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COMMONWEALTH OF AUSTRALIA

DEPARTMENT OF NATIONAL DEVELOPMENT

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

REPORT No. 106

A Chemical Investigation into the Role of Sorption Processes in Ore Genesis

BY

J. R. BEEVERS

Issued under the Authority of the Hon. David Fairbairn,
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MINISTER: THE HON. DAVID FAIRBAIRN, D.F.C., M.P.

SECRETARY: R. W. BOSWELL.

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

DIRECTOR: J. M. RAYNER

THIS REPORT WAS PREPARED IN THE GEOLOGICAL BRANCH

ASSISTANT DIRECTOR: N. H. FISHER

Published by the Bureau of Mineral Resources, Geology and Geophysics

Canberra A.C.T.

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SUMMARY

Experimental evidence suggests that sorption processes in nature play a greater part in ore genesis than is generally believed. The results, as a whole, indicate that syngenetic accumulation of base metals by sorption is at least possible. In the case of uranium, the sorption process alone is able to explain the occurrence of some of the ore-grade uraniferous carbonaceous sediments. For other heavy-metal ores occurring in sedimentary rocks (possibly syngenetic), sorption processes are likely to have played a role in the early stages of ore development. However, the present-day structure of the orebodies and the texture of the contained minerals demonstrate that the sorption process was not the sole factor involved in the formation of the orebodies.

Sorption of ions from solution by a wide variety of naturally occurring sorbents is usually a rapid process. One exception to this rule is bentonite, which displays a seemingly slow sorption (owing to the slow penetration of ions to the basal planes), in addition to the rapid sorption of ions on the surface.

Using solutions containing one ion-species only and sorbents composed of only one material, it was shown that the amount of metal ion sorbed from solution depended primarily on the nature of the sorbent and sorbate, the actual and relative concentrations of the two, the pH of the solution, and the addition of alkali or alkaline-earth metal ions or both to the same solution. Peat, as representative of the organic sorbents occurring in nature, was found to be by far the most efficient of all the sorbent materials used, and kaolinite the least.

Lead, copper, and uranyl ions are the ions most strongly sorbed from solution by all the sorbents, but particularly by peat and ferric hydroxide. The maximum weight of lead, copper, and uranium obtained by sorption of their ions from dilute solution by peat was 16.4, 14.0, and 18.9 gm per 100 gm of peat respectively, while for ferric hydroxide in the presence of 0.1 M magnesium nitrate the corresponding figures were 7.2, 1.2, and 6.5. Generally, in accordance with classical adsorption work, it was found that the greater the number of charges on the ion the greater the amount sorbed, and for ions with the same number of charges, the greater the atomic weight, the greater the amount sorbed. All the ions studied were sorbed to some extent by one or more of the sorbents.

The unexpected behaviour of ferric hydroxide-sol as a sorbent was particularly interesting. Without exception, all the ions used showed the anomalous effect of being better sorbed by ferric hydroxide the greater the concentration of alkaline-earth salts added.

Sorption of pairs of ion-species by single sorbents showed that some ions are preferentially sorbed. Lead, uranium, or copper ions in the presence of one other ion-species at the same concentration are always preferentially sorbed. This behaviour is most clearly shown by peat as sorbent. Preferential sorption is due either to the greater ease with which some ions fit into the crystal lattice of the sorbent material, or to the preferential formation of insoluble compounds on the surface of the sorbent (Fajans-Hans Rule).

The cations can be arranged into a general sequence according to their sorption enrichment factors:

$$Fe^{+++} > UO_2^{++} > Pb^{++} > Cu^{++} > Co^{++} > Zn^{++} > Ni^{++} > Mg^{++} > Cd^{++} > Tl^{+} > Na^{+}.$$

Lead, copper, zinc, and cadmium ions present in the same solution and at the same initial molar concentration were sorbed to different extents by single adsorbents. Under these conditions it was demonstrated how great is the selective mechanism, e.g. for Pb^{++} sorption onto peat or dolomite. The Fajans-Hans rule was clearly applicable. Moreover, the freshly sorbed metal-ions could be easily displaced (though not completely) by magnesium ions. The ability of a mixture of ferric hydroxide and clay to sorb base-metal ions seemed to be little affected by large concentrations of alkali or alkaline-earth metals, such as are found in the oceans. When the four ion-species - that is, lead, copper, zinc, and cadmium - were initially present at unequal concentrations, the preferential sorption of the lead and copper ions was even more pronounced.

The results of the work using sorption columns corroborated the finding that copper and lead were preferentially sorbed by sorbents occurring in nature. This investigation also indicated that the sorptive capacity of the sorbents was approximately the same whether the sorbent was exposed to a small volume of a more concentrated metal-ion solution or a large recurrent supply of a more dilute solution. In addition, the studies showed that, although the freshly sorbed ions could be displaced, this was no longer true on long standing, when the metal-ions became fixed.

INTRODUCTION

In recent years the opinion has been gaining ground among geologists that some base-metal deposits are of syngenetic origin. Whether or not this is true of any given deposit need not concern us here; we are investigating the potency of a factor, in the environment of deposition, in concentrating base metals to the point where an orebody could form syngenetically. Knowledge of environment, as Raggatt (1958) pointed out, is becoming increasingly important in the search for new orebodies.

The work presented in this Report was undertaken in order to ascertain what concentration of various heavy metals could be reasonably expected to accumulate in natural sediments by sorption of ions from solutions, and also to investigate whether these concentrations can approach ore-grade without any further concentrating mechanism.

The main objections to a syngenetic origin for many ore deposits lie in the quantity of metal involved and the lack of a suitable mechanism which could reasonably be responsible for the accumulation of large quantities of metals in natural sediments. It has been established that the sediments containing many of the ores thought to be syngenetic were deposited along an old shoreline, as, for instance, in the Rhodesian copperbelt (Garlick, 1953), or in a trough-like depression in the sea floor as at Broken Hill (Thomas, 1961), or on the margins of a geosyncline as at Rum Jungle (B.P. Walpole, pers.comm.), or in depressions close to the shoreline such as the copper-bearing shale deposited in the Kupferschiefer Sea (Deans, 1948).

These are just the areas where rivers carrying suspended and soluble material from denuded landmasses enter the sea, depositing their detrital material in decreasing particle size away from the shoreline. The soluble material could be either precipitated as insoluble material, sorbed by colloidal material and carried into the sediments, or remain in solution. The material remaining in solution could be taken up by one or more of the many marine plants and animals which seem capable of extracting certain elements from solution; for example, oysters are known to possess a high content of copper and seaweed a high content of iodine (Goldschmidt, 1954), to mention just two organisms capable of concentrating elements in their tissues. After the death of the organisms, their remains settle to the ocean floor, enriching the sediment in whatever element is concentrated in the organism, in the same manner as oil is known to accumulate.

Schneiderhöhn (1932) originally made the suggestion that sulphate-reducing bacteria are capable of precipitating insoluble metal sulphides, thus enriching the sediments. This view has received support from many workers. Recently, Baas Becking & Moore (1961) have succeeded in synthesizing a few simple sulphide minerals (such as covellite and sphalerite) in laboratory experiments using sulphate-reducing bacteria and a source of metal ions provided by relatively insoluble minerals such as chrysocolla or smithsonite. Garlick (in Mendelsohn, 1961) believes that the minerals of the Rhodesian copperbelt originated by a sulphide-precipitation mechanism, the hydrogen sulphide being produced by bacterial action in an anaerobic environment; and he cites some laboratory evidence in support of this hypothesis.

It is clear then that concentrations of metal ions in sediments could arise by at least four completely different processes, that is by:

(i) deposition from mobile waters in which they were carried as detrital or colloidal suspensions;

(ii) precipitation from solution, possibly as carbonate, sulphate, etc;

(iii) sorption;

(iv) biological processes, i.e., by the activity of the living cell.

In this Report it is proposed to give the results of a systematic study of the third of these processes, that is, of the factors affecting the sorption of various ions by certain naturally occurring sorbents.

The word 'colloid' refers only to the size of the particle and not to the material from which the particle is made; the accepted definition of a colloidal particle is that the largest dimension of the particle shall fall into a range between 10 and 10^4 Å. Such particles, if they can be considered as molecules, can have an enormous molecular weight, but their shape is still not visible to the naked eye. They have properties much different from those of smaller molecules or ions when dispersed in a liquid medium. These are:

(i) undetected lowering of freezing point;

(ii) easily visible turbidity;

(iii) negligible diffusion rate;

(iv) increase in viscosity;

(v) optical properties.

Fundamentally, colloids are particles, just as are the small ions or molecules, and, like the smaller particles, are subject to thermal motion, mechanical, gravitational, coulombic, and Van der Waal forces, etc. What differs frequently is the relative importance and extent of these effects.

If we imagine a centimetre cube of a particular material ground to colloidal size i.e. to cubes of side 10^{-4} cm, then the surface area will increase by a factor of 10^4. Thus, colloids readily supply large areas on which surface phenomena can be studied, and therefore a close interrelation between surface and colloid chemistry must exist. Surface phenomena, however, may be (and often are) best studied on surfaces not involving colloids, e.g. the dropping mercury electrode. In this Report studies on colloidal surfaces only are described.

It has been known for over a century that naturally occurring colloidal particles can remove ions from solution. Way (1850) recognized a sorption process in soils which he attributed to the clay, although he did not recognize it as a cation-exchange phenomenon.

The occurrence of trace elements in sediments has been explained either on the basis of the insolubility constants of the hydroxides and sulphides or in terms of the pH and E_H values of the aqueous media (Ginsberg, 1960). There are, however, complications at high dilutions, where surface forces of the liquid medium and the colloidal state of the freshly formed hydroxides or sulphides prevent precipitation. Although the solubility product might be exceeded, the substance is not precipitated because the surface forces oppose flocculation (see section on double layer p.) Even if the concentration of sorbate in solution is very small, addition of more sorbent will reduce the sorbable-ion concentrations still further. In other words, at low concentration, removal of ions from solution takes place by sorption process in preference to precipitation.

The number of different sorbents occurring in nature is very large indeed; however, for the purposes of sorption studies they can be classified into a few definite groups, depending essentially on their chemical structure (see pp). For example, organic materials and the clay minerals are regarded as separate groups. Ferric hydroxide (hydrated ferric oxide) and hydrated manganese oxide belong to another group, and dolomite and limestone constitute yet another. Ferrous sulphide, as representative of the sulphide minerals, forms a fifth group. It seems worthwhile at this stage to review briefly the evidence that these five groups of materials do in fact behave as sorbents in nature, and particularly to examine their association with heavy metals such as lead, zinc, copper, and uranium in sediments. It is well known that colloidal particles are not unique in their ability to sorb ions, but their frequent appearance in nature can be taken as an indication that they make a fairly large contribution to the total sorption processes.

Organic Material

It has been known for a long time that organic matter is a good sorbent for many ions; Boutwell (1904) seems to have been the first to notice the association of organic material and mineral deposits. The numerous cases of mineral occurrences in coal and mineral oils reported by British (Davidson & Ponsford, 1954), Russian (Nekrasova, 1958), and Hungarian (Szalay, 1954) workers show that lead, zinc, copper, uranium and other minerals in coal are present in amounts considerably greater than the average in the earth's crust. It is the general belief that the uranium was concentrated by sorption of the metal from solution by the decaying organic matter.

A thin but widespread cupriferous bed of black shale occurring in the Mansfeld Kupferschiefer contains 2 to 3 percent copper. The ore minerals constitute about 12 percent of the ore and organic substances 15 percent (Bateman 1956).

Breger & Deul (1958) drew attention to the fact that limestones not carrying carbonaceous matter carry no appreciable concentrations of uranium, in contradistinction to some carbonaceous limestones which are known to be unusually radioactive. They concluded that the carbonaceous material was responsible for the concentration of the uranium, possibly by a sorption process. In the Colorado Plateau area of the U.S.A. Breger (1955) reported a black, lustrous, carbonaceous material, with a large amount of uranium, having no cellular structure. The uranium is homogeneously dispersed in the carbonaceous matter, and Breger suggested that the organic material and uranium separated from solution together. Krauskopf (1956) has made a study of the enrichment of over thirty metals in some common sedimentary rocks, and has shown quite conclusively that many metals (including all the chalcophile elements) are enriched in black shale to a far greater extent than in shale containing less carbonaceous material.

The common occurrence of organic material in some high-grade ore deposits has been recognized for a long time. Thus, the Rum Jungle uranium orebody is highly carbonaceous (Raggatt, 1958), and the lead-zinc ore at Mount Isa is reported to contain as much as 4 percent by weight of carbon as graphite (Croxford, Draper, & Harraway, 1961). The presence of carbonaceous material is believed by some to be highly significant and indicative of the environment prevailing at the time of ore deposition.

Clay Minerals

Clays are widespread, and are present to some extent in all rivers and sediments throughout the world; their occurrence in ore deposits is also well recognized. Kohlar (quoted by Emmons, 1904) observed that most of the copper ores occurring in the Permo-Triassic beds of Europe are intimately associated with finely divided clays, and suggested that the copper was absorbed from solution by the clays. Even where copper is associated with organic remains, as for instance in the Kupferschiefer, Kohlar suggested that a thin film of clay around them was responsible for the precipitation. Krauskopf (1956) suggested that possibly the clay fraction is in part responsible for the presence of heavy metals in the shales. The suggestion is not unreasonable, considering the known cation-exchange capacity of clay minerals, which can reach 100 milli-equivalents per 100 gm for a montmorillonite clay.

Ferric Hydroxide

Ferric hydroxide (or hydrated ferric oxide) is common in nature, and is generally formed by atmospheric oxidation of solutions containing dissolved ferrous salts (e.g. mine waters). Considering its widespread occurrence, it is surprising that so little experimental work has been done on its ion-exchange properties until quite recently, when these properties have been exploited and used in exchange columns for separation of various metal ion mixtures (Kraus, Phillips, Carlson & Johnson, 1958). The formation of ferric hydroxide in nature depends on the E_H - pH relationship; the charge on the ferric hydroxide precipitate is dependent on pH, and results from the amphoteric nature of the compound. Consequently the pH of the environment determines whether ferric hydroxide is a good cation or a good anion exchanger.

Goldberg (1954) points out that the hydrous iron and manganese oxides are important collectors of trace elements during weathering and sedimentation, and he tried to explain certain mineral assemblages in hydrated oxides in terms of the charge on the surface of the hydrated oxide.

Bates & Strahl (1958) reported various amounts of iron oxide in the uranium bearing shales of the U.S.A. and Europe and noted that the higher the iron oxide content, the lower the uranium, except in the carbonaceous shales. They considered that the varying amount of iron oxide is a logical result of variation of E_H and pH, which, in turn, depended on the variation in geological conditions during the deposition of the sediments. The fact that uranium generally does not occur together with the iron oxide may, according to these authors, also be a result of E_H - pH relationships.

Lovering (1955) examined many samples of radioactive limonite from western U.S.A. From the colloidal size of the particles, and the high radioactivity, though only traces of definite uranium minerals were present, he suggested that a sorption process was responsible for the fixation of uranium from solution.

Although the common presence of hydrated iron oxides in soils is recognized, there seems to be little agreement on their contribution to the total cation or anion exchange capacity of the soil. Hawkes (1958) suggests that occlusion may be responsible for much of their trace element content. It is possible that aged hydrated ferric oxide has properties different from those of freshly precipitated material, as reported by Kolthoff & Overholzer (1939) and by Kraus, Phillips, Carlson & Johnson (1958). Kraus et al. used hydrated ferric oxide (which had been completely dried out at room temperature) as a selective cation exchanger for the alkali metals, and showed that it possesses excellent selectivity, in addition to an appreciable adsorption.

Kurbatov, Wood & Kurbatov (1951) used a radioactive tracer technique to study the sorption of cobalt from very dilute (10^{-6} molar) solutions by hydrated ferric oxide. They studied the influence of temperature, pH, cobalt concentration, and added electrolyte concentration on the sorption, and found that the sorptive capacity of the hydrated ferric oxide for cobalt is quite high, particularly at high pH.

Calcareous material

Carbonate minerals form and exist in nature over a wide temperature range, from temperatures of groundwater and oceans to the highest encountered in regional metamorphism. Undoubtedly many ore minerals in calcareous rocks are epigenetic, a chemical change being brought about by interaction of the limestone or dolomite with hydrothermal solutions carrying base metal, e.g. the zinc ores mined in the Tri-state district of the U.S.A; however, there is evidence suggesting that many calcareous rocks containing quite high concentrations of base metals have never been in contact with hydrothermal solutions. Instances are to be found in the MacArthur River (Smith, 1964) and Calvert Hills (Roberts, Rhodes, & Yates, 1963) areas of the Northern Territory, where lead and copper sulphides are found disseminated throughout dolomite rocks; the metals are regarded as being syngenetic. Although these sulphides are undoubtedly syngenetic, the presence of hydrothermal solutions cannot be entirely ruled out in the MacArthur River area because of the presence of syenite dykes close by.

Most of the known uranium deposits at Rum Jungle occur in black shale of the Golden Dyke Formation at or near its contact with the Coomalie Dolomite; mineralization also occurs in shale above the carbonate rocks (Raggatt, 1958). In the South Alligator field most of the uranium mined has been won from the carbonaceous and dolomitic rocks of the Koolpin Formation (but there are also deposits in the overlying volcanic rocks). Condon & Walpole (1955) believe that the presence of calcareous rocks in the area is highly significant, because it seems to indicate that the sedimentary environment was connected with the formation of uranium ore-deposits in that area. It is also noteworthy that the copper-cobalt deposits of the Belgian Congo are confined to a suite of sedimentary rocks composed almost entirely of dolomite (mentioned by Knight, 1957). Similarly, Gregory (1930), after making a study of the Mansfeld Kupferschiefer, concluded that the heavy metals were probably originally deposited together with (or as) carbonate; the Kupferschiefer contains up to 50 percent carbonate rocks.

Knight (1957), discussing the occurrence of 108 country rocks containing ore deposits, noted that 56 are actually limestone or dolomite, and a further seven have limestone or dolomite in the immediate vicinity. As Knight points out, this limestone host rock seems out of all proportion to the percentage of carbonate rock in the earth's crust, and at the very least suggests that certain Pb-Zn-Cu ores were deposited only in particular sedimentary environments.

Dolomite is abundant at Mount Isa, where silica and dolomite constitute a major part of the copper orebodies; significantly, too, they are the main simple constituents of the surrounding shales. Though present-day evidence would be more in favour of an epigenetic origin for the Mount Isa copper than a syngenetic one (Fisher, 1960) the possibility of a syngenetic origin cannot be completely discounted.

Sulphide Materials

The occurrence of heavy metal sulphides in some recent sediments is generally considered to be due to the action of heterotrophic bacteria. These organisms thrive in the conditions prevailing in the oxygen-free sediments, and are able to produce hydrogen sulphide by reduction of sulphate ion to sulphide. Hydrogen sulphide is also formed by the bacterial decomposition of proteins. In areas such as the Black Sea, the Baltic, some fjords, and some tropical lagoons behind a protective barrier reef (Goldschmidt, 1954), quite large amounts of hydrogen sulphide gas are produced by bacterial action. Strøm (1939) reports a concentration of 40cc of hydrogen sulphide per litre of water in the bottom waters of a Norwegian fjord. However, not all of the sulphidic sulphur escapes into the supernatant waters in the form of hydrogen sulphide gas; some is bound in the sediments in the form of metallic sulphides such as hydrotroilite, Fe(OH)SH, and recently Baas Becking & Moore (1961) have shown in the laboratory how these sulphate-reducing bacteria are able to form other metal sulphides. It is assumed that when freshly formed, these sulphides will be colloidal in size, and thus possess the property of all colloidal-size particles of being able to sorb ions, particularly those of similar charge and size to those making up its own lattice. In order to obtain some quantitative data on this possibility, the sorptive properties of freshly precipitated ferrous sulphide were studied, during the present investigation. Ferrous sulphide was chosen because pyrite, which is present in all base metal sulphide deposits, is probably the diagenetic product of ferrous sulphide, and it is known from studies of recent sediments, for instance in the Black Sea, that copious supplies of iron sulphides are produced in nature (Volkov, 1959).

