RADIOACTIVITY AND WATER SUPPLIES

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PROEFSCHRIFT

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I. GENERAL INTRODUCTION

Almost immediately after the discovery of X-rays and radioactivity and before the turn of the century the ill effects caused by ionizing radiation to living tissues was demonstrated. Since that time much has been learned about ionizing radiation and its biological effects (genetic and somatic). Although still much is yet to be understood, the fact remains that more is known about the biological and medical effects of ionizing radiation than about other important health hazards.

Since the risks involved in the use of radioactivity and nuclear fission in regard to public health are well recognized, considerable attention is being devoted to the safety aspects. As a consequence we are faced with the unique situation that the wastes resulting from its use are handled quite cautiously and are not discharged into the environmental surroundings (ground, atmosphere or surface water) unless a thorough study has first been made of the hazards involved. Nevertheless the release of radioactivity into the environment is a matter of considerable concern, because with a strongly increasing use of atomic energy and the use of radioactivity in medicine, industry and research work, the desire to discharge radioactive effluents may well increase.

Concerning the discharge of radioactive wastes into surface waters, fundamental information is required concerning the physical, chemical and biological processes in the aquatic environment.

The evaluation of radiation safety as related either to continuous or intermittent discharge of radioactive materials involves knowledge of the types and concentrations of the radionuclides present in the water, and an understanding of the accumulation and retention of radionuclides in organic and inorganic constituents (e.g. aquatic foodstuffs) at various locations in the river system. Attention should be devoted to:

1. Chemical properties, chemico-physico form, values of the maximum permissible concentration (MPC) and the concentrations of the various radionuclides present in the waste.
2. Composition of the surface water as related to the nature and concentration of the dissolved and suspended organic and inorganic matter and the presence of biological organisms accumulating and retaining radionuclides.
3. Nature and composition of natural bottom sediments of streams and estuaries.
4. Hydrology of the aquatic system and the dilution effect.
5. The extent to which the water will be used for drinking water supply, fishing, irrigation and recreation.
6. The places where the radioactive compounds finally could accumulate.

The total process of the distribution of radioactivity over the environment is extremely complex. On the one hand many factors have to be considered, whereas on the other hand several factors are interrelated and/or influenced by temporary and local circumstances.

In a somewhat indirect form this study intends to contribute to the knowledge of this field, more in particular about the physico-chemical aspects of the interaction of radionuclides with materials, especially with organic matter, present in the aquatic system. Rather than release hazardous compounds to the environment, it is preferable to remove them from the waste as completely as necessary prior to discharge. Moreover techniques are available to remove the radioactivity in waste water to any desired level.

The removal of radioactive compounds from aqueous waste solutions is far from a simple problem because on the one hand the radionuclides differ considerably in chemical behaviour, whereas on the other hand wastes may vary greatly in character, e.g. in inactive salt content, in composition, in pH, in the presence or the absence of chelating or complexing compounds, etc. As a matter of fact waste solutions frequently need their own particular approach. However, since an economic treatment tends to use standard and cheap purifying techniques which are not as effective for all radionuclides, specific nuclides can be expected to dominate in the final discharge of the waste treatment plant. This may lead to specific environmental problems. Moreover, other more or less accidental discharges of radioactivity in surface water do not seem altogether impossible. Therefore it seems a matter of good management to develop techniques which enable the production of good drinking water from surface waters which are contaminated by radioactivity.

Convential water treatment processes are, as a rule, not effective in the removal of radioactive compounds. As a consequence it is desirable to have a clear idea about the situation concerning the contamination of the various water supplies, the provisional measures which have to be taken and, more important, to have available a decontamination technique in case an emergency situation might arise.

The main intention of this study is therefore to investigate the various factors involved in an emergency situation and to develop a method which is simple and cheap and which can be applied successfully for drinking water purification and, possibly, in the treatment of radioactive wastes. For this purpose the application of peat seems to be attractive. The choice of peat as a sorbent was based on the following considerations:

1. Peat is a cheap raw material which is available in large quantities in many countries. Even in its natural state it shows a very interesting ion exchange capacity. Moreover, it shows a pronounced selectivity for higher valent cations over univalent cations.
2. An application of the material in its natural location might be considered for the decontamination of large quantities of water.
3. The chemical, physical and ion exchange properties of peat can probably be improved by means of a relatively simple chemical treatment.

The ion exchange properties of peat originate mainly from the humic acids present in it. Since humic acids occur in surface water in rather high concentrations, the results obtained with peat can also be used for the study of the behaviour of radionuclides in surface water.

In this report studies of the ion exchange properties of peat have been described. Special attention has been paid to the interaction of peat with radionuclides of Sr, Cs, Ce, Ru, Co, Mn and I. The sorption of these radionuclides has been investigated mainly as a function of the pH and of the concentration of the various ions present in the solution. Attempts have been made to prepare a modified peat which has superior properties as compared to the natural peat. The ion exchange properties of the modified peat were investigated. The results concerning the ion exchange equilibria have been interpreted in terms of the Donnan theory.

As peat is not very effective in the removal of cesium and iodine, it appeared useful to include experiments with clay and activated carbon for the removal of these radionuclides.

II. RADIOACTIVE CONTAMINATION OF WATER SUPPLIES AND PURIFICATION METHODS

Water supplies can become contaminated by radioactivity when, as a result of a nuclear event, radionuclides are released into the environment. However, there will be a considerable variation in the extent and in the form in which the various supplies will become contaminated by such an event, depending also on the period of time elapsed, since the water supplies differ widely in character. Moreover, various factors determine how far a contamination will represent a serious hazard, viz. the nature, the form and the maximum permissible concentrations (MPC-values) of the constituent radionuclides and whether there is a temporary or a permanent contamination. Should a situation arise in which all available supplies are contaminated, effective purification methods must be applied. Much effort has already been made in this field.

In the following a survey is presented of the literature dealing with radioactive contamination of drinking water supplies and with results of research and measurements made in the decontamination of drinking water and of radioactive waste water.

II-1. **Radioactive contamination of water supplies** (1–3, 7)

II-1-1. REFLECTIONS ON THE POSSIBLE CAUSES

There are many ways in which a water source may become contaminated with radioactive compounds.

1. Fallout from nuclear detonations.
2. Accidents in nuclear installations, e.g. in nuclear fuel reprocessing plants, in atomic power installations, in radioisotope manufacturing plants etc.
3. Accidents during transport of high activity wastes.
4. Disposal of radioactive wastes from nuclear power installations and small amounts from radioisotope manufacturing plants and from industrial, research and medical users.
5. Destruction of nuclear installations in war time by conventional explosives (sabotage).

Undoubtedly the most serious hazard for an extensive and prolonged radioactive contamination is that of radioactive fallout from nuclear explosions. The radionuclides present in fallout are produced by some sort of nuclear event:

fission of ^{235}U or ^{239}Pu,
capture of neutrons by elements.

A wide range of radionuclides are formed, e.g., fission products with very short and very long half lives. After some hours only the longer living ones are left such as ^{131}I, ^{90}Sr, ^{90}Y, ^{137}Cs, ^{95}Zr, ^{106}Ru, ^{144}Ce etc., and induced radioactivity e.g. ^{54}Mn, ^{65}Zn, ^{24}Na, ^{239}Pu, ^{14}C, etc. (4–6). Table II-1 gives an idea of the quantity of fission products formed in the fission of 1 Megaton ^{235}U.

The extent of contamination of the environment due to nuclear explosions depends on many factors (3–6, 11, 17).

1. Type of bomb detonated, e.g., fission or fusion bomb, and the composition of the metallic shield with respect to the induced radionuclides. Considerable more radioactive compounds are produced in the detonation of a fission bomb as compared to that produced in the detonation of a fusion bomb of the same energy.
2. Localization, force and height of the detonation are important as it will influence:
   2.1. nature and amount of induced radioactive compounds (activation of earth's crust materials),

2.2. size, weight, form and composition of the fallout particles,
2.3. solubility of the various nuclides in the particles,
2.4. spreading of the fallout from the point of detonation.

If the explosions are surface or near surface bursts, fallout will start near the point of detonation. Radiation intensities will be high in that case, because there will be less opportunity for dispersal and decay. Consequently much local fallout will result. On the other hand air bursts in which the fire ball does not touch the earth crust do not produce local fallout in any appreciable quantity because no soil is incorporated into the regions of high neutron fluxes. Worldwide fallout of fission products will then occur.

The following has been reported concerning the solubility of radionuclides in fallout particles ([5, 8–10, 17]).

a. Solubility of tower-mounted (near surface) shot fallout in water or acid increases with decreasing particle size. The reverse has been observed for balloon-mounted (air) shot fallout.
b. The water solubility is for tower-mounted shot fallout about 2% of the total β-activity and for balloon-mounted shot fallout about 14% of the total β-activity (for particles <44 micron).
c. The solubility in 0.1 N HCl of tower-mounted fallout is 5% for particles >44 micron and 14-36% for particles <44 micron. For fallout particles <44 micron resulting from balloon-mounted shots the solubility is about 65%.
d. Some of the more hazardous nuclides are rather soluble in water, e.g. ^{90}Sr, ^{131}I and ^{106}Ru, ^{103}Ru.

3. Meteorological factors such as wind direction and intensity, wind currents and precipitation at the moment of the burst, are important ([11]). The radioactive materials present in the troposphere are washed out continuously by precipitation so that the residence time here is one month at the maximum. The residence time in the stratosphere, however, is considerably longer, viz. 7-17 months in polar regions and 15 months to 7 years for detonations in the equatorial regions. As a consequence the fallout originating from the stratosphere consists mainly of long-living radionuclides. Due to atmospheric circulations a maximum descent of radioactive matter occurs in spring-time.

Contamination due to accidents in nuclear installations and/or transport of high activity wastes as a rule will be predominantly local and temporary of character. In the accident at Windscale in 1957, when a fuel element burned in the cooling air of the reactor, 20,000 Curies of ^{131}I and 13,000 Curies of other radionuclides were released into the atmosphere. Nevertheless it was only necessary to withdraw from consumption the milk produced over an area of about 200 square miles. This type of event therefore offers in general no serious hazard for water supply contamination, the more since the chance of occurence of events of this sort is extremely small and the forces leading to distribution of radioactivity will also be small. A possible exception is a nuclear fuel reprocessing plant of the type which applies equipment in which nuclear criticality can occur.

In the disposal of radioactive wastes in surface waters only small quantities of radioactive matter are involved, provided the directions are strictly followed. However even very low concentrations in surface water may lead to a severe accumulation of radioactive compounds in the river system (sediments). A sudden change of the pH and/or the salt concentration of the river water, although rather hypothetical, may result in a release radioactive compounds in the river water and possibly in a contamination of the drinking water produced from it down-stream. However, a drinking water contamination can usually be prevented easily, if a good alarm system functions so that the water purification plants can be warned in time. As the result of a strongly increased nuclear power industry in future an environmental contamination may possibly arise from tritium ([63]), for which no corrective actions can be taken. In conclusion it may be stated that a real emergency situation may arise in the case of a calamity in a big nuclear plant and, much more important, in the case of an extensive use of nuclear weapons and/or destruction of nuclear installations by conventional means during war time.

II-1-2. MAXIMUM PERMISSIBLE CONCENTRATION OF RADIOISOPES IN DRINKING WATER (14, 17)

In dealing with the maximum permissible concentrations of radioisotopes in drinking water two extreme situations have to be distinguished:

1. Normal peace time situation,
2. Emergency situation, e.g. war time and reactor calamity.

With respect to the normal peace time situation frequently the recommendations of the ICRP (13a) are followed. These recommendations require that the individual members of the population should not receive more than 1/10th and the population as a whole not more than 1/30th of the radiation dose set for occupational workers. They are based on research and calculations concerning the permissible damage for the population as a whole; moreover they are based on the simplification that drinking water is the sole source of the contamination. Furthermore it has to be recognized that they are applicable only to adults and not to children. The MPC-values recommended by Euratom (13b) as a rule are somewhat higher than those of the ICRP. MPC-values for a number of important radionuclides, which hold for the population as a whole, are given in Table II-2. Since MPC-values are based on a concept which can be hardly accurately quantified, a revision of some of these values is well likely in future.

The situation becomes quite different when fallout is the main source of the contamination. In this case the contribution of the radioactivity in drinking water with respect to the total uptake of radioactivity with the normal human diet will be rather small if no special actions are taken, viz. about 5%. Many different foods will be contaminated by fallout in direct and indirect ways. It is evident that products which are contaminated severest and for which any adequate decontamination method is not available, should be withdrawn for consumption as far as possible. Others, for which a decontamination method is available, should be purified sufficiently. Concerning drinking water, being an essential component of the dayly diet, it is evident that a decontamination as good as possible must be strived after. This holds certainly good when a prolonged contamination by fallout can be foreseen. Otherwise, in war time situations, the total intake of radioactivity may temporary amount 10 to 100 times the MPC-values, the more so because in war time, due to the social upheaval, the application of any sophisticated decontamination method may be impracticable.

A prediction of the extent of the contamination of water supplies by fallout, which originates from nuclear detonations and/or from accidents in nuclear installations is difficult. Various factors have to be considered:

1. The amount, the composition and the form of the mixture of the radionuclides formed in the event.
2. The dispersion which will take place in the atmosphere resulting in variations of activity over various localities.
3. The disproportionation of the original mixture occurring on its way to the place of intake of the water supply.

The maximum permissible total activity of a mixed fission product alters with its age. This is the consequence of the very different decay times of the various radionuclides in the mixture and of the greatly different MPC-values of the individual isotopes. Haberer (15, 16) calculated the relative hazards of a number of radionuclides (only fission products) in a fallout mixture on the basis of the yields in the fission of ^{235}U, the decay time and the MPC values of the radionuclides. It followed from these calculations that ^{131}I is predominant with regard to relative hazard during the first 50 days. Then follow ^{140}La, ^{140}Ba, ^{90}Sr, ^{89}Sr, ^{144}Ce, ^{106}Ru and ^{95}Zr. However, in a mixture older than 100 days ^{90}Sr is by far the most hazardous radioisotope; then follow ^{144}Ce and ^{106}Ru. The calculated MPC-value of the mixture should be 3000-4000 pCi/l after 10 days, 9000 pCi/l after 80 days, 2000 pCi/l after 2 years and 300 pCi/l after 5 years. As a matter of fact the estimate of Haberer gives a flattering picture, because various of the abovementioned factors were ignored.

II-1-3. RELATIVE HAZARD FOR CONTAMINATION OF WATER SOURCES

It is evidently of predominant importance to know which water sources will, in the first instance, not be seriously contaminated in the event of a high and prolonged fallout.

A high contamination will undoubtedly always occur first in rain water. A high contamination of rain water has been observed in various parts of the world ($^{18-21}$) during and following the period of testing of nuclear weapons. The highest contamination was recorded in 1963 (New York, Minnesota, Vienna, Scotland, Florence). This is illustrated clearly in Table II-3, in which measurements made in New York are summarized. Frequently a ^{90}Sr-activity higher than the MPC-value of 30 pCi/l has been observed in three or more successive months, sometimes reaching values of 173 pCi/l (mean value over one month).

Data are also available for other nuclides ($^{9,\,18-20}$) and for the total β-activity. For the total β-activity of rain water values up to 17,000-32,000 pCi/l have been reported ($^{22,\,43}$).

As follows from Table II-3 even after the termination of the testing of nuclear devices (1962/1963) a high ^{90}Sr-activity persists in the rain water during several years.

A much lower contamination will occur in surface water due to decay, to sorption in soil and to the dilution effect. It has been stated ($^{22-24}$) that a decontamination factor of 6-90 or even higher is encountered in the transport of fallout radionuclides to the surface water. However, the more hazardous radionuclides (^{90}Sr and ^{131}I) are, relatively speaking, poorly retained on their way to the surface water. Furthermore surface waters receiving a larger part of their water directly from precipitation will certainly be contaminated to a higher extent.

An important aspect with respect to the contamination of surface water concerns the extent of self cleaning as a result of flow. This evidently is much more important in rivers than in reservoir- or impounded waters (^{41}).

Up till now an alarming contamination of surface waters has never arisen ($^{19,\,20}$). Concerning the river Rhine a maximum ^{90}Sr-activity of about 2.5 pCi/l was observed in July, August and September 1963. The total β-activity never reached values higher than about 35 pCi/l (mean value over one month), of which 6-8 pCi/l consisted of ^{40}K-activity (^{20}). A slightly higher value of the total β-activity was observed in the river Schelde, namely about 50 pCi/l in 1963. The average concentration of ^{90}Sr in twelve impounded waters in England was 2.25 pCi/l in 1964. The average values for individual water supplies ranged from 1.0 to 3.1 pCi/l. Corresponding values for ^{137}Cs were 0.67 pCi/l with extremes of 0.11 to 3.4 pCi/l (^{41}).

Whatever the cause may be, should a high contamination of surface water by radioactive fallout take place, it has to be recognized that:

1. It certainly will extend over several years. This already is the case for rain water, but even more so for surface water because the drainage area acts as a buffer, spreading the release of accumulated radioactive fallout over a period of several years.
2. A serious contamination can occur only in the case of a very high fallout, and consequently will coincide with a high contamination of other components of the diet. An additional high contamination of drinking water then should be avoided.

An even lower chance of contamination exists for ground water, especially when it originates from precipitation. Practically all radioactive nuclides will be retained in the upper layers of the soil. This is the result of the ion exchange properties of soil and, quite important, of the very low salt content of rain water (25, 26, 34, 42, 44, 46). The situation evidently becomes much less favourable when the ground water is supplemented mainly by infiltration of surface water, and the more if the ion exchange capacity of the soil is low (e.g. sand) and the salt content of the water is high (e.g. Rhine water).

Concerning the penetration depth of ^{90}Sr, it was shown by Herbst (38) that it penetrates considerably deeper in a pure sand-soil than in a sand-soil which contains appreciable amounts of humus (viz. the upper layers of the ground).

In addition to the exchange capacity, the selectivity of the soil in the sorption of the various nuclides, its acidity, cation occupation, texture as well as its filtration properties are quite important in the binding and migration of the radioactive compounds. Moreover radioisotopes may be sometimes retained as the result of a chemical reaction, e.g. the incorporation of strontium in grandellite, apatite etc. (25, 26, 30, 31).

Soils containing clay, in particular illite and vermiculite (because of their selectivity for cesium), retain ^{137}Cs quite efficiently (25–29, 32, 35, 45, 60). The sorption of ^{137}Cs is affected mainly by cations which are sorbed themselves selectively, e.g. K^+, Rb^+, $NH_4{}^+$ and Cs^+. The effect of H^+-ions is relatively small. The latter is also the case in the sorption of rare earth elements, which are retained very effectively by soils (25, 26, 28, 32, 34).

Much more hazardous for ground water contamination are certainly the radioisotopes of Sr, I and Ru. The sorption of Sr and Ru is reduced seriously by H^+- and more valent cations (25–28, 32–37).

Anions as a rule have little influence, though phosphate ions may promote the sorption of strontium to calcite (31). Otherwise the formation of complexes and/or colloids may result in a higher migration rate (30, 35, 36, 40).

In view of the foregoing it may be concluded that ground water, which is not supplemented by infiltration of surface water, in the first instance is protected reasonably well from a fallout contamination. Nevertheless in the long run even here a slight contamination may occur. This will be the case especially for soils having a low exchange capacity. Small amounts of ^{90}Sr, ^{106}Ru and ^{95}Zr have already been detected in ground- and wellwater (39, 41).

A contamination of ground water will certainly take place when it is supplemented by infiltration of contaminated surface water. In particular ^{90}Sr will appear in this sort of ground water. A determination of decontamination factors based on gross β-measurements is therefore of little value (see (42, 44)).

II-1-4. THE OCCURRENCE OF RADIONUCLIDES IN DRINKING WATER SOURCES (1, 23, 33, 47, 48, 50)

In addition to the type and the amount of radioactive compounds present in the water, it is undoubtedly important whether or not these compounds occur in soluble or insoluble form. In the latter case removal can be effected by relatively simple means such as filtration and or sedimentation. Moreover the MPC-value of specific types of suspended radioactive matter may be somewhat higher than of dissolved radioactive matter (compare Table II-2).

In rain water the radionuclides will be present in soluble form as well as in insoluble particles ("hot particles"). In ground water, on the other hand, they will appear almost exclusively in soluble form.

The behaviour of radionuclides in surface waters is quite complex. Many factors are involved, which are interrelated and/or affected by temporary (e.g. meterological), accidental or local circumstances.

1. *Nature, properties and amount of suspended solids* (23, 33, 51, 52, 61, 62)

The presence of clay minerals may result in a rather complete removal of ^{137}Cs from the solution. A significant sorption of other radionuclides such as ^{60}Co, ^{106}Ru and those of the rare earth's elements etc. may also take place, particularly when suspended organic substances are present in the water ([55, 56, 62]).

The ratio of dissolved to total activity obviously depends on the concentration of suspended solids and, consequently on the extent of the agitation of the water. In natural and artificially impounded waters ([48, 49, 58, 59]) a considerable sedimentation of suspended particles will occur. As a consequence the main part of the radionuclides present in the water are left in dissolved form. Also some retention of radioactive compounds may take place in streams, but this will occur mainly between the cribs and in seasons of slow flow. The sedimentated solids will be redispersed when the velocity of the water increases ([32, 49]).

Studies of the behaviour or radioisotopes in Clinch river ([61, 62]) revealed that only 1.5% of the total amount of radioactive compounds released to the river is accumulated in the river system, i.e. mainly ^{137}Cs and a small amount ^{60}Co. The radioisotopes ^{90}Sr, ^{106}Ru and ^{60}Co are predominantly associated with "dissolved solids" and ^{137}Cs with suspended solids. According to studies of EURATOM ([64]) and W. Block ([65]) a significant retention of radioactive compounds in the river Rhine is unlikely.

2. *Composition of the water*

The sorption of radionuclides to solid materials is strongly affected by the salt concentration and the pH of the water. The sorption of ^{137}Cs is reduced mainly by the presence of K^+-ions, while that of ^{90}Sr and other divalent radionuclides is strongly affected by di- and trivalent cations ([33, 51, 55, 61, 62, 65, 66]).

Dependent on the pH, carrier concentration and precipitating anions it is also possible that a precipitation (as hydroxide, or carbonate) or co-precipitation with $Fe(OH)_3$ or Mn-oxides of some nuclides will take place ([52, 66]).

The presence of dissolved humic acids in the water will certainly be of special importance with respect to the behaviour of various radionuclides (e.g. of Co, Ce, Zr, Ru etc.) as they may form soluble compounds. This has not been recognized up to now.

3. *The form in which the radionuclides arrive in the water*

4. *Accumulation of radionuclides by aquatic organisms* ([1, 49, 53, 54, 57, 61–63, 65])

The biota of a stream (plankton, larvaes, fishes etc.) can affect the dispersion of radioactive contamination by accumulating and retaining radioisotopes, especially those of P, Zn, Cu and Co. However, this will probably not result in a significant retention of radioactive matter in a river system ([62]).

From the foregoing one would tend to conclude that the disposal of radioactive wastes in a fast flowing river system at a level not exceeding the MPC-value could be allowed. However, for the discharge of wastes not only the river system itself has to be considered. Other, more critical parts of the environment may be involved, in which radioisotopes, associated with suspended matter or in a form easily taken up by organisms, may be retained. Evidently this can be in natural or artificial impoundments which are used for drinking water supply, in or upon infiltration areas, in waters used for oyster- and mussel cultures and/or fishing (Zeeland-Waddenzee, etc.) and in areas of land reclamation (sea-coast of Friesland and Groningen, IJselmeer).

II-2. **Decontamination of radioactively contaminated water** ([67, 81, 147])

II-2-1. MEASUREMENTS MADE IN WATER-PURIFYING PLANTS ([68])

In periods of high fallout, measurements could be made on various water-purifying plants in order to establish the decontamination efficiency of the treatment processes applied, which included as a rule coagulation and flocculation of iron- and aluminium salts, settling, filtration and/or desinfection. From these observations it appeared that:

1. The decontamination varies between 0-90% (39, 43, 68–76), being at maximum in case of a fresh fallout contamination and at minimum if an old fission product mixture is involved (43, 69–73). Moreover considerable fluctuations can occur daily in the decontamination (70–72).
2. The suspended activity can as a rule easily be removed by means of filtration and/or coagulation and settling (e.g. 43, 69, 73, 74).
3. Sand filtration, especially fast sand filtration, is not effective in the removal of dissolved radioactive compounds. In slow sand filtration a rather high removal of ^{90}Sr, of ^{131}I and of ^{32}P has been observed, i.e. from 80 to 99% (78). However, this seems to be true only with a fresh filter and during a relatively short time (77, 79, 80). The removal of radiostrontium in particular is unsatisfactory (77).

II-2-2. Decontamination by chemical precipitation methods

For the decontamination of water, especially of radioactive waste water, considerable attention has been devoted to the application of chemical methods. Many cationic fission products form insoluble compounds such as hydroxides, carbonates and phosphates. By means of chemical precipitation therefore at least a partial removal of radionuclides can be achieved. Since the radionuclides frequently occur in an extremely low concentration in the water, their removal is mainly the result of co-precipitation, e.g. formation of mixed crystals, occlusion and/or adsorption. It is therefore important that the precipitation is effected under conditions, that a voluminous precipitate is formed with a charge opposite to that of the ions which have to be removed.

II-2-2-1. *Decontamination by means of* $Fe(OH)_3$ *and/or* $Al(OH)_3$

A common method in water treatment consists of the addition of aluminum- or ferric salts to the water, and raising the pH by addition of lime, soda ash or caustic soda, etc. to precipitate the hydrous oxides of these metals (47, 81, 82). The originally formed colloids coagulate and adsorb, entrap or otherwise bring together suspended matter, particularly suspended matter which is colloidal. When formed under alkaline conditions the floc is charged negatively and positive ions, especially the higher valence cations, are sorbed. Moreover hydroxides and basic carbonates of many of the higher valence cations co-precipitate. However, the alkali- and to some extent the alkaline earth cations remain unaffected.

Coagulation in association with settling and/or filtration has been studied intensively in the laboratory and at pilot plant level for the removal of radionuclides (e.g. 82, 83). The efficiency of the method depends on many factors such as the conditions of the flocculation, (e.g. amount and nature of coagulants, contact time, pH, rate of mixing, way of floc separation, etc.), the composition of the contaminated water and the nature of the contamination.

The method is quite effective for the removal of particulate associated radioactive compounds and of the higher valence cationic radionuclides, and amounts to 85-100% (e.g. 82–91, 93, 95). Moreover it has been reported that up to 96% of ruthenium can be removed (82, 84, 85, 91, 93, 95); ferrosulphate seems to be somewhat more effective than ferrisulphate for this purpose (92).

