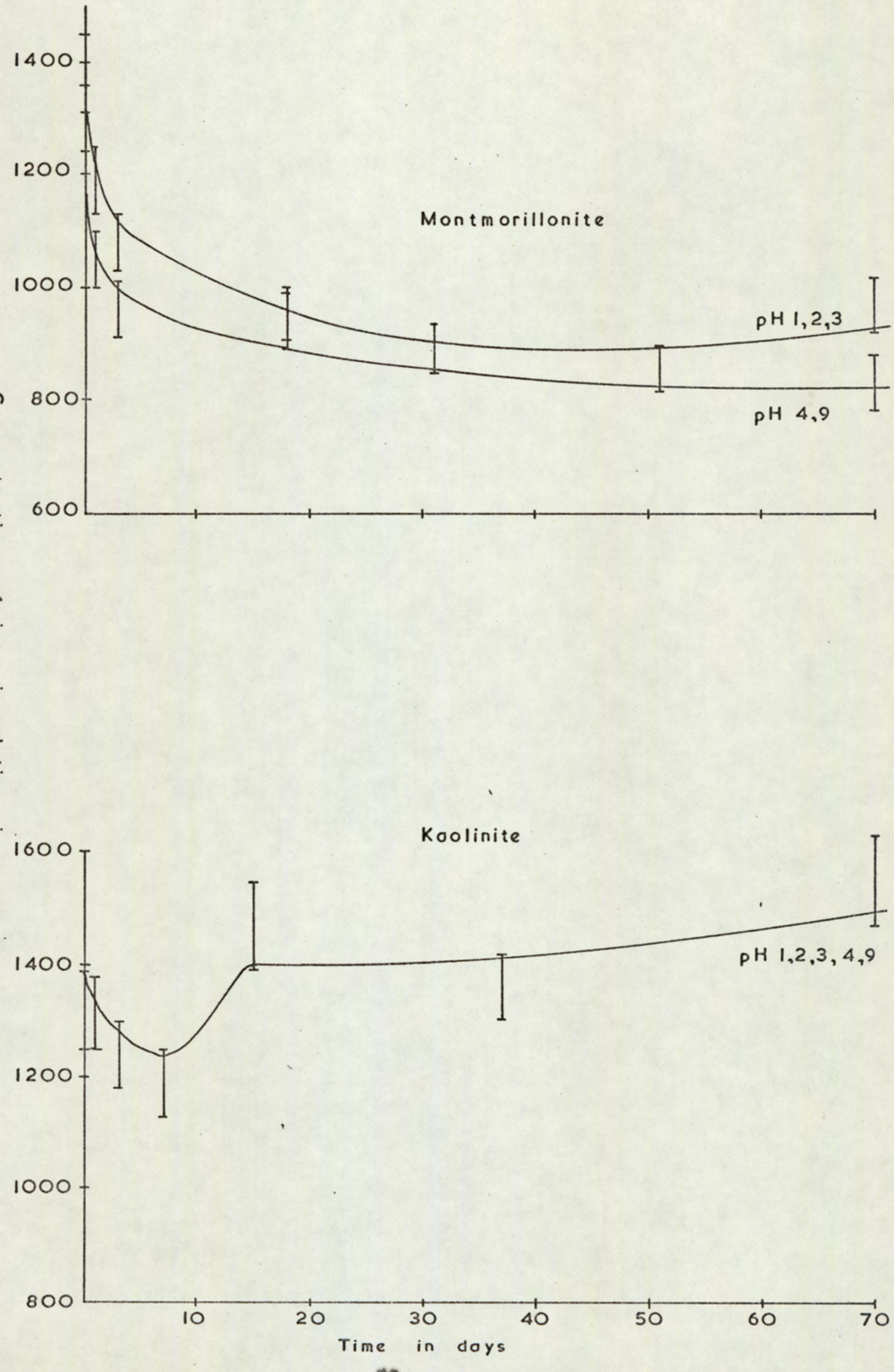
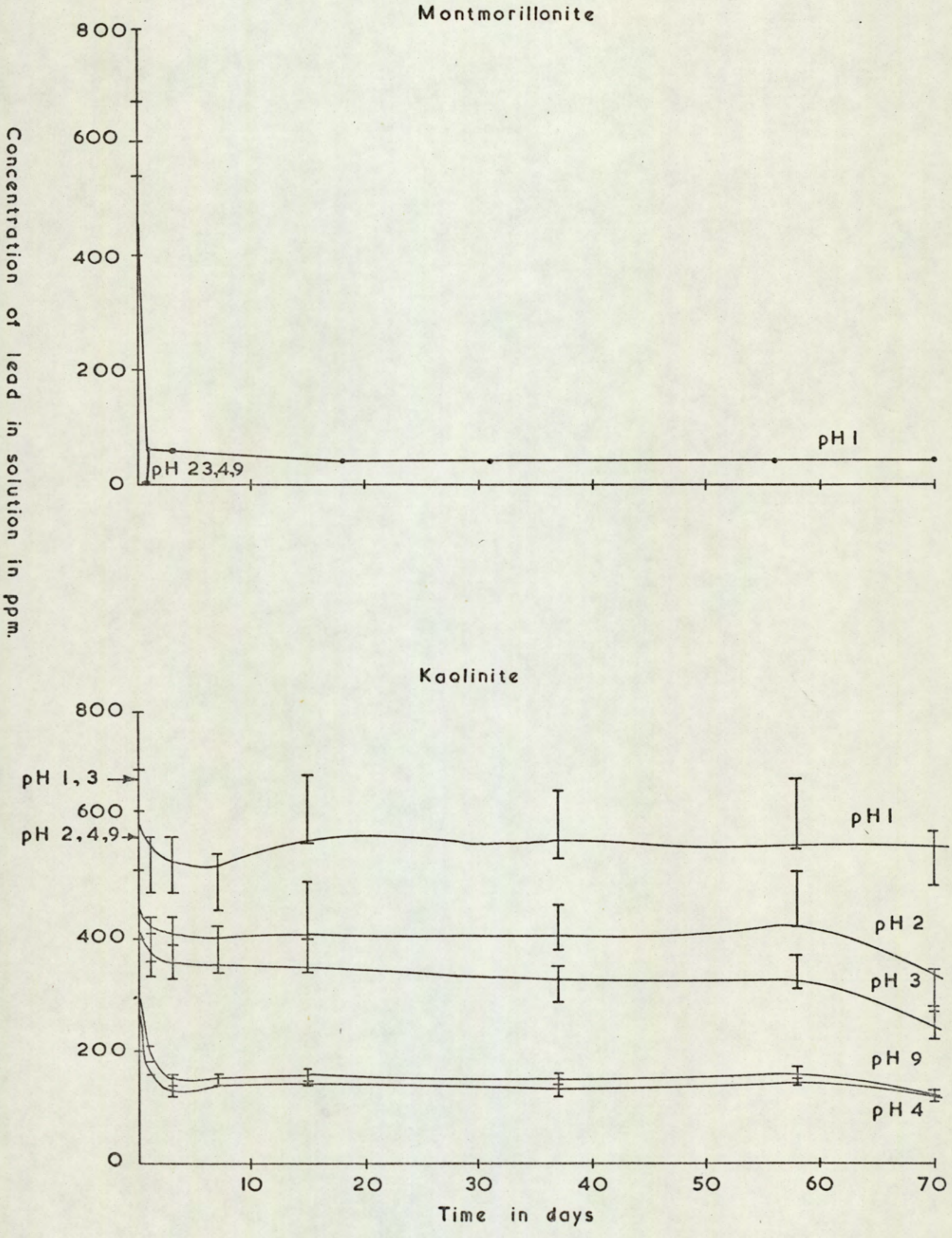


FIG. 22.8

Variation in concentration of lead on Montmorillonite and Kaolinite at pH 1,2,3,4,9



5.3.3 Experiments to Determine the Total Capacity of the Pure Minerals for adsorption of each Metal Species

The experiment was carried out using perchloric acid at pH3 for preparation of the metal solutions. The choice of these conditions was governed by the possibility of complex formation being smaller with the perchlorate anions than with the chloride or nitrate ion, and by the fact that adsorption is a maximum at pH3. The metal ion concentrations were chosen by an appraisal of the past results, increasing the concentrations where adsorption was 100% in previous experiments, and reducing the concentration where little adsorption was observed.

The results are presented as a function of the adsorption in milliequivalents per 100 grams of clay mineral against the original concentration of the solution.

Fig 23. Graph of the variation in adsorption of metal from solution in milliequivalents per 100 grams of clay against the original concentration of metal in solutions for montmorillonite and kaolinite.

Fig 23. 1.)
) Montmorillonite
Fig 23. 2.)

Fig 23. 3.)
) Kaolinite
Fig 23. 4.)

FIG. 23.1

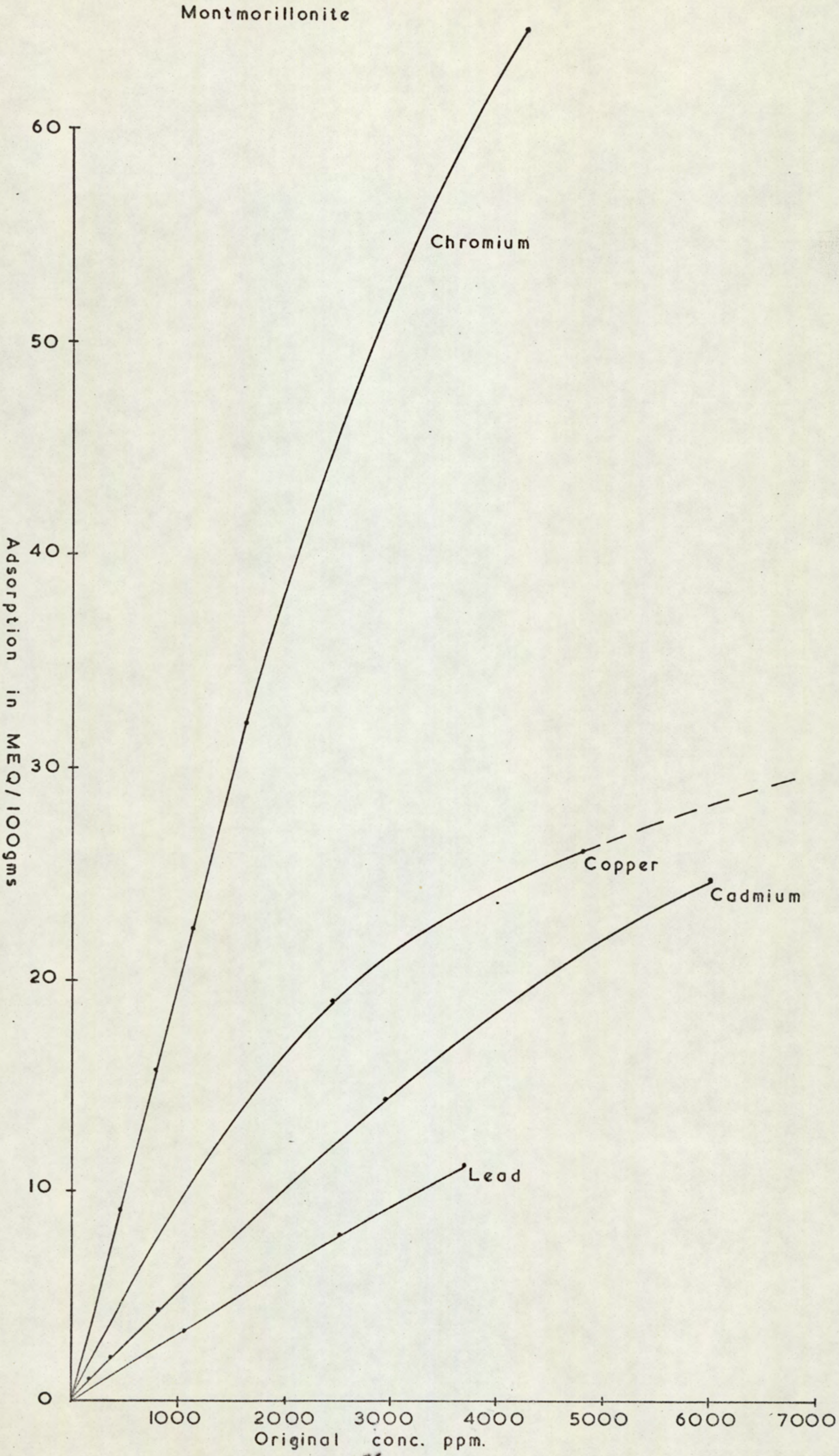

Montmorillonite
Chromium
Copper
Cadmium
Lead
Adsorption in MEQ/100gms
60
50
40
30
20
10
0
1000
2000
3000
4000
5000
6000
7000
Original conc. ppm.

FIG. 23.2

Montmorillonite

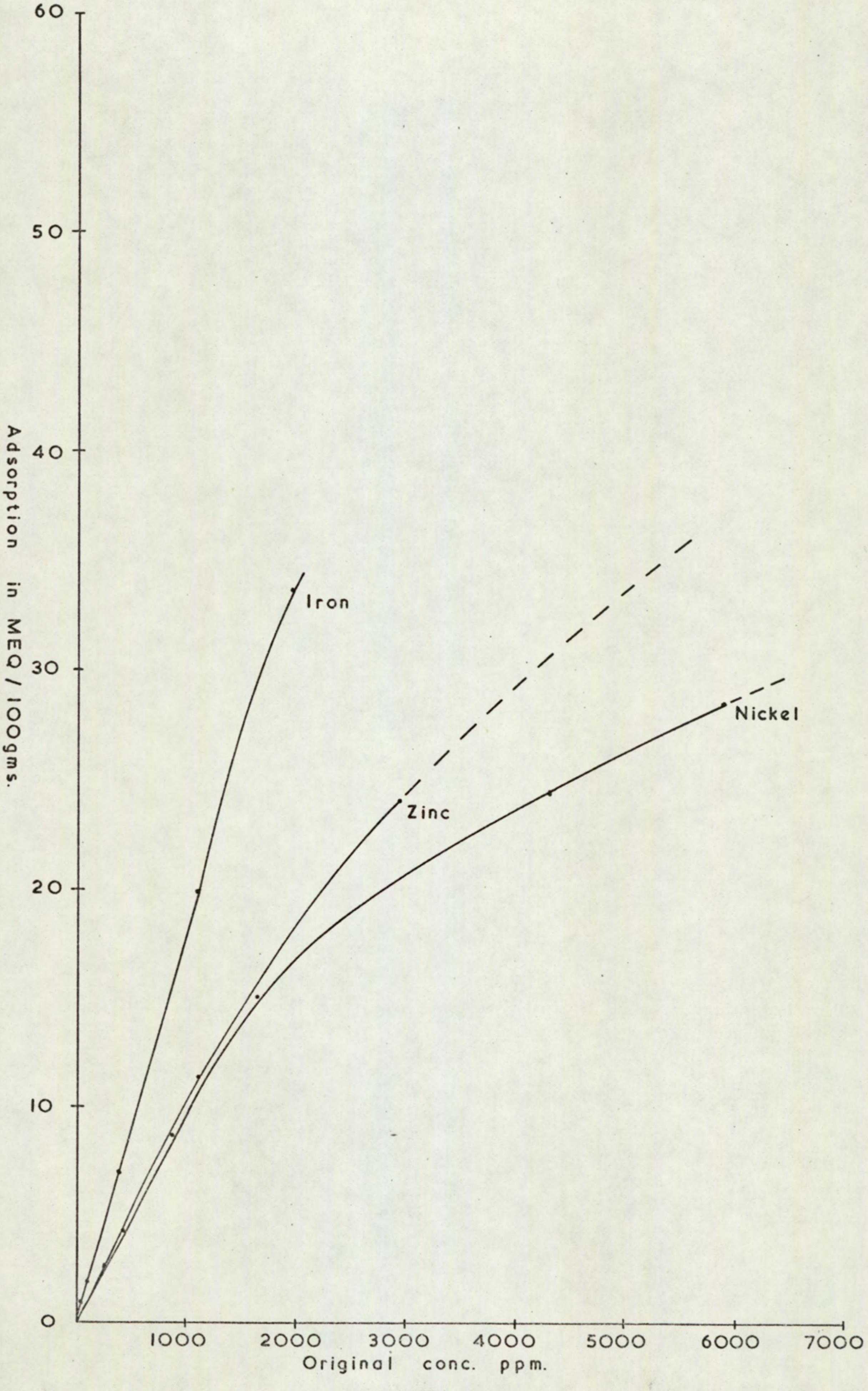
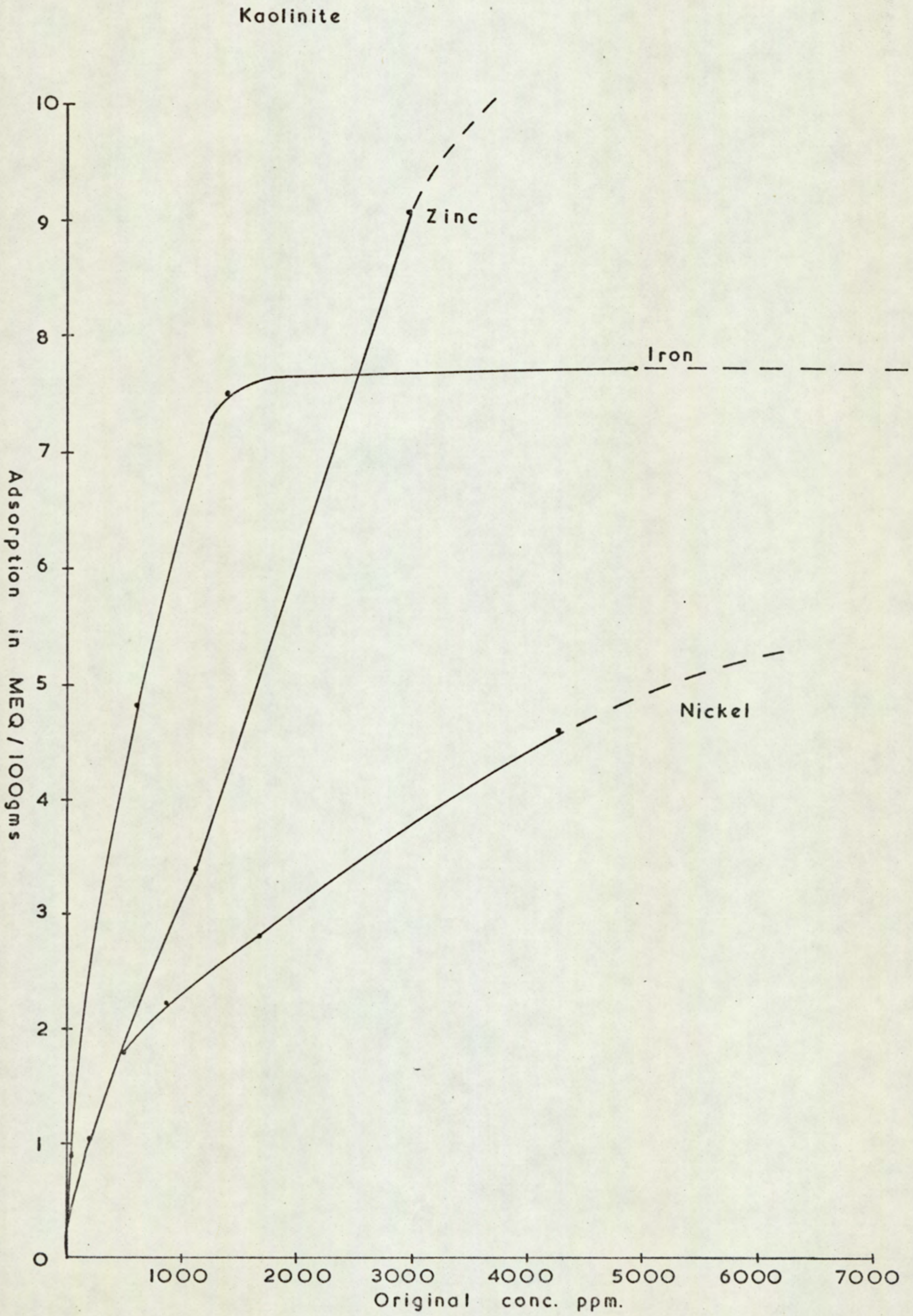


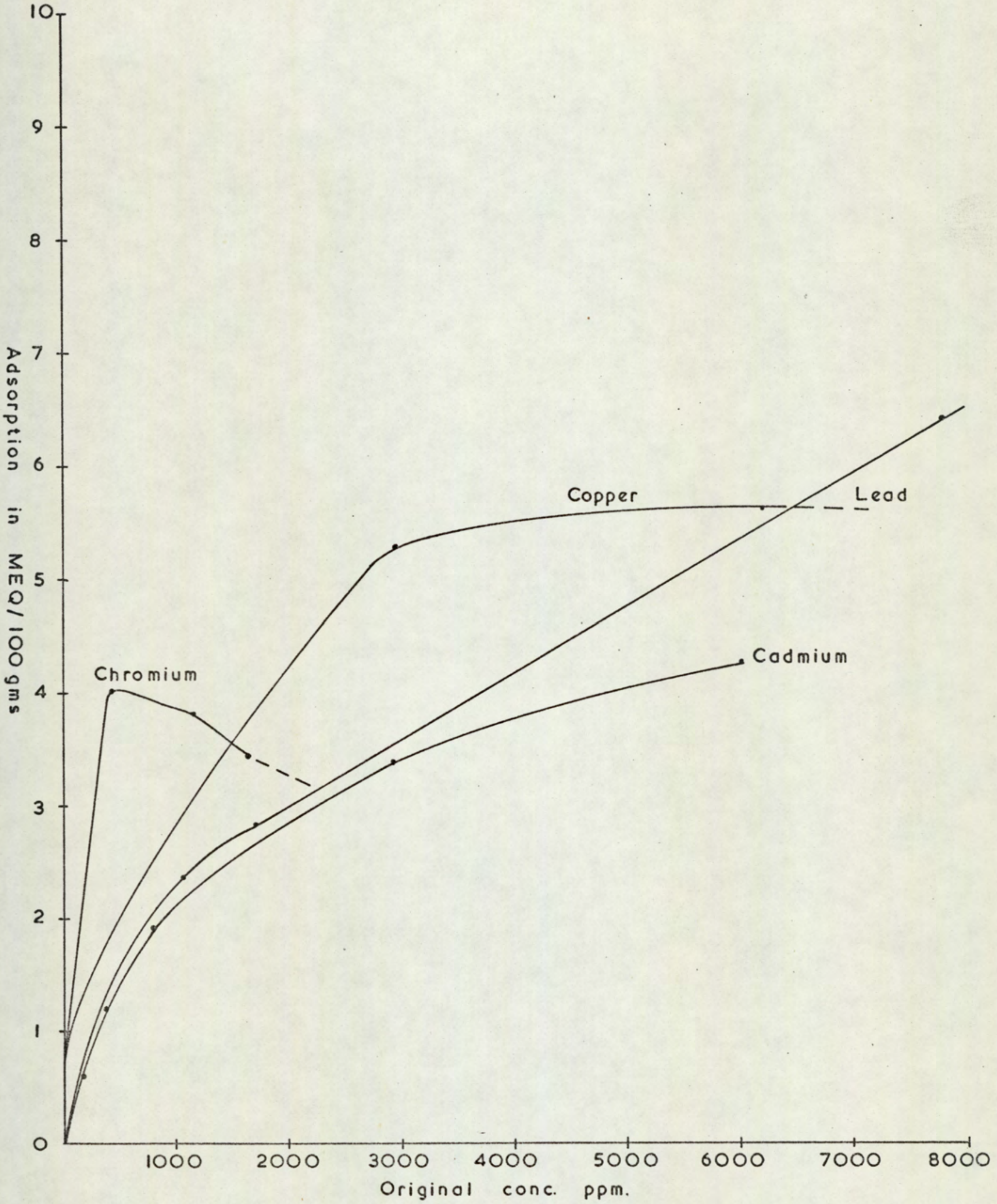
FIG. 23. 3



Kaolinite
Zinc
Iron
Nickel
Adsorption in MEQ / 100gms
Original conc. ppm.
0
1
2
3
4
5
6
7
8
9
10
1000
2000
3000
4000
5000
6000
7000

FIG. 23. 4

Kaolinite



5.3.4. Experiments to investigate the affects of the presence of Sulphate anions on the adsorption of metals from solution, and the possible exchange reactions between the metals and sodium and potassium in the clay minerals.

Solution of the seven metals were prepared in sulphuric, nitric and hydrochloric acid at pH3. The solutions were mixed with montmorillonite and kaolinite, and analysed for sodium and potassium in addition to the metal in solution. The results of the experiments were plotted as a function of the adsoprtion of metal ions, and release of sodium and potassium ions against time.

Fig 24. Graphs of the adsorption of metals from solution, and the leaching of sodium and potassium into solutions in contact with kaolinite and montmorillonite, against time.

Fig 24. 1. Iron

Fig 24. 2. Copper

Fig 24. 3. Zinc

Fig 24. 4. Chromium

Fig 24. 5. Cadmium

Fig 24. 6. Lead

Fig 24. 7. Nickel

FIG. 24.1

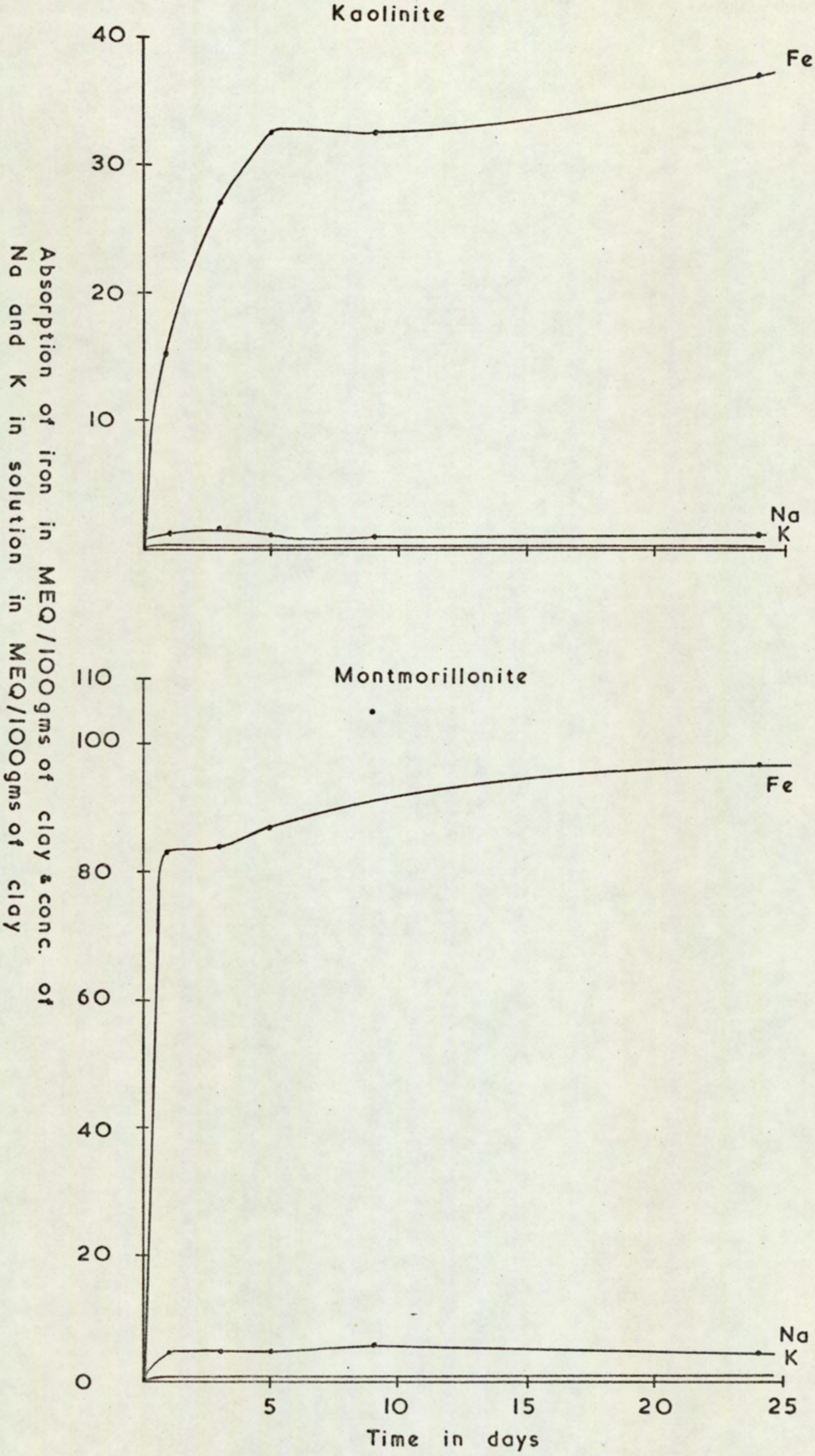

Kaolinite
40
30
20
10
Fe
Na
K
Montmorillonite
110
100
80
60
40
20
0
Fe
Na
K
5
10
15
20
25
Time in days
Absorption of iron in MEQ/100gms of clay & conc. of
Na and K in solution in MEQ/100gms of clay

FIG. 24.2

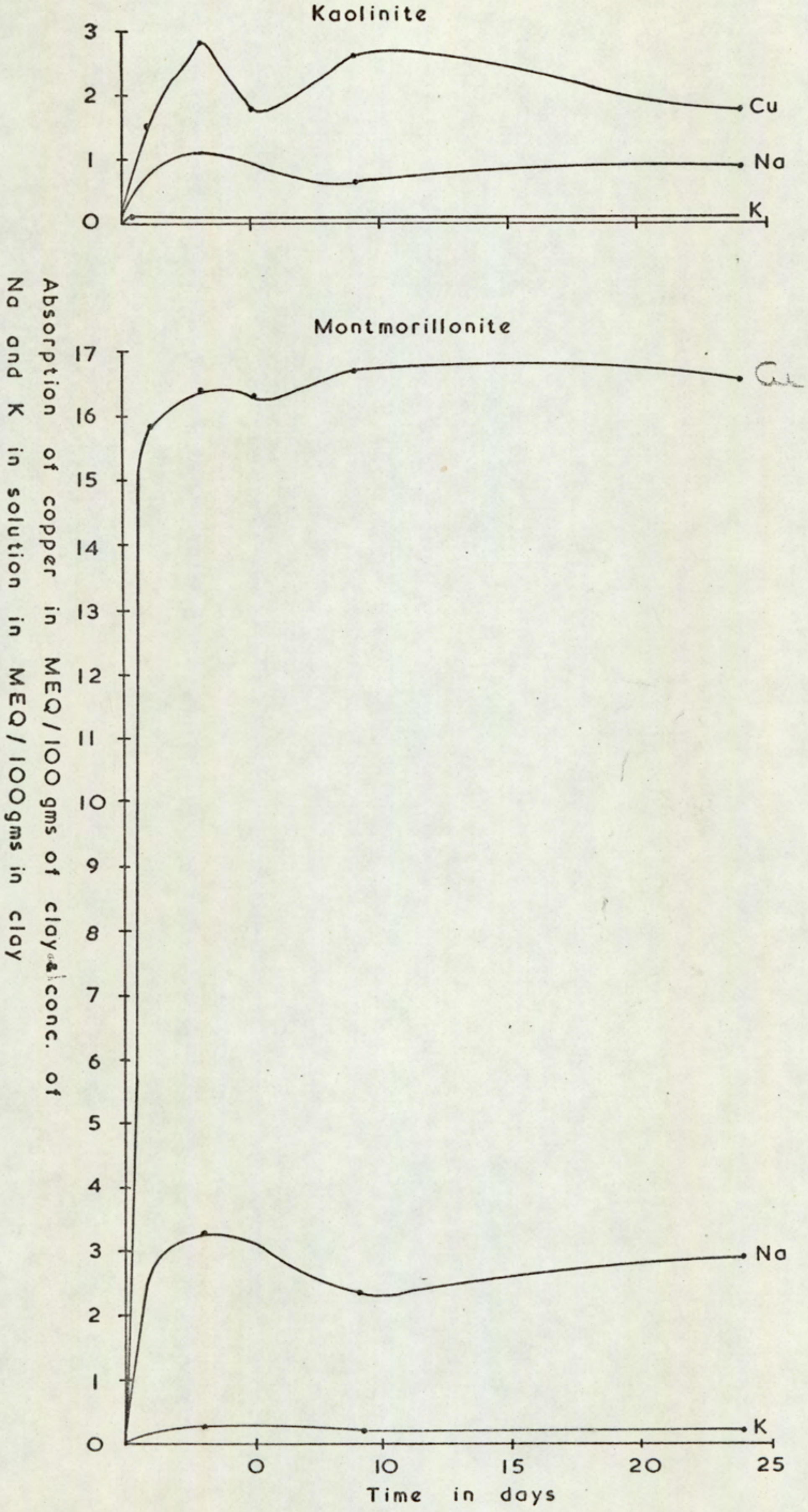

Kaolinite
3
2
1
0
Cu
Na
K
Montmorillonite
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Cu
Na
K
Absorption of copper in MEQ/100 gms of clay & conc. of
Na and K in solution in MEQ/100gms in clay
0
10
15
20
25
Time in days

FIG. 24. 3

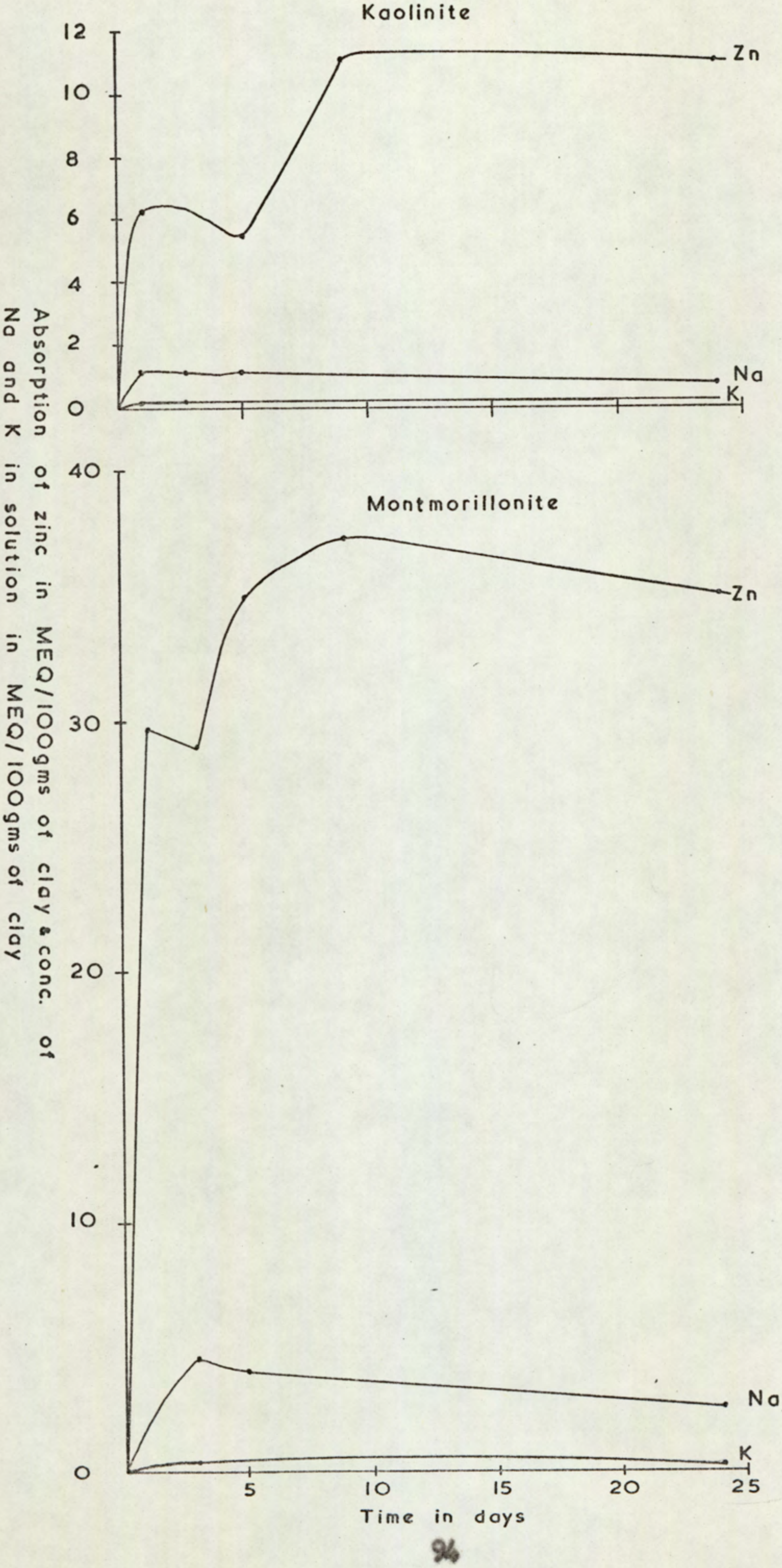

Kaolinite
12
10
8
6
4
2
0
Zn
Na
K
40
30
20
10
0
Montmorillonite
Zn
Na
K
5
10
15
20
25
Time in days
Absorption of zinc in MEQ/100gms of clay & conc. of Na and K in solution in MEQ/100gms of clay

FIG. 24. 4

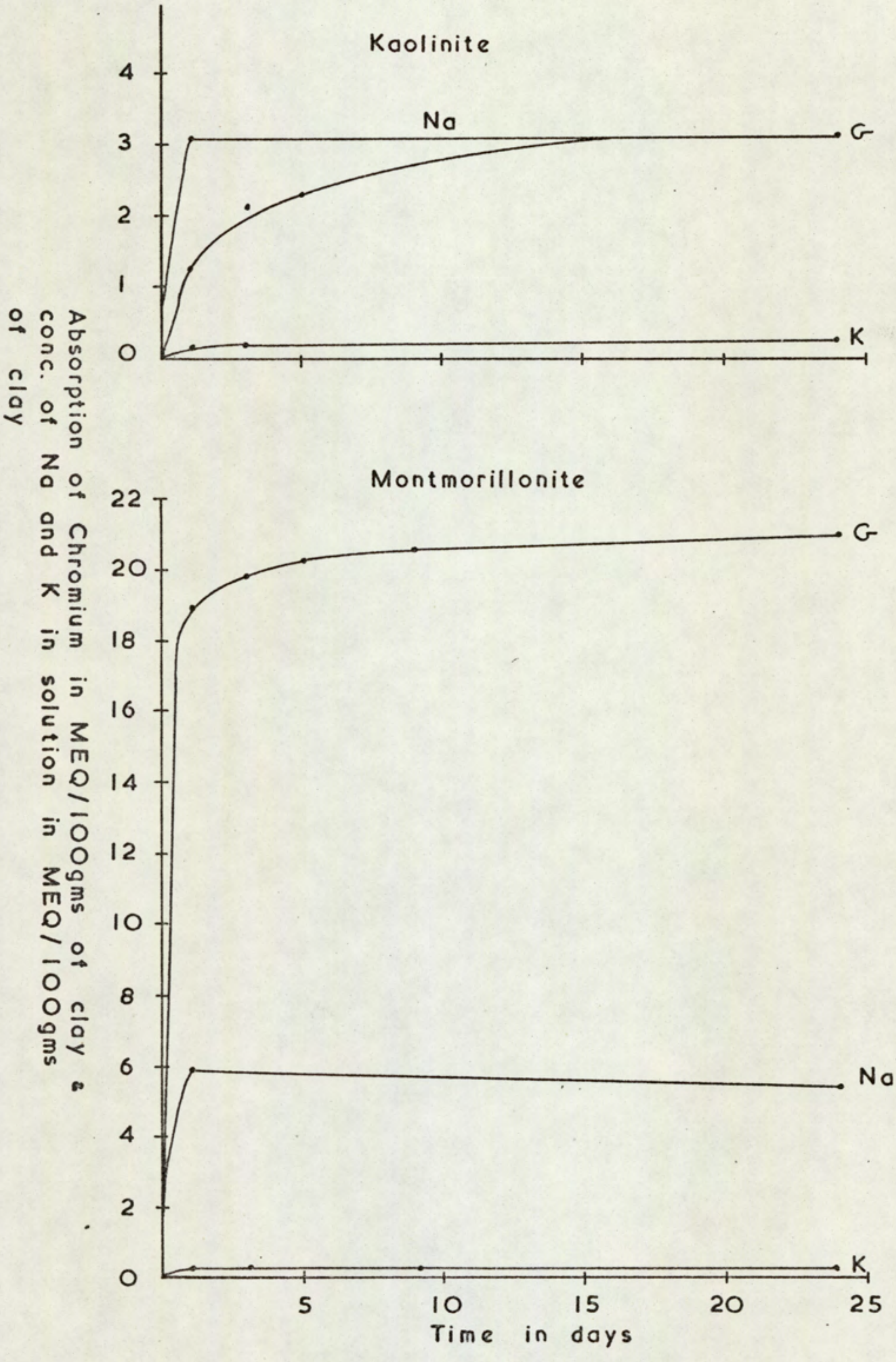

Kaolinite
Montmorillonite
Na
G
K
Na
G
K
0
1
2
3
4
0
2
4
6
8
10
12
14
16
18
20
22
5
10
15
20
25
Time in days
Absorption of Chromium in MEQ/100gms of clay & conc. of Na and K in solution in MEQ/100gms of clay

FIG. 24.5

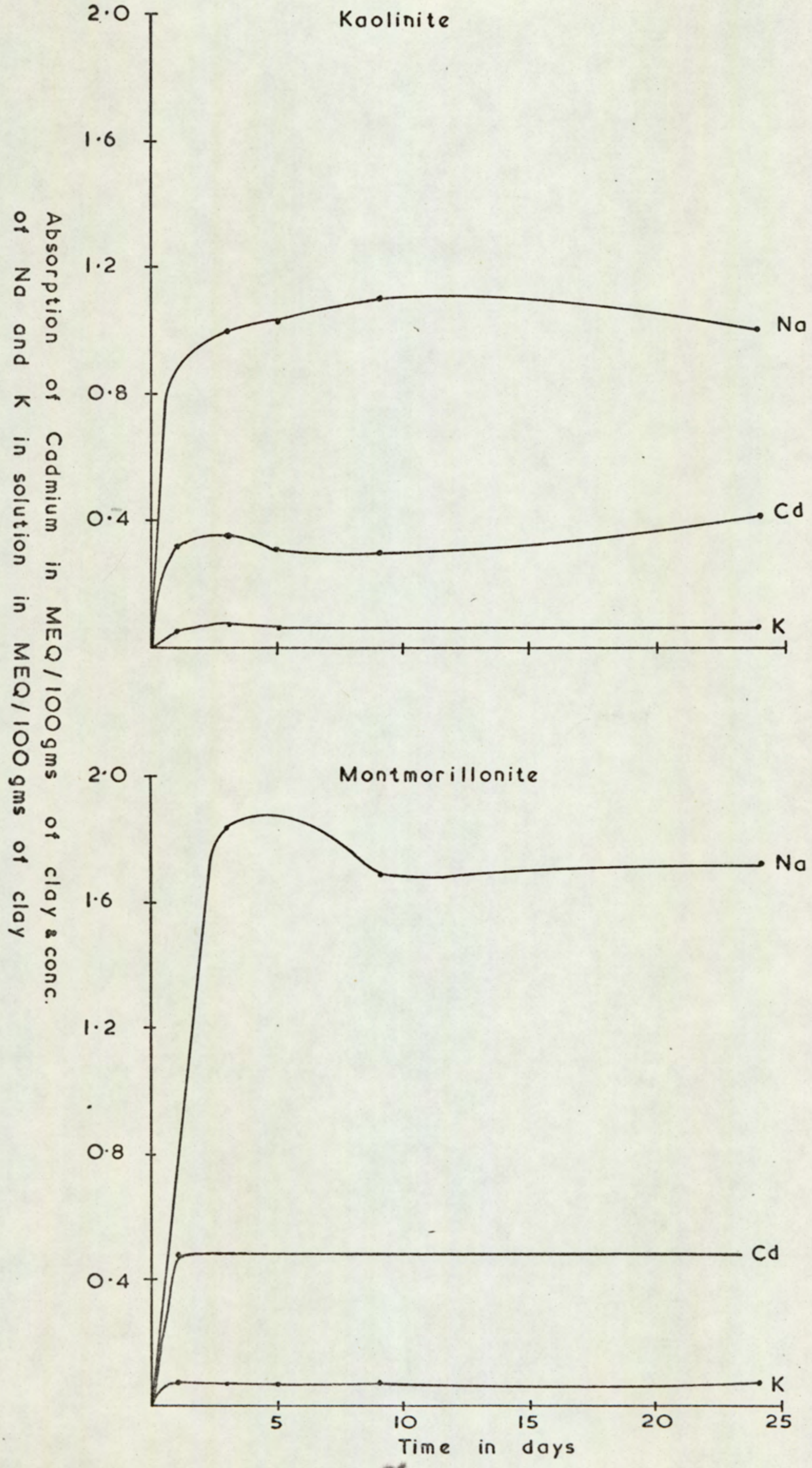

Absorption of Cadmium in MEQ/100gms of clay & conc. of Na and K in solution in MEQ/100gms of clay
Kaolinite
2·0
1·6
1·2
0·8
0·4
Na
Cd
K
Montmorillonite
2·0
1·6
1·2
0·8
0·4
Na
Cd
K
5
10
15
20
25
Time in days

FIG. 24. 6

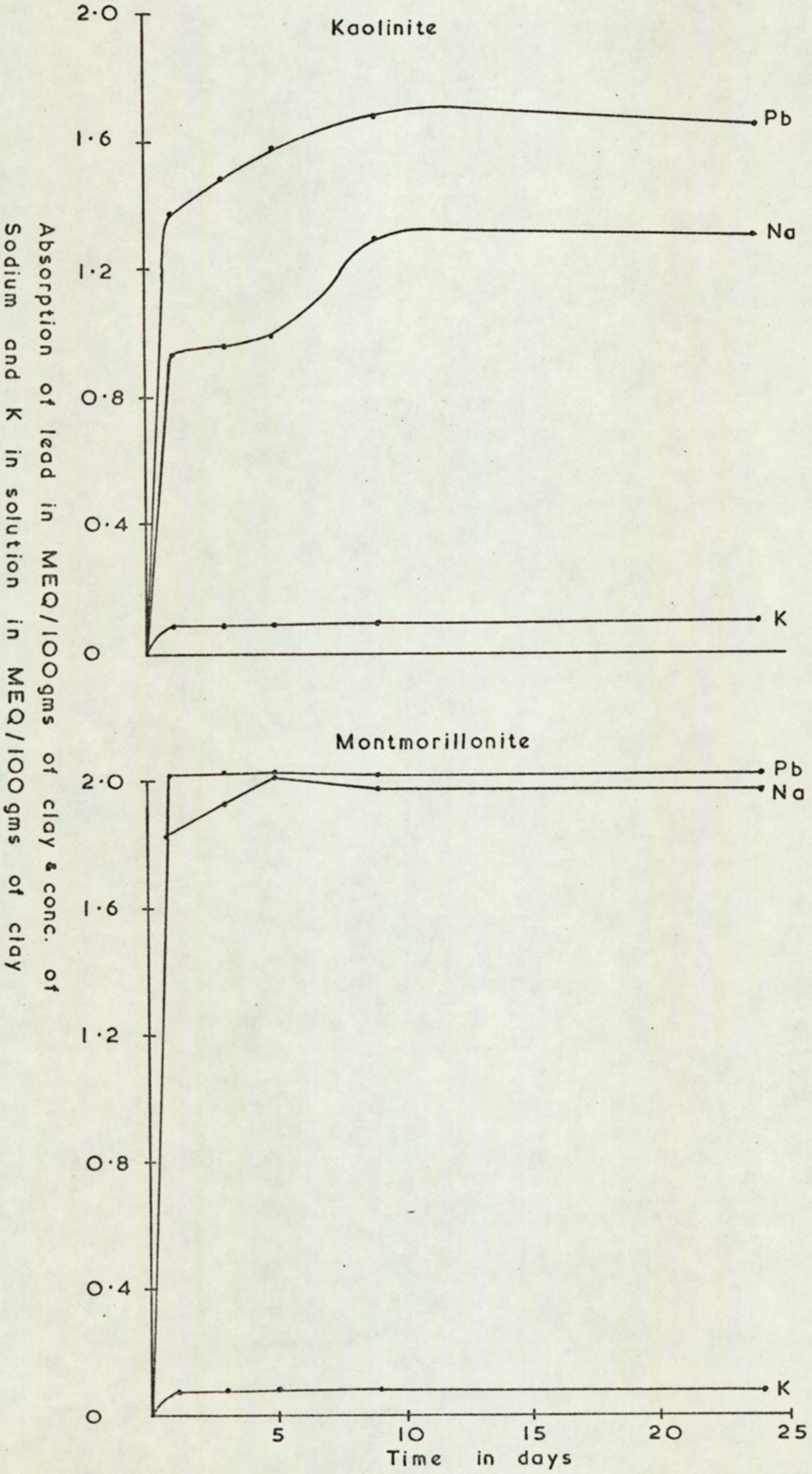
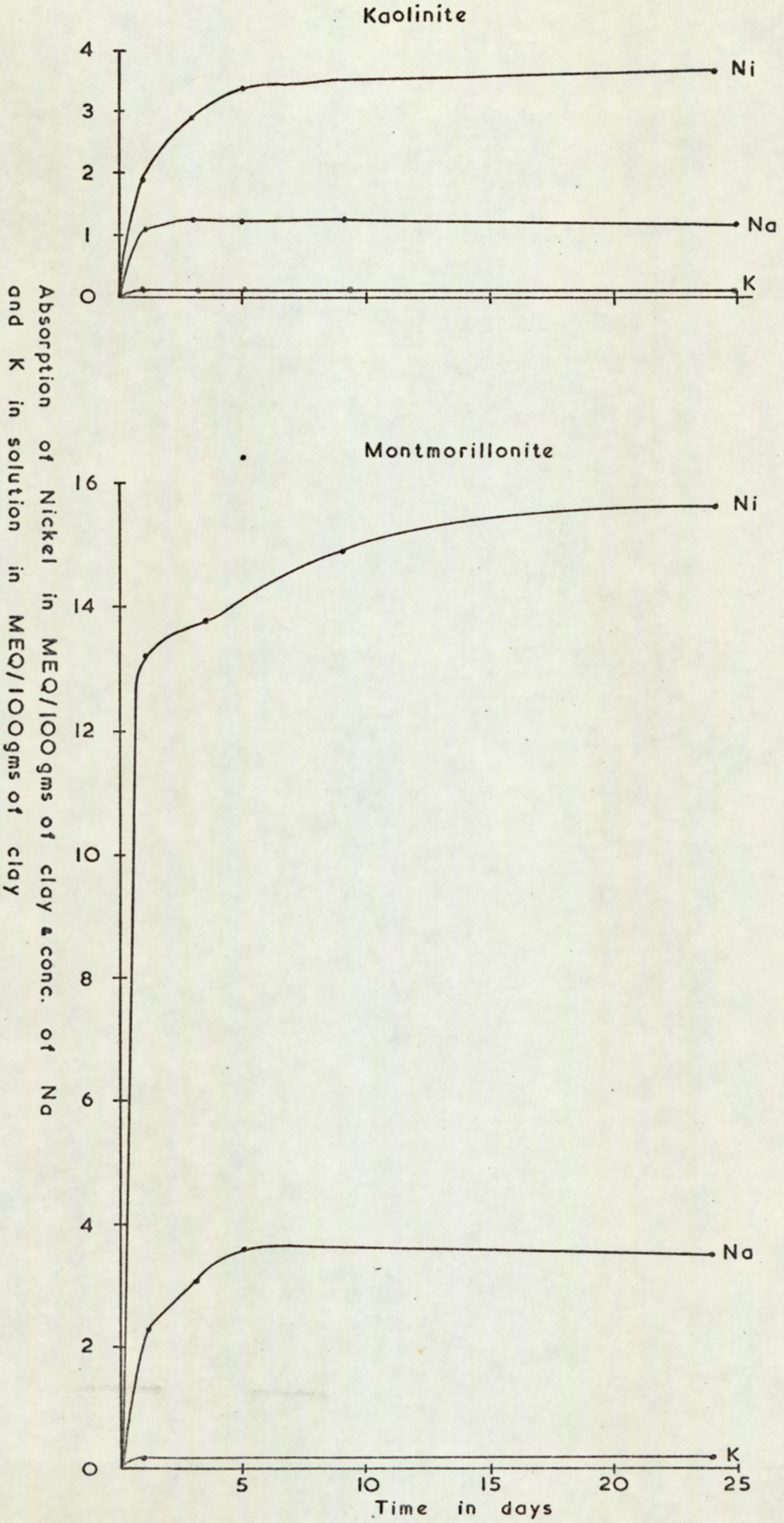

Kaolinite
Montmorillonite
Pb
Na
K
Pb
Na
K
2·0
1·6
1·2
0·8
0·4
0
2·0
1·6
1·2
0·8
0·4
0
5
10
15
20
25
Time in days
Absorption of lead in MEQ/100gms of clay & conc. of Sodium and K in solution in MEQ/100gms of clay

FIG. 24.7


Kaolinite
4
3
2
1
0
Ni
Na
K
Montmorillonite
16
14
12
10
8
6
4
2
0
Ni
Na
K
5
10
15
20
25
Time in days
Absorption of Nickel in MEQ/100gms of clay & conc. of Na and K in solution in MEQ/100gms of clay

5.3.5. Adsorption of metal ions by Kaolinite, Montmorillonite and Coal Measure Shale, from solutions containing more than one metal.