APPARATUS AND SUPPORTING ELECTROLYTES USED

The apparatus used was essentially the same as that described by Breyer, Gutmann & Hacobian (1950). It was modified slightly to enable the use of some commercial equipment in place of the self-built apparatus; thus, a Philips amplifier GM4574 in combination with a Philips Voltmeter GM6015 was used. Details are shown in Figure 1. The superposed alternating voltage had a value of 14mV(r.m.s) and a frequency of 50 c/s. A compensator-current device was also fitted to permit the suppression of interfering d.c. steps; it was particularly useful in the d.c. polarography of mixtures containing an ion species in the presence of a large excess of a more noble one; its use entailed no loss in sensitivity. Experiments were carried out at $20^{\circ} \pm 0.5^{\circ}$C except where otherwise stated.

The capillary characteristics were as follows:

$m = 2.4$ mg/sec.

$t = 2.24$ secs

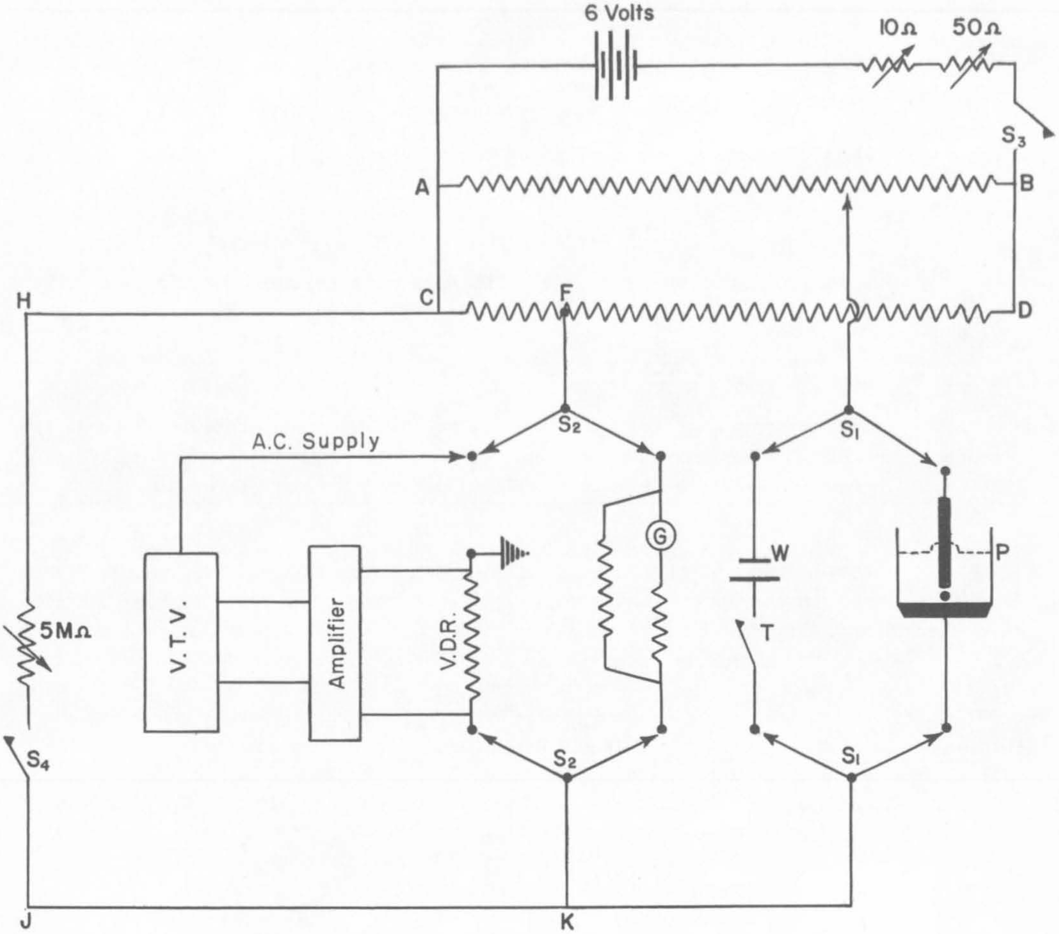
at $h = 70.0$ cm (10^{-1} M KCl: open circuit)

The supporting electrolytes are shown below. In some cases, it proved possible to estimate the component ions of a mixture by taking a single polarogram. In others, different supporting electrolytes had to be used in order to get satisfactory results. The metal ions estimated and the supporting electrolytes used to give satisfactory polarograms were:

Lead, uranyl, zinc, cadmium and thallium ions: 10^{-1} M sodium nitrate or 10^{-1} M sodium perchlorate.

Ferric ion: 10^{-1} M hydrochloric acid.

Chromium as chromic ion: 10^{-1} M sodium perchlorate + 5.10^{-2} M perchloric acid.



A B	*Variable Potentiometer 20 Ω*
C D	*Potentiometer - divided at fixed point F 20 Ω*
S_1, S_2, S_3, S_4	*Switches*
T.	*Tapping Key*
W	*Weston Cell*
V. T. V.	*Philips Vacuum Tube Voltmeter G M 6015*
Amplifier	*Philips G M 4574*
P	*Polarographic Cell*
G	*Galvanometer in Combination with Ayrton Shunt*
CHJK	*Compensator Current Circuit*

Fig. 1. Polarograph used.

Chromium as chromate ion: M potassium hydroxide.

Copper and cobalt ions: 10^{-1} M sodium perchlorate.

Nickel ion: 3+ potassium thiocyanate solution.

Manganese ion: M potassium chloride solution.

Vanadate ion: 10^{-1} M hydrochloric acid.

Molybdate ion: 5.10^{-1} M sulphuric acid / M sodium perchlorate.

Before elements were estimated in the sorption experiments, calibration curves were prepared for the various metal ions in the appropriate media.

SORBENT MATERIALS

The sorbents used, chosen because of their widespread natural occurrences and possible connexion with the genesis of ore deposits, were: kaolinite; peat; dolomite; hydrated iron oxide; hydrated manganese oxide; estuarine silt; freshly prepared ferrous sulphide; and vermiculite.

Kaolinite was found to be the most suitable of the available clay minerals. It was readily available in the large quantities required and it was found to be the best to handle experimentally. By contrast, bentonite, as will be discussed later in more detail, displayed two types of sorption, one very slow, the other relatively fast, the slow process being, of course, the rate-controlling factor. The slow sorption process lengthened considerably the time required for an experiment and the use of bentonite therefore was not convenient. A sample of illite was found to contain a basic ion sulphate which itself was a sorbent and therefore interfered with a study of the sorption properties of the illite. The kaolinite was a commercial sample, supplied by Quality Earths Pty Ltd Sydney. It was untreated chemically, but it was graded so that more that 99 percent was less than 1 micron in diameter. The bentonite was also supplied by Quality Earths Pty Ltd and the small quantity of illite used (from Morris, Illinois, U.S.A.) was obtained from the Department of Geology, University of Sydney.

The peat was a very finely ground sample from Mount Gambier, South Australia, and was supplied by Karl Baumgartner, Sydney.

Dolomite was the natural material occurring at Mount Knowles, New South Wales, graded to pass a 200 B.S.S. mesh.

Ferric hydroxide was prepared in the following way. 200 ml of a M/20 solution of ferric chloride was boiled for half an hour, after which time the pH was raised to 7 by addition of dilute ammonia solution. After standing for half an hour the supernatant liquid was decanted. The precipitated iron hydroxide was shaken with boiling water, centrifuged, and the supernatant liquid again decanted. The operation was repeated several times until, after 10 minutes of centrifuging at 3000 revs/min., a part of the ferric hydroxide remained in suspension, indicating that the washing had been completed. Suspensions of this ferric hydroxide were used in all sorption experiments. In order to estimate the iron content of the suspensions, an aliquot of 50 ml was dissolved in hydrochloric acid and the iron estimated by the standard dichromate procedure. The bulk of the ferric hydroxide solutions was then made up to the required concentration. The composition of the hydrated iron oxide is so very much affected by the method of preparation that great care must be taken to carry out the preparation exactly as described.

The present method of preparation results in the formation of a positive colloid as the subsequent experimental results show.

Hydrated manganese oxide was made from manganous nitrate, using the same technique as that described for the preparation of ferric hydroxide, except that sodium hydroxide was used as precipitant because of the solubility of manganese hydroxide in ammonium salts. The white manganous hydroxide initially formed rapidly oxidized to the brown form of uncertain composition, but most probably $MnO(OH)_2$. The manganese hydroxide suspension was standardized by dissolving the manganese in one aliquot in nitric acid, and estimating by the periodate method.

As with the hydrated iron oxide the standardized method of preparation of the hydrated manganese oxide must be strictly adhered to, so that consistent sorption values are obtained.

Estuarine silt was collected from the top foot of the bottom mud in Botany Bay, Sydney, in the vicinity of Shell Point. The material was air-dried, passed through a 200 B.S.S. mesh sieve in order to remove the coarse sand, etc., and then resuspended in distilled water to the required concentration.

The sediments in the estuaries and harbours in and around Sydney are derived from Triassic fresh shale. Grim & Loughnan (1962) have described a silt similar to that used in these experiments, from Sydney Harbour, just north of Botany Bay. Its clay mineral components were kaolinite, illite, and a mineral of uncertain composition which changes to illite in a marine environment. Other components were hydratic iron oxides and organic material.

Owing to the ease and rapidity with which ferrous sulphide material is oxidized by atmospheric oxygen, it had to be prepared in an atmosphere of nitrogen, and also had to be stored in oxygen-free water. It was prepared by direct precipitation, using yellow ammonium sulphide on a solution of a ferrous salt. The precipitate was filtered (in an atmosphere of nitrogen) and washed with oxygen-free distilled water until clear of free sulphide ion; finally it was resuspended in oxygen-free distilled water and stored under nitrogen.

The commercial preparation of the heat-treated expanded variety of vermiculite was supplied by Neuchatel Asphalte Co. (A/sia) Pty Ltd, Sydney. Two grades were used: (i) passed through 200 B.S.S. mesh for the usual sorption studies and (ii) passed through 100 B.S.S. to remove coarse material, then transferred on to 200 B.S.S. to remove undesirable fine particles; this material was used in the chromatographic work.

A.R. chemicals were used throughout. Stock solutions of ferric chloride, chromic chloride, ammonium vanadate, sodium molybdate, and the nitrates of all other metal ions used were prepared in distilled water at a concentration 8.5×10^{-4} M. Stock solutions containing two ion-species were also made up, together with a stock solution of a mixture of lead, copper, cadmium, and zinc nitrate, all at a concentration 8.5×10^{-4} M.

A solution containing lead, copper, cadmium, and zinc, all at 10^{-4} M. concentration, was used for the chromatographic work.

Sorption processes were allowed to go to equilibrium in stoppered 25 ml graduated cylinders; the use of these vessels greatly facilitated repeated mixing of the solutions and suspensions and also allowed good separation of the sorbents on standing.

The tubes used in the moving solution sorption experiments were of two kinds; in one the flow was vertically upwards, in the other vertically downwards. The tubes, which were made from 1/2 inch glass tubing, were about 10 inches long, with a sintered glass filter fused about 1 inch from one end. The end nearest to the sintered glass filter was then drawn out to about 1/8 inch diameter. The tubes used for downwards flow experiments were ordinary chromatography tubes; the ones used for upward flow experiments were provided with a side arm at a distance of about 2 inches from the end farthest away from the sinter disc. The two types of tube are shown in Figure 2.

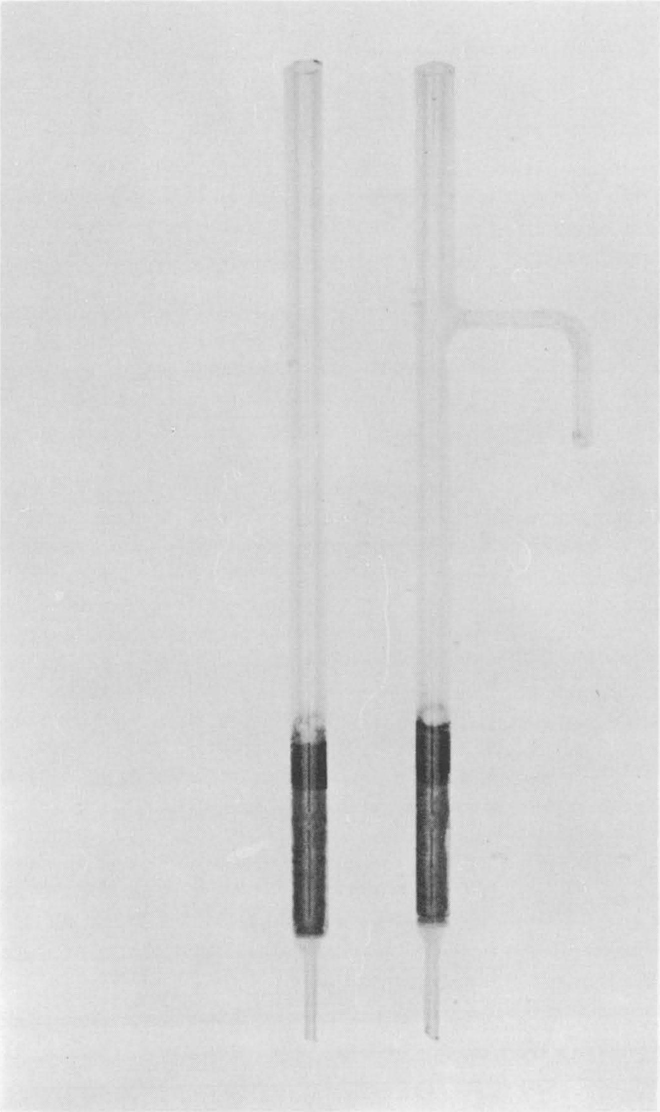


Fig. 2. Tubes used in the flowing-solution experiments.

THE DOUBLE-LAYER

Mechanisms of Sorption

The tendency for a solute to accumulate at an interface is known as adsorption, and absorption refers to a more or less uniform penetration of the solute. Since it is often impossible to separate the effects of adsorption from absorption, the noncommittal term sorption is frequently employed. This term covers all types of adsorption and absorption, including chemisorption, and throughout this Report, the term sorption is used except where the precise form of sorption is positively known.

There are three main classes of attraction between particles; electrical, van der Waals, and chemical. Although any one may lead to sorption, the different types often combine, frequently making it difficult to distinguish between them, although there is a difference in the type of bond formed. The electric forces may be looked on as giving rise to most of the ion-exchange properties, the vander Waals forces as being responsible for physical absorption, and the chemical forces for chemisorption.

The arrangement of ions around a charged surface, whether this be a colloidal particle or a flat surface, has been the subject of a great amount of research, and it is only with a knowledge of this charge distribution that many of the properties associated with the solid-liquid interface can be understood. This area of charge distribution is known as the double-layer and excellent summaries are to be found in review papers by Grahame (1947) and by Bockris et al. (1963).

Since the study described in this Report is concerned to a large extent with clay minerals and with the dropping-mercury electrode it seems logical to describe in detail the double-layer structure around a clay particle dispersed in an aqueous medium and indicate where this differs, if at all, from that around other colloid particles and from that in the water phase at the mercury-water interface.

The charge on the surface of a clay particle can arise in many different ways. These are:

(1) By isomorphous replacement of Si^{4+} by Al^{3+} in the octahedral layer, and by crystal lattice defects.

(2) By attachment of OH ions to ruptured bonds.

(3) By preferential adsorption of either positive or negative ions from the electrolytic medium in which the particles are dispersed. Ions which are similar to those of the clay lattice are particularly important.

(4) By acidic or basic ionization of OH groups which constitute a normal part of every clay lattice e.g.

$$M - OH + H_2O \rightleftharpoons M - 0^- + H_30+$$

or

$$M - OH + \text{Water} \rightarrow M^+ + OH^- \text{ solvated.}$$

(5) Polarization of the clay surface due to the strong polarizing power of the ions.

The fourth postulated mechanism is a feature of the behaviour of amphoteric metal oxide, such as iron hydroxide, which is used in the studies to be described, and depends on the extent to which the OH groups are polarized by the lattice cations which they coordinate. The acidic ionization of -OH and -COOH groups is very probably responsible for much of the surface charge on peat.

The earliest attempt to formulate a structure for humic acid (the principal component of peat) was made by Fuchs (1931), and his proposed structure is shown in Figure 3. It has since been shown that humic acid cannot be represented quite as simply as that, but it does carry -OH and -COOH groups which are capable of ionization. Coulson, Davies & Khan (1959) have shown that it consists of a complex group of poly-ions containing bound protein fragments; however, so far, they have not been able to formulate a definite structure.

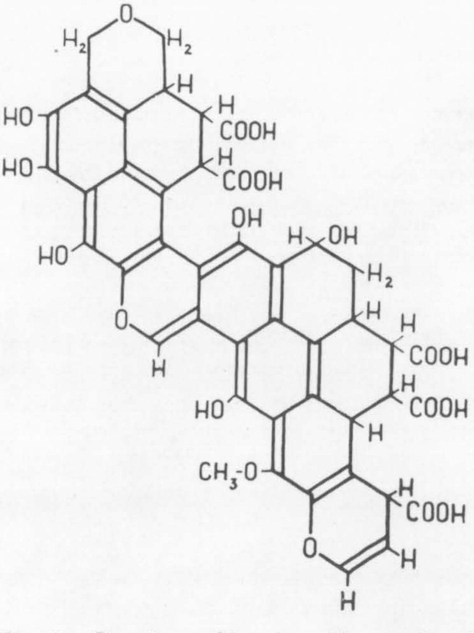


Fig. 3: Structure of humic acid according to Fuchs (1931).

The clay-water system, in fact any electrical system, must retain electrical neutrality, and thus, in the vicinity of the negatively charged surface, there is an excess of cations, or gegenions as the counter ions are commonly called (around a positively charged surface the gegenions would be negatively charged). Electrostatic attraction between the charged clay particle surface and the positively charged gegenions is responsible for this build-up. Thermal agitation, overcoming in part the electrostatic attractions, causes a diffuseness in the arrangement of the cations, and hence a diffuse layer of ions, commonly called the Gouy-Chapman layer after the workers who first suggested it. Co-ions (ions of the same charge sign as the surface) are also present in the diffuse double-layer. According to the Gouy-Chapman hypothesis the electrical potential in the double-layer can be represented as in Figure 4.

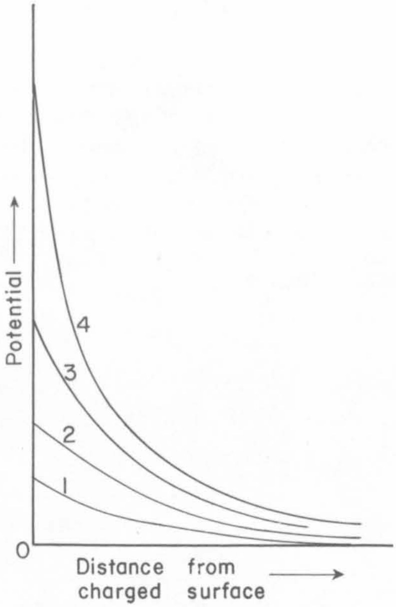


Fig. 4: Electrical potential in the double-layer according to Gouy-Chapman; 1, 2, 3, 4 increasing surface charge.

However, if the electrostatic forces are too strong, or if they are reinforced by van der Waal forces, thermal agitation cannot overcome them, and part of the gegenions remain in a compact layer at the charged surface. According to this idea the electrical potential in the double layer can be represented as in Figure 5. There seems to be some disagreement in the various review papers on the exact nature of what has become known as the Stern layer.