The results obtained for the removal of mono-valent and many divalent cations are less satisfactory. Radiocobalt can be co-precipitated up to 70% (65, 87, 89, 94), but also much lower values, i.e. about 23%, have been found (79, 86). Likewise, the decontamination obtained for radiostrontium varies between wide limits, viz. from 0 to 70% (e.g. 79, 82–85, 87, 95, 115), which may be attributed, at least partly, to the different calcium concentrations of the experimental solutions used in the various investigations. A considerable improvement in the removal of radiostrontium can be achieved by using Na_2CO_3 for pH-adjustment, rather than any other substance (82, 85, 90, 95, 96). This obviously is the result of a precipitation of $CaCO_3$, possibly accompanied by a co-precipitation of the strontium. In most investigations a somewhat higher efficiency towards the removal of radiostrontium (79, 82–84, 88, 93) and other radionuclides, such as ^{60}Co (65, 89, 94) and ^{144}Ce, ^{95}Zr etc. (85) was found with $Fe(OH)_3$ rather than with $Al(OH)_3$. The efficiency of the $Al(OH)_3$-flocculation can be somewhat improved by adding $NaAlO_2$ rather than $AlCl_3$ (91, 98).

When ^{137}Cs is present in the water in soluble form, little if any decontamination can be achieved by means of flocculation (82, 84–86, 90, 93, 99). However, the removal of this nuclide can be improved considerably by adding specific types of clay to the water (47, 82, 93, 99, 100).

The removal of radioiodine is very poor, viz. ranging from 0 to 44% (79, 82, 86, 87, 90, 95).

A rather high decontamination has been observed for ^{32}P, viz. ranging from 68 to 99% (79, 82, 87, 95).

Komatsu (115) investigated the co-precipitation of radionuclides with $Ti(OH)_4$, $Fe(OH)_3$ and $Al(OH)_3$. It was observed that $Ti(OH)_4$ was superior in the removal of ionic radiostrontium; titanium hydroxide removes about five times the amount of strontium than other hydroxides do under the same conditions.

II-2-2-2. *Lime-soda softening* (81, 82)

A considerable part of radiostrontium can be removed from aqueous solution by means of a $CaCO_3$-precipitation. This is even true for carrier free* solutions of radiostrontium, where the solubility product of $SrCO_3$ is not reached (79, 101, 102). This effect has been attributed to the incorporation of strontium ions in the crystal lattice of $CaCO_3$ (101, 102). The extent of co-precipitation seems to depend on the crystal form of the calcium-carbonate, viz. less strontium co-precipitates with calcite, which is formed in cold lime-soda softening, than with aragonite, which is formed predominantly in hot lime-soda softening. It has been shown that aragonite and strontianite, which are both of the ortho-rhombic crystal system, form mixed crystals in all proportions. Calcite, which has a hexagonal crystal structure, and strontianite only do so to a limited extent.

A removal efficiency for strontium of 20 to 80% can be obtained under stoichiometric conditions. A small amount of strontium carrier, viz. up to 10 ppm in the presence of 125 ppm Ca, does not have any effect on the removal efficiency (79, 101, 102). A maximum removal of calcium and strontium is achieved when the precipitation is performed at pH 10 and when an excess of soda is used (79, 101–103). Otherwise a higher percentage of calcium than of radiostrontium is always removed, especially when the non-carbonate hardness is relatively high (79). Although little if any strontium is sorbed by calcite crystals, the presence of calcite crystals is favourable towards decontamination, mainly because they stimulate the precipitation (101, 102). The modern solids-contact softening plants, where preformed crystals are present in the coagulation zones, are therefore more effective than plants which use separate mixing, coagulation and settling (105). Instead of $CaCO_3$ other solids, such as sand, can be used for this purpose (106). Furthermore a very high strontium removal can be achieved by applying a repeated $CaCO_3$-precipitation (101, 102).

Phosphate-ions and complexing agents decrease the removal efficiency (104, 105). Lime-soda softening removal efficiencies for some other radionuclides are summarized in Table II-4.

II-2-2-3. *Specific chemical methods*

Certain radionuclides, e.g. ^{90}Sr, ^{131}I, ^{137}Cs and ^{60}Co, cannot if at all be removed efficiently by any of the precipitation methods commonly used in drinking water purification practice.

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* Carrier free means that non-radioactive forms of the same element are not present.

Attempts have been made to find more specific methods which can be applied separately and/or in combination with the above-mentioned coagulation methods.

A calcium-phosphate precipitation appeared to be quite effective for the removal of strontium and of many other higher-valence radionuclides, such as ^{144}Ce, ^{90}Y, ^{95}Zr, ^{106}Ru etc. ([82, 89, 91, 108–110]). However the removal of radioisotopes of Cs, I and P is poor, unless they are associated with suspended matter ([85, 88, 99, 100, 109, 111]). The optimal conditions for the removal of radiostrontium are: $Na_3PO_4/Ca(OH)_2 = 2.2$ and $pH = 10.5$-11.3 which corresponds to a precipitation of hydroxy-apatite ($3Ca_3(PO_4)_2.Ca(OH)_2$). Up to 98% of the radiostrontium can be removed under these conditions ([108, 110]). However, the method is not attractive for application in the purification of drinking water, due to the rather extreme conditions and the chance of algae-growth in the drinking water. In order to meet the objection of the high pH, Eschle ([112]) investigated the precipitation of $AlPO_4$ in weakly alkaline solutions for the removal of radiostrontium. In distilled water a decontamination of 99% was observed. The method is much less effective, however, when the solutions contain calcium ([83, 89]).

A co-precipitation of radiostrontium with $BaSO_4$ seems to be more promising, because a high removal of strontium can be achieved, e.g. of about 97% with 120 ppm $BaSO_4$, whereas calcium-ions up to a concentration of 8 meq/l have only a small detrimental effect ([89]).

The efficiency of coagulation for the removal of radioiodine can be improved by adding specific reagents such as $AgNO_3$ ([79, 82, 91]), AgCl ([90]), $AgNO_3$ + hypochlorite ([79]), $CuSO_4$ ([82]), $CuSO_4 + Na_2S_2O_3$ ([96]) and activated charcoal ([79, 82, 90]), together with or prior to the addition of the coagulants.

An effective method for the removal of radiocesium consists of a precipitation of nickel-, copper-, cobalt- or iron-ferrocyanides or nickel-ferricyanide, in particular at $pH < 6$ ([85, 94, 96, 113, 114]). Due to the requirement of the low pH, the method cannot be combined with the normal coagulation methods.

II-2-3. DECONTAMINATION BY ION EXCHANGE ([47, 67, 81, 82, 120])

Ion exchange is a very effective method for the removal of ionic radionuclides from water. Synthetic as well as natural ion exchangers can be used for this purpose.

II-2-3-1. *Synthetic ion exchangers*

Synthetic ion exchangers are, as a rule, superior to their natural counterparts in various respects such as capacity, chemical and mechanical stability, column properties. Nevertheless the application of these materials in decontamination of low radioactive wastes is limited. The main reason for this is the relatively high price which necessitates a regeneration of the material after exhaustion. This operation can be omitted if cheap natural materials are applied. However, synthetic ion exchangers are used extensively in nuclear projects for cases where a very low level of dissolved solids in the water must be maintained, e.g. water for reactor moderator and for cooling circuits, and frequently as a second step in the decontamination of radioactive wastes in combination with chemical treatment ([67, 81, 104]). Strongly acidic ion exchangers such as Dowex-50 ([121]), sulphonated coal ([79]), as well as weakly acidic ion exchangers such as Amberlite IRC-50 ([67, 79, 121]) all remove radiostrontium rather efficiently from solutions containing calcium. However, none of these materials has a pronounced specificity for strontium relative to calcium, although the sulphonated coal is somewhat better in this respect than the other materials.

In the last decennium much attention has been paid to the study and the development of synthetic inorganic ion exchangers, e.g. of hydrous oxides of Fe, Al, Si, Sn, Zr etc. and of insoluble salts of polybasic metals such as zirconium-phosphate. In particular zirconium-phosphate has been investigated extensively (e.g. 118,119). This compound has a high exchange capacity, viz. 4-6 meq/g at pH 7-8, and is quite selective for cesium-ions, especially at low pH. However, its stability at high pH is unsatisfactory and it is also difficult to prepare in a suitable particle size range. Many salts of the type of zirconium phosphate are known. Among the metals studied are thorium, titanium, cerium, aluminium, etc. The anions used include phosphate, arsenate, antimonate, vanadate, molybdate, tungstate, chromate, silicate and carbonate (120,124). Another group of synthetic inorganic compounds which have been investigated during recent years are compounds of ferrocyanide-molybdate (120,123) and ammonium molybdophosphate (120,124). These materials have a rather low capacity but are very selective in the sorption cesium.

The application of synthetic resins in the decontamination of surface water for the sake of drinking water production has been suggested by some investigators (91, 98,122). However, for economic reasons this can be considered only when the salt content of the water is low, whether naturally so or as a result of some pretreatment.

II-2-3-2. *Natural ion exchangers*

The high price of synthetic ion exchangers stimulated many attempts to apply natural ion exchangers in the decontamination of radioactive wastes. Of the organic natural ion exchangers especially peat (126–132), and browncoal (96,133,134) have been studied. The ion exchange properties of these materials are mainly derived from their large humic-acid content. Humic acids are complex high molecular compounds which contain at least two kinds of acid groups, namely carboxyl- and phenolic hydroxyl groups. In addition a number of other groups such as $C{=}O$, OCH_3, alcoholic OH, NH_2, etc. are present. These groups also can play a substantial part in the interaction of metal ions and peat. Depending on the conditions, e.g. pH, amount and nature of competing cations, a significant uptake of fission products can take place (126,128,129). Moreover, peat seems to be reasonably suitable for application in colums (126,128), especially after it has been dried at 110°C (130).

The use of peat has already been suggested for the decontamination of cistern water, particularly for the removal of radiostrontium (132).

However, according to A. Szalay and M. Szilagyi (126) anionic fission-products cannot be removed sufficiently with peat. On the other hand E. Raja *et al.* (116) observed that a considerable part of radioiodine is retained in peaty soils, i.e. about 86% after seven days of contact. The use of a humic acid clay preparation has been suggested for the removal of ^{137}Cs (130). Peat alone is not effective in the removal of this radionuclide.

Other organic natural materials which have been investigated are saw-dust (133,134), chemically pretreated saw-dust (135) and sugar-beet pulp (136).

A rather intensive use in the decontamination of radioactive wastes has already been made of natural inorganic ion exchangers such as clays and zeolites. These materials are often extremely selective for cesium. Whether or not a clay mineral exerts a preference for cesium can be explained on the basis of its structure. Basically the alumino silicate "backbone" of clays is composed of alternating parallel layers formed from silicate tetrahedra and aluminate octahedra. The disposition of these layers and the extent and the nature of isomorphous substitution present here, determine to a great extent the chemical and physical properties of the material.

In illite, in montmorillonite and in the micaceous derivatives the repeating unit consists of one aluminate layer sandwiched between two silicate layers. The degree of substitution in either the tetra-hedral (Si^{4+} by Al^{3+}) or octahedral layers (Al^{3+} by Mg^{2+}, Fe^{2+} etc.) determines strongly the properties of the material. Since the parent ion is always replaced by an ion of lower positive charge, the back-bone acquires a negative charge. This negative charge is compensated for by the incorporation of cations in the interlayer spaces between each pair of triple units. These cations are exchangeable when water can penetrate between the units. The degree of isomorphous substitution in the above-mentioned classes of clay minerals is considerably higher than in the kaolinite clay minerals, which consist of units of one silicate and one aluminate layer with negligible substitution in both. Kaolinite clays therefore have a very low exchange capacity, viz. 0.02 to 0.10 meq/g which is derived almost exclusively from cation exchange at the edges and the corners of sheets.

When isomorphous substitution occurs in the octahedra, e.g. such as in montmorillonite, in nontronite and in sapronite, the resulting clay mineral swells strongly when it comes into contact with water. The counter ions are then easily exchangeable and the material therefore has a high exchange capacity, i.e. 0.6 to 1.5 meq/g. This may also be true when the substitution occurs in the tetrahedral layers, provided the counter ion is Mg^{2+} or Ca^{2+}. Such an example is found in vermiculite where a quarter of the Si^{4+} is replaced by Al^{3+}.

Vermiculite has an expanding structure but it loses this when Mg^{2+} is replaced by K^+. Then biotite is formed. This clay-mineral does not expand, because the electrostatic forces between the negatively charged "backbone" and the balancing K^+-ions, which just fit into the hexagonal perforations between the layers of two successive structure units, are much stronger than in vermiculite and in montmorillonite. The capacity of biotite is therefore very low, i.e. about 0.03 meq/g. The same phenomena can be observed in illite and in muscovite. In illite about a sixth of Si^{4+} is replaced by Al^{3+} and the negative charge is neutralized mainly by K^+-ions.

A fixation* is observed in the exchange of certain cations such as K^+, Rb^+ and Cs^+ on non-expanding clay-minerals, but also on vermiculite. Due to their affinity for Cs^+-ions, illite and vermiculite have been applied intensively in the treatment of radioactive wastes, frequently in combination with flocculation (32, 43, 82, 99, 100, 107, 108, 139–145). Ions which are sorbed selectively, e.g. K^+ and Rb^+, show the strongest competing action. Other cations have a much smaller influence. With respect to the removal of radiostrontium clay-minerals with a high exchange capacity, e.g. montmorillonite and vermiculite, have been considered. Since strontium is sorbed much less selectively than cesium, the competing action of cations, especially the higher valency cations, is quite important (30, 104, 107, 110, 133, 141, 142, 145).

In zeolites, e.g. clinoptilolite, analcite, natrolite and sodalite, the structures are built up from tetrahedral groupings (AlO_4^{5-} and SiO_4^{4-}) in such a way that the corners, the edges and the faces of the tetrahedra are shared to give condensed rigid structures. The zeolites may be regarded as being derived from $(SiO_2)_n$ by replacing Si by Al to varying extents. The resulting negative charge is balanced by cations. The consequence of their three dimensional rigidity is that the lattice is unable to swell, so that ions exceeding a certain size cannot enter the structure. In clinoptilolite, which mineral is quite selective for cesium, Ca^{2+} and Na^+ are, as a rule, the counter-ions. This mineral is sometimes applied in the decontamination of radioactive wastes (30, 35, 134, 141, 146).

II-3. **Conclusions**

1. A real emergency situation concerning a radioactive contamination of water is in fact only possible in the case of an extensive and uncontrolled use of nuclear weapons. This will result in a prolonged and probably in a severe contamination.

2. The relative hazard for a radioactive contamination of water supplies depends on the nature of the water supplies and increases in the sequence: ground water < surface water < rain water.

The form in which the radionuclides will be found in the water is closely connected with the

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* The term "fixation" denotes a form of exchange in which the inchanged ion is held by the exchangers in a relatively unexchangeable form.

hydrodynamical, chemical and physical properties of the aquatic system and with the form in which the nuclides arrive in the water. In general it may be stated that the proportion of dissolved activity increases in the sequence: surface water in agitation $<$ rain water $<$ stagnant surface water $<$ ground water.

The nuclides, which as a rule will occur in soluble form are strontium and iodine, but this may also be valid to some extent for other radionuclides such as those of cesium, cobalt, ruthenium, manganese and others.

3. Conventional water treatment processes (coagulation, sedimentation and filtration) effect a satisfactory removal of particulate associated radionuclides and 3-, 4-, and 5-valence radionuclides. However, this is not true for dissolved nuclides, which are in fact the most hazardous for public health. More specific methods have been developed and are already being applied in the treatment of radioactive wastes for the removal of ^{90}Sr (i.e. lime-soda, phosphate and barium sulphate precipitation), of ^{131}I (addition of $AgNO_3$, or activated charcoal), and of ^{137}Cs (co-precipitation with the ferrocyanides of heavy metal ions). However, it is questionable to what extent these methods can be used in the production of drinking water, because of the price of the chemicals, of drinking water requirements, of difficulties in the handling of large amounts of sludge and of difficulties in the adjustment of the treatment processes. Moreover the efficiency of some of these methods is questionable, as is true for the application of activated charcoal in the removal of iodine.

4. In the production of drinking water the application of cheap natural ion exchangers may represent an attractive method, provided these materials combine a high specificity with a reasonable exchange capacity. Moreover their chemical, mechanical and physical properties should be satisfactory.

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TABLE II-1

Quantity of long living fission products formed in and after the detonation of an ^{235}U *atomic bomb* (41)

Radioisotope	Fission yield (%)	$t_{0.5}$	Starting activity % of total activity		
			MCi/Mton	After 8 weeks	After 12 weeks
^{95}Zr	4.7	65 d	22	10.4	8.0
^{103}Ru + ^{103}Rh	4.5	40 d	34.2	22.0	4.2
^{131}I	2.7	8.04 d	160	1.3	—
^{137}Cs	5.4	30 y	0.15	0.14	1.18
^{140}Ba + ^{140}La	4.6	12.8 d	109	9.3	—
^{141}Ce	4.3	32.5 d	40	10.55	0.8
^{144}Ce + ^{144}Pr	3.3	285 d	3.53	5.22	25.4
^{90}Sr	3.0	28 y	0.089	0.08	0.63
^{89}Sr	2.6	51 d	15.24	5.7	2.6

TABLE II-2

MPC-*values for various radionuclides in drinking water as recommended for the population as a whole*

Radioisotope	MPC-value (pCi/l)	
	Soluble form	Insoluble form
^{3}H	100,000	
^{24}Na	70,000	100,000
^{54}Mn	30,000	30,000
^{60}Co	20,000	10,000
^{65}Zn	30,000	60,000
^{89}Sr	3,000	9,000
^{90}Sr	30	13,000
^{90}Y	6,000	6,000
^{95}Zr	20,000	20,000
^{103}Ru	24,000	24,000
^{106}Ru	3,000	3,000
^{131}I	700	20,000
^{137}Cs	7,000	15,000
^{140}Ba	11,000	9,000
^{144}Ce	3,000	3,000
^{226}Ra	3	10,000
U-Nat	6,000	6,000
^{239}Pu	1,500	9,000
Fission product mixture of unknown composition containing ^{90}Sr.	30	

TABLE II-3

^{90}Sr-*activity and precipitation in New York* (HASL-172, July 1966)

Year	Month	1	2	3	4	5	6	7	8	9	10	11	12
1959	^{90}Sr pc/l	7.7	15.6	20.5	50	14.8	16	1.8	2.3	1.8	1.1	1.1	1.7
	Prec. ml	5.9	4.3	9.6	4.8	3.4	10.7	10.9	11.3	2.8	12.3	10.7	11.8
1960	^{90}Sr pc/l	2.8	2.8	1.6	2.1	3.7	3.8	0.5	0.5	0.4	0.6	0.6	0.5
	Prec. ml	6.1	11.2	7.5	7.8	7.5	4.4	21.0	15.9	13.7	7.2	7.8	9.7
1961	^{90}Sr pc/l	0.8	0.7	2.4	2.9	3.5	2.3	0.6	0.6	0.5	2.4	5.3	7.3
	Prec. ml	4.8	10.1	10.7	12.9	9.1	7.3	12.5	7.9	4.3	5.6	6.9	7.7
1962	^{90}Sr pc/l	7.4	10.3	6.6	23.4	33.8	12.3	29.2	6.4	5.7	9.8	6.2	18.3
	Prec. ml	6.6	9.5	7.5	7.6	3.2	9.9	4.2	14.5	7.8	8.0	10.0	5.7
1963	^{90}Sr pc/l	18.8	31.6	19.1	22	2 58.8	23.6	40.5	3 46.4	16.2	25	8.5	14.4
	Prec. ml	4.9	6.5	9.2	3.2	5.5	6.9	5.5	8.1	10.3	0.4	21	5.9
1964	^{90}Sr pc/l	8.9	28.2	28	5 36.7	35.9	4 37.6	12.1	64 1	5.4	6.6	4.9	5.3
	Prec. ml	11.7	7.4	6.5	12.9	1.4	6.7	10.6	0.6	4.3	4.4	6.5	10.6
1965	^{90}Sr pc/l	4.8	8.2	13	13	10.7	19.5	16.3	5.6	2.6	3.5	4.0	2.5
	Prec. ml	7.8	9.3	6.3	7.4	4	3.2	3.4	6.3	4.3	5.5	3.7	4.4

TABLE II-4

Removal of radionuclides by lime soda softening

Radionuclide	Removal (%)	Additions	Literature
^{137}Cs	0-20	—	99, 105-107
	> 80	with clay	107
^{60}Co	> 50	with clay	105, 107
^{106}Ru	about 50		105, 107
	about 80	with clay	107
rare earth's	> 90		99, 105-107
^{131}I	0-10		95
^{32}P	99		95

III. THEORY OF ION EXCHANGE (¹)

An important part of the work described in this report deals with the sorption of radionuclides by peat and chemically modified peat. Therefore a study was made of the ion exchange properties of peat, because the sorption of ions on peat and similar materials can be frequently interpreted exclusively in terms of an ion exchange mechanism. Before discussing the results it is therefore desirable to present first the fundamentals of the theory of ion exchange such as it will be applied to peat.

III-1. Ion exchange equilibria

When an ion exchanger is placed in a solution containing an ion which is different from that in the ion exchanger, a redistribution of the ions takes place over the solution and the ion exchanger according to:

$$b\,AR_a + aB^{b+} \rightleftharpoons a\,BR_b + b\,A^{a+} \qquad \text{(III-1)}$$

where AR_a and BR_b represent the ions A^{a+} and B^{b+} in the resin.

The concentration ratio of two competing counter ion species in the ion exchanger is usually different from that in the solution. As a rule the ion exchanger selects one species in preference to the other. This selectivity and its physical causes are of great practical and theoretical importance. However, since various hardly measurable phenomena affect the distribution of ions over both phases, such as swelling of the ion exchanger matrix, size and solvation tendency of the counter ions, ion pair formation and association, an adequate and quantitative description of ion exchange equilibria has been developed for only a few relatively simple cases. Whereas a quantitative description is already quite difficult for the chemically well-defined synthetic ion exchangers, it is not surprising that practically all attempts at describing ion exchange equilibria on a material as complex as peat were not very successful until now.

Nevertheless, it seems possible to interpret the ion exchange equilibria on the basis of a more or less simplified model (²) in a qualitative or semi-quantitative way. For that purpose the ion exchange resin will be presented as a network of elastic springs carrying ionic groups. When the resin swells, the network is stretched and exerts a pressure on the internal ‚pore' liquid. Swelling of the resin takes place as a result of the tendency of the fixed and mobile ions to form solvation shells, as a result of electrostatic interactions (adjacent fixed groups repel one another and thus tend to stretch the chains of the matrix) and because of the tendency of the highly concentrated solution inside the ion exchanger to take up additional solvent. Swelling equilibrium is attained when the elastic forces of the matrix balance the dissolution tendency of the fixed ionic groups. The extent of swelling depends on a number of factors, e.g. nature of the solvent (polar solvents give a higher swelling because they interact more strongly with the ions than do non-polar solvents), degree of crosslinking, capacity, nature of the fixed groups and of the counter ions (viz. size, valency and hydration), the extent of ion pair formation and association, and the concentration of the solution (resins in contact with a dilute solution are subjected to a high osmotic pressure difference and consequently tend to swell strongly).

All ions, except those attached to the matrix of the polymer can move freely in the inside (phase II) and outside solution (phase I). The negative charge of the ionized groups of the cation exchanger is compensated by cations in the surrounding solution. In contrast to the cation concentration, the concentration of anions in the inner solution as a rule is very small. Because the concentration differences of the counter ions and co-ions in both phases tend to level out by diffusion, an electrical potential difference establishes between both phases. This so-called ‚Donnan potential' pulls back cations into the ion exchanger and anions into the solution. Thus it is prevented that the existing concentration differences level out. The electrical potential difference between an ion exchanger and a dilute solution can attain very high values. However, since migration of just a few ions is sufficient to build up a strong electrical field, the deviation from electro-neutrality remains far below the detection limit of any analytical method. Consequently, for all practical purposes, the condition of electro-neutrality is still valid.

Equations concerning ion exchange equilibria are dictated by thermodynamics. At equilibrium the electro-chemical potential of a dissolved ionic species i must be the same in both phases:

$$(\eta_i)^{\mathrm{I}} = (\eta_i)^{\mathrm{II}} \tag{III-2}$$

or since $\eta_i = \mu_i + z_i \mathrm{F}\psi$

$$(\mu_i)^{\mathrm{I}} + z_i \mathrm{F}\psi^{\mathrm{I}} = (\mu_i)^{\mathrm{II}} + z_i \mathrm{F}\psi^{\mathrm{II}} \tag{III-2a}$$

where μ_i = chemical potential;
z_i = valency of species i;
F = Faraday constant;
ψ = electric potential.

For the solvent holds accordingly:

$$(\mu_S)^{\mathrm{I}} = (\mu_S)^{\mathrm{II}} \tag{III-3}$$

where μ_S = the chemical potential of the solvent.

The pressure dependency of the chemical potential is

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial V}{\partial x_i} = v_i \text{ (at } T = \text{constant)} \tag{III-4}$$

where G = free energy;
x_i = number of moles of species i;
P = pressure;
V = volume;
v_i = partial molar volume of species i.

Assuming that v_i is constant, which holds fairly well for solutions and defining the activity a_i of species i by:

$$\mu_i(P, m) = \mu_i^0(P) + RT \ln a_i$$

where $\mu_i(P, m)$ = the chemical potential of species i in a solution of molality m and under pressure P,

for the ‚swelling pressure' (π), which is the pressure difference between phase I and phase II, the following relation can be obtained:

$$\pi v_S = -RT \ln \frac{a_S^{\mathrm{II}}}{a_S^{\mathrm{I}}} \tag{III-5}$$

where v_S = partial molar volume of the solvent,
a_S = activity of the solvent.

It follows from Eq. III-5 that π increases with increasing a_S^{I}, consequently with decreasing salt content of the external solution.