Solutions containing combinations of the seven elements previously studied were prepared in perchloric acid at pH3. When selecting the concentrations of the metals, the chemical analyses of effluents disposed at Walsall Wood were taken as a guide. Hence, solution A represented the loads with fairly low concentrations of all seven elements, while combination F was similar but with a high iron content. Solution B represented an effluent with a high iron concentration, and fairly high copper and nickle concentration. Solution E was similar to B, but with no iron. Combination C contained only high quantities of iron and zinc, while Combination D contained a high concentration of copper and nickel, with lower concentrations of chromium and zinc but no iron.

The solutions were reacted with montmorillonite, kaolinite and Coal Measures shale, and the results represented on graphs showing the reduction in concentration of the metal ion in solution with time. To facilitate the comparison of the results from the different combinations the maximum percentage adsorptions for each element were tabulated (Table 4).

TABLE 4

Combination Experiment results: total adsorption for each combination

COMBINATION A - MONTMORILLONITE

Element		Max % abs	Orig Conc in meq 100 gm	Absorption in Meq/100 gms	Total	
					Abs in Meq/100 gms	% of Orig Conc
a.		b.	c.	d.	e.	f.
	Orig Conc					
Copper	33ppm	100	0.34	0.34		
Iron	99	100	1.74	1.74		
Lead	136	100	0.44	0.44		
Cadmium	13	77	0.08	0.06		
Chromium	69	100	1.35	1.35		
Zinc	53	100	0.54	0.54		
Nickel	653	85	7.43	6.40	10.87	91.2
COMBINATION A - SHALE						
Copper	33	100	0.34	0.34		
Iron	99	100	1.74	1.74		
Lead	136	100	0.44	0.44		
Cadmium	13	38	0.08	0.03		
Chromium	69	100	1.35	1.35		
Zinc	53	64	0.54	0.25		
Nickel	653	47	7.43	3.34	7.49	62.8
COMBINATION A - KAOLINITE						
Copper	33	0	0.34	-		
Iron	99	90	1.74	1.56		
Lead	136	29	0.44	0.13		
Cadmium	13	0	0.08	-		
Chromium	69	57	1.35	0.76		
Zinc	53	0	0.54	-		
Nickel	653	7.5	7.43	0.56	3.00	25.3

a	b	c	d	e	f
COMBINATION B - MONTMORILLONITE					
Copper 3671	24.3	37.42	9.09		
Iron 6439	47	114.78	53.2		
Zinc 52	5[illegible]	0.53	0.31		
Nickel 434	26	4.94	1.26		
Chromium 14	50	0.27	0.14	64.00	40.5
COMBINATION B - SHALE					
Copper 3671	10	37.42	3.85		
Iron 6439	21	114.78	23.23		
Zinc 52	42	0.53	0.25		
Nickel 434	12	4.94	0.63		
Chromium 14	0	0.27	-	27.94	17.7
COMBINATION B - KAOLINITE					
Copper 3671	10	37.42	3.58		
Iron 6439	-	114.78	-		
Zinc 52	21	0.53	0.12		
Nickel 434	12	4.94	0.61		
Chromium 14	0	0.27	-	4.31	2.7
COMBINATION C - MONTMORILLONITE					
Iron 1617	94	28.82	26.75		
Zinc 3747	48	38.43	18.63	45.38	67.5
COMBINATION C - SHALE					
Iron 1617	36	28.82	10.88		
Zinc 3747	10	38.43	3.79	14.57	21.7
COMBINATION C - KAOLINITE					
Iron 1617	8	28.82	2.14		
Zinc 3747	4	38.43	1.54	3.68	5.5
COMBINATION D - MONTMORILLONITE					
Copper 6999	28	71.35	19.81		
Zinc 1438	38	14.75	5.58		
Nickel 6382	28	72.6	20.22		
Chromium 2312	67	45.33	30.55	76.16	37.3

a		b	c	d	e	f
COMBINATION D - SHALE						
Copper	6999	5.52	71.35	3.93		
Zinc	1438	11	14.75	1.62		
Nickel	6382	14	72.6	9.89		
Chromium	2312	33	45.33	15.14	30.58	15
COMBINATION D - KAOLINITE						
Copper	6999	1.12	71.35	0.85		
Zinc	1438	12	14.75	1.77		
Nickel	6382	10	72.6	7.35		
Chromium	2312	6	45.33	2.69	12.66	6.2
COMBINATION E - MONTMORILLONITE						
Copper	3627	67	36.97	24.77		
Zinc	24	58	0.25	0.14		
Nickel	264	70	3.00	2.09		
Chromium	16	100	0.31	0.31	27.31	67.4
COMBINATION E - SHALE						
Copper	3627	33	36.97	12.35		
Zinc	24	-	0.25	-		
Nickel	264	40	3.00	1.21		
Chromium	16	100	0.31	0.31	13.87	34.0
COMBINATION E - KAOLINITE						
Copper	3627	20	36.97	7.4		
Zinc	24	-	0.25	-		
Nickel	264	32	3.00	0.97		
Chromium	16	100	0.31	0.31	8.69	21
COMBINATION F - MONTMORILLONITE						
Copper	31	45	0.32	0.14		
Iron	10990	31	195.9	61.96		
Lead	101	21	0.32	0.80		
Zinc	57	41	0.38	0.15		
Cadmium	19	21	0.11	0.02		
Chromium	43	26	0.51	0.24	63.41	32.1

a	b	c	d	e	f
COMBINATION F - SHALE					
Copper 31	-	0.32	-		
Iron 10990	5	195.9	9.51		
Lead 101	11	0.32	0.04		
Zinc 57	-	0.38	-		
Nickel	-	-	-		
Cadmium 19	-	0.11	-		
Chromium 43	-	0.51	-	9.55	4.8
COMBINATION F - KAOLINITE					
Copper 31	10	0.32	0.97		
Iron 10990	4	195.9	6.93		
Lead 101	-	0.32	-		
Zinc 57	-	0.38	-		
Nickel -	-	-	-		
Cadmium 19	-	0.11	-		
Chromium 43	-	0.51	-	7.90	4.0

Fig 25. Graphs of the variation in concentration of metal in solution with time, for solutions containing more than one element in contact with montmorillonite, kaolinite, and Coal Measures shale.

Fig 25. 1. Combination A. Copper, lead, nickel

Fig 25. 2. Combination A. Iron, zinc, chromium, cadmium

Fig 25. 3. Combination B. Copper, zinc, chromium

Fig 25. 4. Combination B. Iron, nickel

Fig 25. 5. Combination C.

Fig 25. 6. Combination D. Copper, nickel

Fig 25. 7. Combination D. Zinc, chromium

Fig 25. 8. Combination E.

Fig 25. 9. Combination F. Iron, zinc

Fig 25. 10. Combination F. Lead, copper, chromium

FIG. 25.1

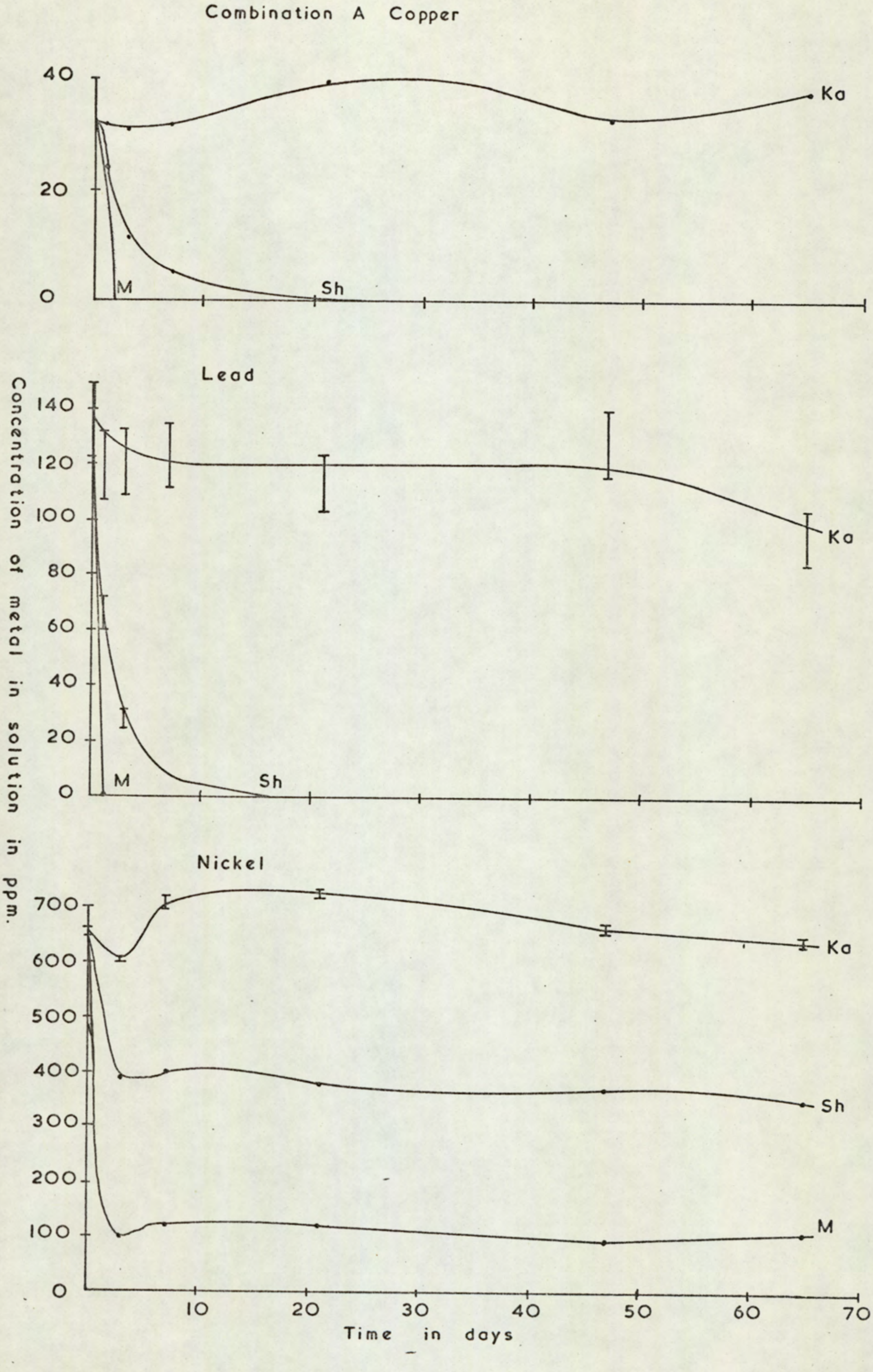

Combination A Copper
40
20
0
M
Sh
Ka
Lead
140
120
100
80
60
40
20
0
M
Sh
Ka
Nickel
700
600
500
400
300
200
100
0
Ka
Sh
M
10
20
30
40
50
60
70
Time in days
Concentration of metal in solution in ppm.

FIG. 25. 2

Combination A

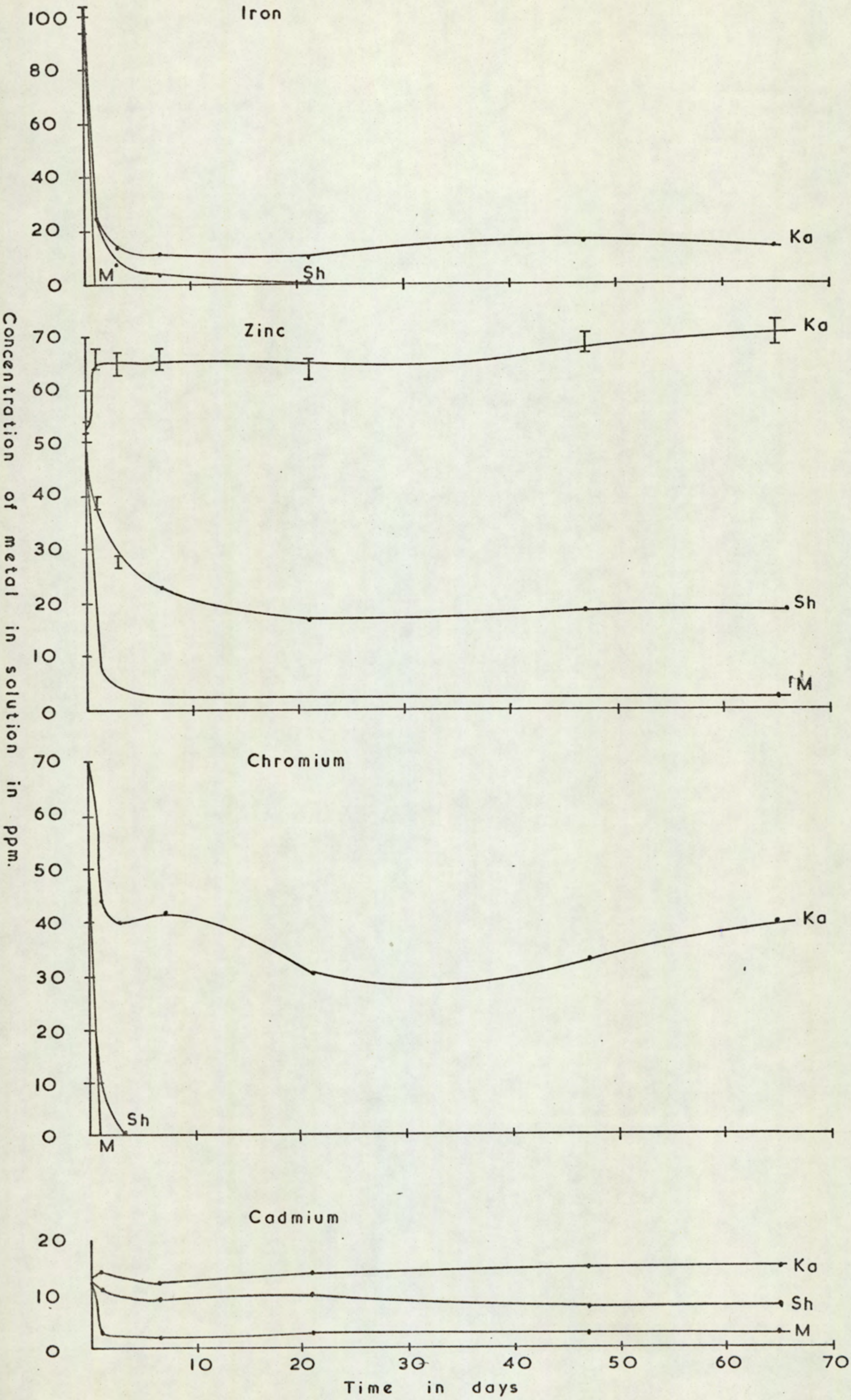
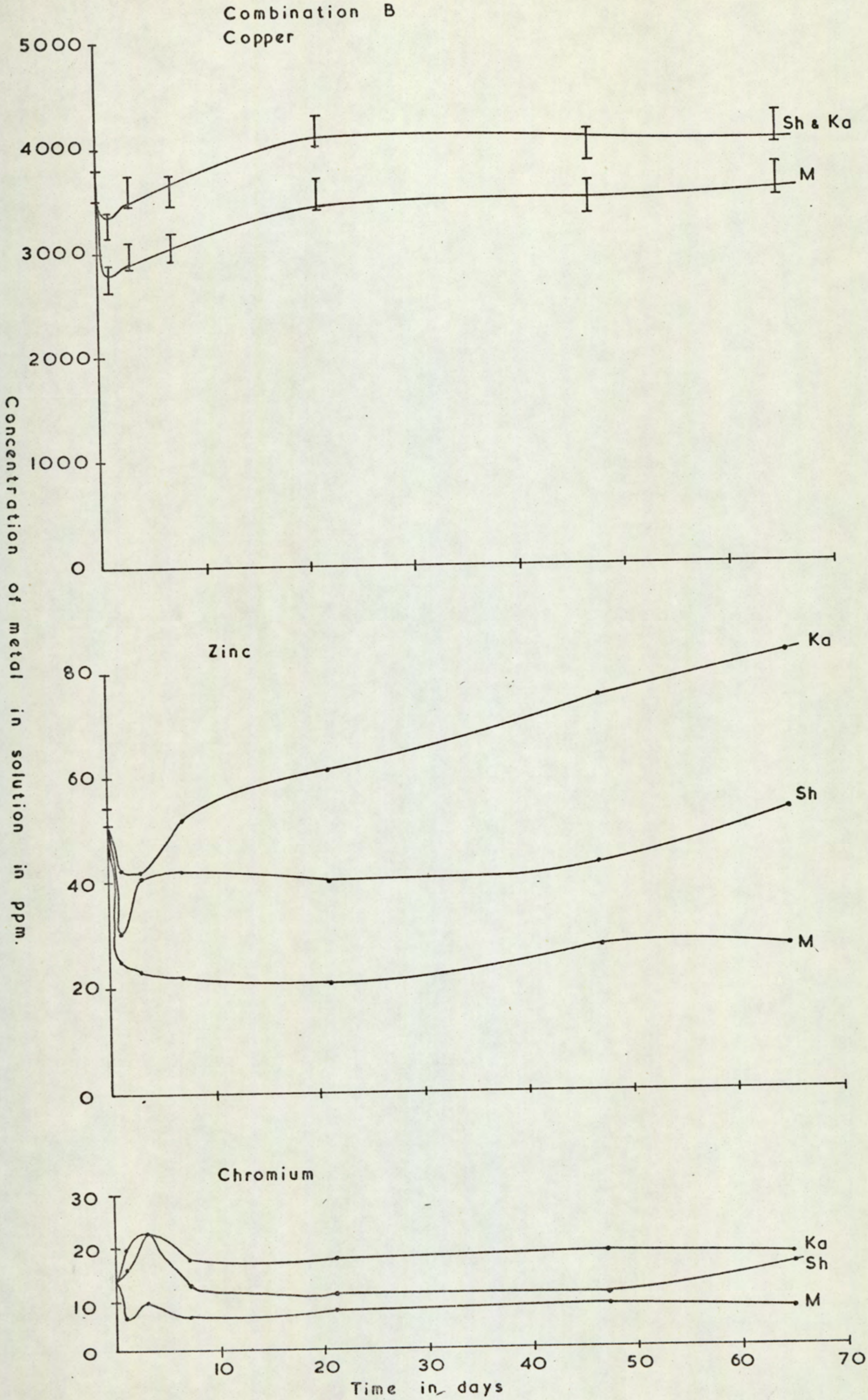


FIG. 25.3



Combination B
Copper
5000
4000
3000
2000
1000
0
Sh & Ka
M
Zinc
80
60
40
20
0
Ka
Sh
M
Chromium
30
20
10
0
Ka
Sh
M
10
20
30
40
50
60
70
Time in days
Concentration of metal in solution in ppm.

FIG. 25. 4

Combination B

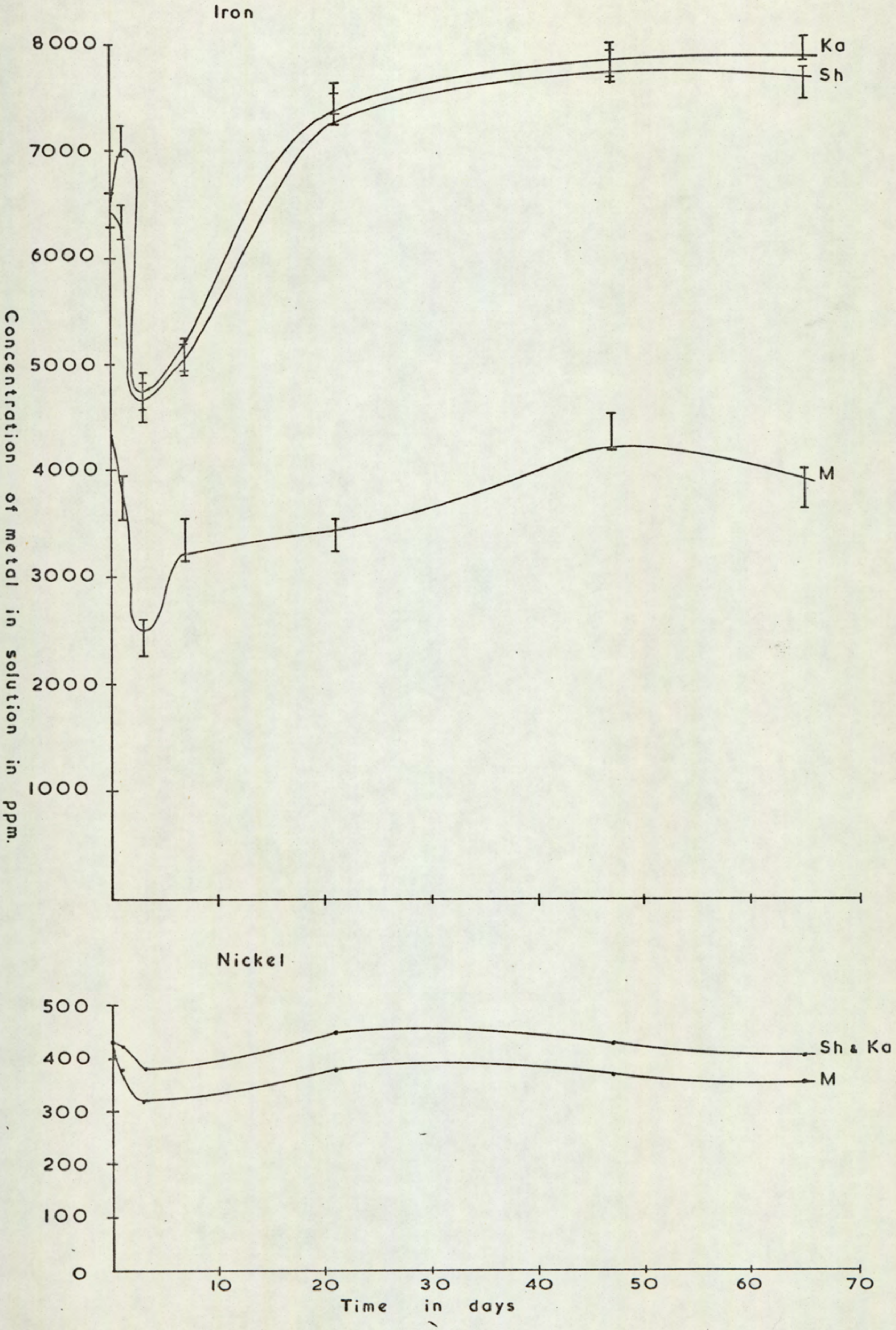


FIG. 25.5

Combination C

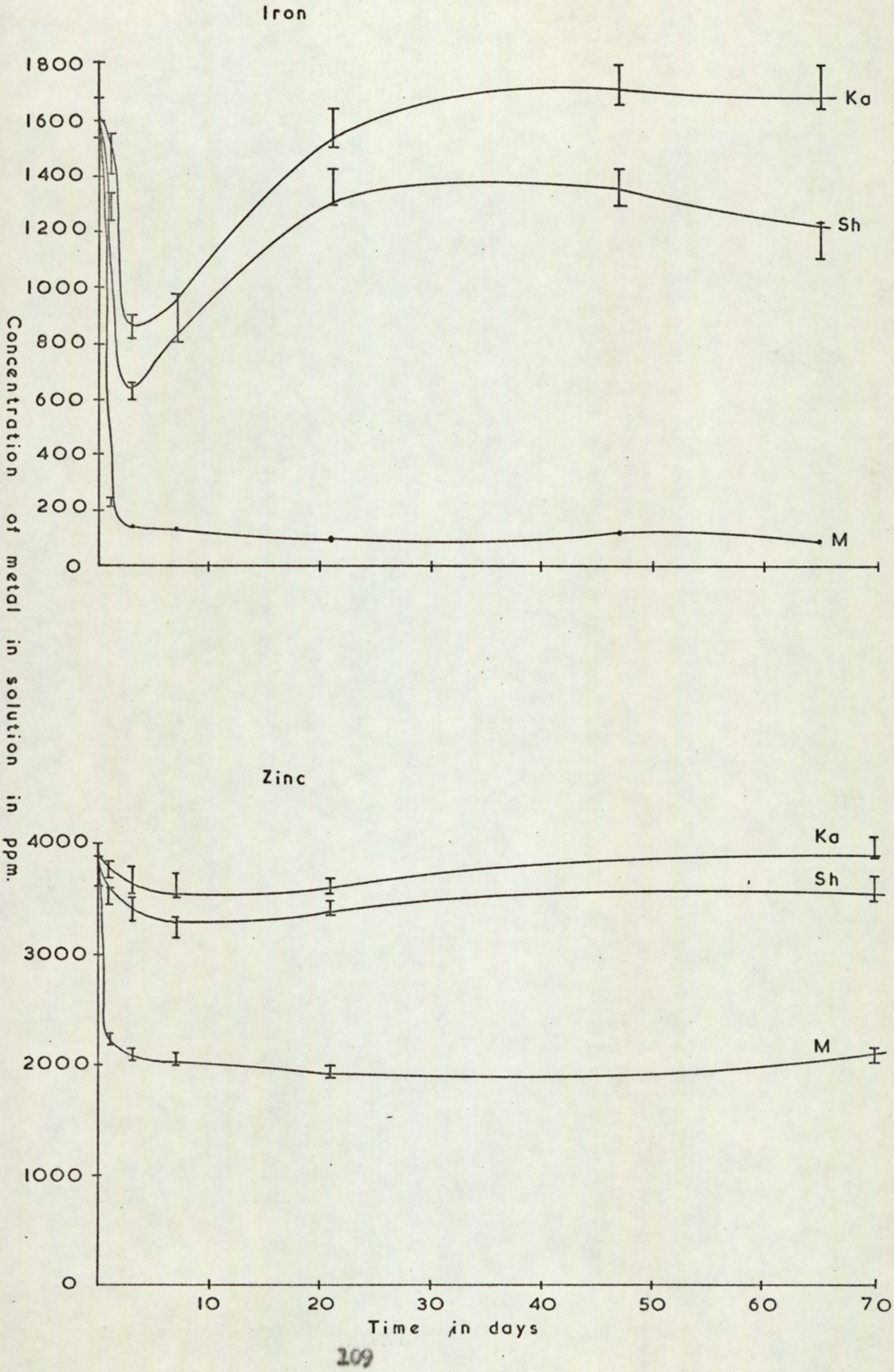
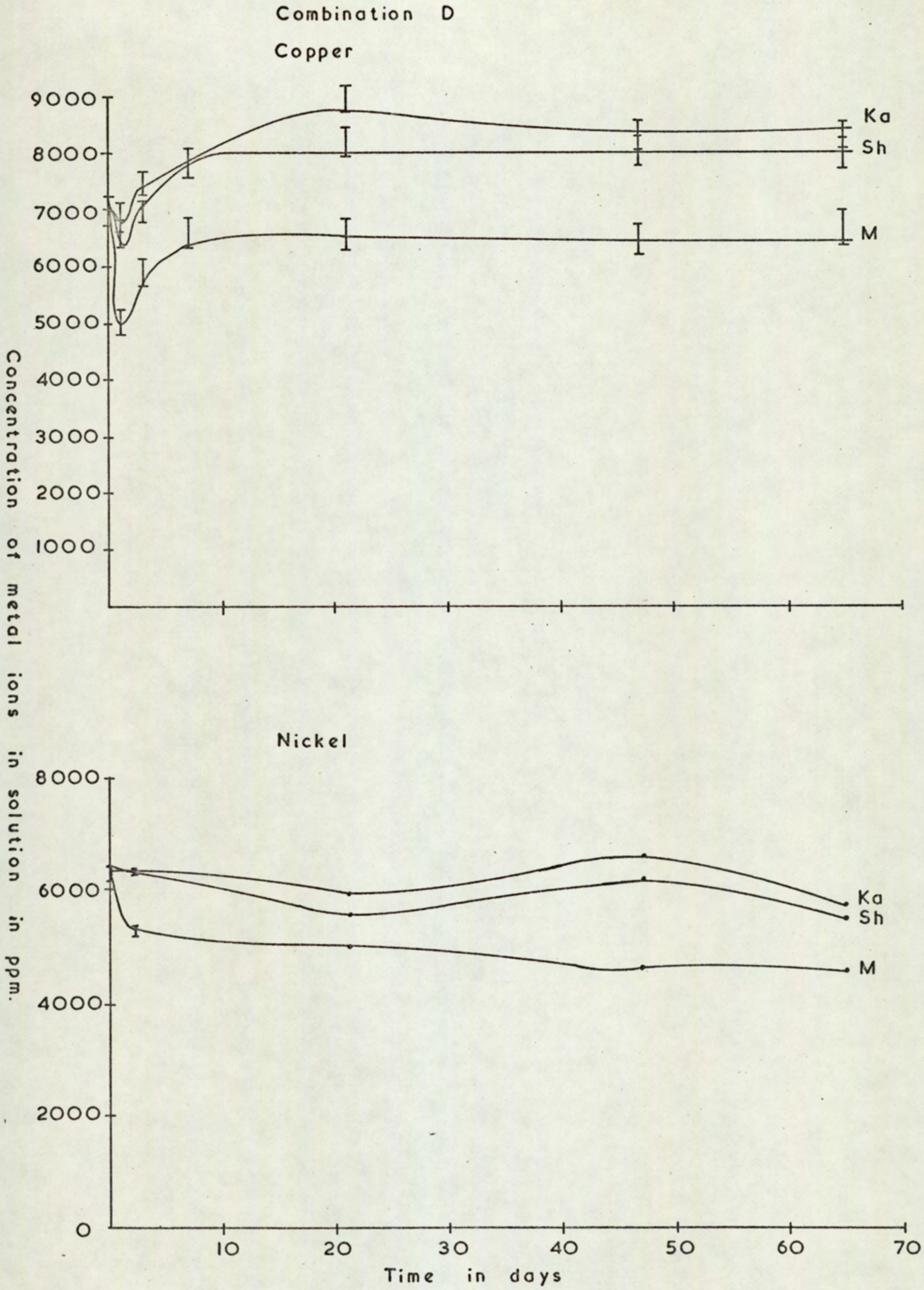


FIG. 25. 6



Combination D

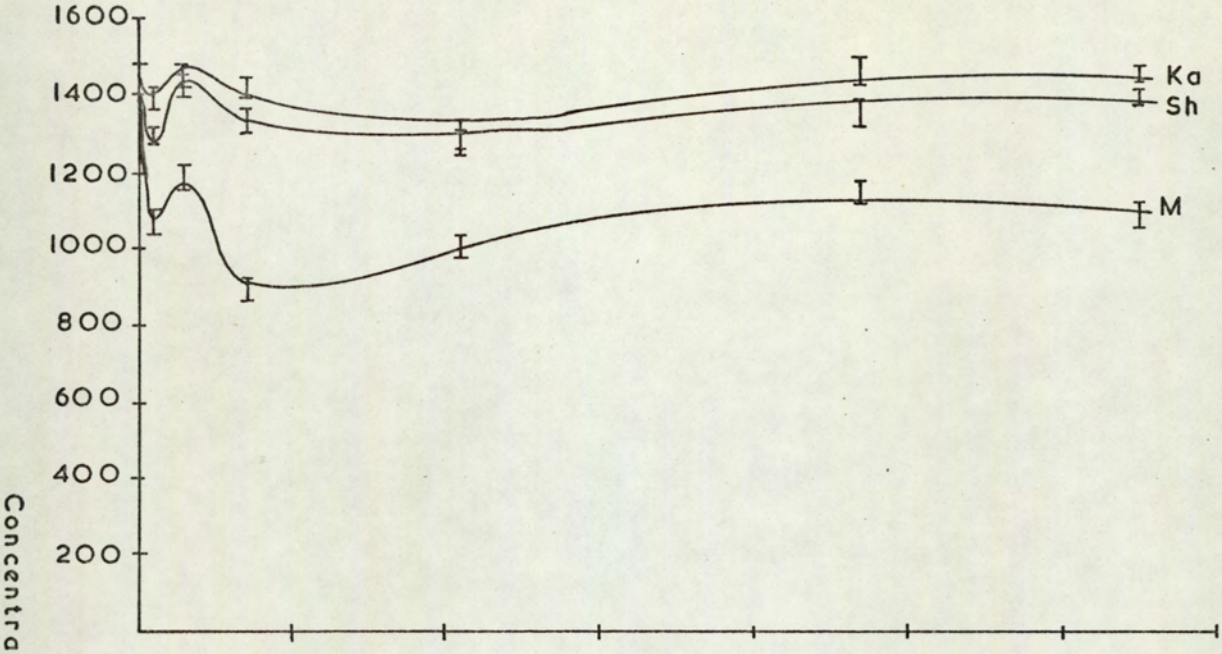
Copper

Nickel

FIG. 25. 7

Combination D

Zinc



Chromium

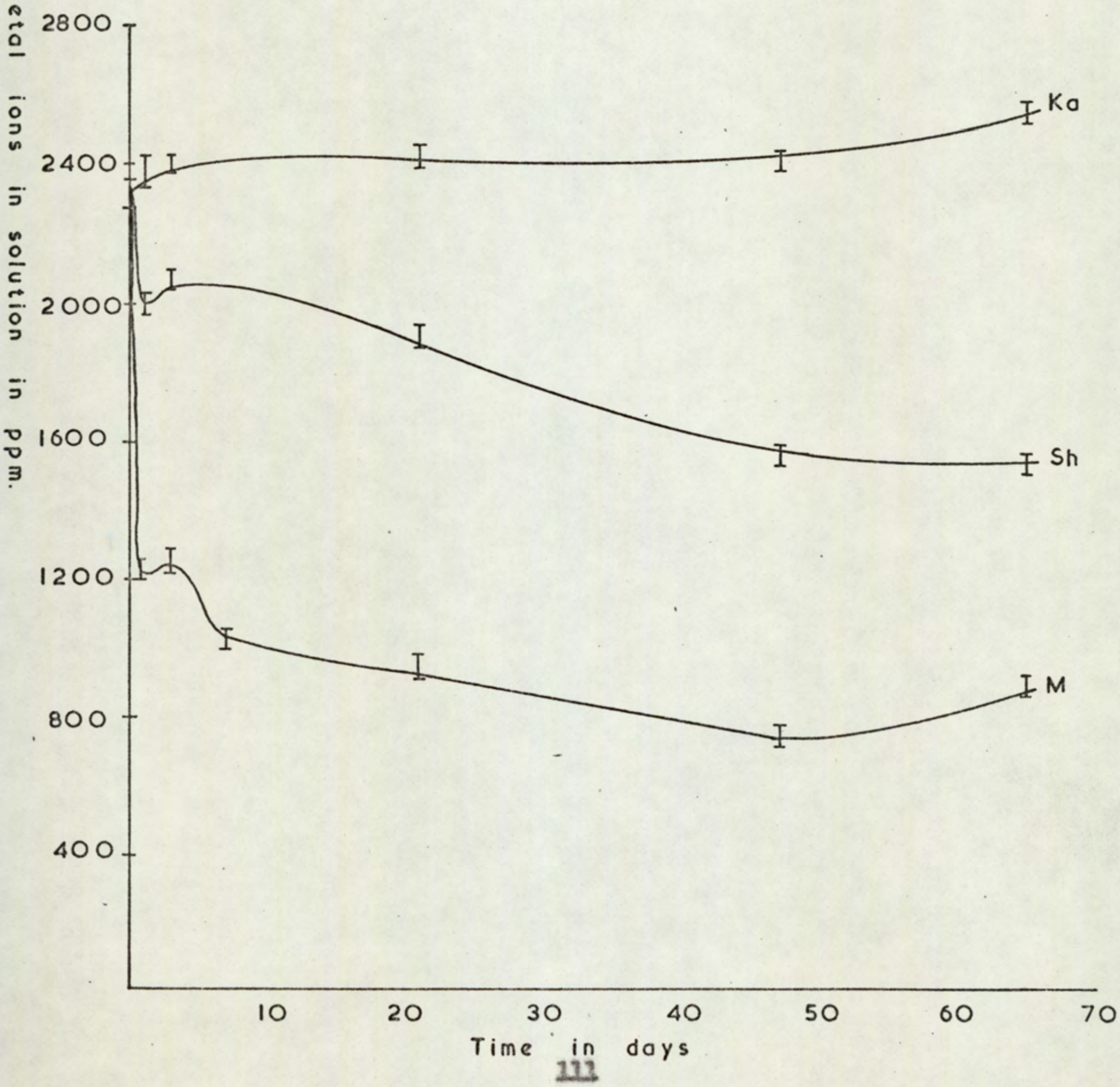


FIG. 25. 8

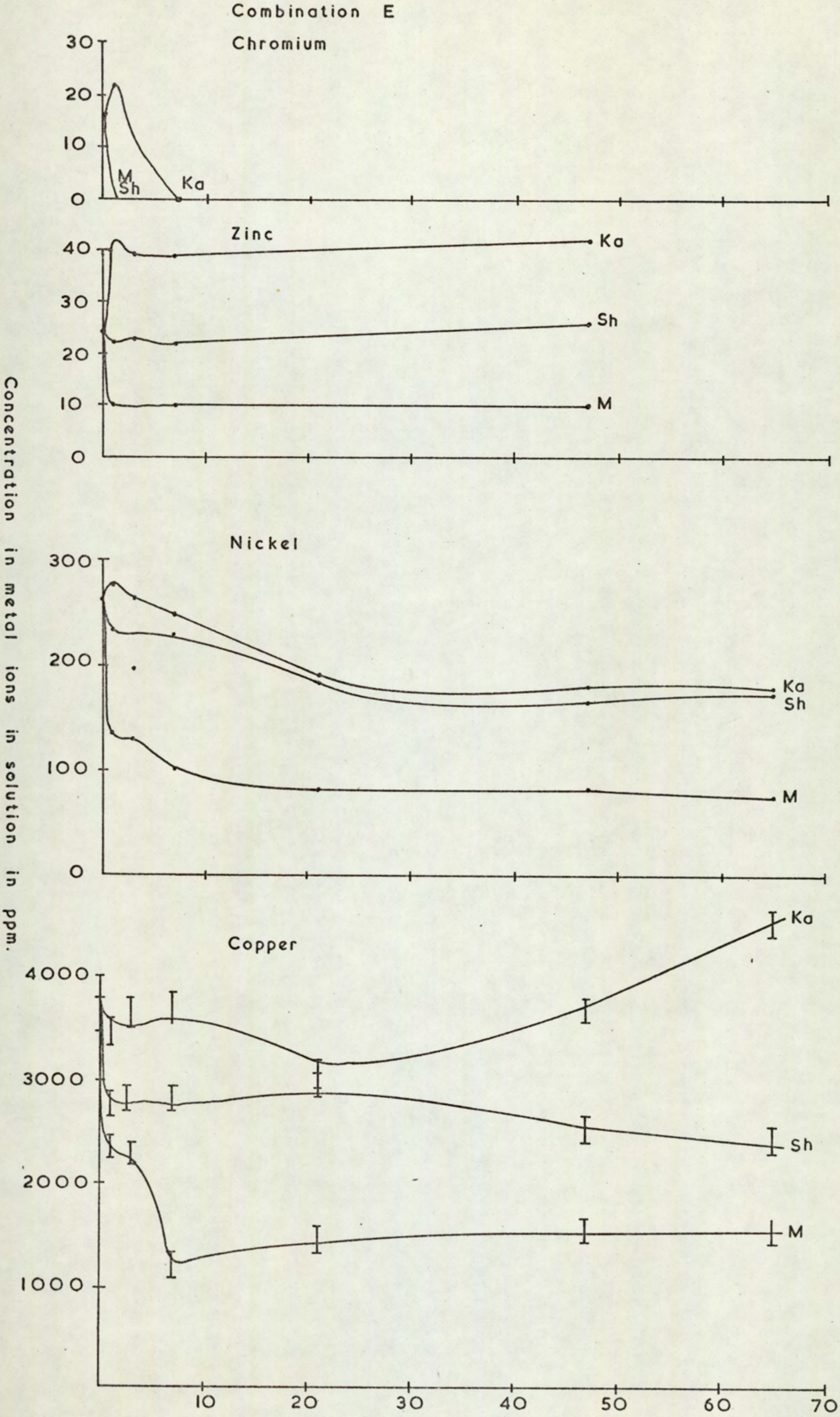

Combination E
Chromium
Zinc
Nickel
Copper
Ka
Sh
M
30
20
10
0
40
300
200
100
4000
3000
2000
1000
10
20
30
40
50
60
70
Concentration in metal ions in solution in ppm.
Time in days

FIG. 25. 9

Combination F

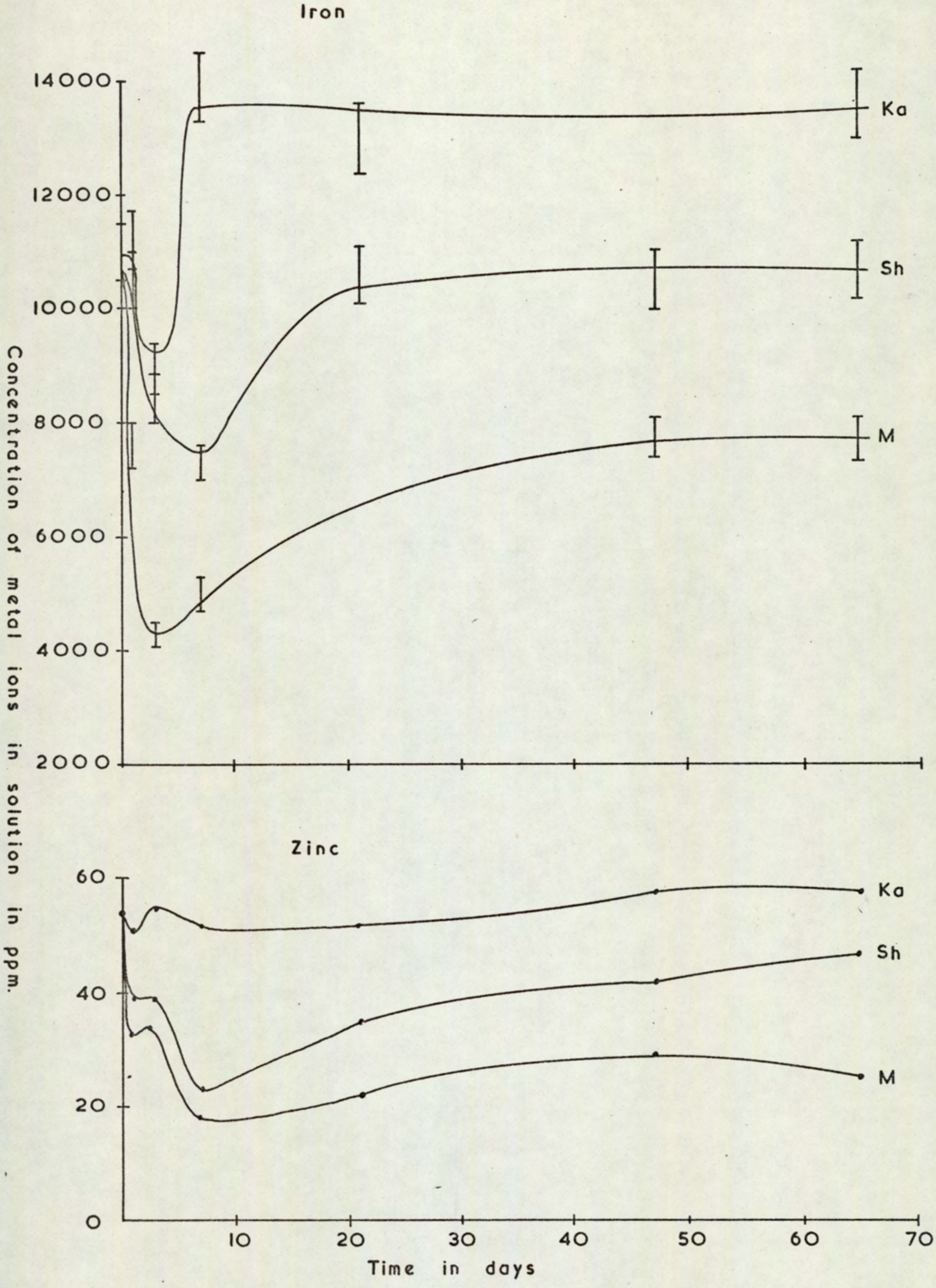
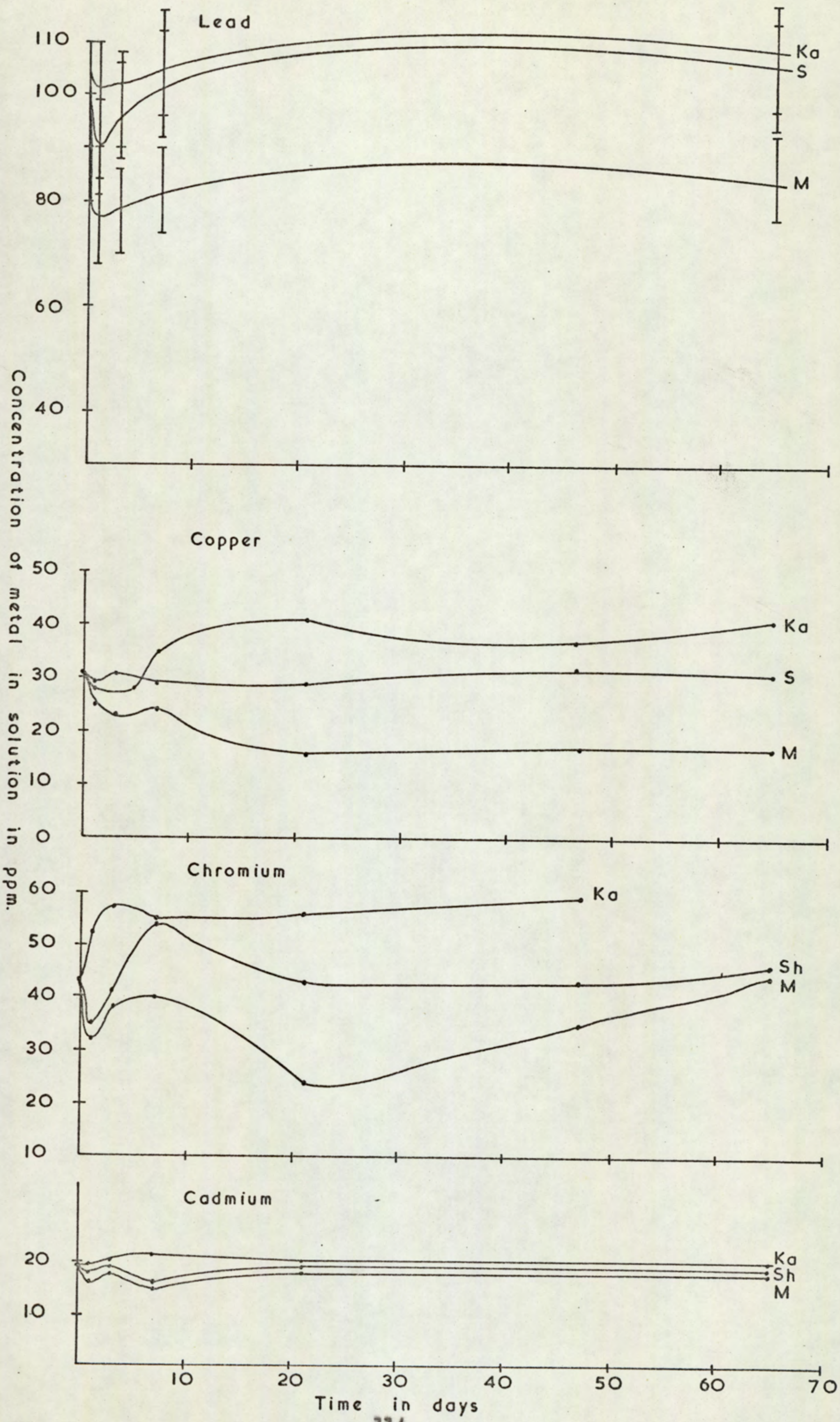


FIG. 25.10

Combination F



5.3.6. Experiments with Coal Measures Rocks

The experiments carried out on the pure clay minerals to determine the effects of varying the pH, of using solutions containing more than one element, and the attempts to saturate the adsorption sites were repeated using Coal Measures rocks. Both sandstone and shale were used for the experiments at different pH values, but as the results were similar for both rock types, only shale was used for subsequent experiments.