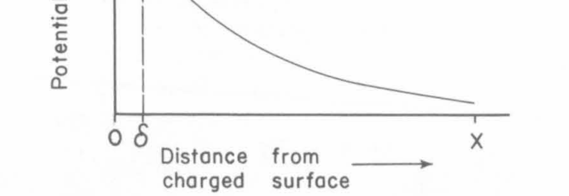


Fig. 5: Electrical potential in the double layer according to Stern.

Some authors like to consider it as being composed only of specifically absorbed particles, but Stern himself considered that any particles (whether gegenions, co-ions, or polar molecules) which are present at the charged surface, and which can be considered to be fixed, are present in the same layer - later called the Stern layer. Bockris et al. (1963) have presented a new model of the double layer structure and this is reproduced in Figure 6. For the present purposes, the locus of the centres of the hydrated cations (Gouy plane ϕ_2 in Fig. 6) shall be considered to be the line of demarcation of the diffuse and fixed parts of the double layer. All particles lying closer to the surface than this plane shall be considered to be in the fixed part of the double-layer. The particles which are farther away from the surface than this plane (including those in the plane) shall be considered to be in the diffuse part of the double layer.

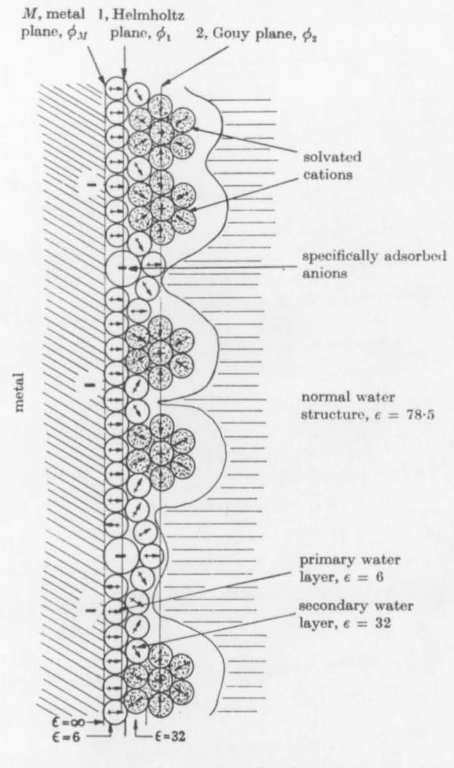


Fig. 6: Present model of the double-layer around a negatively charged surface (after Bockris et al., 1963).

Grahame (1947), whose main interest was the double-layer at the mercury-water interface, introduced the concept of the inner and outer Helmholtz planes. The locus of the centre of charge of the hydrated cations at the point of closest approach to the surface he called the outer Helmholtz plane (the Gouy plane in Fig. 6). Unhydrated anions or water molecules can approach much closer to the surface and are held either by electrostatic forces, covalent bonds, or van der Waal forces. The locus of the electrical centres of unhydrated ions is called the inner Helmholtz plane (Helmholtz plane ϕ_1 in Fig. 6). A negatively charged surface does not necessarily adsorb positively charged particles preferentially, nor does a positively charged surface necessarily adsorb negatively charged particles preferentially. These points will be brought out more fully when discussing some of the experimental results reported in the text.

Specific sorption refers to that sorption which is over and above that to be expected solely on charge considerations. The bonding may be of the covalent type or may be due to van der Waal forces or, infact, to image forces. Grahame, Poth, & Cummings (1952) explained the specific sorption of halide ions on a mercury surface as due to covalent bonding of the anions to the mercury. If this is in fact the correct explanation, one would expect the bond strength of Hg - X to decrease in the order $I > Br > Cl > F$ judging from the sorbabilities of the respective halide ions. But, as pointed out by Bockris et al. (1963), the bond strength decreased in order $F > Cl > Br > I$, and these authors suggest that the degree and type of ionic hydration is the principal factor which determines specific sorption, and not the bond strength of the mercury halides. Thus, the fluoride ion, generally (if not exactly) referred to as non-specifically sorbed, has a much greater heat of hydration than chloride, bromide, or iodide and, in accordance with Bockris' suggestion, it is the least specifically sorbed of the halide ions. Bockris et al. do not mention polarization phenomena, but it is generally recognized that the larger the ion, the greater its polarizability and the greater the expected adsorbability. Specific sorption takes place only within the Stern layer and the innermost layer of the diffuse part of the double-layer (the outer Helmholtz plane); non-specific sorption occurs in both the diffuse and the fixed parts of the double-layer.

One must not assume from this that specific sorption is a phenomenon restricted almost entirely to anions. On the contrary, if the cation is sufficiently large it will tend to be specifically sorbed. Generally speaking, ions tend to be specifically sorbed if they are bereft of a primary hydration sheath. According to Bockris et al., cations tend to be specifically sorbed at a given charge about 1/3 to 1/4 as much as anions of the same radius, and this may be one of the reasons why specific sorption of cations has been much harder to demonstrate than the specific sorption of anions, particularly at the mercury-water interface. Specific sorption of cations on the negatively charged clay surface is claimed by many workers; the earliest appears to have been Elgabaly (1950). He noted that, in addition to the common cation-exchange reactions, montmorillonite appears to combine with zinc ion in such a way that the zinc remains fixed, in the sense that it is not exchangeable with ammonium acetate. Hodgson(1960) studied the specific sorption of cobalt by montmorillonite in the presence of a large excess of calcium chloride, and concluded that there were two relatively specific reactions involved. One of these was due to chemisorption (Hodgson suggests broken bonds on the surface as being responsible) and the chemisorbed cobalt was slowly exchangeable over a period of three days. The other was due to cobalt ions entering holes left in the crystal lattice by the isomorphous substitution of Si^{4+} by Al^{3+}, and the cobalt was not exchangeable.

Whether a particular ion will be sorbed on a clay surface depends on its ability to polarize the clay lattice or coordinating water. Ion-exchange pertains only to gegenions in the double-layer, and the co-ions play only a minor role in exchange reactions unless they are specifically sorbed. Co-ions play a much greater part in reactions at the mercury surface.

Chemisorption involves the formation of bonds between the sorbed particle and the sorbent surface, which are almost as strong as those existing in stable stoichiometric compounds. Chemisorption is often irreversible, and because of the formation of chemical bonds (as distinct from physical bonds due to van der Waals adsorption) the heat of sorption is often very high. A measure of the heat of sorption is frequently the only factor available to enable one to determine the type of sorption. It is considered likely that part, if not all, of the specific sorption on peat is due to chemisorption.

Flocculation of colloids

Flocculation is a rather complex process and is not yet completely understood. The phenomenon can however be partially understood by the present ideas on double-layer theory, and it is sufficiently pertinent to the colloid studies described in this Report that a brief discussion of it in this section seems desirable.

Colloids owe their stability when dispersed in an aqueous medium to their charge and the surrounding double-layer. The inner part of the Stern layer, which is bound to the colloid particle surface, consisting usually of adsorbed polar molecules such as water, moves with the particle in an applied electric field. The surface of shear is the exterior of this adhering layer, and the zeta potential, analogous to the work required to bring unit charge from infinity to this surface of shear, is a measure of the stability of the particle in that medium. Tuorila (1928) has shown diagrammatically the relationship between the zeta-potential and the ease of flocculation of a kaolinite suspension (Fig.7).

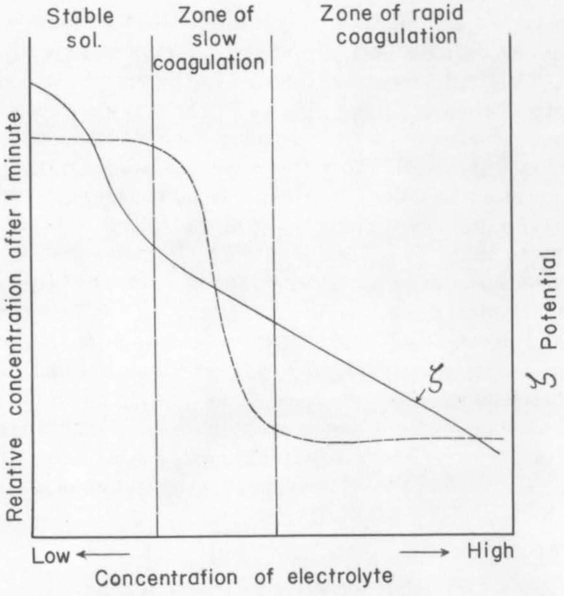


Fig. 7. The relationship between the zeta-potential and the ease of flocculation of a kaolinite suspension (after Tuorila).

The more highly hydrated the ion forming the fixed part of the double-layer or the lower the concentration of gegenions in the double-layer, the higher the zeta-potential and the greater the stability of the colloid. At lower potentials, brought about by the addition of electrolytes, floccules of particles form and this gives great apparent bulk to the solid in suspension. At much higher surface charge densities the floccule structure is destroyed by mutual electrostatic repulsion and the apparent bulk of the solid diminishes very considerably. Flocculation of colloids takes place because the double-layer is reduced in thickness to such an extent by the addition of electrolyte that the particles can approach each other sufficiently closely to be attracted by van der Waal forces, with concomitant interaction of the double-layers. The extent by which the zeta potential and the structure of the double-layer is affected by changing electrolyte concentrations is shown in Figure 8.

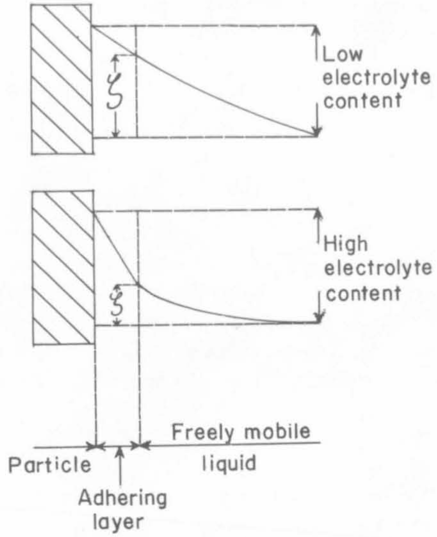


Fig.8. The influence of electrolytes on the structure of the double-layer and the zeta-potential.

The flocculation value is defined as the minimum concentration of electrolyte that is required to effect rapid coagulation. The stability of colloids is a question of velocity of flocculation, which means therefore that one has to consider the kinetics of the system when discussing flocculation. Quite generally speaking, it can be said that two factors combine to bring about flocculation. These are:

(i) Brownian movement, which is the movement of particles due to the quite random collisions of all the ions and molecules in the system, including molecules of the medium in which the particles are suspended.

(ii) Interaction of the particles when they are close enough, i.e. when the double-layer is reduced in thickness sufficiently for the short range van der Waal forces to become operative between colloid particles.

The character of the counter-ions which bring about flocculation has a great effect on the flocculation rate. For instance, the Schulze-Hardy rule states that trivalent cations are much more effective than divalent ones in the flocculation of negatively charged colloids, and divalent than monovalent. In an analogous way, polyvalent anions are much more effective than monovalent anions in the flocculation of positively charged colloids.

The Hofmeister series refers to the order of flocculation of ions of the same sign and valence. Ions which can approach close to the colloid, i.e. those having a small hydration shell, have greater powers of flocculation than those with much larger hydration shells. Thus, large cations, with small polarizing power, and therefore less attraction between the ion and the water molecule dipoles, have greater powers of flocculation than the equivalent amount of a smaller ion of the same valence.

For monovalent cations, in order of decreasing flocculating power, the Hofmeister series is:

$$H^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+$$

and for anions

$$F^- > Cl^- > Br^- > NO_3^- > CIO_4^- > I^-$$

A colloidal particle may be protected against flocculation if polar particles are sorbed, whose hydrophilic groups are oriented towards the aqueous medium. The surface of these colloid particles is thus effectively formed by hydrophilic groups and these determine the character of the surface of the colloid particle. The sorption of polar particles can also profoundly affect the reactions occurring at the dropping mercury electrode surface.

SORPTION OF SINGLE ION-SPECIES

Although sorption from solutions containing a single metal-ion species will hardly ever occur in nature, any attempt to study sorption of ions from a mixture must be preceded by a study of sorption of single ions.

Experiments were carried out to investigate factors which could influence the quantity of metal ion sorbed by some of the more common or more relevant natural sorbents. Thus, it was necessary to know how the relative concentrations of sorbents and of sorbate ions influence the weight of metal ion sorbed per unit weight of sorbent; to what extent ions which occur in large quantities in nature (such as Na^+ and Mg^{++}) affect the sorption of heavy metal ions; what factors affect the sorption rate; to what extent is the pH of the solution important; and whether there are interfering substances present in the various sorbents which could give misleading or erroneous analytical results.

The early part of the study was devoted to answering these questions and the relevant experiments and their results will be described in the following sections. It was soon established that the answers were fundamentally the same for all metal ions investigated; most of the experiments described here refer to the lead ion only.

Sorption rate

First it was necessary to study the sorption rate in order to know the time needed for the establishment of equilibrium before proceeding to the analysis of the supernatant liquid in contact with the sorbent. The following procedure was adopted:

Twelve 25 ml graduated tubes were set up, each containg 20 ml of the kaolinite suspension (20 gm kaolinite/litre) in 10^{-1} M sodium nitrate solution, containing also 2 ml of the stock lead solution (see p.); the blank solution contained 20 ml 10^{-1}M sodium nitrate without kaolinite and 2 ml of the stock lead solution. The tubes were shaken and the kaolinite allowed to settle. After 20 minutes the lead content of the supernatant liquid of one of the tubes was determined, and this analysis repeated on four other tubes at 20-minute intervals, thereafter every 4 hours on three further tubes, and at daily intervals on the remainder. The difference between the lead ion remaining in the supernatant after sorption, and the lead ion in the solution not containing kaolinite, gave the amount of lead sorbed. The quantity of lead sorbed was plotted as a function of time (Fig. 9).

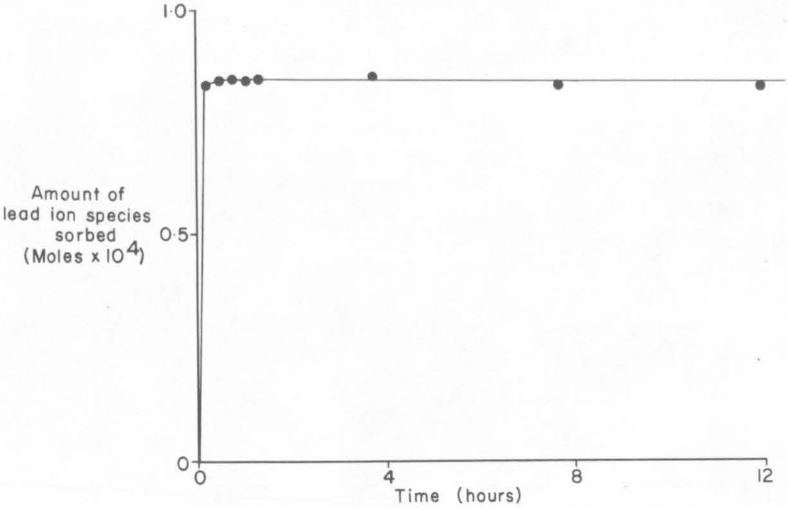


Fig. 9 Rate of sorption of lead ion species by kaolinite.

It is clear that the sorption by kaolinite is rapid; in fact less than 20 minutes was required for equilibrium to be established.

The experiment was repeated using bentonite as sorbent (5 gm/ litre). The result is shown in Figure 10, which clearly shows a rapid initial sorption, followed by a very slow sorption which most probably could be attributed to the slow penetration of the sorbed ions into the inner layers of the bentonite crystals, or to chemisorption, or to a combination of both.

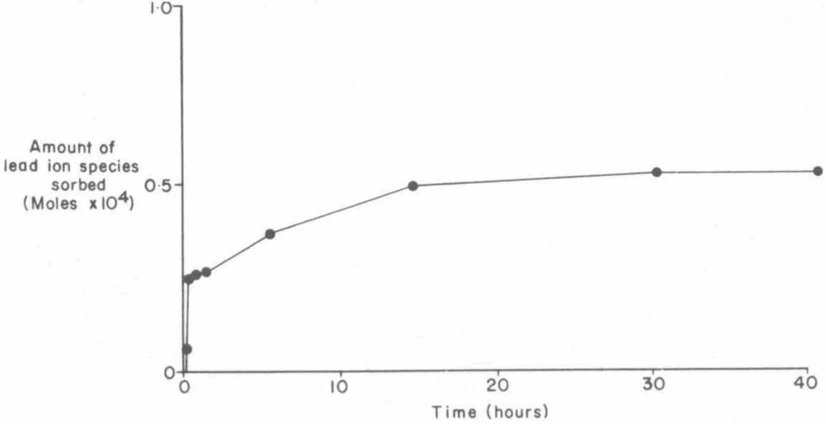


Fig. 10 Rate of sorption of lead ion species by bentonite.

Experiments using other sorbents such as peat, ferric hydroxide, dolomite, and vermiculite showed that the sorption rates for all of them were high and did not exhibit the dual sorption mechanism shown by bentonite; equilibrium was reached in less than one hour.

Dialysis experiments

The effect of surface-active compounds on the reduction of inorganic ions at the dropping-mercury electrode are well known; in some cases a distorted step is produced (sometimes accompanied by a reduced step height) (Meites & Meites, 1950); in others the surface-active compound has no apparent effect (Beevers & Breyer, 1959/60). It was thought that some of the sorbents used, particularly the peat, might contain surface-active compounds which could interfere with the polarographic estimations.

The presence of surface-active compounds was shown by the non-coalescence of the mercury drops in the polarographic cell when peat was used as sorbent. To investigate whether these surfactants interfere with the polarographic analysis, dialysis experiments were carried out as follows: A cellophane bag, containing 100 ml of a 10^{-1} M sodium nitrate solution, to which varying amounts of peat were added, was immersed into 100 ml of a 10^{-1} M sodium nitrate solution containing also 2×10^{-4} M lead nitrate.

The results show that equilibrium was certainly established within three days (Table 1).

	Peat Suspension (gm/100 ml)	Nil	0.0025	0.01	0.05	0.10
Lead step height (arbitrary units)	Control	33.7	26.3	17.0	2.6	2.4
	Dialysis experiment after 3 days	33.5	23.5	14.8	2.3	1.8
	Dialysis experiment after 4 days	33.5	22.9	14.7	2.4	1.9

Table 1. The quantities of lead ion remaining in solution at equilibrium, after dialysis experiment using peat suspension and lead ion.

Simultaneously with these experiments, a series was run using 100 ml of the peat suspensions in 10^{-1} M sodium nitrate and mixing directly with 100 ml of the solution of 2.10^{-4} M lead in 10^{-1} M sodium nitrate. After three days the equilibrium concentration of lead was determined and used as the control (Table 1).

The results of these two series of experiments show that the control results are higher, indicating that there is no interference with the polarographic results in the presence of peat. The higher results could be due to sorption of lead by cellophane.

An analogous series of experiments using copper, zinc, and cobalt salts showed that the surfactants contained in peat do not interfere with the polarographic estimation of these metal ions either. A further series of experiments using in turn dolomite, ferric hydroxide, and kaolinite, in place of peat, showed also that these sorbents did not contain surfactants which interfered with the estimation of lead, copper, zinc, and cobalt ions.

Influence of pH on sorption

Because of its small size relative to other cations, the hydronium ion behaves uniquely in sorption processes; considering the very wide range of pH values observed in natural waters it seemed worthwhile to investigate the influence of pH on the sorption equilibrium obtained.

It was not intended to control by buffers the pH of the solutions in the main sorption experiments because the use of buffer solutions would almost certainly mean the formation of complexes. Since such complexes (acetates, phosphates, borates, etc.) are rare in nature the results of laboratory experiments involving their use would have only a limited application. Nevertheless it was considered desirable to know just how the sorptive properties of the various adsorbents vary with the pH of the medium in which they are suspended.