A relation for the Donnan potential can be derived by developing Eq. III-2a:

$$E_{\text{Donnan}} = \psi^{\mathrm{II}} - \psi^{\mathrm{I}} = \frac{1}{z_i P}\left| RT \ln \frac{a_i^{\mathrm{I}}}{a_i^{\mathrm{II}}} - \pi v_i \right| \tag{III-6}$$

This equation holds for any mobile ionic species present in the system. Applied to a salt AY_a the following equation is obtained:

$$\left(\frac{a_A^{\mathrm{I}}}{a_A^{\mathrm{II}}}\right)^{1/a}\left(\frac{a_Y^{\mathrm{I}}}{a_Y^{\mathrm{II}}}\right) = \mathrm{e}^{\pi v_{AYa}/RT} = \left(\frac{a_S^{\mathrm{I}}}{a_S^{\mathrm{II}}}\right)^{v_{AYa}/v_S} \tag{III-6a}$$

and when applied to two cations A^{a+} and B^{b+} one obtains

$$\left(\frac{a_A^{\mathrm{II}}}{a_A^{\mathrm{I}}}\right)^{b}\left(\frac{a_B^{\mathrm{I}}}{a_B^{\mathrm{II}}}\right)^{a} = \mathrm{e}^{\pi(av_B - bv_A)/RT} \tag{III-6b}$$

Replacing in Eq. III-6b the activities by $C_i f_i$ leads to:

$$\ln\left[\frac{([A]^{\mathrm{II}})^b([B]^{\mathrm{I}})^a}{([A]^{\mathrm{I}})^b([B]^{\mathrm{II}})^a}\right] = \ln K_{A/B} = \ln\frac{(f_B^{\mathrm{II}})^a}{(f_A^{\mathrm{II}})^b} + \ln\frac{(f_A^{\mathrm{I}})^b}{(f_B^{\mathrm{I}})^a} + \frac{\pi(av_B - bv_A)}{RT} \tag{III-7}$$

Here $K_{A/B}$ refers to the so-called selectivity coefficient and $[A]$ and $[B]$ are the concentrations of A^{a+} and B^{b+} respectively and f_A and f_B their activity coefficients.

Eq. III-7 involves single activity coefficients and partial molar volumes of the ions. The former appear only as ratios, which are thermodynamically defined and the latter can be expressed in terms of partial molar volumes of the electrolytes AY_a and BY_b:

$$av_B - bv_A = av_{BY_b} - bv_{AY_a}$$

Relation III-7 reflects the various effects discussed before, i.e. swelling pressure effects appear in the third term, interactions with the co-ion in the solution in the second term and specific interactions in the ion exchanger appear in the first term. In the absence of all these effects $K_{A/B} = 1$. In that case only electrical selectivity for the counter ions is operative, which means that the ion exchanger prefers the counter ion with higher valency. This effect increases with dilution of the solution and is stronger with ion exchangers of high internal concentration.

In practice the actual preference of the ion exchanger frequently is expressed by the separation factor $\alpha_{A/B}$, which is defined as follows:

$$\alpha_{A/B} = \frac{[A]^{\mathrm{II}}[B]^{\mathrm{I}}}{[B]^{\mathrm{II}}[A]^{\mathrm{I}}} \tag{III-8}$$

In contrast to the selectivity coefficient the separation factor does not contain the ionic valencies as exponents. The two quantities are interrelated by:

$$(\alpha_{A/B})^a = K_{A/B}\left[\frac{[A]^{\mathrm{II}}}{[A]^{\mathrm{I}}}\right]^{a-b} \tag{III-9}$$

The relation III-9 shows that $\alpha_{A/B}$ becomes larger than $K_{A/B}$ if A^{a+} is the ion of higher valency, since $[A]^{\mathrm{II}}$ is as a rule higher than $[A]^{\mathrm{I}}$.

The effect of the swelling pressure term on $K_{A/B}$

The relative importance of the swelling pressure term on the selectivity is usually very small, because the differences in the partial equivalent volumes of the ions are, as a rule, of the order of only a few milliliters.

Even at a swelling pressure of several hundred atmospheres the contribution of this term to the selectivity coefficient rarely exceeds 0.01 ($R = 0.082$ liter atm. mole^{-1}).

However, the picture can become quite different when the solvation of the ions is explicitly taken into account. Assuming that the system behaves ideally (activity coefficient unity) except for solvation, Eq. III-7 simplifies to

$$\ln K_{A/B} = \pi(av_B^* - bv_A^*)/RT \tag{III-7a}$$

where v_A^* and v_B^* are the equivalent volumes of the solvated ions A^{a+} and B^{b+}.

Eq. III-7a may represent a very useful approximation in systems where solvation is the most important factor in the selectivity. The swelling pressure and the solvated volumes of the ions have to be known for this purpose. However, solvation of ions is thermodynamically ill-defined and swelling pressures are difficult to determine, expecially for ion exchangers of inhomogeneous structure. For ion exchange resins in which the degree of cross-linking can be varied without significant change of the structure and the weight capacity, the swelling pressure can be calculated from vapor-sorption isotherms. Such a situation is found in styrene type anion- and cation exchangers. The degree of cross-linking can be adjusted here in a relatively simple and reproducible manner by varying the amount of cross-linking agent (viz. divinyl benzene). It has been found with these ion exchangers that π is a linear function of the equivalent volume of the resin:

$$V_e = m\pi + n \tag{III-10}$$

Here V_e is the equivalent volume of the ion exchanger and m and n are empirical parameters which are independent of the ionic composition of the ion exchanger and of the relative humidity.

The determination of π for resins of inhomogeneous structure is much more difficult. Moreover it is quite doubtful if a simple relation like III-10 holds in that case.

In principle the Eq. III-5 can be used for the calculation of π. The solvent activities in the outside solution, a_S^{I}, and in the inside solution, a_S^{II}, have to be determined for this purpose. In general a_S^{I} can be calculated from the osmotic coefficients, which are tabulated for strong electrolytes, by means of

$$\ln a_S^{\mathrm{I}} = -\frac{\nu_{AY_a}\phi_{AY_a} m_{AY_a} M_w}{1000} \tag{III-11}$$

where ν_{AY_a} = the number of ions formed in the dissociation of AY_a;
ϕ_{AY_a} = the osmotic coefficient;
M_w = the molecular weight of water.

A similar equation can be defined for the internal solution:

$$\ln a_S^{\mathrm{II}} = -\frac{\phi \sum m_i^{\mathrm{II}} M_w}{1000} \tag{III-11 a}$$

in which the summation is carried out over all mobile species. The activity of the solvent in the internal phase (being water in our case) can be calculated by means of this relation, provided the osmotic coefficient is known. Unfortunately this factor cannot be determined, and it also cannot be predicted theoretically.

The effect of specific interactions in the ion exchanger on the selectivity

Frequently selectivity in ion exchange is not only caused by differences in solvation, but also by the formation of ion-pairs or even covalent bonds between the counter ions and the immobile ionic groups. These effects appear in the first term of Eq. III-7. In ion-pairs the interaction is electrical in nature. The ions approach each other so closely that they do not contribute anymore to the potential of the environment. Especially poorly hydrated cations and more atomic easily polarizable anions tend to enter in this kind of interactions. Thermodynamically, ion pairs are defined as poorly as the solvation of ions.

Covalent bonds can be formed between fixed groups in the ion exchanger, which have an unshared pair of electrons (e.g. amino-, imino-, keto-aldehyde-groups) and certain cations. Bond formation between weakly acidic groups (e.g. carboxylic and phenolic) and H^+-ions is a trivial example. The ion exchanger prefers the counter ion which forms the stronger ion-pairs or bonds with the fixed ionic groups.

As a result of the formation of ion-pairs and/or of covalent bonds between a metal ion and the fixed ionic groups of a weakly acid ion exchanger, a lowering of the charge of the ion exchanger takes place and because of that (disturbance of the dissociation equilibrium) a further dissociation of the weakly acidic groups can occur. As a matter of fact it concerns here a competition between metal ions and protons in specific bond formation. Interactions of this kind can be regarded as belonging exclusively to a third (solid) phase III.

At equilibrium the chemical potentials of species i in phase II and III are equal:

$$\mu_i^{\mathrm{II}} = \mu_i^{\mathrm{III}} \tag{III-12}$$

or

$$\mu_{0_i}^{\mathrm{II}} + RT \ln a_i^{\mathrm{II}} = \mu_{0_i}^{\mathrm{III}} + RT \ln a_i^{\mathrm{III}} \tag{III-12a}$$

Before anything definite can be said about the competition of metal-ions and protons in the ‚specific bond' formation, at first the stability coefficient of the binding of protons to the fixed groups in the ion exchanger has to be determined. This is possible by performing a titration of the material. Since the internal pH, ($\mathrm{pH}^{\mathrm{II}}$) has to be determined for this purpose, whereas only the external pH (pH^{I}) can be measured, it is necessary to perform the titration in the presence of an inert salt. It is then possible to calculate the internal pH by means of the Donnan theory, viz. from the distribution of the inert cations over both solution phases ([3, 4]). The method has been worked out for a weakly acidic ion exchanger (e.g. peat) below.

Assuming that no specific interactions take place between Na^+-ions and the fixed groups of the ion exchanger, and that in the Eqs. III-6 and III-6b concentrations rather than activities may be used, one obtains (upon neglecting the swelling pressure term)

$$\frac{[\mathrm{Na}^+]^{\mathrm{II}}}{[\mathrm{Na}^+]^{\mathrm{I}}} = \frac{[\mathrm{H}^+]^{\mathrm{II}}}{[\mathrm{H}^+]^{\mathrm{I}}} = \frac{[\mathrm{Cl}^-]^{\mathrm{I}}}{[\mathrm{Cl}^-]^{\mathrm{II}}} = \lambda \tag{III-13}$$

where the brackets refer to the concentration (in meq/kg) and

$$\lambda = \mathrm{e}^{(\psi^{\mathrm{II}} - \psi^{\mathrm{I}})/RT}$$

In addition, since both phases must be almost electrically neutral:

$$[\mathrm{Na}^+]^{\mathrm{I}} + [\mathrm{H}^+]^{\mathrm{I}} = [\mathrm{Cl}^-]^{\mathrm{I}} + [\mathrm{OH}^-]^{\mathrm{I}} \tag{III-14a}$$

$$[\mathrm{Na}^+]^{\mathrm{II}} + [\mathrm{H}^+]^{\mathrm{II}} = S(1-\theta)/v + [\mathrm{Cl}^-]^{\mathrm{II}} + [\mathrm{OH}^-]^{\mathrm{II}} \tag{III-14b}$$

where S = the total amount of sites in the ion exchanger which are capable of splitting off a proton (meq/kg);
θ = the fraction of the sites being occupied by a proton and;
v = the amount of water in the internal phase (kg/kg).

Furthermore the material balances for Na^+ and Cl^- give:

$$a(p+q) = (a-v)\,[\mathrm{Na}^+]^{\mathrm{I}} + v[\mathrm{Na}^+]^{\mathrm{II}} \tag{III-14c}$$

$$ap = (a-v)\,[\mathrm{Cl}^-]^{\mathrm{I}} + v[\mathrm{Cl}^-]^{\mathrm{II}} \tag{III-14d}$$

where p = the concentration of NaCl in the starting solution (meq/kg);
q = the concentration of NaOH in the starting solution (meq/kg);
a = the amount of water in the starting solution per weight quantity ion exchanger.

When only solution of $\mathrm{pH} < 9$ are considered, the OH^--concentrations in the Eqs. III-14a and III-14b can be neglected.

Eliminating $[\mathrm{Cl}^-]^{\mathrm{I}}$, $[\mathrm{Cl}^-]^{\mathrm{II}}$, $[\mathrm{Na}^+]^{\mathrm{I}}$, $[\mathrm{Na}^+]^{\mathrm{II}}$ from the Eqs. III-13, III-14a, III-14c and III-14d one obtains:

$$a(p+q) = \left[\frac{ap}{v\frac{[H^+]^{I}}{[H^+]^{II}}+(a-v)} - [H^+]^{I}\right]\left[v\frac{[H^+]^{II}}{[H^+]^{I}}+(a-v)\right] \qquad \text{(III-15)}$$

and since $v\frac{[H^+]^{I}}{[H^+]^{II}}$ is negligible compared with $(a-v)$:

$$[H^+]^{II} = \frac{a-v}{v}[H^+]^{I}\left[\frac{aq+(a-v)[H^+]^{I}}{ap-(a-v)[H^+]^{I}}\right] \qquad \text{(III-16)}$$

Further it follows from Eqs. III-14a and III-14d:

$$S(1-\theta) = aq+v[H^+]^{II}+(a-v)\,[H^+]^{I} \qquad \text{(III-16a)}$$

Combination of the Eqs. III-16 and III-16a and neglecting the term $v|H^+|^{II}$, which is usually very small, results in

$$[H^+]^{II} = \frac{S(1-\theta)}{ap-(a-v)[H^+]^{I}}\,\frac{(a-v)}{v}[H^+]^{I} \qquad \text{(III-17)}$$

In the case of peat the term $(a-v)\,[H^+]^{I}$ can be neglected compared with ap, provided ap is not very small (viz. <0.01 meq) and $pH^{I}>4.5$.

Consequently Eq. III-17 reduces to:

$$[H^+]^{II} = \frac{a-v}{v}[H^+]^{I}\,\frac{S(1-\theta)}{ap} \qquad \text{(III-17a)}$$

It will be evident that at the same degree of ionization but at different NaCl-concentrations, the same value of $[H^+]^{II}$ should always be found. As a consequence all titration curves should coincide when plotted on a $S(1-\theta)$ versus pH^{II} scale.

The assumption of complete absence of specific interactions between Na^+-ions and the fixed ionic groups of the ion exchanger (e.g. peat) is somewhat questionable, but even there is some specific interaction it certainly will be relatively small. Some association or ion-pair formation of alkali metal ions with carboxyl groups has been postulated to take place ([5]), especially at higher degree of dissociation, and decreasing in the sequence $Li^+>Na^+>K^+$. An indication for this is found also in the mean activity coefficients of alkali metal acetates, which decrease in the sequence $K^+>Na^+>Li^+$. The same sequence holds for the solubility of the salts of dicarboxylic acids of these cations.

The replacement of activities by concentrations in Eq. III-13 means in fact that a constant ratio of activity coefficients of the ions in phase I and phase II is presumed. Since the activities of the ions in phase II cannot be measured by any method this assumption cannot be verified experimentally.

In the same way an equation can be derived when $CaCl_2$ is present as neutral salt, viz.

$$[H^+]^{II} = [H^+]^{I}\sqrt{\frac{a-v}{v}\,\frac{S(1-\theta)}{as-(a-v)[H^+]^{I}}} \qquad \text{(III-18)}$$

where s = the concentration of $CaCl_2$ in the starting solution (meq/kg).

Once the relationship between pH^{II} and $S(1-\theta)$ is known, the problem consists of further evaluation of Eq. III-12. Considering the case of a polyacid which contains n identical and independent acid groups, it can be shown by a statistical treatment ([6]) that the activity of H^+-ions in the polyacid may be equated to $\theta/(1-\theta)$.

This leads to the following dissociation relation:

$$pK_a = pH-\log\frac{1-\theta}{\theta} \qquad \text{(III-19a)}$$

where $$K_a = \frac{\mu^{\mathrm{II}}_{0_{\mathrm{H}^+}} - \mu^{\mathrm{III}}_{0_{\mathrm{H}^+}}}{RT}$$

This equation holds for a polyacid of which K_a is independent of the degree of ionization. However, this is never actually so for polyacids, because as a rule K_a increases with θ.

The variation of K_a is caused mainly by electrostatic interactions; in fact the acid groups do not dissociate independently. Therefore electrostatic effects have to be taken into account in the dissociation equation ([7, 8]). However, this leads to quite complicated equations, which are only applicable to a few well-defined polyacids.

Frequently an empirical relation is applied for the description of the titration behaviour of polyacids, viz. ([4, 9–13]).

$$\mathrm{pH}^{\mathrm{I}} = pK_m + n \log \frac{1-\theta}{\theta} \qquad \text{(III-19b)}$$

where K_m and n are empirical parameters.

The Eq. III-19b is known as the modified Henderson-Hasselbalch equation. The parameters K_m and n are strongly dependent on experimental conditions, e.g. polyacid concentration, base used in the titration and the nature and the concentration of the neutral salt. Nevertheless frequently the titration curves of polymeric acids can be fitted reasonably well by this equation. This has also been suggested with respect to the titration curves of humic acids (e.g. [14–17]). However, since only a relatively short part of the titration curve can be fitted, the application of this equation seems to be of little if any value. Peat is a very complex material; at least two kinds of acid groups are present. The derivation of a theoretical dissociation relationship for such a material seems to be wishful thinking.

As mentioned before, the net result of specific interactions of metal ions with the fixed ionic groups is a further dissociation of the acid groups in the (weakly acid) ion exchanger, consequently a decrease of pH.

When the dissociation of the polymeric acid can be described by a constant 'dissociation constant', the method of Bjerrum would offer a means for the calculation of the stability constant of a metal-complex with this acid from the occurring pH-shift ([18]). However, the method cannot be applied in a simple manner, since in general K_a varies with θ and acid groups are withdrawn from the dissociation equilibrium. Additional assumptions have to be made in order to be able to calculate the concentration of the dissociated acid groups (see Chapter VI).

Another difficulty arises in the definition of the stability coefficient of the complex ([19–21]).

According to the reactions

$$\mathrm{A}^{2+} + \mathrm{RH} \rightleftharpoons \mathrm{AR}^+ + \mathrm{H}^+$$

$$\mathrm{AR}^+ + \mathrm{RH} \rightleftharpoons \mathrm{AR}_2 + \mathrm{H}^+$$

an overall complex constant can be defined as follows:

$$K_b = \frac{[\mathrm{AR}_2]\,[\mathrm{H}^+]^2}{[\mathrm{A}^{2+}]\,[\mathrm{RH}]^2} \qquad \text{(III-20)}$$

where RH represents a polymer unit carrying an acid group in H-form. However, with polymeric acids the situation is less simple, because the second reaction takes place independently, at least to some extent, of the overall concentration of RH. Therefore, the polymeric acid can be represented better as consisting of dibasic units (of $\mathrm{R}_2\mathrm{H}_2$). The reaction then becomes

$$\mathrm{A}^{2+} + \mathrm{H}_2\mathrm{R}_2 \rightleftharpoons \mathrm{AR}_2 + 2\mathrm{H}^+ \qquad \text{(III-21)}$$

which gives for the stability constant* the following equation:

$$K_c = \frac{[AR_2][H^+]^2}{[A^{2+}][H_2R_2]} \qquad \text{(III-22)}$$

Accordingly for trivalent cations tribasic units may be assumed.

A further discussion of this matter will be presented in Chapter VI in connection with the experimental data.

III-2. **Ion exchange equilibria involving trace components**

A comparatively simple situation is encountered when one counter ion species predominates and the others are present only as tracers. In that case the ion exchanger phase and the solution do not alter considerably during the ion exchange process. Furthermore, the exchange of trace quantities is only covered by a short section of the ion exchange isotherm near the origin. The ion exchange isotherm gives, for example, the equivalent ionic fraction of A in the ion exchanger (Y_A) as a function of the equivalent fraction of A in the solution (X_A). This short section of the isotherm may be considered as linear, if A is a trace component. Consequently

$$q_{A/Q} = Y_A = K_d C_A/C_t = K_d X_A \qquad \text{(III-23)}$$

where q_A = the concentration of A in the ion exchanger (meq/ml);
Q = total concentration of cations in the ion exchanger (meq/ml);
C_A = concentration of A in the solution (meq/l);
C_t = total concentration of cations in the solution (meq/l);
K_d = proportionality factor (being the slope of the isotherm near the origin), which is known as the distribution factor.

At low concentrations of A the distribution coefficient is almost independent of the concentration of A. It further decreases in magnitude at increasing concentration of the macrocomponent B.

In case of radioisotopes the concentrations are frequently presented in μCi/ml or in μCi/g and consequently the distribution coefficients as

$$K_d^* = \frac{(\mu\text{Ci/g})_{\text{ion exchanger}}}{(\mu\text{Ci/ml})_{\text{solution}}}$$

or

$$K_d' = \frac{(\mu\text{Ci/ml})_{\text{ion exchanger}}}{(\mu\text{Ci/ml})_{\text{solution}}}$$

Since by a close approximation

$$\begin{aligned} q_A + q_B &= q_B \simeq Q \\ C_A + C_B &= C_B \simeq C_t \end{aligned} \qquad \text{(III-24)}$$

the relation for the selectivity coefficient (see Eq. III-7)

$$K_{A/B} = \left[\frac{q_A}{C_A}\right]^b \left[\frac{C_B}{q_b}\right]^a \qquad \text{(III-25)}$$

can be written

$$K_{A/B} = (K_d')^b \left[\frac{C_t}{Q}\right]^a \qquad \text{(III-26)}$$

---

* Theoretically this coefficient is the stability constant but because a constant value is an exception in ion exchange equilibria the indication stability coefficient is preferred.

In logarithmic form $\log K_d' = 1/b \log K_{A/B} + a/b \log Q - a/b \log C_t$ (III-27)

When $K_{A/B}$ and Q remain constant, a plot of $\log K_d'$ versus $\log C_t$ must result in a straight line with slope $-a/b$.

III-3. **Kinetics of ion exchange**

In judging the applicability of an ion exchanger the kinetical aspects always have to be considered. It is obvious that the usefulness of an ion exchanger reduces to zero even in the case of a pronounced selectivity, when the rate of the process becomes extremely small.

Although a chemical reaction can occasionally be the rate determining step, ion exchange as a rule is purely a diffusion phenomenon. As a consequence of the electro-neutrality requirement, ion exchange is inherently a stoichiometric process. The fluxes of the exchanging counter ions are equal in magnitude, even when the mobilities of the ions are quite different. This is because the fluxes are electrically coupled.

In fact three rate determining steps can be distinguished, viz.

1. interdiffusion of the counter ions within the ion exchanger (Particle diffusion),
2. interdiffusion of the counter ions in the adherent films (Film diffusion),
3. chemical reaction.

In ideal particle diffusion control (no concentration differences in the film) the exchange flux is approximately proportional to the concentration of the fixed charges and to the interdiffusion coefficient in the beads and is inversely proportional to the bead radius; on the other hand it is independent of the film thickness, solution concentration and diffusion coefficients in the film. In ideal film diffusion control (concentration gradients only in the film) the flux is proportional to the solution concentration and the interdiffusion coefficient in the film and inversely proportional to the film thickness. However, it is independent of the fixed charge concentration, interdiffusion coefficient in the bead and bead radius. Film diffusion may prevail in systems of high ionic concentration of fixed ionic groups, with low degree of crosslinking, with particles small in size, with dilute solutions and with inefficient agitation.

Rate laws of ion exchange

In the derivation of rate laws complications arise from diffusion-induced electric forces (no constant diffusion coefficient), selectivity, specific interactions and changes in swelling. As a consequence non-linear differential equations and boundary conditions are obtained.

Well-developed theories are available for isotopic exchange (e.g. exchange in a system in equilibrium except for isotopic distribution) and for exchange of traces of a counter ion in the presence of a large excess of another ion; most of the complicating factors are then absent.

In the ion exchange of traces a linear equilibrium relationship holds, since only the linear part of the exchange isotherm close to the origin is used:

$$Y_A = K_d X_A \qquad \text{(III-23)}$$

or

$$q_A = K_d' C_A$$

where

$$K_d' = K_d \frac{Q}{C_t}.$$

The proportionality factor K_d (distribution coefficient) is dependent on the concentration of the macro component.

For spherical particles the following differential equation must be solved:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\mathbb{D}\, r^2 \frac{\partial \eta}{\partial r}\right) = \frac{\partial \eta}{\partial t} \qquad \text{(III-28)}$$

where

η = the relative concentration of A in the particle at a distance r from the center and at time t, as compared to the equilibrium concentration C_A^∞;

$\eta = \dfrac{C_{A\,(r,\,t)}}{C_A^\infty}$

r = radial space co-ordinate;

$\overline{\mathbb{D}}$ = diffusion coefficient in the particle.

The ion exchange between the solution and the interface of the ion exchanger can be described by a mass transfer coefficient k.

The differential equation can be solved under the following initial and boundary conditions:

$$\begin{array}{lll} t=0 & 0 \leqslant r < r_0 & \eta = 0 \\ t \geqslant 0 & r = 0 & \eta \neq \infty \\ t \geqslant 0 & r = r_0 & k\, C_A^\infty(\bar{x}-\bar{x}_w) = \mathbb{D}\, q_A^\infty \dfrac{\partial \eta}{\partial r} \end{array} \qquad \text{(III-29)}$$

where $\bar{x}$ = mean dimensionless concentration of A in the solution, viz.; $\bar{x} = C_A/C_A^\infty$;

q_A^∞ = equilibrium concentration of A in the ion exchanger;

$\bar{x}_w$ = the value of $\bar{x}$ at the interface;

r_0 = radius of the bead.

Assuming that $\overline{\mathbb{D}}$ is independent of η or r and that a linear equilibrium relation holds (e.g. Eq. III-23) the following solution is obtained (22)

$$1 - y = \sum_{i=1}^{i=\infty} \frac{6}{\beta_i^3} \frac{(\sin\beta_i - \beta_i \cos\beta_i)^2}{\beta_i - \sin\beta_i \cos\beta_i}\, e^{-\beta_i^2 \overline{\mathbb{D}}\, t/r_0^2} \qquad \text{(III-30)}$$

where $\beta_i \cos\beta_i = 1 - k r_0/\overline{\mathbb{D}}\, K_d'$, and $y = q_A/q_A^\infty$.

From Eq. III-30 it follows that y is a function of two dimensionless parameters $\overline{\mathbb{D}}t/r_0^2$ and $kr_0/\overline{\mathbb{D}}K_d$. This function is tabulated in the literature for the various values of

$$kt/K_d' r_0 (= \overline{\mathbb{D}}\, t/r_0^2 \times k r_0/\overline{\mathbb{D}}\, K_d') \text{ and } k r_0/\overline{\mathbb{D}}\, K_d'.$$

If $kr_0/\overline{\mathbb{D}}K_d{}' = 0$ (film diffusion control), the following simple solution is obtained:

$$1 - y = e^{-3kt/r_0 K_d'} \qquad \text{(III-31)}$$

Description with an overall mass transfer coefficient

In principle the use of an overall mass transfer coefficient is not possible, because in that case at all values of the factor $kr_0/\overline{\mathbb{D}}K_d{}'$ the following relation would describe the process:

$$1 - y = e^{-3Kt/r_0 K_d'} \qquad \text{(III-32)}$$

Consequently a linear relationship should always hold between $\log(1-y)$ and $3Kt/r_0 K_d{}'$. This is not the case. However, after a sufficiently long period of time only the first term of β_i in

Eq. III-30 is still important. The following then holds:

$$\frac{\mathrm{d}\ln(1-y)}{\mathrm{d}t} = -\beta_1^2\,\bar{\mathbb{D}}/r_0^2 \tag{III-33}$$

This equation represents a linear relationship between $\ln(1-y)$ and t. Consequently an overall mass transfer coefficient can then be used.