The results are presented as graphs of the reduction in concentration of the metal in solution against time for the experiments at different pH values and the multi element experiments. For the saturation experiments the maximum adsorption in milliequivalents per 100 gm of rock is plotted against the original concentration. Results for the multi element experiments are in Appendix 3.5, and the graphs of these results in Section 5.3.5.

Fig 26. Graphs of the results of experiments carried out on Coal Measures rocks.

a. Experiments at pH 1, 2, 3, 4 and 9

b. Experiments to saturate the adsorption sites.

Fig 26. a. 1 Chromium

Fig 26. a. 2 Iron, copper

Fig 26. a. 3 Lead, cadmium

Fig 26. a. 4 Nickel, zinc

Fig 26. b. 1 Iron, copper, lead, cadmium

Fig 26. b. 2 Zinc, nickel, chromium

FIG. 26.a.1

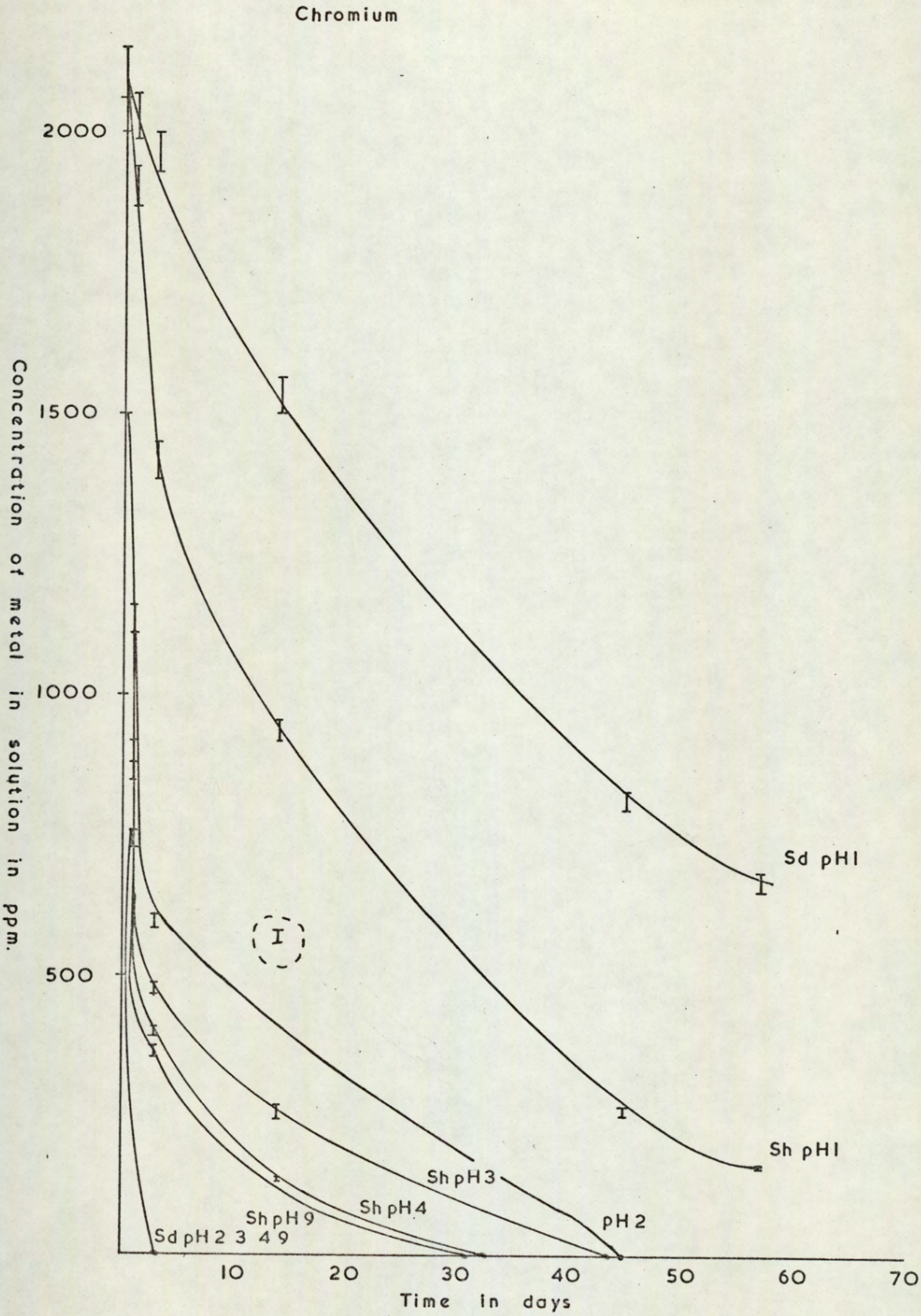

Chromium
Concentration of metal in solution in ppm.
2000
1500
1000
500
10
20
30
40
50
60
70
Time in days
Sd pH1
Sh pH1
Sh pH3
pH 2
Sh pH4
Sh pH9
Sd pH 2 3 4 9

FIG. 26.a. 2

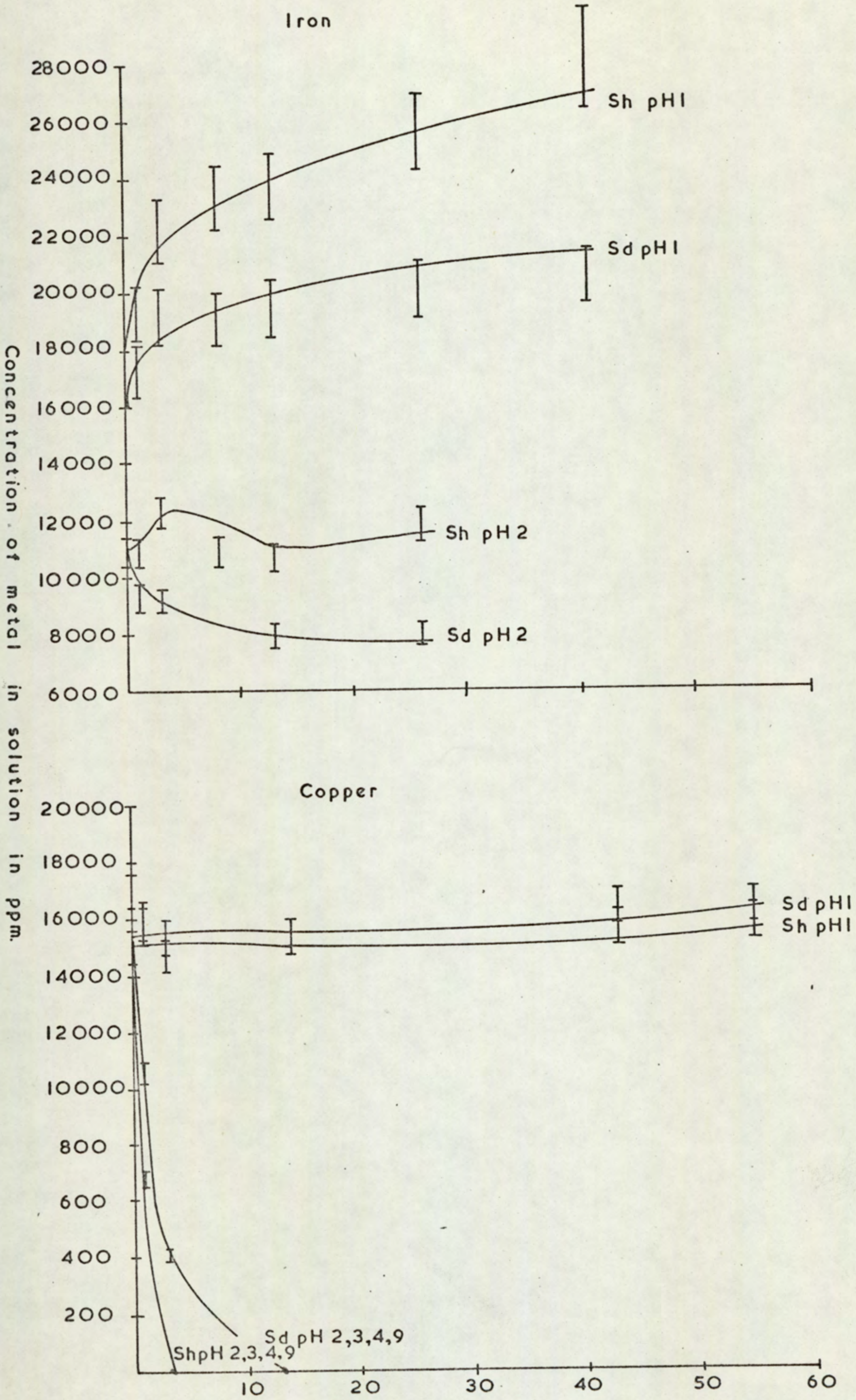

Iron
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
Sh pH1
Sd pH1
Sh pH 2
Sd pH 2
Concentration of metal in solution in ppm.
Copper
20000
18000
16000
14000
12000
10000
800
600
400
200
Sd pH1
Sh pH1
Sd pH 2,3,4,9
ShpH 2,3,4,9
10
20
30
40
50
60

FIG. 26. a. 3

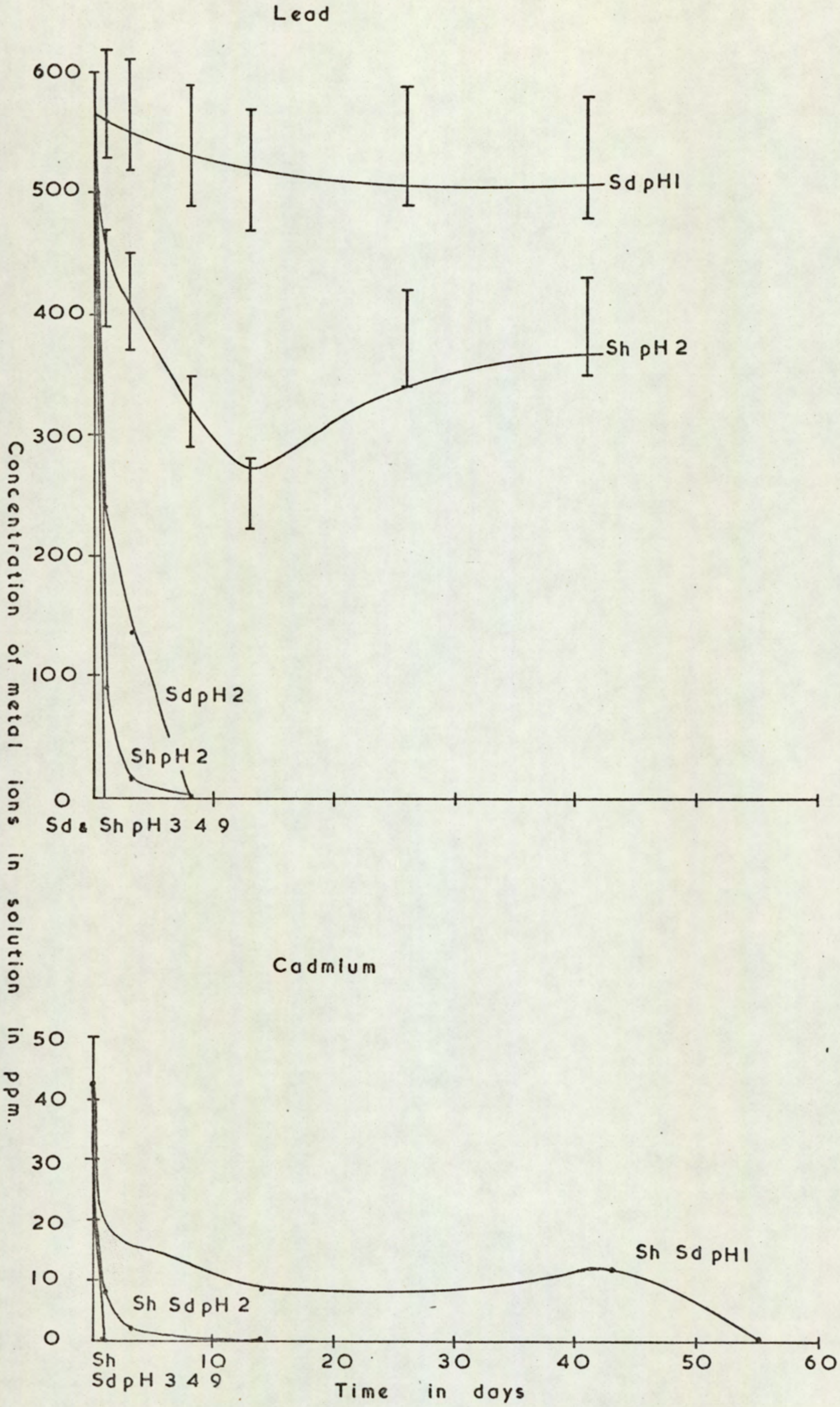

Lead
600
500
400
300
200
100
0
Sd pHI
Sh pH 2
Sd pH 2
Sh pH 2
Sd & Sh pH 3 4 9
Concentration of metal ions in solution in ppm.
Cadmium
50
40
30
20
10
0
Sh Sd pHI
Sh Sd pH 2
Sh
Sd pH 3 4 9
10
20
30
40
50
60
Time in days

FIG. 26. a. 4

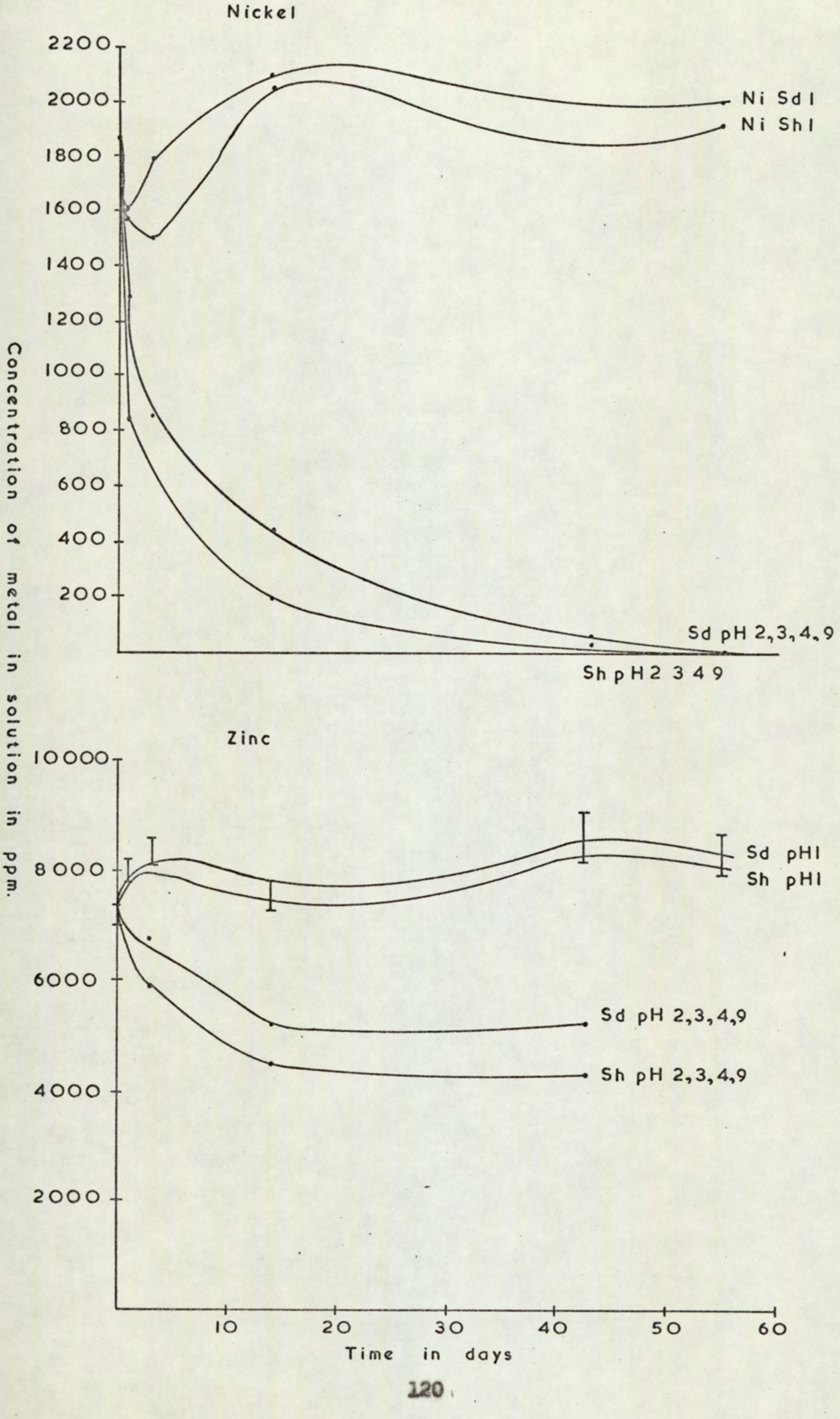
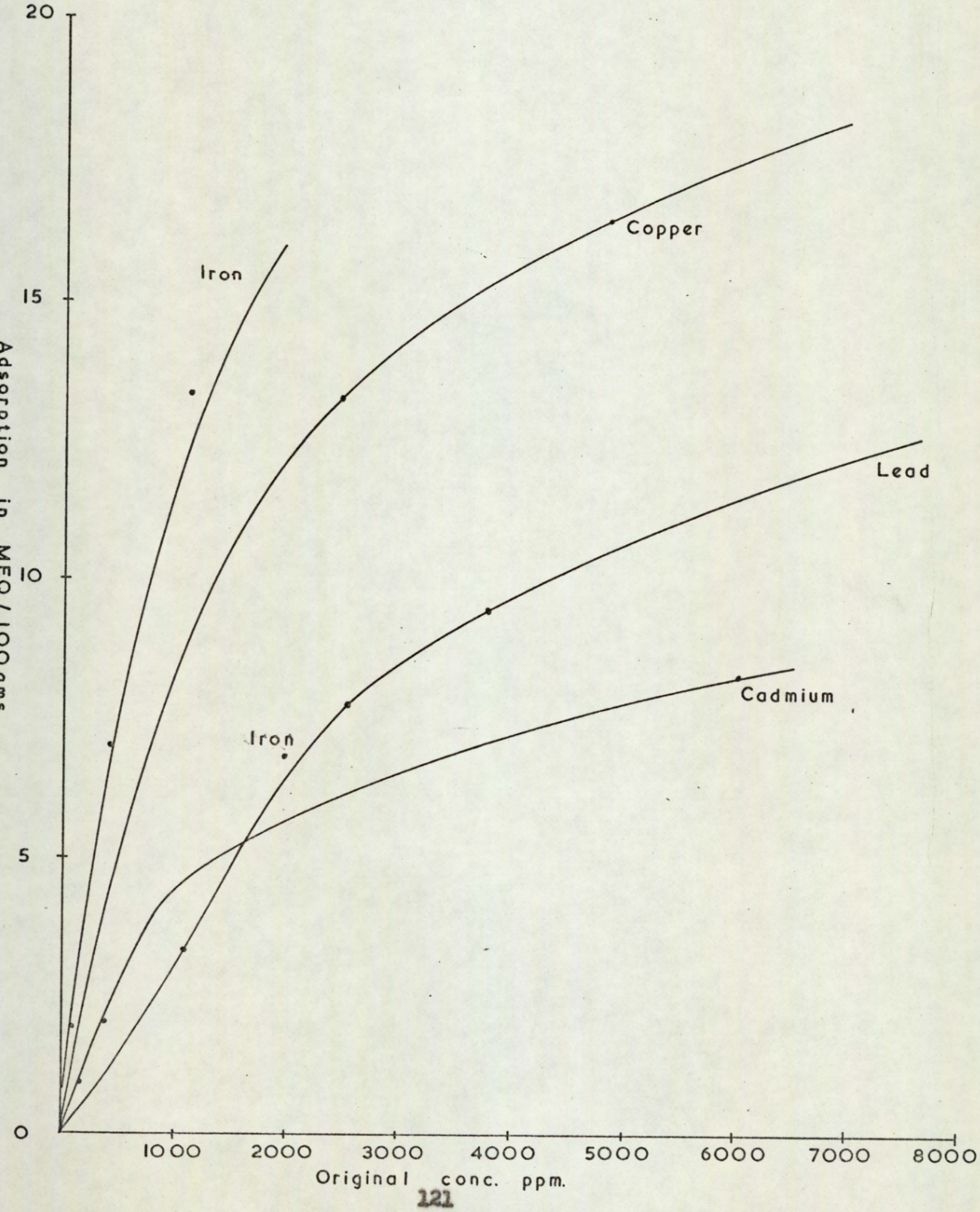
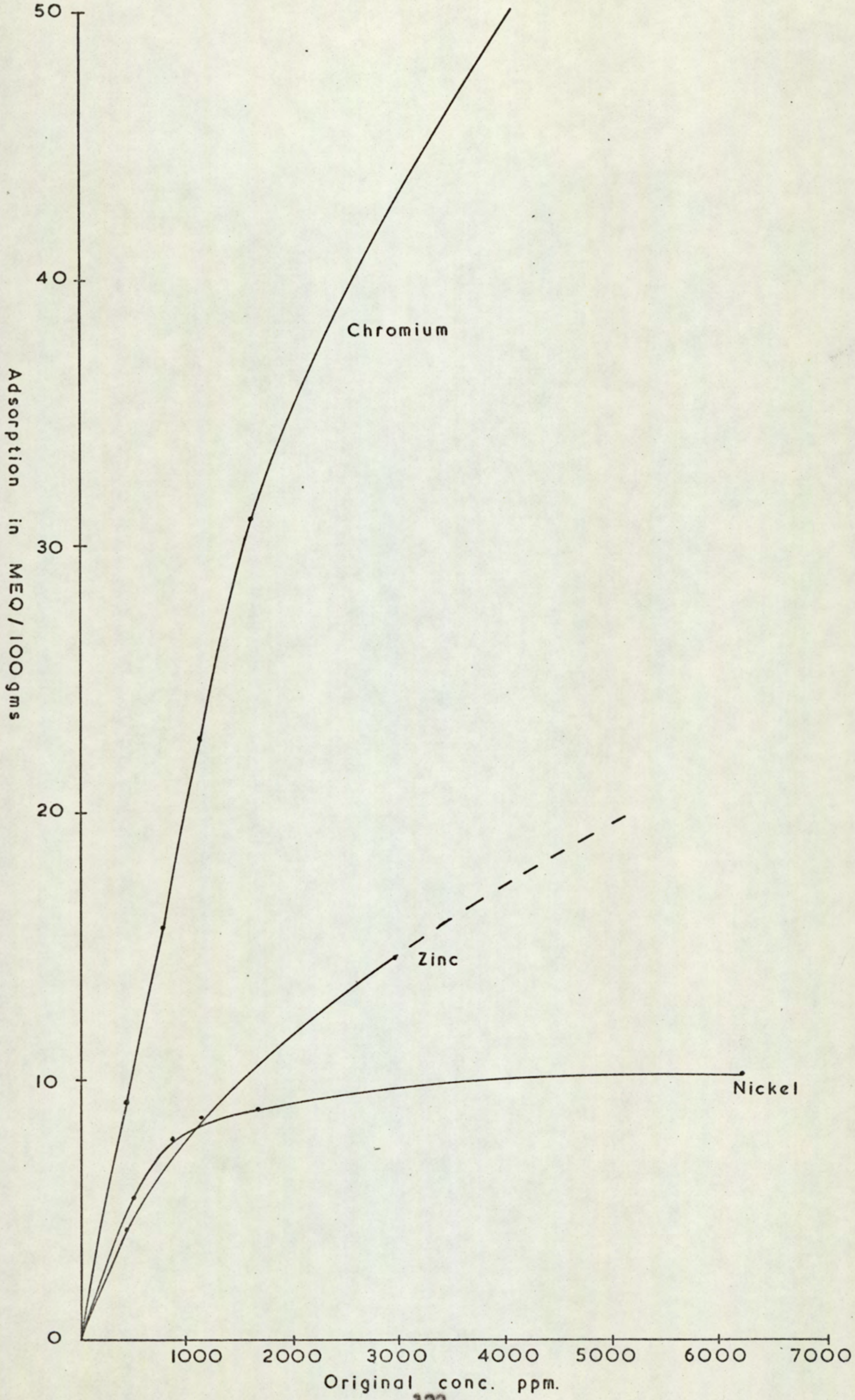

Nickel
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
Ni Sd I
Ni Sh I
Sd pH 2,3,4,9
Sh pH 2 3 4 9
Zinc
10000
8000
6000
4000
2000
Sd pH I
Sh pH I
Sd pH 2,3,4,9
Sh pH 2,3,4,9
Concentration of metal in solution in ppm.
10
20
30
40
50
60
Time in days

FIG. 26. b. 1



20
15
10
5
0
Adsorption in MEQ / 100 gms
Iron
Copper
Lead
Iron
Cadmium
1000
2000
3000
4000
5000
6000
7000
8000
Original conc. ppm.

FIG. 26. b. 2


50
40
30
20
10
0
Adsorption in MEQ / 100 gms
Chromium
Zinc
Nickel
1000
2000
3000
4000
5000
6000
7000
Original conc. ppm.

5.3.7 Experiments with Betton Abbotts Site Rocks

Acid solutions at pH3 were prepared containing metals in concentrations similar to those found in effluents likely to be disposed of at the Betton Abbotts site. Solutions were also prepared at pH9. Iron copper and zinc were each prepared in two different concentrations, one in hundreds of ppm and the other in thousands of ppm reflecting the variation in concentration of these elements in the effluent types as indicated by analyses supplied by the operators of the site.

To examine the effects of the presence of more than one metal in solution, two solutions containing mixtures of the elements were prepared. Combination 1 contained all seven elements in quantities similar to those of the single element solutions, with copper, iron and zinc in the lower concentration. Combination 2 contained only copper, iron and zinc in high concentrations. As the original concentrations of the single element and mixed element solutions are similar, the effects of competition of other elements present may be assessed. These solutions were mixed with each of the four rock types from the site. The results are presented as graphs indicating the adsorption by each rock type of the elements from the single metal solution, and the combination solutions. The adsorption of each element is presented in milliequivalents per 100 gm of rock for each solution in Table 5 to facilitate comparison of the single and mixed element solutions.

TABLE 5

Results of the experiments on the adsorption of metal ions by the Betton Abbotts Site rocks in percentage adsorption and the absolute adsorption in milliequivalents per 100 grams of rock.

RED CLAY (BOULDER CLAY)

SINGLE ELEMENT SOLUTIONS			MIXED ELEMENT SOLUTIONS		
Solution	Max % Abs	Abs in Meq/100 gm	Solution	Max % Abs	Abs in Meq/100 gm
Fe 590 pH3	100	10.5	Fe 610 pH3	100	10.9
Fe 626 pH9	100	11.2	Fe 582 pH9	100	10.3
Pb 113 pH3	100	0.36	Pb 450 pH3	100	1.4
Pb 113 pH9	100	0.36	Pb 46 pH9	100	0.15
Cr 94 pH3	100	1.8	Cr 94 pH3	100	1.8
Cr 94 pH9	100	1.8	Cr 85 pH9	100	1.7
Cd 19 pH3	100	0.11	Cd 25 pH3	92	0.14
Cd 19 pH9	100	0.14	Cd 17 pH9	88	0.09
Ni 1278 pH3	92	13.3	Ni 1334 pH3	85	12.9
Ni 1278 pH9	92	13.0	Ni 1353 pH9	97	14.9
Cu 133 pH3	100	1.4	Cu 202 pH3	100	2.1
Cu 133 pH9	100	1.3	Cu 209 pH9	100	2.1
Zn 211 pH3	100	2.2	Zn 594 pH3	95	5.8
Zn 211 pH9	100	2.2	Zn 423 pH9	97	4.2
Fe 19553 pH3	58	201	Fe 8595 pH3	59	105
Fe 19553 pH9	58	204	Fe 18309 pH9	58	190
Cu 8715 pH3	100	89	Cu 10485 pH3	21	22
Cu 8988 pH9	100	92	Cu 10255 pH9	16	17
Zn 11576 pH3	41	49	Zn 25750 pH3	16	43
Zn 11011 pH9	37	42	Zn 13096 pH9	20	27
GREY SAND (WEST END SAND)					
Fe 590 pH3	100	10.5	Fe 610 pH3	100	10.9
Fe 626 pH9	100	11.2	Fe 582 pH9	100	10.3
Pb 113 pH3	100	0.36	Pb 450 pH3	100	1.4
Pb 113 pH9	100	0.36	Pb 46 pH9	100	0.15
Cr 94 pH3	100	1.8	Cr 94 pH3	100	1.8
Cr 93 pH9	100	1.8	Cr 85 pH9	100	1.7
Cd 19 pH3	100	0.11	Cd 25 pH3	64	0.10
Cd 23 pH9	100	0.14	Cd 17 pH9	59	0.06

SINGLE ELEMENT SOLUTIONS			MIXED ELEMENT SOLUTIONS		
Solution	Max % Abs	Abs in Meq/100 gm	Solution	Max % Abs	Abs in Meq/100 gm
Ni 1278 pH3	92	13.3	Ni 1334 pH3	78	11.8
Ni 1278 pH9	92	13.0	Ni 1353 pH9	88	13.6
Cu 133 pH3	100	1.4	Cu 202 pH3	100	2.1
Cu 127 pH9	100	1.3	Cu 209 pH9	100	2.1
Zn 211 pH3	100	2.2	Zn 594 pH3	89	5.4
Zn 211 pH9	100	2.2	Zn 423 pH9	89	3.9
Fe 19553 pH3	58	201	Fe 8595 pH3	56	86
Fe 19553 pH9	58	204	Fe 18309 pH9	26	82
Cu 8715 pH3	100	89	Cu 10485 pH3	15	16
Cu 8988 pH9	100	92	Cu 10255 pH9	13	14
Zn 11576 pH3	41	48	Zn 25750 pH3	10	25
Zn 11011 pH9	37	42	Zn 13096 pH9	7	10
GREY CLAY					
Fe 590 pH3	100	10.5	Fe 610 pH3	73	8.0
Fe 626 pH9	100	11.2	Fe 582 pH9	73	10.0
Pb 113 pH3	100	0.36	Pb 450 pH3	96	1.4
Pb 113 pH9	100	0.36	Pb 46 pH9	74	0.11
Cr 94 pH3	100	1.8	Cr 94 pH3	96	1.8
Cr 93 pH9	100	1.8	Cr 85 pH9	94	1.6
Cd 19 pH3	100	0.11	Cd 25 pH3	16	0.02
Cd 23 pH9	100	0.14	Cd 17 pH9	-	-
Ni 1278 pH3	32	4.6	Ni 1334 pH3	15	2.3
Ni 1278 pH9	30	3.0	Ni 1353 pH9	18	2.8
Cu 133 pH3	98	1.3	Cu 202 pH3	34	0.7
Cu 127 pH9	97	1.25	Cu 209 pH9	41	0.87
Zn 211 pH3	27	0.58	Zn 594 pH3	26	1.6
Zn 211 pH9	29	0.64	Zn 423 pH9	5	0.2
Fe 19553 pH3	9	11.2	Fe 8595 pH3	9	13.2
Fe 19553 pH9	12	30.2	Fe 18309 pH9	10	33.4
Cu 8715 pH3	6	5.4	Cu 10485 pH3	16	17.5
Cu 8988 pH9	6	5.3	Cu 10255 pH9	16	16.5
Zn 11576 pH3	4	4.2	Zn 25750 pH3	5	12.9
Zn 11011 pH9	9	10.2	Zn 13096 pH9	6	8.3

RED SAND (BORE HOLE SAND)

SINGLE ELEMENT SOLUTIONS			MIXED ELEMENT SOLUTIONS		
Solution	Max % Abs	Abs in Meq/100 gm	Solution	Max % Abs	Abs in Meq/100 gm
Fe 518 pH3	72	6.6	Fe 539 pH3	72	7.0
Fe 567 pH9	71	7.1	Fe 539 pH9	81	7.8
Pb 50 pH3	100	0.16	Pb 41 pH3	17	0.02
Pb 50 pH9	100	0.16	Pb 45 pH9	18	0.03
Cr 93 pH3	100	1.8	Cr 90 pH3	96	0.78
Cr 95 pH9	100	1.9	Cr 90 pH9	100	0.61
Cd 18 pH3	100	0.11	Cd 25 pH3	28	0.04
Cd 25 pH9	100	0.15	Cd 19 pH9	17	0.02
Ni 1161 pH3	14	1.9	Ni 1310 pH3	4	0.69
Ni 1171 pH9	9	1.2	Ni 1214 pH9	2	0.34
Cu 172 pH3	100	1.8	Cu 202 pH3	16	0.3
Cu 197 pH9	100	2.0	Cu 186 pH9	10	0.19
Zn 582 pH3	20	1.7	Zn 594 pH3	16	0.96
Zn 531 pH9	14	3.5	Zn 537 pH9	6	0.36
Fe 12627 pH3	-	-	Fe 9039 pH3	3	5.1
Fe 18070 pH9	-	-	Fe 16485 pH9	2	5.8
Cu 11290 pH3	20	23	Cu 9184 pH3	8	7.9
Cu 11061 pH9	14	16	Cu 9151 pH9	4	3.8
Zn 13227 pH3	10	14	Zn 27973 pH3	7	16.8
Zn 13374 pH9	10	14	Zn 12077 pH9	6	7.8

Fig 27. Graphs of the variation in concentration of metal in solution against time for single element and mixed element solutions in contact with rocks from the Betton Abbotts Site.

Fig 27. 1. Iron, Red sand

Fig 27. 2. Iron, Grey clay

Fig 27. 3. Iron Grey sand

Fig 27. 4. Iron, Red clay

Fig 27. 5. Copper, Red sand

Fig 27. 6. Copper, Grey clay

Fig 27. 7. Copper, Grey sand

Fig 27. 8. Copper, Red clay

Fig 27. 9. Zinc, Red sand

Fig 27. 10. Zinc, Grey sand

Fig 27. 11. Zinc, Grey clay

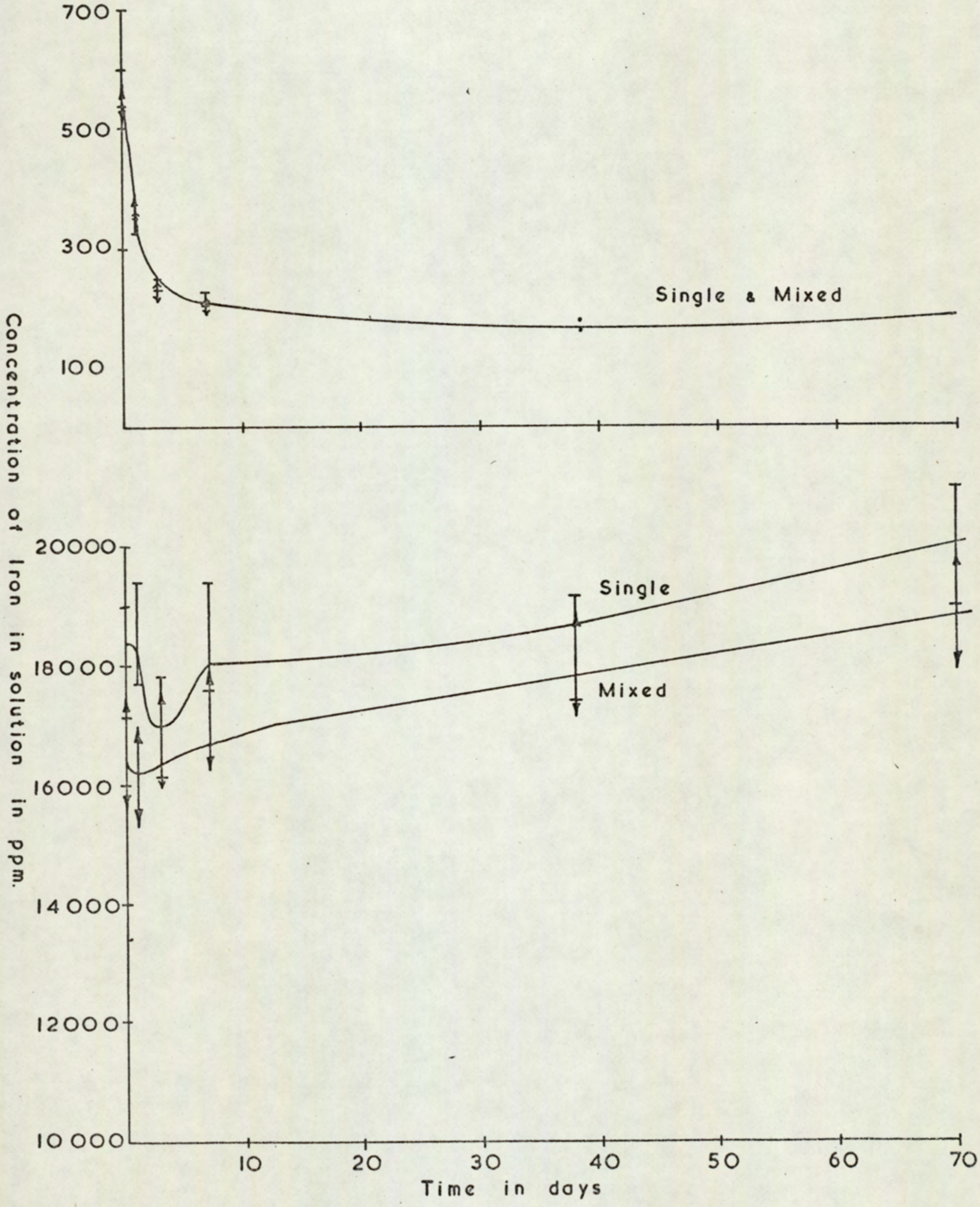
Fig 27. 12. Zinc, Red clay

Fig 27. 13. Chromium

Fig 27. 14. Nickel

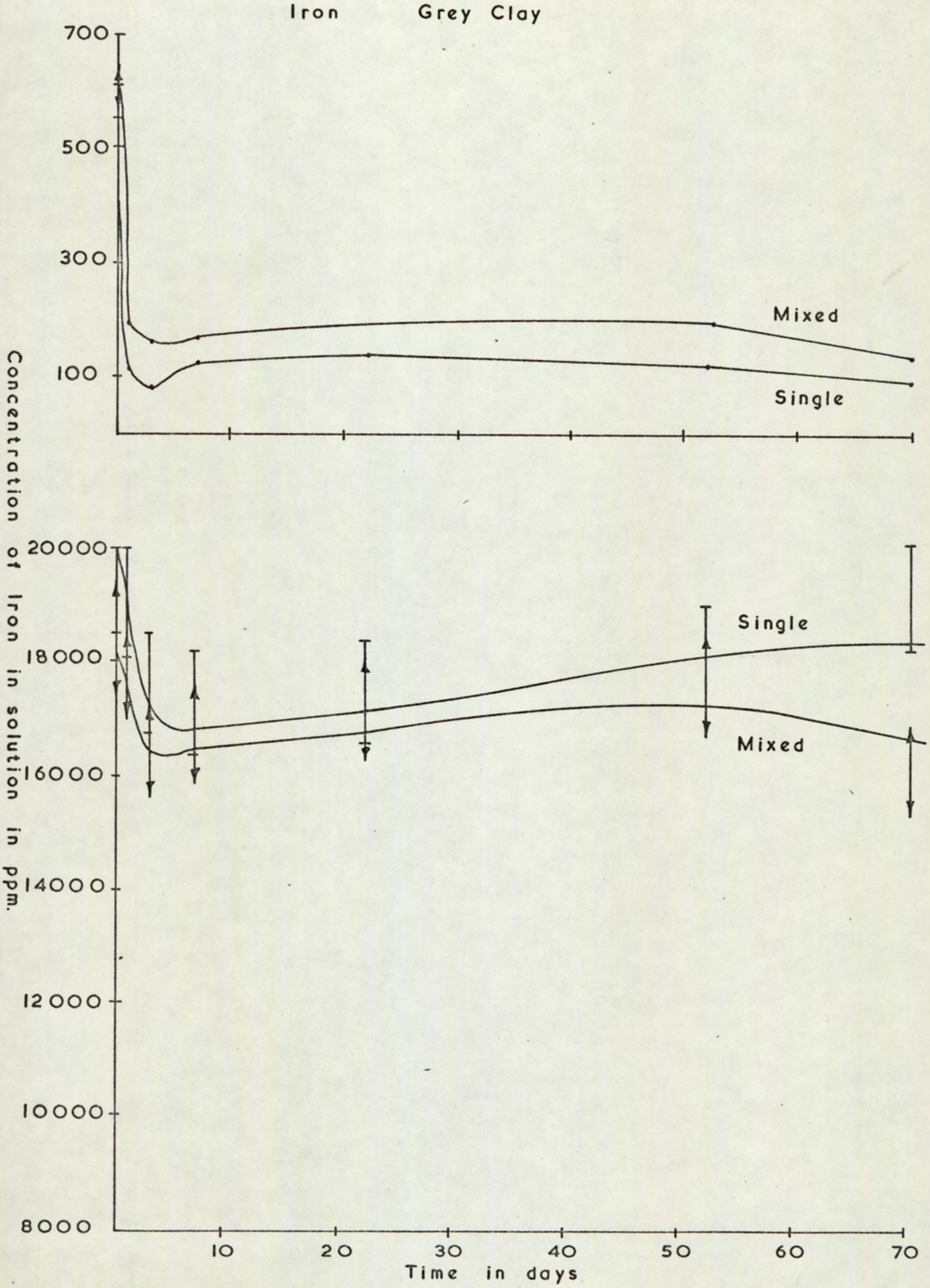
Fig 27. 15. Cadmium

FIG. 27.1



Iron Red Sand

FIG. 27. 2



Iron Grey Clay
700
500
300
100
Mixed
Single
20000
18000
16000
14000
12000
10000
8000
Single
Mixed
10
20
30
40
50
60
70
Time in days
Concentration of Iron in solution in ppm.