The effect of pH on the sorptive properties of dolomite could not be studied because any attempt to acidify the suspension was countered by the dissolving of an equivalent amount of dolomite. The effect of pH on the sorptive properties of ferric hydroxide is much the same as the effect of pH on the sorptive properties of kaolinite, except that the point of zero sorption occurs about pH 4.5.

pH measurements were made on every solution used in the sorption studies reported here and the results showed that, except where free acid or free alkali was added, the pH of the clay and river silt suspensions was always 6.4 ± 0.2 irrespective of the composition of the solution; that is, the clay materials behaved as mild buffers. The peat suspensions were so dilute that the pH of the solution was almost identical with the pH of the water before addition of the peat.

Effect of pH on sorptive properties of kaolinite: Into each of six 25 ml graduated glass tubes was put 20 ml of a suspension of kaolinite (10 gm/litre) and 2ml of the stock solution of lead. A seventh tube contained 20 ml of water and 2 ml of the stock lead solution; this was used as control. By addition of a few drops of either very dilute hydrochloric acid or dilute ammonia solution, the pH of the solution in the tubes containing clay was adjusted to give a range of pH values from 7 to 2. The tubes were shaken, the kaolinite allowed to settle overnight, and the lead in the supernatant liquid determined. There was no change in the pH value of any of the solutions on standing overnight. The lead sorbed was then plotted against the pH of the solution (Fig. 11).

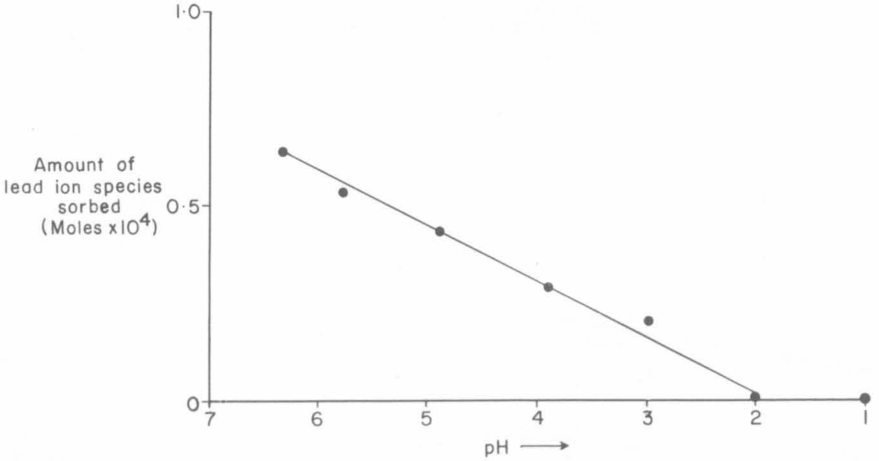


Fig. 11. Sorption of lead ion species by kaolinite in solutions of varying pH.

A curve of almost identical shape was obtained for the ions Cu^{++}, UO_2^{++}, Co^{++}, Cd^{++}, Zn^{++}, and Ni^{++}. It can be seen that in the range pH 2 to 6 the sorption of metal ions is linearly proportional to the pH of the medium. Exactly the same type of behaviour was found with silt.

Effect of pH on the sorptive properties of peat: Employing the same technique as that used with kaolinite, but using a suspension containing 0.1 gm/litre of peat, the effect of pH on the sorptive properties of peat was studied. The results obtained with lead ion are shown diagrammatically in Figure 12.

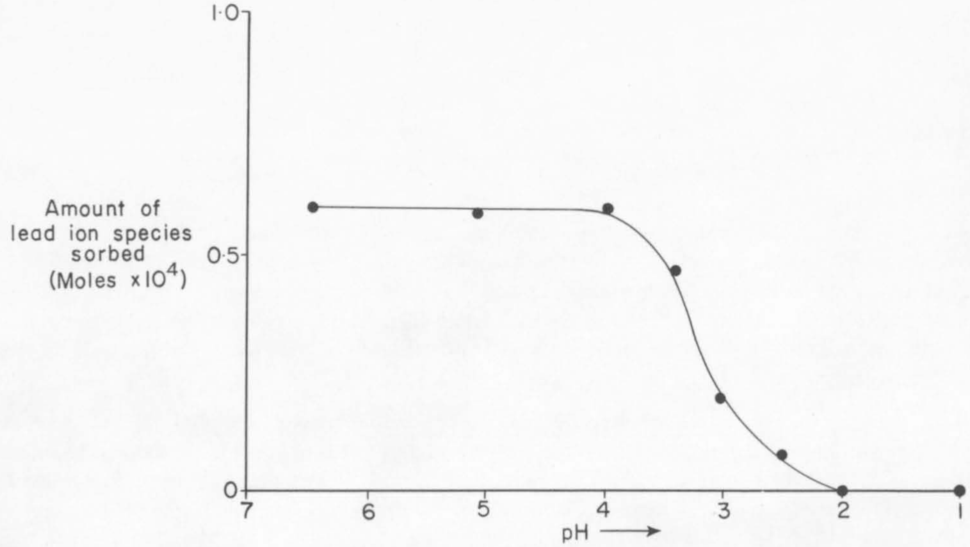


Fig. 12. Sorption of lead ion species by peat in solutions of varying pH.

Cu^{++}, UO_2^{++}, Co^{++}, Cd^{++}, Zn^{++} and Ni^{++} gave diagrams almost identical in shape with that shown in Figure 12. It is obvious that the high sorption values above pH 4 are independent of pH; sorption diminishes rapidly at lower pH values until at a pH below 2 the sorption is very small indeed. These results are in very close agreement with those reported by Szalay (1957) for the uranyl ion and a Hungarian peat.

In view of these results subsequent experiments were so ordered as to ensure that changes in sorption were not due to changes in pH. With kaolinite and silt the pH had to be kept at a fixed value within very narrow limits; this fortunately was easy since, as was stated previously, kaolinite and silt behave as mild buffers and, except where free acid or free alkali was added, the pH was found to be 6.4 ± 0.2. Peat on the other hand does not behave as a buffer in the small concentrations used; but, since its sorption properties are independent of pH above pH4, the only control required was to ensure that the pH of the test solution did not fall below 4, nor rise above 6.5.

Sorption as a function of sorbable-ion concentration

Into each of six cylinders was put 20 ml of kaolinite suspension (20 gm/litre); six similar cylinders contained 20 ml of distilled water. The cylinders were arranged in pairs, one cylinder from each group, and to each pair was added the same amount of lead ion; the range of lead concentrations used varied from 10^{-3} to 10^{-5} M. After addition of the lead solution, the cylinders were shaken and the kaolinite allowed to settle overnight. Then polarograms were run on the supernatant liquids to determine the amount of lead ion sorbed. The results, given in Table 2, are also shown graphically in Figure 13.

Results of an analogous experiment using peat as sorbent are shown in Table 3 and Figure 14.

Initial lead nitrate concentration $M \times 10^4$	Equilibrium concentration of lead in supernatant $M \times 10^4$	Moles of lead sorbed per 100 gm kaolinite $\times 10^4$
0.30	0.012	1.4
0.74	0.20	2.7
1.44	0.70	3.7
1.70	0.88	4.1
2.12	1.24	4.5
2.73	1.71	5.0
3.35	2.20	5.7
3.93	2.74	5.8
6.04	4.53	7.6
8.20	6.20	9.9
10.00	7.92	10.4

Table 2. Lead ion sorbed by kaolinite (20 gm/litre) as a function of initial lead ion concentration.

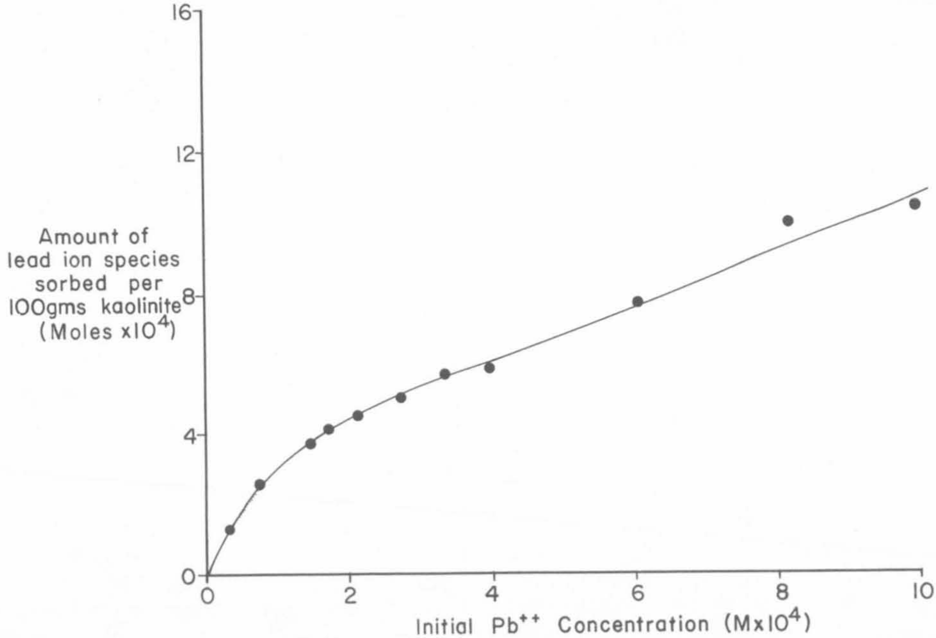


Fig. 13. Results of Table 2 shown graphically.

Initial lead nitrate concentration $M \times 10^4$	Equilibrium concentration of lead in the supernatant $M \times 10^4$	Moles of lead sorbed per 100 gm of peat $\times 10^2$
0.30	0.02	1.35
0.74	0.17	2.76
1.44	0.54	4.51
1.70	0.75	4.97
2.12	1.07	5.31
2.73	1.64	5.60
3.35	2.26	5.40
3.93	2.70	6.10
6.04	4.80	6.30
8.20	6.82	6.78

Table 3. Lead ion sorbed by peat(0.2 gm/litre) as a function of initial lead ion concentration.

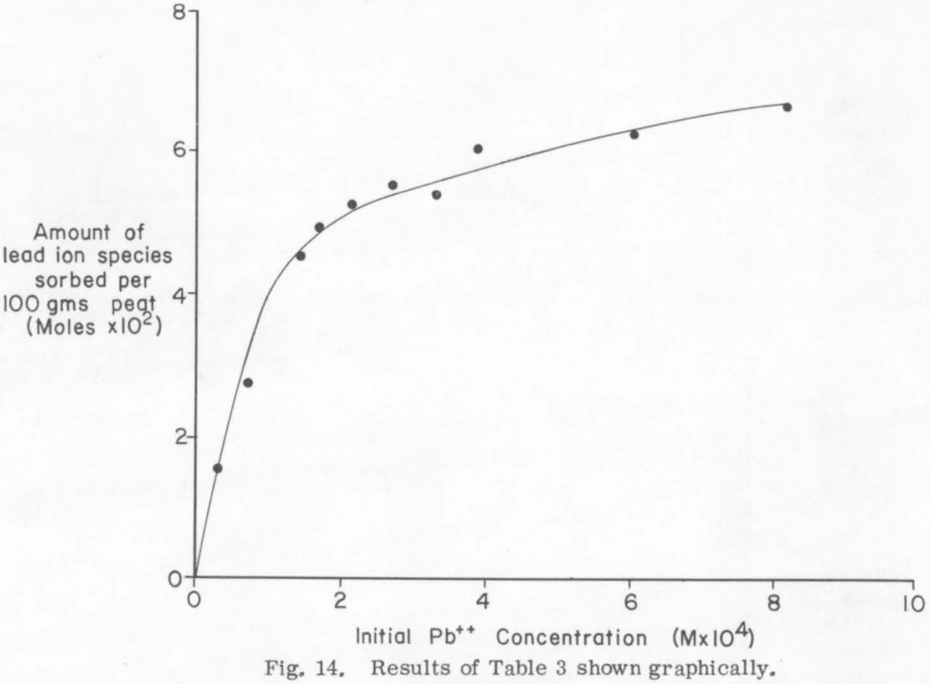


Fig. 14. Results of Table 3 shown graphically.

The results are in good agreement with the sorption isotherms obtained by Rozhkova et al. (1958), using uranyl ion and various lignites and peats as sorbents.

Effect of Sodium and Magnesium salts on the Sorption Equilibrium

The effects of sodium and magnesium salts on the sorption equilibrium obtained with various metal ions and different sorbents occurring in nature were studied because sodium and magnesium salts are present in high concentration in seawater, and such a study could clarify the possible effect of seawater when brought into contact with a sorbent containing sorbed metal ions. The experiments were carried out as follows:

To each of five tubes, four of which contained 20 ml of kaolinite suspension (5 gm/litre), and the remaining one 20 ml of distilled water, was added 2 ml of the stock lead ion solution. Sodium nitrate was added to each of the four tubes containing kaolinite so that the solutions in the tubes were 10^{-1} M, 10^{-2} M, 10^{-3} M, 10^{-4} M and 0 M with respect to sodium nitrate after they had been made up to a final volume of 25 ml with distilled water. The tubes were thoroughly shaken and allowed to stand overnight. The lead ion remaining in the supernatant was determined and a plot made of lead sorbed as a function of the sodium salt concentration. The solution in the fifth tube served as a control.

The whole experiment was repeated using magnesium nitrate instead of sodium nitrate. Both experiments were then repeated using the other sorbable ion-species shown in Table 4. The whole series of experiments were repeated with peat and ferric hydroxide as sorbents. The results are shown in Tables 4, 5, and 6.

The control tube showed, in every case, that no loss of sorbable ion-species occurred in the absence of sorbent (kaolinite, peat, or ferric hydrate). In other words, the glass containers exhibited negligible sorption effects.

Sorbable ion species	Added electrolyte	Concentration of added electrolyte			
		10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M
		Moles of sorbate ion sorbed per 100 gm kaolinite x 10^4			
Pb^{++}	$NaNO_3$	5.2	10.8	12.6	12.6
	$Mg(NO_3)_2$	2.4	4.1	7.2	10.7
Cu^{++}	$NaNO_3$	3.1	7.8	10.9	12.7
	$Mg(NO_3)_2$	3.1	3.1	4.7	9.4
UO_2^{++}	$NaNO_3$	7.6	10.5	10.5	10.5
	$Mg(NO_3)_2$	4.6	5.4	7.6	9.7
Zn^{++}	$NaNO_3$	2.2	7.1	10.2	10.2
	$Mg(NO_3)_2$	n.d.*	0.6	6.1	7.4
Cd^{++}	$NaNO_3$	0.4	6.5	9.8	9.8
	$Mg(NO_3)_2$	n.d.	1.4	3.1	7.3
Co^{++}	$NaNO_3$	n.d.	7.8	10.3	10.3
	$Mg(NO_3)_2$	n.d.	3.2	4.7	8.3
Tl^{+}	$NaNO_3$	n.d.	1.7	3.0	3.0
	$Mg(NO_3)_2$	n.d.	n.d.	0.9	2.8

Table 4. Effect of presence of varying concentrations of added sodium or magnesium salts on sorption of various cations from a 7.6 x 10^{-5} M solution by a kaolinite suspension (5 gm/litre).

* (n.d. = not detected)

Sorbable ion species	Added electrolyte	Concentration of added electrolyte			
		10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M
		Moles of sorbate ion sorbed per 100 gm of peat x 10^{2}			
Zn^{++}	$NaNO_3$	2.5	3.5	3.6	4.5
	$Mg(NO_3)_2$	0.8	0.9	2.4	3.1
Cd^{++}	$NaNO_3$	1.8	3.5	3.6	4.5
	$Mg(NO_3)_2$	0.2	1.0	2.7	3.5
Pb^{++}	$NaNO_3$	4.6	6.5	6.7	7.9
	$Mg(NO_3)_2$	2.0	4.7	5.7	5.9
Co^{++}	$NaNO_3$	Trace	3.4	3.6	3.6
	$Mg(NO_3)_2$	Trace	2.0	2.6	3.3
Tl^{+}	$NaNO_3$	n.d.	n.d.	n.d.	n.d.
	$Mg(NO_3)_2$	n.d.	n.d.	n.d.	n.d.
UO_2^{++}	$NaNO_3$	7.3	7.2	7.2	7.2
	$Mg(NO_3)_2$	4.3	5.6	5.7	6.7

Table 5. Effect of presence of varying concentrations of added sodium or magnesium salts on sorption of various cations from a 7.6 x 10^{-5} M solution by a peat suspension (0.05 gm/litre)

Sorbable ion species	Added electrolyte	Concentration of added electrolyte			
		10^{-1} M	10^{-2} M	10^{-3} M	10^{-4} M
		Moles of sorbate ion sorbed per 100 gm ferric hydroxide x 10^{3}			
Zn^{++}	$NaNO_3$	6.3	5.4	2.5	2.2
	$Mg(NO_3)_2$	5.7	5.2	2.6	2.2
Pb^{++}	$NaNO_3$	25.0	21.7	12.5	9.0
	$Mg(NO_3)_2$	35.0	30.6	14.4	10.4
Co^{++}	$NaNO_3$	4.7	3.6	0.8	n.d.
	$Mg(NO_3)_2$	5.1	3.9	3.1	0.8
Cd^{++}	$NaNO_3$	4.8	4.8	1.7	n.d.
	$Mg(NO_3)_2$	3.8	3.7	2.0	1.3
Cu^{++}	$NaNO_3$	16.4	15.6	13.8	10.9
	$Mg(NO_3)_2$	18.9	18.6	14.1	11.4

Table 6. Effect of presence of varying concentrations of added sodium or magnesium salts on sorption of various cations from a 7.6 x 10^{-5} M solution by ferric hydroxide sol (0.2 gm/litre).

The results show that for kaolinite and peat, the sorption of a particular ion decreased as the concentration of magnesium or sodium ion increased. This was to be expected, as was the fact that divalent Mg^{++} ion had greater powers of displacement than had the monovalent Na^{+} ion. The results obtained with ferric hydroxide, however, were different; here, the addition of Na^{+} or Mg^{++} ions caused increased sorption. This behaviour was undoubtedly due to the fact that the ferric hydrate was a positive colloid, whereas the kaolinite and peat were both negative colloids (this was established by electrophoresis experiments).

Sorption as a function of mass of sorbent per unit volume of solvent

Kaolinite suspensions containing 1.25, 2.5, 5.0, 7.0, and 10.0 gm/litre were used. The sorption experiments were carried out in solutions containing the relevant metal ions at a concentration of 7.6×10^{-5} M, dissolved either in distilled water or in a 10^{-1} M solution of sodium or magnesium nitrate. After the kaolinite had settled overnight (if it had not settled the suspension was centrifuged) the concentration of metal ion in the supernatant was determined. Peat, silt, dolomite, and ferric hydroxide were also used as sorbents. The results of these experiments are summarized in Tables 7 to 11.

The quotient of the mass of ions/ mass of adsorbent and the mass of ions/ mass of solvent in the original solution is called the enrichment factor (after Szalay, 1957); the enrichment factors found in the present series of experiments are presented in Tables 12 to 16. The enrichment factor changes from one metal ion to another for the same sorbent, but varies much more widely from one sorbent to another. The enrichment factors for peat and ferric hydroxide are surprisingly high, even in the presence of a 10^{-1} M solution of sodium or magnesium nitrate. In fact, using ferric hydroxide as sorbent, the enrichment factor in the presence of sodium or magnesium nitrate solution is greater than in distilled water.

The figures quoted refer of course to a single ion-species and to one type of sorbent only; quite different figures are found when mixtures of ions or of sorbents or both are used, as will be shown later.

It seems that the only similar type of work published is that due to Szalay (1957) who investigated the uptake of uranyl ion from dilute solutions by various peats. He quotes a maximum enrichment factor of 10,000 for uranium and peat, which is in good agreement with the present results.