The overall mass transfer coefficient is composed of partial mass transfer coefficients in the particle (k_p) and in the solution (k). In case of a linear equilibrium relationship the relation between K, k and k_p is given by:

$$\frac{1}{K} = \frac{1}{k} + \frac{1}{K_d' k_p} \tag{III-34}$$

The Eqs. III-32, III-33 and III-34 can be combined to:

$$\frac{k}{k_p K_d'} = \frac{3kr_0}{\beta_1^2\,\bar{\mathbb{D}}\,K_d'} - 1 \tag{III-35}$$

It has been shown that this equation can be approximated by:

$$\frac{1}{k_p} \simeq \frac{1}{3.5}\,\frac{r_0}{\bar{\mathbb{D}}} \tag{III-36}$$

so that the overall mass transfer coefficient becomes:

$$K \simeq k\left(1 - \frac{2kr_0}{7\,\bar{\mathbb{D}}\,K_d'}\right)^{-1} \tag{III-37}$$

The mass transfer coefficients in both phases are about equal in magnitude at $kr_0/\bar{\mathbb{D}}k_d' \simeq 3.5$, or according to Glueckauf (^{23}) at

$$\frac{kr_0}{\bar{\mathbb{D}}\,K_d'} \simeq 8.$$

For column operations the mass transfer coefficient in the external solution is quite important. It can be calculated by means of the relation of Thoenes (^{24}):

$$\frac{2kr_0}{\mathbb{D}} = 1.0\left(\frac{v_0 d_p}{(1-\varepsilon)\,\nu\gamma}\right)^{1/2}\left(\frac{\nu}{\mathbb{D}}\right)^{1/3} \tag{III-38}$$

or $\mathrm{Sh} = 1.0\,(\mathrm{Re}_p)^{1/2}\,(\mathrm{Sc})^{1/3}$

where v_0 = velocity of the solution as related to the empty column;
ν = kinematic viscosity of the solution;
Sh = $2kr_0/\mathbb{D}$ = Sherwood number;
Re_p = $v_0 d_p/(1-\varepsilon)\gamma\nu$ = Reynolds number;
Sc = $\nu/\mathbb{D}$ = Schmidt number;
γ = a form factor (external surface area = $\pi d_p^2 \gamma$).

Eq. III-38 can be applied to a packed bed with a porosity $0.25<\varepsilon<0.50$ and in the region $40<\mathrm{Re}_p<2.10^3$ and $\mathrm{Sc}<4\,000$. At $\mathrm{Re}_p<1$ the following equation can be applied:

$$\mathrm{Sh} = 1.26\,\mathrm{Re}^{1/3}\,.\,\mathrm{Sc}^{1/3} \tag{III-39}$$

III-4. **Ion exchange in columns**

Ion exchangers are applied as a rule in columns. In column operation the capacity of the ion exchanger is effectively used, whereas also a complete removal of ions from solutions can be achieved easily.

However, the mathematical treatment of column processes is difficult and until now no rigorous quantitative theory is available. Nevertheless various approaches have been presented which can be used to find the optimum conditions operation.

A rather rigorous solution has been presented by Rosen (^{25}). His solution is based on the rate Eqs. III-30 and III-31 and holds for linear equilibria. The effect of longitudinal diffusion was not included. Furthermore a constant interdiffusion coefficient was assumed, which holds in fact only for isotopic exchange and exchange involving traces.

The relative concentration x of the ion in the effluent solution is given as a function of three dimensionless parameters:

$$x = f\left(\frac{k\bar{S}z}{v_0}, \frac{kr_0}{\mathbb{D}K'_d}, \frac{\varepsilon(v_f t - z)}{K'_d(1-\varepsilon)z}\right) \tag{III-40}$$

where $\bar{S}$ = surface area of the ion exchanger per unit bed volume $(= 6(1-\varepsilon)\gamma/d_p)$;
v_f = linear flow velocity in the packed bed;
ε = porosity;
z = height of the column.

The function III-40 has been calculated by computer and is tabulated in the literature for various values of the dimensionless parameters (^{26}).

When the process is described with an overall mass transfer coefficient K a solution for x is found, being dependent on two dimensionless parameters (Schumann (^{27})), e.g.

$$x = f\left(\frac{K\bar{S}z}{v_0}, \frac{\varepsilon(v_f t - z)}{K'_d(1-\varepsilon)z}\right) \tag{III-41}$$

Function III-41 holds for a linear equilibrium relation. Like III-40 it has been calculated by computer (^{28}).

In case of a sharp boundary 50% breakthrough takes place at about

$$\frac{\varepsilon(v_f t - z)}{K'_d(1-\varepsilon)z} \simeq 1 \tag{III-42}$$

Sharp boundaries are obtained at large values of the column capacity parameter $N(= K\bar{S}z/v_0)$, viz. $N > 50$. In that case III-41 can be approximated by:

$$x = \tfrac{1}{2}[1 + \mathrm{erf}\,(\sqrt{\zeta} - \sqrt{N})] \tag{III-43}$$

where

$$\zeta = \frac{v_0 t - z}{(1-\varepsilon)\,K'_d v_0/K\bar{S}}$$

The Eqs. III-40, III-41 and III-43 can be applied to the description of breakthrough curves obtained with peat columns in the removal of radionuclides from aqueous solutions, because a linear equilibrium relation is valid there.

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IV. EXPERIMENTS WITH NATURAL PEAT SAMPLES

IV-1. **Introduction**

IV-1-1. GENERAL INTRODUCTION

To consider the possible application of peat for the purification of water which is contaminated with radioactive compounds, first of all information is required about the sorption capacity of peat for radioisotopes in relation to the cations which are usually present in the water. Furthermore the physical, chemical and mechanical properties of peat have to be considered with respect to such an application. The organic matter of peats consists of a mixture of partially decomposed plant and animal residues, together with substances synthesized from breakdown products, generally referred as "humus". Humus represents the main component of peat responsible for the sorption of cations. Humus, an amorphous brown or black product, can be divided into fractions differing in solubility in sodium hydroxide, water, alkalis, acids and organic solvents. The term humic acids is, as a rule, used for the portion of humus which is soluble in a dilute sodium hydroxide solution and which will be precipitated by acidification of the alkali extract. The fraction which remains in solution after acidification, is frequently denoted with the term "fulvic acids". This fraction includes, together with low molecular weight humic acids, also relatively simple compounds such as carbohydrates, phenols, aminoacids, etc. The term "humins" refers to the fraction of humus being insoluble in dilute (cold) NaOH; part of the humins is soluble in hot dilute NaOH. The various compounds of humus, which can be simply defined as polycondensates or polymers of the polyphenol type, differ greatly in degree of polymerization. Within the various fractions wide differences exist also in the number, the type and arrangement of active groups such as phenolic and carboxylic acid groups, methoxy and amino groups. Due to the big variety of such arrangements formed under various natural conditions from materials of different origin, it is impossible to present one characteristic formula or to characterize them by molecular weight.

Under natural conditions the composition, the physical and chemical properties of peat will alter continuously and in an irreversible way, due to natural degradation processes. Change brought about in composition, in chemical and physical properties by the action of chemical agents like acids and alkali also can not be restored.

With respect to the amount of humic acids which can be extracted from peat with alkali several factors are important, including composition and salt content of the solution, cation occupation of the peat, time of contact, procedure applied in the extraction etc. Moreover, the character of dissolved humic acids may alter to some extent during extraction.

Since humic acids contain a large number of reactive groups, such as phenolic hydroxyl, methoxyl, carboxylic, amino and other groups, electrostatic as well as specific interactions (covalent bonds) may be involved in the binding of metal ions to peat.

It is well-known in the chemistry of metal-chelate compounds that covalent bonds are frequently formed between electron donors and metal ions of the transition series ([1]). The chelates of the alkaline earth metal ions however, are predominantly ionic in nature. Irrespective of the ligand involved, it has been shown by Mellor and Maley ([2]) that the stability constants of metal chelates decrease in the sequence:

$$\mathrm{Pd} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Fe} > \mathrm{Mn} > \mathrm{Ca} > \mathrm{Ba}$$

The series is known as the Irving-Williams series.

Various techniques have been used in the study of the interaction of metal ions with humic acids, viz. potentiometric titration of humic acids in solutions of different composition ([3–11, 28]), electrophoresis ([12–18]), electro-dialysis ([19]), flocculation ([5, 18, 20]), infrared spectrometry ([13, 21, [23, 24]) and ion exchange methods ([9, 25–28, 30]). In general it is well accepted now that specific interactions play a predominant part in the binding of the higher valence metal ions to humic acids. Otherwise still much has to be solved. Concerning the stability of the compounds formed, sometimes the Irving Williams series seems to hold ([3–6, 29]), but strongly different series of stability have also been observed ([30]). Most authors agree that the interaction between humic acids and alkaline and alkaline earth ions is predominantly electrostatic in nature. In the binding of the transition metal ions to humic acids, however, also covalent bonds may be involved. Very little information is available about the interaction of the rare earth elements with humic acids. However, since these elements form stable complexes with poly-basic organic acids and amino-poly-acetic acids ([32]), it is likely that these elements also form stable complexes with humic acids.

In view of the above and of studies made concerning the sorption of various radioisotopes on peat and/or humic acids e.g. of radiostrontium ([19, 26, 33–37]), of radiocesium ([34–36]), of radiocerium ([28, 33–36]), of radiocobalt ([32, 34, 38]) of radioruthenium ([33, 36, 39]) and of uranium and radium ([16, 22, 31, 33]), peat may represent an attractive sorbent for application in the decontamination of water contaminated with radioactive isotopes.

IV-1-2. MATERIALS USED

The investigations were carried out with a number of peat samples of different origins collected from several locations in the Netherlands*.

The exchange sites of natural peat are, as a rule, occupied by various cations such as H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+} and others. Moreover, soluble and/or insoluble salts may also be present in the peaty soils.

The presence of these compounds hampers the interpretation of the sorption results seriously. For this reason the peat samples were treated with a 2N HCl solution (20 g peat per liter HCl-solution). By means of this treatment all exchangeable metal ions are replaced by H^+-ions. Moreover, the soluble salts which may be present are removed from the material. After the treatment with the HCl-solution the peat was washed thoroughly with demineralized water until it was free of HCl. Subsequently the material was dried in air. The peat thus prepared is referred to as H-peat. Small amounts of metal ions (e.g. of Al and Fe) not removed from the peat sample by means of this treatment are present in unexchangeable form and, consequently do not interfere.

In a similar way a "Ca-peat" was prepared, viz. by bringing the peat into contact with a 2N calcium-acetate solution (during 24 hours). This treatment has only been applied to the moor-peat, which in its natural state is almost completely in H-form (viz. 140.5 meq H/100 g, 8.4 meq Ca/100 g, 8.3 meq Mg/100 g, 1.4 meq K and Na/100 g) and does not contain any appreciable amount of soluble or insoluble salts. After the treatment the peat was washed with demineralized water until the washwater was free of calcium. Subsequently the material was dried in air. The designation Ca-peat requires some further explanation, because it does not mean that all exchange sites in the material are occupied by Ca-ions. This is only true for those acid groups in the peat which are dissociated at the applied end-pH of the solution, which is about 6.5. The acid groups which dissociate at higher pH are still in H-form after the treatment.

Some data about the peat samples are summarized in Table IV-1.

IV-1-3. EXPERIMENTAL

The sorption of radioisotopes on peat was studied by means of slurry tests as well as column experiments. The following procedure was applied in the slurry tests, unless cited otherwise.

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* Obtained through kind co-operation with the "Instituut voor Bodemkartering" in Alphen a/d Rijn.

Portions of 50 ml of the radioactive solution were pipetted in polythene bottles of 100 ml. Subsequently a known amount of 0.1 N NaOH was added to the solution, whereupon the solution was made up to 55 ml with demineralized water. Then 110 mg of the peat sample was immersed into the solution after which the bottle was closed and shaken for 20-24 hours. Such a contact-time suffices for the equilibration of suspensions of end-pH 6 (pH^1) and lower, because any change in pH does not take place on continuation of shaking. However, this is not true for suspensions which have an end-pH higher than 6.5 after 24 hours shaking; in those cases a further slight decrease of the pH takes place upon continuation of shaking, especially in the pH-region 7.0-8.5. Nevertheless also these experiments have been analysed after 24 hours.

After shaking, the peat was separated from the suspension by filtration over a S & S-filter 1575 or occasionally by centrifuging, viz. in the experiments with ^{60}Co. In the filtrate the radioactivity (comp. § IV-1-4) and pH were determined, the latter potentiometrically by using a Philips pH-meter type RP 9600. The concentration of the competing cations Ca, Mg, was determined by complexometric titration and/or by flame photometry.

Column experiments were performed in the arrangement shown in Fig. IV-1. Details about these experiments are discussed in the relevant chapter.

The sorption of radiostrontium has been investigated with all peat samples mentioned in Table IV-1. The sorption of other radioisotopes has been investigated exclusively with moor peat (sample 1).

IV-1-4. MEASUREMENT OF THE RADIOACTIVITY

In all experiments, except some column experiments, γ-emitting radioisotopes have been used and thus not always the radioisotopes which can really be expected in contaminated surface water. This is done because the measurement of γ-radiation can be accomplished, as a rule, more conveniently than of β-radiation. The measurement of the activity of γ-emitting radioisotopes was carried out in a well type sodium iodide (thallium activated) scintillation detector using a single channel analyser; the assembly was equiped with a sample changer. As a rule a series of samples were counted overnight. Counting times of 5-30 minutes were used, depending on the activity of the samples so that the error due to statistical variations never exceeded 2%.

Unless cited otherwise, in the experiments discussed in this study, carrier free solutions of the various isotopes were used, as a rule in a concentration of 5.10^{-3} μCi/ml. In pure carrier free solutions the weight quantity in g of the radioisotopes per liter of the solution (G) can be calculated with the formula:

$$G = 8.85 . M . t_h . c . 10^{-20}$$

where M = the atomic weight;
t_h = half life in seconds;
c = concentration in μCi/ml.

The concentration in ppm for carrier free solutions of 5.10^{-3} μCi/ml of the various isotopes can be specified as follows;

Concentration (ppm) for solutions of specific activity 5.10^{-3} μCi/ml

^{90}Sr	^{89}Sr	^{85}Sr	^{90}Y	^{137}Cs	^{144}Ce	^{106}Ru	^{131}I	^{60}Co	^{54}Mn
$3.6.10^{-8}$	$1.7.10^{-10}$	$2.1.10^{-10}$	$9.2.10^{-12}$	$5.8.10^{-8}$	$1.6.10^{-9}$	$1.5.10^{-9}$	4.10^{-11}	$4.5.10^{-9}$	6.10^{-10}

Actually the commercial supplied carrier free solutions may contain a quantity 100 to 1000 times that calculated for pure carrier free solutions, because of the addition of a small amount of carrier by the manufacturer in order to reduce wall adsorption effects. However, for the experiments discussed in this thesis the influence of these concentrations can also be neglected.

For instance precipitation of hydroxides does not take place at any pH below 7 at these concentrations.

In some column experiments the *β-emitting* ^{89}Sr has been used *in* stead of ^{85}Sr. The activity of ^{89}Sr in the solution was then continuously measured by passing the solution through a flow-through cell, which was packed with grains of anthracene. The cell was combined with a fotomultiplier + preamplifier; they were enclosed in a light-tight box. Although the activity of ^{89}Sr could be measured conveniently and accurately in this way, the method was not very satisfactory on the long run, mainly because of clogging of the cell by materials present in the effluent of the column. This was frequently accompanied by some accumulation of ^{89}Sr in the cell. For this reason ^{85}Sr was used in later column experiments. In a few preliminary experiments ^{90}Sr in equilibrium with its radioactive daughter ^{90}Y was used. The ^{90}Sr adsorption is found by comparing the initial activity, measured in a liquid GM-counter, with that of the supernatant after three weeks storage, which is necessary to allow ^{90}Y to grow to equilibrium. The ^{90}Y sorption is found from the activity increase during this storage by using the predetermined counting efficiency of the liquid GM-counter.

IV-2. **Results**

IV-2-1. THE SORPTION OF RADIOSTRONTIUM

The sorption of radiostrontium has been investigated in relation to pH and the concentration of Ca- and Mg-ions of the solution. Carrier free ^{85}Sr, present in the solution in a concentration of 5.10^{-3} μCi/ml, was used in these experiments. In addition to Ca or Mg always 5 meq Na/l (added as NaCl and Na_2SO_4) was present in the starting solution.

IV-2-1-1. *Slurry tests* (peat in H-form)

The competing action of Ca-*ions*

The results of experiments carried out with ^{85}Sr-Ca solutions are shown in Figs. IV-2–IV-6. In these figures the relative concentration of strontium and calcium has been plotted versus the end-pH of the solution.

These graphs show clearly the strong influence of the pH on the sorption of ^{85}Sr and Ca. Moreover, it appears from the relative positions of the curves of ^{85}Sr and of Ca that both elements behave almost identically; the sorption of ^{85}Sr is slightly better at low pH and the sorption of Ca slightly better at high pH.

Since the absolute concentration of Sr is small relative to the Ca-concentration and since Ca-ions are strongly preferred by the peat in stead of Na-ions (see paragraph IV-2-4), the exchange capacity of the peat can be calculated roughly from the amount of Ca which is removed from the solution. Appreciable deviations from the actual capacity (i.e. total amount of exchangeable cations per weight quantity peat) are only found when the Ca-concentration of the solution becomes very small (consequently at low Ca-concentrations of the starting solution and/or at high end-pH). The separation factor $\alpha_{Sr/Ca}$ can be calculated with (see Eq. III-9)

$$\alpha_{Sr/Ca} = \sqrt{K_{Sr/Ca}} = \frac{[Sr]_{pe}}{[Sr]_{sol}} \cdot \frac{[Ca]_{sol}}{[Ca]_{pe}} = \frac{100-(C/C_0)_{Sr}}{(C/C_0)_{Sr}} \, \frac{(C/C_0)_{Ca}}{100-(C/C_0)_{Ca}}$$

where $[Sr]_{pe}$ and $[Ca]_{pe}$ are the concentrations of Sr and Ca in the peat (in μCi/g and meq/g respectively) and $[Sr]_{sol}$ and $[Ca]_{sol}$ are their concentrations in solution (in μCi/l and meq/l respectively). Values of $[Ca]_{pe}$ and of $\alpha_{Sr/Ca}$ were calculated at a number of selected pH-values. The results are summarized in Tables IV-2 and IV-3 respectively.

Only gradual differences between the various peat samples exist; moor peat has a slightly lower exchange capacity and also its specificity for Sr is somewhat lower than the other peat species.

The titration curves as measured for the peat samples 1, 4 and 5 are presented in Fig. IV-7. These curves are very similar to those found for soluble humic acids (e.g. [3, 5, 10, 11]). Inflection points in the titration curves are absent, although the peat humic acids contain carboxylic and phenolic acid groups, which in fact differ appreciably in acid strength.

Obviously there is a gradual transition in acid strength between the two classes of acid groups, so that they do not manifest themselves separately. Moreover, a titration end-point cannot be detected, because the acid strength of the greater part of the phenolic acid groups is extremely low.

It further appears from Fig. IV-7 that the titration curves are affected by the Ca-concentration of the solution. This effect must be attributed to the dissipation of H-ions from the inside solution into the bulk of the solution. This phenomenon can be explained on the basis of the Donnan theory (see Eq. III-13). A detailed discussion about this matter is presented in Chapter VI in connection with the results obtained in the titration of modified peat.

As set forth in Chapter III, a linear relation with slope -1 should hold between the logarithm of the distribution coefficient and the logarithm of the Ca-concentration of the solution, provided $K_{Sr/Ca}$ and the exchange capacity remain constant (see Eq. III-27). This condition is not fully met. However, the resulting deviations are in opposite directions and not very significant. As a consequence the concerning relationship may be expected to hold approximately. As shown in Fig. IV-8 this is indeed the case. Moreover the slope of the lines is very near to -1.

Competing action of Mg-*ions*

The results of experiments carried out with ^{85}Sr-solutions which contain Mg as competing cation are summarized in Table IV-4. Compared to the experiments with solutions containing Ca as competing cation (in about the same concentration) the following is observed.

1. The peat has a slightly lower exchange capacity when Mg is the competing cation instead of Ca. This may be attributed to the larger equivalent volume of the hydrated Mg-ions (being 180 Å^3) as compared to that of the hydrated Ca-ions (being 155 Å^3). Otherwise Mg-ions probably exert less tendency to appear in a specific interaction than do Ca-ions. Both these effects result in a lower dissipation of H-ions from the peat into the bulk of the solution.
2. The separation factor $\alpha_{Sr/Mg}$ is considerably higher than $\alpha_{Sr/Mg}$ which is the logical consequence of the above.
3. In accordance with the experiments with Ca-solutions the moor peat is less effective in the removal of radiostrontium than the other peat species.

Effect of the ^{85}Sr-*concentration*

When a species is present in trace amounts in a solution, in the sorption of such a species a linear relation is found, as a rule, between its concentration in the sorbent and in the solution. This is the consequence of the fact that the sorption covers a very short range at the origin of the sorption isotherm (see Chapter III, paragraph 2). This has been checked for radiostrontium with moor peat in Ca-form (the Ca-content of the peat was 1.15 meq/g) and ^{85}Sr-solutions containing 7.5 meq/l Ca, 5 meq/l Na and different concentrations of ^{85}Sr. The results of these experiments are summarized in Table IV-5. From these results it may be concluded that in the sorption of radiostrontium such a linear relationship indeed holds.

Rate of exchange

The rate of exchange was determined by measurement of the activity of filtered samples, which were taken from the stirred mixture of the peat (moor peat in H-form) in the ^{85}Sr solution after various time intervals, starting directly after the immersion of the peat into the solution. In addition the rate of exchange was also determined on two synthetic carboxylic cation exchangers, viz. Amberlite IRC-75 and Amberlite IRC-84.

The ^{85}Sr-solutions used in these experiments contained 5 meq/l $CaCl_2$ (in the experiment with peat) or 10 meq/l $CaCl_2$ (in the experiment with Amberlite), 5 meq/l Na^+ (2.5 meq/l added as sulphate and 2.5 meq/l added as chloride) and 7.5 meq/l NaOH (in the experiments with peat) or 10 meq/l NaOH (in the experiments with the Amberlite products).

The results are presented graphically (C/C_0 in relation to the contact time) in Fig. IV-9. A very high rate of exchange is found with moor peat. Since the peat sample consists for a considerable part of a fine powder, a high exchange rate could be expected for this material. Much more time is required for the equilibration of the synthetic ion exchangers, but these materials consist of larger particles. Evidently a comparison between both materials cannot be made in this respect. However it is clear that a high exchange rate prevails with peat when used under natural conditions.

IV-2-1-2. *Column experiments* (peat in Ca- and H-form)

The application of an ion exchanger in a column is as a rule preferred over a batch-wise application, as a more efficient use is made of the ion exchange capacity in column operation. Moreover, ions can easily be removed completely from the solution by means of column operations. With a batch-process a large excess of the ion exchanger or a series of repeated equilibrations with fresh portions of the ion exchanger is required to reach the same removal. However, the application of ion exchangers in columns is not always possible. Such a situation arises when the ion exchanger consists of particles of very small size and/or when the rigidity of the particles is low (soft particles) or the material has a strong tendency to swell. A high flow resistance, channeling or even blocking of the column is found to occur under such circumstances.

Unfavourable properties as mentioned above are frequently found for peat. This holds especially for peat species of high degree of decomposition. Peat species of low degree of decomposition, such as the moor peat used in our investigations, can be applied in columns reasonably well. Therefore column experiments were performed with this type of peat.

A column of diameter 2.4 cm was filled to a height of 20 cm with 10.6 g of the moor peat. The moor peat consisted of particles which ranged in size from a very fine powder up to particles (fibrous of appearance) of about 2 mm.

Experiments were performed with the H- and Ca-form of the peat. In the former regeneration was carried out by percolating the column with a solution of pH 2.19. In the experiments with the Ca-form of the peat a Ca-acetate solution of pH 7.2 was used for regeneration. Always the regeneration was followed by washing with demineralized water.

All experiments were carried out at the same flow rate v_0, i.e. 1.6 m/hr.

Column experiments with moor-peat in Ca-form

Experiments have been carried out with ^{85}Sr or ^{89}Sr solutions of different pH which contained 5 meq/l Ca-acetate and 6.5 meq/l NaCl. In addition one experiment was carried out with a ^{85}Sr solution which contained 5 meq/l $CaCl_2$, 2.5 meq/l Na_2SO_4 and 7.5 meq/l $NaHCO_3$.

The results, i.e. the relative concentration of Sr in the effluent and the effluent pH in relation to the effluent volume, are shown in Fig. IV-10. The following is concluded from these data.

1. As expected a certain amount of the effluent is completely free of ^{85}Sr.
2. The first break-through always takes place at about the same stage with Ca-acetate solutions and somewhat later with the $CaCl_2$–$NaHCO_3$ solution.
3. The break-through curves are sharper when the pH of the solution is lower.
4. The complete exhaustion of the peat proceeds slowly with solutions of $pH > 6$.

The slow equilibration of the peat with solutions of high pH, indicated by the lower slope of the break-through curves (expecially beyond 80-90% break-through) and the small increase in the effluent pH, may be attributed to the fact that regeneration of the peat was performed with Ca-acetate solutions of pH 7.2. The weakly acid exchange sites which contribute to the exchange capacity at higher pH values (> 7.2) are still in H-form under these circumstances. When brought in contact with a solution of $pH > 7.2$, these sites tend to exchange H for a cation from the solution (e.g. Ca, Sr, Na). As a result of this exchange the pH of the solution will decrease and adjust itself to a value of 7.2. The rate of exchange of the weakly acid groups against Sr, Ca or other cations is very small for two reasons. First of all the concentration gradient of H-ions is small, because the concentration of these ions in the inside solution is extremely low and the buffer capacity of the outside solution is small at the concerning pH-values. Secondly the concentration gradient for Ca-ions is high.

The rate of exchange is larger with a solution of pH 5.1. This time the peat contains more Ca at the start than corresponds to the Ca-concentration and pH of the external solution. As a result Ca-ions from the peat are replaced by H-ions from the solution, bringing on an increase of the pH and of the Ca-concentration of the solution. This process, which starts at the top of the column, will continue during the downward movement of the solution through the column till in lower layers of the column an equilibrium has been reached between peat and solution. Finally, when the Ca–H exchange zone reaches the bottom of the column, a decrease of the effluent pH and Ca-concentration will be observed. The exchange between Ca and H proceeds relatively fast, because the Ca-concentration gradient is high, and the concentration gradient of H-ions can work also temporarily in positive direction, viz. if $pH^{II} > pH^{I}$. The exchange of ^{85}Sr and Ca from the solution for Ca from the peat is further not affected by H-ions.