FIG. 27.3

Iron Grey Sand

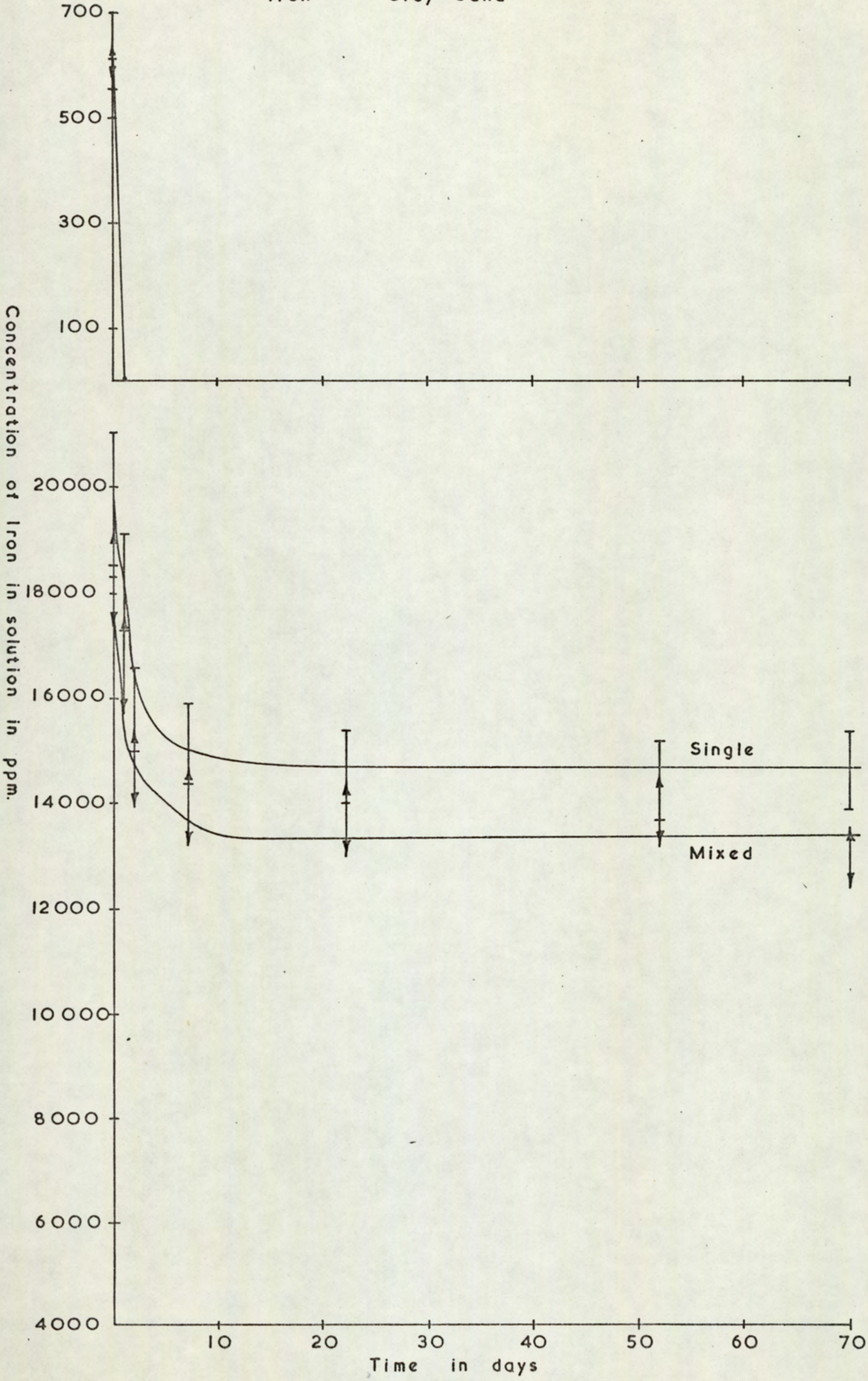


FIG. 27. 4

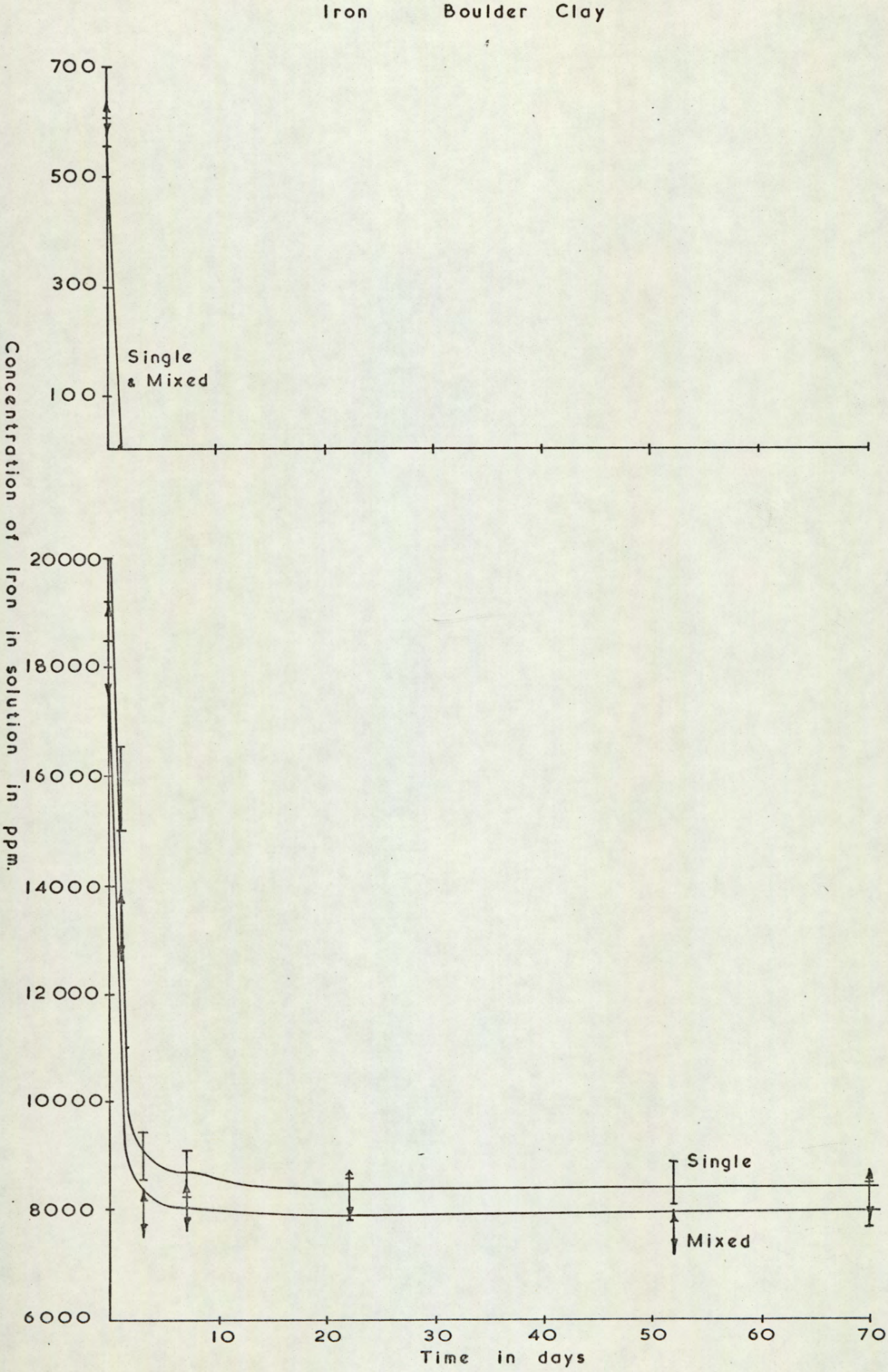

Iron Boulder Clay
700
500
300
100
Single
& Mixed
20000
18000
16000
14000
12 000
10000
8000
6000
Concentration of Iron in solution in ppm.
Single
Mixed
10
20
30
40
50
60
70
Time in days

FIG. 27. 5

Copper Red Sand

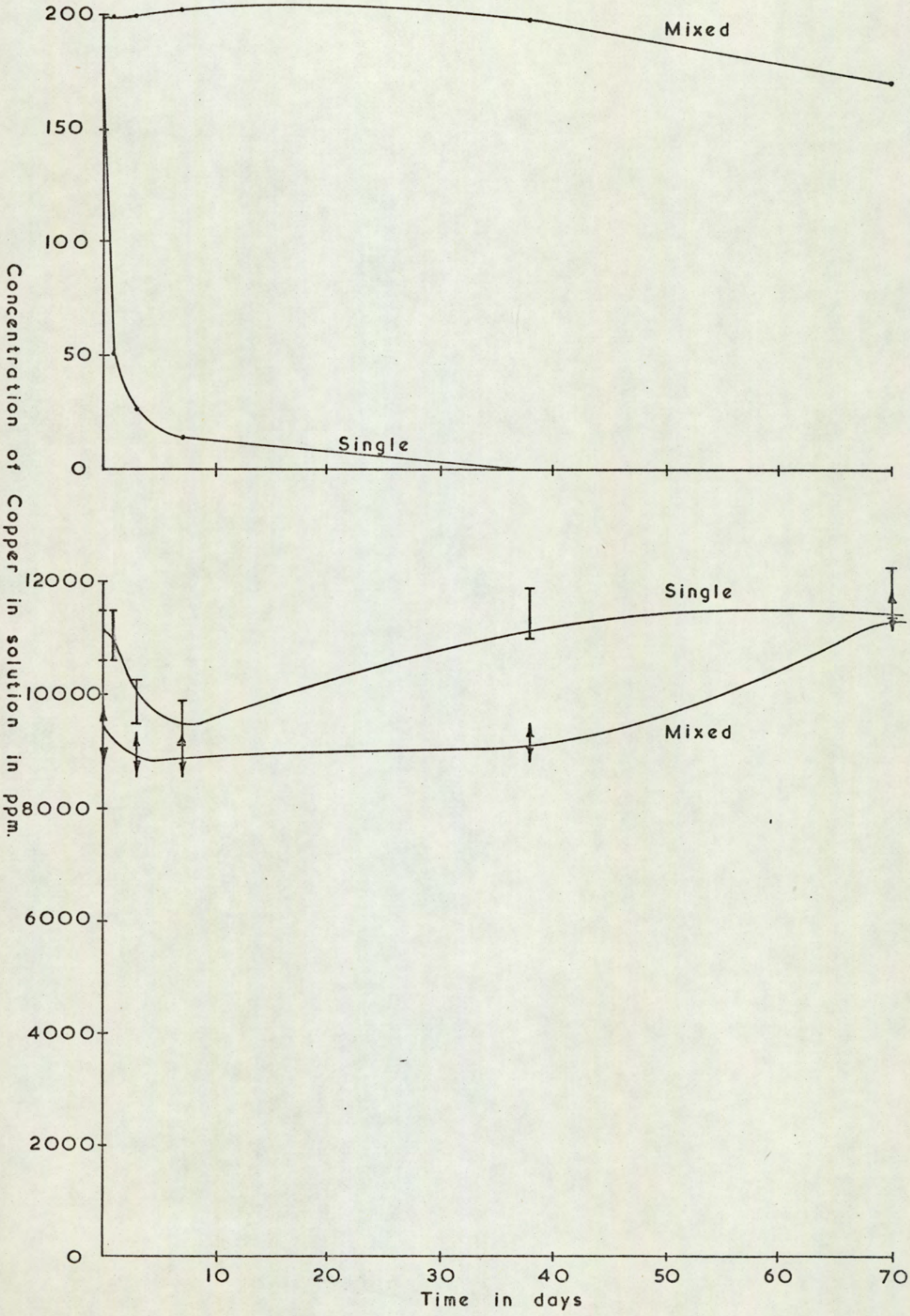


FIG. 27. 6

Copper Grey Clay

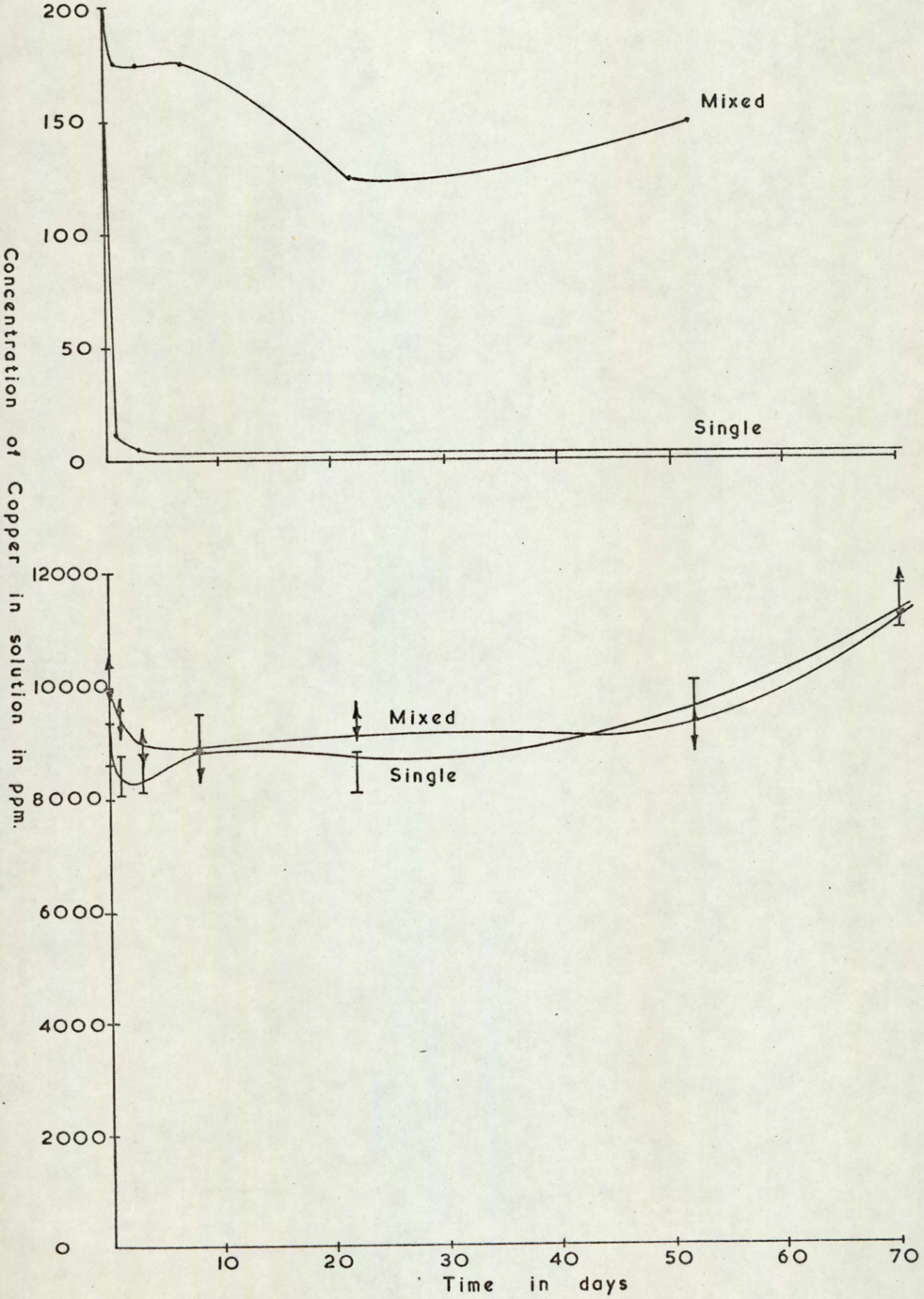


FIG. 27.7

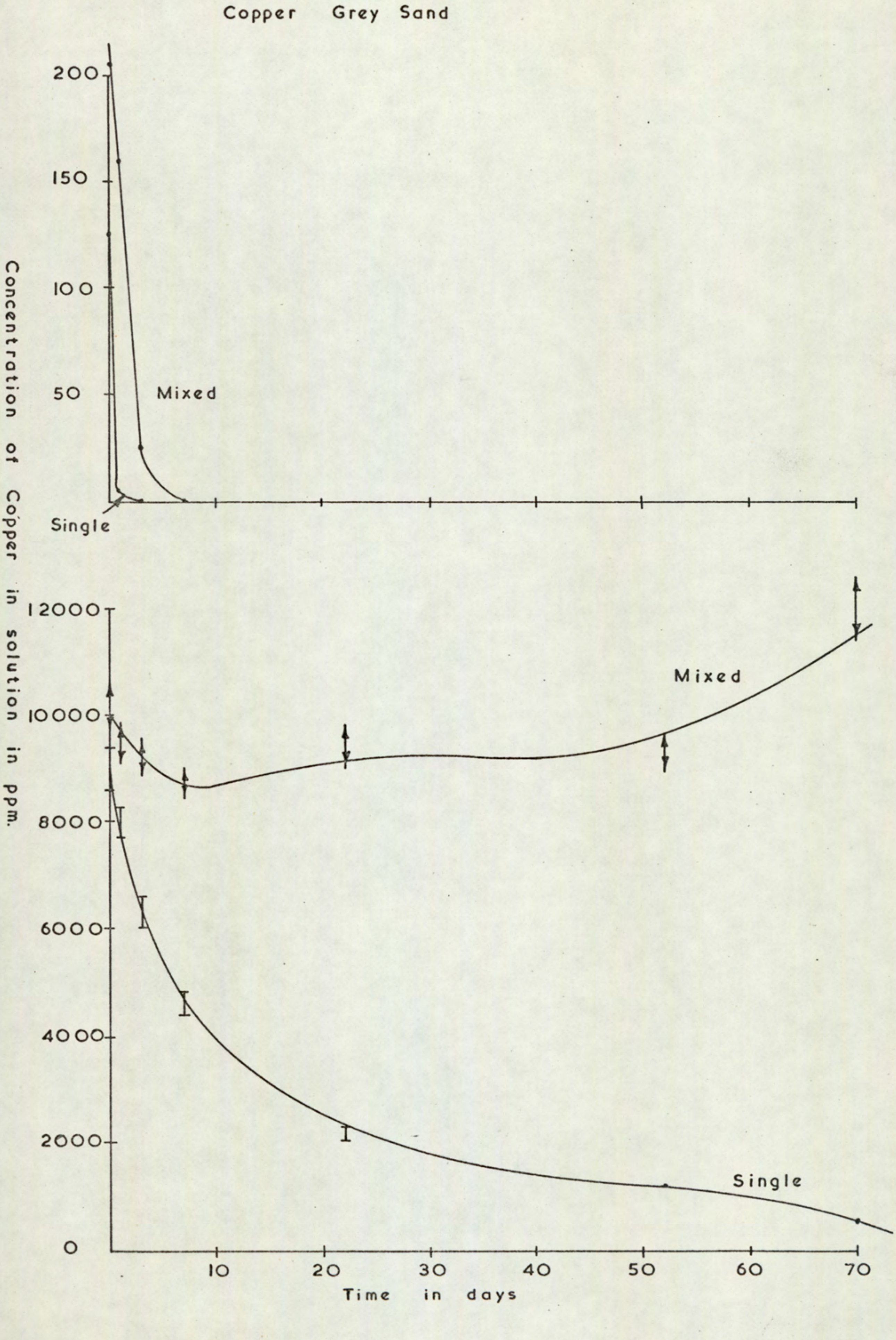

Copper Grey Sand
200
150
100
50
Mixed
Single
12000
10000
8000
6000
4000
2000
0
Mixed
Single
10
20
30
40
50
60
70
Time in days
Concentration of Copper in solution in ppm.

FIG. 27.8

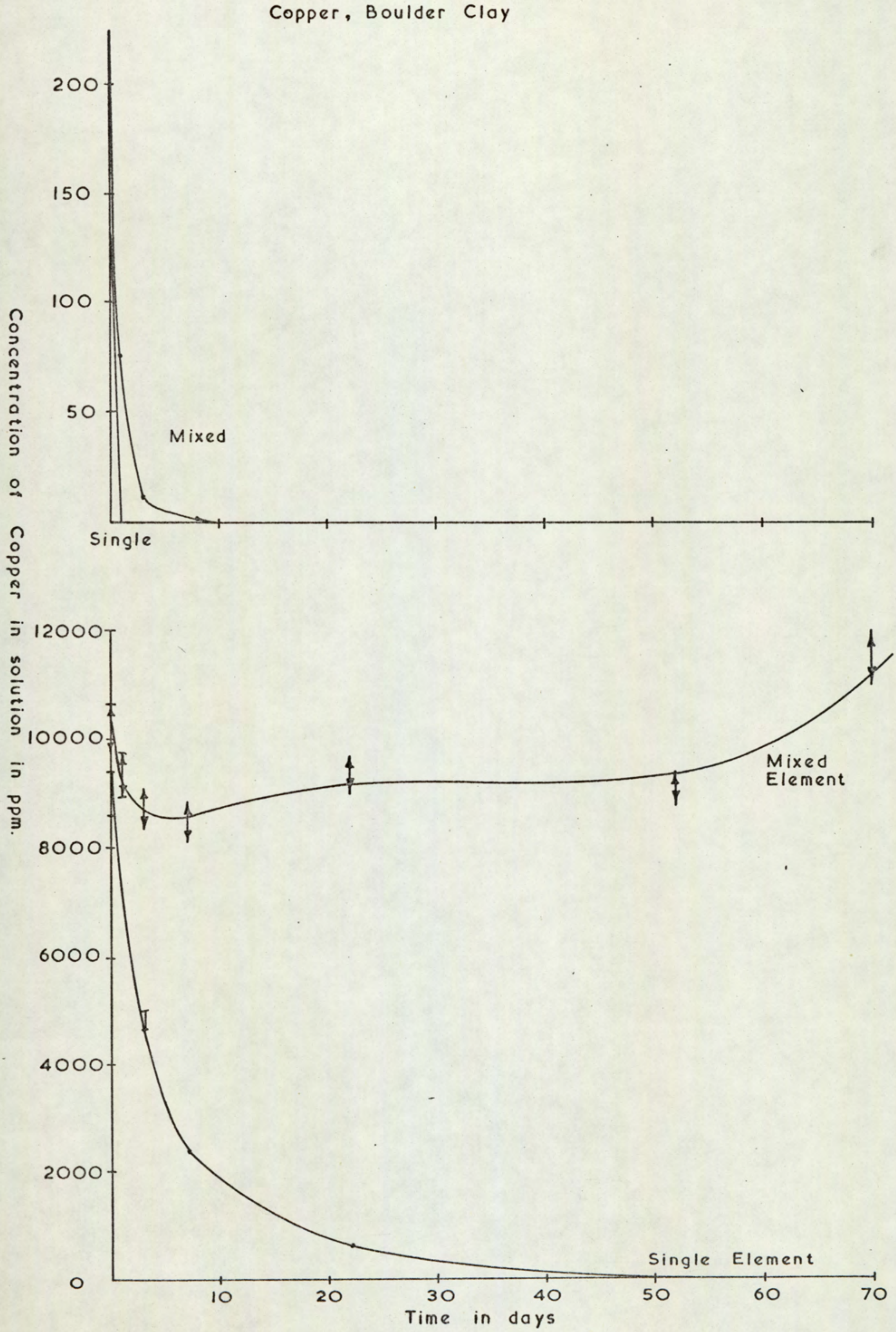

Copper, Boulder Clay
Concentration of Copper in solution in ppm.
200
150
100
50
Mixed
Single
12000
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
70
Time in days
Mixed Element
Single Element

FIG. 27. 9

Zinc Red Sand

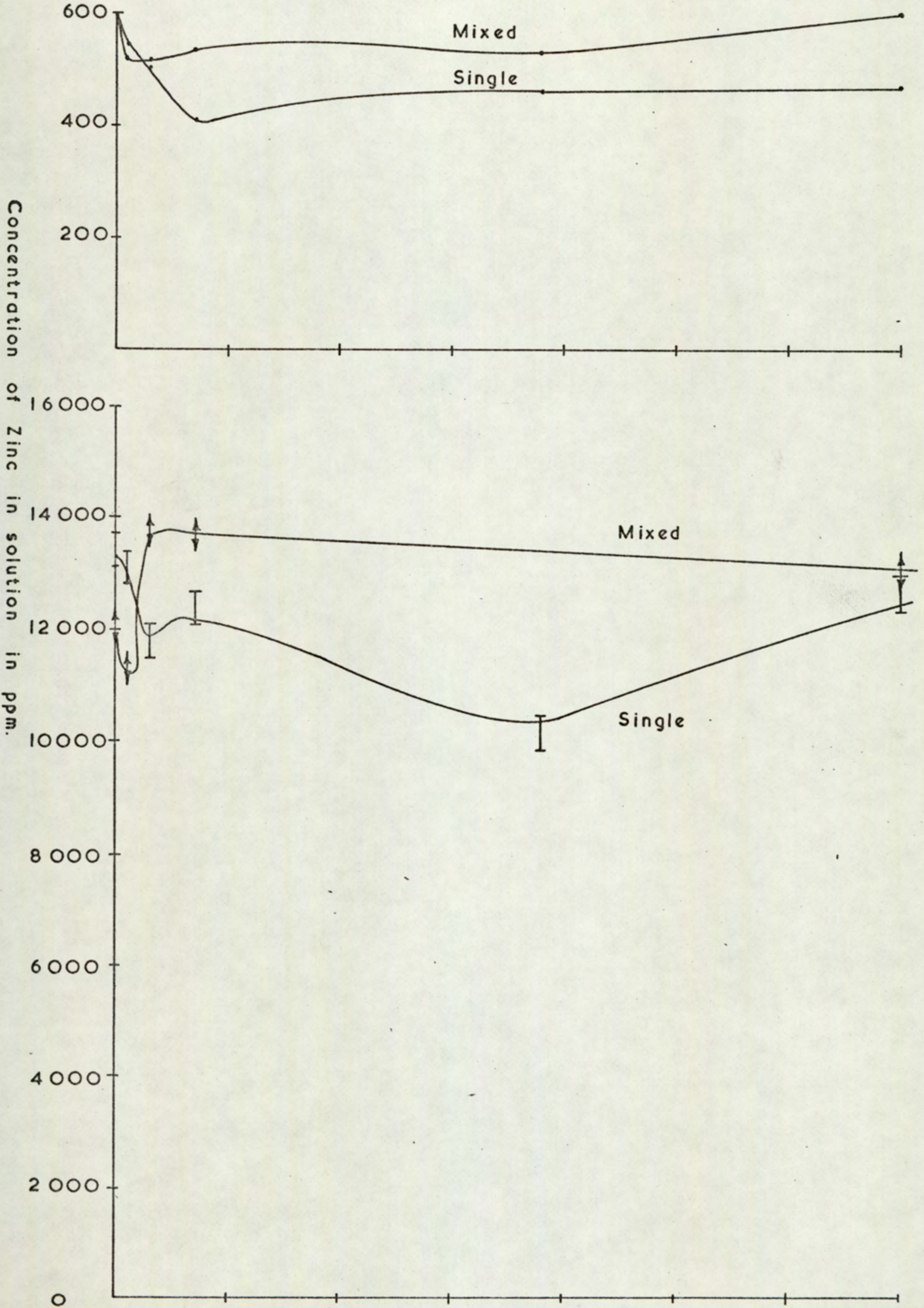


FIG. 27. 10

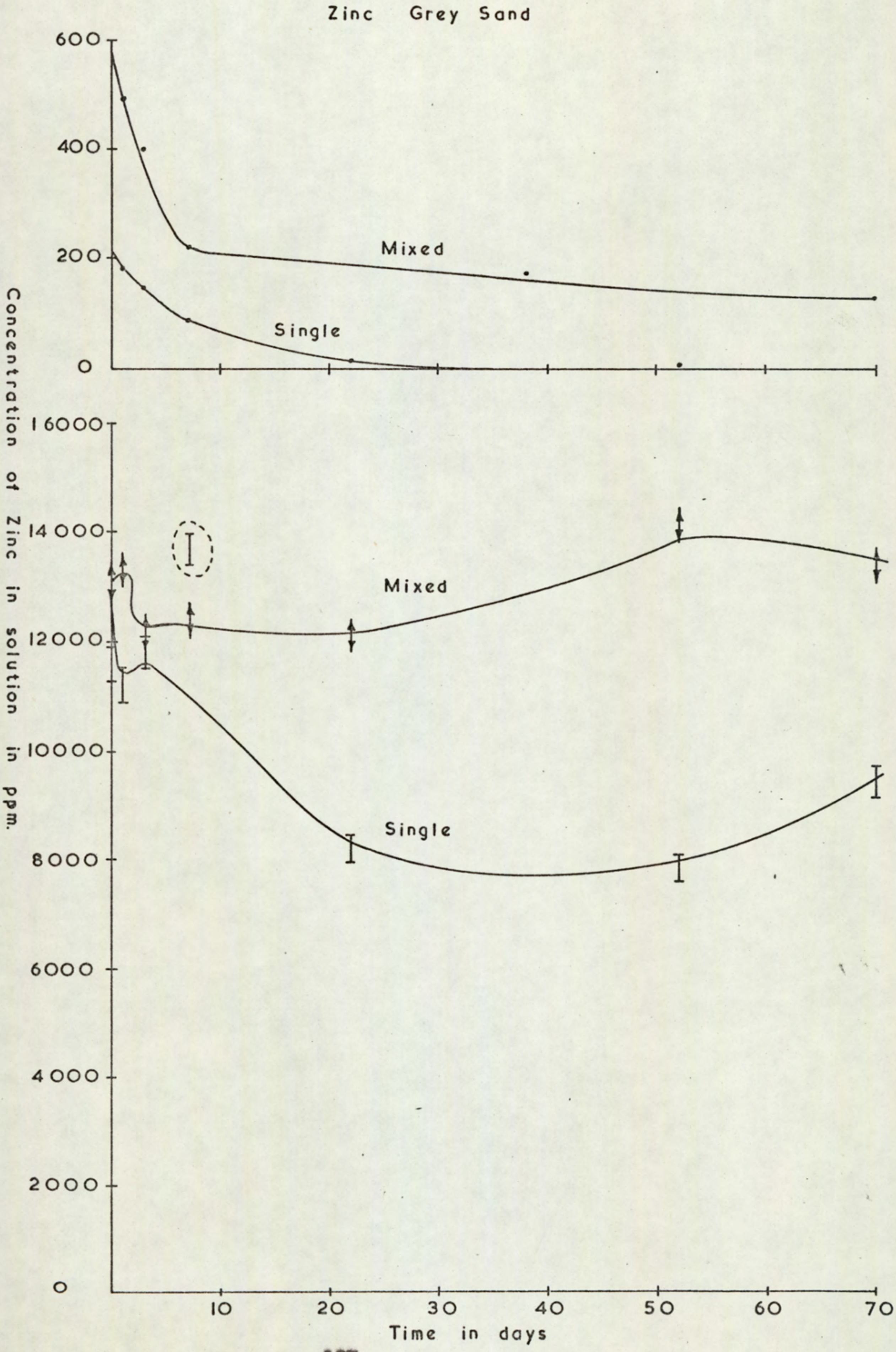

Zinc Grey Sand
Concentration of Zinc in solution in ppm.
600
400
200
0
Mixed
Single
16000
14000
12000
10000
8000
6000
4000
2000
0
Mixed
Single
10
20
30
40
50
60
70
Time in days

FIG. 27. II

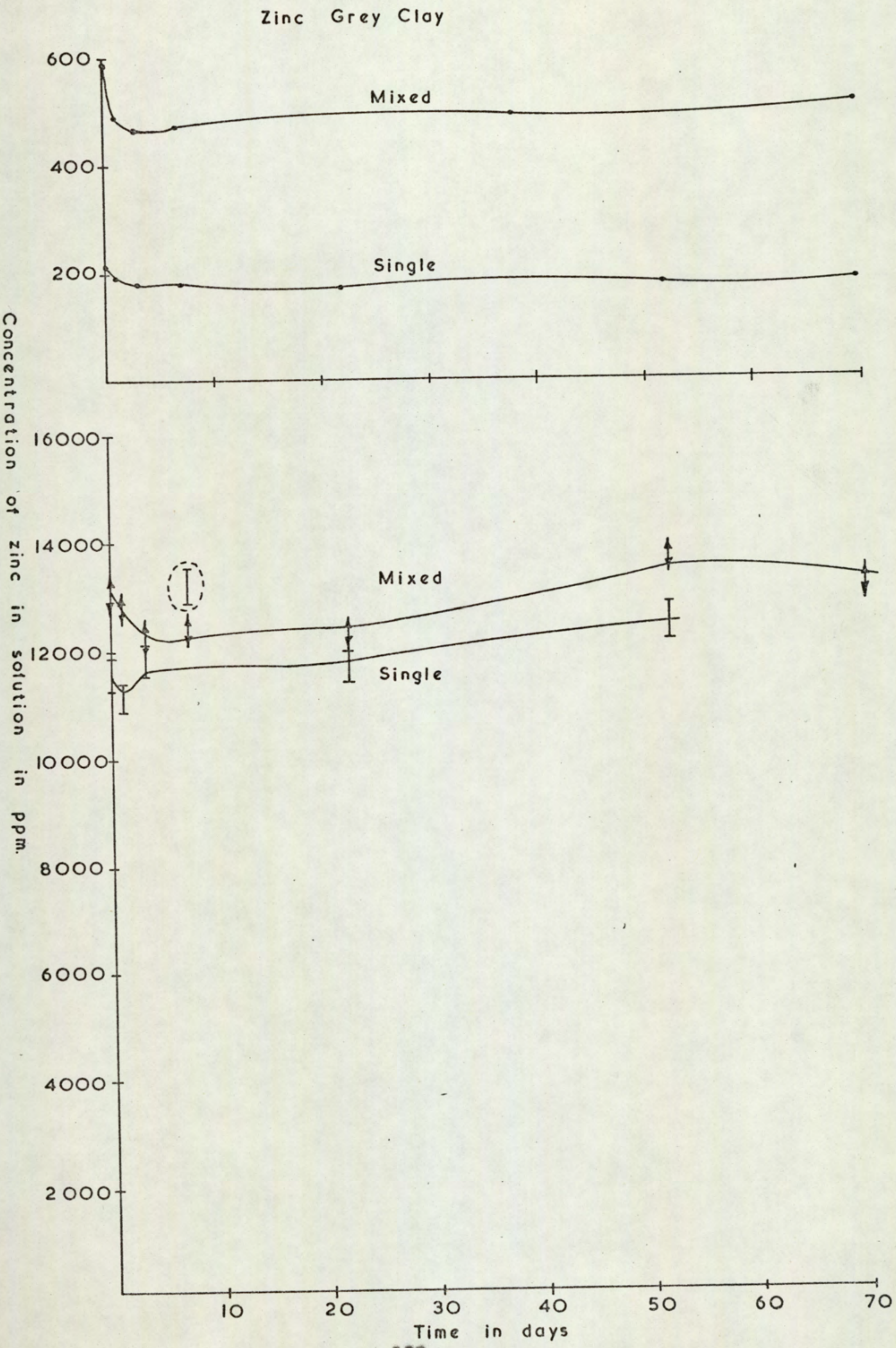

Zinc Grey Clay
600
400
200
Mixed
Single
16000
14000
12000
10000
8000
6000
4000
2000
Mixed
Single
10
20
30
40
50
60
70
Concentration of zinc in solution in ppm.
Time in days

FIG. 27.12

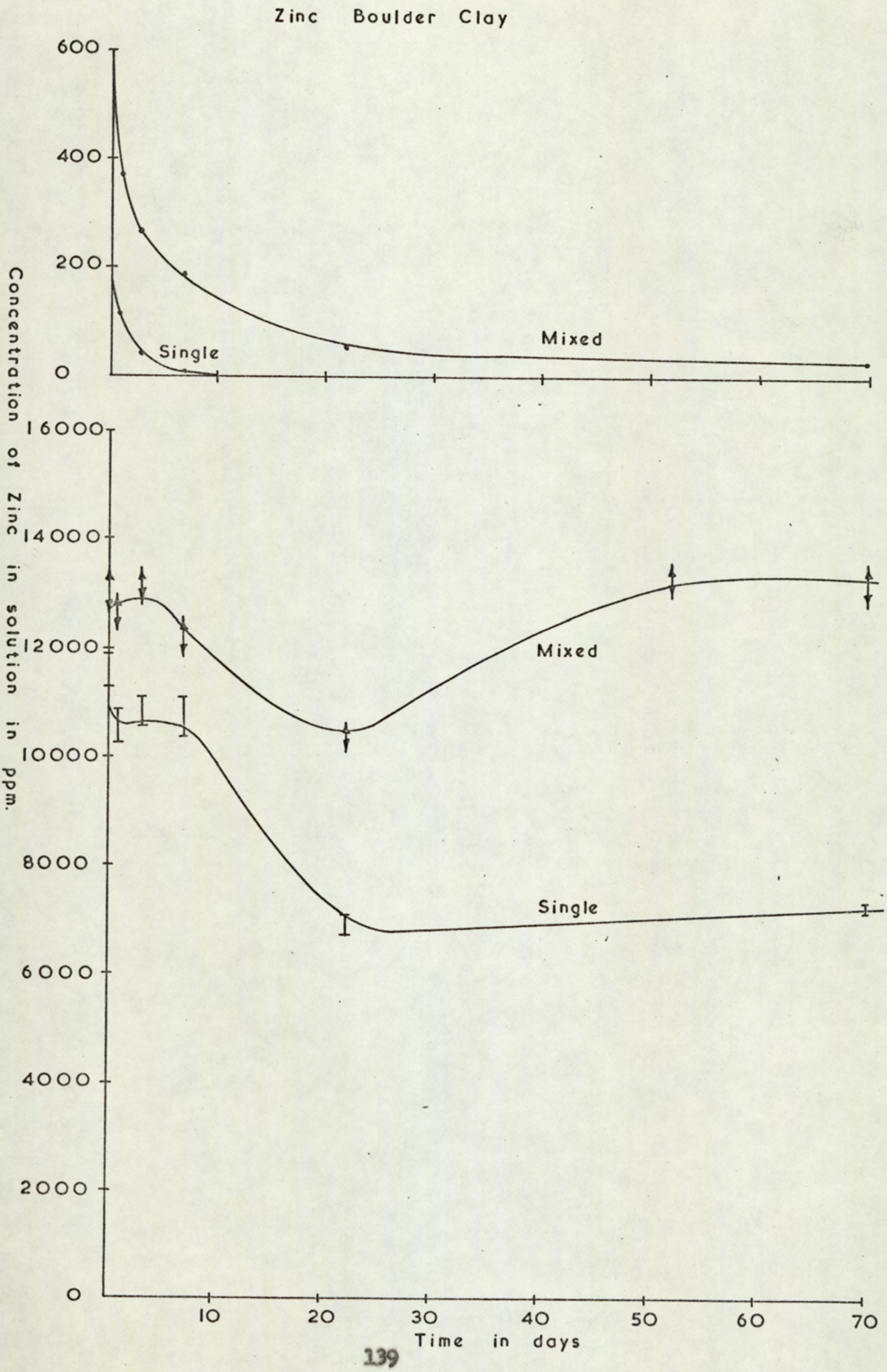
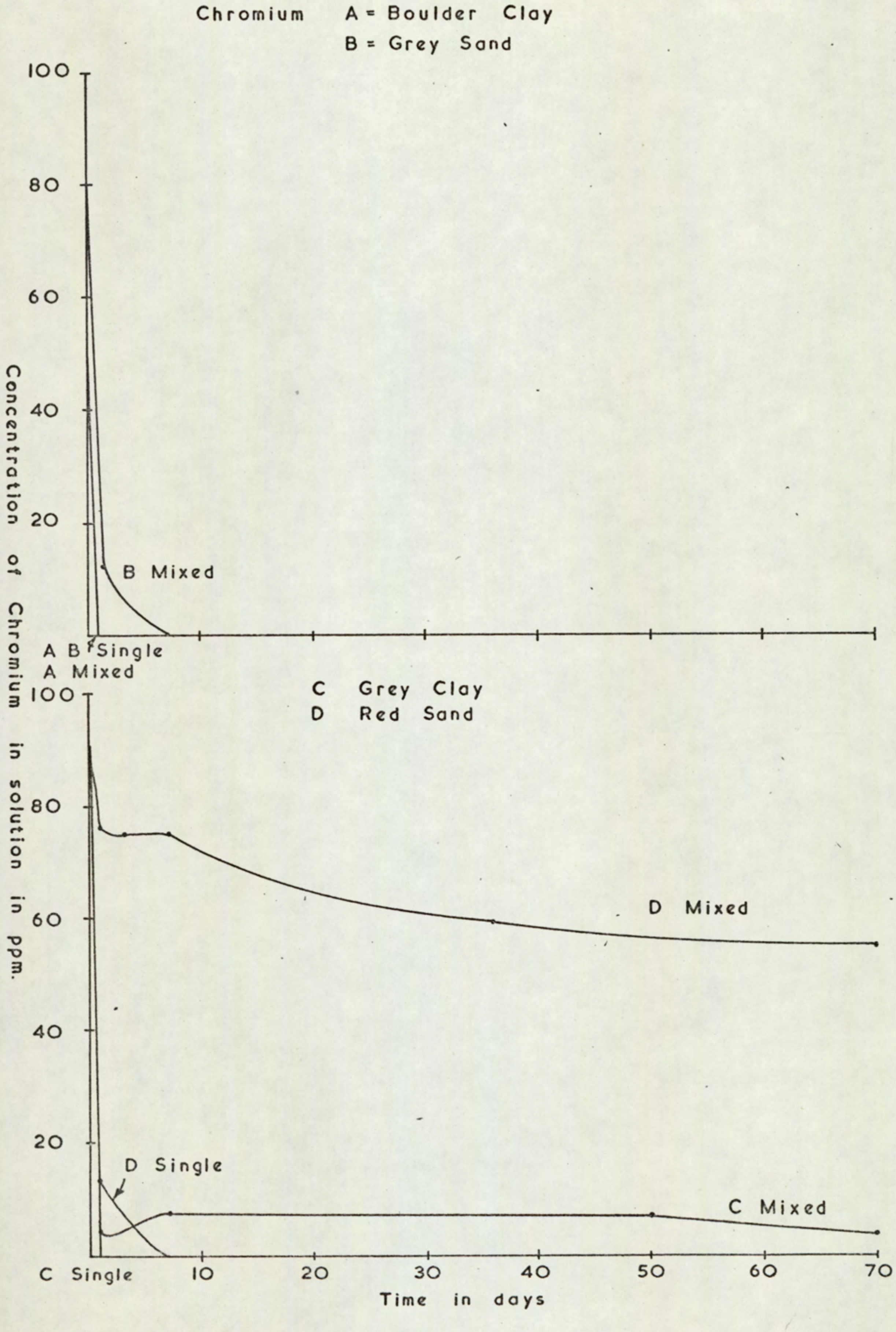

Zinc Boulder Clay
600
400
200
0
Mixed
Single
16000
14000
12000
10000
8000
6000
4000
2000
0
Mixed
Single
Concentration of Zinc in solution in ppm.
10
20
30
40
50
60
70
Time in days

FIG. 27.13



Chromium A = Boulder Clay
B = Grey Sand
100
80
60
40
20
B Mixed
A B Single
A Mixed
C Grey Clay
D Red Sand
100
80
60
40
20
D Mixed
D Single
C Mixed
C Single
10
20
30
40
50
60
70
Concentration of Chromium in solution in ppm.
Time in days

FIG. 27.14

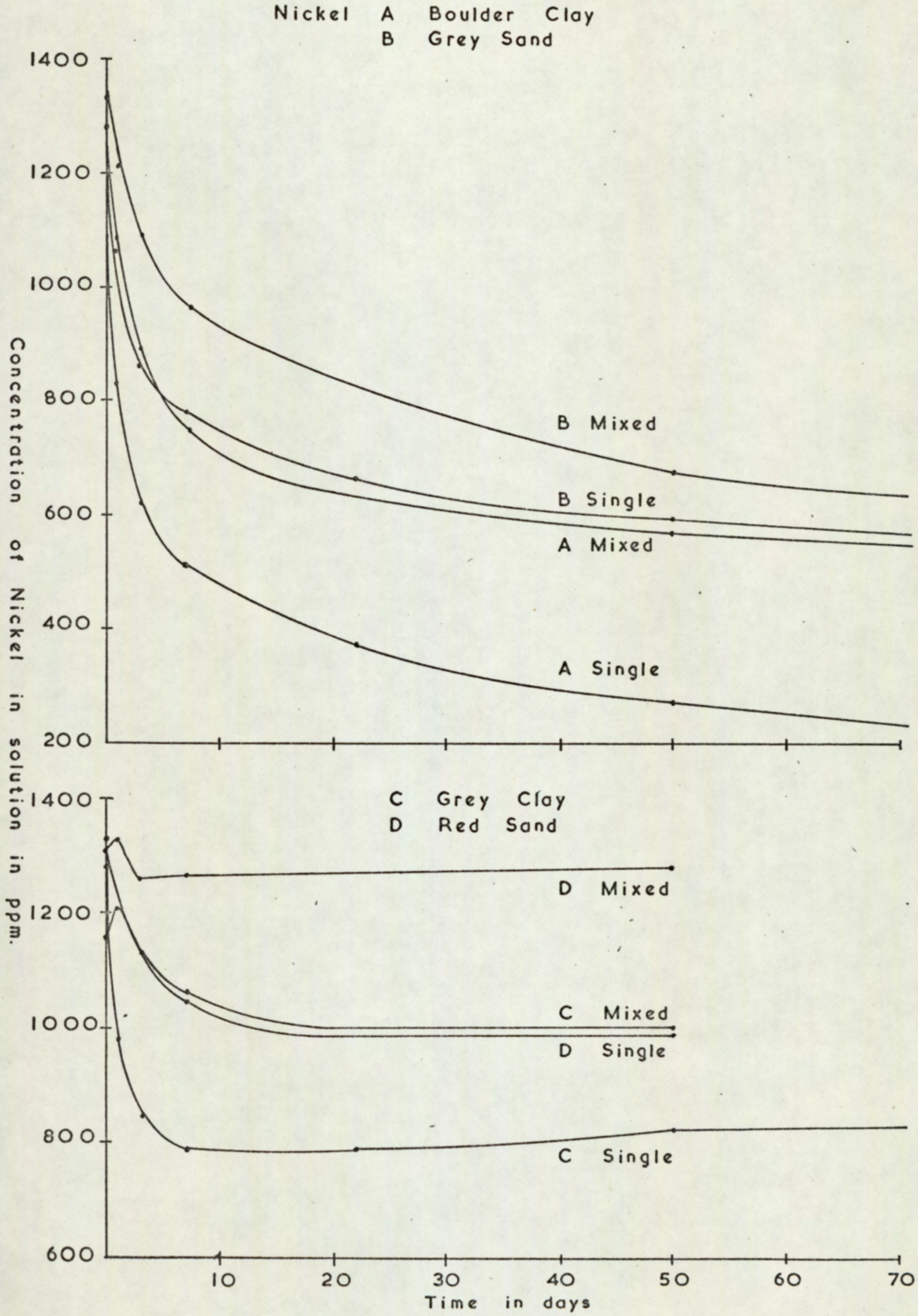
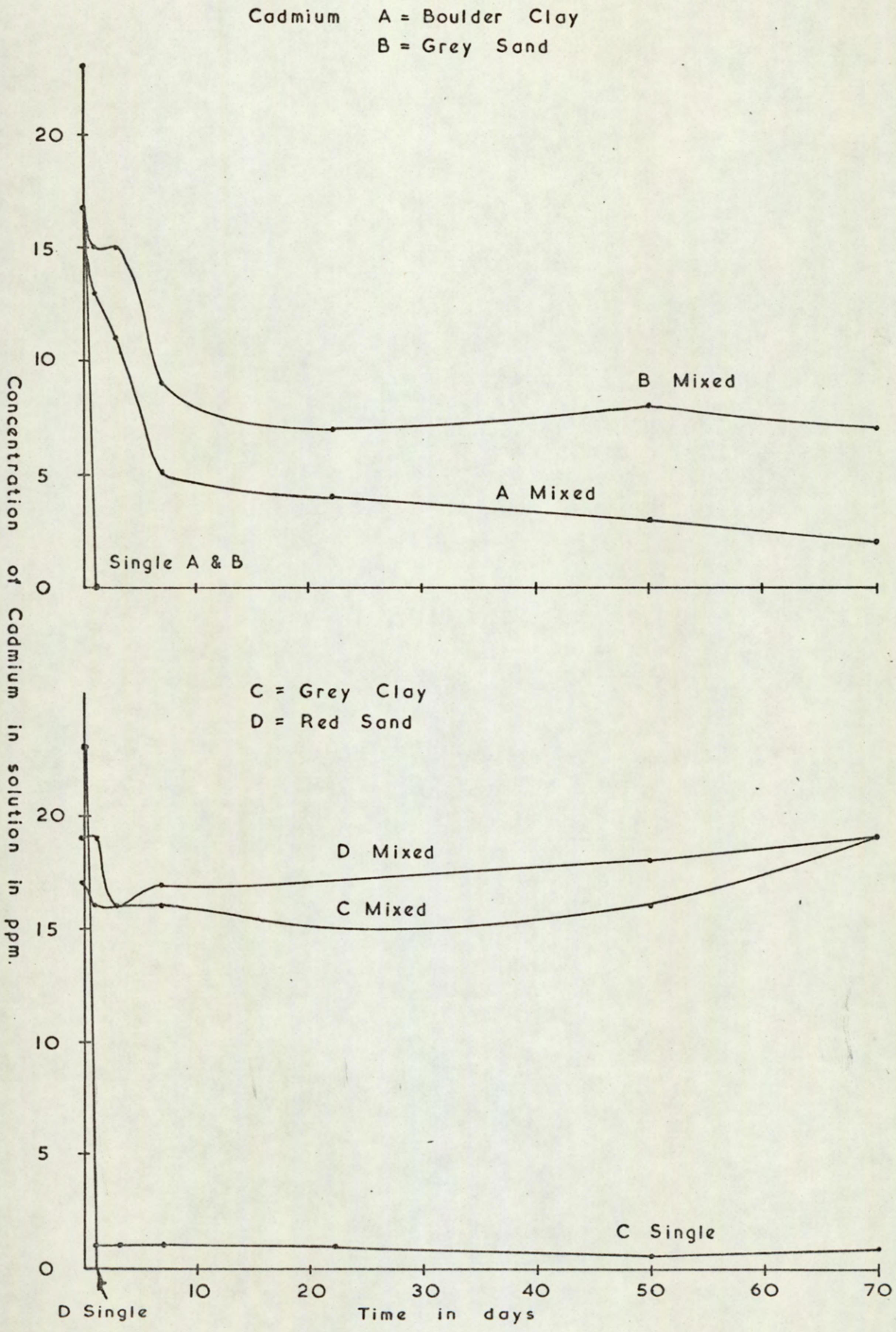

Nickel A Boulder Clay
B Grey Sand
1400
1200
1000
800
600
400
200
B Mixed
B Single
A Mixed
A Single
C Grey Clay
D Red Sand
1400
1200
1000
800
600
D Mixed
C Mixed
D Single
C Single
Concentration of Nickel in solution in ppm.
10
20
30
40
50
60
70
Time in days

FIG. 27.15


Cadmium A = Boulder Clay
B = Grey Sand
B Mixed
A Mixed
Single A & B
C = Grey Clay
D = Red Sand
D Mixed
C Mixed
C Single
D Single
Concentration of Cadmium in solution in ppm.
Time in days
0
5
10
15
20
10
20
30
40
50
60
70

5.3.8. Experiments on Rocks from Mitco Tip

Experiments were carried out on Etruria Marl Series red clay from Mitco tip. The concentrations and combinations of elements were similar to those used for the Betton Abbotts rock experiments. Again the results are represented graphically as a function of the reduction in concentration of metal ions in solution against time, and in tabular form in Table 6 to allow comparison of the results for single and mixed element solutions.