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Sorbable ion-species	Distilled water					10^{-1} Sodium nitrate				
	Kaolinite (gm/litre)									
	1.25	2.5	5.0	7.5	10.0	5.0	10.0	20.0	30.0	40.0
	Moles of metal ion sorbed per 100 gm kaolinite x 10^4.									
Cr^{+++}	47.3	27.3	15.0	11.2	7.5	4.6	4.2	2.7	1.5	1.2
Fe^{+++}	38.0	25.6	15.0	11.3	7.4	7.7	7.1	4.6	2.7	2.1
Pb^{++}	33.7	23.1	13.8	10.0	7.5	4.5	4.5	2.9	2.2	1.8
Cu^{++}	21.2	19.1	11.7	8.6	7.0	4.7	4.5	3.0	2.2	2.0
Ni^{++}	19.5	14.4	9.7	7.3	6.1	1.2	1.0	0.7	0.5	0.5
Zn^{++}	19.1	15.1	9.9	7.7	6.2	2.3	2.3	2.2	2.0	1.5
Cd^{++}	21.0	15.2	10.7	8.4	6.6	2.7	2.1	1.7	1.4	1.2
Co^{++}	11.4	6.5	4.7	4.1	3.4	1.2	1.2	1.0	1.0	0.8
Mn^{++}	19.3	13.7	8.9	6.5	5.1	1.3	1.3	1.1	0.5	0.5
Tl^{+}	11.4	8.1	5.8	4.9	4.2	1.2	1.1	1.0	0.9	0.7
UO_2^{++}	7.5	3.7	3.4	2.8	2.5	3.4	3.4	3.4	2.7	2.1
VO_3^{-}	3.9	3.3	3.3	3.1	2.4	3.9	2.9	1.8	0.8	0.5
MoO_4^{--}	1.6	1.3	1.0	0.8	0.7	1.6	1.4	1.3	1.0	0.6
CrO_4^{--}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 7. Quantities of metal ions sorbed on to kaolinite from 7.6 x 10^{-5}M solutions in the presence and absence of sodium nitrate.

Sorbable ion species	Distilled water					10^{-1}M sodium nitrate				
	Peat (gm/litre)									
	0.025	0.05	0.10	0.15	0.20	0.05	0.10	0.20	0.30	0.40
	Moles of metal ion sorbed per 100 gm of peat x 10^2.									
Cr^{+++}	12.8	9.2	4.2	3.2	2.5	7.5	4.0	2.2	2.0	1.4
Fe^{+++}	12.8	9.7	5.7	3.9	3.2	7.2	5.1	2.4	2.0	1.4
Pb^{++}	7.9	6.1	3.0	2.1	1.7	5.7	2.7	1.6	1.6	1.2
Cu^{++}	22.0	12.5	7.2	4.9	3.3	5.9	4.2	2.5	1.6	1.3
Ni^{++}	5.4	4.4	3.4	2.8	2.2	3.4	3.2	2.1	1.8	1.5
Zn^{++}	4.5	2.7	2.2	1.7	1.4	1.9	1.7	1.5	1.3	1.1
Cd^{++}	4.5	2.7	2.2	1.7	1.4	2.5	2.0	1.3	1.0	0.8
Co^{++}	2.3	1.5	0.8	0.6	0.5	1.7	0.7	0.4	0.3	0.3
Mn^{++}	3.5	3.3	2.1	1.4	1.4	0.7	0.7	0.4	0.2	0.2
Tl^{+}	1.2	1.0	0.6	0.4	0.3	0.3	0.3	0.1	0.1	0.1
UO_2^{++}	7.9	7.8	4.7	3.6	2.8	5.7	5.1	3.6	2.4	1.7
VO_3^{-}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MoO_4^{--}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CrO_4^{--}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 8. Quantities of metal ions sorbed onto peat from 7.6 x 10^{-5}M solutions in the presence and absence of sodium nitrate.

Sorbable ion-species	Distilled water				10^{-1}M Magnesium nitrate		
	Silt (gm/litre)						
	0.5	1.5	3.0	7.0	3.0	7.0	10.0
	Moles of metal ion sorbed per 100 gm silt x 10^4						
Pb^{++}	40.7	22.3	11.6	5.8	12.6	8.5	7.0
Cu^{++}	40.6	20.3	14.1	6.3	14.8	8.6	6.3
Ni^{++}	23.7	11.9	11.9	8.5	n.d.	n.d.	n.d.
Zn^{++}	24.6	18.5	10.8	7.7	n.d.	n.d.	n.d.
Cd^{++}	24.2	10.7	8.9	5.4	n.d.	n.d.	n.d.
Co^{++}	11.9	10.2	5.1	1.7	n.d.	n.d.	n.d.
Tl^{+}	4.4	2.5	2.0	2.0	n.d.	n.d.	n.d.
UO_2^{++}	40.3	42.0	21.0	11.0	9.8	9.1	7.0
VO_3^{-}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MoO_4^{--}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 9. Quantities of metal ions sorbed on to silt from 7.6 x 10^{-5}M solutions in the presence and absence of magnesium nitrate.

Sorbable ion-species	Distilled water					10^{-1}M Magnesium nitrate			
	Dolomite (gm/litre)								
	0.125	0.250	0.375	0.50	1.00	0.5	1.0	1.5	2.0
	Moles of metal ion sorbed per 100 gm dolomite x 10^3								
Pb^{++}	19.4	15.8	12.8	10.0	7.5	7.7	4.3	2.4	1.9
Cu^{++}	7.1	4.7	3.5	3.5	3.5	3.1	1.6	0.9	0.5
No^{++}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn^{++}	Trace	Trace	4.8	4.8	4.6	n.d.	n.d.	n.d.	n.d.
Cd^{++}	Trace	3.9	3.5	2.2	1.8	n.d.	n.d.	n.d.	n.d.
Co^{++}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tl^{+}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UO_2^{++}	4.7	4.7	2.4	1.8	1.4	3.2	1.9	1.3	1.0
VO_3^{-}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MoO_4^{--}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 10. Quantities of metal ions sorbed on to dolomite from 7.6 x 10^{-5}M solutions in the presence and absence of magnesium nitrate.

Sorbable ion-species	Distilled water				10^{-1}M magnesium nitrate				10^{-1}M sodium nitrate
	Ferric hydroxide (gm/litre)								
	0.125	0.250	0.375	0.500	0.125	0.250	0.375	0.500	0.125
	Moles of metal ion sorbed per 100 gm ferric hydroxide x 10^3								
Pb^{++}	10.4	9.1	7.2	6.2	35.1	20.1	13.6	10.0	25.2
Cu^{++}	11.4	7.2	5.3	4.7	18.9	11.7	9.4	6.3	16.4
Zn^{++}	2.2	1.4	0.9	1.5	5.9	3.8	2.5	1.5	5.9
Cd^{++}	1.8	1.1	0.8	0.7	4.4	1.8	1.3	1.0	5.5
Co^{++}	Trace	n.d.	n.d.	n.d.	4.9	2.7	1.5	0.8	4.6
Tl^{+}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
UO_2^{++}	15.2	10.5	8.4	6.0	27.3	18.9	13.2	10.2	27.3
MoO_4^{--}	5.2	3.2	2.4	3.0	5.2	4.2	3.6	3.1	5.2

Table 11. Quantities of metal ions sorbed on to ferric hydroxide from 7.6 x 10^{-5}M solutions in the presence and absence of magnesium and sodium nitrates.

Sorbable ion-species	Distilled water					10^{-1}M sodium nitrate				
	Kaolinite (gm/litre)									
	1.25	2.5	5.0	7.5	10.0	5.0	10.0	20.0	30.0	40.0
	Enrichment factors									
Cr^{+++}	620	358	197	146	100	61	55	35	20	15
Fe^{+++}	510	337	205	148	111	101	94	61	35	28
Pb^{++}	443	304	182	132	103	60	60	38	29	24
Cu^{++}	278	252	154	114	93	62	60	39	29	27
Ni^{++}	257	190	127	96	80	15	13	9	0	0
Zn^{++}	250	198	129	100	80	30	30	28	26	20
Cd^{++}	276	200	141	111	87	35	27	22	19	15
Co^{++}	150	85	62	54	45	16	16	13	13	11
Mn^{++}	254	180	117	86	67	17	17	14	0	0
Tl^{+}	149	106	76	65	55	16	15	13	12	9
UO_2^{++}	99	49	44	37	33	44	44	45	36	28
VO_3^{-}	52	44	44	41	31	52	39	23	10	7
MoO_4^{--}	21	16	14	11	10	21	19	16	14	8
CrO_4^{--}	0	0	0	0	0	0	0	0	0	0

Table 12 Enrichment factors for kaolinite after sorption from 7.6 x 10^{-5}M solutions of various ions, in the presence and absence of sodium nitrate.

Sorbable ion-species	Distilled water					10^{-1} sodium nitrate				
	Peat (gm/litre)									
	0.025	0.05	0.10	0.15	0.20	0.05	0.10	0.20	0.30	0.40
	Enrichment factors									
Cr^{+++}	16900	12200	5530	4220	3300	9900	5290	2950	2600	1910
Fe^{+++}	16800	12700	7460	5180	4200	9400	6700	3150	2580	1880
Pb^{++}	10500	8100	3900	2840	2230	7500	3600	2080	2070	1620
Cu^{++}	29000	16500	9500	6480	4330	7720	5480	3260	2160	1690
Ni^{++}	7150	5820	4420	3640	2860	4460	4250	2820	2320	1920
Zn^{++}	5970	3530	2900	2200	1860	2430	2240	1980	1700	1400
Cd^{++}	5920	3530	2880	2180	1850	3240	2680	1660	1330	1080
Co^{++}	2970	1960	1120	848	670	2240	870	558	446	357
Mn^{++}	4550	4350	2730	1890	1800	960	860	455	310	240
Tl^{+}	1570	1320	790	528	423	385	320	160	109	77
Uo_2^{++}	10500	10300	6150	4710	3670	7530	7110	6500	5200	4500
VO_3^{-}	0	0	0	0	0	0	0	0	0	0
MoO_4^{--}	0	0	0	0	0	0	0	0	0	0
CrO_4^{--}	0	0	0	0	0	0	0	0	0	0

Table 13. Enrichment factors for peat after sorption from 7.6 x 10^{-5} M solutions of various ions, in the presence and absence of sodium nitrate.

Sorbable ion-species	Distilled water				10^{-1}M magnesium nitrate		
	Silt (gm/litre)						
	0.5	1.5	3.0	7.0	3.0	7.0	10.0
	Enrichment factors						
Pb^{++}	535	293	153	76	331	229	185
Cu^{++}	537	268	185	82	392	227	165
Ni^{++}	312	156	156	112	0	0	0
Zn^{++}	323	242	140	100	0	0	0
Cd^{++}	317	141	118	70	0	0	0
Co^{++}	156	134	67	22	0	0	0
Tl^{+}	58	32	26	26	0	0	0
UO_2^{++}	532	552	378	155	388	360	277
VO_3^{-}	0	0	0	0	0	0	0
MoO_4^{--}	0	0	0	0	0	0	0

Table 14. Enrichment factors for silt after sorption from 7.6 x 10^{-5} M solutions of various ions, in the presence and absence of magnesium nitrate.

Sorbable ion-species	Distilled water					10^{-1}M magnesium nitrate			
	Dolomite (gm/litre)								
	0.125	0.25	0.375	0.50	1.00	0.5	1.0	1.5	2.0
	Enrichment factors								
Pb^{++}	2560	2080	1690	1310	1120	1020	568	320	248
Cu^{++}	928	618	453	450	450	410	200	124	62
Ni^{++}	0	0	0	0	0	0	0	0	0
Zn^{++}	0	0	624	624	600	0	0	0	0
Cd^{++}	0	506	460	294	236	0	0	0	0
Co^{++}	0	0	0	0	0	0	0	0	0
Tl^{+}	0	0	0	0	0	0	0	0	0
UO_2^{++}	615	615	322	233	183	415	255	166	138
VO_3^{-}	0	0	0	0	0	0	0	0	0
MoO_4^{--}	0	0	0	0	0	0	0	0	0

Table 15. Enrichment factors for dolomite after sorption from 7.6 x 10^{-5}M solutions of various ions, in the presence and absence of magnesium nitrate.

Sorbable ion-species	Distilled Water				10^{-1} magnesium nitrate				10^{-1}M sodium nitrate
	Ferric hydroxide (gm/litre)								
	0.125	0.250	0.375	0.500	0.125	0.250	0.375	0.500	0.125
	Enrichment factors								
Pb^{++}	1370	1200	957	820	4620	2650	1790	1320	3310
Cu^{++}	1500	948	700	620	2590	1550	1240	825	2170
Zn^{++}	283	182	121	200	768	505	323	200	768
Cd^{++}	236	141	106	94	578	235	177	129	720
Co^{+}	0	0	0	0	648	357	200	122	602
Tl^{+}	0	0	0	0	0	0	0	0	0
UO_2^{++}	2020	1390	1110	800	3600	2500	1740	1330	3600
MoO_4^{--}	687	425	315	397	687	548	480	412	687

Table 16. Enrichment factors for ferric hydroxide after sorption from 7.6 x 10^{-5}M solution of various ions, in the presence and absence of magnesium nitrate and sodium nitrate.

Tables 7 to 16 imply that small amounts of sorbent are more efficient per gram than larger amounts. This is not a general conclusion, and is only true in these experiments because the amount of sorbent present is greater, in nearly all cases, than the amount needed to become fully saturated with the available sorbable ion-species. Thus the ratio of sorbent to sorbable ion-species is most important and the lower the ratio of amount of sorbent to available sorbable ion-species, the more nearly does the sorption equilibrium approach the true cation exchange capacity of the sorbent. Sorption values at low sorbent concentrations are thus approximating to the cation exchange capacities (see Figs 13 and 14).

SORPTION INVOLVING TWO ION-SPECIES

Much more time than was available would have been required to carry out a complete study of the behaviour of the various sorbents with respect to the simultaneous sorption of two ion-species present at equal concentrations. Since clay and organic matter are the sorbents most commonly found in nature and thought capable of concentrating metal ions from solution as a first stage in syngenetic ore formation, it was considered that a detailed study of these two types of sorbents would be the most worthwhile. Moreover, since more detailed studies, involving a number of sorbents and solutions containing four ion-species, are reported on pages 36-46 , the limited experimental results presented in this section might be considered sufficient for the purposes of this investigation.

The experimental technique was the same as that described on pages 8-12. Kaolinite or peat was used as sorbent; the kaolinite suspensions contained 1.25, 2.50, 3.75, and 5.0 gm/litre, the peat suspensions 0.025, 0.05, 0.075, and 0.10 gm/litre. Both ion-species in the solution were present at a concentration of 7.6×10^{-5} M. The results are shown in Tables 17 and 18. The equilibrium concentration of each of the two metal ion-species remaining in solution is compared to the equilibrium concentration of the same single ion-species (7.6×10^{-5} M) when exposed to the same amount of sorbent. These results are shown graphically in Figures 15 and 16.

The results clearly show which ions are preferentially sorbed, and, as is to be expected, the order of preferential sorption of the ions was the same as that found in the study of the sorption of single ions by kaolinite and peat. Thus, the ions of copper, lead, uranium, and iron were the most strongly sorbed, while the alkali and alkali earth ions appear to be the least sorbed. However, the equilibrium concentration of the ion-species sorbed by kaolinite is clearly influenced by the presence of another ion-species, and with peat the interference seems to be still greater, as seen by the wider spread of the curves reproduced in Figure 16, compared with those of Figure 15 (with the possible exception of uranyl ion). This could indicate that possibly a different sorption mechanism exists for peat from that described for clay-minerals - maybe a reversible type of chemisorption.

The fact that the uranyl ion seems to be more tenaciously held by peat than the other metal ions may be significant; it will be discussed in a later section in the light of field-work evidence.

SORPTION INVOLVING FOUR ION-SPECIES AT EQUAL CONCENTRATION

It has been shown in previous sections that many sorbents, closely allied to those occurring in nature, are able to sorb metal ions from solution. It has also been established that certain ion-species are preferentially sorbed; this was most evident in the experiments involving the simultaneous sorption of two ion-species. In consequence, it became of interest to investigate even more complex ion-mixtures. The multitude of possibilities and analytical difficulties did not permit the study of all the possible combinations; hence, only one ion-mixture, together with seven different types of sorbents, was used throughout.

Original ion-species present 7.6×10^{-5}M	Added ion-species 7.6×10^{5}M	Kaolinite (gm/litre)			
		1.25	2.50	3.75	5.00
		Equilibrium concentration of original ion species M x 10^5			
UO_2^{++}	None	5.7	4.5	3.3	2.4
	Fe^{+++}	6.4	5.7	5.0	4.6
	Pb^{++}	6.2	5.2	4.6	4.2
	Co^{++}	6.2	5.0	4.3	4.0
	Mg^{++}	6.2	4.9	4.1	3.6
	Cd^{++}	6.2	4.9	4.1	3.4
	Tl^{+}) Na^{+})	5.7	4.5	3.3	2.4
Cu^{++}	None	5.1	3.3	2.8	2.4
	Fe^{+++}	6.9	5.8	4.9	4.6
	Pb^{++}	6.0	5.1	4.2	3.7
	Mg^{++}	5.6	4.1	3.5	3.2
	Tl^{+}) Na^{+})	5.1	3.6	3.0	2.7
Zn^{++}	None	5.5	4.0	3.1	2.4
	Fe^{+++}	7.0	6.2	5.3	5.1
	Cu^{++}	6.3	5.5	5.0	4.7
	Pb^{++}	6.4	5.6	4.9	4.8
	Cd^{++}	5.9	4.9	4.5	4.3
	Tl^{+}) Na^{+})	5.6	4.0	3.1	2.5
Pb^{++}	None	4.6	2.0	1.3	1.1
	UO_2^{++}	4.9	3.7	2.8	2.2
	Cu^{++}	4.9	3.3	2.4	1.8
	Fe^{+++}	5.2	4.1	3.3	2.9
	Co^{++}	4.9	3.3	2.3	1.7
	Ni^{++}) Cd^{++}) Ba^{++}) Mg^{++})	5.0	3.1	2.2	1.7
	Tl^{+}) Na^{+})	4.6	2.0	1.3	1.1
Cd^{++}	None	5.7	4.2	3.3	2.7
	UO_2^{++}	6.5	5.9	5.0	4.5
	Pb^{++}	6.4	5.9	5.0	4.5
	Co^{++}	6.1	5.1	4.6	4.4
	Zn^{++}	6.5	5.6	4.6	4.0
	Mg^{++}	6.1	5.0	4.2	3.6
	Tl^{+}	5.7	4.5	3.6	3.1
	Na^{+}	5.7	4.2	3.4	2.7
Co^{++}	None	5.3	3.6	3.1	2.7
	Pb^{++}	6.4	5.5	4.4	3.7
	Mg^{++}	6.4	5.3	4.4	3.6
	Ni^{++}	5.9	4.6	3.7	3.4
	Cd^{++}	5.5	4.5	3.7	3.3
	Tl^{+}) Na^{+})	5.3	3.7	3.2	2.8

Table 17. Equilibrium concentrations of metal ions after sorption by kaolinite, in the presence of a competing ion-species at the same concentration.