In the experiment with the $CaCl_2$–$NaHCO_3$ solution, the pH of the effluent reaches the high value of 7.95 in a relatively early stage. The reason for this is the high buffer capacity of the solution and the fact that in this case regeneration of the peat was accomplished with a $CaCl_2$-solution which contained 2.5 meq/l $NaHCO_3$ (pH 8.1). Nevertheless the break-through curve after about 80% break-through is quite similar to that obtained in the experiment with a Ca-acetate solution of high pH, again indicating to the very low exchange rate of the weakly acid groups even under a somewhat stronger pH-gradient.

As stated in Chapter III, at 50% break-through the following relation may hold in close approximation:

$$\frac{\varepsilon(v_f t - z)}{K_d'(1-\varepsilon)\, z} \simeq 1 \qquad \text{(III-42)}$$

As a rule this is true for steep break-through curves which are obtained under conditions in which equilibrium is nearly reached.

Concerning the break-through curves obtained with a "bi- or poly-functional" ion exchanger like peat, equilibrium may be nearly reached with the carboxylic groups, but not with the phenolic groups. Therefore, when alkaline solutions are percolated through the peat column, break-through curves will be obtained which consist roughly of two parts, namely a steep part mainly concerning the exchange on carboxylic groups and a slowly rising part belonging to the exchange on weakly acid groups (compare Fig. IV-10). As a consequence of these effects, the distribution coefficient calculated from the break-through curves by means of the relation III-42 will be, at higher pH values, considerably lower as compared to the values for this coefficient determined from the results of the slurry experiments in which a contact-time of 20 hours was maintained (see Fig. IV-8). The distribution coefficients as determined by both methods are summarized in Table IV-6.

The break-through curves of the experiment with the Ca-acetate solution of pH 5.1 can be fitted reasonably well with the relation of Schumann (Eq. III-41) by taking $N = 40$ (compare Fig. IV-10a, in which some theoretical curves are shown together with experimental curves).

Break-through curves for columns of other length can then easily be calculated by introducing the corresponding value of $N(= k\bar{S}z/v_0)$. The same holds with respect to the break-through curves obtained with other flow rates.

As appears from Fig. IV-10a the other curves (viz. those obtained with solutions of pH 7.8 and 9.75; see Fig. IV-10) can be fitted by the theoretical curves by taking for N a value of about 20-30. However, this is only true up to about 80% break-through. The reason for this must be found in the slow rate of equilibration of the phenolic groups.

Column experiments with peat in H-*form*

In the experiments with peat in H-form the break-through curves of Ca and radio-Sr were determined separately, using the same column after intermediate treatment with 2N HCl. The results with Ca-acetate containing solutions are shown in Fig. IV-11. As appears from this figure the relative concentration of Sr in the effluent is higher than that of Ca in most experiments, except in the experiment with a solution of relatively low pH. This obviously must be attributed to the pH-dependency of the selectivity coefficient $K_{Sr/Ca}$. As appeared in the slurry experiments strontium is preferred by the peat at low pH and Ca at high pH (compare Table IV-3, paragraph IV-2-1-1).

As compared to the experiments with Ca-peat sharper break-through curves are obtained (compare Figs. IV-11 and IV-10). This must be attributed to the fact that the concentration gradient of the out-changed ion (H^+) between peat and solution is maintained on a high level, as a result of the buffer action of the acetate ions present in the solution The rate of exchange on H-peat (Ca and Sr for H) will therefore be faster than with Ca-peat, because there the outchanged ion is not removed from the solution.

In the experiment with a solution of pH 5.05 already part of the acetate is present in acid form. For this reason here the pH of the solution will drop to a lower value, at the same removal of Ca, than will occur with solutions of higher pH. As a result the concentration gradient of H-ions will be lower, and consequently the rate of exchange.

In the experiment at pH 5.05, the last remainders of Ca (and Sr) are removed from a nearly unbuffered solution (pH 2.7-3.0) in the lower parts of the exchange zone; the sorption capacity of peat is very low here, due to the low pH of the solution. The removal of Ca in the upper parts of the exchange zone takes place at a higher pH-level, and consequently from a more strongly buffered medium. For this reason it may be expected that the first part of the break-through curve will correspond to a lower value of N than the medium part of the curve. Theoretical and experimental plots as shown in Fig. IV-11a confirm this interpretation. It further follows from Fig. IV-11a that the break-through curves correspond to higher values of N, when the pH of the starting solution is higher. The reason for this must be found in the higher buffer capacity of solutions of higher pH.

Values of the equilibrium and non-equilibrium distribution coefficient, which were obtained in the same way as described above, are summarized in Table IV-7.

To investigate the influence of available buffer capacity, some experiments were carried out with ^{85}Sr-solutions which contained $CaCl_2$ and various amounts of $NaHCO_3$. Break-through curves obtained are shown in Fig. IV-12. Very steep break-through curves are found in the experiment with 7.5 meq/l $NaHCO_3$. Apparently in the experiment with 2.5 meq/l $NaHCO_3$ the buffer capacity of the solution is too low, because a complete removal of Ca and Sr in then not achieved.

It further appears from Fig. IV-12 that in the experiment with 7.5 meq/l $NaHCO_3$, the ^{85}Sr-concentration in the effluent reaches a value higher than in the starting solution during a short time after break-through. This phenomenon must be attributed to the rather low value of $\alpha_{Sr/Ca}$ (or $K_{Sr/Ca}$) at pH-values higher than 4-5. As a consequence the removal of Ca continuously is somewhat better than of Sr, resulting in a relative increase of Sr in the lower parts of the exchange zone and consequently in a first break-through of Sr as well as in higher concentration of Sr (relative to the influent concentration) in the effluent after break-through. The very steep break-through curve obtained in this experiment obviously must be attributed to the fact that $NaHCO_3$ buffers at a relatively high pH.

Concerning the quality of the effluent it has to be noted that the solution is clear, and is not or only slightly coloured when the pH of the effluent does not exceed a value of about 6.5. The solubility of the humic acids in the peat increases rapidly at higher pH, leading to a yellow effluent.

IV-2-2. THE SORPTION OF RADIOCOBALT ON MOOR PEAT IN H-FORM AND CA-FORM

The sorption of radiocobalt was investigated exclusively by means of slurry experiments. Two somewhat different procedures were applied so that two types of experiments can be distinguished:

1. "Shaking experiments", which were performed in the way described in paragraph IV-1-3.
2. Experiments in which the pH of the solution was changed step-wise by addition of small amounts of 2N NaOH or 2N HCl into the stirred or shaken mixture, always after establishment of the sorption "equilibrium". The sorption of cobalt was followed by filtering or centrifuging samples of the mixture and counting.

Carrier free ^{60}Co was used in the experiments in a concentration of about 5.10^{-3} μCi/ml.

IV-2-2-1. *Shaking experiments*

Results of experiments performed with Ca-peat and H-peat are shown in Fig. IV-13a and IV-14a respectively. Apparently the peat behaves differently in the sorption of cobalt as compared with that of strontium, as considerable differences are found between the relationships of $(C/C_0)_{^{60}Co}$ and of $(C/C_0)_{^{85}Sr}$ with pH^I. A significant decrease of the sorption of cobalt is found in solutions of pH^I above a value between 6-8, dependent on the cation-form of the peat. For strontium and calcium such an effect is only found, but to a much lower extent, at pH-values above 9 and at low Ca-concentration (compare Fig. IV-2).

In the sorption of cobalt the curves shift to higher pH when the Ca-concentration of the solution is higher (see Fig. IV-13a). Apparently the effect of Ca-ions on the sorption of cobalt in the acid pH-region is opposite to that in the alkaline pH-region. Further it appears that the nature of the ions originally present in the peat influences the sorption of cobalt.

Oreshko *et al.* ([38]), who found approximately the same sorption characteristic for cobalt on peat did not recognize the effect of Ca-ions or that of the original cation occupation of the peat. According to these authors the decreased sorption in the acid and in the alkaline pH-region is the result of the formation of complexes of cobalt with sulphonic acid groups in the peat at low pH and with carboxylic acid groups at high pH. Apart from the fact whether complex formation takes place or not, it is obscure how this would result in a decrease of the sorption. The explanation has to be found in quite another direction.

The decreasing sorption with decreasing pH in the lower pH-region evidently is caused by a decrease of the dissociation of the carboxylic acid groups.

Less clear, at first sight, is the reason of the decrease of the sorption at increasing pH in the higher pH-region. Some other mechanism must predominate here, because an increase of the Ca-concentration results in a better removal of cobalt. Apparently this mechanism is already operative at much lower pH when H-peat is the sorbent, because the optimum pH is lower and the minimum value of C/C_0 is higher as compared with the results obtained with Ca-peat.

The poor sorption of cobalt at high pH probably must be attributed to the presence of peat humic acids in the solution. At high pH part of the humic acids dissolve from the peat possibly accompanied with disrupture of original linkages in the humus substances and mainly in the form of sodium salts. The extent of dissolution of organic matter from the two forms of the peat at various pH-values and the influence of the Ca-concentration on this effect was measured in part of the experiments. This was done by titration of an appropriate sample of the solution with standardized $KMnO_4$ according to the directions given for routine water analyses ([40]). The amount of $KMnO_4$ consumed herein, denoted as $KMnO_4$-value (mg $KMnO_4$ per liter), may be considered as a rough measure of the concentration of humic acids in solution. According to investigations of Obenaus ([42]) made on moorwater, 1 mg $KMnO_4$ corresponds to about 0.65 mg humic acids.

Results of $KMnO_4$-titrations carried out in the experiments with Ca-peat and H-peat with solutions containing about 5 meq/l $CaCl_2$, are shown in Fig. IV-13b and Fig. IV-14b respectively together with the rest Ca-concentration of the solution. From the $KMnO_4$-value-pH^I plots it appears that the solubility of humic acids strongly increases with pH^I in the pH-region above about 7, reaching values of about 150 mg $KMnO_4$/l at pH^I 10 with Ca-peat (90-100 mg/l humic acids!) and even 500-600 mg $KMnO_4$/l (about 350 mg/l humic acids!) with H-peat. An additional experiment was performed with Ca-peat to investigate the influence of the Ca-concentration on the solubility of humic acids. Portions of 1900 ppm peat were shaken for 24 hrs with solutions containing 0, 2.5, 4.65 and 9.3 meq/l $CaCl_2$ respectively and always 4.75 meq/l NaOH. After determination of the $KMnO_4$-values of filtered samples of the mixtures, the pH of the mixtures was decreased by addition of N HCl (to pH 2.6 in all cases) and shaking was continued for another 24 hrs. Then again the $KMnO_4$-values were determined. From the results shown in Fig. IV-15 it appears that:

1. The solubility of humic acids from the peat at pH 10 decreases strongly with increasing Ca-concentration of the solution, especially in the Ca-concentration region 0-5 meq/l.
2. After acidification of the mixtures, the $KMnO_4$-values of all solutions were the same, and equal to the value at pH 10 for 9.3 meq Ca/l. This minimum solubility amounts to approx. 100 mg/l humic acids. Apparently in systems with a high Ca-concentration (>5 meq/l) higher molecular weight humic acids do not dissolve at pH 10 and no notable precipitation takes place upon acidification of that solution.

As will be shown in the experiments which will be discussed in the next paragraph the solubility of peat humic acids is even smaller when Co-ions are present in solution in a concentration of about 1 meq/l (see Figs. IV-18b and -19b).

The dissolved Na-humates in the solution meet the remainder of Ca- and Co-ions, which displace Na-ions as counter ion, dependent on their relative concentrations and affinities for humic acids. Co-ions (or hydrolized Co-ions) combine fast and well with humic acids, because these compounds exert a high affinity for cobalt (very high sorption under optimal conditions). Moreover the cobalt is present in extremely small concentrations, so that a relatively small amount of humic acids suffices for its binding.

Of course the main part of the humic acids is still present in the peat. This follows directly from the relative Ca-concentration; even at high pH-values (>8) and at the lowest Ca-concentration in the starting solution investigated, consequently at conditions of maximum solubility of the humic acids, the main part of the calcium is present in dissolved form (see Figs. IV-13b and 14b). Therefore the ^{60}Co is not randomly distributed over all exchange sites which are present in the system, viz. over dissolved and undissolved humic acids. However, a redistribution of Co may last a long time, when cobalt and humic acids form compounds which are poorly and only partly dissociated. Since cobalt exerts a strong tendency to form coordination bonds with donor atoms like oxygen, nitrogen and sulfur, which all are present in humic acids in greater or smaller amounts, the existence of stable chelates of cobalt and humic acids may be well accepted.

The stability of these chelates, in the peat and certainly also in the solution, apparently increases with pH. This can be deduced from the increase of $\alpha_{Co/Ca}$ (as calculated from the results in Figs. IV-13a and IV-13b, see Table IV-8) as long as the solubility of the peat does not increase appreciably ($pH < 7$). The apparent decrease of the competitive action of calcium at higher pH values will then be the result of preferential binding of cobalt by the increased fraction of dissolved humic acids. Since humic acids differ widely in nature, the character and stability of the various cobalt chelates (with low molecular weight and high molecular weight material) may vary greatly. Moreover, in spite of the possibly different stabilities of the various cobalt chelates, ligand exchange, even in solution, may be low in rate, especially at pH-values above 7. In this respect attention should be paid to information obtained from chelate chemistry ([1]). This seems to point to the fact that ligand exchange frequently is slow if the central metal ion is bound to several active groups of the same molecule. As humic acids contain many active groups, which could be involved in chelate formation, it seems reasonable to accept that a Co-humic acid complex of high stability is formed.

Although not systematically studied, the existence of stable bonds (covalent?) between Co and humic acids is supported by the results of desorption experiments, which were performed with the peat samples obtained in the sorption experiment with Ca-peat (Fig. IV-13a). The peat samples, separated from the ^{60}Co-solution by filtration, were washed on the filter under suction with 50 ml demineralized water. Then vacuum was removed and 1 ml of a 2N HCl solution, containing 50 ppm Co as chloride, was poured on the filter where it remained in contact with the peat*. After 5 minutes this solution was removed under suction. Then the peat was washed with 75 ml demineralized water. The HCl-eluate and washwater were combined, diluted to 100 ml and counted for ^{60}Co activity.

The percentage desorption, as calculated from the activities of the starting solution, the filtrate and the eluate, has been plotted versus the end-pH obtained in the sorption ($pH_{sorption}$) in Fig. IV-13c. It appears from this figure that the desorption of cobalt is nearly complete from peat which had adsorbed cobalt at $pH < 6$. However, from peat which had adsorbed cobalt at higher pH, much less ^{60}Co is removed by the same treatment. Neither the low pH, nor the presence of inactive cobalt results in a complete desorption, indicating that the rate of desorption decreases with increasing $pH_{sorption}$.

This experiment shows that the type of the bonds formed between Co and humic acid depends on pH. Moreover, the reaction in which the strong bond is formed is not completely reversible. At the same time it means that redistribution of cobalt over all solid and dissolved humic acids will not always take place easily if by some reason the cobalt was originally bound either to the dissolved or to the solid material. In the experiments described in Figs. IV-13 and IV-14 the peat is added to the cobalt solution so that on the one hand humic acids are diffusing into the solution and at the other hand Co-ions diffuse into the peat. Insufficient information is available to judge which of the two processes is the slowest. However, the preference of cobalt for reaction with the dissolved humic acids, assuming that this is the reason for the effects observed, indicates

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* From data given in Fig. IV-7 it can be seen that about 0.5 meq OH^- is required for 200 mg H-peat to increase the pH of the peat mixture (200 mg H-peat in 100 ml solution) to 9. In a treatment with 1 ml 2N HCl sufficient acid is added to regenerate the acid groups and to bring the pH of the surrounding solution to a very low level.

that diffusion of humic acids is the most important. This seems likely because an excess of humic acids with respect to the very low concentration of cobalt, is soon available in solution. Moreover the pH of the solution in the beginning is higher, resulting in the formation of more stable Co-compounds. In this light it also becomes clear that addition of calcium improves the sorption of cobalt by the solid peat, because it hampers the formation of dissolved humic acids.

The preference of cobalt for dissolved humic acids could theoretically also be the result of a difference in stability of the undissolved and dissolved cobalt-humic acids compounds. However results of Fig. IV-13c and experiments described in the next paragraph indicate that redistribution of cobalt is also slow in those experiments where Co is primarily adsorbed by solid peat.

Evidence of the association of cobalt with humic acids is found in the results of paper electrophoresis*. This was applied to Co-containing filtrates of peat at different pH-values and to the corresponding pure cobalt solutions. It appears (see Fig. IV-16) that the mobility of ^{60}Co is lower in the peat-filtrates than in the pure Co-solutions for all pH-values between 3 and 10. In alkaline filtrates even negatively charged Co-complexes are present. In pure ^{60}Co-solutions further a decreasing mobility can be observed at increasing pH. This apparently is the result of decreasing charge and/or increased mass.

Results of experiments performed with different concentrations of Ca-peat and solutions composed of 4.4 meq/l $CaCl_2$ and 1 meq/l $NaHCO_3$ are summarized in Table IV-9. The distribution coefficient appears to be almost independent on the peat concentration for these circumstances where pH is nearly constant.

The rate of exchange was determined in the way described in previous paragraph by counting filtered samples taken from a stirred mixture of peat and solution. It appears that cobalt is sorbed sufficiently fast for technical applications at all pH-values investigated (Fig. IV-17).

IV-2-2-2. *Experiments in which* pH *was changed stepwise*

In view of the strong effect of dissolved humic acids on the sorption of cobalt to peat, and because of the strong influence of pH, salt content and salt composition of the solution on the solubility of peat humic acids, it may be expected that the removal of ^{60}Co from the solution will depend on various factors such as origin of the peat sample, the conditions of pretreatment and the circumstances under which peat and cobalt are brought together and the pH of the solution. Because of the formation of strong bonds between peat and cobalt at higher pH considerable differences may for instance be expected in the binding of cobalt between systems in which the pH is stepwise raised and systems in which the pH is stepwise lowered. To confirm this, experiments were performed with moor peat in H-form in which the pH was raised, starting from a low pH, by small additions of 1N NaOH, or lowered (starting from a high pH) by small additions of 1N HCl. Experiments were carried out with ^{60}Co-solutions containing various amounts of $CaCl_2$ and/or $CoCl_2$. Always a contact time of 20 hours or more was maintained for each new condition. Stirring or shaking was carried out in closed containers. Samples were taken from the mixtures for determination of the radioactivity and the $KMnO_4$-value. The remainder of the samples were returned, together with the filtered peat, into the suspension after analyses; no corrections were made for the small amounts of the filtrate (0.5% of the solution or less) lost in the determination of the $KMnO_4$-value.

The results of these experiments are presented graphically in Figs. IV-18a and IV-19a, (C/C_0 versus pH^I), and in Figs. IV-18b and IV-19b ($KMnO_4$-value versus pH^I).

With respect to the solubility of humic acids it may be noted that the solubility curves

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* For this work use was made of high voltage electrophoresis in an instrument obtained from Virus kg (type E 100).

obtained in the stepwise increase of pH (Fig. IV-18b) have the same slowly rising form as those measured in the shaking experiments (Fig. IV-14b), though a somewhat higher solubility at pH-values below 7 is obtained in the stepwise procedure. This might be related to slow dissolving rates in the acid region.

For the stepwise decrease of pH a complete different picture is obtained. The solubility curves stay horizontal and humic acids are only precipitated at pH-values below 4 to 5. In the pH-region below 4 to 5 the charge of the dissolved humic acids reduces fastly to zero, as a result of which attractive forces can initiate a coagulation of the organic matter. These phenomena point clearly to the irreversible character of the processes which take place, when the peat is brought in contact with either alkali or acid.

Addition of calcium decreases the solubility of humic acids in both types of experiments as was already found earlier (Fig. IV-15). It is now shown that at low calcium concentrations a considerable portion of the humic acids present in the peat passes into the solution and not only at high pH. The total amount of soluble humic acids present in the peat corresponds to roughly 2200 mg/l $KMnO_4$, as estimated by extrapolation from the results in Fig. IV-19b taking into account that in the absence of Ca a $KMnO_4$-value of 2050 mg/l is measured at pH 11.5. Thus percentages of the humic acids varying between 80 and 10% are dissolved at high pH, dependent on the cations present and the procedure applied.

Addition of cobalt reduces the solubility of humic acids even stronger than calcium.

The relationships between C/C_0 and pH^1 are less easily explainable. The curves for stepwise increase of pH are somewhat comparable to those measured in the shaking experiments, though a sharp increase in the solubility of cobalt at high pH is absent here. This seems to be in agreement with the observed fact that cobalt is bound much less strongly at lower pH, and consequently can distribute itself relatively easily over dissolved and undissolved humic acids. When cobalt and peat solution are directly mixed at high pH the cobalt is preferentially bound to the soluble humic acids and in such a form that it exchanges very slowly if at all, as we have seen.

In this respect it seems interesting to look more closely to the ratio between dissolved cobalt and dissolved humic acid during the stepwise increase of pH.

The dissolved Co can be expressed as fraction of the total amount of cobalt available by comparing the concentration C with the starting concentration C_0. The dissolved humic acids can be calculated from the $KMnO_4$ number (KW) and may be expressed relative to the total amount of soluble humic acids which is represented by a KW of 2200.

Two types of ratio factors have been calculated. Factor R_1 relates to total cobalt and humic acid concentration whereas R_2 involves only the increases in dissolved cobalt and humic acids as compared to the situation at the pH where C/C_0 for cobalt has its minimum value. This situation is indicated by m.

$$R_1 = C/C_0 : \mathrm{KW}/2200$$

$$R_2 = \frac{C/C_0-(C/C_0)_m}{100-(C/C_0)_m} : \frac{\mathrm{KW}-(\mathrm{KW})_m}{2200-(\mathrm{KW})_m}$$

The ratio-factors plotted versus pH, are shown graphically in Fig. IV-18c and Fig. IV-18d respectively. It appears from Fig. IV-18c, that the ratio-factor, is approximately constant in the nearly neutral pH-region, and is lower in magnitude at higher Ca-concentration of the solution. This phenomenon can be attributed to the fact that KW/2200 decreases strongly at increasing Ca-concentration, whereas in media of pH < 6-7, (C/C_0) is higher for increased Ca-concentration, due to the competitive action of Ca-ions. In the pH-region in which the ratio-factor approaches a constant value, the increase in KW/2200 is approximately compensated by the increase in (C/C_0).

Ratio-factor R_2 is continuously increasing with increasing pH (see Fig. IV-18d). Moreover it appears that this ratio-factor is approximately equal in magnitude for the various Ca-concentrations, though the total amount of humic acids dissolved from the peat decreases with increasing Ca-concentration. This seems to indicate that during dissolution of peat material the humic acid complexes with high cobalt content are dissolved by preference. It is not clear to what extent the free humic acids play a role in the attack of parts of the peat, which contain high amounts of cobalt. However, in view of the equality of the ratio-factor found in the various experiments for which large differences in the free humic acid concentration are present, the role of the dissolved humic acids in the dissolution of cobalt seems to be small. The relative concentration of cobalt in solution, (C/C_0), at pH above 5 is probably mainly governed by solution processes of solid peat, in which the cobalt seems to be distributed inhomogeneously. Of course these effects will only be found for the very low concentrations (about 5.10^{-9} ppm) of tracer cobalt. At higher cobalt concentrations different results are found. At low pH the cobalt is kept in solution (carrier effect) but at high pH the low solubility of Co-humic acid compounds will dominate.

In the experiments where pH was stepwise decreased the peat was added to the cobalt solution directly after the addition of NaOH (25 ml 0.1 N NaOH in 200 ml solution). Under these highly alkaline conditions (end-pH about 11.3) appreciable amounts of the humic acids dissolve, viz. about 20 to 80% depending on calcium concentration. As we have seen a more or less selective bonding between the few cobalt atoms and the overwhelming amounts of dissolved humic acids takes place (strong bonds). When decreasing the pH no great change in the distribution of cobalt can be expected at first, unless a preferential precipitation of humates with high Co content would take place. Such a precipitation indeed seems to occur to some extent, since down to about pH 5 the values of the ratio factor $R_1 = \mathrm{KW}/2200:(C/C_0)$ increase upon acidification (see Fig. IV-19c), whereas the relative concentration of the humic acids does not change significantly in this pH-region. At pH-values lower than 5 the ratio-factor tends to decrease. But here of course a counter action by the exchange for H^+ and also for Ca^{2+} (increasing competitive action at decreasing pH) becomes more and more important. It further follows from Fig. IV-19c that the ratio-factor is higher as a result of higher relative dissolved humic acid concentration. This confirms the former conclusion that because of kinetic factors the trace amounts of cobalt at these pH-values lead to a selective reaction with dissolved humic acids when the calcium concentration of the solution is lower.

The same effects seem to hold when cobalt carrier is present; but then the precipitation of cobalt humates is greater and the carrier effect will decrease the binding of cobalt at low pH.

IV-2-3. THE SORPTION OF RADIOMANGANESE

The sorption properties of peat were also investigated for Mn-ions in a way which made it comparable to the sorption of Co. In shaking experiments at various pH-values moor peat in H-form was brought into contact with a carrier free solution of manganese at the same time containing 9.72 meq Ca/l. The results shown in Fig. IV-20 show a curve similar to the one obtained for cobalt. However, the minimum is shifted to a higher pH and is somewhat lower for manganese. A direct comparison with cobalt is impossible because the calcium concentration was not identical for both series of experiments. However, a higher C/C_0 at lower pH for manganese indicates that the manganese bond is less strong than that of cobalt. The lower minimum also shows that the formation of complexes with soluble humic acids is less strong as compared with cobalt.

IV-2-4. THE EFFECT OF NA -IONS ON THE SORPTION OF CA -IONS BY MOOR PEAT

Surface waters frequently contain a relatively high concentration of calcium and sodium salts. Therefore information is required about the sorption of both ions on peat when they are present simultaneously in the solution, especially in the pH-region of 6.0 to 6.5, because the conditions for the application of peat are optimal under these circumstances.

For this purpose experiments were carried out with moor peat in Ca-form, which was prepared by equilibrating the natural peat with a 2N Ca-acetate solution (see Paragraph IV-1-1). The Ca-content of the peat was 1.15 meq/g.

The Ca-content of the peat was determined by suspending a weighed sample of the peat in a certain amount of concentrated HCl; Ca is replaced by H practically completely under these circumstances. After filtration of the peat and washing, the Ca-content of the filtrate (combined with wash-water) is determined by EDTA-titration.

Appropriate portions of the peat (always 2000 ppm) were suspended in neutral solutions of different concentrations of $CaCl_2$, viz. 0, 0.52, 2.76 and 5.00 meq/l, and of NaCl in concentrations varying between 0 and 50 meq/l. The Na-concentration range investigated in these series of experiments include values which are much higher than usually found in surface waters, approximately 5-8 meq/l in Rhine water. This has been done to obtain a more clear idea of the effect of Na-ions on the sorption of Ca. The suspensions were shaken for about 20 hours and then filtered. Subsequently the Ca-concentration and pH of the filtrate were determined.