TABLE 6

The results of the experiments on the adsorption of metal ions by the Mitco red clay rock type in percentage adsorption and absolute adsorption in milliequivalents per 100 gms of rock.

MITCO CLAY

SINGLE ELEMENT SOLUTION			MIXED ELEMENT SOLUTION		
Solution	Max % Abs	Abs in Meq/100 gm	Solution	Max % Abs	Abs in Meq/100 gm
Fe 518 pH3	100	9.2	Fe 539 pH3	100	9.6
Fe 567 pH9	100	10.1	Fe 539 pH9	100	9.6
Fe 12627 pH3			Fe 9039 pH3	20	31.9
Fe 18070 pH9	3	10.2	Fe 16485 pH9	3	7.2
Pb 50 pH3	100	0.16	Pb 41 pH3	100	0.13
Pb 50 pH9	100	0.16	Pb 45 pH9	100	0.14
Cr 93 pH3	100	1.8	Cr 90 pH3	100	1.8
Cr 95 pH9	100	1.9	Cr 90 pH9	100	1.8
Cd 18 pH3	100	0.11	Cd 25 pH3	16	0.02
Cd 25 pH9	100	0.15	Cd 16 pH9	16	0.02
Ni 1161 pH3	50	6.6	Ni 1310 pH3	26	3.9
Ni 1171 pH9	52	6.9	Ni 1214 pH9	22	3.04
Cu 172 pH3	100	1.8	Cu 93 pH3	93	0.9
Cu 197 pH9	100	2.0	Cu 186 pH9	94	1.8
Cu 11290 pH3	48	55.2	Cu 9184 pH3	8	7.2
Cu 11061 pH9	47	52.5	Cu 9151 pH9	5	4.2
Zn 582 pH3	97	5.8	Zn 594 pH3	41	2.5
Zn 531 pH9	98	5.3	Zn 537 pH9	34	1.8
Zn 13227 pH3	17	22.6	Zn 27973 pH3	11	31.4
Zn 13374 pH9	16	22	Zn 12077 pH9	6	7.8

Fig 28. Graphs of the variation in concentration of metal in solution against time for single element and mixed element solutions in contact with red clay from the Mitco Site.

Fig 28. 1. Iron

Fig 28. 2. Copper

Fig 28. 3. Zinc

Fig 28. 4. Nickel

Fig 28. 5. Chromium, Cadmium

FIG. 28.1

Mitco Rock Iron

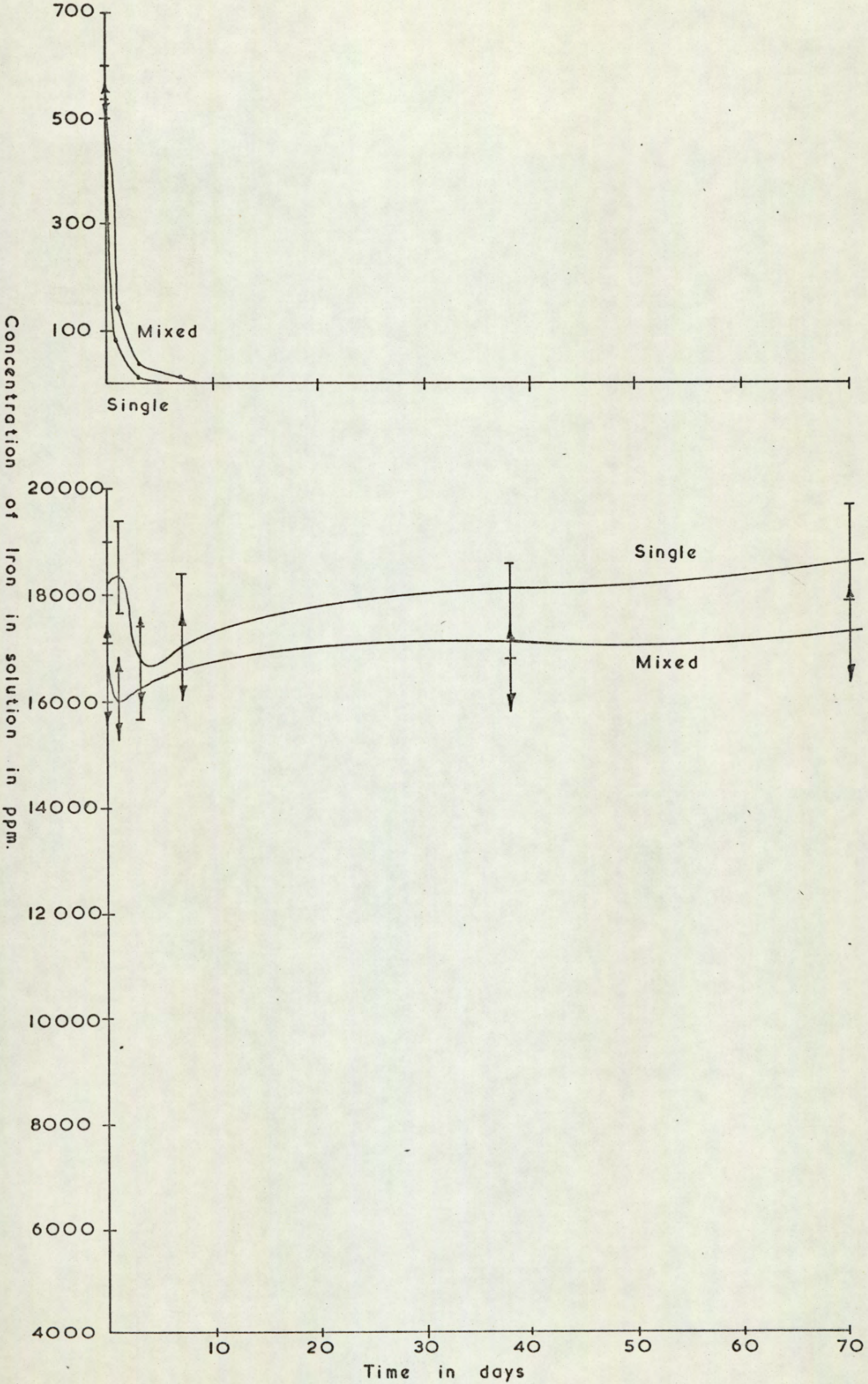


FIG. 28. 2

Mitco Rock Copper

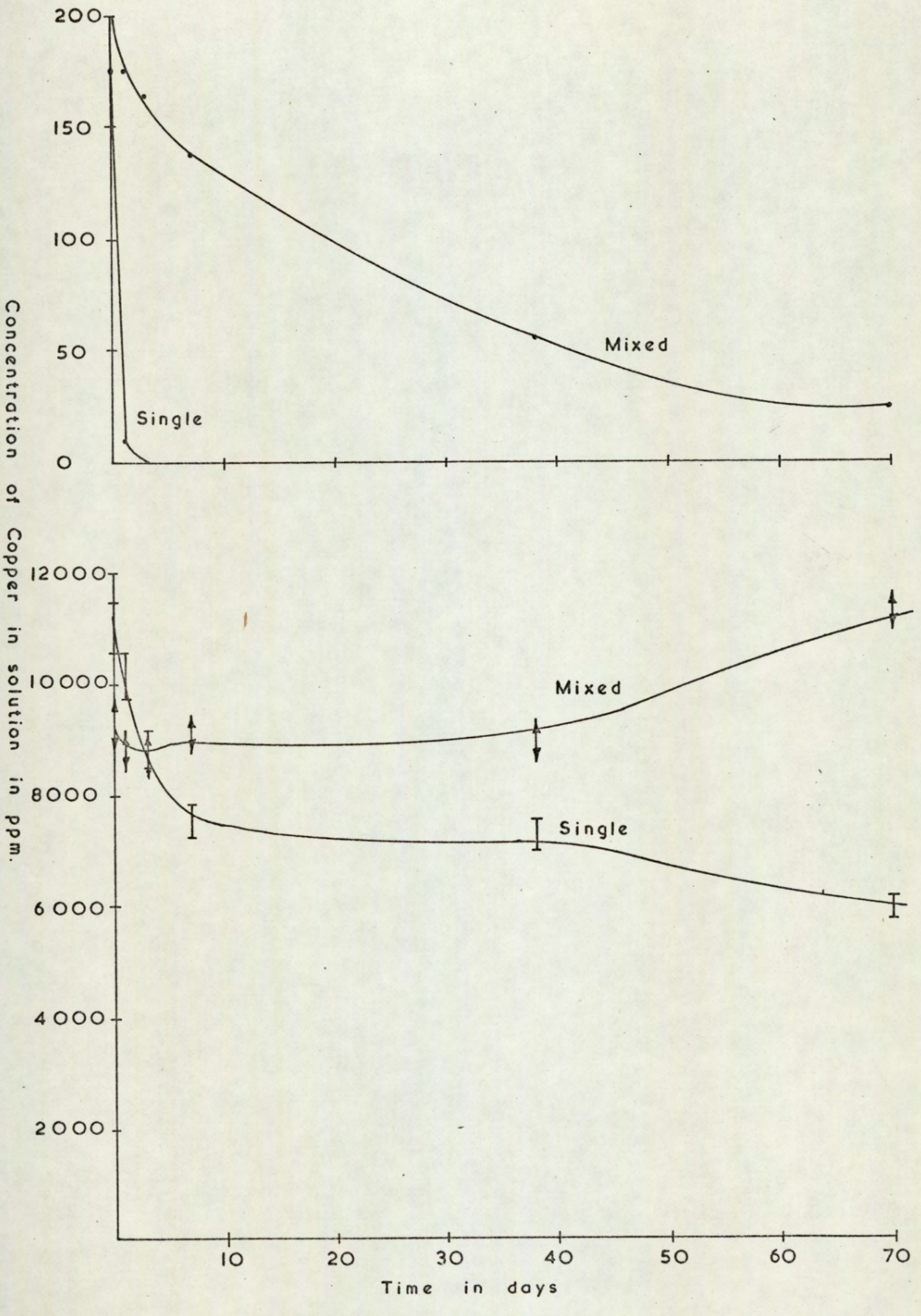


FIG. 28.3

Mitco Rock Zinc

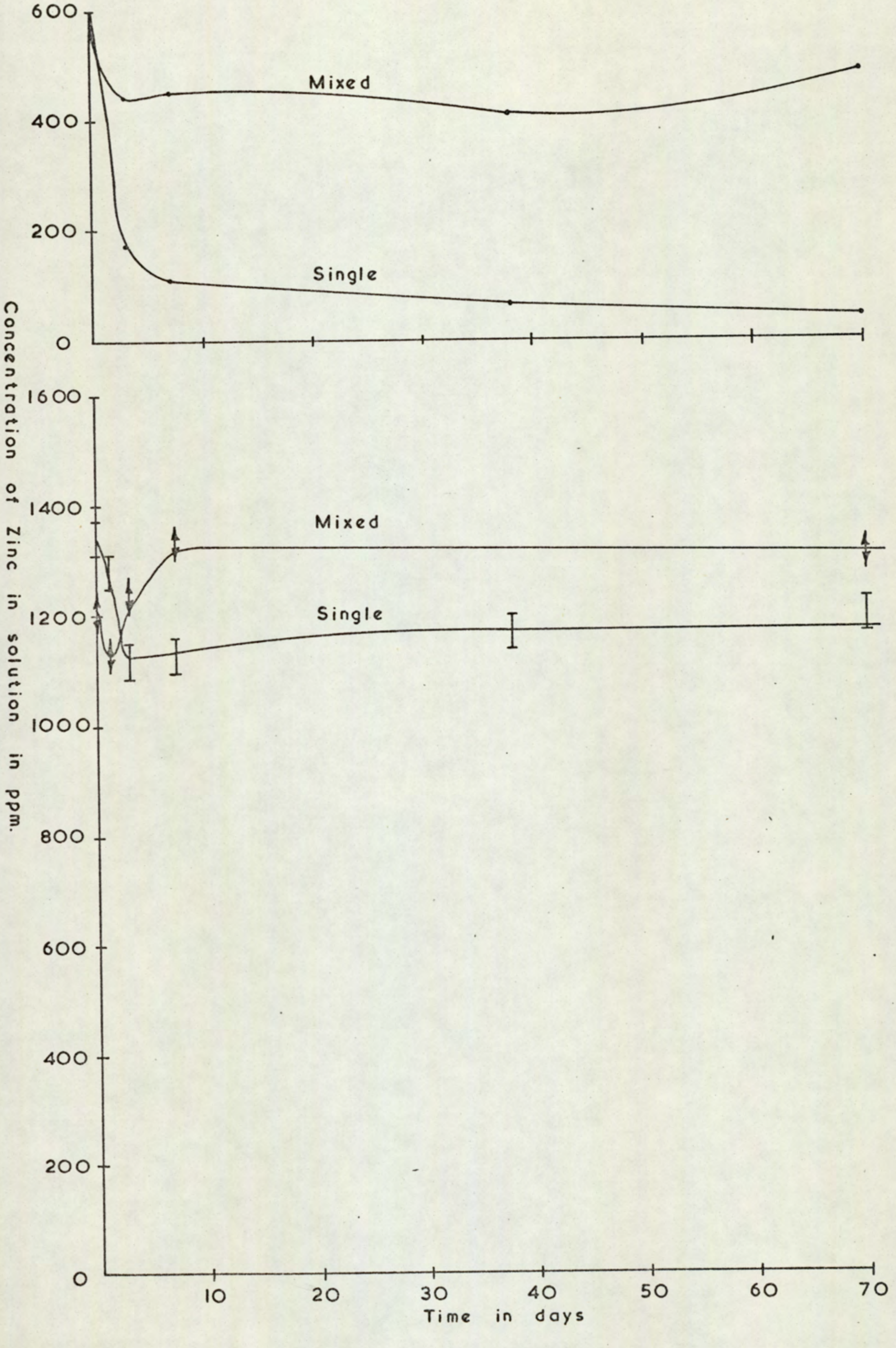


FIG. 28.4

Mitco Rock Nickel

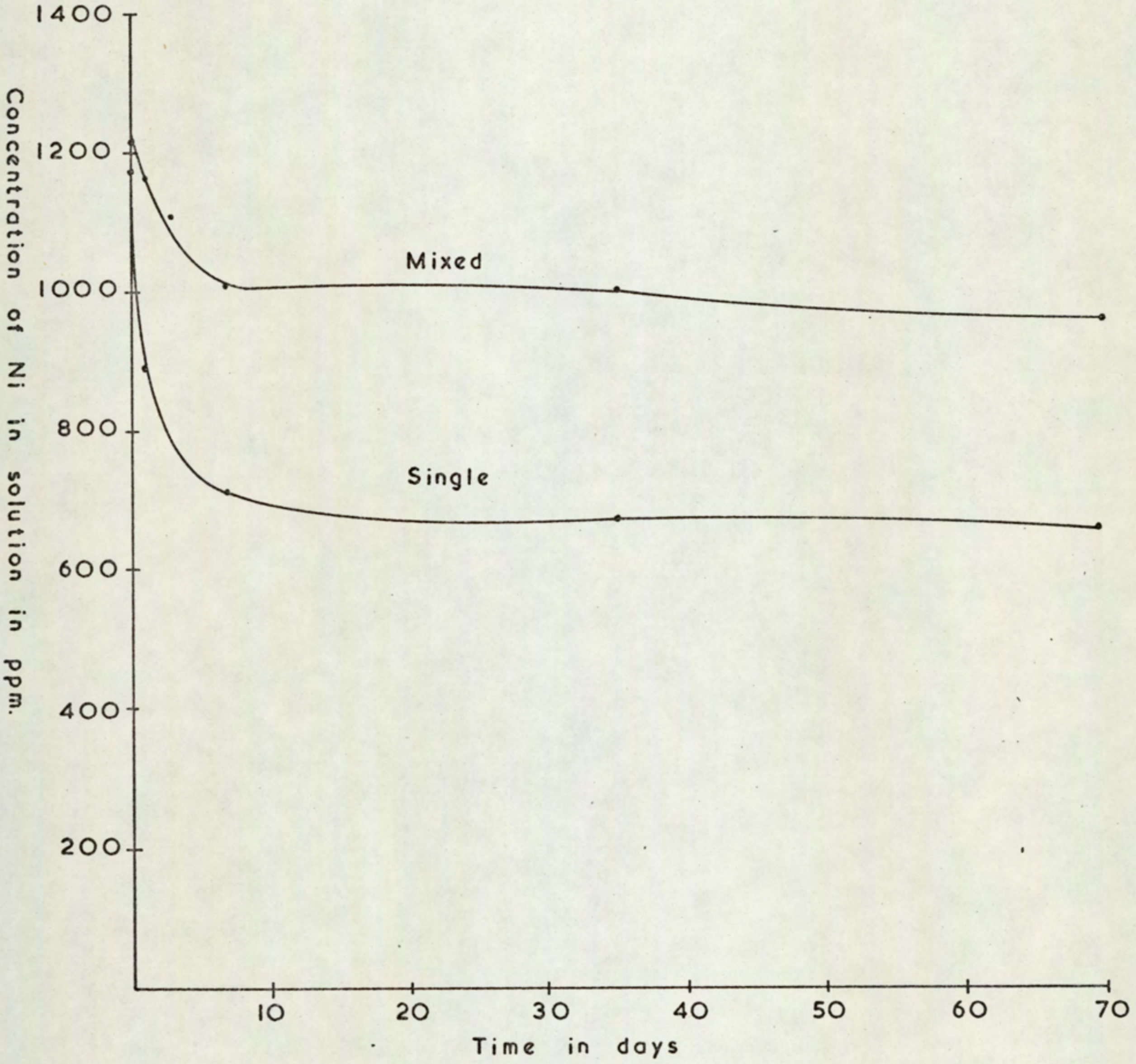
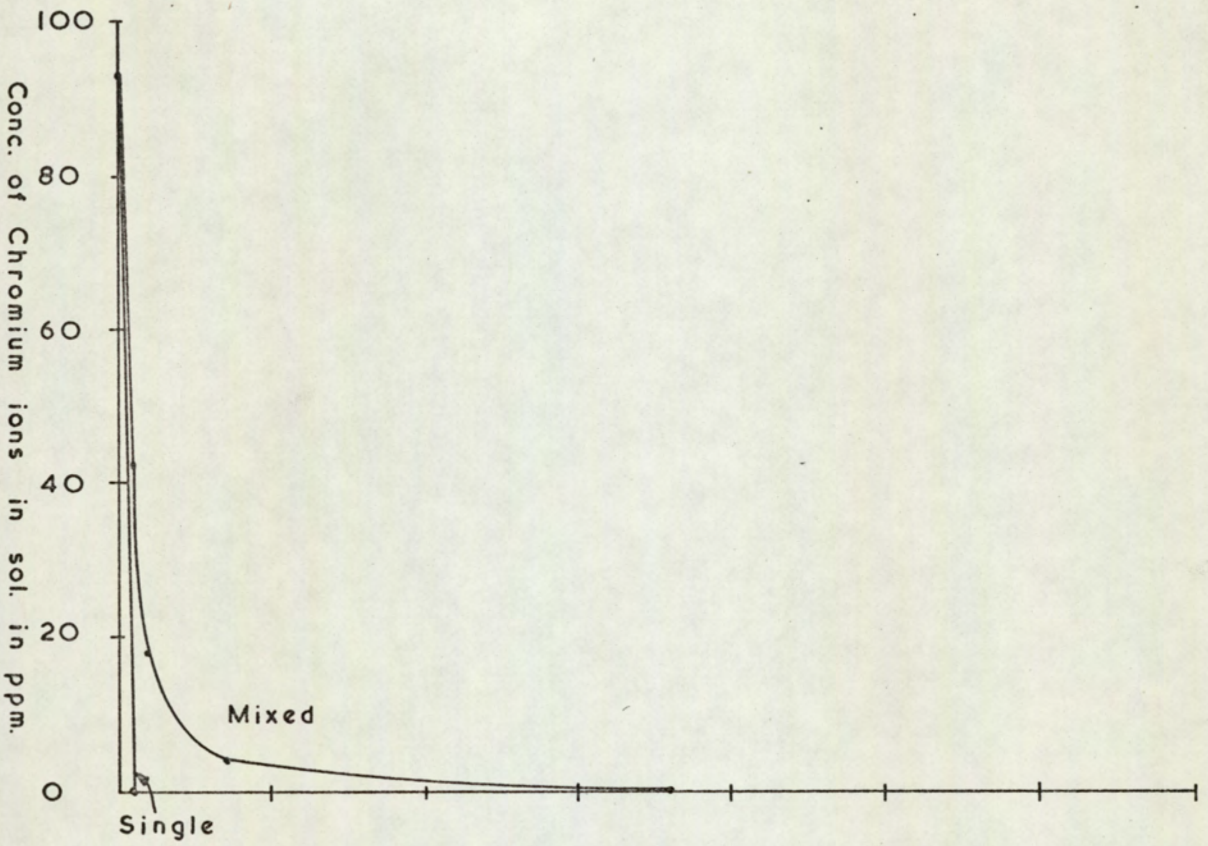
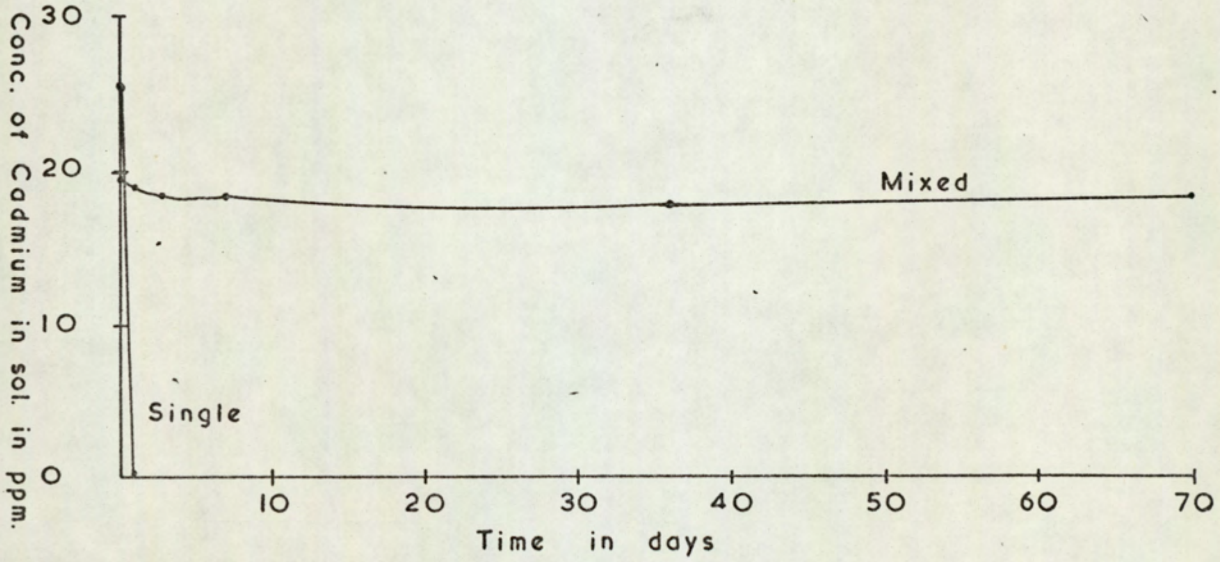


FIG. 28. 5

Mitco Rock Chromium



Cadmium



5.3.9. Experiments with Effluent Samples

Finally, a series of experiments were carried out using the effluent samples supplied by the disposal companies. The effluent from the Walsall Wood site was reacted with Coal Measures shales, kaolinite and montmorillonite. The four Betton Abbotts rock types together with montmorillonite and kaolinite were reacted with the effluent from the Shrewsbury site. The experiments set up using Mitco rock types and the effluent from the site were only analysed once as the concentration of metal ions present was below detection levels.

The results are represented graphically as a function of the reduction in concentration of metal ions in solution with time, and as a table giving the maximum percent adsorption, and the amount of metal ion adsorbed in meg/100 gms of rock to allow comparison with the adsorption expected for the elements in similar concentrations, but in pure acid solutions (Table 7), for the reaction with Walsall Wood site effluent. For the experiments with effluent from the Betton Abbotts site, the results are presented in a table showing the maximum percent adsorption and the adsorption in milliequivalents per 100 grams of rock (Table 8).

TABLE 7

The results of the adsorption of metal from effluent in contact with Coal Messure Shale, Kaolinite and Montmorillonite

Original Concentration

Total meq/100 grams rock = 741.92

MINE - EFFLUENT

	Max % Abs	Abs Meq/100gm		% Redcn in Ads		Max % Abs	Abs Meq/100gm		% Redcn in Ads
		Effluent	Pure Soln				Effluent	Pure Soln	
Pb 0.16 meq/ 100gm					Zn 45.78 meq/ 100gm				
S1	48	0.08	0.1	20	S1	19	8.5	18.4	54
S2	38	0.06		40	S2	15	6.87		63
K1	-	-	0.13	100	K1	15	6.91	7.85	12
K2	-	-		100	K2	16	7.11		10
M1	80	0.13	0.13	0	M1	15	6.91	31.25	78
M2	82	0.13		0	M2	18	8.26		74
Cr 18.65 meq/ 100gm					Fe 668.45 meq/ 100gm				
S1	25	4.47	18.2	76	S1	-	-		
S2	25	4.53		75	S2	-	-		
K1	30	5.31	4.26		K1	-	-		
K2	30	5.25			K2	-	-		
M1	26	4.59	17.75	74	M1	0.3	1.8		
M2	29	5.12		71	M2	2.02	13.53		
Cu 8.66 meq/ 100gm					Ni 1.22 meq/ 100gm				
S1	23.65	2.05	7.7	73	S1	4	0.05	1.1	96
S2	21	1.86		76	S2	4	0.05		96
K1	41	2.24	2.67	16	K1	8.4	0.10	0.2	50
K2	24	2.09		22	K2	10	0.10		50
M1	21	1.79	8.4	79	M1	10	0.10	1.2	92
M2	27	2.3		78	M2	7	0.08		92

TABLE 8

The results of the adsorption of metal from effluent in contact with Betton Abbotts Site rocks, kaolinite and montmorillonite.

SHREWSBURY EFFLUENT

Cadmium 182	Max % Abs	Abs in Meq/100 gm	Zinc 583	Max % Abs	Abs in Meq/100 gm
BC 1	5	0.0595	BC 1	45	2.6872
2	3	0.0536	2	47	2.8000
WES 1	3	0.0298	WES 1	41	2.4410
2	4	0.0476	2	39	2.3282
GCC 1	3	0.0298	GCC 1	1	0.6150
2	5	0.0298	2	10	0.6256
BHS 1	3	0.0298	BHS 1	10	0.6256
2	3	0.0298	2	9	0.5641
Ka1	4	0.0476	Ka1	3	0.1949
2	5	0.0536	2	2	0.1333
M 1	6	0.0655	M 1	28	1.6923
2	3	0.0298	2	28	1.6923
Copper 858	(Still reducing)		Iron 52319		
BC 1	83	7.2987	BC 1	14	288
2	79	6.9011	2	14	125
WES 1	81	7.07	WES 1	10	91
2	81	7.0642	2	7	68
GCC 1	86	7.5229	GCC 1	14	126
2	85	7.4108	2	12	114
BHS 1	89	7.7574	BHS 1	6	53
2	86	7.6656	2	7	70
Ka1	86	7.5229	Ka1	6	59
2	87	7.5841	2	6	56
M 1	77	6.6157	M 1	16	148
2	88	7.7166	2	16	148

Fig 29. Graphs of the variation in concentration of metals in an effluent sample which is in contact with kaolinite, montmorillonite and Coal Measures shale, against time.

Fig 29. 1. Zinc, Copper

Fig 29. 2. Nickel, Iron

Fig 29. 3. Lead, Chromium, Cadmium

FIG. 29.1

Walsall Wood Effluent

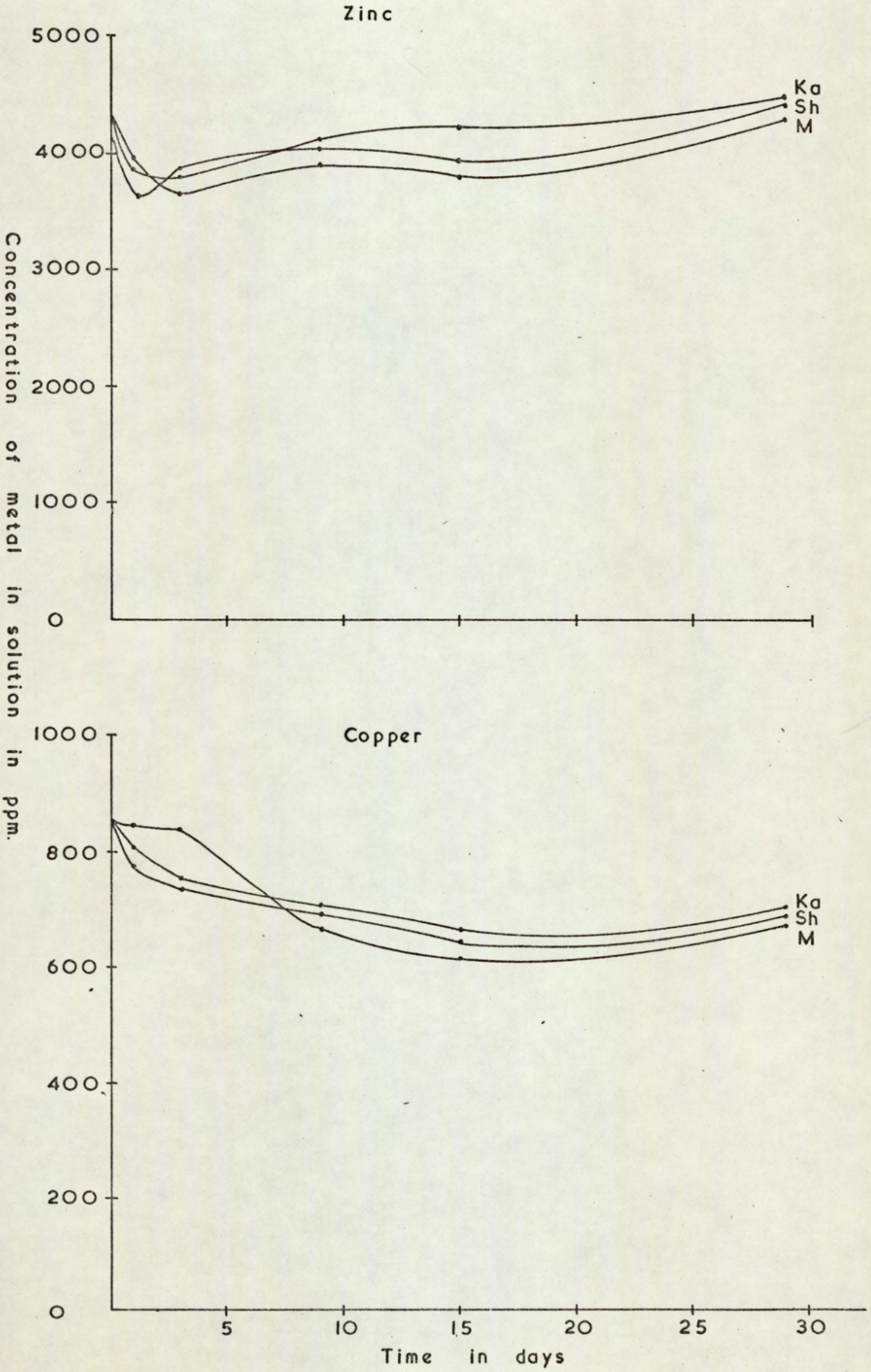


FIG. 29. 2

Walsall Wood Effluent

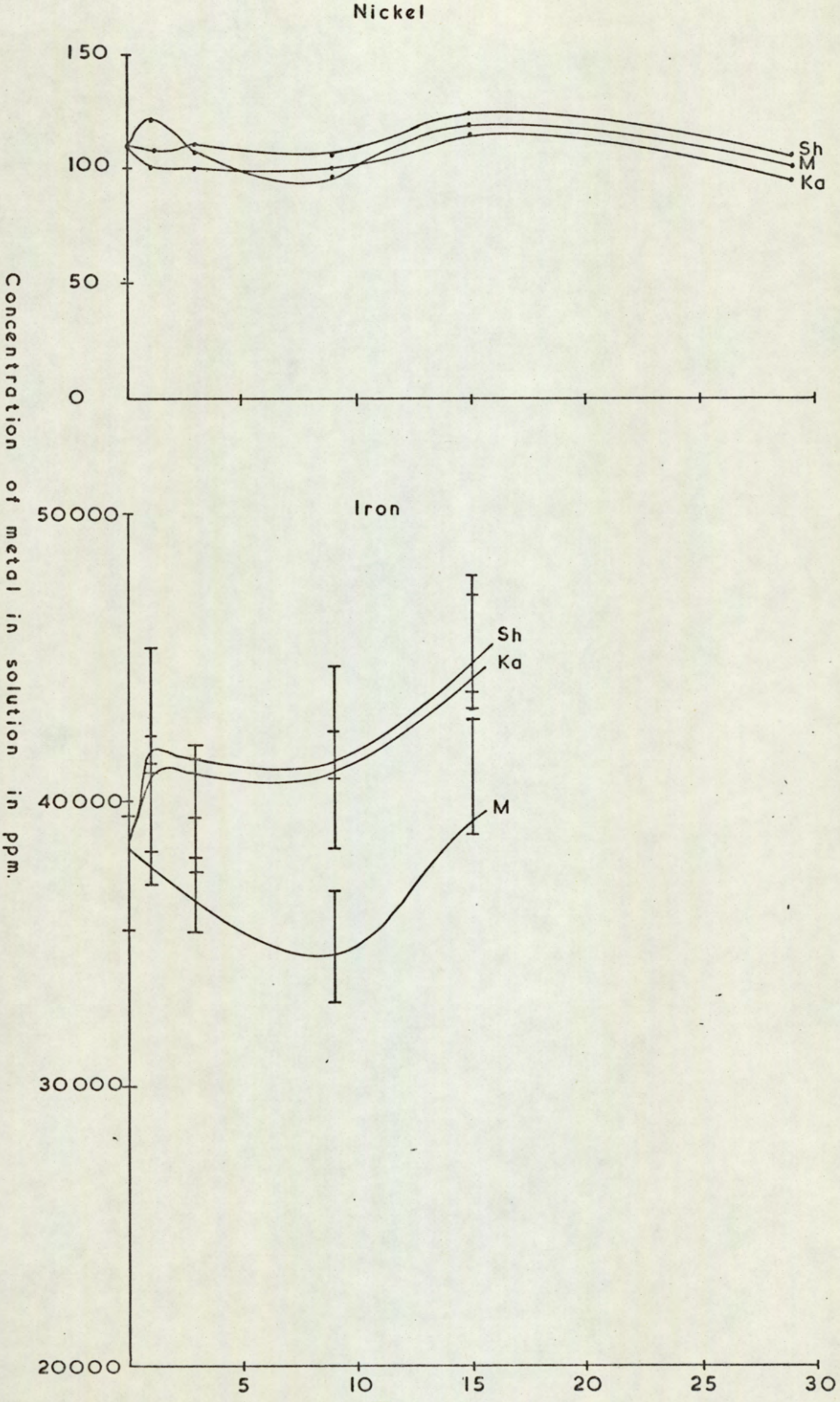
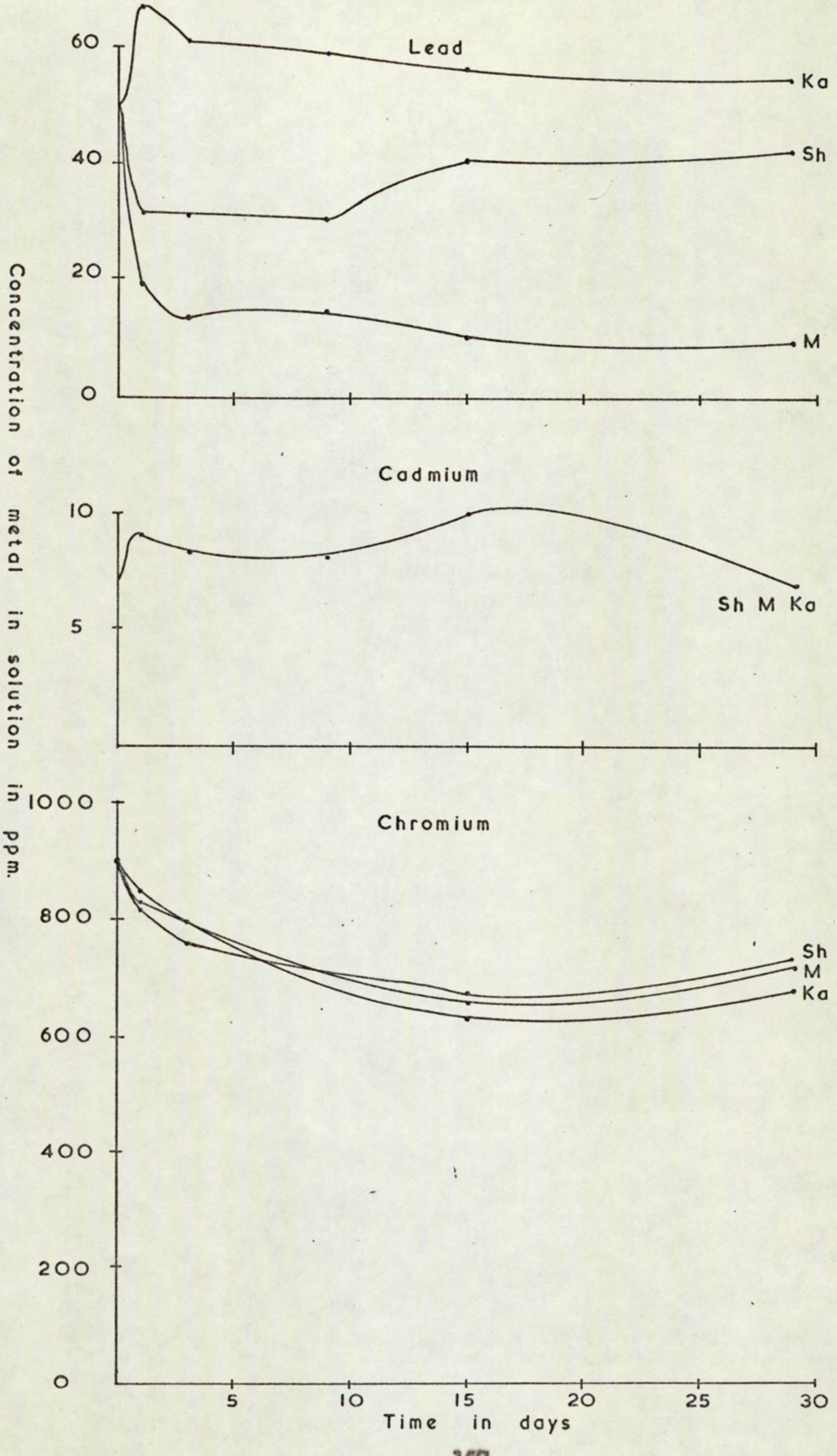


FIG. 29.3

Walsall Wood Effluent



CHAPTER 6

Analysis of the rocks used for adsorption experiments

6.1 Clay Minerals

The chemical specifications for the pure clay minerals, montmorillonite and kaolinite, were given in section 5.1.

6.2 Coal Measures Rocks

The Coal Measures shale and sandstone were examined by X ray diffraction spectrometry (X.R.D.) to establish their clay mineral content. Traces were obtained for samples of grain size below 600μ, 20μ, 10μ, and 2μ. As the grain size of the sample decreased the coarser elements such as quartz were reduced and the clay mineral peaks became more apparent. The traces were run at a speed of 1° 2θ per minute from 2° to 60° covering the peaks which identify clay minerals. From the traces quartz, kaolinite, and illite were recognised. The presence of chlorite was indicated by a small peak at d = 14.255, but the main chlorite peak at d = 7.1379 was masked by the prominent kaolinite peak at this point. A peak at d = 4.9828 and a smaller peak at d = 1.9976 showed the presence of muscovite.

A small peak at d = 2.82 was present on the trace for the sub 2μ sample. d Values nearest to this peak, for minerals which may be expected to occur in these rocks, are those of the carbonate minerals, although they are not an exact fit. In an analysis of clay formations[54] values of 0.8 - 1.2% CaO, 1.0 - 1.6% CaO, 1.0 - 2.0% CO_2 are quoted, indicating that carbonate minerals may be present. Thus, although the peak cannot be positively identified it would seem likely that it represents a carbonate mineral.

The trace for the 2μ slide showed no evidence for the presence of expansible clay minerals in the 2° to 20° range. This was confirmed by the trace for the glycolated 2μ sample slide which appeared identical to the trace for the untreated sample slide.

The peak area for the quartz and clay minerals indicate that there is more quartz present in the sand than the shale, and more clay present in the shale.

The presence of illite, kaolinite, and chlorite was confirmed by an infra red (I.R.) trace. In the region between 3600 cm^{-1} to 4000 cm^{-1} on the I.R. trace a triplet was present, the pattern of which was similar to that found by Kodama et al.[55] for an experimentally prepared mixture of kaolinite, illite, and chlorite in a 1:1:1 ratio. After separately treating the Coal Measures shale with molar hydrochloric, nitric, and sulphuric acids, the rocks were again analysed using I.R. absorption. The only indication of any alteration occurred in the rocks treated with nitric acid, where an additional peak was present at 1383 cm^{-1}. This peak indicated that the nitrate ion had been adsorbed onto the clay minerals.

Atomic absorption analysis (A.A.) was carried out on the Shale (See Appendix 4 for the method), revealing a very high (35816 μgm gm^{-1}) iron content. This high value was expected from black shales where a high iron sulphide content was present. Nickel, copper and zinc were present in concentrations of 147, 193 and 145 μgm gm^{-1} respectively. Chromium was present in much smaller concentrations, 63 μgm gm^{-1} and cadmium was not detected by the instrument.

6.3. Rocks from the area of the Mitco Site.

X.R.D. analysis of rocks from the Mitco site revealed the presence of quartz, kaolinite and illite. The illite peak at d = 10.048 had a shoulder which was interpreted as being due to the presence of a mixed layer illite - montmorillonite clay mineral. A peak at d = 3.1977 showed that a feldspar was present. The peak at d = 2.82, seen on the traces produced for the Coal Measures Shale, tentatively identified as a carbonate mineral, was present on the traces from the coarser (sub 600μ , and sub 20μ) samples for Mitco clay. Peaks at d = 2.69 and d = 2.45 were interpreted to represent the presence of goethite, an iron-carbonate mineral.

A.A. analysis revealed a very high iron content, 52,032 μgm gm^{-1}. This was expected from the red colouration (iron oxides) of the rock. The second most abundant metal in the rocks was zinc, present in quantities of up to 1000 ugm gm^{-1}. (Appendix 5) Nickel and chromium were less abundant, with concentrations of 148 and 123 ugm gm^{-1} respectively, while copper was present in a concentration of 600 ugm gm^{-1}.

6.4. Betton Abbotts Site Rocks

Quartz was identified, by X.R.D. analysis, in all four rocks from this site; the borehole (red) sand; the boulder (red) clay; the grey sand: the grey clay. Kaolinite also was present in all four rocks, but the relative size of the d = 7.1379 peak indicated that there was a smaller quantity of the mineral in the borehole sand than in the other three rock types. Similarly, illite was present in all four rock types, but to a lesser degree in the borehole sand. However, the peak for illite at d = 10.048, on the trace of the sub 2μ sample for the borehole sand had a shoulder indicating the presence of mixed layer clays, probably illite - montmorillonite. A double peak at d = 3.53 to 3.59 suggests the presence of chlorite in these rocks, confirmed by peaks at d = 4.7199 and d = 14.255. After glycolation the peak was still present at d = 14.255 confirming that it represents chlorite, and not an expansible clay. Again, the borehole sand had less chlorite present relative to the other three rock types, Muscovite was present in the grey and red clays, and in the grey sand.

This was identified from the peak at d = 1.9893, and the nature of the quartz peak at d = 3.351 where it overlaps with a muscovite peak. Feldspars were detected in the coarser fractions of all the rock samples, identified by an indeterminate feldspar peak at d = 3.24. In addition, a peak at d = 2.50, present on the traces for the grey and red clays, and the grey sand was identified as a plagioclase feldspar peak.

The two clay samples and the grey sand are similar in their mineral content, but the borehole sand differs considerably in that it has a much lower clay content.

A.A. analysis revealed a high iron content in the grey sand and in the boulder clay, 39,308 and 33,864 μgm gm^{-1} respectively. The borehole sand and grey clay have a lower iron content than the other two rock types, 17,381 and 26,414 μgm gm^{-1} respectively. The relatively low iron content for the borehole sand can be explained as being the result of iron oxides occurring only as very thin coatings on the rock grains and that little or no iron is present as clay minerals or other cementing material. Copper is the second most abundant metal present, with values of 300 μgm gm^{-1} for the two clays ' 500 μgm gm^{-1} for the grey sand and 650 μgm gm^{-1} for the borehole sand. Nickel is present in all four rock types in concentrations of 150 μgm gm^{-1}, while zinc and chromium are present in tens of μgm gm^{-1}. The results of the AA analyses are given in Appendix 5.

CHAPTER 7

DISCUSSION

7.1 Objectives

A literature survey had indicated that reaction with clay minerals results in a removal of metal ions from solution [26, 28, 30, 31]. The present work was carried out to determine whether any significant removal of metal ions could be expected when effluent reacts with rocks at disposal sites. Effluents are generally of such a complex nature that it would be difficult to establish the reason for any reduction of metal concentration which may be observed. Hence, to achieve any understanding of the mechanism involved it was decided to use solutions of pure metal salts in solution to eliminate any effects of organic materials which may be present in effluents. Pure clay minerals were used in addition to site rocks, again to reduce the number of variables in the experiments. As the work progressed, more complex solutions were developed, containing more than one element, and eventually the actual effluent was used, with the early results being used to understand the results achieved with the more complex situations.

7.2 Adsorption Experiments

7.2.1 Restricted Variable Experiments. Although simple solutions of single metals in an acidic solution were used the choice of concentration was governed by analyses of typical effluents. When solutions were prepared containing more than one metal, again the relative concentrations were governed by analyses of actual effluent samples. The experiments were carried out on the pure clay minerals montmorillonite and kaolinite. Both minerals adsorbed metals ions although the efficiency of montmorillonite was far higher than that of kaolinite, as is expected from the greater cation exchange capacity of the former (Section 3.1).

The results of the experiments to establish the adsorptive capacity of montmorillonite and kaolinite (Section 5.3.3) demonstrate the difference in the adsorptive capacity of the minerals. The saturated state was achieved when further increase in the original concentration of metal ions in solution failed to increase the quantity of metal adsorbed by the clay mineral. For montmorillonite this state was not reached with the concentration of metal ions used (Fig 23). Saturation of kaolinite was achieved with chromium, copper and iron, while the decrease in the gradient of the curves for cadmium, nickel and lead indicate that saturation was approached (Fig 23). For zinc greater adsorption was observed with the increasing concentrations applied indicating that saturation was not achieved with the quantity of metal used. The concentration of metal was not increased to saturation for all the elements as the concentrations used were sufficient to cover the range found in the majority of effluents.