Original ion-species present 7.6×10^{-5} M	Added ion-species 7.6×10^{-5} M	Peat (gm/litre)			
		0.025	0.050	0.075	0.10
		Equilibrium concentration of original ion species $M \times 10^5$			
Zn^{++}	None	6.0	4.6	3.9	3.5
	Cu^{++}	7.2	6.8	6.4	6.0
	Pb^{++}) Fe^{++})	7.2	6.8	6.5	6.3
	Cd^{++}) Co^{++})	6.6	5.9	5.3	5.0
	Ba^{++}) Mg^{++}) Na^{+})	6.0	4.6	4.0	3.5
Co^{++}	None	5.9	4.7	4.1	3.7
	Cu^{++}) Pb^{++})	7.0	6.8	6.6	6.5
	Cd^{++}	6.7	6.0	5.6	5.4
	Zn^{++}) Ba^{++})	6.7	6.0	5.3	4.9
	Mg^{++}	6.4	5.5	4.7	4.2
	Na^{+}) Tl^{+})	5.9	4.7	4.1	3.7
UO_2^{++}	None	5.5	3.7	2.6	2.2
	Pb^{++}) Fe^{+++})	5.9	4.9	4.4	3.3
	Zn^{++}) Cu^{++}) Co^{++}) Cd^{++}) Ba^{++}) Mg^{++}) Tl^{+}) Na^{+})	5.5	3.9	2.8	2.4
Pb^{++}	None	4.6	2.4	1.6	1.2
	UO_2^{++}	6.2	5.0	4.3	3.6
	Fe^{+++}	6.2	5.2	4.4	3.6
	Cu^{++}	5.5	4.0	3.3	2.7
	Ba^{++}) Mg^{++}) Zn^{++}) Co^{++}) Cd^{++})	4.6	2.4	1.7	1.3
Cu^{++}	None	5.2	3.1	2.4	1.9
	UO_2^{++}	6.8	6.0	5.4	4.5
	Fe^{++}	6.8	6.2	5.4	4.6
	Pb^{++}	6.2	5.2	4.6	4.0
	Zn^{++}) Cd^{++}) Co^{++}) Ba^{++}) Mg^{++})	5.0	3.6	3.0	2.1
	Na^{+}) Tl^{+})	6.1	4.8	3.9	3.5
Cd^{++}	None	6.1	4.8	4.0	3.5
	UO_2^{++}	7.1	6.9	6.8	6.5
	Pb^{++}	7.1	6.8	6.5	6.3
	Cu^{++}	7.1	6.6	5.9	5.6
	Fe^{+++}	7.1	6.6	6.1	5.6
	Zn^{++}	6.4	5.3	4.6	4.2
	Co^{++}	6.2	4.8	4.6	4.3
	Na^{++}) Mg^{++})	6.1	4.8	3.9	3.5

Table 18. Equilibrium concentration of metal ions after sorption by peat in the presence of a competing ion-species at the same concentration.

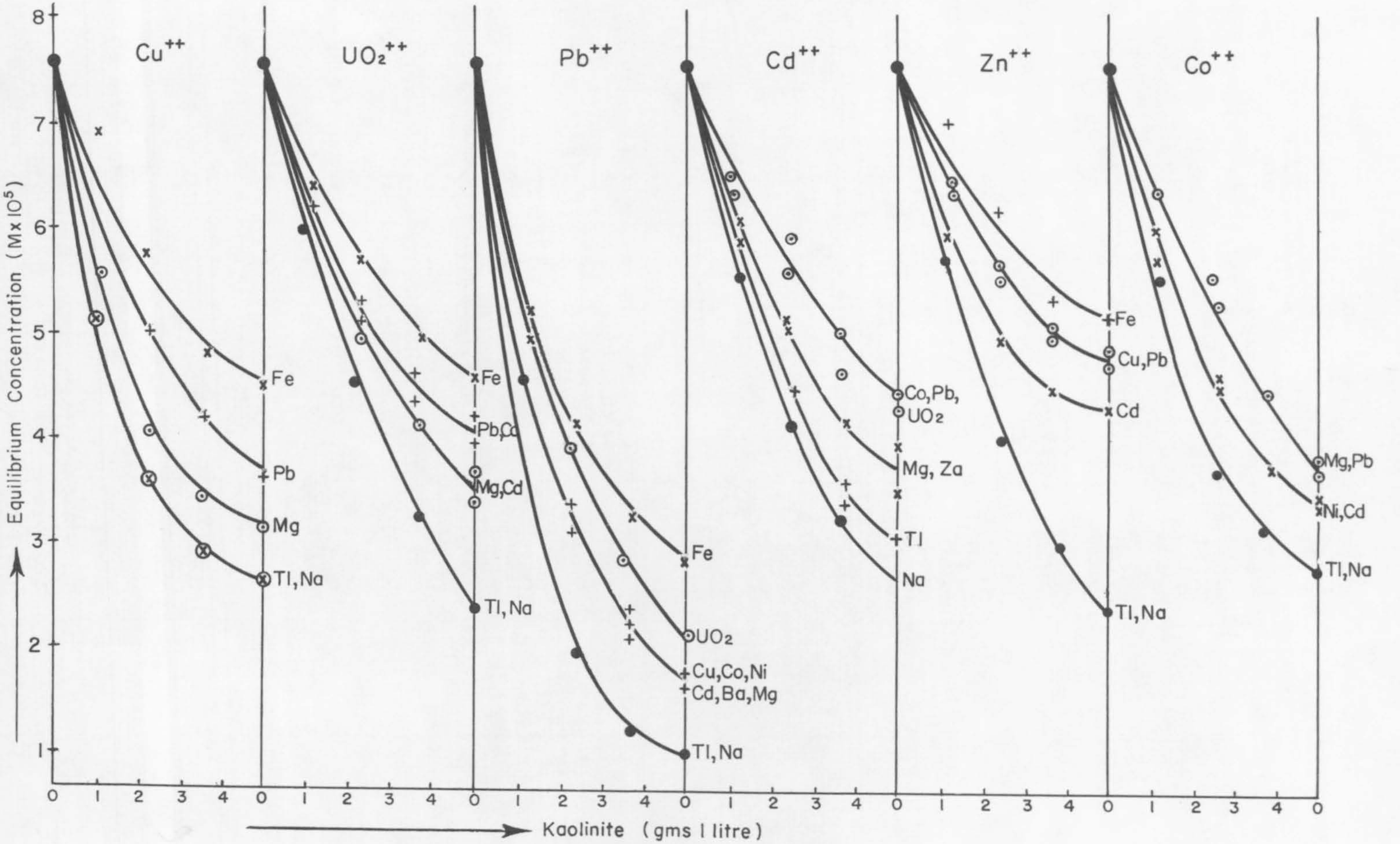

Fig. 15. Effect of a competing ion species on sorption of heavy metal ions onto kaolinite.

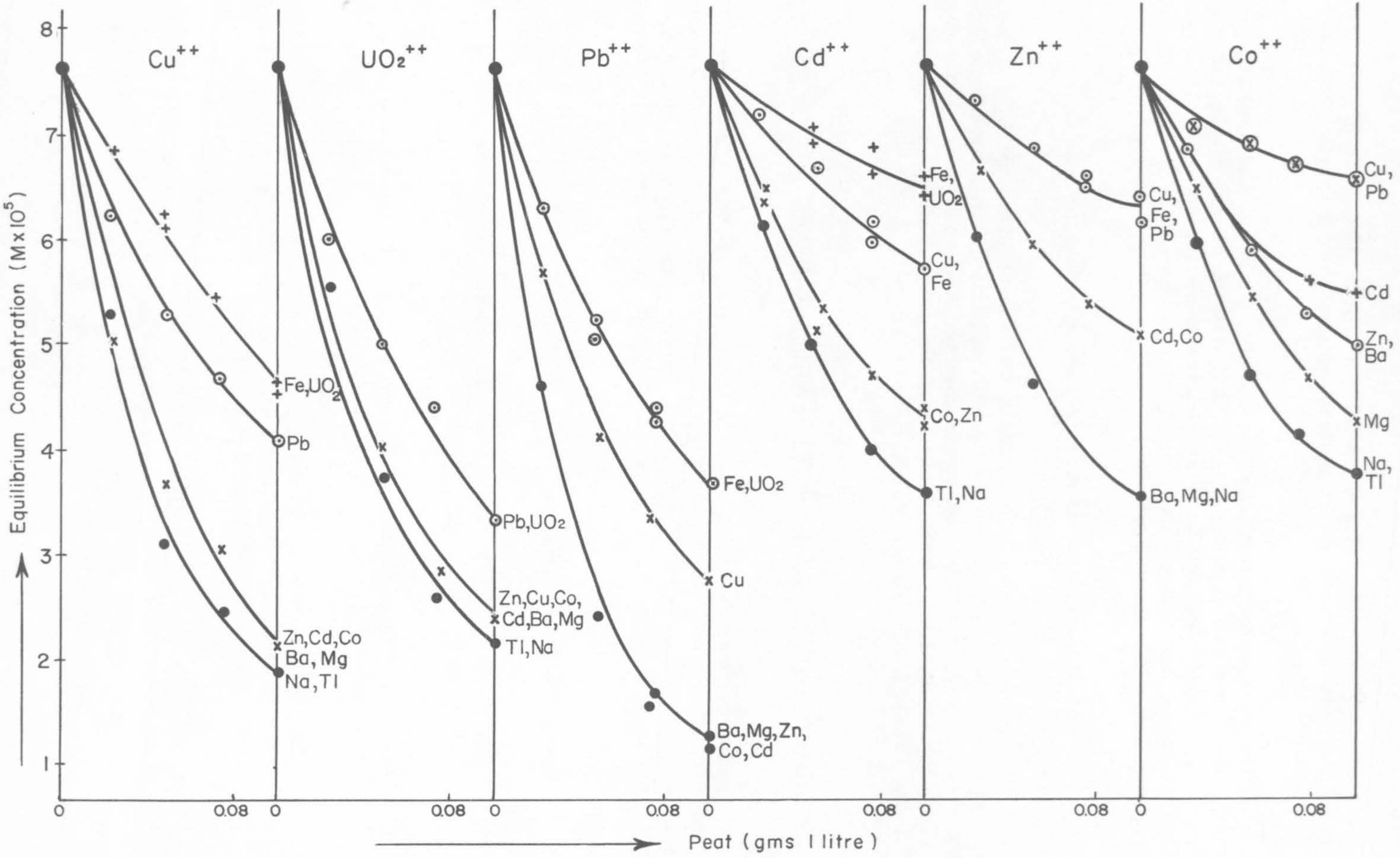

Fig. 16. Effect of competing ion-species on sorption of heavy metal ions onto peat.

The solution used contained 7.6×10^{-5} M copper, lead, cadmium, and zinc as nitrates. These metal ions were chosen because the metals are frequently associated in base-metal sulphide deposits.

The sorbents were peat, kaolinite, dolomite, ferric hydroxide, estuarine silt, vermiculite, and a hydrated manganese oxide. The experiments were carried out both in the presence and in the absence of a large excess of sodium or magnesium ion. The experimental procedure was the same as that described on page ; polarography proved particularly suited to the analysis of the ion-mixture used.

The experimental conditions and results are to be found in Table 19.

The results in Table 19 show quite distinctly that lead is generally sorbed to a greater extent than copper, which in turn is sorbed to a substantially larger extent than either cadmium or zinc. The hydrated manganese oxide appears to exhibit the same type of sorption effect as does ferric hydroxide, i.e. increased sorption in the presence of sodium or magnesium salts; it appears to be a better sorbent than ferric hydroxide.

SORPTION INVOLVING FOUR ION-SPECIES AT UNEQUAL CONCENTRATIONS

The experiments were carried out as described above. The sorbents were kaolinite, peat, dolomite, silt, and ferric hydroxide. The total ionic strength of the solutions used was identical in all cases, but the individual concentrations of the ions in the mixture, that is copper, lead, cadmium, and zinc, varied widely; the results are given in Tables 20 to 29.

Conclusions to be drawn are:

1. Lead is preferentially sorbed over other metals, particularly when dolomite is the sorbent.

2. When the ratio of sorbent to sorbable ion is low, the preferential sorption of lead is greatest.

3. Using kaolinite, peat, or silt as sorbent, copper seems to be almost as strongly sorbed as lead, but using dolomite or ferric hydroxide, the sorption of copper appears to be much less strong than that of lead.

4. Neither cadmium nor zinc is appreciably sorbed by dolomite, and no sorption at all could be detected using ferric hydroxide as sorbent.

Sorbent	Quantity of Sorbent (gm/litre)	Distilled water or added electrolyte (10^{-1}M)	Moles of metal ions sorbed per 100 gm of sorbent x 10^4			
			Cu	Pb	Cd	Zn
Kaolinite	2.5	Distilled water	3.1	14.0	7.2	10.8
" "	5.0	" "	3.1	9.7	4.5	4.6
" "	7.5	" "	4.7	6.3	4.5	4.6
" "	5	Sodium nitrate	1.5	2.9	n.d.	n.d.
" "	5	Magnesium "	1.5	2.4	n.d.	n.d.
Peat	0.05	Distilled water	152.0	580.0	91.0	40.0
"	0.10	" "	250.0	510.0	67.8	37.0
"	0.15	" "	303.0	300.0	56.2	35.4
"	0.1	Sodium nitrate	273.0	387.0	64.2	35.4
"	0.1	Magnesium "	197.0	220.0	50.0	33.8
Mixture (Peat (Kaolinite	0.05) 2.5)	Distilled water	10.9	15.9	8.9	9.2
Mixture (Peat (Kaolinite	0.10) 5.0)	" "	7.8	11.1	4.5	7.7
Mixture (Peat (Kaolinite	0.15) 7.5)	" "	7.8	8.7	4.5	3.1
Silt	3	" "	18.8	21.7	3.6	7.7
"	3	Magnesium nitrate	14.1	13.5	n.d.	n.d.
"	7	Distilled water	7.8	9.2	5.4	6.2
"	7	Magnesium nitrate	7.8	8.7	0.9	3.1
"	10	Distilled water	4.7	6.8	5.4	6.2
"	10	Magnesium nitrate	4.7	6.3	3.6	3.1
Ferric hydroxide	0.7	Distilled water	18.8	64.2	n.d.	n.d.
" "	0.7	Sodium nitrate	92.0	100.8	n.d.	n.d.
" "	0.7	Magnesium nitrate	100.0	104.0	n.d.	13.8
Hydrated)	0.1	Distilled water	167.0	280.0	n.d.	67.7
Manganese)	0.1	Sodium nitrate	199.0	348.0	n.d.	61.6
Oxide)	0.1	Magnesium nitrate	228.0	318.0	n.d.	n.d.
Vermiculite	0.25	Distilled water	212.0	147.0	11.6	n.d.
"	0.50	" "	200.0	154.0	40.2	41.5
"	1.00	" "	100.0	87.5	26.8	50.8
"	0.50	Magnesium nitrate	122.0	80.4	n.d.	n.d.
"	0.50	Sodium nitrate	136.0	80.4	n.d.	n.d.
Dolomite	0.2	Distilled water	18.8	272.0	n.d.	n.d.
"	0.4	" "	31.2	164.0	n.d.	n.d.

Table 19. Quantities of four metal ion-species sorbed on different sorbents from 7.6 x 10^{-5}M solutions.

Quantity of kaolinite (gm/litre)	Original Solution Cu^{++}	Equil. Conc'n Cu^{++}	Original Solution Pb^{++}	Equil. Conc'n Pb^{++}	Original Solution Cd^{++}	Equil. Conc'n Cd^{++}	Original Solution Zn^{++}	Equil. Conc'n Zn^{++}
12.5	100	61	200	90	300	240	500	350
12.5	500	345	300	132	200	164	100	75
12.5	300	168	100	24	500	400	200	160
12.5	200	132	500	255	100	100	300	246
25.0	100	50	200	60	300	201	500	255
25.0	500	285	300	160	200	132	100	55
25.0	300	123	100	10	500	310	200	124
25.0	200	94	500	145	100	83	300	183
37.5	100	33	200	28	300	159	500	200
37.5	500	215	300	33	200	102	100	47
37.5	300	84	100	5	500	240	200	102
37.5	200	72	500	40	100	73	300	144
50.0	100	23	200	14	300	126	500	180
50.0	500	155	300	6	200	94	100	40
50.0	300	63	100	2	500	215	200	94
50.0	200	50	500	40	100	65	300	123

Table 20. Sorption on to kaolinite when using mixtures containing copper, lead, cadmium, and zinc ions (all concentrations uM).

Quantity of Peat (gm/litre)	Original Solution Cu^{++}	Equil. Conc'n Cu^{++}	Original Solution Pb^{++}	Equil. Conc'n Pb^{++}	Original Solution Cd^{++}	Equil. Conc'n Cd^{++}	Original Solution Zn^{++}	Equil. Conc'n Zn^{++}
0.2	100	52	200	82	300	300	500	475
0.2	500	425	300	156	200	200	100	95
0.2	300	174	100	19	500	500	200	196
0.2	200	136	500	335	100	100	300	300
0.4	100	21	200	36	300	285	500	400
0.4	500	320	300	99	200	200	100	92
0.4	300	84	100	11	500	470	200	192
0.4	200	106	500	220	100	95	300	300
0.6	100	6	200	14	300	207	500	395
0.6	500	220	300	54	200	194	100	90
0.6	300	48	100	8	500	405	200	182
0.6	200	46	500	100	100	89	300	288
0.8	100	0	200	10	300	162	500	365
0.8	500	165	300	30	200	178	100	84
0.8	300	30	100	7	500	330	200	160
0.8	200	32	500	50	100	82	300	282

Table 21. Sorption on to peat when using mixtures containing copper, lead, cadmium, and zinc ions (all concentrations uM).

Quantity of dolomite (gm/litre)	Original Solution Cu^{++}	Equil. Conc'n Cu^{++}	Original Solution Pb^{++}	Equil. Conc'n Pb^{++}	Original Solution Cd^{++}	Equil. Conc'n Cd^{++}	Original Solution Zn^{++}	Equil. Conc'n Zn^{++}
0.5	100	89	200	16	300	300	500	500
0.5	500	500	300	63	200	200	100	96
0.5	300	198	100	25	500	500	200	200
0.5	200	200	500	100	100	100	300	300
1.0	100	85	200	16	300	300	500	500
1.0	500	500	300	33	200	200	100	87
1.0	300	198	100	23	500	500	200	200
1.0	200	200	500	30	100	100	300	300
1.5	100	87	200	16	300	300	500	500
1.5	500	500	300	n.d.	200	200	100	93
1.5	300	192	100	15	500	500	200	200
1.5	200	200	500	n.d.	100	100	300	300
2.0	100	69	200	16	300	300	500	500
2.0	500	475	300	n.d.	200	200	100	90
2.0	300	198	100	4	500	500	200	200
2.0	200	178	500	n.d.	100	90	300	300

Table 22. Sorption on to dolomite when using mixtures containing copper, lead, cadmium, and zinc ions (all concentrations uM).

Quantity of silt (gm/litre)	Original Solution Cu^{++}	Equil. conc'n Cu^{++}	Original Solution Pb^{++}	Equil. Conc'n Pb^{++}	Original Solution Cd^{++}	Equil. Conc'n Cd^{++}	Original Solution Zn^{++}	Equil. Conc'n Zn^{++}
0.5	100	n.d.	200	16	300	285	500	430
0.5	500	245	300	78	200	200	100	82
0.5	300	54	100	7	500	500	200	158
0.5	200	64	500	155	100	100	300	285
1.0	100	n.d.	200	n.d.	300	222	500	290
1.0	500	95	300	30	200	200	100	70
1.0	300	n.d.	100	n.d.	500	435	200	112
1.0	200	18	500	n.d.	100	86	300	255
1.5	100	n.d.	200	n.d.	300	183	500	220
1.5	500	n.d.	300	n.d.	200	184	100	50
1.5	300	n.d.	100	n.d.	500	360	200	96
1.5	200	n.d.	500	n.d.	100	73	300	189
2.0	100	n.d.	200	n.d.	300	144	500	155
2.0	500	n.d.	300	n.d.	200	125	100	30
2.0	300	n.d.	100	n.d.	500	295	200	54
2.0	200	n.d.	500	n.d.	100	46	300	75

Table 23. Sorption on to silt when using mixtures containing copper, lead, cadmium, and zinc ions (all concentrations in uM).

Quantity of ferric hydroxide (gm/litre)	Original Solution Cu^{++}	Equil. Conc'n Cu^{++}	Original Solution Pb^{++}	Equil. Conc'n Pb^{++}	Original Solution Cd^{++}	Equil. Conc'n Cd^{++}	Original Solution Zn^{++}	Equil. Conc'n Zn^{++}
0.5	100	93	200	150	300	300	500	500
0.5	500	465	300	234	200	200	100	100
0.5	300	270	100	55	500	500	200	200
0.5	200	200	500	470	100	100	300	300
1.0	100	80	200	120	300	300	500	500
1.0	500	465	300	219	200	200	100	100
1.0	300	252	100	53	500	500	200	200
1.0	200	168	500	365	100	100	300	300
1.5	100	66	200	76	300	300	500	500
1.5	500	450	300	177	200	200	100	100
1.5	300	198	100	17	500	500	200	200
1.5	200	162	500	335	100	100	300	300
2.0	100	45	200	50	300	300	500	500
2.0	500	400	300	135	200	200	100	100
2.0	300	185	100	9	500	500	200	200
2.0	200	152	500	295	100	100	300	300

Table 24. Sorption on to ferric hydroxide when using mixtures containing copper, lead, cadium, and zinc ions; (all concentrations in uM).