The pH was found to vary rather arbitrarily between 6.0 and 6.3. These fluctuations in the pH must be mainly attributed to the inaccurate pH-measurement at the time the experiments were performed. Any influence of the NaCl-concentration on the pH therefore cannot be observed.

As a matter of fact, according to the Donnan concept (see Chapter III), a decrease of pH should take place at increasing NaCl concentration. However, as appeared in some preliminary experiments, concerning the titration of a modified peat* in solutions containing 7.5 meq/l $CaCl_2$ and different NaCl concentrations, a distinct influence of the NaCl concentration on the end pH was absent. As an illustration some of these results are presented in Table IV-10.

Apparently the dissipation of H-ions from the peat is mainly the result of the action of the Ca-ions.

Na-ions to some extent can remove Ca-ions from the peat. This is reflected in an increase of the Ca-concentration of the solution as can be seen in Fig. IV-21 in which the increase of the Ca-concentration of the solution (relative to the Ca-concentration of the starting solution), as obtained in the experiments with Ca-peat, was plotted versus the Na-concentration of the solution. As appears from this figure already at zero Na-concentration a certain amount of Ca is removed from the peat depending on the Ca-concentration of the starting solution. This dissipation of Ca-ions is not accompanied with any notable change in the pH of the solution. Obviously this phenomenon must be attributed to the presence of a small amount of free calcium salts in the peat (e.g. acetate or soluble humates), which must have been left as a result of incomplete removal during washing due to a slow rate of dissolution (see Paragraph IV-1-2). In view of the effect of the Ca-concentration on the solubility of these calcium salts, probably mainly calcium humates are involved.

It is evident that these effects prevent the calculation of a correct value of the selectivity coefficient. However, a rough impression of the magnitude of this factor can be obtained in the following way. The exchange capacity of the peat is put equal to its Ca-content at zero NaCl concentration. Furthermore it is assumed that the exchange between Na and Ca is stoichiometric. The concentration of Na in the peat can then be calculated from the difference $[Ca]_{sol\ NaCl=x}$-$[Ca]_{sol\ NaCl=0}$. The values of $[Ca]_{pe}$, $[Ca]_{sol}$ can be calculated from the original Ca-content of the peat and the NaCl and $CaCl_2$ concentrations of the starting solutions. The selectivity coefficients, as calculated in this way, are summarized in Table IV-11.

Apparently the peat exerts a strong preference for calcium. Furthermore, it appears from the data in Table IV-11 that the selectivity coefficient decreases with increasing Na-concentration

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* See for the preparation of this peat Chapter V. Though this peat has additional sulphonic groups the experiment described is also indicative for normal peat.

and decreasing Ca-concentration.

Obviously the Ca-ions in the peat become more difficult exchangeable for Na-ions when the Ca-occupation of the peat is lower.

IV-3. **Discussion of the results**

Natural peat represents an attractive material in the purification of water which is contaminated with radioactive cationic isotopes. Compared with synthetic cation exchangers the cation exchange capacity of peat is reasonably high, provided the pH of solution is maintained at a level of about 6. According to literature the capacity of the material under these conditions is derived mainly from the carboxylic acid groups. The rate of exchange on these groups was found to be rather high. In the sorption of cations, peat shows a pronounced selectivity for the higher valency ions; this especially is true for the transition element metal ions, such as Co^{2+} and Mn^{2+}.

If necessary, peat can be applied in water treatment plants. Preferentially it has to be applied in columns, because then a complete removal of radionuclides can easily be achieved. Column operations can be applied reasonably well for peat species of low degree of decomposition, such as the moor peat used in our investigations. Peat species of high degree of decomposition are much less or not suitable for column operation since they are composed almost completely of very small particles.

As was shown with ^{85}Sr-solutions, extremely steep break-through curves can be obtained, provided the pH and the buffer capacity of the solution are well adjusted to the cation occupation of the peat.

One of the most serious limitations of the application of peat is the absence of specificity for radiostrontium relative to calcium. Since the Ca-content of most surface waters is rather high, it is evident that the application of peat (just as the application of synthetic ion exchangers) in water treatment plants cannot be considered for the removal of Sr, unless the production and distribution of drinking water is separated from that of process water. Then much smaller quantities of water have to be treated.

An attractive alternative technique for the use of peat in the decontamination of water, especially in case of emergency, undoubtedly would be its application in its natural location. For this purpose it should be shown that an infiltration technique involving large production rates per unit of surface area is techniqually possible and, will at the same time lead to a sufficient contact between the infiltered water and peat particles. It has been observed that the water permeability of undisturbed and slightly decomposed peaty soils is about $2\text{-}3 . 10^{-3}$ cm/sec which certainly is not extremely small. Moreover, only a relatively small quantity of decontaminated water per head of the population is required for pure consumption purposes.

With respect to a discharge of radioactive wastes in surface water the following may be noted. It is known from recent investigations that appreciable amounts of humic acids occur in surface water ([41]).

As was found in the investigations described in this chapter humic acids exert a strong affinity for radioisotopes of the transition elements. Therefore such an interaction may also be expected in surface water. At a humic acid concentration of 8-15 ppm in the water at least 10-15% of ^{60}Co will be associated with these compounds (comp. Table IV-9). Since only about 50% of humic acids are removed by water treatment processes, a limited purification of surface water from ^{60}Co can be expected to take place. To the contrary by means of peat column a removal of at least 85 to 90% of the cobalt will take place.

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TABLE IV-1

Peat samples investigated in the sorption of radioisotopes

Number	Peat sample [1])	Origine	Location	Moisture content [2]) %
1	moor peat	sphagnum	Drente	11.3
2	low land peat R-1 40/55	reed	Reeuwijk polder	10.2
3	low land peat R-1 70/90	reed	Reeuwijk polder	10.7
4	low land peat Nw 40/55	reed	Nieuwerkerk polder	11.1
5	low land peat Nw 95/100	reed- sedge	Nieuwerkerk polder	11.0

1) Numbers reveal depth of the samples in cm.

2) Moisture content of the samples in H-form as determined by drying at 110 °C.

TABLE IV-2

Exchange capacity of the various peat samples (in meq/g)

Peat sample	$(Ca)_0$ meq/l	$pH^{I} = 3.5$	$pH^{I} = 4.25$	$pH^{I} = 5$	$pH^{I} = 6$	$pH^{I} = 7$
Moor peat	9.88	0.34	0.56	0.77	1.07	1.39
	7.68	0.33	0.57	0.78	1.10	1.41
	4.94	0.30	0.53	0.76	1.06	1.33
	2.49	0.24	0.44	0.66	0.90	1.07
$Nw^{95/100}$	7.48	0.53	0.79	1.07	1.39	1.70
	4.63	0.39	0.63	0.87	1.19	1.49
	2.49	0.37	0.62	0.82	1.02	1.12
$Nw^{40/55}$	7.48	0.56	0.80	1.03	1.35	1.62
	4.63	0.48	0.71	0.94	1.24	1.49
	2.49	0.42	0.66	0.88	1.08	1.13
$R\text{-}1^{40/55}$	7.48	0.54	0.81	1.06	1.36	1.62
	4.96	0.44	0.69	0.93	1.19	1.45
	2.49	0.37	0.58	0.77	0.96	1.09
$R\text{-}1^{70/90}$	7.48	0.48	0.66	0.87	1.17	1.46
	4.96	0.36	0.58	0.80	1.10	1.36
	2.49	0.30	0.53	0.75	1.00	1.12

TABLE IV-3

Separation factor $\alpha_{Sr/Ca}$ *as determined for the various samples*

Peat sample	$(Ca)_0$ meq/l	$pH^I = 3.5$	$pH^I = 4.25$	$pH^I = 5$	$pH^I = 6$	$pH^I = 7$
Moor peat	9.88	1.08	0.90	0.84	0.75	0.72
	7.68	1.12	0.96	0.94	0.87	0.84
	4.94	1.14	0.99	0.92	0.87	0.83
	2.49	1.24	1.16	1.10	1.00	0.90
$Nw^{95/100}$	7.48	1.22	1.10	1.02	0.98	0.92
	4.63	1.42	1.28	1.17	1.05	0.98
	2.49	1.33	1.14	1.10	1.28	1.29
$Nw^{40/55}$	7.48	1.24	1.16	1.12	1.03	0.95
	4.63	1.38	1.26	1.17	1.05	1.00
	2.49	1.43	1.27	1.08	1.01	1.81
$R\text{-}1^{40/55}$	7.48	1.15	1.22	1.02	0.96	0.91
	4.96	1.39	1.23	1.09	1.00	0.93
	2.49	1.37	1.62	1.88	2.12	1.63
$R\text{-}1^{70/90}$	7.48	1.10	1.10	1.04	0.95	0.86
	4.96	1.43	1.24	1.13	1.03	0.97
	2.49	1.37	1.08	1.19	1.23	1.22

TABLE IV-4

Results of experiments with Mg *as competing cation (starting solution:* 6.16 meq Mg/l *for samples* 1 *and* 2, *and* 6.20 meq Mg/l *for samples* 3 *and* 4; Na-*concentration* 5 meq/l *in all experiments)*

Peat sample		$pH^I = 3.5$	$pH^I = 4$	$pH^I = 5$	$pH^I = 6$	$pH^I = 7$
1. Moor peat	$[Mg]_{pe}$ meq/g	0.22	0.37	0.68	0.98	1.25
	$(C/C_0)_{Sr}$ %	69.4	58.7	41.0	32.7	27.1
	$\alpha_{Sr/Mg}$	5.7	5.05	5.1	4.4	3.95
2. $Nw^{95/100}$	$[Mg]_{pe}$ meq/g	0.32	0.48	0.78	1.10	1.41
	$(C/C_0)_{Sr}$ %	45.6	35.9	22.5	17.5	14.2
	$\alpha_{Sr/Mg}$	10.2	9.8	10.1	8.5	7.1
3. $R\text{-}1^{40/55}$	$[Mg]_{pe}$ meq/g	0.32	0.47	0.76	1.06	1.35
	$(C/C_0)_{Sr}$ %	47.3	36.7	24.8	19.5	16.5
	$\alpha_{Sr/Mg}$	9.8	9.7	9.35	7.95	6.5
4. $R\text{-}1^{70/90}$	$[Mg]_{pe}$ meq/g	0.21	0.34	0.63	0.96	1.28
	$(C/C_0)_{Sr}$ %	50	40.1	28.5	22.7	18.6
	$\alpha_{Sr/Mg}$	14.0	13.0	9.8	7.15	6.25

TABLE IV-5

Removal of ^{85}Sr *from solutions containing different concentrations of* ^{85}Sr *(sorbent: moor peat in* Ca-*form; starting solution:* 7.5 meq Ca/l and 5 meq Na/l*)*

Starting activity μCi/ml	$(C/C_0)_{Sr}$ %	End-pH	End-Ca concentration meq/l
10.10^{-2}	78.8	4.9	7.52
5.10^{-2}	78.5	4.9	7.48
3.10^{-2}	78.0	5.0	7.40
6.10^{-3}	78.7	4.8	7.54
2.10^{-3}	78.8	4.9	7.50
5.10^{-4}	78.5	5.0	7.50

TABLE IV-6

Distribution coefficients under equilibrium (from slurry tests) and under non-equilibrium conditions (from break-through curves)

Solution	Equilibrium K_d^* ml/g	Non-equilibrium K_d^* [1] ml/g
$Ca(CH_3COO)_2$, $pH = 5.1$	153	146
$Ca(CH_3COO)_2$, $pH = 7.8$	240	177
$Ca(CH_3COO)_2$, $pH = 9.75$	340	200
$CaCl_2 + NaHCO_3$, $pH = 8.2$	270	193

1) The porosity of the bed is about 0.67. This value is based on a wet volume of the peat $V_b = 2.75$ ml/g air dry peat.

TABLE IV-7

Distribution coefficients under equilibrium (from Fig. IV-8) and non-equilibrium conditions (from break-through curves)

Solution	Equilibrium K_d^* ml/g	Non-equilibrium K_d^* ml/g
Ca-acetate $pH = 5.05$	148	141
Ca-acetate $pH = 6.8$	208	161
Ca-acetate $pH = 10.9$	—	230

TABLE IV-8

The distribution coefficient and separation factor as calculated at some selected pH^I*-values from Fig. IV-13*

$[Ca]_0$ meq/l	1.59		4.92		7.44	
pH^I	K_d^* ml/2 g	$\alpha_{Co/Ca}$	K_d^* ml/2 g	$\alpha_{Co/Ca}$	K_d^* ml/2 g	$\alpha_{Co/Ca}$
4.0	877	3.0	585	3.8	365	3.4
5.0	3 850	6.3	1 860	7.2	1 170	6.5
6.0	7 200	16	7 300	19.5	4 260	16.6
7.0	49 000	28	49 000	95	27 600	82
8.0	11 500	4	35 000	50	55 000	125
9.0	3 540	0.6	9 650	10.5	14 100	25

TABLE IV-9

Effect of the peat concentration on the removal of ^{60}Co

Peat conc. ppm	2000	1000	402	210	86	25	8
C/C_0 %	3.5	7.0	14.0	22.4	47.8	76.7	90.9
K_d^* ml/g	13 800	13 300	14 800	16 500	12 100	12 200	12 500
pH	7.9	7.95	7.99	8.07	8.12	8.15	8.16

TABLE IV-10

Results of the titration of modified peat N_B *in* H*-form in a solution containing* 7.87 meq/l $CaCl_2$ *and different concentrations of* NaCl
(pH *was determined in the suspension after 24 hrs shaking; accuracy* pH*-measurement* 0.05 pH*-units*)

NaOH added	NaCl = 0 meq/l	NaCl = 10 meq/l	NaCl = 30 meq/l	NaCl = 70 meq/l
meq/l	end-pH			
0	3.33	3.40	3.38	3.36
1.36	4.47	4.47	4.45	4.49
3.64	6.28	6.32	6.25	6.30
4.55	6.85	6.85	6.81	6.90
5.46	7.33	7.32	7.29	7.30
6.82	7.95	7.91	7.90	7.93

TABLE IV-11

The effect of the Ca- *and* Na-*concentration on the selectivity coefficient* $K_{Na/Ca}$ *of moor peat in* Ca-*form*

$[Ca^{2+}]_0$ meq/l	$[Na^+]_0 = 5$ meq/l	$[Na^+]_0 = 25$ meq/l	$[Na^+]_0 = 50$ meq/l
	$K_{Na/Ca}$		
0	$0.3\ .10^{-3}$	$0.26.10^{-3}$	$0.20.10^{-3}$
0.52	$0.38.10^{-3}$	$0.29.10^{-3}$	$0.23.10^{-3}$
2.76	$0.35.10^{-3}$	$0.31.10^{-3}$	$0.27.10^{-3}$
5.00	$0.37.10^{-3}$	$0.32.10^{-3}$	$0.29.10^{-3}$

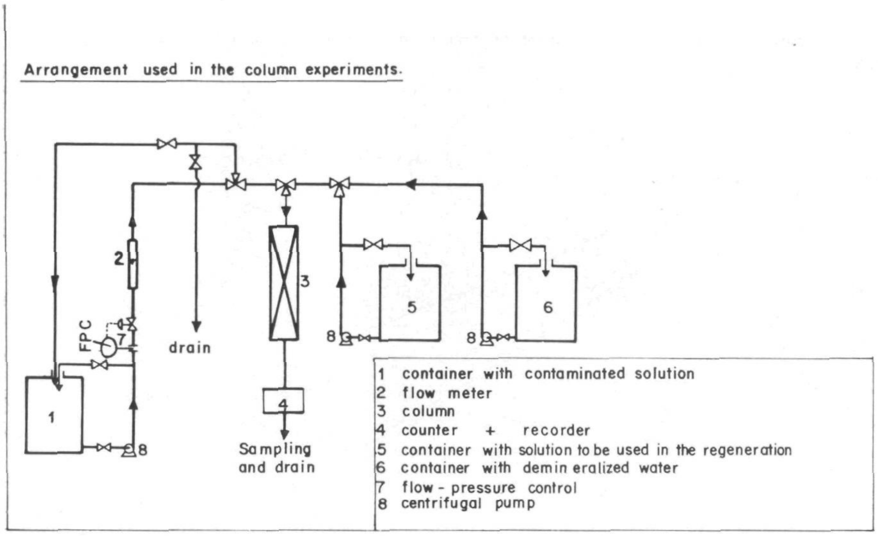

Fig. IV-1

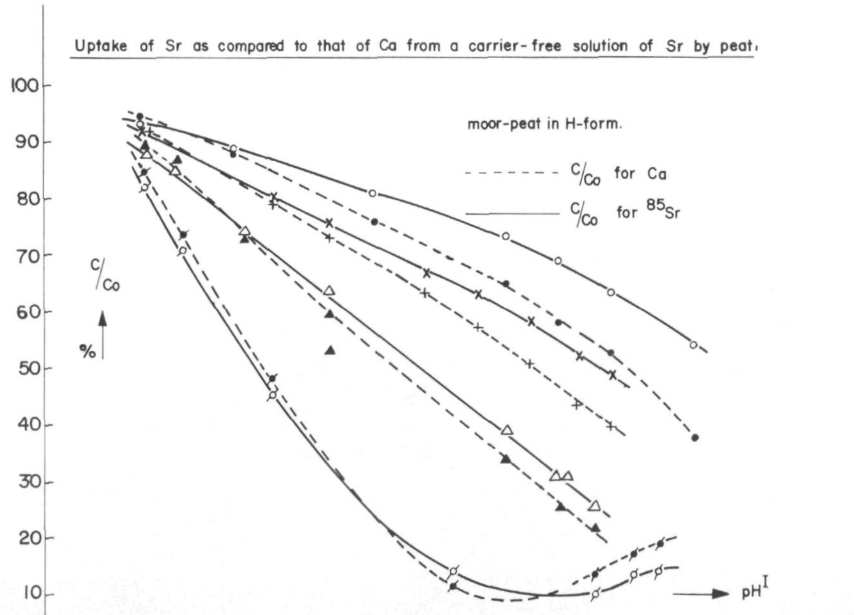

Fig. IV-2

Sorbent: 2000 ppm moor-peat in H-form; — Contact time: 20-24 hrs.

Starting solutions: ○ ● 9.88 meq $CaCl_2$/l + × 7.68 meq $CaCl_2$/l

△ ▲ 4.94 meq $CaCl_2$/l ϕ ɸ 2.49 meq $CaCl_2$/l

in addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l and 2.5 Na_2SO_4/l.

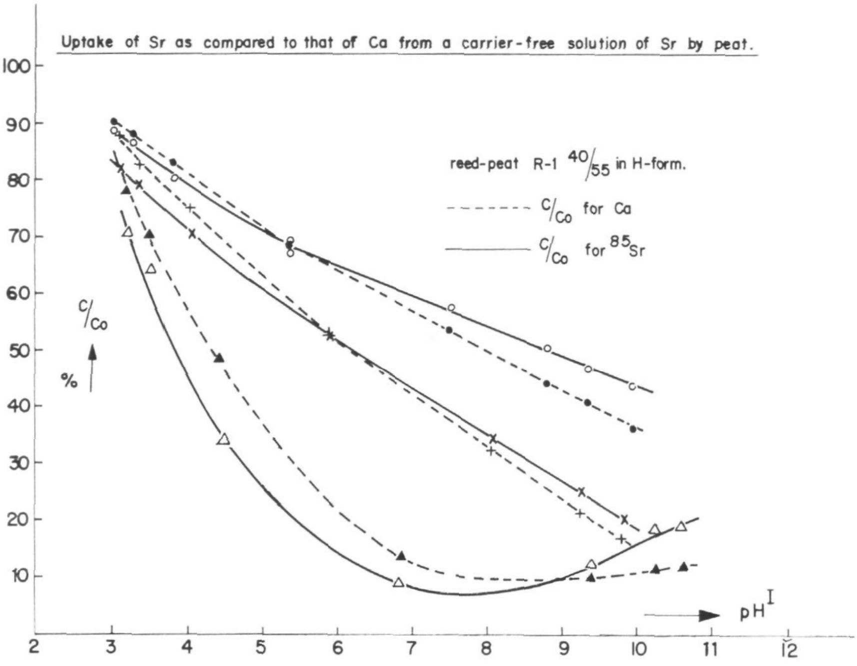

Fig.. IV-3

Sorbent: 2000 ppm reed-peat R-1 40/55 in H-form; — Contact time: 20-24 hrs.
Starting solutions: ○ ● 7.48 meq $CaCl_2$/l + × 4.96 meq $CaCl_2$/l △ ▲ 2.49 meq $CaCl_2$/l
in addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{85}Sr/ml.

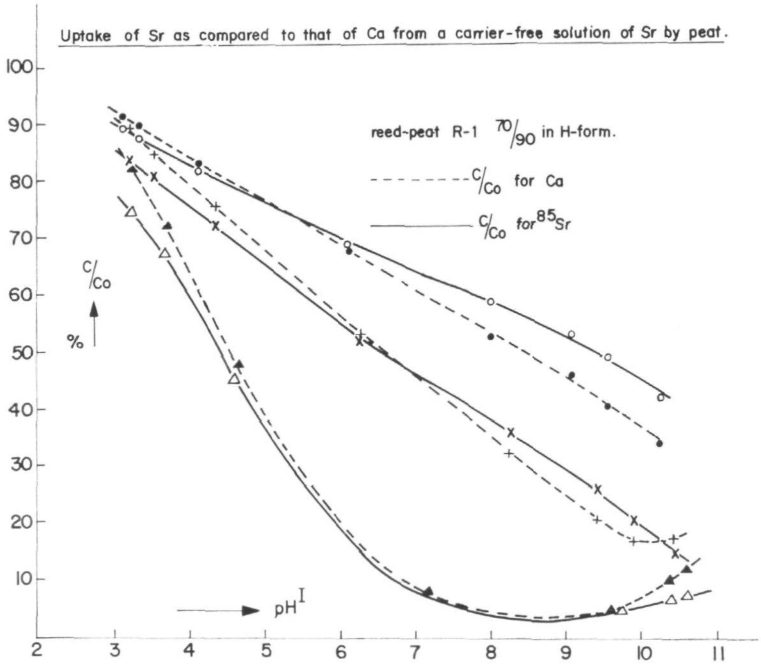

Fig. IV-4

Sorbent: reed-peat R-1 70/90 in H-form; — Contact time: 20-24 hrs.
Starting solutions: ○ ● 7.48 meq $CaCl_2$/l + × 4.96 meq $CaCl_2$/l △ ▲ 2.49 meq $CaCl_2$/l
in addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{85}Sr/ml.

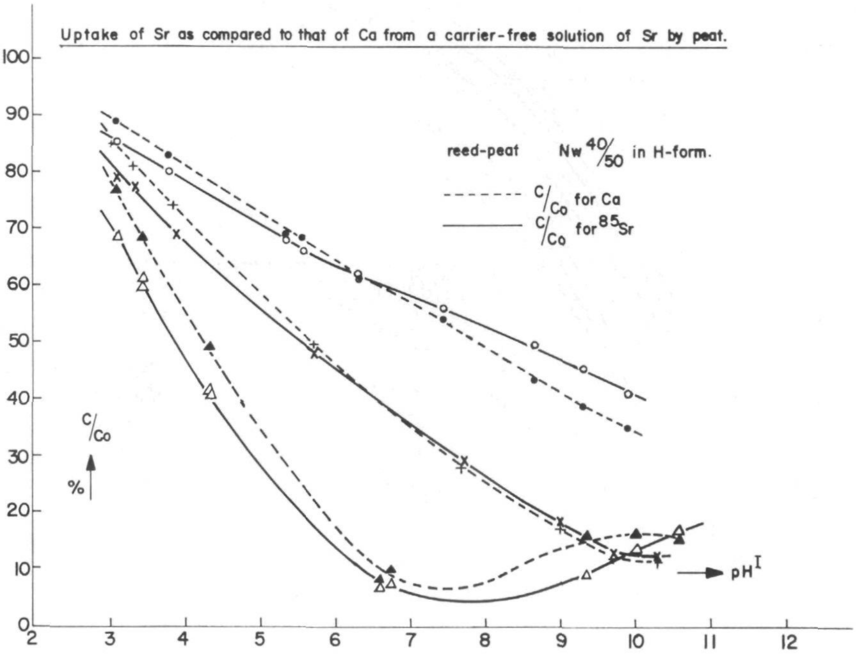

Fig. IV-5

Sorbent: 2000 ppm reed-peat Nw 40/55 in H-form; — Contact time: 20-24 hrs.

Starting solutions: ○ ● 7.48 meq $CaCl_2$/l + × 4.63 meq $CaCl_2$/l △ ▲ 2.49 meq $CaCl_2$/l in addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{85}Sr/ml.

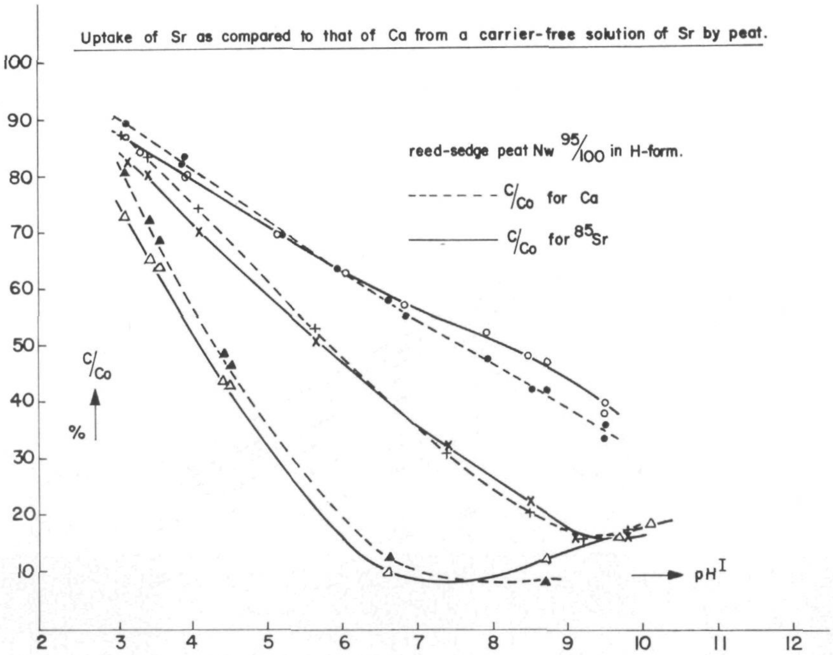

Fig. IV-6

Sorbent: 2000 ppm reed-sedge peat Nw 95/100 in H-form; — Contact time: 20-24 hrs.