The number of milli equivalents of metal adsorbed before the saturation state was achieved, varied with the metal species, suggesting that the position of equilibrium for the adsorption process is not the same for all the metal species. Kaolinite readily demonstrates this fact with a maximum adsorption of 4 meq/100 gm clay and 7 meq/100 gm clay for chromium and iron respectively. Surprisingly, zinc is adsorbed to the greatest extent. A plausible, though currently unsupported explanation is that zinc may be able to isomorphically substitute for Mg^{2+} ions present in the clay minerals [26]. This would not be possible for tripositive ions and is less probable for the other dipositive transition metal ions whose chemistry and stereochemistry differ from those of zinc. Although tripositive cations cannot isomorphically substitute for Mg^{2+} it is possible that they may substitute for Al^{3+}. However, atomic absorption analysis of solutions for aluminium showed that the metal is not present in sufficient quantities to lend support to this hypothesis.

Thus the experiments of section 5.3.3. demonstrate that montmorillonite has a greater capacity than kaolinite, to adsorb metal ions. Comparison of the relative quantities of metal adsorbed by kaolinite before saturation was reached indicates the dependence of the adsorption process on both the metal species and clay species. The majority of adsorption for montmorillonite will

will be due to ion exchange [26], as exchangeable ions are available, mainly between the clay structural units [26, 30]. Electrostatic attraction is likely to occur on kaolinite where broken bonds at the surface account for the majority of surface charge [26]. Co-ordination is equally favourable for both clay minerals as they both have oxygen molecules exposed at the surface.

The results of the experiments in sections 5.3.3. and 5.3.5. show the effects of the presence of more than one metal ion in solution on the adsorbance by montmorillonite and kaolinite. From the graphs of Fig 23 the adsorption from a single element solution of a particular concentration in contact with montmorillonite and kaolinite may be ascertained. From these graphs the adsorption for the elements used in the combination solutions C and D (Section 5.3.5) if in a single element solution, can be calculated. The values are compared with the actual adsorption observed for the combination experiments in Table 9. There is a reduction in the adsorption for a particular element when in competition with other elements, although the percentage reduction is inconsistant.

Where zinc and iron are in competition (Combination C) iron is more selectively adsorbed, with a smaller reduction in adsorption, compared to the single element solution, than for zinc. The original concentration of zinc in this case is higher than that of iron, which would give an advantage in the competition for adsorption sites if the only process involved was one of equilibrium adsorption.

Where four elements are in competition (Combination D) they may be placed in the order of their ability to compete for exchange sites. The elements are arranged in the order of their percentage reduction in adsorption from the multi-element solution, compared with the single element solutions, for each rock type:

Montmorillonite	Zn > Cu > Ni > Cr
Kaolinite	Cu > Zn > Cr > Ni

TABLE 9

Comparison of the adsorption of metal ion with and without competition **from** other metals

COMBINATION C		MONTMORILLONITE			KAOLINITE			SHALE		
Metal	Original Conc ppm	Adsorption from mixed element soln meq/100 gm	Adsorption from single element soln	% reduction in adsorption	Adsorption from mixed element soln meq/100 gm	Adsorption from single element soln	% reduction in adsorption	Adsorption from mixed element soln meq/100 gm	Adsorption from single element soln	% reduction in adsorption
Iron	1617	26.75	28.25	5.3	2.14	7.6	71.8	10.88	15	73.3
Zinc	3747	18.63	28	33.5	1.54	10	84.6	3.79	16.2	76.6
COMBINATION D										
Copper	6999	19.81	30	34	0.85	5.63	85	3.93	18.25	78.5
Zinc	1438	5.58	13.75	59.4	1.77	4.3	58.8	1.62	9.6	83.1
Nickel	6382	20.22	29.25	30.9	7.35	5.35		9.89	10.1	2.1
Chromium	2312	30.55	42.13	27.5	2.69	3.2	16	15.14	37.7	59.8

Many variables contribute to the series of metals including their charge, size, ligand field of the co-ordinated species, concentration and the nature of the clay mineral. Chromium being trivalent, will compete favourably with the divalent metals for adsorption sites, and is therefore in the anticipated position. Nickel shows comparatively little reduction in adsorption when in competition, which may be attributed to the high concentration of the element in the solution. However copper, which was present in a similar concentration, has competed less well.

The effect of the presence of iron in solution may be observed in combinations A, B, E and F. Combinations A and F differ in that F has a larger concentration of iron than A. B and E differ in that iron is absent from B. The percentage reductions for the adsorption of elements in Combination F compared to A, and E compared to B (Table 4) must be due to the presence of large quantities of iron in solutions E and F giving this element an advantage in the equilibrium adsorption process. However, even in Solution A, where iron is present in small quantites it still achieves the greatest percentage adsorption and the greatest absolute adsorption for kaolinite (for montmorillonite there is 100% adsorption for other elements), suggesting that iron competes successfully for adsorption sites despite the disadvantages of a low concentration. The relative ease with which metals are adsorbed is therefore dependent on the mineral involved, as shown by the differences in the series for each mineral where four minerals are observed. Iron appears to compete favourably irrespective of the other metals present. or of the mineral.

7.2.2 Site Rock Experiments. Experiments were carried out using rocks from the disposal sites studied. The simple solutions containing single elements and combinations of elements were used for the first experiments, followed by experiments with effluent (Section 7.2.3). The adsorption observed may be related to the mineralogy of the rocks.

Walsall Wood Site

Reactions of the rocks similar to those present at Walsall Wood Site with solutions containing metals indicate that there is adsorption of metal ions by the clay minerals present. Adsorption by the shale was always greater than that of the sandstone. This was expected as adsorption capacity is dependent on the clay mineral content. XRD analysis confirmed the presence of kaolinite, illite and chlorite in the Coal Measures Shale (Section 6.2). The poor adsorption capacity of kaolinite, which appears from the XRD analysis to be the dominant mineral, is compensated by the higher capacities of illite and chlorite, although they are present in smaller quantities (Section 3.1). The Coal Measures Sandstone has less illite and chlorite present which gives a lower adsorptive capacity as the majority of adsorption is achieved in this case by the kaolinite present.

The experiments of Section 5.3.1. carried out on Coal Measures Sandstone and Shale demonstrate the difference in the adsorptive capacity of the two rock types. In the case of iron, there is an increase in the concentration of metal ion in solution for both sandstone and shale, with a greater increase for shale due to the higher iron content in this rock type. In all other cases, except chromium in nitric acid, there is a greater adsorption of metal by the shale than by the sandstone. In Section 5.3.6. a similar pattern is seen for the experiments at pH 1, 2, 3, 4 and 9. The graphs of Fig 26.b. show the results of the attempts to saturate the adsorption sites on Coal Measures Shale. It can be seen that the saturated state was not reached with the concentrations of metal ion used although the curve for nickel was beginning to flatten.

Where there is competition between metal ions for adsorption sites (section 5.3.5) the Coal Measures Shale gives a similar result to that for the pure clay minerals. Table 9 shows the reduction in the percentage adsorption from mixed element solutions compared to pure element solutions. The series of elements in their order of percentage reduction in adsorption from a multi element solution is:

$$Zn > Cu > Cr > Ni$$

As explained for the pure clay minerals, this series depends not only on the nature of the metals but also on the nature of the minerals present, and is therefore not the same as that for the pure clay minerals. Again, for the Coal Measures rocks iron competes very favourably against other metals for the adsorption sites. The results of the experiments on the Coal Measures Shale in fact reflect the results of kaolinite and monmorillonite, with an adsorptive capacity for the shale between that of montmorillonite and kaolinite which reflects the mineralogy of the rock.

Control experiments (Section 5.3.1) show that little leaching of metals from the shale occurs even at pH0. Only iron is leached in significant quantities (up to 200 meq 100 gm rock at pH 0 and 1). At higher pH values there was no leaching of iron from the rock. Effluent disposed of in this site, at a low pH value (less than 1) will leach iron as it moves through the rocks. As the effluent moves through the broken ground, neutralisation will occur (Section 8.2.) increasing the pH of the effluent to a value above which leaching of iron will cease. By this time the liquid will have adsorbed large quantities of iron, which will compete with metals in the effluent for exchange sites or the clay minerals. The neutralising effect of the Coal Measures rocks will cease when the carbonate and oxides present have reacted. The pH of the effluent passing through such rock will not be altered, and it will leach both iron and other elements which have been adsorbed from previously neutralised effluent. Further neutralisation will occur when the effluent reaches unreacted rocks. Thus a belt of adsorbed metal ions will move through the rocks in the mine as they are alternately adsorbed and leached.

The effects of the high iron content of Coal Measures rocks must be considered with respect to adsorption processes. The black shales of the Coal Measures were deposited in a reducing environment hence the iron present will be divalent. During the working life of a colliery the circulation of air will oxidise iron, in minerals exposed, to the trivalent state. Fe II will compete with other metal ions less successfully than Fe III for exchanges sites on clay minerals. However, as nitric acid accounts for a significant volume of the effluent disposed in the mine, much of the Fe II present will be oxidised to Fe III. Thus the complete role of iron in the mine remains a matter of speculation. However sufficient evidence is presented here to show that the presence of acid leachable iron in large quantities can assist the movement of a band of metal ions through a mineral medium. This will be less of a problem if the site contains minerals which can neutralise the acid effluent efficiently, however it must be emphasised that the seepage of acid solution from such a site could be serious.

Betton Abbotts Site

The experiments with these rocks were designed to determine the adsorption which can be achieved by reaction of the rocks with solutions containing single elements and combinations of elements in concentrations similar to those of effluents to be disposed of at the site.

Of the four rock materials from this site, the red boulder clay most efficiently adsorbs metal ions from solution (Section 5.3.7). The grey clay rich sand from the west end of the site, has a similar adsorption capacity to the red clay, with only slightly lower adsorption values for iron and nickel. The grey clay, and red sand from the borehole, have an appreciably lower capacity for adsorption compared with the other two materials seen from the results of the mixed element experiment (Table 5). The low clay mineral content of the red borehole sand shown by XRD analyses (Section 6.3) accounts for the low adsorption capacity of this rock type. The low adsorption by the grey clay may be due to the very fine grained nature of the material which would restrict the movement of metal bearing liquids. If a filter bed method is to be used to reduce the toxic metal content of effluents at the site (Section 2.4) it should contain the grey sand. The boulder clay is unsuitable for use as a filter as the permeability is too low to allow movement of liquids.

The effects of competition between elements for adsorption sites on clays in the Betton Abbotts site rocks may be determined by comparison of the results for the single element, and multi element solutions. No reduction in adsorption was observed when the red clay and grey sand were mixed with the combination 1 solution, compared with adsorption from the single element solutions of similar concentrations (Section 5.3.7). This observation suggests that both these materials have sufficient capacity to adsorb the total amount of metal present in the particular multi element solution. Adsorption of copper and zinc from the Combination 2 solution, where the original concentrations are high, is lower than from the single element solutions in contact with these materials (Figs 27.7, 27.8, 27.10 and 27.12). Adsorption of zinc was reduced by approximately 50%, from 50 meq/100 gm to 27 meq/100 gm for the same original concentrations. Copper adsorption fell by 80% from 90 meq/100 gm, for the single element solution, to 15 meq/100 gm for the mixed element solution. The grey clay and the red borehole sand showed a reduction in adsorption for both multi element solutions compared with the single element solutions (Table 5).

Thus, there is a reduction in the adsorption from mixed element solutions, as observed for the experiments with the pure clay minerals. Where iron is in competition it is seen to compete favourably with a similar percentage adsorption observed for the mixed and single element solutions, while lead, copper, nickel and zinc adsorption is reduced by competition, unless there is sufficient capacity for adsorption of all metals in solution. However, the results suggest that metal content of liquids disposed of at the site will be reduced by adsorption of metal ions from the solution on the clay minerals.

7.2.3 Experiments with Effluent Samples. The results in Section 5.3.9 show the effects of reacting a typical effluent sample with Coal Measures Shale, kaolinite and montmorillonite. In all cases for kaolinite and Coal Measures shale, and in the majority of cases for montmorillonite, there is a reduction in the amount of adsorption compared to that for the pure metal solution (Table 7). The series of adsorption observed for the pure element solutions, with montmorillonite showing the greatest adsorption, shale intermediate, and kaolinite the least, is observed for the reactions with the effluent in the majority of cases. The percentage reductions in adsorption for the effluent compared to the pure element solutions, for montmorillonite and shale are in general lower than for kaolinite, although the absolute adsorption is lower for kaolinite. For chromium there was a greater amount of adsorption from the effluent sample than for the pure element sample for kaolinite. Similarly for the reactions of the Betton Abbotts site rocks with a typical effluent, there is little adsorption compared with that observed for the pure element solutions. Zinc illustrates the effect with a decrease in adsorption capacity for all four rock materials from Betton Abbotts when in contact with the effluent sample. A 40% reduction was observed in the concentration of the effluent sample in contact with the red boulder clay and the red sand, but the borehole sand and the grey clay reduced the concentration by only 10%. Similar concentrations of zinc in single element solutions were 100% adsorbed by the red clay and grey sand, and 20% adsorbed by the grey clay and red sand. Similar, though slightly lower results were found for the mixed element solution.

The reduction in the adsorption observed for the reactions with effluent solutions may result from the presence of organic material in the solutions which are likely to occupy adsorption sites [26], and solids which will block the adsorption sites. However the results do show that some cleaning of effluent samples occur when they are in contact with typical site rocks.

7.3 The Chemistry of the adsorption of metal ions by clay minerals

Previous studies of ion exchange reactions of clay minerals [44, 45, 46] show the loss of sodium and potassium from the minerals. To ascertain the contribution of ion exchange to the adsorption observed during this work, the concentrations of sodium and potassium present were determined before and after the adsorption process. Pure clay minerals were used for this examination (Section 5.3.4). Analyses showed that very small quantities of sodium and potassium (less than 10 ppm and 0.5 ppm respectively) were present in the solutions before reaction with the clay minerals. The concentration of both elements in solution increased after reaction indicating that the adsorption process was accompanied by release of sodium and potassium. Both kaolinite and montmorilonite released 0.1 meq of potassium per hundred grams of clay mineral. Sodium was released in greater quantities, and varied with the metal ion present. Reaction of montmorillonite with solutions containing chromium and iron released 6 meq/100 gm clay mineral, while the other metal solutions released less than 3 meq/100 gm clay. These observations may be explained by considering the equilibrium between sodium both in solution and adsorbed on the clays, and metal ions in solution and adsorbed on the clays.

$$\text{Clay } (Na^+)m + xM^{n+} \rightleftharpoons \text{clay } (Na^+)_{m-nx} (M^{n+})_x + nx\ Na^+$$

The equilibrium constant for this reaction may differ for di- and trivalent metal ions, which would explain the difference in the quantity of sodium released by the trivalent iron and chromium species compared with that released by the divalent metals.

Release of sodium and potassium occurred during the first five days of the experiment, after which the concentrations of these elements in solution remained constant. This is consistent with the majority of the adsorption of metal ions from solution during the first week of the experiment. Except in the case of cadium, the total amount of metal ion adsorbed in meq/100 gm clay is greater than the quantity of sodium and potassium released (Fig 24). This suggests that, although some of the adsorption may be due to ion exchange, a second mechanism is necessary to account for the excess metal adsorbed. This additional capacity may be explained by a variety of mechanisms (Section 3.1). Firstly, electrostatic attraction between positively charged metal ions and the negatively charged faces of the clay minerals [27, 44] may lead to the adsorption of metal ions onto the clays. Subsequent electrostatic attraction between anions present in solution may restore the negative charge at the surface, giving rise to further attraction of metal cations (Fig 30a). Secondly, co-ordination between the metal ions and oxygen molecules present at the surface of the minerals may be responsible for the adsorption of metals from solution. The E.S.R. data obtained (Section 8.3) has shown that Ni II is present on the clay minerals studied in a distorted configuration, and that Cu II is present in a configuration not consistant with the hexaquo ion. These observations are explained by substitution of a proportion of the water molecules in the co-ordination shell, present in the aqueous environment, by oxygen atoms on the clay minerals (Fig 30b). Finally when the pH is above 6, additional adsorption capacity may be made available since precipitation of the metal as a hydroxide may occur. This may form a coating on the clay surface onto which metals are adsorbed. The mechanism is likely to be of particular importance for solutions containing large concentrations of iron.

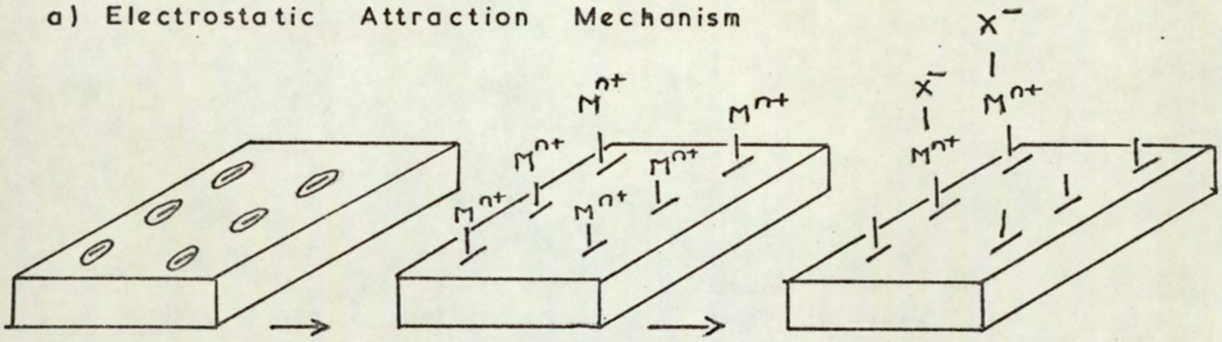
For cadmium there is a greater release of sodium than adsorption of metal for both kaolinite and montmorillonite. This suggests that the release of sodium and potassium is dependent upon the total cation concentration, and not only on the metal ion concentration. The excess sites available, when all the metal ions present have been adsorbed, may be occupied by hydrogen ions present in the acid solution.

Some information on the nature of the adsorption sites for copper and nickel was obtained from E.S.R. spectroscopy (Section 8.3). For the sample of kaolinite which had been in contact with a Cu II solution a rhombic spectrum was observed from which three g factors were calculated. From the work of Dudley and Hathaway [56] we can define:

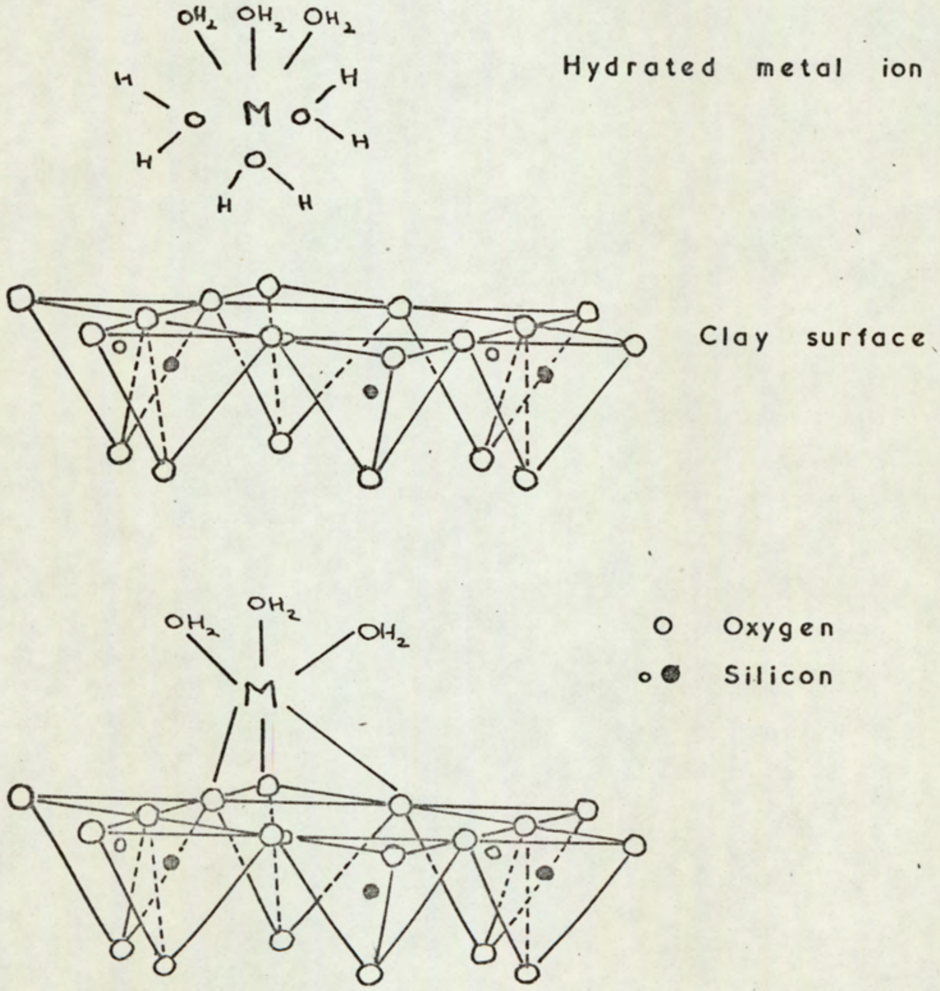
FIG. 30

Diagrammatic representation of the Adsorption Mechanisms

a) Electrostatic Attraction Mechanism



b) Co-ordination Mechanism



$$R = \frac{g_2 - g}{g_3 - g_2} \quad \text{where } g, < g_2 < g_3$$

If $R < 1$ $\quad d_x 2 - y^2$ ground state

$R > 1$ $\quad d_Z 2$ ground state

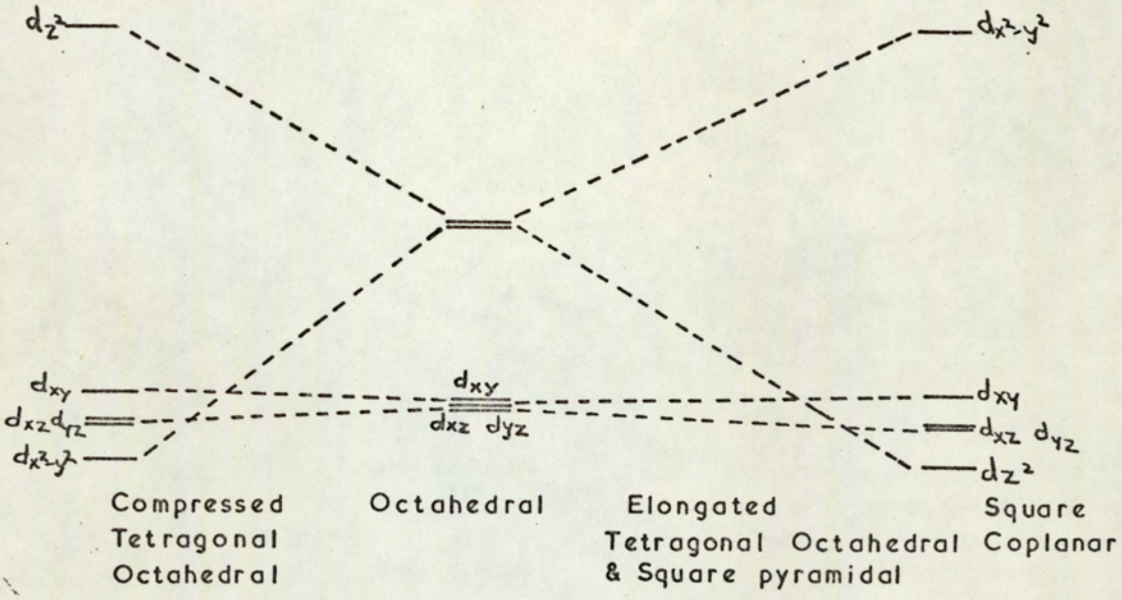
Substituting values for the g factors (Table 11) we obtain R = 0.8 or $R < 1$ which implies a $d_x 2 - y^2$ ground state [57,58] (Fig 31). Thus we may eliminate such geometrics as trigonal bipyramidal as this has a $_Z2$ ground state. In fact a distorted six co-ordinate environment is most likely; and 'cis octahedral' distortion may also be eliminated as it has a d_Z2 ground state [57, 58] (Fig 31 b).

For montmorillonite in contact with Cu II an axial trace of copper, with fine structure on the weakest component, was obtained. This indicates a coupling of the electron with the 3/2 nuclear spin of copper giving rise to four components for g_{11}. This interaction is not resolved for g_1. The spectrum suggests a tetragonal environment for the copper atom. The lowest g factor from this spectrum is g = 2.05 which implies a $d_x 2 - y_2$ ground state ie a distortion along the $_Z$ axis of the octahedron leaving the unpaired election in the $d_x 2 - y_2$ orbital. One spectrum was taken of kaolinite, which had been in contact with nickel nitrate solution. A two g factor (axial) spectrum was obtained indicating that, in the case of Ni II also, sites of lower symmetry than octahedral were occupied thus eliminating Ni $(H_2O)_6$ as the adsorbed species. Some evidence of fine structure due to coupling of electron and nuclear spin, were noted on both the perpendicular and parallel components. The E.S.R. evidence suggests that copper and nickel need not simply be adsorbed as the hexaqus ion, supporting the previous suggestion that more than one mechanism of adsorption is operative.

The results of the experiments on kaolinite, montmorillonite and Coal Measures Rocks (Sections 5.3.1, 5.3.2 and 5.3.6) illustrate the pH dependence of metal ion adsorption. The original experiments

FIG. 31

a)



The splitting of the one-electron energy levels of the copper (II) ion in crystal fields of axial symmetry.

b) Cis octahedral distortion

Cis octahedral $d_{z}2$ ground state

carried out on Coal Measures Shale at pH 0 (Section 5.3.1) showed that little adsorption occurred, and in the case of copper, zinc and cadmium an increase in the concentration of metal in solution was observed. For copper and cadmium the effect is within experimental error. In the case of zinc, part of the increase is due to evaporation of the solution as is evident in later experiments, particularly where the metal is present in high concentrations (Section 5.2). Some zinc is naturally present in rocks (Section 6.2) but control experiments show that it is not leached in sufficient quantities to explain the increase in concentration observed (Section 5.3.1). For chromium and iron (Fig 21) there is a two stage adsorption with a period of little adsorption indicated by the flattening of the curve. This effect is discussed later.

When the pH of the solution was raised adsorption of the metals present increased, with a particularly marked increase at pH 2. At pH values above 3, a plateau value was reached, above which the metal ion adsorption remained constant with further increase in pH.

The results of the experiments with montmorillonite illustrated the distinction between adsorption at pH 1, and that at pH values of 2 and above (Table 10). Generally results from the kaolinite experiments did not show as marked a discontinuity, however for cadmium no adsorption was observed until pH 3, after which adsorption of 60% of the original concentration occurred, and for lead adsorption of 20% was observed at pH 1, 34% at pH 2, and 70% at pH 3, 4 and 9. Similarly Coal Measures shale adsorbed larger quantities of metal at pH values above 2 (Table 10). The variation in the percentage adsorption is therefore related to the hydrogen ion concentration. Adsorption is an equilibrium process in which the concentration of the cations present determine the equilibrium position. If a high concentration of hydrogen ions is available, ie the pH is low, they will compete with the metal cations for adsorption sites. When the hydrogen ion concentration drops, ie the pH is increased, the

TABLE 10

A summary of the variation in adsorption of metals by montmorillonite and Coal Measures shale at pH 1, 2, 3, 4 and 9.

Metal	% adsorption at pH				
	1	2	3	4	9
MONTMORILLONITE					
Chromium	75	97	97	98	98
Copper	72	95	92	94	93
Zinc	46	58	58	60	60
Nickel	49	76	80	83	82
Cadmium	61	100	100	100	100
Lead	94	100	100	100	100
Iron	22	26	23	26	26
COAL MEASURES SHALE					
Chromium	92	100	100	100	100
Copper	0	100	100	100	100
Zinc	0	38	54	49	41
Nickel	20	100	98	100	100
Cadmium	100	100	100	100	100
Lead	37	100	100	100	100
Iron	0	0	11	9	13

metal cations compete more favourably for the exchange sites. In addition to the concentration factor hydrogen ions, although monovalent and solvated, are smaller than monovalent metal ions, consequently they have a greater charge density which will enable them to compete as effectively as a di- or trivalent metal cation.

The effects observed when the pH was varied may also be due to the achievement of the point of zero charge for the minerals (Section 3.1). At this point the charge on the clay minerals reverses from positive to negative. This state is achieved below pH 3 for montmorillonite and at a pH between 3 and 4 for kaolinite[26] hence the increase in adsorption up to a pH value of 3, when the clay charge reversal is complete, after which the change in pH does not affect the quantity of metal adsorbed.

Thus, the pH dependence of the adsorption of metal cations from solutions is probably due to the effects of both the hydrogen ions and the physical state of the clay minerals. The process of adsorption was shown to be reversible, and dependent on the pH value of the medium, for lead. After reaction with Coal Measures Shale, solutions containing lead were decanted and replaced with an equal quantity of acid at pH 1. Lead previously adsorbed onto the minerals was leached into solutions in quantities equal to those of the original solutions applied.

To assess the effects of the anionic species in solution, four acids were used to prepare the metal solutions (Sections 5.3.1, 5.3.2, 5.3.4) Nitrate salts of the metals were used to ensure solubility hence nitrate ions were present in all the solutions in a concentration rate of n : 1 for the metal salt $M(NO_3)_n$. Perchloric, hydrochloric, and nitric acids were used for the original experiments at pH 0 (Section 5.3.1). Perchloric acid provides an ion which is theoretically less likely to form complexes with the metal ions than chloride or nitrate anions. Complex formation, between the anion and a metal, will result in a lower percentage adsorption of the metal from solution as fewer metal ions will be available, and will therefore compete less favourably in the equilibrium process of adsorption. Where solutions contain more than one metal, the nature of the anion present may cause a reversal in the order of adsorption of metals from solution due to the relative stability of the complexes formed.

Significant variation in adsorption of zinc and lead was observed in the experiments carried out on Coal Measures shale at pH 0 for hydrochloric acid, compared with nitric and perchloric acid. The concentration of zinc in the hydrochloric acid solution was reduced by 10%, while the concentrations of the solutions in nitric acid and perchloric acid were reduced by 20%. This may be explained by the formation of a complex between zinc and chloride ions which reduced the concentration of zinc ions available for adsorption. The concentration of the lead, in nitric acid solution, remained constant, while the concentration of the perchloric acid solution was reduced by 60%. It appears that nitrate ions effectively reduce the concentration of lead available for adsorption.

The results of the experiments of Section 5.3.4. and those at different pH values (Sections 5.3.2, 5.3.6) show that the variation in adsorption with anionic species is not observed at p^H values above 2. However it must be remembered that the anion concentration falls proportionally with the hydrogen ion concentration as the pH is increased. In the case of disposal sites where neutralisation occurs the anion concentration remains stable when the pH value falls:

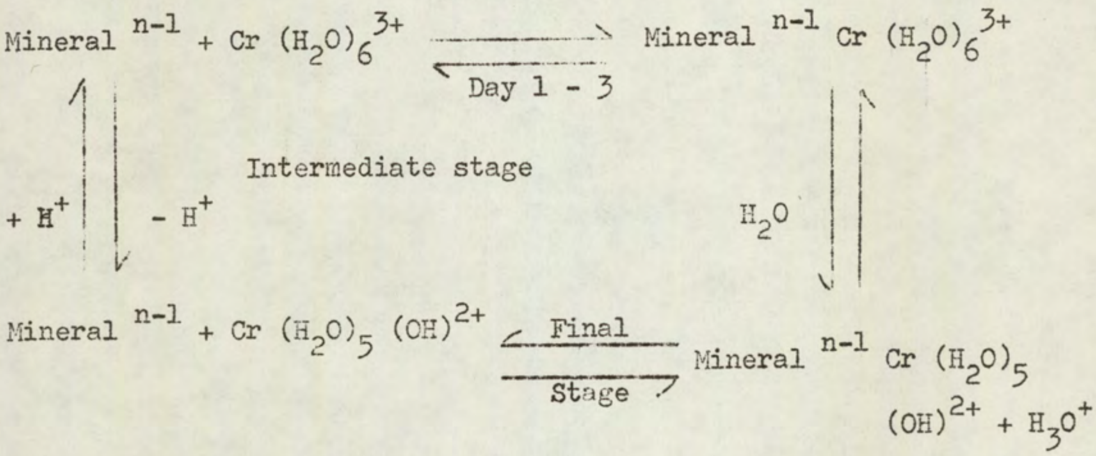
$HCl\ (Cl^-) = 1M$ pH 0 Pure solution
$(Cl^-) = 10^{-2}M$ pH 2

$HCl\ (Cl^-) = 1M$ pH 0 Neutralisation
$\downarrow Na_2CO_3$
$(H^+) = 10^{-2}M$ pH 2
$(Cl^-) = 1M$

Of the anions considered, only chloride is likely to form complexes with the metal ions under the prevailing conditions, particularly with zinc. If hydrochloric acid is deposited at disposal sites and neutralised by carbonates and oxides present, the chloride ion concentration would not be affected. If the disposal pattern at a facility involves large quantities of strong hydrochloric acid the question of chloro-complex, formation must be considered. In this work, experimental data shows that the concentration of chloride, nitrate, sulphate and perchlorate in acid solutions of pH 2 and above are insufficient for complex formation to interfere with other adsorption phenomena observed. This could be an important factor in disposal at the Walsall Wood facility where high concentrations of hydrochloric acid are deposited.

The adsorption of chromium and iron is represented by graphs which are different from those for the other metal ions (Figs 21, 22). It appears that chromium is adsorbed in two distinct stages; (a) during the first three days adsorption by the clay occurs and an equilibrium situation is reached; (b) further adsorption occurs after the next 3 or 4 days, and a second equilibrium situation approached after ten days (Fig 21.1). This phenomenon was observed for both kaolinite and Coal Measures shale which contain large quantities of kaolinite (Section 6.2). A possible explanation is that the original rapid adsorption occurs on the surface of the clay, typical of adsorption by kaolinite [26], followed by a slower adsorption onto sites with the clay mineral when the metal has had time to migrate to these areas. This second stage will comprise isomorphic substitution of trivalent cations by chromium within the clay lattice (Section 3.1). Alternatively the observations may be related to the hydrolysis of the trivalent cations. Chromium may be adsorbed as the $Cr(H_2O)_6^{3+}$ species, which will be efficiently adsorbed because of its high charge. When the chromium ion is attached to the clay mineral, deprotonation of the hydrated ion may occur, in which a hydrogen ion is lost from one of the water molecules acting as ligands (Fig 32). The effect would be to reduce the charge on the chromium from 3 to 2, which would make the ion less competitive for the occupation of exchange sites. Thus the reduction in the rate of adsorption of chromium can be explained and it may even result in an increase in the concentration of chromium in solution, after a period of time, depending on the position of equilibrium for the two processes. If the deprotonation mechanicsm is slow, this will be the rate determining step for the final equilibrium between Cr $(H_2O)_6^{3+}$ and Cr $(H_2O)_5(OH)^{2+}$. This in turn will determine the final amount of chromium adsorbed by the mineral. If this explanation is applied to the adsorption of iron, the increase in concentration of the metal in solution after five days (Fig 21) may be accounted for.

FIG 32



7.4 Conclusions

The work has produced some useful data related to the Walsall Wood Mine and the other sites. From the data derived from the mine facility it may be possible to predict the extent of contamination of the workings by calculation of the pH change in the effluent from an estimation of the surface area of contact. Although this will only give a very rough estimation, it could be useful for future planning of disposal facilities. The importance of keeping the pH high to promote adsorption of metals by clay minerals has been demonstrated. This will be particularly important in controlled leakage sites where the contaminants leaving the site must be kept to a minimum. Similarly the importance of iron both in the effluent and the rocks into which the effluent passes has been shown. Where iron is present in solution it will compete very favourably with other metal ions, hence the desireability of preventing leaching of iron from the rocks.

The work has developed a method of obtaining data from simple laboratory experiments, which may be used when assessing new sites. Samples of the rock types from proposed sites may be taken and reacted with effluents to be tipped at the site to determine the changes which can be expected in the effluent.

Future work could usefully be directed towards investigating the reactions of organic materials in effluents with clay minerals. In addition, more work on the reactions of metal ions could be achieved by use of the H.G.A.

CHAPTER 8

ADDITIONAL WORK

8.1 Monitoring of the Mitco Borehole Liquid

Two 40m deep boreholes were drilled at the Mitco site to determine any movement of liquids from the tip into the surrounding rocks. Borehole No 1 is situated on the north side of the site between the lagoon and Aldridge Brixancole No 2 quarry, and the second borehole is situated approximately 200m west of the site (Fig 7). Water samples from these boreholes were collected and analysed for phenol at frequent intervals.

The phenol analyses were carried out using a Pye Unicam SP 1800 ultra violet spectrophotometer. The phenolate ion was detected, at neutral to alkaline pH, by measuring absorption at a wavelength of 287 nm. The concentration was obtained assuming Beers Law to be obeyed, and taking E_{287} for $C_6 H_5 O^-$ as 2600.[59] Although this method is not as accurate as Gas Liquid Chromatography, being subject to interference from other organic materials present, it is rapid and convenient.

The first analyses of water samples from Borehole 1 revealed a phenol content of approximately 125 ppm. No metal was present in detectable quantities. Subsequent analyses of samples collected over a six month period showed a decrease in the phenol concentration in the water to a concentration of 50 ppm. The concentration remained at this level, with small fluctuations, for ten months, until sampling was discontinued (Table 11). The water from Borehole 2 contained no phenol in detectable quantities over this period.

The liquid in Mitco Tip has a phenol concentration of approximately 600 ppm, which remained relatively constant over the sampling period. The water in Borehole 1 therefore appears to be a diluted solution of the liquid present in the Mitco site. The high phenol values

TABLE 11

Results of the phenol analyses of liquid from the boreholes at Mitco Site and the depth of the water table

Date	Borehole	Depth to Water Table in Metres	Phenol Concentration µgm ml
18.7.73	1	13.8	125
	2	9.0	Not detected (n.d)
24.7.73	1	13.4	129
	2	9.6	n.d.
4.9.73	1	12.85	97
	2	9.25	n.d.
11.9.73	1	12.9	90
	2	9.2	n.d.
18.9.73	1	12.9	85
	2	9.2	n.d.
26.9.73	1	13.0	90
	2	9.1	n.d.
5.10.73	1	13.0	92
	2	9.3	n.d.
16.10.73	1	12.7	87
	2	8.9	n.d.
24.10.73	1	13.6	83
	2	8.9	n.d.
31.10.73	1	12.9	78
	2	8.7	n.d.
14.11.73	1	12.9	75
	2	8.7	n.d.
30.11.73	1	12.7	61
	2	8.55	n.d.
3.12.73	1	12.6	50
	2	8.6	n.d.
7.12.74	1	12.8	52
	2	8.5	n.d.

Date	Borehole	Depth to Water Table in Metres	Phenol Concentration µgm ml
18.12.73	1	12.6	61
	2	8.35	n.d.
18.1.74	1	12.5	50
	2	8.5	n.d.
1.2.74	1	12.2	53
	2	8.0	n.d.
8.2.74	1	12.9	61
	2	8.2	n.d.
11.3.74	1	12.03	54
	2	-	n.d.
18.4.74	1	12.1	64
	2	7.6	n.d.
3.9.74	1	11.6	38
	2	7.2	n.d.
23.10.74	1	Not recorded	60
	2	" "	n.d.
26.11.74	1	11.4	79
	2	7	n.d.
17.1.75	1	11.6	51
	2	6.7	n.d.

for the early analyses are probably the result of contamination introduced during permeability testing of Borehole 1. The water used was transported in a tanker previously used for Mitco Tip liquid. This water would be contaminated with phenol and dilution by the ground water has removed the effects. If the level of 50 ppm is taken as the phenol content in Borehole 1, this represents a dilution of 90% during movement of the water from the lagoon, through approximately 20 m of rock, to the borehole. The absence of phenol in water samples from Borehole 2 is due to the greater distance from the lagoon, and the fact that movement of contaminants will be down dip (to the north) rather than along the strike of the beds.

8.2. To assess the change in pH of an acidic solution in contact with Coal Measures Shale.

100m of hydrochloric acid, pH 0.89, were added to 30gm of Coal Measures Shale in a beaker. The mixture was stirred, and the pH value of the solution recorded each day for a period of two weeks.

Day	pH of the acid
1	0.89
2	1.10
3	1.14
4	1.46
5	1.41
8	1.46
9	1.44
10	1.30
11	1.41
12	1.56

This shows that 30 gm of rock has reduced the pH from 0.89 to 1.56. This represents a reduction of 0.101 moles in the concentration of hydrogen ion. The capacity of the rock for neutralising acid expressed in terms of moles per 100 gm of rock is therefore 0.3366.

8.3. Electron Spin Resonance (E.S.R.)

Electron spin resonance spectra were obtained to give information about the co-ordination environment of the absorbed ions. Kaolinite and montmorillonite samples which had been reacted with solutions containing copper and nickel, were selected to evaluate the technique. Spectra were obtained on a Varian instrument at 78K with a microwave frequency of 9.146 G.Hz. The g values obtained from the traces are given below:

TABLE 12. g values for E.S.R. spectra

Sample	g_1	g_2	g_3
Copper, Kaolinite	2.025	2.039	2.056
Copper, Montmorillonite	2.050	2.2112	
Ni, Kaolinite	2.008	2.015	

8.4. Mössbauer Spectrophotometry

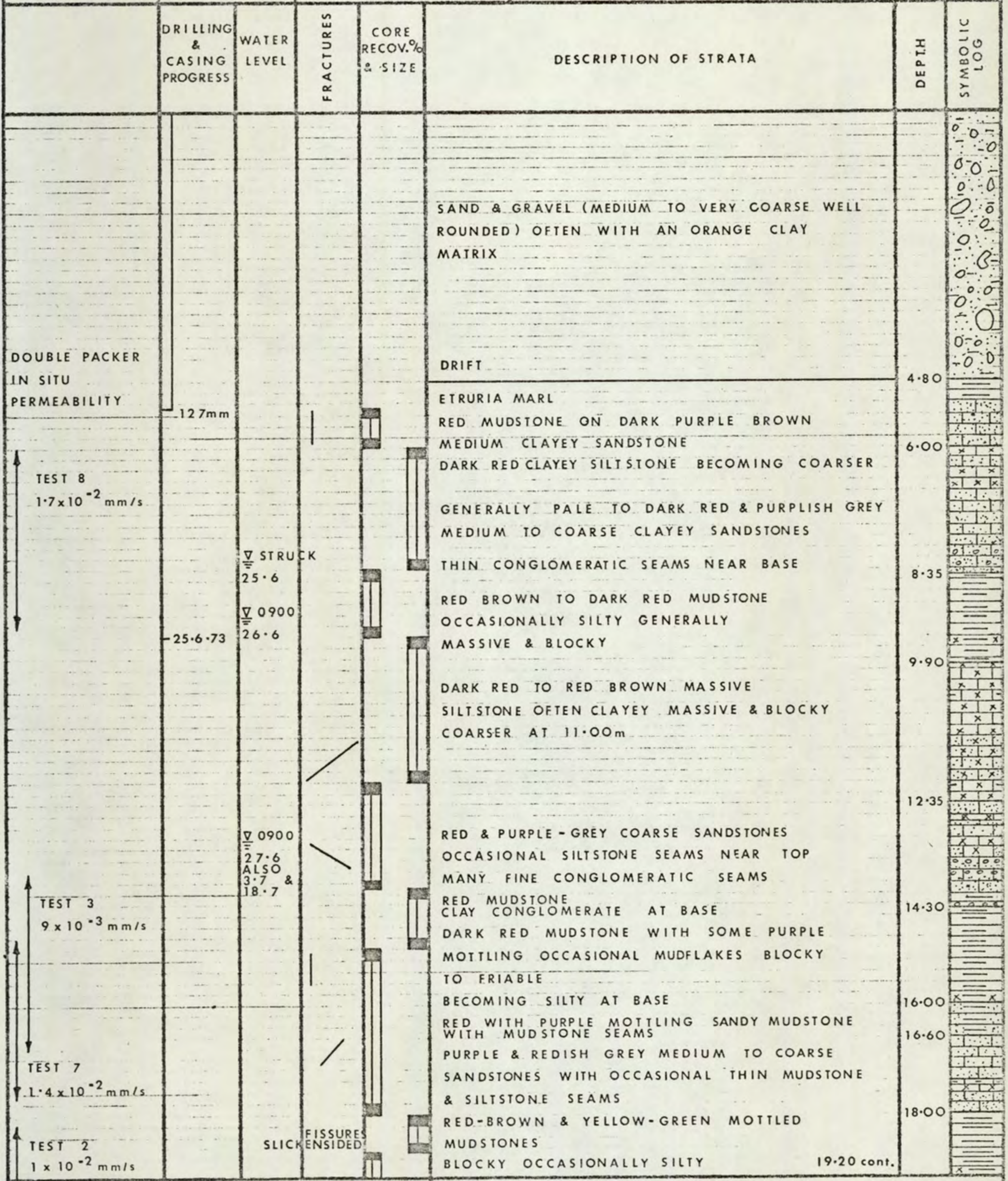
It was hoped that this technique would give information about the oxidation state of iron adsorbed onto clay minerals. Weaver et al[60] used this technique for the analysis of iron in clay minerals, to establish the presence of Fe II and Fe III, and in sheet structure silicates they distinguished octahedrally coordinated iron from tetrahedrally coordinated iron in pure clay minerals.

Samples of the Coal Measures Shales were prepared between perspex plates, and attempts made to obtain a spectrum on a Centronic Mössbauer Spectrometer. Although the preparation of the samples was varied to obtain a range of thicknesses, no spectra were obtained. As the work progressed the need for this information appeared to diminish and the technique was abandoned.

APPENDIX 1

Mitco Site Borehole Logs

DRILLING METHOD ROTARY AIR FLUSH	GROUND LEVEL 146m O.D. approx.	CO-ORDINATES SK 0480 0245	BOREHOLE NO. 1
MACHINE GRYPHON MARK 5	CORE BARREL & BIT DESIGN DOUBIE TUBE 4·12 TUNGSTEN	ORIENTATION VERTICAL	SITE ALDRIDGE COLLIERY



DOUBLE PACKER IN SITU PERMEABILITY

TEST 8 1·7 x 10^{-2} mm/s

TEST 3 9 x 10^{-3} mm/s

TEST 7 1·4 x 10^{-2} mm/s

TEST 2 1 x 10^{-2} mm/s

DESCRIPTION OF STRATA	DEPTH
SAND & GRAVEL (MEDIUM TO VERY COARSE WELL ROUNDED) OFTEN WITH AN ORANGE CLAY MATRIX DRIFT	4·80
ETRURIA MARL RED MUDSTONE ON DARK PURPLE BROWN MEDIUM CLAYEY SANDSTONE	6·00
DARK RED CLAYEY SILTSTONE BECOMING COARSER GENERALLY PALE TO DARK RED & PURPLISH GREY MEDIUM TO COARSE CLAYEY SANDSTONES THIN CONGLOMERATIC SEAMS NEAR BASE	8·35
RED BROWN TO DARK RED MUDSTONE OCCASIONALLY SILTY GENERALLY MASSIVE & BLOCKY	9·90
DARK RED TO RED BROWN MASSIVE SILTSTONE OFTEN CLAYEY MASSIVE & BLOCKY COARSER AT 11·00m	12·35
RED & PURPLE - GREY COARSE SANDSTONES OCCASIONAL SILTSTONE SEAMS NEAR TOP MANY FINE CONGLOMERATIC SEAMS RED MUDSTONE CLAY CONGLOMERATE AT BASE	14·30
DARK RED MUDSTONE WITH SOME PURPLE MOTTLING OCCASIONAL MUDFLAKES BLOCKY TO FRIABLE BECOMING SILTY AT BASE	16·00
RED WITH PURPLE MOTTLING SANDY MUDSTONE WITH MUDSTONE SEAMS	16·60
PURPLE & REDISH GREY MEDIUM TO COARSE SANDSTONES WITH OCCASIONAL THIN MUDSTONE & SILTSTONE SEAMS	18·00
RED-BROWN & YELLOW-GREEN MOTTLED MUDSTONES BLOCKY OCCASIONALLY SILTY	19·20 cont.