Kaolinite (gm/litre)	Weight of ions (gm) sorbed per 100 gm kaolinite				Solution* number
	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	
12.5	0.019	0.180	0.054	0.075	1
12.5	0.077	0.280	0.032	0.013	2
12.5	0.066	0.126	0.090	0.020	3
12.5	0.034	0.407	n.d.	0.027	4
25	0.013	0.116	0.041	0.061	1
25	0.058	0.200	0.031	0.011	2
25	0.044	0.075	0.086	0.019	3
25	0.027	0.295	0.008	0.029	4
37.5	0.011	0.095	0.042	0.050	1
37.5	0.047	0.148	0.030	0.009	2
37.5	0.036	0.053	0.078	0.016	3
37.5	0.021	0.254	0.008	0.026	4
50	0.009	0.077	0.039	0.040	1
50	0.043	0.123	0.024	0.008	2
50	0.029	0.042	0.064	0.013	3
50	0.019	0.191	0.008	0.022	4
Range	0.009 - 0.077	0.042 - 0.407	n.d. - 0.090	0.008 - 0.075	

Table 25. Weight of various metal ions sorbed per 100 gm kaolinite, computed from data given in Table 20.

* Solution 1 is 100 uM with respect to Cu^{++}, 200 uM with respect to Pb^{++}, 300 uM with respect to Cd^{++}, 500 uM with respect to Zn^{++}.

* Solution 2 is 500 uM with respect to Cu^{++}, 300 uM with respect to Pb^{++}, 200 uM with respect to Cd^{++}, 100 uM with respect to Zn^{++}.

Solution 3 is 300 uM with respect to Cu^{++}, 100 uM with respect to Pb^{++}, 500 uM with respect to Cd^{++}, 200 uM with respect to Zn^{++}.

Solution 4 is 200 uM with respect to Cu^{++}, 500 uM with respect to Pb^{++}, 100 uM with respect to Cd^{++}, 300 uM with respect to Zn^{++}.

Peat (gm/litre)	Weight of ions (gm) sorbed per 100 gm peat				Solution number (See table 25)
	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	
0.2	1.50	12.30	n.d.	0.78	1
0.2	2.34	15.00	n.d.	0.16	2
0.2	3.93	8.42	n.d.	0.13	3
0.2	2.00	17.16	n.d.	n.d.	4
0.4	1.24	8.54	0.42	0.63	1
0.4	2.81	10.40	n.d.	0.13	2
0.4	3.37	4.68	0.85	0.12	3
0.4	1.47	14.60	0.14	n.d.	4
0.6	0.97	6.44	1.75	1.09	1
0.6	2.91	8.53	0.06	0.09	2
0.6	2.62	3.22	1.81	0.29	3
0.6	1.59	13.84	0.21	0.13	4
0.8	0.78	4.94	1.94	1.06	1
0.8	2.63	7.02	0.31	0.13	2
0.8	2.12	2.31	2.40	0.31	3
0.8	1.31	11.73	0.25	0.14	4
Range	0.78 - 3.93	2.31 - 17.16	n.d. - 2.40	n.d. - 1.09	

Table 26. Weight of various metal ions sorbed per 100 gm peat, computed from the data given in Table 21.

Dolomite (gm/litre)	Weight of ions (gm) sorbed per 100 gm dolomite				Solution number (See table 25)
	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	
0.5	0.14	7.65	n.d.	n.d.	1
0.5	n.d.	9.85	n.d.	0.05	2
0.5	1.26	3.12	n.d.	n.d.	3
0.5	n.d.	16.60	n.d.	n.d.	4
1.0	0.09	3.83	n.d.	n.d.	1
1.0	n.d.	5.57	n.d.	0.08	2
1.0	0.65	1.58	n.d.	n.d.	3
1.0	n.d.	9.77	n.d.	n.d.	4
1.5	0.05	2.53	n.d.	n.d.	1
1.5	n.d.	4.15	n.d.	0.03	2
1.5	0.45	1.16	n.d.	n.d.	3
1.5	n.d.	6.93	n.d.	n.d.	4
2.0	0.10	1.91	n.d.	n.d.	1
2.0	0.08	3.12	n.d.	0.03	2
2.0	0.32	1.00	n.d.	n.d.	3
2.0	0.07	5.40	n.d.	n.d.	4
Range	n.d. - 1.26	1.00 - 16.60	n.d.	n.d. - 0.08	

Table 27. Weight of various metal ions sorbed per 100 gm dolomite, computed from data given in Table 22.

Silt (gm/litre)	Weight of ions (gm) sorbed per 100 gm silt				Solution number (See table 25)
	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	
5	0.12	0.77	0.034	0.09	1
5	0.32	0.92	n.d.	0.02	2
5	0.31	0.39	n.d.	0.05	3
5	0.17	1.44	n.d.	0.02	4
10	0.06	0.42	0.088	0.13	1
10	0.25	0.56	n.d.	0.02	2
10	0.19	0.21	0.073	0.05	3
10	0.11	1.04	0.016	0.03	4
15	0.04	0.28	0.088	0.12	1
15	0.21	0.42	0.010	0.02	2
15	0.12	0.14	0.103	0.04	3
15	0.08	0.70	0.020	0.05	4
20	0.03	0.21	0.088	0.11	1
20	0.15	0.31	0.042	0.2	2
20	0.09	0.10	0.114	0.05	3
20	0.06	0.52	0.031	0.06	4
Range	0.03 - 0.32	0.10 - 1.44	n.d. - 0.114	0.02 - 0.13	

Table 28. Weight of various metal ions sorbed per 100 gm silt, computed from data given in Table 23.

Ferric hydroxide (gm/litre)	Weight of ions (gm) sorbed per 100 gm ferric hydroxide				Solution number (See table 25)
	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	
0.5	0.087	2.08	n.d.	n.d.	1
0.5	0.430	2.75	n.d.	n.d.	2
0.5	0.370	1.87	n.d.	n.d.	3
0.5	n.d.	1.25	n.d.	n.d.	4
1.0	0.124	1.66	n.d.	n.d.	1
1.0	0.217	1.67	n.d.	n.d.	2
1.0	0.298	0.98	n.d.	n.d.	3
1.0	0.198	2.80	n.d.	n.d.	4
1.5	0.140	1.71	n.d.	n.d.	1
1.5	0.207	1.71	n.d.	n.d.	2
1.5	0.421	1.00	n.d.	n.d.	3
1.5	0.157	2.28	n.d.	n.d.	4
2.0	0.170	1.56	n.d.	n.d.	1
2.0	0.310	1.71	n.d.	n.d.	2
2.0	0.360	0.94	n.d.	n.d.	3
2.0	0.149	2.12	n.d.	n.d.	4
Range	n.d. - 0.430	0.94 - 2.80	n.d.	n.d.	

Table 29. Weight of various metal ions sorbed per 100 gm ferric hydroxide, computed from data given in Table 24.

SORPTIVE PROPERTIES OF A FERRIC HYDROXIDE/KAOLINITE MIXTURE

In view of the unexpected sorptive properties of ferric hydroxide in the presence of large concentrations of mangesium or sodium salts (see Table 16) it was felt that it might be interesting to study the sorptive properties of various mixtures of ferric hydroxide and kaolinite in the presence of varying concentrations of Mg^{++} or Na^{+} or both; once again Pb^{++} served as the sorbable ion-species. The quantities of ferric hydroxide and kaolinite used are shown in Table 30. The initial concentration of lead ion in all cases was 10^{-4} M i.e. 100 umole per litre. The sorptive properties of the ferric hydroxide/kaolinite mixtures were tested in the presence of four different concentrations of magnesium ion, as well as in the absence of magnesium ion.

The equilibrium concentration of lead ion is given in Table 30 and the weight of lead ion sorbed per 100 gm of the mixed sorbent in Table 31. These results show what might be expected to occur under similar conditions in nature. For example, looking only at general tendencies, the following is true:

1. For a given kaolinite concentration, the smaller the concentration of magnesium ion, the less the effect of the ferric hydroxide on the sorption.
2. For a given ferric hydroxide concentration, the smaller the concentration of magnesium ion, the greater the effect of the kaolinite on the sorption.
3. The sorptive properties of a given mixture of kaolinite and ferric hydroxide vary greatly with the magnesium nitrate concentration, but not regularly. For example, the sorption is favoured by very high or very low salt concentrations. Much less sorption occurs in the intermediate salt ranges.
4. The less the ratio of total sorbent to sorbable ion the more concentrated is the sorbed ion in the sediments.

Magnesium nitrate concentration	Kaolinite (gm/litre)	Ferric hydroxide (gm/litre)			
		0.36	0.18	0.09	0.045
M	10	46	49	61	68
M	5	39	56	64	72
M	2.5	37	55	69	75
M	1.25	41	59	69	79
10^{-1} M	10	37	47	63	73
10^{-1} M	5	42	55	71	78
10^{-1} M	2.5	46	62	80	85
10^{-1} M	1.25	47	65	79	89
10^{-2} M	10	42	44	52	57
10^{-2} M	5	48	59	63	73
10^{-2} M	2.5	54	68	76	78
10^{-2} M	1.25	56	73	81	87
10^{-3} M	10	36	39	45	45
10^{-3} M	5	48	54	55	58
10^{-3} M	2.5	61	63	69	78
10^{-3} M	1.25	65	71	72	82
None present	10	26	29	28	24
None present	5	35	36	38	40
None present	2.5	51	39	48	46
None present	1.25	56	56	65	66

Table 30. Lead ion equilibrium concentration (uM) after sorption by various sorbent mixtures, from a solution containing lead, concentration 100 (uM) and magnesium nitrate at the indicated concentrations.

Magnesium nitrate concentration	Kaolinite (gm/litre)		Ferric hydroxide (gm/litre)			
		0.36	0.18	0.09	0.045	
M	10	0.104	0.100	0.077	0.064)	
M	5	0.227	0.170	0.141	0.111)	Range
M	2.5	0.440	0.336	0.277	0.196)	0.064 -
M	1.25	0.732	0.573	0.463	0.324)	0.732
10^{-1}M	10	0.122	0.104	0.073	0.054)	
10^{-1}M	5	0.216	0.174	0.114	0.087)	Range
10^{-1}M	2.5	0.378	0.284	0.154	0.118)	0.054 -
10^{-1}M	1.25	0.658	0.490	0.313	0.170)	0.658
10^{-2}M	10	0.112	0.110	0.095	0.087)	Range
10^{-2}M	5	0.194	0.158	0.145	0.107)	0.087 -
10^{-2}M	2.5	0.322	0.239	0.185	0.173)	0.547
10^{-2}M	1.25	0.547	0.378	0.284	0.201)	
10^{-3}M	10	0.124	0.120	0.109	0.110)	Range
10^{-3}M	5	0.194	0.178	0.176	0.167)	0.110 -
10^{-3}M	2.5	0.273	0.276	0.239	0.173)	0.435
10^{-3}M	1.25	0.435	0.406	0.418	0.278)	
None present	10	0.143	0.139	0.143	0.151)	
None present	5	0.243	0.247	0.244	0.238)	Range
None present	2.5	0.343	0.455	0.402	0.424)	0.139 -
None present	1.25	0.547	0.615	0.522	0.525)	0.615

Table 31. Mass of sorbed lead ion (gm) per 100 gm of a ferric hydroxide/kaolinite mixture after sorption of the lead from a 100 uM solution, and magnesium ion at the indicated concentration.

SORPTION STUDIES WITH FLOWING SOLUTIONS

In nature, one might expect that a sorbent material, when compacted in a sediment, will sorb ions from a percolating solution flowing through it. The experiments described in this section were conducted with a view to studying the sorption effects which might be the result of such conditions.

The experiments consisted in passing solutions containing a mixture of ions through columns of sorbents contained in specially prepared tubes. The sorbents used were dolomite, fine estuarine silt, and vermiculite (all in 1-gm quantities); and mixtures of each of them with peat (0.02 gm) were used in other tubes. Thus, six different sorbents (or sorbent mixtures) were used. The experiments were carried out under both upward and downward flow using the two types of tubes shown in Figure 2, making twelve columns in all.

Because of the very small particle size, and the frequently encountered imbibition swelling, most of the sorbents used packed down very tightly in the columns and were very slowly permeable to aqueous solutions. By mixing the sorbents with 5 gm of acid-washed sand of negligible cation-exchange capacity, the filtration speed was very much increased. Each column was packed by preparing a slurry of the particular sorbent with sand; the mixture was allowed to settle on the sinter glass filter.

The twelve tubes were then conncected by means of polythene tubing to a reservoir containing the ion mixture. The tubes with side arms had the polythene tubing fitted to the narrow lower end, while the other tubes had the polythene tubing connected to the upper end. The solution contained a mixture of copper, lead, cadmium, and zinc ions all at a concentration 10^{-4} M.

The volume of liquid leaving each of the columns was noted and collected at suitable time intervals, and analysed for copper, lead, cadmium, and zinc. Although every precaution was taken, the columns were not identically packed, as witnessed by the wide variation in the rates of flow. Differences in the sorptive capacity of the columns were therefore expected, not only because of the different sorbents but also because of the differences in packing and exposure of the colloidal sorbents to the percolating solution. Results are given in Tables 32 to 37, which show the volume of liquid leaving the column, the average metal content of that volume, and the time over which that volume was collected. From these figures was calculated the total weight of each metal ion sorbed by the column when saturated or at the time of termination of the experiment. Some of the columns were either too impervious, or the exchange capacity too great, to achieve saturation. In these cases, the flow of liquid was stopped after a given period of time; however, in all cases at least one of the sorbent ions was present in the liquid leaving the column.

After the flow of liquid was stopped, the polythene tubes were removed, and the liquid allowed to drain to the top of the sorbents; 10^{-1} M magnesium nitrate solution was passed through the columns. The eluate was collected, the volume collected was noted, and it was analysed for Cu, Pb, Cd, and Zn. The total weight of metal desorbed was calculated, and this weight, compared to the weight originally sorbed, is shown in Table 38. In all cases, after collection of a few millilitres of eluate, the flow stopped, presumably because of a blockage in the column. The desorption figures therefore only represent the respective concentrations of eluted ions before this blockage occurred. Hence desorption was incomplete.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
1	28	n.d.	n.d.	30	31
2	22	36	trace	95	98
3½	26	90	29	94	92
4½	20	89	71	88	89
6	24	92	70	88	87
Average rate of flow = 20 ml/hour					
Desorption					
	10	n.d.	156	77	58
	14	n.d.	49	19	23

(b)

Time in hours	ml	Concentrations of ions (uM)			
		Cu	Pb	Cd	Zn
22	20	n.d.	n.d.	n.d.	n.d.
48	12	n.d.	n.d.	n.d.	n.d.
70	9	n.d.	n.d.	n.d.	n.d.
94	10	n.d.	n.d.	18	13
118	10	n.d.	n.d.	82	65
142	11	n.d.	n.d.	108	114
166	11	n.d.	n.d.	127	140
190	11	n.d.	n.d.	137	154
286	48	83	22	110	118
430	82	92	71	93	97
574	80	103	98	91	95
Average rate of flow = 0.704 ml/hour					
Desorption					
	5	89	650	123	117

Table 32. Concentration of Cu^{++}, Pb^{++}, Cd^{++} and Zn^{++} in eluates from columns containing silt only. The original solution was 100 uM with respect to each of the ions.
(a) Upward flow (b) Downward flow.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
5	20	n.d.	n.d.	n.d.	n.d.
22	20	n.d.	n.d.	14	23
48	19	n.d.	n.d.	38	56
70	13	n.d.	n.d.	54	68
94	13	n.d.	n.d.	80	78
118	12	12	n.d.	90	95
142	11	10	Trace	97	99
166	10	19	3	101	104
190	9	26	4	117	109
286	31	29	4	124	121
430	38	34	8	126	121
574	26	62	30	105	108
810	36	69	48	110	104
1108	35	82	69	96	95
1444	36	74	76	99	101
1832	31	73	70	99	100
2332	34	83	53	99	101
2832	25	87	60	98	99
3232	22	90	74	108	90
Average rate of flow = 0.136 ml/hour					
Desorption					
	2	75	510	85	45

(b)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
22	9	n.d.	n.d.	n.d.	n.d.
70	7	n.d.	n.d.	n.d.	n.d.
142	8	n.d.	n.d.	n.d.	n.d.
286	11	n.d.	n.d.	n.d.	n.d.
430	8	n.d.	n.d.	n.d.	n.d.
810	15	n.d.	n.d.	n.d.	n.d.
1108	9	n.d.	n.d.	n.d.	n.d.
1444	9	n.d.	n.d.	n.d.	n.d.
1832	9	n.d.	n.d.	n.d.	n.d.
2332	10	n.d.	n.d.	16	5
2832	9	n.d.	n.d.	56	55
3232	8	n.d.	n.d.	85	90
Average rate of flow = 0.035 ml/hour					
Desorption					
	2	60	410	150	160

Table 33. Concentration of Cu^{++}, Pb^{++}, Cd^{++}, and Zn^{++} in eluates from columns containing silt and peat mixture. The original solution was 100 uM with respect to each of the ions.

(a) Upward flow (b) Downward flow.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
9	20	n.d.	n.d.	n.d.	15
22	19	n.d.	n.d.	64	46
48	24	Trace	n.d.	105	110
70	19	Trace	Trace	100	109
94	18	15	Trace	102	111
118	16	16	6	100	106
142	16	27	12	102	106
166	14	26	13	104	100
190	13	25	12	104	102
286	44	31	9	109	109
430	55	23	8	114	110
574	45	49	8	125	115
810	61	54	8	120	112)*
1108	59	65	8	132	105)
1444	59	68	8	130	119)
1832	43	86	8	123	140)
Average rate of flow = 0.291 ml/hour					
Desorption					
	4	70	2070	1520	-

* Cu^{++} crystallizing out in the outlet tube.

(b)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
2	20	n.d.	n.d.	n.d.	n.d.
4	20	13	n.d.	69	46
5	27	47	6	124	111
6	29	101	22	102	109
7	22	121	57	100	87
8	28	113	73	100	89
9	30	75	84	90	91
Average flow rate = 19.56 ml/hour					
Desorption					
	20	n.d.	98	76	100
	16	n.d.	29	15	12
	21	n.d.	12	2	n.d.

Table 34. Concentration of Cu^{++}, Pb^{++}, Cd^{++}, and Zn^{++} in eluates from columns containing dolomite only. The original solution was 100 uM with respect to each of the ions.

(a) Upward flow

(b) Downward Flow.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
1	23	n.d.	n.d.	n.d.	Trace
3	23	n.d.	n.d.	23	29
4	28	25	n.d.	80	96
6	23	53	Trace	106	100
7	22	49	12	108	108
9	32	93	15	108	94
10	13	120	22	109	83
Average rate of flow = 16.4 ml/hour					
Desorption					
	10	8	182	180	124
	10	5	80	40	46
	10	n.d.	42	10	26

(b)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
7	20	n.d.	n.d.	n.d.	n.d.
22	46	n.d.	n.d.	n.d.	Trace
48	60	n.d.	n.d.	117	112
70	48	n.d.	n.d.	135	141
94	54	37	15	115	120
118	58	74	46	104	94
142	57	85	68	95	100
166	56	89	74	96	101
190	49	81	60	98	93
Average rate of flow = 2.04 ml/hour					
Desorption					
	10	33	235	100	104

Table 35. Concentration of Cu^{++}, Pb^{++}, Cd^{++}, and Zn^{++} in eluates from columns containing dolomite and peat mixture. The original solution was 100 uM with respect to each of the ions.