Starting solutions: ○ ● 7.48 meq $CaCl_2$/l + × 4.63 meq $CaCl_2$/l △ ▲ 2.49 meq $CaCl_2$/l in addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{85}Sr/ml.

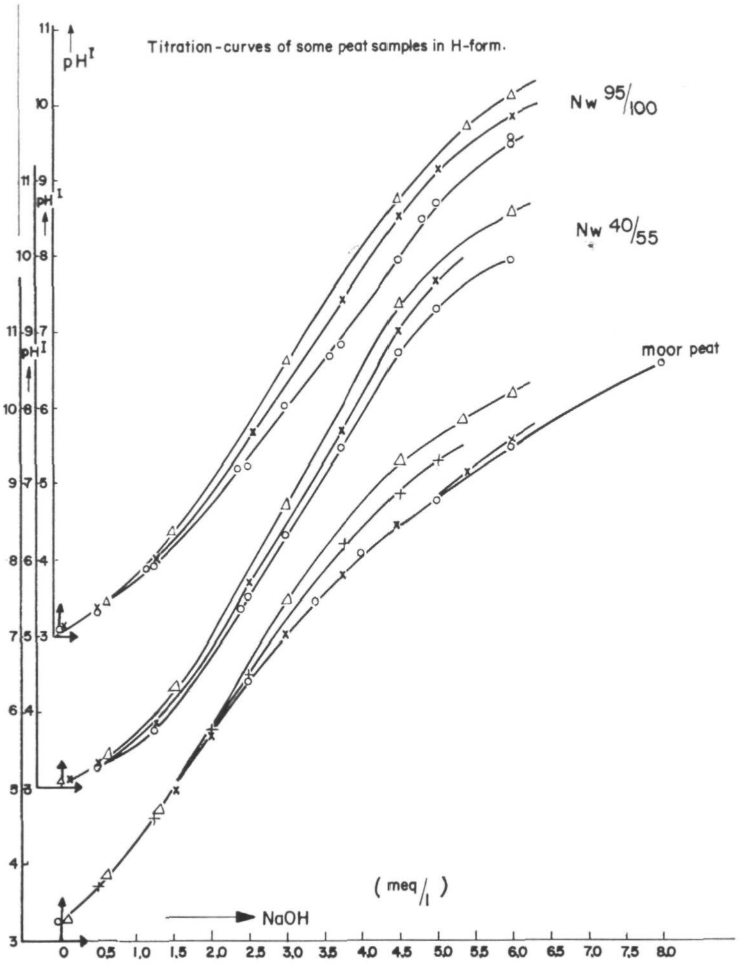

Fig. IV-7

Peat concentration: 2000 ppm
Contact time: 20-24 hrs.
For symbols see Fig. IV-2 for moor peat, Fig. IV-5 for reed peat Nw 40/55 and Fig. IV-6 for reed-sedge peat Nw 95/100.

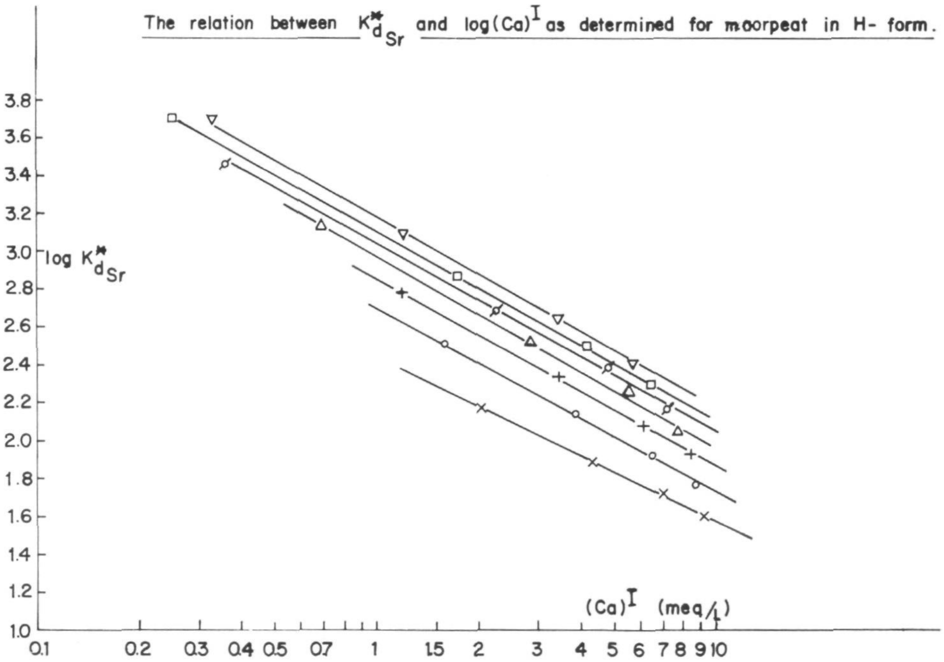

Fig. IV-8

Peat concentration: 2000 ppm. — Contact time: 20-24 hrs.
▽ $\mathrm{pH}^{\mathrm{I}} = 9$; □ $\mathrm{pH}^{\mathrm{I}} = 8$; ϕ $\mathrm{pH}^{\mathrm{I}} = 7$; △ $\mathrm{pH}^{\mathrm{I}} = 6$; + $\mathrm{pH}^{\mathrm{I}} = 5$; ○ $\mathrm{pH}^{\mathrm{I}} = 4.25$; × $\mathrm{pH}^{\mathrm{I}} = 3.5$

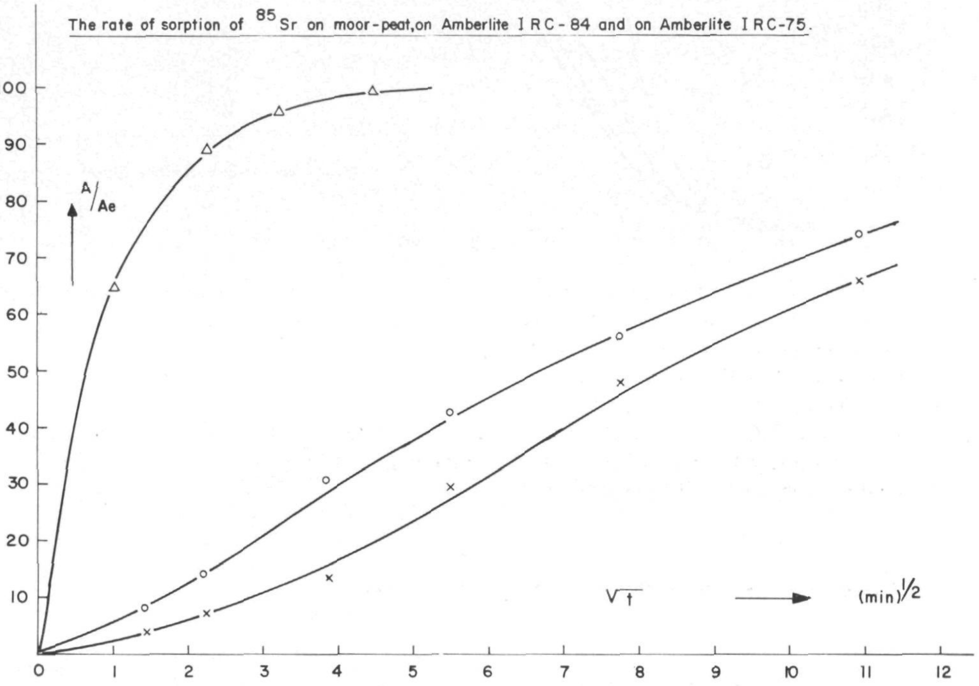

Fig. IV-9. — Concentrations of peat and Amberlite species: 2000 ppm.

△ experiment with moor peat; starting solution: 5 meq $CaCl_2$/l, 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 7.5 meq NaOH/l ($A_e = 86.7\%$).

○ experiment with Amberlite IRC-84; starting solution: 10 meq $CaCl_2$/l, 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 10 meq NaOH/l ($A_e = 94.1\%$).

× experiment with Amberlite IRC-75; starting solution as used in the experiment with Amberlite IRC-84 ($A_e = 90.7\%$).

A_e = percentage of ^{85}Sr sorbed after 24 hrs contact; A = percentage ^{85}Sr sorbed after contact time t.

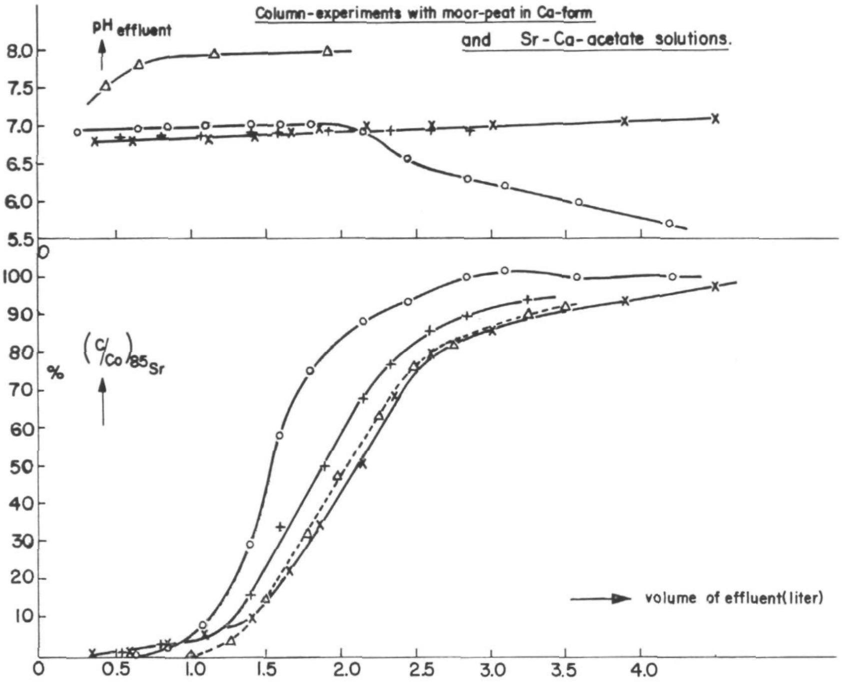

Fig. IV-10 — Moor peat treated beforehand by percolating the column with a Ca-acetate solution of pH 7.2. Column diameter: 2.4 cm; column height: 20 cm; amount of peat 10.6 g; flow rate $v_0 = 1.6$ m/hr.

× solution: 5 meq $Ca(CH_3COO)_2$/l, 6.5 meq NaCl/l; pH 9.75
\+ solution: 5 meq $Ca(CH_3COO)_2$/l, 6.5 meq NaCl/l; pH 7.8
○ solution: 5 meq $Ca(CH_3COO)_2$/l, 6.5 meq NaCl/l; pH 5.1
△ solution: 5 meq $CaCl_2$/l, 7.5 meq $NaHCO_3$/l, 2.5 meq Na_2SO_4/l; pH 8.2. In this experiment the column was pretreated with a $CaCl_2$-solution containing 2.5 meq $NaHCO_3$/l.

All solutions contained 5.10^{-3} μCi ^{85}Sr/ml.

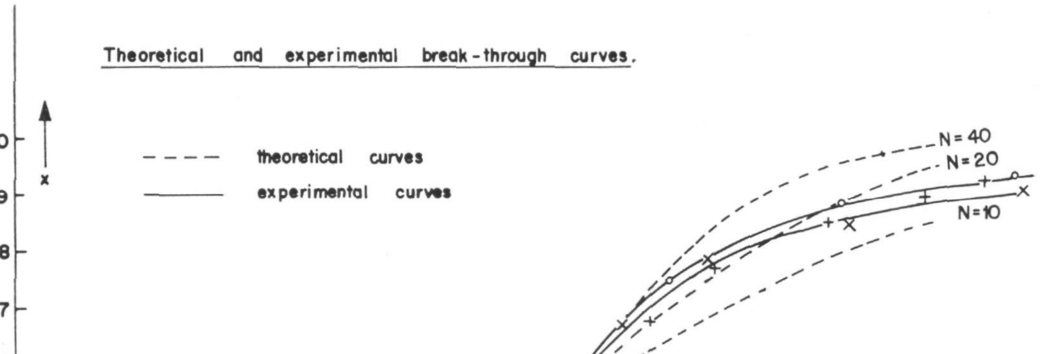

Fig. IV-10a — For symbols see Fig. IV-10.

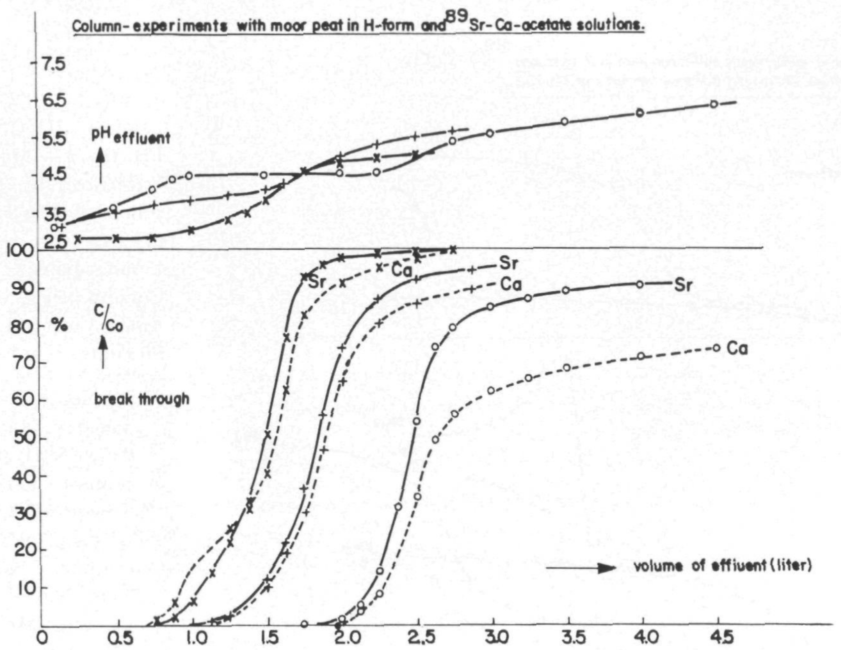

Fig. IV-11 — Moor peat treated beforehand by percolating the column with a HCl-solution of pH 2.19. Column diameter: 2.4 cm; column height: 20 cm; amount of peat 10.6 g; flow rate $v_0 = 1.6$ m/hr.

× solution: 5 meq $Ca(CH_3COO)_2$/l, 5 meq NaCl/l; pH 5.05
+ solution: 5 meq $Ca(CH_3COO)_2$/l, 5 meq NaCl/l; pH 6.80
○ solution: 5 meq $Ca(CH_3COO)_2$/l, 5 meq NaCl/l; pH 10.9
All solutions contained 5.10^{-3} μCi ^{89}Sr/ml.

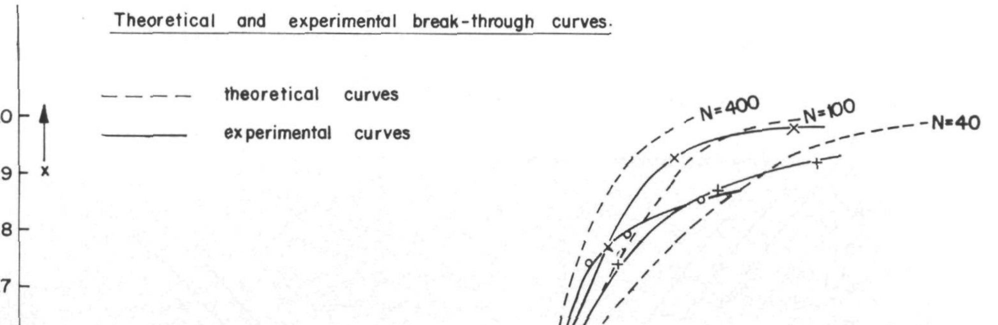

Fig. IV-11a — For symbols see Fig. IV-11

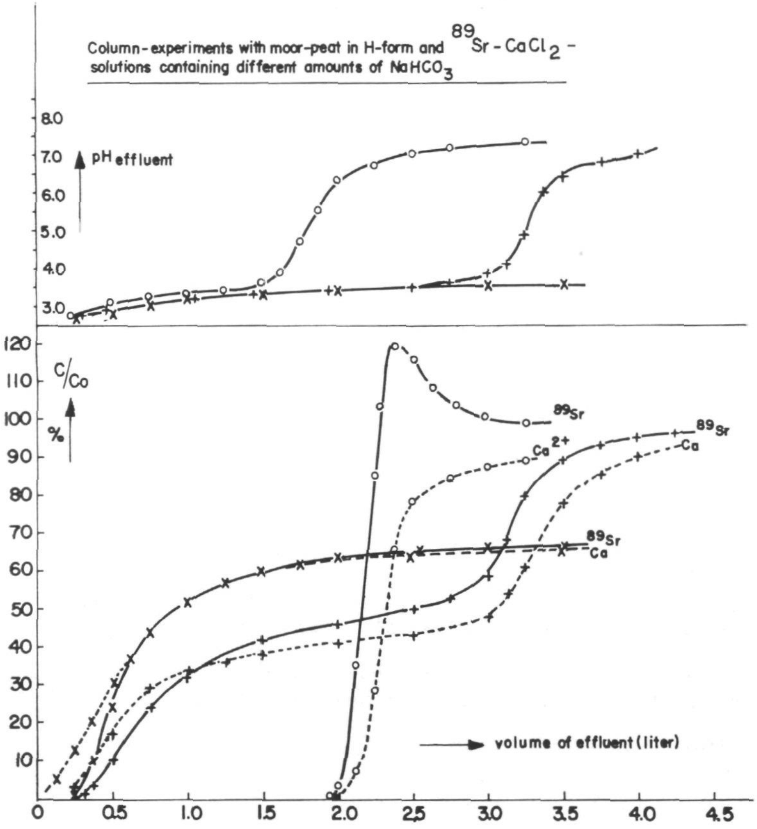

Fig. IV-12 — Moor peat treated beforehand by percolating the column with a HCl-solution of pH 2.19.

Column diameter: 2.4 cm

Column height: 20 cm

Amount of peat: 10.6 g

Fow rate: $v_0 = 1.6$ m/hr.

× solution: 5 meq $CaCl_2$/l,
5 meq NaCl/l,
0 meq $NaHCO_3$/l; pH 10.8

\+ solution: 5 meq $CaCl_2$/l,
5 meq NaCl/l,
2.5 meq $NaHCO_3$/l; pH 8.0

○ solution: 5 meq $CaCl_2$/l,
5 meq NaCl/l,
5.0 meq $NaHCO_3$/l; pH 8.2

All solutions contained 5.10^{-3} μCi ^{89}Sr/ml.

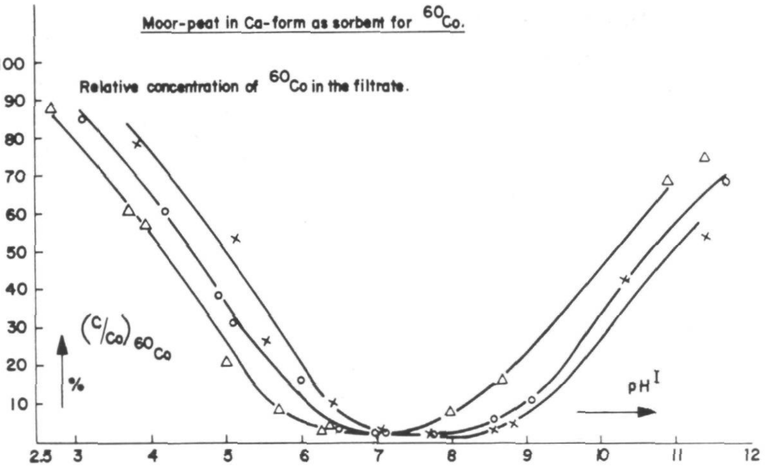

Fig. IV-13a

Sorbent: 2000 ppm moor peat in Ca-form. — Contact time: 20-24 hrs.

Starting solutions: △ 1.59 meq $CaCl_2$/l
○ 4.92 meq $CaCl_2$/l
× 7.44 meq $CaCl_2$/l

In addition to $CaCl_2$ all solutions contained 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{60}Co/ml.

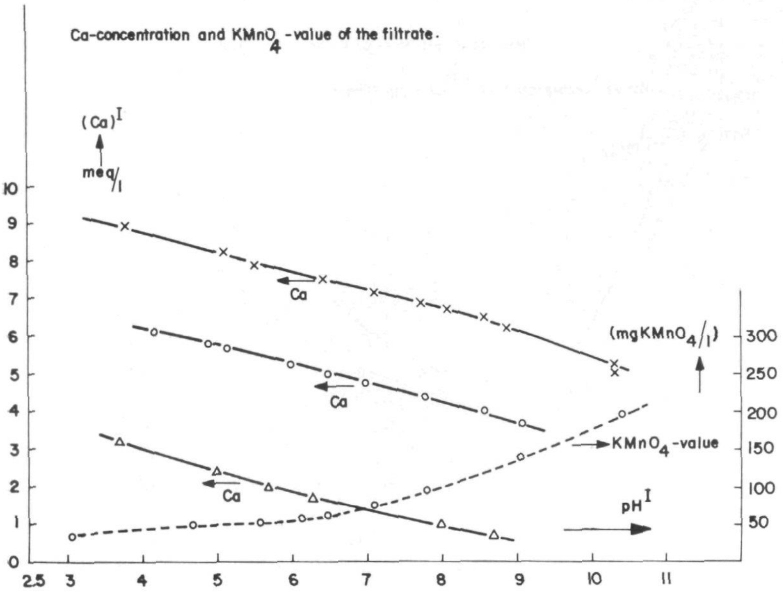

Fig. IV-13 b — See subscription of Fig. IV-13 a.

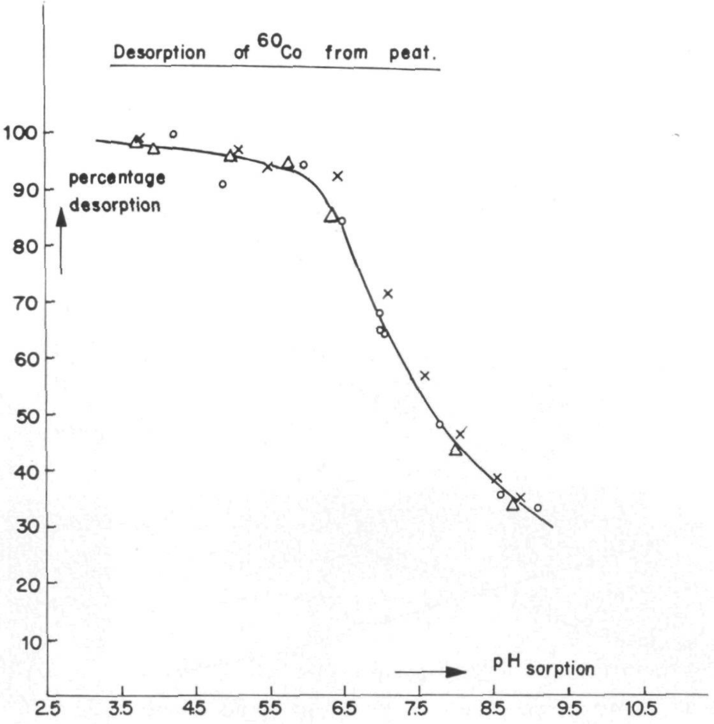

Fig. IV-13 c — See subscription Fig. IV-13 a.

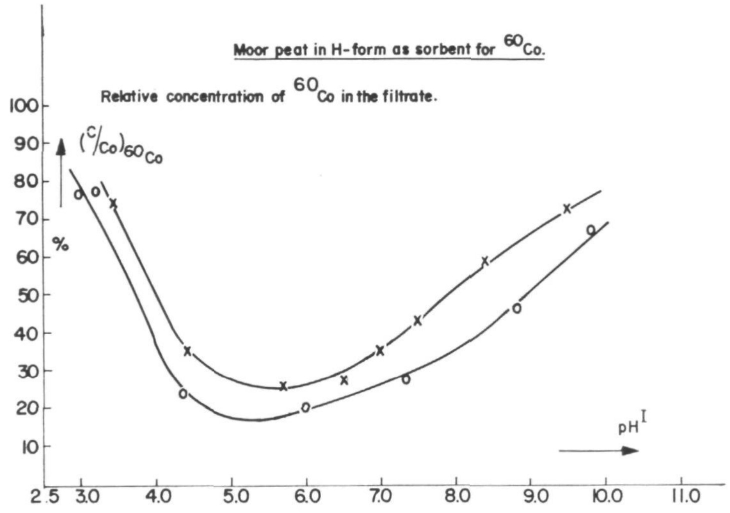

Fig. IV-14 a

Sorbent: 1870 ppm moor peat in H-form. — Contact time: 20-24 hrs.

Starting solutions: × 4.84 meq $CaCl_2$/l

○ 4.92 meq $CaCl_2$/l

In addition to $CaCl_2$ *the solutions contained* 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} μCi ^{60}Co/ml.

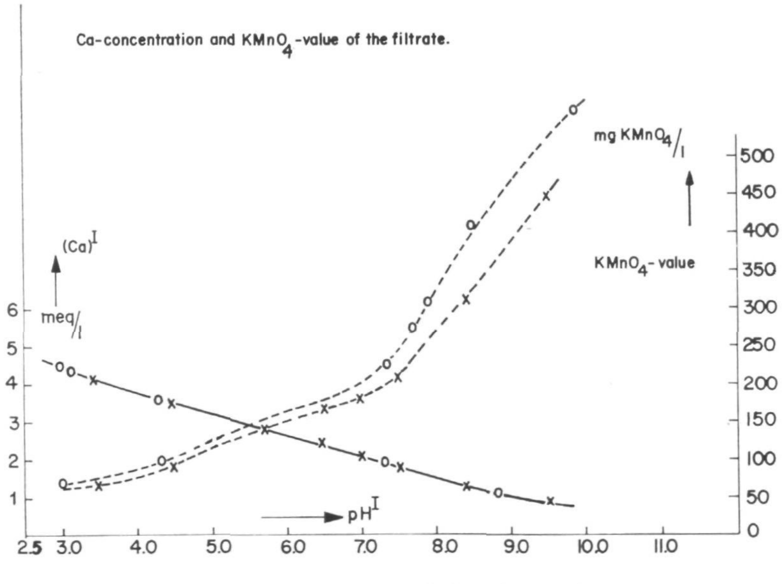

Fig. IV-14 b — See subscription Fig. IV-14 a.