MAJOR FRACTURES INDICATED ONLY MANY SHOW SLICKENSIDES AND A CLAY COATING

STANDPIPE (75mm) INSERTED TO 40m

WATER LEVELS		
3·7·73	13. 70	below top of standpipe
18·7·73	13. 80	"
24·7·73	13. 40	"

LOGGED BY: J.A.M./J.W.G. SCALE 1:100

CLIENT E.D.L.

REF. M 773

FIG. 2

SITE

ALDRIDGE COLLIERY

CONTINUATION SHEET 1

BOREHOLE NO. **1 Cont.**

IN SITU PERMEABILITY TESTS	DRILLING & CASING PROGRESS	WATER LEVEL	FRACTURES	CORE RECOV.% & SIZE	DESCRIPTION OF STRATA	DEPTH
					Cont.	19·20
TEST 2			SLICKEN-SIDES		RED BROWN & DARK RED MUDSTONES OFTEN	
1×10^{-2} mm/s					MOTTLED GREEN AND/OR YELLOW	
					SOME SILTY SEAMS	
					MASSIVE & BLOCKY	
					BECOMING SANDY	
					CONGLOMERATIC SEAM	
		WATER STRUCK 26·6			OCCASIONAL PURPLE MOTTLING	
TEST 1					THINLY LAMINATED SEAMS	
$1{\cdot}5 \times 10^{-2}$ mm/s	26.6.73					
					BECOMES SILTY	
TEST 6					RED CLAYEY SANDSTONE ON	23·95
9×10^{-3} mm/s					SILTSTONES WITH CONGLOMERATIC SEAMS	
						24·75
					RED MUDSTONES & SILTY MUDSTONES WITH	
					SUBORDINATE SILTSTONES	
						26·50
					RED-BROWN LAMINATED SILTY FINE SANDSTONE	26 80
		WATER STRUCK 27·6				
					RED-BROWN SILTY MUDSTONE & SILTSTONE	
					SOME REDUCTION SPOTS	
					GENERALLY LAMINATED	
					SOME SEAMS OF RED MUDSTONE	
						28·90
					RED-PURPLE GREY FINE-MEDIUM SANDSTONE	
TEST 5					ON DARK RED SILTSTONE	
$9{\cdot}2 \times 10^{-3}$ mm/s						30·30
					RED MUDSTONE WITH SEAMS OF PALE	
					GREY-GREEN FRIABLE MUDSTONE	
					MUDFLAKE HORIZON AT 31·50	
	27.6.73					
					MOTTLED PURPLE-GREY & YELLOW SILTSTONES	32·15
					OFTEN CLAYEY	32·75
					PURPLE-GREY FINE TO COARSE SANDSTONES	
		TRACES 28·6				
						34·50
					DARK RED BROWN & PURPLE-GREY CLAYEY	
					COARSE CONGLOMERATIC SANDSTONES	
					OCCASIONAL SEAMS OF MUDSTONE	
					SOME CLAY CONGLOMERATES	
TEST 4						36·10
					RED & GREY-GREEN MOTTLED MUDSTONES	
5×10^{-3} mm/s						36·50
					MOTTLED CLAY CONGLOMERATE (FINE) ON	
					FINE SANDSTONES WITH CONGLOMERATIC SEAMS	
						38·00
					RED & GREEN & YELLOW MOTTLED MUDSTONES	
					& CLAYEY SILTSTONES MASSIVE & BLOCKY	
						39·00
					GREY-BROWN WITH PURPLE MOTTLING	
					CLAYEY FINE TO MEDIUM SANDSTONE	
	28.6.73				POORLY LAMINATED	40·00

SYMBOLIC LOG

CLIENT **E.D.L.**

REF. M 773

FIG. 2A

DRILLING METHOD **ROTARY AIR FLUSH**	GROUND LEVEL **146m O.D. approx.**	CO-ORDINATES **SK 0462 0235**	BOREHOLE NO. **2**
MACHINE **GRYPHON MARK 5**	CORE BARREL & BIT DESIGN DOUBLE TUBE 4·12 TUNGSTEN	ORIENTATION **VERTICAL**	SITE **ALDRIDGE COLLIERY**

DRILLING & CASING PROGRESS | WATER LEVEL | FRACTURES | CORE RECOV.% & SIZE

SINGLE PACKER OPEN TAIL-PIPE TESTS

▽ 2·7 PARTIALLY SEALED OFF

127

▽ 18/7

IN SITU PERMEABILITY TEST I 3 x 10^{-4} mm/s

▽ 0900 3·7

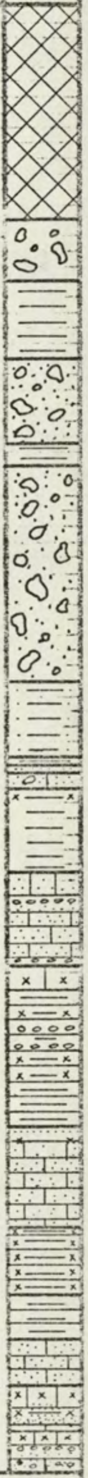
2.7. 73.

TEST 2 1·7 x 10^{-3} mm/s

FRAGMENTARY

DESCRIPTION OF STRATA	DEPTH
BLUE-GREY CLAY WITH GRAVEL & ASH BRICK ETC. FILL	0·00
WELL ROUNDED MEDIUM TO COARSE GRAVEL WITH A LITTLE SAND	2·80
RED CLAY	3·65
SAND & MEDIUM TO COARSE WELL ROUNDED GRAVEL	4·60
RED CLAY	5·70
SAND & MEDIUM TO COARSE WELL ROUNDED GRAVEL DRIFT	6·00
ETRURIA MARL RED-BROWN SANDY MUDSTONE	8·80
THIN RED MUDSTONE ON RED BROWN FINE TO MEDIUM CLAYEY SANDSTONE WITH RED MUDFLAKES	9·80
RED WITH PURPLE MOTTLING MUDSTONE & SILTSTONE	10·20
DARK RED FINE TO COARSE SANDSTONES WITH FINE CONGLOMERATIC SEAMS GENERALLY WITH A CLAY MATRIX	11·30
RED TO RED-BROWN MOTTLED PURPLE-GREY SILTSTONE SILTY MUDSTONE & MUDSTONE WITH THIN CONGLOMERATIC SEAMS WITH YELLOW-GREEN MOTTLING	12·50
DARK RED TO RED-BROWN FINE SANDSTONE OCCASIONAL SEAMS OF SILTY MUDSTONE WITH REDUCTION SPOTS AND SOME PURPLE MOTTLING	14·65
RED BROWN SILTY MUDSTONE BLOCKY AND HIGHLY FRACTURED	15·85
PALE RED MUDSTONE WITH PALE GREY MOTTLING	16·80
PALE RED FINE SANDSTONE WITH THIN MUDSTONE SEAMS	17·40
DARK RED SILTSTONE & CLAYEY SILTSTONE WITH CLAYEY CONGLOMERATIC SEAMS Cont.	18·05
	19·20

SYMBOLIC LOG



MAJOR FRACTURES INDICATED ONLY, MANY SHOW SLICKENSIDES & A CLAY COATING

STANDPIPE (75mm dia.) INSERTED TO 40m ON COMPLETION

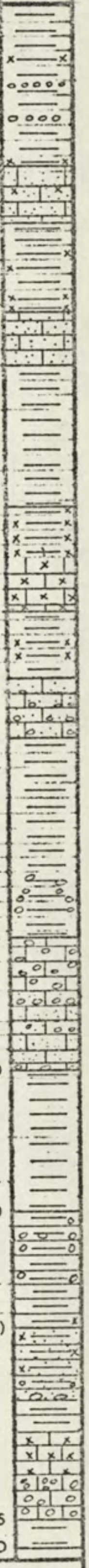
WATER LEVEL
24·7·73 9·60 below top of standpipe

LOGGED BY: J.W.G./J.A.M.	SCALE 1 : 100	CLIENT EFFLUENT DISPOSAL LTD. **E.D.L.**	REF. M 773 FIG. 3

SITE	CONTINUATION SHEET 1	BOREHOLE NO.
ALDRIDGE COLLIERY		2 Cont.

IN SITU PERMEABILITY TESTS	DRILLING & CASING PROGRESS	WATER LEVEL	FRACTURES	CORE RECOV. % & SIZE	DESCRIPTION OF STRATA	DEPTH
IN SITU PERMEABILITY					Cont. RED MUDSTONES MASSIVE & BLOCKY LOCALLY SILTY WITH OCCASIONAL CLAYEY CONGLOMERATIC SEAMS PURPLE & YELLOW MOTTLING COMMON	19·20
				FRAGMENTARY	DARK RED FINE SANDSTONE WITH CLAY MATRIX OCCASIONALLY LAMINATED GREENISH WITH CLAY PARTINGS	21·35
TEST 3 5 x 10^{-4} mm/s					DARK RED-BROWN MUDSTONE & SILTY MUDSTONE REDUCTION SPOTS COMMON	22·10
	3.7.73	TRACE 0900 4.7.73			DARK RED FINE SANDSTONE WITH A RED MUDSTONE SEAM	23·30
					RED & GREEN MOTTLED MUDSTONE LOCALLY SILTY	23·95
					DARK RED-BROWN RED & GREEN MOTTLED SILTY MUDSTONES & CLAYEY SILTSTONES REDUCTION SPOTS COMMON SOME YELLOW MOTTLING TOWARDS BASE	25·90
					RED BROWN MUDSTONE BECOMING GREEN & SILTY	27·25
TEST 4 4 x 10^{-4} mm/s					PALE PINK GREY FINE TO VERY COARSE SANDSTONE WITH FINE CONGLOMERATIC SEAMS	28·15
	4.7.73.	TRACE 0900 5.7.73.		80%	RED-BROWN MUDSTONE SOME GREEN AND YELLOW MOTTLING WITH CONGLOMERATIC SEAMS TOWARDS BASE (MUDFLAKES)	29·05
					MOTTLED RED GREEN BROWN BECOMING DARK PURPLE RED FINE CONGLOMERATE WITH CLAY MATRIX WITH FINE TO COARSE SANDSTONES	31·70
					RED YELLOW & GREEN MOTTLED MUDSTONE BLOCKY MANY REDUCTION SPOTS RED MUDSTONE	33·50
					RED SILTY MUDSTONE WITH MUDFLAKES & FINE GRAVEL	35·40
					GRADING INTO RED SILTY FINE SANDSTONE RED MUDSTONE BECOMING CONGLOMERATIC BOTH SANDY & CLAYEY	(37·00)
					DARK RED MUDSTONE ETRURIA MARL	39·65 40·00

SYMBOLIC LOG



	CLIENT	
	E.D.L.	REF. M773 FIG. 3A

APPENDIX 2

LOGS OF AUGER BOREHOLES AROUND BETTON ABBOTTS SITE

Borehole 1

0.0 - 1.0m	Sandy brown soil
1.0 - 1.3	Light brown clay/sand
1.3 - 1.9	Brown sand
1.9 - 10.0	Chocolate brown clay

(Draw of water on withdrawal @ 6.0m)

Borehole 2

0.0 - 0.6m	Yellow/brown sandy soil
0.6 - 1.2	Chocolate brown clayey sand (wet)
1.2 - 2.5	Chocolate brown firm sandy clay
2.5 - 5.5	Firm brown clay
5.5 - 10.0	Chocolate brown sandy clay

Borehole 3

0.0 - 0.6m	Brown sandy soil
0.6 - 1.3	Yellow clayey sand
1.3 - 2.0	Brown sandy clay, with thin grey clay layer at top
2.0	Traces of organic materials
2.0 - 10.0	Wet brown sand. Water produced at 3.5m
10.0	Chocolate brown clay traces on end of bit

Borehole 4

0.0 - 1.0m	Yellow sand
1.0 - 1.5	Grey sand
1.5 - 2.0	Brown sand. Water produced at 2.0m
2.0 - 10.0	Brown sand, water saturated, yellow sand at extreme end of hole

Borehole 5

0.0 - 0.75m	Brown sandy soil
0.75 - 1.5	Yellow sandy clay
1.5 - 1.75	Brown sand
1.75 - 2.5	Brown sandy clay
2.5 - 3.5	Light brown sandy clay. Water produced at 3.5m
3.5 - 4.0	Liquid clayey material
4.0 - 10.0	Stiff brown clay

Borehole 6

0.0 - 0.6m	Brown sandy soil
0.6 - 2.25	Yellow sand
2.25 - 4.0	Wet yellow sand
4.0 - 5.3	Brown sandy clay - sticky. Slight greyness at base
5.3 - 8.0	Wet clay, brown
8.0 - 10.0	Stiff brown clay

Borehole 7

0.0 - 0.8m	Brown sandy soil
0.8 - 1.75	Wet yellow sand
1.75 - 2.0	Wet yellow sand with some clay
2.0 - 2.25	Light brown sandy clay
2.25 - 3.2	Brown clayey sand becoming progressively sandier downwards
3.2 - 3.9	Brown sand
3.9 - 5.0	Brown sand. Water at 5.0m
5.0 - 8.6	Wet brown sand
8.6 - 10.0	Stiff dark brown clay

Borehole 8

0.0 - 10.0m	Stiff brown clay

Borehole 9

0.0 - 0.75m	Brown clayey soil
0.75 - 3.0	Chocolate brown clay with pebbles
3.0 - 3.6	Sandy brown gravelly clay
3.6 - 4.2	Sandy clay with pebbles
4.2 - 4.5	Pebble free chocolate brown clay
4.5 - 4.8	Brown sand
4.8 - 5.0	Dark brown clay

(Hole terminated as auger would not penetrate deeper)

Borehole 10

0.0 - 0.4m	Brown clay soil
0.4 - 1.0	Yellow-brown sandy clay
1.0 - 1.8	Light grey sticky clay
1.8 - 4.5	Light grey sandy clay - wet
4.5 - 5.5	Lighter grey, sandier clay
5.5 - 9.25	Less sandy grey clay, clay content increasing with depth and the colour changes to a more brown and less liquid clay
9.25 - 10.0	Stiff brown clay

Borehole 11

0.0 - 0.5m	Dark brown soil
0.5 - 1.5	Dark brown clay - dry
1.5 - 1.8	Dark brown clay - sticky
1.8 - 2.0	Sandy dark brown clay
2.0 - 2.8	Yellow brown fine sandy clay
2.8 - 2.9	As above with decreasing sand content
2.9 - 4.5	Stiff chocolate brown clay
4.5 - 4.8	Stiff chocolate brown clay with a few rounded pebbles up to ½" diameter
4.8 - 5.0	Pebble free chocolate brown clay
5.0 - 7.0	Chocolate brown clay - sticky at top becoming stiffer to base

(Hole terminated because of drilling difficulties in stiff clay)

Borehole 12

0.0 - 0.4m	Dark brown clayey soil
0.4 - 1.5	Khaki brown clay
1.5 - 2.3	Wet khaki brown clay
2.3 - 3.5	Liquid clay, grey/khaki colour becoming slightly sandy
3.5 - 4.5	Sandier clay
4.5 - 5.0	Sand content increasing, though still clay
5.0 - 6.5	Grey liquid sand
6.5 - 10.0	Brown sandy clay - relatively liquid
at 10.0	Bit has firm sandy clay adhering to it

Borehole 13

0.0 - 0.5m	Sandy clay soil
0.5 - 1.3	Brown sand and clay
1.3 - 1.7	Brown sandy clay
1.7 - 2.5	Stiff brown sandy clay
2.5 - 3.5	Light brown sandy clay
3.5 - 8.0	Very stiff brown clay
8.0 - 9.5	Wet dark brown clay
9.5 - 10.0	Hard dry brown clay

Borehole 14

0.0 - 0.2m	Peaty deposits
0.2 - 1.1	Dark grey clay
1.1 - 2.0	Brown/grey clay
2.0	Obstruction met. Hole abandoned to be redrilled Clay on end of bit is plastic and brown in colour

Borehole 14 (Redrilled)

0.0 - 0.8m	Black peaty deposit
0.8 - 1.6	Sticky grey clay
1.6 - 1.9	Peaty deposit
1.9 - 3.0	Sticky grey clay with water content increasing to base
3.0 - 4.5	Chocolate brown clay, quite plastic

(Hole terminated because of difficulty in penetrating deeper in clays of this consistency)

Borehole 15

0.0 - 0.7m	Black peaty deposits, some clay content
0.7 - 2.8	Liquid very dark brown clay
2.8 - 4.0	Liquid brown clay, with some plant remains
4.0 - 5.8	Light grey/brown liquid clay
5.8 - 7.8	Light grey/brown sandy liquid clay
7.8 - 10.0	As above, though on withdrawal there was some sandy clay adhering to the last flight

Borehole 16

0.0 - 0.75m	Brown clay soil
0.75 - 1.5	Yellow-brown dry sand
1.5 - 2.0	Chocolate brown sandy clay
2.0 - 2.1	Chocolate brown clay - dry
2.0 - 2.6	Chocolate brown clay - moist, with some small pebbles
2.6 - 3.7	Red-brown moist clay - some sand content
3.7 - 4.2	Wet sticky light brown chocolate sandy clay
4.2 - 5.0	Semi-liquid light chocolate brown sandy clay
5.0 - 5.5	Stiff brown clay
5.5 - 6.1	Liquid chocolate brown clay, some sand content
6.1 -	End of hole. Boulder struck Clay on end of bit is chocolate brown and stiff.

Borehole 17

Location between holes 14 and 15 and some 30 metres to the east

0.0 - 2.5m	Grey clay, wet. Very thin deposit of peaty material occurs at the top of the ground
2.5 - 5.0	Liquid brown clay with some sand content
5.0 - 6.0	Liquid brown sandy clay
6.0 - 7.0	Wet brown clay with some sand content, getting stiffer
7.0 - 8.5	Brown sandy clay, quite plastic
8.5 - 10.0	Stiff plastic brown clay with some sand content

Borehole 18

0.0 - 1.0m	Sandy clay soil
1.0 - 1.5	Sandy clay
1.5 - 2.0	Stiff brown clay
2.0 - 2.7	Sandy brown clay
2.7 - 6.0	Stiff chocolate brown clay
6.0 - 9.0	Slightly wet brown clay
9.0 - 9.3	Crumbly dry brown clay
9.3 - 9.4	Dry brown clayey sand
9.4 - 10.0	Dry hard brown clay

Borehole 19

0.0 - 1.0m	Grey clay mixed with peaty interlayers
1.0 - 3.0	Dark brown clay interlayered with considerable quantities of peaty material
3.0 - 4.0	Wet red brown sand
4.0 - 5.5	Wet red brown sand, getting more clay content downwards
5.5 - 9.0	Hard chocolate brown clay

(Hole ended because of augering difficulties in clay of this consistency. At end of drilling hole filled with water to within 45cm of surface)

APPENDIX 3

The results of the experimental work on the adsorption of metal ions from solutions by clay minerals.

BC	Boulder Clay (Red Clay)
BHS	Borehole Sand (Red Sand)
GC	Grey Clay
Ka	Kaolinite
M	Montmorillonite
Sd	Coal Measures Sandstone
Sh	Coal Measures Shale
WES	West End Sand (Grey Sand)

APPENDIX 3.1

Results of experiments with Perchloric, Nitric and Hydrochloric Acid at pHO on Coal Measures Sandstone and Shale

Solution	Concentration of solution in ppm after a period of time given in days from the commencement of the experiment				
	Day				
	1	3	6	17	55
Cr is $HCLO_4$	3061				
Cr Sd	2925	2722	2778	2759	
Cr Sd	2903	2722	2726	2938	
Cr Sd*	2765	2766	2726	2523	2505
Sd Control	1	2	3	3	3
Cr Sh	2864	2766	2726	2690	
Cr Sh	2841	2766	2778	2690	
Cr Sh*	2713	2550	2572	2321	2190
Sh Control	1	2	2	3	3
Cr in HCL	2347				
Cr Sd*	2433	2426	2367	2179	2244
Cr Sd	2390	2396	2287	2249	
Cr Sd	2339	2396	2247	2165	
Sd Control	3	5	6	7	7
Cr Sh	2239	2321	2192	2043	
Cr Sh*	2272	2321	2208	2110	2048
Cr Sh	2272	2474	2208	2110	
Sh Control	2	5	5	6	7
Cr in HNO_3	2038				
Cr Sd	2152		1633	1737	
Cr Sd	2378		1674	1511	
Cr Sd*	2072		1633	1796	1623
Sd Control	1		3	3	4

Solution	Day				
	1	3	6	17	55
Cr Sh	2210		1810	1796	
Cr Sh*	2095		1810	1808	1678
Cr Sh	2175		1651	1796	
Sh Control	2		3	2	2

*Results used for plotting graph of reduction in concentration of metal ion in solution against time.

Solution	Day						
	1	3	7	11	28	47	64
Zn in HCLO$_4$	8049						
Zn Sd	7954		8101	7549	6040		
Zn Sd*	8049		8101	7217	6304	7749	7735
Zn Sd	8176		8150	7268	6304		
Sd Control	-		-	-	-	8	13
Zn Sh	7923		8101	7176	6432		
Zn Sh*	7923		7633	6912	6304	7749	7597
Zn Sh	5986		7519	7267	6304		
Sh Control	-		-	-	-	25	33

	1	3	7	16	31	70
Zn in HCL	9357					
Zn Sd	9568	9165		9491		
Zn Sd*	9392	9099		8996	8917	9526
Zn Sd	9357	8969		8488		
Sd Control	4	5		9	14	15
Zn Sh*	9357	9165		8439	8689	8814
Zn Sh	9357	8656		8610		
Zn Sh	9357	8656		8865		
Sh Control	3	12		16	25	35

Solution	Day					
	1	3	7	16	32	70
Zn in HNO_3	9176					
Zn Sd*	9176	8437		8371	8917	9526
Zn Sd	9176	8464		8787		
Zn Sd	9176	8043		8317		
Sd Control	2	3		9	8	14
Zn Sh*	8990	8303		8591	8679	9346
Zn Sh	9176	8172		8291		
Zn Sh	9176	7868		8291		
Sh Control	3	8		20	26	52
Solution	1	3	6	17	38	54
Ni in $HClO_4$	2480					
Ni Sd*	2692	3009	2844	2851		
Ni Sd	2841	3009	2844	2770	2775	
Ni Sd	2742	2950	2783	2691		
Sd Control	7	-	9	11	13	14
Ni Sh	2742	3009	2783	2691		
Ni Sh*	2821	3033	2664	2691	2775	2882
Ni Sh	2821	3033	2723	2691		
Sh Control	6	-	7	10	11	14
Solution	1	3	7	16	31	70
Ni in HCl	1789					
Ni Sd	2326	2280	2317	2141		
Ni Sd*	2271	2238	2183	2141	2122	2372
Ni Sd	2235	2238	2222	2141		
Sd Control	4	7	9	11	11	14
Ni Sh	2280	2255	2261	2154		
Ni Sh*	2280	2255	2183	2076	2122	2324
Ni Sh	2280	2255	2222	2154		
Sh Control	4	7	10	13	16	24

Solution	Day					
	1	3	6	16	31	70
Ni in HNO_3	2485					
Ni Sd*	2792	2485	2251	2270	2475	2673
Ni Sd	2673	2561	2322	2353		
Ni Sd	2566	2460	2233	2270		
Sd Control	4	5	6	14	10	12
Ni Sh*	2682	2452	2190	2186	2475	2621
Ni Sh	2700	2452	2207	2270		
Ni Sh	2583	2435	2190	2210		
Sh Control	6	9	9	10	19	22
Solution	1	3	6	17	38	54
Cd in $HClO_4$	102					
Cd Sd	102	89	88	88		
Cd Sd*	100	89	88	87	93	95
Cd Sd	99	88	87	88		
Sd Control	-	-	-	-	-	-
Cd Sh	95	88	87	88		
Cd Sh*	95	89	88	89	95	95
Cd Sh	92	87	87	88		
Sh Control	-	-	-	-	-	-
Solution	1	3	7	16	31	70
Cd in HCL	77					
Cd Sd	82	72	70	69		
Cd Sd*	82	70	65	69	50	80
Cd Sd	82	70	65	67		
Sd Control	-	-	-	-	-	-
Cd Sh	82	68	72	67		
Cd Sh	82	69	70	66		
Cd Sh*	82	73	68	66	50	75
Sh Control	-	-	-	-	-	-

Solution	Day					
	1	3	7	16	31	70
Cd in HNO_3	51					
Cd Sd*	53	51	52	49	44	54
Cd Sd	53	51	51	49		
Cd Sd	53	50	52	48		
Sd Control	-	-	-	-	-	-
Cd Sh*	54	50	49	48	45	54
Cd Sh	54	50	51	48		
Cd Sh	54	39	50	48		
Sh Control	-	-	-	-	-	-

Solution	1	4	7	11	28	46	67
Cu in $HCLO_4$	1469						
Cu Sd*	1402	1447	1454	300	1608	1731	
Cu Sd	1469	1469	1476	313	1564		1485
Cu Sd	1469	1469	1493	313	1564		
Sd Control	-	-	-	2	2	2	2
Cu Sh	1421	1394	1371	391	1417	1546	
Cu Sh*	1421	1409	1505	472	1458		1399
Cu Sh	1518	1462	1382	391	1478		
Sh Control	-	-	-	2	2	2	2

Solution	1	3	7	16	32	70
Cu in HCL	2462					
Cu Sd*	2436	2521	2220	2194	2094	2214
Cu Sd	2462	2536	2226	2172		
Cu Sd	2462	2521	2214	2116		
Sd Control	2	2	1	2	2	5
Cu Sh*	2441	2521	2189	2116	2161	2148
Cu Sh	2441	2408	2201	2102		
Cu Sh	2441	2521	2127	2068		
Sh Control	1	1	1	2	4	6

Solution	Day					
	1	3	7	16	32	70
Cu in HNO_3	1876					
Cu Sd*	1876	2006	1930	1627	1441	1710
Cu Sd	1876	2029	1930	1645		
Cu Sd	1876	2001	1930	1645		
Sd Control	1	1	2	2	2	2
Cu Sh*	1795	1978	1870	1580	1302	1649
Cu Sh	1820	1906	1923	1627		
Cu Sh	1795	1861	1802	1566		
Sh Control	1	1	2	3	7	13

Solution	1	4	7	11	28	46	67
Fe in $HCLO_4$	13390						
Fe Sd	21182	24649	25952	28157	24990		
Fe Sd*	21624	24465	25952	27191	25820	29097	28963
Fe Sd	20744	24189	23871	26241	25403		
Sd Control		8639		12232	10169	11446	
Fe Sh	23426	26549	29079	29139	28313	31609	
Fe Sh*	26261	29179	30074	31157	30856	34255	32359
Fe Sh	24816	29718	31282	30139	29379		
Sh Control		11612		15017	12930	14543	

Solution	1	3	7	16	32	70
Fe in HCL	19034					
Fe Sd*	24337	26042	27872	35403	29181	28121
Fe Sd	25417	24060	27872	37500		
Fe Sd	24337	26042	27706	37500		
Sd Control	6424	12339	11454	13875	15151	16797
Fe Sh*	25056	27456	29137	38600	31133	30056
Fe Sh	26068	27040	28458	39200		
Fe Sh	25056	27456	28881	38200		
Sh Control	5799	11628	13104	13811	15655	16797

Solution	Day 1	3	7	16	32	70
Fe in HNO_3	12404					
Fe Sd*	16967	22247	23149	24723	22738	24002
Fe Sd	18524	21504	23149	24723		
Fe Sd	16510	20775	21964	22664		
Sd Control	4521	8778	9112	10821	11425	10341
Fe Sh*	17584	23004	24547	27767	27120	25522
Fe Sh	17197	23620	25691	27767		
Fe Sh	16057	23776	24547	25601		
Sh Control	7731	13291	13409	15330	18488	16193

Solution	1	4	7	11	28	46	67
Pb in $HClO_4$	524						
Pb Sd	529	528	468	342	341		
Pb Sd	578		397	304	304		
Pb Sd*	539	536	458	342	353	357	393
Pb Control	3	-	-	2	2	2	
Pb Sh*	294	249	199	176	180	177	
Pb Sh	403	384	335	284	286		232
Pb Sh	268	222	191	169	163		
Sh Control	3	-	-	5	4	4	

Solution	1	3	7	16	32	70
Pb in HNO_3	626					
Pb Sd*	649	649	639	661	602	667
Pb Sd	643	649	639	693	664	
Pb Sd	632	642	639	666	670	
Sd Control	2	2	2	3	2	2
Pb Sh*	630	630	639	656	644	645
Pb Sh	630	642	639	666	598	
Pb Sh	644	630	615	595	549	
Sh Control	6	8	8	7	6	5

APPENDIX 3.2

Results of experiments with three acids at pH 1, 2, 3, 4 and 9 on Montmorillonite and Kaolinite, given in ppm of metal ions in solution

CHROMIUM - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Perchloric Acid pH1		2013				
MpH1	500	528	504	511	420	597
Acid pH2		1945				
MpH2	136	89	55	48	56	55
Acid pH3		2092				
MpH3	141	94	60	50	48	43
Acid pH4		2013				
MpH4	109	74	40	36	36	34
Soln pH9		2052				
MpH9	109	70	40		36	30
Hydrochloric Acid pH1		2104				
MpH1	395	387	354	389	312	394
Acid pH2		2013				
MpH2	125	77	46	47	48	47
Acid pH3		1922				
MpH3	94	57	29	27	28	23
Acid pH4		2078				
MpH4	123	81	41	42	44	41
Nitric Acid pH1		2013				
MpH1	355	339	305	330	268	327
Acid pH2		2104				
MpH2	152	110	59	65	64	67
Acid pH3		2013				
MpH3	116	76	41	38	40	35
Acid pH4		2039				
MpH4	116	78	43	39	40	37

CHROMIUM - KAOLINITE

Solution	Days						
	1	3	7	15	37	58	70
Perchloric Acid pH1		2215					
KapH1	2360	2000	2169	2354	1473	1849	1985
Acid pH2		2000					
KapH2	1965	1803	1858	1888	1345	1694	1689
Acid pH3		2271					
KapH3	2201	1966	2056	1933	1416	1725	1619
Acid pH4		2160					
KapH4	2099	1880	1964	1856	1290	1631	1537
Soln pH9		2215					
KapH9	2099	1900	1942	1824	1325	1725	1523
Hydrochloric Acid pH1		2327					
KapH1	2099	1900	2056	1856	1437	1209	1592
Acid pH2		2160					
KapH2	2099	1867	1928	1824	1346	1656	1606
Acid pH3		1967					
KapH3	1930	1803	1824	1792	1207	1521	1372
Acid pH4		2327					
KapH4	2201	1966	2000	1888	13 0	1689	1606
Nitric Acid pH1		2327					
KapH1	2099	1900	1964	1920	1423	1779	1933
Acid pH2		2442					
KapH2	2201	1966	2033	1953	1402	1758	1759
Acid pH3		2271					
KapH3	2201	1900	1949	1856	1360	1590	1640
Acid pH4		2384					
KapH4	2253	1900	1949	1856	1346	1590	1654

Solution	1	3	8	16	30	50	64
Perchloric Acid pH1	1065						
KapH1	992	993	865	955	855	1338	1110
Acid pH2	1020						
KapH2	951	854	817	876	781	1026	912

Solution	Days						
	1	3	8	16	30	50	64
Acid pH3	1044						
KapH3	939	773	797	842	749	832	808
Acid pH4	1032						
KapH4	918	764	797	827	749	817	808
Soln pH9	1061						
KapH9	951	769	797	832	756	800	796

ZINC - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Perchloric Acid pH1	8499					
MpH1	5708	5508	4589	5000	3842	5578
Acid pH2	8141					
MpH2	4959	4207	3453	3736	2814	4136
Acid pH3	8571					
MpH3	5041	4268	3560	3926	2775	4197
Acid pH4	8248					
MpH4	4636	3807	3334	3423	2974	3774
Acid pH9	8177					
MpH9	4636	3899	3269	3423	2619	3834
Hydrochloric Acid pH1	8248					
MpH1	5538	5352	4235	4433	3437	4946
Acid pH2	8899					
MpH2	5102	4515	3750	3897	2904	4321
Acid pH3	9082					
MpH3	5246	4886	3750	3867	3025	4228
Acid pH4	7975					
MpH4	4676	3654	3140	3243	2515	3700
Nitric Acid pH1	10097					
MpH1	5878	5821	4659	5052	3877	5596
Acid pH2	8212					
MpH2	4676	3747	3230	3353	2329	3760
Acid pH3	8248					
MpH3	4676	3411	2937	3106	2726	3525
Acid pH4	10824					
MpH4	4676	4176	3165	3479	2619	3894

ZINC - KAOLINITE

Solution	Days						
	1	3	7	15	37	58	70
Perchloric Acid pH1		7615					
KapH1	6493	6947	6569	6804	7044	9270	9403
Acid pH2		8481					
KapH2	6639	6947	6159	7161	7114	8950	9403
Acid pH3		7615					
KapH3	7083	6637	6707	7161	7206	9018	9460
Acid pH4		7027					
KapH4	6348	6947	6104	6923	7044	8520	9151
Soln pH9		7174					
KapH9		6637	6131	6686	6813	8458	9096
Hydrochloric Acid pH1		6589					
KapH1	6348	6180	6294	6568	7392	8597	9460
Acid pH2		6881					
KapH2	7384	6947	6294	6804	7392	8987	9574
Acid pH3		6735					
KapH3	7384	6791	6376	7161	7392	9393	7421
Acid pH4		7027					
KapH4	6204	6180	6757	6450	6698	8213	8906
Nitric Acid pH1		7321					
KapH1	7283	6947	6707	7161	7578	8241	10004
Acid pH2		6298					
KapH2	6321	5732	5836	6215	6744	9679	8276
Acid pH3		6444					
KapH3	6056	6637	5677	6215	6652	8366	8798
Acid pH4		6589					
KapH4	7283	6444	6077	6333	6522	8404	8987

NICKEL - MONTMORILLONITE

Solution	1	3	18	31	56	70
Perchloric Acid pH1		1648				
MpH1	826	844	917	1182	766	897
Acid pH2		1556				
MpH2	420	376	369	447	304	363
Acid pH3		1731				
MpH3	383	376	345	416	292	340

NICKEL - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Acid pH4		1609				
MpH4	331	291	281	347	243	288
Acid pH9		1615				
MpH9	335	305	296	358	255	302
Hydrochloric Acid pH1		1620				
MpH1	756	735	784	982	600	730
Acid pH2		1545				
MpH2	380	340	334	406	278	328
Acid pH3		1498				
MpH3	287	266	254	307	214	251
Acid pH4		1599				
MpH4	345	312	-	366	256	308
Nitric Acid pH1		1754				
MpH1	734	706	742	951	578	711
Acid pH2		1637				
MpH2	392	345	340	410	279	340
Acid pH3		1561				
MpH3	301	266	266	327	224	245
Acid pH4		1637				
MpH4	323	289	288	364	244	290

NICKEL - KAOLINITE

Solution	1	3	7	15	37	58	70
Perchloric Acid pH1		1699					
KapH1	2070	1808	1750	1827	1812	1936	1688
Acid pH2		1618					
KapH3	1982	1753	1623	1710	1798	1789	1582
Acid pH3		1672					
KapH3	2117	1808	1699	1797	1847	1781	1670
Acid pH4		1645					
KapH4	1912	1699	1593	1681	1754	1647	1548
Soln pH9		1591					
Ka9	1912	1699	1562	1768	1749	1668	1461

Solution	Days						
	1	3	7	15	37	58	70
Hydrochloric Acid pH1		1672					
Ka. pH 1	2117	1753	1686	1681	1847	1899	1697
Acid pH2		1564					
Ka pH 2	1912	1672	1593	1554	1774	1710	1692
Acid pH3		1484					
Ka. pH 3	1810	1564	1490	1287	1633	1508	1410
Acid pH4		1538					
Ka pH 4	1912	1618	1611	1312	1745	1626	1530
Nitric Acid pH1		1645					
KapH1	2070	1835	1718	1768	1867	1914	1670
Acid pH2		1538					
KapH2	1947	1699	1562	1642	1754	1717	1565
Acid pH3		1538					
KapH3	1878	1591	1490	1570	1653	1529	1427
Acid pH4		1591					
KapH4	1912	1645	1562	1598	1711	1617	1478

CADMIUM - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Perchloric Acid pH1		49				
MpH1	17.6	20	19	18		21
Acid pH2		44				
MpH2	1.7	1.7	1.6	1.5		1.4
Acid pH3		48				
MpH3	0.8	0.8	0.7	0.6		0.6
Acid pH4		48				
MpH4	0.6	0.6	0.4	0.3		0.4
Soln pH9		50				
MpH9	0.6	0.7	0.5	0.4		0.4

Solution	Days					
	1	3	18	31	56	70
Hydrochloric Acid pH1		44				
MpH1	22	27	23	20		25
Acid pH2		49				
MpH2	1.8	1.6	1.6	1.2		1.2
Acid pH3		43				
MpH3	0.6	0.6	0.4	0.3		0.3
Acid pH4		46				
MpH4	0.6	0.6	0.4	0.3		0.4
Nitric Acid pH1		36				
MpH1	9	12.1	9.2	8		14
Acid pH2		45				
MpH2	1.5	1.3	1.3	1.1		1.2
Acid pH3		49				
MpH3	0.6	0.6	0.5	0.4		0.4
Acid pH4		49				
MpH4	0.6	0.7	0.5	0.3		0.4

CADMIUM - KAOLINITE

Solution	1	3	7	15	37	58	70
Perchloric Acid pH1		48					
KapH1	45	46	48	47	48	47	49
Acid pH2		42					
KapH2	27	36	39	38	42	37	37
Acid pH3		50					
KapH3	27	35	37	53	41	35	35
Acid pH4		46					
KapH9	14	13	12	14	24	14	12
Soln pH9		47					
	13	12	11	12	21	11	11
Hydrochloric Acid pH1		32					
KapH1	40	41	43	41	44	40	44
Acid pH2		35					
KapH2	36	42	46	41	46	42	43
Acid pH3		41					
KapH3	14	12	11	11	21	8	10

				Days			
Solution	1	3	7	15	37	58	70
Acid pH4		44					
KapH4	12	-	9	10	14	8	9
Nitric Acid pH1		44					
KapH1	27	30	32	31	37	28	28
Acid pH2		48					
KapH2	32	38	40	39	43	38	40
Acid pH3		46					
KapH3	19	16	17	14	23	11	12
Acid pH4		45					
KapH4	14	13	10	11	15	9	11

COPPER - MONTMORILLONITE

Solution	1	3	18	31	56	70
Perchloric Acid pH1		2268				
MpH1	660	403	634	635	742	698
Acid pH2		2446				
MpH2	231	207	262	218	242	229
Acid pH3		2300				
MpH3	210	187	262	203	221	215
Acid pH4		2416				
MpH4	165	139	150	152	165	164
Acid pH9		2339				
MpH9	164	147	150	159	177	177
Hydchloric Acid pH1		2398				
MpH1	606	438	534	572	647	617
Acid pH2		2398				
MpH2	191	183	192	196	213	207
Acid pH3		2403				
MpH3	157	140	154	152	165	162
Acid pH4		2446				
MpH4	149	132	140	143	157	174
Nitric Acid pH1		2300				
MpH1	594	443	550	568	644	620
Acid pH2		2355				
MpH2	231	206	174	212	233	229

Solution	Days					
	1	3	18	31	56	70
Acid pH3		2384				
MpH3	163	147	156	155	174	170
Acid pH4		2282				
MpH4	186	160	178	167	191	193

COPPER - KAOLINITE

Solution	1	3	7	15	37	58	70
Perchloric Acid pH1		1548					
KapH1	1472	1494	1468	1487	1483	1517	1536
Acid pH2		1745					
KapH2	1544	1575	1524	1588	1563	1585	1620
Acid pH3		1772					
KapH3	1647	1690	1650	1669	1665	1657	1688
Acid pH4		1745					
KapH4	1781	1496	1513	1512	1541	1495	1502
Soln pH9		1851					
KapH9	1879	1520	1570	1562	1574	1567	1595
Hydrochloric Acid pH1		1745					
KpH1	1879	1520	1553	1599	1590	1633	1585
Acid pH2		1745					
KapH2	1813	1520	1582	1562	1546	1553	1585
Acid pH3		1693					
KapH3	1813	1520	1496	1512	1536	1477	1512
Acid pH4		1693					
KapH4	1720	1569	1441	1463	1473	1389	1442
Nitric Acid pH1		1772					
KapH1	1620	1660	1641	1669	1701	1682	1688
Acid pH2		1745					
KapH2	1620	1603	1582	1562	1641	1562	1662
Acid pH3		1745					
KapH3	1520	1521	1547	1539	1579	1495	1560
Acid pH4		1799					
KapH4	1595	1575	1629	1588	1590	1504	1585

IRON - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Perchloric Acid pH1		13790				
MpH1	11900	10792	9556	8917	8564	9676
Acid pH2		13888				
MpH2	11309	10314	9744	9304	9818	8887
Acid pH3		13790				
MpH3	11505	10553	9892	9304	9818	9043
Acid pH4		13016				
MpH4	10536	9602	9492		9200	8340
Soln pH9		13546				
MpH9	11066	10076	9528	7478	9444	8581
Hydrochloric Acid pH1		13546				
MpH1	12099	11031	9948	9226	10388	9805
Acid pH2		13160				
MpH2	10776	9744	9808	7268	9248	8430
Acid pH3		13401				
MpH3	11066	11029	9808	7394	9518	8919
Acid pH4		13546				
MpH4	10776	9839	9912	7101	9346	8430
Nitric Acid pH1		13304				
MpH1	11358	10314	8360	15209	9896	9199
Acid pH2		14036				
MpH2	11751	10553	10832	8030	10048	9356
Acid pH3		13790				
MpH3	11260	10076	9808	7562	9618	8826
Acid pH4		14283				
MpH4	10920	10076	9808	7689	9644	8826

IRON - KAOLINITE

Solution	1	3	7	15	37	58	70
Perchloric Acid pH1		13216					
KapH1	13154	12442	11946	14733	13677	896	15482
Acid pH2		13216					
KapH2	13769	12188	12266	14976	13739	931	16497

Solution	Days						
	1	3	7	15	37	58	70
Acid pH3		13742					
KapH3	14081	12442	11626	15469	13862	920	16118
Acid pH4		12698					
KapH4	13666	12188	11466	14733	13125	886	15016
Soln pH9		13216					
KapH9	13666	12698	12748	15222	12575	988	16065
Hydrochloric Acid pH1		13741					
KapH1	14448	13742	12426	15469	13616	920	16118
Acid pH2		13216					
KapH2	13666	12698	12426	14976	13060	899	16065
Acid pH3		13478					
KapH3	13821	13216	12426	15469	13125	903	15016
Acid pH4		13216					
KapH4	13409	12698	11946	14976	13187	879	15274
Nitric Acid pH1		15648					
KapH1	13925	13216	11946	14733	13125	900	15798
Acid pH2		14546					
KapH2	14448	13742	13231	15222	13800	942	15535
Acid pH3		13478					
KapH3	13925	13216	11946	15222	13309	921	15274
Acid pH4		14008					
KapH4	13666	12956	12748	14733	13309	886	14760

LEAD - MONTMORILLONITE

Solution	Days					
	1	3	18	31	56	70
Perchloric Acid pH1		617				
MpH1	57.5	60	40	40	37	44
Acid pH2		608				
MpH2	3.75	4	3.75	-	-	2.9
Acid pH3		675				
MpH3	-	-	-	-	-	-
Acid pH4		536				
MpH4	-	-	-	-	-	-
Soln pH9		572				
MpH9	-	-	-	-	-	-

Solution	Days					
	1	3	18	31	56	70
Nitric Acid pH1		638				
MpH1	50	45.3	37	36	32	37
Acid pH2		601				
MpH2	3.5	2.5	-	-	-	2
Acid pH3		579				
MpH3	-	-	-	-	-	-
Acid pH4		601				
MpH4	-	-	-	-	-	-

LEAD - KAOLINITE

Solution	1	3	7	15	37	58	70
Perchloric Acid pH1		647					
KapH1	528	542	508	634	608	628	543
Acid pH2		584					
KapH2	407	412	387	451	423	470	310
Acid pH3		669					
KapH3	373	359	332	371	329	360	251
Acid pH4		521					
KapH4	174	134	152	152	135	149	122
Soln pH9		563					
KapH9	190	151	152	165	150	160	122
Nitric Acid pH1		647					
KapH1	528	542	541	610	590	697	132
Acid pH2		584					
KapH2	390	394	394	411	388	426	367
Acid pH3		584					
KapH3	223	168	170	196	163	139	159
Acid pH4		563					
KapH4	174	151	133	174	150	79	14

APPENDIX 3.3

Results of the experiments to saturate the exchange sites of montmorillonite and kaolinite, given in ppm of metal ions in solution

MONTMORILLONITE

Solution	Day						
	1	4	8	18	22	45	61
Pb 1075	-	-	-	-	-	-	-
Pb 2176	17	23	24	18	26	16	21
Pb 3719	249	216	215	190	227	176	244
Solution	1	3	5	23	45	65	90
Pb 2510	44	42	33	32	31	35	36
Pb 7864	1678	1394	1338	1321	1474	1537	1468
Pb 17278	12552	8768	4273	5474	6342	6162	6342
Solution	1	4	8	18	22	45	61
Cd 160	3	2	2	2	2	2	2
Cd 371	54	22	15	16	18	14	19
Cd 820	83	83	83	79	84	79	85
Solution	1	3	5	23	45	65	90
Cd 2973	581	564	512	542	515	589	613
Cd 6009	3103	2042	1886	2014	1853	2162	2271
Cd 14369	7008	6254	5799	6112	5794	6489	6955
Solution	1	4	8	18	22	45	61
Cu 2461	798	744	598	611	623	544	697
Cu 4821	2458	2395	2306	2500	2478	2455	2769
Solution	1	3	5	23	45	65	90
Cu 14154	8779	7327	7275	7837	7951	8353	9048
Solution	1	4	8	18	22	45	61
Cr 463	2	-	-	-	-	-	-
Cr 799	21	38	7	3	2	4	2
Cr 1156	39	13	22	8	14	11	-
Solution	1	3	5	23	45	65	90
Cr 1621	187	106	137	75	66	60	60
Cr 4228	1476	1091	982	979	922	919	933
Cr 14816	4409	4284	4887	4184	4249	3918	3905

Solution	Day						
	1	4	8	18	22	45	61
Ni 4336	2089	1635	2001	2187	2271		1789
Ni 5900	4177	3882	4162	4382	4270	3952	3393
Solution	1	3	5	23	45	65	90
Ni 871		105	115	89	97	89	91
Ni 1665		334	348	336	377	337	337
Solution	1	4	8	18	22	45	61
Fe 52	-	-	-	-	-	-	-
Solution	1	3	5	23	45	65	90
Fe 113	-	-	-	-	-	-	-
Fe 400	-	-	-	-	-	-	-
Fe 1135	20	12	10	5	5	4	7
Fe 1986	188	187	187	80	94	79	79
Solution	1	4	8	18	22	45	61
Zn 266	1	5		4	5	6	4
Zn 434	22	19	16	16	16	12	13
Zn 2945	683	660	651	669	670	599	621
Solution	1	3	5	23	45	65	90
Zn 1130	161	130	126	133	122	121	124

KAOLINITE

Solution	Day						
	1	4	8	18	22	45	61
Pb 1075	450	405	582	384	409	337	341
Pb 1763	967	901	1126	781	928	904	889
Solution	1	3	5	23	45	65	90
Pb 2510	1840	1684	1523	1513	1670	1700	1722
Pb 7864	7099	6585	5867	6603	7049	7226	7542
Pb 17278	16712	14421	14420	14325	16043	16308	16315

Solution	Day						
	1	4	8	18	22	45	61
Cd 160	61	61	63	47	47	63	66
Cd 371	299	168	292	172	163	297	307
Cd 820	302	471	619	467	449		363
Solution	1	3	5	23	45	65	90
Cd 2973	2553	2703	2409	2532	2685	3045	3148
Cd 6009	6132	5568	5294	5780	5312	6123	6245
Cd 14369	13277	12566	11120	12336	11415	12774	14263
Solution	1	4	8	18	22	45	61
Cu 68	-	-	-	-	-	-	-
Solution	1	3	5	23	45	65	90
Cu 2974	2417	2458	2480	2689	3415	2761	3093
Cu 6187	5678	5634	5309	5818	6560	6543	6978
Cu 14154	13639		12120	11045	12903	13397	14201
Solution	1	4	8	18	22	45	61
Cr 463	238	235	213	214		253	190
Cr 799		651	634	640	608	612	581
Cr 1156	1110	1053	997	1011	960	978	954
Solution	1	3	7	23	45	65	90
Cr 1621	1470	1323	1556	1485	1526	1441	1406
Solution	1	4	8	18	22	45	61
Ni 500	370	377	364	416	338	420	413
Solution	1	3	7	23	45	65	90
Ni 871		715	883	529	681	666	719
Ni 1665		1475	989	1430	1592	1440	1531
Ni 4247		4176	4740	3842	4346	4122	4166
Ni 6236		6158	6613	6060	6591	6239	6419
Solution	1	4	8	18	22	45	61
Fe 52	-	-	-	-	-	-	-

Solution	Day				
	1	3	10	33	69
Fe 635	485	457	386	403	365
Fe 1407	1192	1141	992	1010	986
Fe 4944	4658	4510	4672	5223	5166

Solution	1	4	8	18	22	45	61
Zn 20	4	3	4	4	5	3	2

Solution	1	3	7	23	45	65	90
Zn 191	99	96	90	97	97	97	102
Zn 788	520	483	485	504	488	544	492
Zn 1130	917	931	899	1009	934	938	890
Zn 2945	2175	1615	2040	2218	2173	2187	2250

APPENDIX 3.4

Results of the experiments to determine the effect of the $SO_4^=$ anion on adsorption, and the concentration of sodium and potassium in the solution, in ppm.