(a) Upward flow (b) Downward flow.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
1	20	n.d.	n.d.	n.d.	n.d.
2	22	n.d.	n.d.	n.d.	n.d.
4	23	n.d.	n.d.	n.d.	n.d.
6	22	n.d.	n.d.	n.d.	n.d.
9	28	n.d.	n.d.	n.d.	n.d.
22	60	n.d.	n.d.	n.d.	n.d.
48	48	n.d.	n.d.	n.d.	n.d.
70	30	n.d.	n.d.	n.d.	Trace
94	24	n.d.	n.d.	n.d.	Trace
118	22	n.d.	n.d.	n.d.	Trace
142	20	n.d.	n.d.	n.d.	Trace
166	18	n.d.	n.d.	n.d.	Trace
190	17	n.d.	n.d.	n.d.	Trace
286	57	n.d.	n.d.	n.d.	Trace
430	65	n.d.	n.d.	n.d.	Trace
574	51	n.d.	n.d.	35	12
810	68	n.d.	n.d.	59	17
1108	70	n.d.	n.d.	90	30
1444	67	n.d.	n.d.	105	41
1832	61	n.d.	n.d.	119	47
2332	59	n.d.	n.d.	129	44
2832	35	n.d.	n.d.	106	56
3232	30	n.d.	n.d.	114	50
Average rate of flow = 0.284 ml/hour					
Desorption					
		2540	7900	5380	4500

(b)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
3	22	n.d.	n.d.	n.d.	n.d.
5	23	n.d.	n.d.	n.d.	Trace
7	23	n.d.	n.d.	n.d.	5
9	35	n.d.	n.d.	n.d.	12
22	173	n.d.	n.d.	n.d.	6
48	232	n.d.	n.d.	42	11
70	185	n.d.	n.d.	106	56
94	218	23	21	114	97
118	233	43	53	99	100
142	248	54	77	95	96
166	253	58	88	92	90
190	237	61	93	91	91
Average rate of flow = 9.91 ml/hour					
Desorption					
	15	235	2830	1500	1200
	12	94	1220	850	975
	18	n.d.	176	30	25

Table 36. Concentration of Cu^{++}, Pb^{++}, Cd^{++}, and Zn^{++} in eluates from columns containing vermiculite only. The original solution was 100 uM with respect to each of the ions.

(a) Upward flow (b) Downward flow.

(a)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
3	28	n.d.	n.d.	n.d.	n.d.
7	24	n.d.	n.d.	n.d.	n.d.
10	17	n.d.	n.d.	n.d.	n.d.
22	48	n.d.	n.d.	n.d.	n.d.
48	57	n.d.	n.d.	n.d.	n.d.
70	39	n.d.	n.d.	n.d.	n.d.
94	35	n.d.	n.d.	n.d.	Trace
118	30	n.d.	n.d.	n.d.	Trace
142	28	n.d.	n.d.	n.d.	Trace
166	27	n.d.	n.d.	n.d.	Trace
190	23	n.d.	n.d.	n.d.	Trace
286	76	n.d.	n.d.	n.d.	Trace
430	80	n.d.	n.d.	n.d.	Trace
574	61	n.d.	n.d.	19	7
810	82	n.d.	n.d.	86	10
1108	81	n.d.	n.d.	134	36
1444	77	n.d.	n.d.	138	57
1832	50	n.d.	n.d.	141	76
2332	37	n.d.	n.d.	140	62
2832	27	n.d.	n.d.	112	66
3232	23	n.d.	n.d.	112	56
Average rate of flow = 0.294 ml/hour					
Desorption					
	1	1880	7070	4120	3750

(b)

Time in hours	ml	Concentration of ions (uM)			
		Cu	Pb	Cd	Zn
6	20	n.d.	n.d.	n.d.	n.d.
22	39	n.d.	n.d.	n.d.	n.d.
48	40	n.d.	n.d.	n.d.	n.d.
70	25	n.d.	n.d.	n.d.	n.d.
94	25	n.d.	n.d.	n.d.	n.d.
118	23	n.d.	n.d.	n.d.	n.d.
142	20	n.d.	n.d.	n.d.	n.d.
166	17	n.d.	n.d.	n.d.	n.d.
190	15	n.d.	n.d.	n.d.	n.d.
286	50	n.d.	n.d.	n.d.	n.d.
430	57	n.d.	n.d.	n.d.	n.d.
574	45	n.d.	n.d.	n.d.	n.d.
810	59	n.d.	n.d.	n.d.	n.d.
1108	61	n.d.	n.d.	n.d.	n.d.
1444	62	n.d.	n.d.	n.d.	n.d.
1832	64	n.d.	n.d.	n.d.	n.d.
2332	72	n.d.	n.d.	30	Trace
2832	57	n.d.	n.d.	116	Trace
3232	58	n.d.	n.d.	141	Trace
Average rate of flow = 0.25 ml/hour					
Desorption					
	4	2120	5880	5600	6000
	3	410	6150	5740	5000

Table 37. Concentration of Cu^{++}, Pb^{++}, Cd^{++}, and Zn^{++} in eluates from columns containing vermiculite and peat mixture. The original solution was 100 uM with respect to each of the ions.

(a) Upward flow (b) Downward flow.

Sorbent	Direction of flow	Weight of metals sorbed (umole/gm)				Weight of metals desorbed (umole/gm)			
		Cu	Pb	Cd	Zn	Cu	Pb	Cd	Zn
Silt	up	4.48	8.14	2.75	2.72	Nil	2.25	1.04	1.94
Silt	down	10.63	15.68	5.12	3.91	0.54	3.90	0.74	0.70
Silt +) Peat)	up	22.36	29.07	1.50	1.44	0.15	1.02	0.17	0.09
	down	11.30*	11.30*	9.96	10.03	0.12	0.82	0.30	0.32
Dolomite	up	30.77	49.61	7.80	-	0.28	8.28	6.04	-
"	down	5.06	10.98	2.21	3.39	-	2.68	1.80	2.19
Dolomite +) Peat)	up	8.87	15.37	3.94	4.28	0.13	3.04	2.30	1.96
	down	18.67	24.32	2.58	2.57	0.33	2.35	1.00	1.04
Vermiculite	up	91.79*	91.79*	56.33	76.25	5.08	15.80	10.76	9.00
	down	130.74	108.00	42.62	61.22	4.65	60.26	33.24	30.15
Vermiculite)	up	95.02*	95.02*	48.50	77.32	1.88	7.07	4.12	3.75
+ Peat)	down	80.80*	80.80*	63.85	80.80	9.71	41.97	39.62	39.00

* Not showing in liquid leaving column when sorption experiment was suspended; so these figures do not represent maximum sorptive capacity.

Table 38. Uptake of copper, lead, cadmium, and zinc ions by various columns, and quantities eluted by magnesium nitrate solution. The weight of sorbent in the columns was 1 gm with an additional 0.02 gm of peat in the cases shown.

Sorbent	Direction of flow	Sorption from flowing solutions				Sorption from stationary solutions			
		Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}	Cu^{++}	Pb^{++}	Cd^{++}	Zn^{++}
Silt	up	0.029	0.168	0.031	0.018	0.12	0.45	0.04	0.05
Silt	down	0.068	0.324	0.057	0.025				
Silt + Peat	up	0.143	0.600	0.017	0.009	0.165^{a}	0.662^{a}	0.055^{a}	0.055^{a}
"	down	0.072^{b}	0.233^{b}	0.112	0.065				
Dolomite	up	0.197	1.025	0.087	n.d.	0.12	5.60	n.d.	n.d.
"	down	0.032	0.277	0.024	0.022				
Dolomite +	up	0.057	0.317	0.044	0.028	0.165^{a}	58.12^{a}	0.015^{a}	0.005^{a}
Peat	down	0.113	0.502	0.029	0.017				
Vermiculite	up	0.588^{b}	1.890^{b}	0.630	0.497	1.28	3.20	0.45	0.27
	down	0.838	2.230	0.477	0.398				
Vermiculite	up	0.610^{b}	1.962^{b}	0.532	0.502	1.31^{a}	3.41^{a}	0.47^{a}	0.28^{a}
+ Peat	down	0.518^{b}	1.670^{b}	0.715	0.525				

a. Calculated from the sorptive capacities of the individual components of the sorbent mixture, using the results given in Tables 25 to 29.

b. Equilibrium not established with respect to these metal-ions, i.e. the columns were not saturated.

Table 39. Quantities of metal-ions on some sorbents as found in sorption from flowing and from an identical but stationary solution. The results are expressed as gm of metal ion sorbed per 100 gm of sorbent.

Discussion

The results do not indicate that one direction of flow is any more favourable to sorption than another. The extreme difficulty of packing two columns identically may, in part, account for the large but not consistent differences.

The sorption results recorded in Tables 32-37 clearly show that a desorption process is occurring concurrently with the sorption process, and a separation of the elements effected in consequence. The metal ions move slowly through the columns at different rates (Cd, Zn, Cu, Pb) giving rise to a separation of the elements in accordance with normal chromatography, and this process offers a means whereby elements in a mixture can be separated in nature into distinct bands. These bands of metal ions could then be subjected to other natural processes during consolidation and diagenesis, ultimately giving rise to banded sulphides such as we often find in the conformable base-metal sulphide deposits.

Comparing the sorptive capacities of the various sorbents in the experiments involving flowing and stationary solutions respectively (Table 39), it is seen that for any one sorbent the values obtained in most cases are rather inconsistent. They are close enough, however, to suggest that if the columns could have been so packed that the whole of the sorbent had been exposed to the flowing solution, the sorption figures would be no less than those obtained in stationary solutions. The sorption figures obtained with flowing solutions are in some cases even higher than the corresponding sorption figures for stationary solutions, which suggests that they might have been higher in every case if the sorbent could have been saturated by extending sufficiently (perhaps for years) the percolation time of the solutions. This may have important implications in nature, for it means that a given mass of sediment could sorb a relatively high amount of metal ion when exposed to a prolonged or recurrent supply of even a dilute pregnant liquor.

Most natural waters carry very small quantities of metal ion in solution, but waters carrying large concentrations of metal ions are quite rare. The latter are produced by denudation of rocks rich in the particular metal, or, as is well known, liberated as hydrothermal solution from magma; Stanton (1962) & Baas Becking have recently commented on the role of hydrothermal solutions in the deposition of base metals in some recent sediments.

The results of these experiments, therefore, suggest that the sorption process in nature is able to concentrate metals in sediments by sorption of metal ions from very dilute solutions filtering through the sediment. Hence, a recurrent supply of a very dilute solution could lead to the same enrichment of the sediment as would a more concentrated solution, providing that the total weight of metal ion brought into contact with the sediment is the same in each case. Rozhkova et al. (1958) reached a similar conclusion using the uranyl and vanadyl ions in solution and lignite and phosphorite as sorbents.

The desorption results seem interesting, because in no case was the sorbed metal ion desorbed quantitatively by the action of a strong solution of magnesium nitrate. Even allowing for the fact that in the given time the desorption process could not go to completion it is obvious that the copper was particularly tenaciously held in the columns. Where copper and lead were sorbed in approximately equal amounts, it was the lead which was desorbed in greater quantities by the elution process; zinc and cadmium seemed to be the most easily desorbed ions.

When comparing the results of the flowing and stationary sorption experiments, the great difference of the time factor must be borne in mind. The duration of some of the experiments with flowing solutions was several months, whereas the sorption experiments with stationary solutions came to equilibrium over a matter of a few hours.

It may be, indeed it is very likely, that changes in the ion species, or changes in the location of the sorbed minerals on the sorbents, take place on standing, the metal ions moving from exchange positions to non-exchange positions in the crystal lattice as already suggested by Elgabaly (1950) for montmorillonite clays. This movement of ions in the crystal possibly represents an early stage in the fixation and utilization of sorbed metal ions to form distinct minerals.

CONCLUSIONS

The results as a whole permit the assertion to be made that sorption processes probably play a part in the collection of metals in sediments. The fact that, even in the presence of large excesses of Mg^{++} or Na^{+} ions, the heavy metal ions are still sorbed (specific sorption), suggests that the sorption process could function both in seawater and in freshwater. This specific sorption of metal ions in the presence of a large excess of a competing ion species is in accordance with the results of Elgabaly (1950) and Hodgson (1960). It is very likely that the high specific sorption of metals by peat, as shown in Table 13, is due to the formation of metal chelate rings by means of coordinate links. The particularly high sorption capacity of mixtures of clay and ferric hydroxide for base metals, even in the presence of a large excess of a competing ion species is very interesting. It seems to the author that such mixtures in nature could, at least in part, be responsible for the fact that trace element concentrations are generally higher in marine than in freshwater argillaceous sediments (Nicholls, 1962).

Sorption processes could be either epigenetic or syngenetic and could occur also during diagenesis. Under the experimental conditions used, high concentrations of base metals were obtained on sediments consisting of pure peat or pure ferric hydroxide. Such pure sediments are unlikely to occur in nature, and consequently, the maximum concentrations expected in nature would be less, by a factor dependent on the composition of the sediment. Sediments which contain large quantities of quartz, micas, etc., (i.e. materials of negligible cation-exchange capacity) would obviously be the least effective. It seems likely then that only in the case of uranium could the natural sediments be responsible for enrichment up to ore-grade; in fact, in the U.S.A., uranium ore is mined in sedimentary rocks containing only 0.2 percent uranium. Only under the most favourable conditions could the other metals concentrate in sediments by sorption processes alone to form ore-grade material. That some sediments are better able to fix metals than others is not seriously questioned. It would seem from the results that a sediment rich in organic material - a type which is found in many bays and estuaries - would be the most effective. According to Waksman (1938) these sediments contain up to 20 percent humus, and, in accordance with the results presented here, it is such sediments that are found to be often enriched in uranium.

Dunham (1961) points out that marine black shales are not necessarily enriched in base metal, even though it is known that the black-shale environment tends to favour their incorporation by precipitation or sorption or both. It follows, then, that some highly special condition is required to produce such ore deposits, and it has been suggested (Kraume, 1966) that submarine springs releasing juvenile or hydrothermal fluids into a stagnant environment, or streams carrying metals in abnormally high amounts, may provide these 'special conditions'. Joplin (1945) has suggested that some of the black shales of New South Wales are volcanic dust deposits, but this idea has received little support.

It was the intention, in this Report, to report on the investigation into the sorptive properties of iron sulphide. No results are reported, however, because it was extremely difficult to be sure that the medium was free of hydrogen sulphide, and it was therefore not certain that what was being inferred as sorption was not in fact a direct precipitation of the sorbable metal ions by the hydrogen sulphide. Indications are, however, that the freshly precipitated iron sulphides are very good sorbents, but until more work is done this cannot be rigorously proved; the instability of the freshly precipitated iron sulphides (rapid oxidation) makes this task a very difficult one. Some recent work on British Carboniferous sediments by Nicholls & Loring (1962) has prompted them to suggest that iron sulphide may first form as colloidal particles and while in this condition act as a sorbent.

The results given in Tables 19 and 27 might, at first sight, imply that the sorption process could not give a mixture of lead and zinc metal in dolomite. This is not so; the experimental conditions were so chosen that there was competition between base-metal ions for the available sorption sites. The figures given in these two tables only indicate the uptake of the base metal ions from a mixture of them all when the number of available sorption sites is limited. If the amount of dolomite were to be increased, eventually cadmium and zinc would be sorbed. The greater the amount of dolomite added, the more nearly would the ratio of sorbed zinc to sorbed lead, and sorbed cadmium to sorbed lead, approach the ratio of zinc ion to lead ion and cadmium ion to lead ion in the initial solution. Thus, the mechanism could well explain the presence of lead in dolomitic rocks with only a trace of zinc or cadmium. It could not explain the occurrence of zinc alone in dolomite rocks unless one assumes that the solution from which the zinc was sorbed was free of lead ion. On the other hand, one must not assume that because the sorption process can explain a particular mineral assemblage, that this was, in fact, the operative one.

A syngenetic explanation of some of the world's base-metal deposits must account for the large quantities of metal involved, no matter what physico-chemical mechanism is postulated for the accumulation of metal in the sediments. A syngenetic submarine-hydrothermal origin has been advanced for certain concordant sulphide deposits, classed by Schneiderhöhn (1932) as submarine exhalative sedimentary orebodies. One deposit of this type at Rammelsberg, in Germany, has been described by Kraume (1955), who suggests that the changing composition of the hydrothermal solutions is responsible for the order of deposition of the metals. Though such a mechanism may be true for the Rammelsberg deposits, other probably syngenetic orebodies show no evidence at all of hydrothermal solutions' having carried the base metals. It seems certain that circulating surface waters can carry enough metal to form orebodies. Garlick (in Mendelsohn, 1961) calculates that the river Nile carries 7200 tons of copper away from the drainage area per year, assuming that the average copper content of the land masses being eroded is 100 ppm. Hence, over a period of 1000 years, a small period in terms of geological time, 7.2 million tons of copper may be carried by the Nile, to say nothing of the other base metals carried by the same river. When one considers that the calculated reserves of copper ore in one of the world's largest copper provinces, that of Northern Rhodesia, are 474 million tons of an average grade ore about 4 percent copper (Bateman, 1956) distributed over an area 140 miles by 40 miles, it is plain that such quantities are well within the carrying capacity of some of the rivers of the world, in a relatively short space of time. If part of the mineral content of the Basement complex that was eroded to form the Katanga sediment were somehow accumulated and concentrated there would be more than enough for the known and probable ore in the copper belt deposits.

Accepting that a sorption process is able to concentrate metals in sediments, generally in insufficient quantity to form ore-grade material, one is faced with the problem of the process or processes that provide the ores as we find them today, and particularly their more common occurrence and greater enrichment in the form of sulphidic ores. The formation of sulphide minerals by bacterial action has been mentioned; any further comments are not within the scope of this Report.

As long ago as 1916, Zies, Allen, & Merwin showed how simple and mixed sulphide minerals of copper and iron could be obtained at normal temperatures and pressures by simple chemical reactions. More recently W.M.B. Roberts (1961) has synthesized mixed sulphides from naturally occurring sulphides and from precipitates, and has shown further that sulphide minerals can be tecturally and compositionally reconstituted at normal temperatures and pressures (Roberts, 1963, 1965), using synthesized sulphide minerals. Using minerals prepared synthetically in the cold, high pressures were needed to effect a textural change rather that the change itself; certainly high temperatures were unnecessary. Some textures produced in this way were very similar in appearance to many natural ones.

Judging by the complexity of most ore deposits, one can conclude that it is extremely doubtful whether any isolated and single phase of metallic segregation has given rise to an orebody. Cumulative concentration processes appear to be essential to the formation of massive sulphides. King (in King & Thompson, 1961) writes: 'As the complexity of Broken Hill is progressively revealed it becomes increasingly difficult to imagine that a single event of mineralisation could simultaneously produce all the observed phenomena. There has been intense igneous and dynamic activity at Broken Hill, even if the deposits were originally made in the sediments.' It is obvious that a final theory for the genesis of uranium and base metal deposits must take into account all the facts. Just as the simple epigenetic theory does not take into account the localization of minerals in sediments, neither does the simple syngenetic theory take into account the possible reconcentration of minerals by later metamorphism or tectonic activity. Only continued research (both in the laboratory and in the field) can provide an answer to the problem. No single theory can explain the genesis of all the orebodies found. The outcome of the work presented here, however, seems to indicate that sorption processes might, at least in part, contribute to the formation of ore deposits in sediments.

ACKNOWLEDGEMENTS

I would like to record my appreciation of the invaluable help and guidance given by Dr B.Z. Breyer, who supervised most of the work contained in this Report when I was a research student at Sydney University.

Others, in particular Professor A.N. Hambly of the Australian National University, Canberra, have been most helpful in checking, editing and objectively criticizing the original script, and it is a pleasure to acknowledge their help.

I have placed much reliance, on the geological side, on the suggestions and criticisms of my colleagues in the Bureau, and to them I would like to express my sincere gratitude. During the summer vacation of 1959-1960, Mr. G.B. Guise, Student, assisted me in some of the analytical work. His help is also acknowledged with gratitude.

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