Solution	Day														
	1			3			5			9			24		
LEAD	Pb	Na	K	Pb	Na	K	Pb	Na	K	Pb	Na	K	Pb	Na	K
HCl Control	636	5	0.3												
HCl Ka 1	209	64	9	174	66	9	147	68	10	115	90	10	122	100	11
HCl Ka 2	201			149			150			106			96		
HCl M 1	7	126	11	3	133	11	1.4	144	10	11	122	10	4	122	9
HCl M 2	2			0.6		11	0.6			9			4		
H_2SO_4 Control	481	4	0.3												
H_2SO_4 Ka 1	127	60	9	91	77	9	128	74	11	53	86	10	54	81	10
H_2SO_4 Ka 2	139			103		9	120			76					
H_2SO_4 M 1	3	136	10	1	139	11	1	142	11	4	121	10	1	130	10
H_2SO_4 M 2	1			0.4		11	0.6			7					
HNO_3 Control	616	4	0.2												
HNO_3 Ka 1	212	56	9	152	75	11	116	72	11	118	84	12	103	81	16
HNO_3 Ka 2	196			136		13	121			119			89		
HNO_3 M 1	2	152	11	1	153	11	0.8	143	11	9	121	10	2		
HNO_3 M 2	2			0.9		12	0.6			9			0.6	81	9
CADMIUM															
HCl Control	81														
HCl Ka 1	22		6	20	69	8	29	71	7	31	76		10	67	8
HCl Ka 2	23			20			23			31			19	69	17
HCl M 1	2		9	1.3	126	9	1.3	130	9	2.2	116		1.1	119	16
HCl M 2	1.5			1.1			1.2			1.9			1.0	137	11
H_2SO_4 Control	85														
H_2SO_4 Ka 1	23		20	22	69	8	24	73	7	34	75		19	70	18
H_2SO_4 Ka 2	23			21			24			33			20	69	17
H_2SO_4 M 1	1		9	1.1	128	9	1.4	131	9	1.8	137		1.1	122	13
H_2SO_4 M 2	1.5			1.3			1.4						0.8		11
HNO_3 Control	95														
HNO_3 Ka 1	30		6	26	71	7	27	71	8	39	76		21	72	15
HNO_3 Ka 2	26			24			26			35			23	70	18
HNO_3 M 1	1.8		9	1.6	123	8	1.6	123	9	1.9	136		1.2	119	
HNO_3 M 2	1.8			1.5						2.4			1.3	132	

Element							Day								
	1			3			5			9			24		
		K	Na		K	Na		K	Na		K	Na		K	Na
ZINC															
HQ Control	7304	-	10												
Ka 1	6688	11	78	6700	17	77	6781	19	76	6115			6225	14	52
Ka 2	7027			7075			6991			6154					
M 1	4168	33		4204	50	299	3895	40	270	3496			3881	31	167
M 2	4006			3887			3368			3269					
H_2SO_4 Control	7304		10												
Ka 1	6857	15	67	7442	33	80	7205	19	80	6154				16	51
Ka 2	7069			6729			6372			6414					
M 1	4207	41		4404	51	290		40	291	3629				34	160
M 2	3445			3473			3621			3307					
HNO_3 Control	7112	-	4												
Ka 1	6688	11	71	6521	34	80	7422	19	79	6135				16	50
Ka 2	6984			7232						6374					
M 1	3645	36		4244	48	299	3846	39	252	3496				33	158
M 2	4329			4046											
NICKEL															
HQ Control	1659														
Ka 1	1490	13	79	1400	17	86	1360	17	84	1458	15	88	1332	15	81
Ka 2	1478		90	1385			1360			1497			1332	16	83
M 1	499	23	160	450	24	213	210	26	249	346	22	156	291	22	244
M 2	502	23	160	352			371			346			294	21	225
H_2SO_4 Control	1641														
Ka 1	1438	13	73	1410	16	83	1364	15	87	1445	14	43	1321	14	79
Ka 2	1472		71	1400			7360			1451			1309	16	81
M 1	357	24	221	484	24	199	375	24	234	352	22	157	278	23	242
M 2	531		149	450			309			312			275	20	235
HNO_3 Control	1629														
Ka 1	1415	16	69	1355	14	81	1346	15	83	1240	15	43	1299	16	81
Ka 2	1380		70	1335			1311			1196			1299	16	80
M 1	357	25	215	361	25	221	309	23	237	273	21	156			242
M2	357		211	361			303			259				27	

	Day														
Element	1			3			5			9			24		
		K	Na		K	Na		K	Na		K	Na		K	Na
IRON															
HQ Control	14766														
Ka 1	13913	16		13258	15		12956	21	83	12943		82	12693	29	78
Ka 2	13913			12979		90	13992			13544			13658		
M 1	10127	60		10067	68		9880	64	341	8883		402	9340	72	313
M 2	9867			9266		344	9230			9209			9045		
H_2SO_4 Control	15034														
Ka 1	14392	17		13393	18		13783	22	87	14188		83	13949	16	79
Ka 2	14608			13188		86	13664						14042		
M 1	9925	62		9493	68		9419	63	354	9209		387	9049	71	313
M 2	9550			9266		373	9682						9143		
HNO_3 Control	14606														
Ka 1	14126	17		12979	19		12759	22	150	11251		145	10846	27	161
Ka 2	14019			13049	11	148	12617						13786		
M 1	9780	61		9493	70		9312	65	414	9013		442	8997	67	388
M 2	9350			8366		421	9608						8997		
COPPER															
HQ Control	1838														
Ka 1	1691	14		1564	16	78	1666			1580	13	42	1668	8	65
Ka 2	1669			1564			1634			1551			1683		
M 1	295	17		232	36	226	239			199	22	155	209	23	198
M 2	322			257			247			219			206		
H_2SO_4 Control	1838														
Ka 1	1675	7		1512	15	78	1634			1530	15	44	1584	10	45
Ka 2	1675			1485			1634			1580			1591		
M 1	299	14		244	39	229	275			207	23	156	246	22	198
M 2	344			276			278			207			247		
HNO_3 Control	1849														
Ka 1	1675	7		1664	15	77	1612			1566	14	43	1021	15	55
Ka 2	1675			1617			1650			1566			984		
M 1	329	14		292	39	223	260			211	22	156	253	22	198
M 2	304			280			257			206			251		

Element	Day														
	1			3			5			9			24		
		K	Na		K	Na		K	Na		K	Na		K	Na
CHROMIUM															
HQ Control	1102														
Ka 1	1037	16		995	18	219	986	16	67	1055	19	152	941	20	219
Ka 2	1059	15		1032			993			1072			1031		
M 1	136	34		92	37	405	68	37	124	53	20	2437	31	20	369
M 2	120			160			62			44			30		
H_2SO_4 Control	1156														
Ka 1	1075	15		995	23	225	1000	19	67	1094	19	153	996	23	218
Ka 2	1113			1051			1019			1077			1027		
M 1	188	32		100	33	378	76	32	114	62	31	2450	39		353
M 2	134			148			59			48			30		
HNO_3 Control	1156														
Ka 1	1075	16		1032	19	244	993	19	68	1089	19	152	1006	21	214
Ka 2	1097			1070			1029			1089			1004		
M 1	126			79	37	405		35	118	48	33	2231	34	31	369
M 2	131			187			67			55			34		

APPENDIX 3.5

Results of experiments with solutions containing combinations of elements on montmorillonite, kaolinite and Coal Measures Shale.

Combination A	Day						
	1	3	7	21	47	65	90
Cu	33	-	-	-	-	-	-
Cu M	-	-	-	-	-	5	1
Cu Sh	24	11	5	-	-	3	-
Cu Ka	32	31	32	40	33	38	
Fe	99						
Fe M	-	-	-	-	2	9	-
Fe Sh	24	7	4	7	-	9	-
Fe Ka	25	13	11	10	16	14	-
Pb	136						
Pb M	-	-	-	-	-	-	-
Pb Sh	66	28	10	-	-	-	-
Pb Ka	120	121	123	114	129	95	96
Zn	53						
Zn M	-	4	4	3	3	9	2
Zn Sh	39	28	23	17	19		19
Zn Ka	66	65	66	64	69	71	
Ni		653					
Ni M		98	120	118	91	105	81
Ni Sh		387	396	380	371	347	359
Ni Ka		604	705	725	663	643	
Cd	13						
Cd M	3	3	2	3	3	3	3
Cd Sh	11		9	10	8	8	8
Cd Ka	14		12	14	15	15	17
Cr	69						
Cr M	-	-	-	-	-	-	-
Cr Sh	15	-	-	-	-	-	-
Cr Ka	44	40	42	30	33	40	30

Combination B	Day 1	3	7	21	47	65	90
Cu	3671						
Cu M	2779	2980	3073	3548	3496	3679	4039
Cu Sh	3293	3619	3604	4147	4033	4152	4055
Cu Ka	3320	3575	3677	4338	4195	4264	
Fe	6439						
Fe M	3764	2424	3410	3392	4368	3813	
Fe Sh	6362	4778	5115	7390	7833	7660	
Fe Ka	7123	4598	5048	7499	7787	7954	
Zn	52						
Zn M	25	23	22	22	27	27	
Zn Sh	30	41	42	40	43	53	
Zn Ka	42	41	52	61	75	83	
Ni	434						
Ni M	384	323	463	386	374	358	371
Ni Sh	426	379	546	449	426	408	420
Ni Ka	426	380	534	441	420	411	
Cr	14						
Cr M	7	10	7	8	9	8	
Cr Sh	20	23	13	11	11	16	
Cr Ka	16	23	17	18	19	18	

Combination C

Fe	1617						
Fe M	229	146	129	94	119	91	93
Fe Sh	1283	628	840	1375	1376	1173	997
Fe Ka	1495	859	923	1581	1736	1725	1642
Zn	3747						
Zn M	2242	2116	2060	1931		2100	2275
Zn Sh	3573	3418	3263	3446		3622	3375
Zn Ka	3692	3668	3612	3597		3960	3987

Combination D	Day						
	1	3	7	21	47	65	90
Cu	6999						
Cu M	5056	5906	6592	6540	6506	6698	8740
Cu Sh	6613	7035	7846	8198	8067	8012	8283
Cu Ka	6916	7474	8952	8341	8391	8704	8667
Zn	1438						
Zn M	1075	1178	894	1016	1150	1090	1494
Zn Sh	1302	1447	1337	1280	1365	1412	1423
Zn Ka	1387	1424	1419	1265	1466	1451	1494
Ni	6382						
Ni M		5368	6453	5003	4625	4605	5967
Ni Sh		6382	7192	5590	6214	5513	6046
Ni Ka		6382	7192	5912	6613	5736	6046
Cr	2312						
Cr M	1233	1262	1032	964	754	907	964
Cr Sh	2000	2071	1609	1900	1576	1540	1576
Cr Ka	2391	2400	1624	2420	2408	2555	2175

Combination E

Cu	3627						
Cu M	2364	2294	1197	1459	1546	1539	1634
Cu Sh	2779	2830	2818	2965	2536	2415	2679
Cu Ka	3458	3634	3697	3054	3660	4548	4243
Zn	24						
Zn M	10	10	10	9	10		10
Zn Sh	22	23	22	23	26		30
Zn Ka	42	39	39		42		36
Ni	264						
Ni M	136	132	100	80	80	75	81
Ni Sh	236	196	231	185	166	170	158
Ni Ka	278	264	251	192	182	179	182
Cr	16						
Cr M	-	-	-	-	-	-	-
Cr Sh	-	-	-	-	-	-	-
Cr Ka	22	11	-	-	-	-	-

Combination F	Day						
	1	3	7	21	47	65	90
Cu	31						
Cu M	25	23	24	16	17	17	17
Cu Sh	29	31	29	29	32	31	37
Cu Ka	28	28	35	41	37	41	42
Fe	10990						
Fe M	7573	4298	5021		7775	7774	7458
Fe Sh	10496	8400	7343	10595	10448	10719	12854
Fe Ka	11190	8960	13920	13095	10768	13630	12769
Pb	101						
Pb M	76	78	82	32	129	85	82
Pb Sh	90	97	102	35	80	108	109
Pb Ka	101	99	106	82	112	104	113
Zn	54						
Zn M	33	34	18	22	29	25	29
Zn Sh	39	39	23	35	42	47	49
Zn Ka	51	55	52	52	58	58	75
Cd	19						
Cd M	16	18	15	18		19	19
Cd Sh	18	19	16	19		19	20
Cd Ka	18	20	21	20		20	20
Cr	43						
Cr M	32	41	40	24	35	44	31
Cr Sh	35	38	54	43	46	52	42
Cr Ka	52	57	53	56	59	66	55

APPENDIX 3.6

Results of the experiments with Coal Measures Shale in ppm of metal ion in solution.

pH Experiments

Solution	Day					
	1	3	8	13	26	41
Fe acid pH1	12008					
Sd pH1	17365	19285	19082	19565	20152	20572
Sh pH1	19274	22223	23374	23771	25684	27809
Fe acid pH2	10922					
Sd pH2	9398	9200		7977	8025	
Sh pH2	10922	12698		10756	11862	
Fe acid pH3	13738					
Sd pH3	11560	12281	10952	11787		
Sh pH3	14049	14306	12356	13716		
Fe acid pH4	12563					
Sd pH4	10583	11057	8525	8808		9033
Sh pH4	12058	12698	11447	12140		
Fe acid pH9	11068					
Sd pH9	8615	8212	6948	6920		7026
Sh pH9	10105	10658	9364	9942		9914
Pb acid pH1	545					
Sd pH1	578	568	544	518	548	535
Sh pH1	432	412	322	253	381	391
Pb acid pH2	584					
Sd pH2	242	136	-	-	-	-
Sh pH2	91	15	-	-	-	-
Pb acid Ph3	744					
Sd pH3	-	-	-	-	-	-
Sh pH3	-	-	-	-	-	-
Pb acid pH4	663					
Sd pH4	-	-	-	-	-	-
Sh pH4	-	-	-	-	-	-
Pb acid pH9	534					
Sd pH9	-	-	-	-	-	-
Sh pH9	-	-	-	-	-	-

Solution	Day				
	1	3	14	43	55
Cd acid pH1	50				
Sd pH1	17	18	9	11	-
Sh pH1	18	16	9	10	-
Cd acid pH2	43				
Sd pH2	8	1	0.08	-	-
Sh pH2	14	1	0.2	-	-
Cd acid pH3	47				
Sd pH3	0.5	1	-	-	-
Sh pH3	0.4	1	-	-	-
Cd acid pH4	50				
Sd pH4	0.5	1	0.02	-	-
Sh pH4	0.4	1	0.03	-	-
Cd acid pH9	70				
Sd pH9	1.0	1	0.06	-	-
Sh pH9	0.6	1	0.08	-	-
Sd pH1			0.08		
Sh pH1			0.11		
Cu acid pH1	1498				
Sd pH1	1597	1530	1527	1629	1636
Sh pH1	1574	1474	1527	1557	1480
Cu acid pH2	1702				
Sd pH2	1065	410	0.6	-	-
Sh pH2	680		4.5	-	-
Cu acid pH3	1967				
Sd pH3	1022	451	0.4	-	-
Sh pH3	870	515	123	-	-
Cu acid pH4	2429				
Sd pH4	1574	730	0.5	-	-
Sh pH4	909	522	11.8	-	-
Cu acid pH9	1929				
Sd pH9	1108	451	0.3	-	-
Sh pH9	556	230	1.0	-	-
Sd pH1	1.1	1.9	1.7	1.4	2.1
Sh pH1	1.3	1.5	3.4	3.9	4.4

Solution	Day				
	1	3	14	43	55
Other pH controls contained no copper					
Zn Sd 1				1.4	
Zn Sh 1				2.6	
N Sd 1				1.8	
N Sh 1				4.4	
Cr Sd 1				1.3	
Cr Sh 1				2.2	
Cd Sd 1				1.4	
Cd Sh 1				3.0	

Solution	1	3	14	43	55
Ni acid pH1	2011				
Sd pH1	1614	1802	2159	2000	2000
Sh pH1	1578	1519	2046	1855	1929
Ni acid pH2	1855				
Sd pH2	1290	853	440	57	9
Sh pH2	839		183	37	15
Ni acid pH3	1649				
Sd pH3	1224	773	459	37	17
Sh pH3	794	428	156	27	24
Ni acid pH4	1977				
Sd pH4	1621	958	639	141	45.5
Sh pH4	963	573	279	63	37.5
Ni acid pH9	1818				
Sd pH9	986	655	306	8.3	5
Sh pH9	848	465	185	35	30
Sd pH1	4	5	7.1	7.1	8
Sh pH1	7	7	13.6	14.5	16
Zn Sd 1				6.2	
Zn Sh 1				13.6	
Cu Sd 1				7.5	
Cu Sh 1				12.5	
Cr Sd 1				7.0	
Cr Sh 1				13.7	

Solution	Day				
	1	3	14	43	55
Cd Sd 1				6.8	
Cd Sh 1				13.1	
Zn Sd 2				1.3	
Zn Sh 2				6.2	
Cr Sh 2				1.5	
Zn Sd 3				1.4	
Zn Sh 3				6.1	
Zn Sh 4				6.0	
Cr Sh 4				1.3	
Zn Sd 9				1.3	
Zn Sh 9				5.3	

Solution	1	3	14	43	55
Zn acid pH1	7204				
Sd pH1	8030	8367	7613	8870	8466
Sh pH1	7974	8000	7246	8429	7953
Zn acid pH2	7204				
Sd pH2	6800	6853	5201	5296	
Sh pH2		5925	4469	4314	4583
Zn acid pH3	7874				
Sd pH3	6690	6791	5416	5416	5522
Sh pH3	6308	6356	3611	4314	4407
Zn acid pH4	7874				
Sd pH4	7368	8194	5744	6638	6768
Sh pH4	6518	6590	4005	5097	4763
Zn acid pH9	9568				
Sd pH9	3858	8467	6583	6513	6338
Sh pH9	8050	8218	5634	6513	7793
Pb 1 Sd	4	4.7	4.4	6.5	9.1
Pb 1 Sh	5	7.5	0.6	1.8	19.5
Cu Sd 1				4.9	
Cu Sh 1				12.8	
Ni Sd 1				6.5	
Ni Sh 1				16.0	

Solution	Day				
	1	3	14	43	55
Cr Sd 1				6.7	
Cr Sh 1				16.5	
Cd Sd 1				7.1	
Cd Sh 1				15.4	

Solution	1	3	14	43	55
Cr Acid pH1	2110				
Cr Sd1	2031	1968	1537	814	670
Cr Sh1	1906	1423	943	260	162
Cr acid pH2	2110				
Cr Sd2	869	17	-	-	-
Cr Sh2	1135	598	570	-	-
Cr acid pH3	2054				
Cr Sd3	1081	352	-	-	-
Cr Sh3	901	481	251	-	-
Cr acid pH4	2190				
Cr Sd4	717	13	-	-	-
Cr Sh4	869	402	136	-	-
Cr acid pH9	1906				
Cr Sd9	798	76	-	-	-
Cr Sh9	744	369	115	-	-
No Cr in Control Experiments					

Saturation Experiments

Solution	Day						
	1	4	7	18	22	45	61
Pb 1075	37	23	-	-	-	-	-
Pb 2176	446	201	93	47	40	-	-
Pb 3719	1918	1610	1460	1125	1242	917	758
Solution	1	3	7	25	49	67	90
Pb 2510	836	432	231	134	102	156	75
Pb 7864	5800	4756	3700	3960	4192	3941	3963
Pb 17278	14674	10938	11363	11409	12492	12163	12163
Solution	1	4	8	18	22	45	61
Cd 160	2	1	1	1	1	1	1
Cd 371	51	36	29	22	24	28	37
Cd 820	142	166	283	176	167	201	168
Solution	1	3	7	25	49	67	90
Cd 2973	1898	1784	1680	1740	1925	2041	2396
Cd 6009	5332	4615	4398	4860	4537	5094	
Cd 14369	12466	11611	10559	11439	10447	11654	13257
Solution	1	4	8	18	22	45	61
Cu 2461	1840	1633	1741	1382	1422	1188	1157
Cu 4821	4833	4717	4627	4370	4108	4277	4446
Solution	1	3	7	25	49	67	90
Cu 14154	12976	12252	11439	11597	11396	11907	12569
Solution	1	4	8	18	22	45	61
Cr 462	23	-		-	-	-	-
Cr 799	246	235	24	2	2	-	-
Cr 1156		1440	152	32	16	3	-
Solution	1	3	7	25	49	67	90
Cr 1621	1331	1045	687	221	100	55	35
Cr 4228	3736	2966	3677	1908	1718	1693	1480
Cr 14816	14907	14308	8264	6683	6554	6256	5858

Solution	Day						
	1	4	8	18	22	45	61
Ni 500	103	57	42	32	24		20
Solution	1	3	7	25	49	67	90
Ni 871		331	270	222	216	200	196
Ni 1665		1040	852	891	906	826	890
Ni 4247		3393	4261	3060	3447	3238	3272
Ni 6236		5340	6194	5461	5884	5513	5348
Solution	1	4	8	18	22	45	61
Zn 266	7	3	1	-	-	-	-
Zn 434	74	38	30	18	4	9	7
Zn 2945	2047	1821	1748	1819	1765	1577	1525
Solution	1	3	7	25	49	67	90
Zn 1130	625	473	363	376	337	351	298
Solution	1	3	7	25	49	67	90
Fe 113	-	-	-	-	-	-	-
Fe 400	250	245	133	56	9	-	-
Fe 1135	687	562	571	433	494	418	355
Fe 1986	1677	1678	1597	1614		1620	

APPENDIX 3.7

The results of the experiments with Betton Abbotts Site rocks in ppm.

Solution	Day 1	3	7	22	52	73
IRON						
Fe Control pH3	590					
BC pH3	-	-	-	-	-	-
WES pH3	-	-	-	-	-	-
GC pH3	110	88	127	143	129	74
BHS pH3	339	242	216	159	138	145
Fe 1 Control pH9	626					
BC pH9	-	-	-	-	-	-
WES pH9	4	-	-	-	-	-
GC pH9	155	99	115	137	130	81
BHS pH9	344	239	225	166	196	166
Combination 1						
Fe Control pH3	610					
BC pH3	-	-	-		-	-
WES pH3	5	-	-		-	-
GC pH3	191	162	168		202	141
BHS pH3	281	259	238	190	188	149
Fe Control pH9	582					
BC pH9	-	-	-	-	-	-
WES pH9	9	-	-	-	-	-
GC pH9	160	160	165	196	200	106
BHS pH9	368	217	199	182	171	167
Fe 2 Control pH3	19553					
BC 2 pH3	15749	9263	8692	8282	8648	8681
WES 2 pH3	17638	15107	15324	14719	15318	15299
GC 2 pH3	19261	17093	17381	17857	18897	18577
BHS 2 pH3	18589	16992	18517	18355	19986	18313
BHS 2 Control	18070					
Fe 2 Control pH9	19611					
BC 2 pH9	14448	9016	8715	8193	8497	8111
WES 2 pH9	18215	15828	15132	14719	14474	14684
GC 2 pH9	19028	17652	17304	17857	18230	19233
BHS 2 pH9	18589	16992	18517	18355	19986	18313
BHS 2 Control	18070					

Solution	Day					
	1	3	7	22	52	73
Combination 2						
Fe Control pH3	8595					
BC pH3	4956	3970		2673		
WES pH3	7003	4778	4420	4583	3774	3871
GC pH3	8366	7839	8059	7854	8362	9640
BHS pH3	8867	8749	8862	8834	9714	10027
BHS Control	9039					
Fe Control pH9	18309					
BC pH9	13313	7915	7969	8312	7638	8385
WES pH9	16679	14620	13922	13726	13945	12808
GC pH9	17638	16434	16739	17194	17734	16094
BHS pH9	16160	16792	17094	17981	18843	19079
BHS Control	16485					

Solution	1	3	7	22	50	73
CADMIUM						
Cd Control pH3	19					
BC pH3	-	-	-	-	-	-
WES pH3	-	-	-	-	-	-
GC pH3	0.7	0.8	4	0.5	5	0.7
BHS pH3	8	7	8		6	7
BHS Control	18					
Cd Control pH9	23					
BC pH9	-	-	-	-	-	-
WES pH9	-	-	-	-	-	-
GC pH9	1.1	1.0	0.9	0.7	0.6	0.7
BHS pH9	2	0.8	0.2	0.6	-	-
BHS Control	25					
Combination 1						
Cd Control pH3	25					
BC pH3	14	11	9	7	5	4
WES pH3	22	16	9	12	10	10
GC pH3	23	21	21	22	22	28
BHS pH3	25	23	23	23	22	20
BHS Control	25					

Solution	Day					
	1	3	7	22	50	73
Cd Control pH9	17					
BC pH9	13	11	5	4	3	2
WES pH9	15	15	9	7	8	7
GC pH9	16	16	16	15	16	19
BHS pH9	19	16	17	18	19	19
BHS Control	19					
Solution	1	3	7	17	50	73
CHROMIUM						
Cr Control pH3	94					
BC pH3	-	-	-	-	-	-
WES pH3	-	-	-	-	-	-
GC pH3	-	-	-	-	-	-
BHS pH3	12	-	-	-	-	-
BHS Control	93					
Cr Control pH9	93					
BC pH9	-	-	-	-	-	-
WES pH9	-	-	-	-	-	-
GC pH9	-	-	-	-	-	-
BHS pH9	11	-	-	-	-	-
BHS Control	95					
Combination 1						
Cr Control pH3	94					
BC pH3	-	-	-	-	-	-
WES pH3	12	-	-	-	-	-
GC pH3	4	7	7	7	7	4
BHS pH3	76	75	75	59	55	50
BHS Control	90					
Cr Control pH9	85					
BC pH9	-	-	-	-	-	-
WES pH9	20	-	-	-	-	-
GC pH9	41	22	22	-	5	4
BHS pH9	75	60	62	59	65	62
BHS Control	90					

Solution	DAY					
	1	3	7	22	50	84
NICKEL						
Ni Control pH3	1278					
BC pH3	828	617	506	371	268	170
WES pH3	1085	862	781	658	590	449
GC pH3	980	804	781	779	817	842
BHS pH3	1214	1134	1056	993	1051	
BHS Control	1161					
Ni Control pH9	1247					
BC pH9	858	627	525	356	263	176
WES pH9	586	880	792	645	571	430
GC pH9	960	812	798	790	824	872
BHS pH9	1214	1120	1091	1076	1062	
BHS Control	1171					
Combination 1						
Ni Control pH3	1334					
BC pH3	1064	890	745		574	271
WES pH3	1219	1088	957		676	466
GC pH3	1219	1134	1133		1148	1221
BHS pH3	1328	1261	1267	1277	1324	1343
BHS Control	1310					
Ni Control pH9	1353					
BC pH9	1285	894	722	422	242	129
WES pH9	1377	1112	947	686	490	336
GC pH9	1205	1168	1124	1103	1118	1175
BHS pH9	1230	1232	1218	1184	1227	1283
BHS Control	1214					
COPPER						
Cu Control pH3	133					
BC pH3	-	-	-	-	-	-
WES pH3	8	-	-	-	-	-
GC pH3	9	5	4	3	3	3
BHS pH3	52	24	14	1	-	-
BHS Control	172					

Solution	Day					
	1	3	7	22	50	84
Cu Control pH9	127					
BC pH9	-	-	-	-	-	-
WES pH9	11	-	-	-	-	-
GC pH9	11	7	5	4	5	4
BHS pH9	70	31	19	3	1	1
BHS Control	197					
Combination 1						
Cu Control pH3	202					
BC pH3	45	1	-	-	-	-
WES pH3	139	18	1	-	-	-
GC pH3	175	166	169	154	154	134
BHS pH3		204	208	197	169	186
Cu Control pH9	209					
BC pH9	68	10	1	-	-	-
WES pH9	169	26	1	-	-	-
GC pH9	177	172	173	124	150	149
BHS pH9	191	167	171	190		216
BHS Control	186					

Solution	1	3	7	22	52	73
Cu Control pH3	8715					
BC pH3	7169	4995	2271	2784	-	-
WES pH3	7963	6726	4839	2626	1466	605
GC pH3	8187	8575	9091	9084	10070	11069
BHS pH3	10681	10457	9043	10507	9703	11326
BHS Control	11290					
Cu Control pH9	8988					
BC pH9	7330	4864	2378	548	-	-
WES pH9	8007	6376	4645	2181	1160	527
GC pH9	8464	8526	9208	8528	9781	11387
BHS pH9	11061	9891	9528	11492	11867	11612
BHS Control	11061					
Combination 2						
Control pH3	10485					
BC pH3	9292	8405	8800	8318	3338	9926

Solution	Day					
	1	3	7	22	52	73
WES pH3	9556	8949	9600	9375	9557	12008
GC pH3	9556	8772	9404	9347	9147	12313
BHS pH3	8952	8410	8896	8851	11706	11244
BHS Control	9184					
Control pH9	10255					
BC pH9	9367	8772	8584	9375	9129	11535
WES pH9	9500	9207	8893	9430	9371	12008
GC pH9	9500	8924	8635	9375	9184	11663
BHS pH9	8919	8776	8896	9147	11509	10858
BHS Control	9151					
ZINC						
Zn Control pH3	211					
BC pH3	115	41	10	1	-	-
WES pH3	180	151	87	7	4	5
GC pH3	190	179	183	168	175	182
BHS pH3	541	498	413	464	473	536
BHS Control	582					
Zn Control pH9	211					
BC pH9	153	62	18	2	1	1
WES pH9	164	143	75	6	4	3
GC pH9	194	178	178	158	169	178
BHS pH9	426	312	306	282	318	196
BHS Control	531					
Combination 1						
Zn Control pH3	594					
BC pH3	369	266	192	59	32	17
WES pH3	494	402	317	175	130	99
GC pH3	494	465	470	487	517	411
BHS pH3	528	509	530	527	598	465
BHS Control						
Zn Control pH9	423					
BC pH9	296	268	184	54	26	13
WES pH9	365	410	427	176	121	97
GC pH9	407	452	524	443	584	573
BHS pH9	518	535	521	502	601	431
BHS Control	537					

Solution	Day					
	1	3	7	22	52	73
Zn Control pH3	11576					
BC pH3	10380	10484	10799	6842	7013	7847
WES pH3	11228	11780	13667	8196	7857	9416
GC pH3	11166	11780	13215	11743	12540	
BHS pH3	13117	11852	12141	12708	13754	10998
BHS Control	13227					
Control pH9	11011					
BC pH9	10617	10958	10748	6921		730
WES pH9	11291	11325	12609	8455	8229	6947
GC pH9	10858	11707	13065	11628	10015	12619
BHS pH9	13117	11852	12451	10192	12725	11837
BHS Control	13374					
Combination 2						
Zn Control pH3	25750					
BC pH3		25859	31055	21572	25967	31726
WES pH3		26212	26573	23275	27735	31921
GC pH3		25166	27461	26508	28277	35523
BHS pH3	29702	26334		27562	30153	
BHS Control	27973					
Zn Control pH9	13096					
BC pH9	12653	13199	12230	10443	13281	13194
WES pH9	13274	12151	12398	12094	14157	13379
GC pH9	12785	12340	12432	12291	13715	13194
BHS pH9	11313	13831		13771	13085	
BHS Control	12077					

APPENDIX 3.8

The results of the experiments with Mitco Rocks in ppm

Solution	Day					
	1	3	7	38	70	85
Fe Control pH3	518					
Fe pH3	95	10	-	-	-	-
Fe Control pH9	567					
Fe pH9	77	9	-	-	-	-
Comb 1 Control pH3	543					
Comb 1 pH3	147	38	7	-	-	-
Comb 1 Control pH9	539					
Comb 1 pH9	145	35	9	-	-	-
Fe Control pH3	12627					
Fe pH3	18680	17173	18006	18023	18577	18835
Fe Control pH9	18070					
Fe pH9	18589	16541	17498	17734	18794	16929
Comb 2 Control pH3	9039					
Comb 2 pH3	8190	7654	7539	7249	7626	7973
Comb 2 Control pH9	16485					
Comb 2 pH9	16052	16792	16842	16597	17207	18629
Cd Control pH3	18					
Cd pH3	-	-	-	-	-	-
Cd Control pH9	25					
Cd pH9	-	-	-	-	-	-
Comb 1 Control pH3	23					
Comb 1 pH3	23	21	21	21	21	21
Comb 1 Control pH9	19					
Comb pH9	18	17	17	16	17	18
Cr Control pH3	93					
Cr pH3	-	-	-	-	-	-
Cr Control pH9	95					
Cr pH9	-	-	-	-	-	-
Comb 1 Control pH3	90					
Comb 1 pH3	42	18	4	-	-	-
Comb 1 Control pH9	90					
Comb 1 pH 9	38	17	5	-	-	-

Solution	Day					
	1	3	7	38	70	85
Ni Control pH3	1161					
Ni pH3	858	770	739		679	673
Ni Control pH9	1171					
Ni pH9	890	770	716		673	664
Comb 1 Control pH3	1310					
Comb 1 pH3	1182	1111	1081		1006	984
Comb 1 Control pH9	1214					
Comb 1 pH9	1161	1106	1040		1000	963
Cu Control pH3	172					
Cu pH3	10	-	-	-	-	-
Cu Control pH9	197					
Cu pH 9	12	-	-	-	-	-
Comb 1 Control pH3	202					
Comb 1 pH3	175	167	137	56	24	22
Comb 1 Control pH9	186					
Comb 1 pH9	169	153	129	50	24	17
Cu Control pH3	11290					
Cu pH3	10302	8805	7333	6879	5873	6541
Cu Control pH9	11061					
Cu pH9	10226	8917	7609	7294	5910	6697
Comb 2 Control pH3	9184					
Comb 2 pH3	9018	8475	8896	9126	19366	11408
Comb 2 Control pH9	9151					
Comb 2 pH9	8919	8737	9117	9018	11366	10919
Zn Control pH3	582					
Zn pH3	506	174	110	64	44	26
Zn Control pH9	531					
Zn pH9	270	142	92		38	11
Comb 1 Control	594					
Comb 1 pH3	478	443	448	415	486	
Comb 1 Control pH9	537					
Comb 1 pH9	586	471	440	411	489	

Solution	Day					
	1	3	7	38	70	85
Zn Control pH3	13227					
Zn pH3	12497	11233	11021	12205	12478	
Zn Control pH9	13374					
Zn pH9	12861	11233	11351	11728	12064	
Comb 2 Control pH3	27973					
Comb 2 pH3	24911	27896		26855	30153	
Comb 2 Control pH9	12077					
Comb 2 pH9	11313	12463		13313	13158	

APPENDIX 3.9

Results of the experiments with effluent samples in ppm

IRON

MINE	1	3	9	15	30
Sh 1	40249	39485	42736	45860	
Sh 2	40597	41154	42736	46487	
Ka 1	43310	40022	54746	45233	
Ka 2	39728	38709	40436	45233	
M 1	39728	37397	37556	40885	
M 2	39381	36741	34926	42101	
Control	37500				
Shrewsbury					
BC 1	50223	47572	36135	50890	
BC 2	51171	47791	45281	55324	
WES 1	51553	49330	47218	49629	
WES 2	51553	49330	48521	49629	
GCC 1	50602	51106	47868	45239	
GCC 2	50602	50215	45924	52153	
BHS 1	51553	49993	50938	49322	
BHS 2	52127	49330	49177	48372	
Ka 1	50223	49330	49177	48998	
Ka 2	52319	49330	49177	50255	
M 1	46869	44117	44003	45233	
M 2	46501	44759	44003	45233	
Control	52319				

CADMIUM

MINE	1	3	9	15	29
Sh 1	9	8	9	10	4
Sh 2	9	8	8	10	4
Ka 1	9	8	9	8	4
Ka 2	9	8	8	10	4
M 1	9	8	8	10	4
M 2	9	8	8	10	4
Control	7				

	1	3	9	15	29
Shrewsbury					
BC 1	185	172	177	178	180
BC 2	185	173	177	174	178
WES 1	181	177	180	177	183
WES 2	183	177	177	174	183
GCC 1	182	180	179	177	186
GCC 2	181	179	173	177	185
BHS 1	181	179	188	177	185
BHS 2	184	179	184	177	186
Ka 1	180	175	174	177	185
Ka 2	183	177	174	173	189
M 1	185	178	177	171	180
M 2	185	178	177	178	185
Control	182				
COPPER MINE					
Sh 1	781	738	695	649	696
Sh 2	753	734	697	668	727
Ka 1	818	723	691	630	703
Ka 2	800	749	710	668	703
M 1	854	843	697	674	688
M 2	955	699	673	624	681
Control	850				
Shrewsbury					
BC 1	962	756	448	263	142
BC 2	964	678	510	278	181
WES 1	912	747	443	249	164
WES 2	930	590	441	253	165
GCC 1	673	519	326	207	120
GCC 2	744	480	358	211	131
BHS 1	722	366	348	229	97
BHS 2	818	596	412	196	106
Ka 1	577	424	213	143	120
Ka 2	577	437	244	161	114
M 1	582	412	192	138	109
M 2	615	403	210	143	101
Control	838				

ZINC

MINE	1	3	9	15	29
Sh 1	3635	3846	4086	3927	4475
Sh 2	3794	4036	4086	3990	4540
Ka 1	3839	3790	4108	4227	4437
Ka 2	3817	3771	4062	4021	4492
M 1	3839	3790	4527	3974	4404
M 2	3953	3659	3923	3788	4300
Control	4464				
Shrewsbury					
BC 1	424	430	371	333	321
BC 2	494	425	371	322	311
WES 1	546	479	436	352	345
WES 2	524	462	420	356	437
GCC 1	582	577	624	647	1026
GCC 2	522	577	599	654	945
BHS 1	522	348	626	638	1049
BHS 2	528	556	615	701	1049
Ka 1	564	582	637	694	1000
Ka 2	570	582	643	698	967
M 1	458	538	605	673	730
M 2	458	538	611	663	918
Control	583				

CHROMIUM

MINE					
Sh 1	823	762	1110	672	737
Sh 2	793	762	1083	669	737
Ka 1	838	802	1009	629	683
Ka 2	785	827	1009	632	683
M 1	850	799	1041	666	722
M 2	829	802	1041	639	718
Control	900				

Shrewsbury - Less than 4 ppm

NICKEL

MINE	1	3	9	15	30
Sh 1	107	108	103	122	105
Sh 2	106	106	103	121	105
Ka 1	122	105	98	101	95
Ka 2	122	107	96	118	95
M 1	103	101	96	118	104
M 2	100	100	100	115	100
Control	107				

Shrewsbury - Less than 6 ppm

LEAD

MINE					
Sh 1	31	26	32	43	44
Sh 2	31	31	32	40	42
Ka 1	67	61	55	46	52
Ka 2	67	62	58	56	54
M 1	19	13	14	9.6	9
M 2	18	13	13	8.9	8
Control	50				

Shrewsbury - Less than 3.75 ppm

APPENDIX 4

The method for dicolving rock samples for atomic absorption analysis

Approximately 0.2 grams of rock was accurately weighed and placed in a sealed, P.T.F.E. lined container to which 3 ml of aqua regia, and 5 ml of 48% hydrofluoric acid were added. The mixture was heated in an oven at 100° C for one hour. 50 ml of saturated boric acid solution was added, and the mixture heated, at 100° C, for one hour. The liquid was cooled and made up to 100 ml with distilled water prior to analysis. Two samples of each rock type were prepared and analysed, and the results are tabulated in Appendix 5.

APPENDIX 5

AA analysis results for the rocks from the three disposal sites in $\mu gm\ gm^{-1}$

Rock	Fe	Zn	Cu	Cr	Ni	Pb	Cd
Coal Measure Shale 1	35154	152	201	65	150	n.d.	n.d.
2	36478	139	177	61	145	n.d.	n.d.
Mitco Red Clay 1	50865	960	621	127	147	53	n.d.
2	53200	1016	591	119	148	88	n.d.
Red (Borehole) Sand 1	17561	89	622	26	101		n.d.
2	17201	82	683	36	78		n.d.
Grey Sand 1	40521	75	540	98	151		n.d.
2	38096	76	430	64	163		n.d.
Red (Boulder Clay) 1	34324	52	316	63	151		n.d.
2	33410	48	308	70	143		n.d.
Grey Clay 1	26605	73	346	98	150		n.d.
2	26223	73	313	99	144		n.d.

REFERENCES

1. E. L. Streatfield. Paper given at the regional meeting of the Engineering Group of the Geological Society (Sept 1973)

2. A. V. Bridgwater. J. W. Gaskarth. Paper given at the conference "Conservation of Materials", Harwell (1974)

3. H.M.S.O. "The Report of the Technical Committee on the Disposal of Solid Toxic Wastes". (1970)

4. Industrial Wastes. A working party document embodying a Provisional Code of Practise for Disposal of Wastes. Inst. Chem, Eng. (1971)

5. J. F. Proctor. I. W. Marine. Nuclear Science and Engineering 22 50-356 (1965)

6. E. C. Donaldson. U.S. Bureau of Mines Information Circular 8212 (1964)

7. J. A. Lee. Chemical Engineering 137-139 (1950)

8. R. P. Selm, B. T. Hulse Proc 14th Industrial Waste Conference. Purdue Univ. Engineering Ext. Series 104 (1959)

9. D. M. Evans. A. Bradford. Environment 11 8. 2-13 (1969)

10. C. A. Caswell. Environmental Science and Technology 4 8. 642-647 (1970)

11. T. Morse. The Engineer 235 6089 (1972)

12. H.M.S.O. Deposit of Poisonous Waste Act (1972)

13. J. J. Geraghty. Water Well Journal 12 (1962)

14. H. E. Skibitzke. G. M. Robinson. Geol Survey Paper 386-B (1963)

15. W. H. Walker. Ground Water 11 2. 11-20 (1973)

16. D. A. Gray. J. D. Mather. I. B. Harrison. Paper given at the regional meeting of the Eng. Group of the Geol Soc. (1973)

17. H. LeGrand. Journal of The American Water Work Association 56 (1964)

18. K. J. Edworth. C. P. Young. Paper given at the joint meeting of the Engineering Group and Hydrogeological Group of the London Geological Society. Geol. Soc. Newsletter *4*. 2 (Abstract) (1975)

19. R. Aspinwall. Paper given at a London conference on Waste Disposal "Planning the Way Ahead" (1974)

20. A. Golwer. *Wasser* *36* 64-92 (1970)

21. H. B. Berridge. Paper given at a London conference on Waste Disposal "Planning the Way Ahead" (1974)

22. E. J. Mesu. *Geologie en Mijnbouw* *53* 4. 171-176 (1974)

23. H. LeGrand. *Wat Sewage Wks* 114 167-170 (1967)

24. R. C. Routson. R. E. Wildung. *Industrial Water Eng.* *7* 25-27 (1970)

25. Geological Survey. "The Geology of the Country around Lichfield" (1919)

26. G. W. Bailey. Federal Water Pollution Control Admin. South-east Water Lab (rept) (1968)

27. C. H. Wayman. In Principles and Applications of Water Chemistry. Rudolfs Research Conf. 4th Rutgers Univ. Proc. New York and London. John Wiley & Sons (1967)

28. E. T. Degens. "Geochemistry of Sediments: a brief survey" Prentice-Hall (1965)

29. B. L. Sawhney. *Clays and Clay Minerals* *20* 93-100 (1972)

30. R. E. Grim. "Clay Mineralogy" New York. McGraw Hill (1953)

31. American Petroleum Research Project 49 "Reference Clay Minerals". Columbia University, New York, N.Y. (1951)

32. W. C. Ormsby. J. M. Schartsis. K. H. Woodside. *J. Am Ceram Soc.* *45* 361-366 (1962)

33. T. B. Dayananda. T. B. Tennekoon. J. M. Thomas. M. J. Tricker. *J. C. S. (Dalton)* *20* 2211 (1974)

34. G. R. Wentink. J. E. Etzel. *J. Water Pollut Centr. Fed.* *44* 8. 1561-1574 (1972)

35. A. Himsley. F. X. McGarvey. *Ion Exchange and Membranes* *1* 3. 143-148 (1973)

36. V. M. Klechkovsky. L. N. Sokolova. G. N. Tselishcheva. Progress in Nuclear Energy. Edited by W. G. Marley and K. Z. Morgan. Vol 12. Health Physics. Pergamon Press N.Y. (1959)

37. D. G. Jacobs. T. Tamura. Trans. Int. Congr. Soil. Sci. *2* 206-214 (1960)

38. N. T. Coleman. F. H. Leroux. *Soil Science* *99* 243-250 (1965)

39. H. G. Von Reickenbach. *Clay Minerals* *7* 331-341 (1968)

40. B. L. Sawhney. C. R. Frink. *Soil Sci. Soc. Am. Proc.* *29* 25-28 (1964)

41. B. L. Sawhney. Proc. Int. Clay Conf. Tokyo 1. Israel University Press (1969)

42. D. E. Hill. B. L. Sawhney. *Soil Sci. Soc. Am. Proc.* *33* 531-534 (1969)

43. D. L. Dolcaster. E. G. Lotse. *Soil Sci. Soc. Am. Proc.* *32* 795-798 (1968)

44. S. Swartzen-Allen. E. Matijevic. *Chem Reviews* *74* 3. 385-399 (1973)

45. B. M. Tucker. *Aust. J. Soil* Res. *5* 173-190 (1967)

46. A. H. Weir. *Clay Minerals* *6* 17-22 (1965)

47. J. B. Page. L. D. Bauer. *Soil Sci. Soc. Am. Proc* *4*. 150-155 (1940)

48. M. Coultard. Computer program. Private communication (1973)

49. R. J. Reynolds. K. Aldous. "Atomic Absorption Spectroscopy; a Practical Guide" London: Griffin (1970)

50. J. A. Dean. T. C. Rains. "Flame Emission and Atomic Spectrometry" Vol I, Marcel Dekker (1969)

51. G. Y. Chaos 2 θ (Cu) Table for Common Minerals. Geological paper 69-2. Carleton University (1969)

52. R. E. Carver. "Procedures in Sedimentary Petrology". New York, London; Wiley Interscience (1971)

53. V. Stubican. R. Roy. Journal of the American Ceramic Society 44. 12. 625 (1961)

54. Open University. "Constructional and other bulk Materials" The Earths Physical Resources 625 - Block 4, (1974)

55. H. Kodama. K. Oinuma. *Clays Clay Minerals* 11. 236-249 (1963)

56. R. J. Dudley, B. J. Hathaway. *J. Chem Soc* (A) 2799 (1970)

57. B. J. Hathaway. D. E. Billings. *Co-Ordination Chem. Rev* *5* 1 (1970)

58. B. J. Hathaway. *J. C. S. Dalton.* *12* 1196 (1972)

59. D. H. Williams. I Fleming. "Spectroscopic Methods in Organic Chemistry" McGraw Hill (1966)

60. C. E. Weaver. J. M. Wampler. T. E. Peacil *Science* 156 504 (1967)