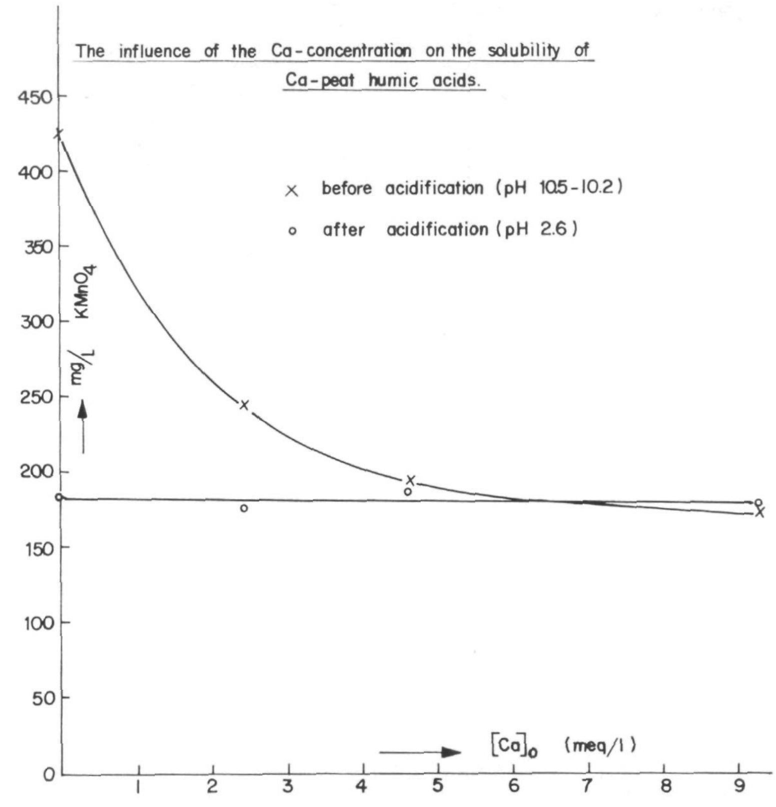

Fig. IV-15

Peat concentration: 1900 ppm. — Contact time: 24 hrs before and after acidification. Starting solutions: various concentrations of $CaCl_2$ and always 4.75 meq NaOH/l.

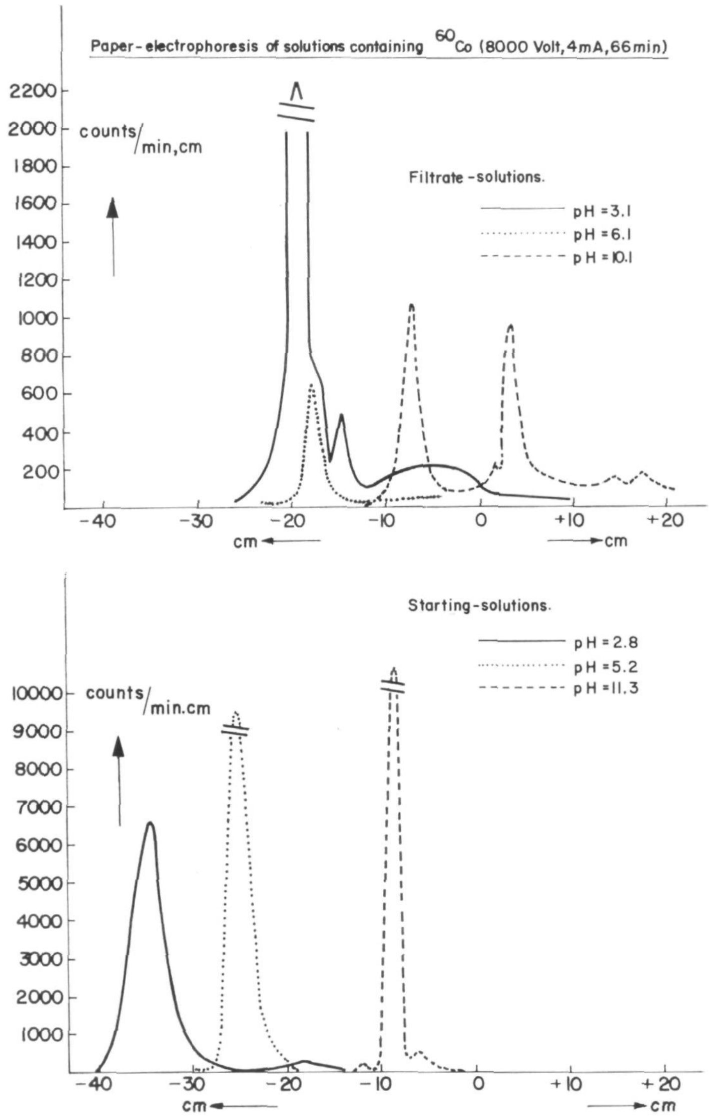
Paper-electrophoresis of solutions containing 60Co (8000 Volt, 4mA, 66min)
counts/min,cm
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
Filtrate-solutions.
pH = 3.1
pH = 6.1
pH = 10.1
-40
-30
-20
-10
0
+10
+20
cm
cm
Starting-solutions.
pH = 2.8
pH = 5.2
pH = 11.3
counts/min.cm
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
-40
-30
-20
-10
0
+10
+20
cm
cm

Fig. IV-16

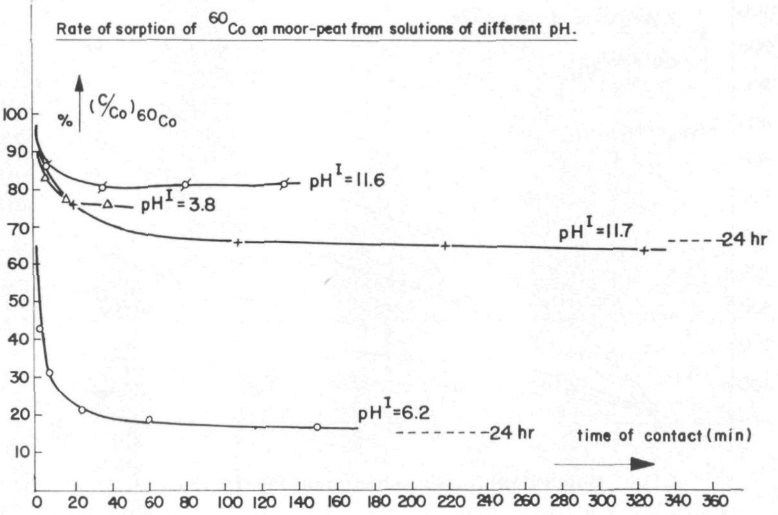

Fig. IV-17

Sorbent: 1900 ppm moor peat in H-form.

Starting solutions: 5 meq $CaCl_2$/l, 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and 5.10^{-3} $\mu Ci^{60}Co$/ml; the various solutions differed in pH.

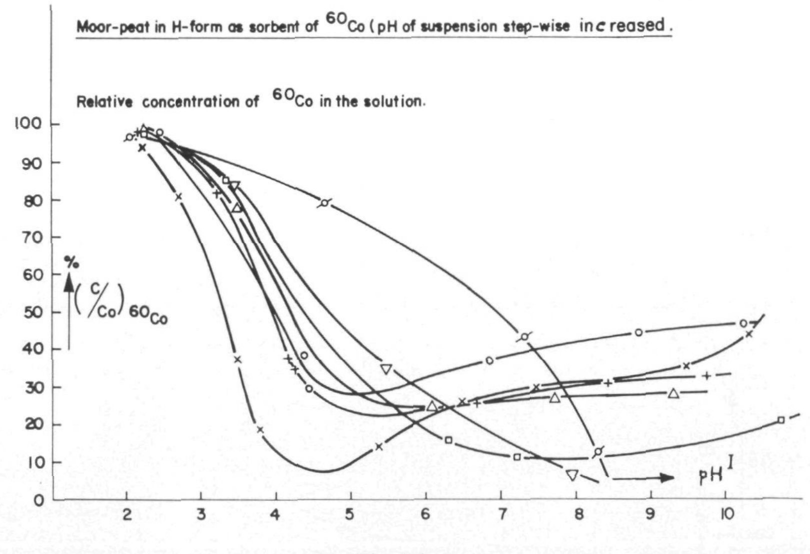

Fig. IV-18a

Sorbent: 1900 ppm moor peat in H-form. — Contact time: 20 hrs at the minimum after each addition of NaOH.

Starting solutions: × 0 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
○ 2.22 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
+ 4.45 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
△ 8.90 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
□ 4.45 meq $CaCl_2$/l and 22.10^{-3} meq $CoCl_2$/l
▽ 4.45 meq $CaCl_2$/l and 28.10^{-2} meq $CoCl_2$/l
ϕ 4.45 meq $CaCl_2$/l and 3.6 meq $CoCl_2$/l
All solutions contained 5.10^{-3} $\mu Ci^{60}Co$/ml and 8 meq HCl/l.

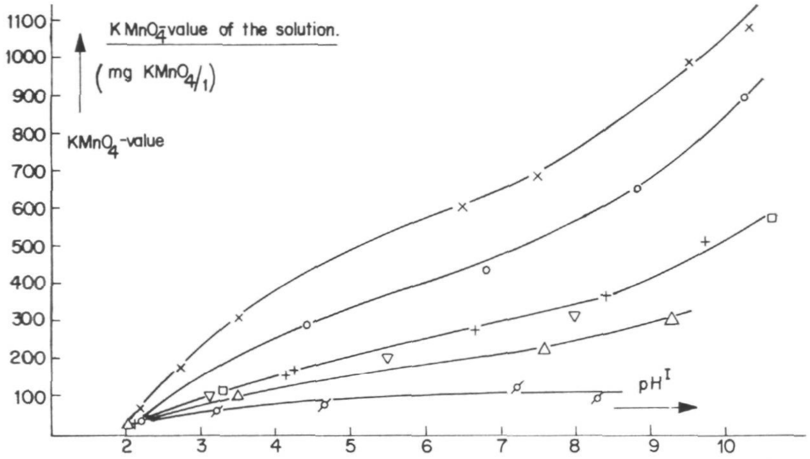

Fig. IV-18b — See subscription Fig. IV-18a.

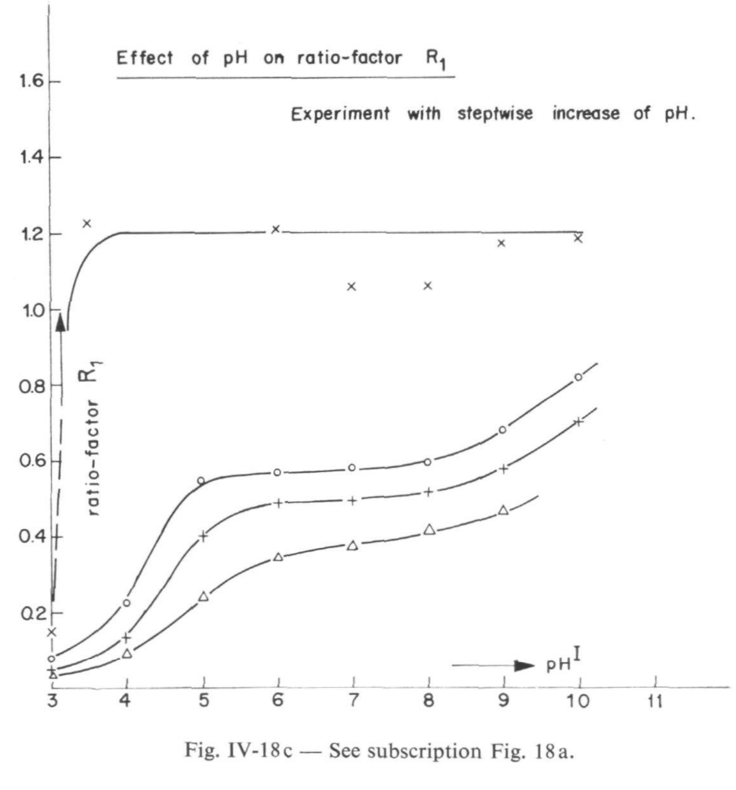

Fig. IV-18c — See subscription Fig. 18a.

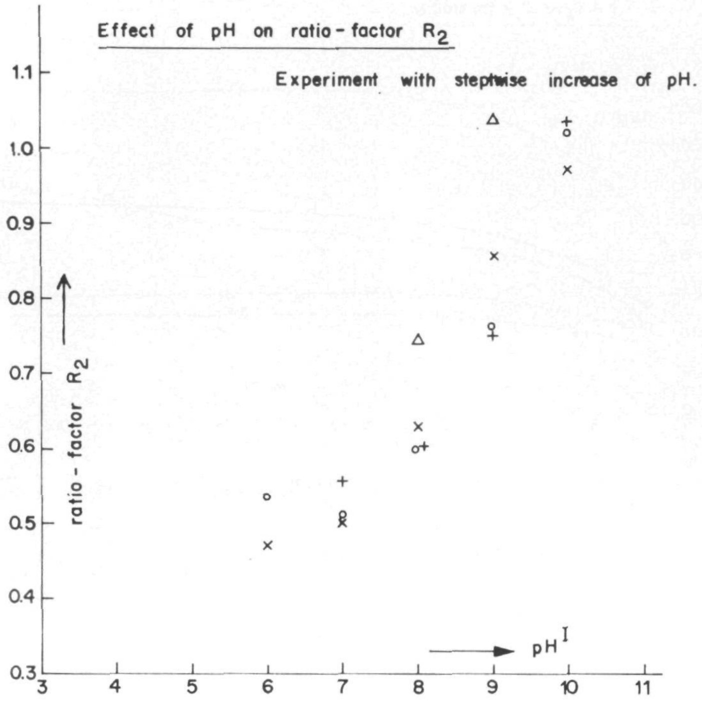

Fig. IV-18 d — See subscription Fig. IV-18 a.

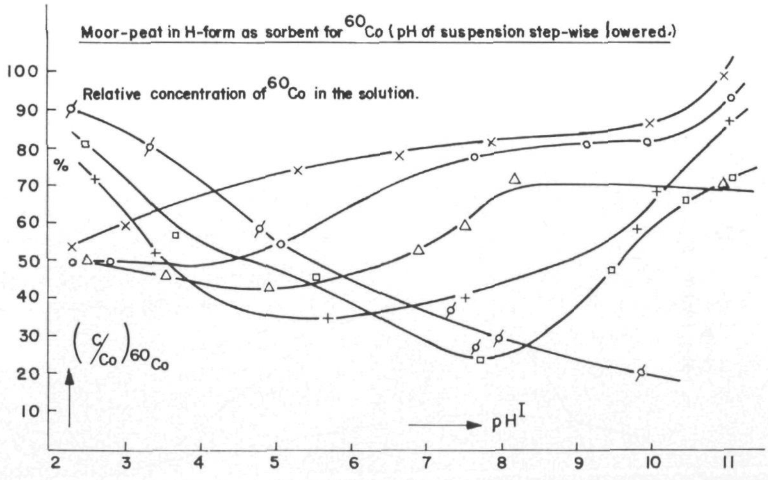

Fig. IV-19 a

Sorbent: 1900 ppm moor peat in H-form. — Contact time: 20 hrs at the minimum after each addition of HCl.

Starting solutions: × 2.25 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
○ 4.45 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
△ 8.90 meq $CaCl_2$/l and 0.0 meq $CoCl_2$/l
+ 4.45 meq $CaCl_2$/l and 22.10^{-3} meq $CoCl_2$/l
□ 4.45 meq $CaCl_2$/l and 28.10^{-2} meq $CoCl_2$/l
ϕ 4.45 meq $CaCl_2$/l and 3.6 meq $CoCl_2$/l.
All solutions contained 5.10^{-3} $\mu Ci\,^{60}Co$/ml and 11 meq NaOH/l.

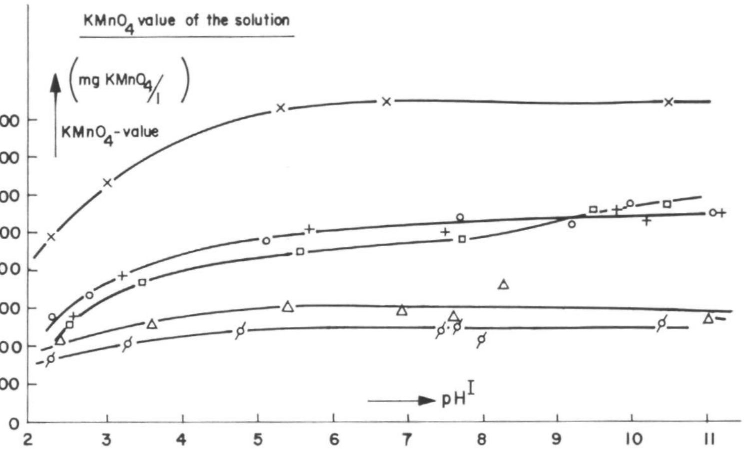

Fig. IV-19 b — See subscription Fig. IV-19 a.

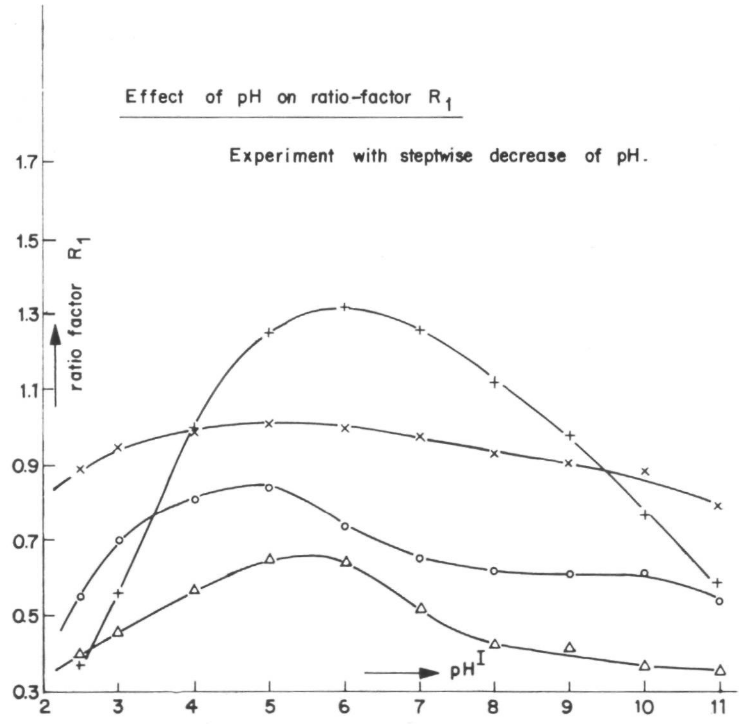

Fig. IV-19 c — See subscription Fig. IV-19 a.

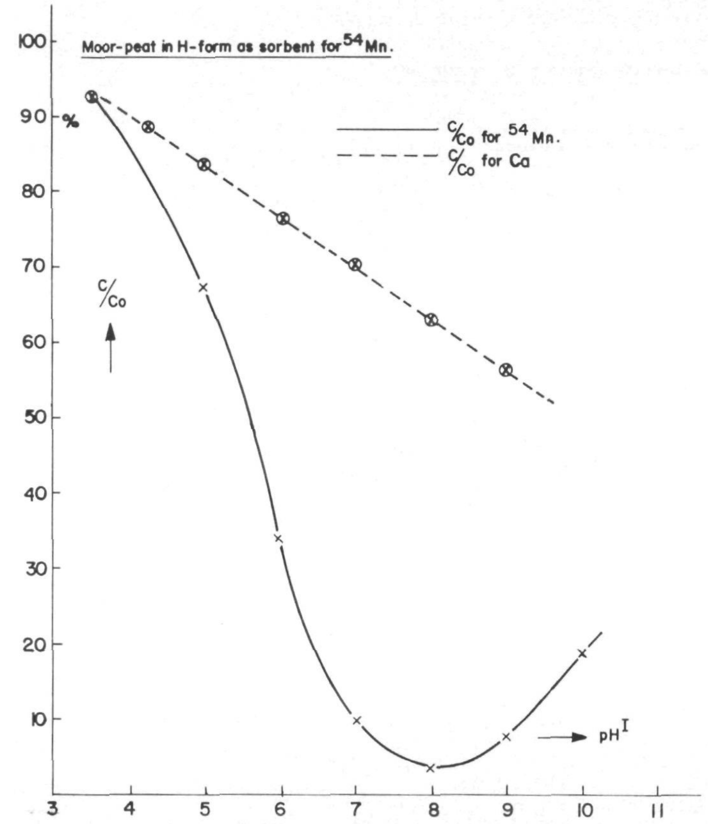

Fig. IV-20

Sorbent: 1820 ppm moor peat in H-form. — Contact time: 20-24 hrs.
Starting solution: 9.72 meq $CaCl_2$/l, 2.5 meq NaCl/l, 2.5 meq Na_2SO_4/l and $5 . 10^{-3}$ μCi ^{54}Mn/ml.

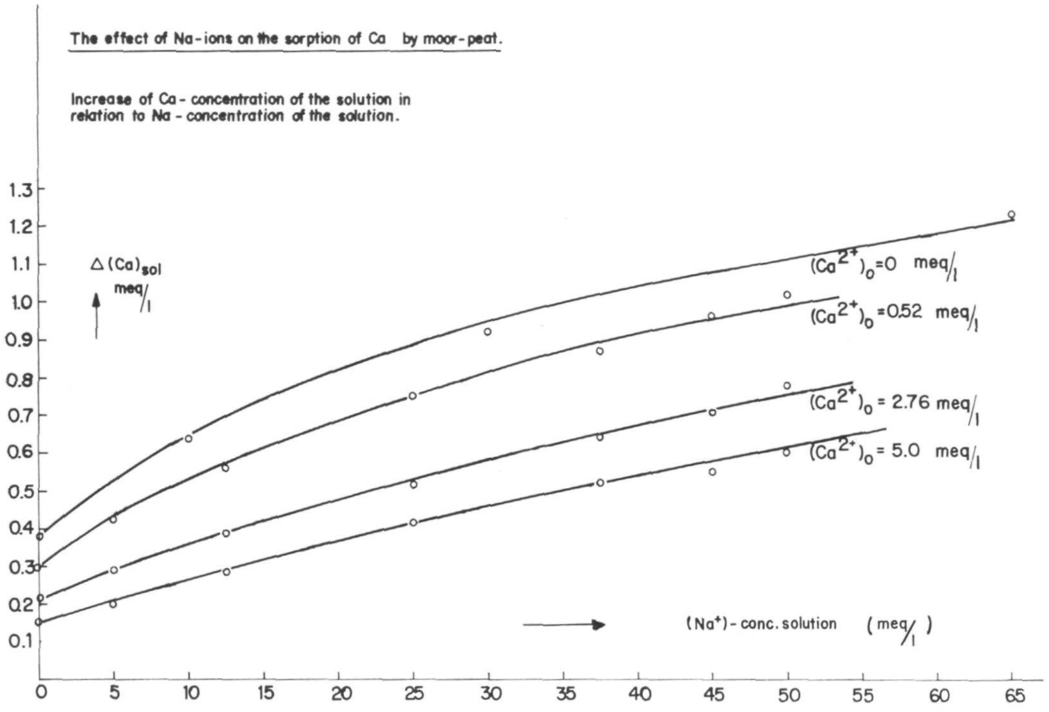

Fig. IV-21

Sorbent: 2000 ppm moor peat in Ca-form. — Contact time: 20-24 hrs.
End-pH supernatant: 6.0-6.3.

V. PREPARATION OF A MODIFIED PEAT WITH SUPERIOR WORKING PROPERTIES

V-1. **Introduction**

Since natural peat as ion exchanger shows some unfavourable properties, attempts were made to prepare from it a product with superior properties.

Evidently an improvement of the properties of peat is required in the following respects:

1. stability against alkalies,
2. exchange capacity,
3. selectivity for strontium relative to calcium,
4. rigidity and swelling properties.

A well-known method for improving the ion exchange capacity and the stability against alkalies of bituminous coals and anthracites consists of a treatment of these materials with fuming sulphuric acid. Sulphonic acid groups are built in and additional carboxylic groups seem to be formed by oxidation. At the same time, the sulphuric acid treatment causes poly-condensation reactions by which the coal is "gelified" and its chemical and mechanical stability is improved ($^{1-3}$).

The treatment with concentrated sulphuric acid has also been applied to peat by some investigators. Schmidt *et al.* (^{4}) reported about the preparation of a rather good ion exchanger from peat by treating the peat with concentrated sulphuric acid (15-20 ml/g) at 180-200 °C during 90-120 min. The exchange capacity of the product was 1.5-1.7 meq/g at $\mathrm{pH} \simeq 6$. The exchange capacity of the starting material was 0.5-0.8 meq/g at $\mathrm{pH} \simeq 6$. M. Dina (^{5}) investigated the sulphonation of peat, lignite and coal using 95% sulphuric acid. The optimal reaction temperature and reaction time were found to be for peat 100 °C and 4-5 hrs respectively. The ion exchange capacity of the products ranged from 0.7 to 1.7 meq/g. M.H. Khundkar (^{6}) performed the sulphonation at 120 °C in the presence of MnO_2 as a catalyst. A reaction time of 3 hrs was applied. The product obtained paired a reasonable capacity (2.25 meq/g) with satisfactory chemical and physical properties. A recent Japanese patent reports about the preparation of low cost ion exchanger from peat (^{12}). A 20% aqueous dispersion of peat is first treated 6 hrs with 5 ml formaldehyde at 60-70 °C. Subsequently a mixture of 50 parts of this product and 50 parts sulphuric acid was kept at room temperature to give an ion exchanger of 2.2 meq/ml capacity.

An attractive method to improve the ion exchange properties of peat might be the method, used by Langenhorst, Tels, Vlughter, Waterman (^{7}), with the object to restrict the swelling properties of sugar beet pulp. According to these authors a treatment of sugar beet pulp with a mixture of formaldehyde and HCl at about 110 °C is quite effective. However, the treatment is accompanied with a decrease of the ion exchange capacity (being 0.62 meq/g before and 0.50 meq/g after the treatment). Otherwise, a considerable improvement leading to an exchange capacity of 1.62 meq/g was obtained when a mixture of formaldehyde, HCl and dilute H_2SO_4 was used in the treatment. According to Deuel (^{8}) the function of formaldehyde is the introduction of cross-links (methylene bridges) in the macro-molecules of the pulp (pectin, cellulose). Cross-links are formed when the OH-groups in the macro-molecules are arranged in trans-position. Cross-link formation is catalysed by acids. For this purpose alone the addition of either HCl or H_2SO_4 may suffice. However, in view of the extra favourable effect of H_2SO_4 on the exchange capacity of the final product, a treatment of the pulp with a mixture of formaldehyde and dilute H_2SO_4 is most attractive.

In our investigations concerning the improvement of the properties of peat as an ion exchanger, the effect of a treatment with both concentrated and dilute H_2SO_4 was investigated. Some preliminary experiments carried out with mixtures of dilute H_2SO_4 and various concentrations of formaldehyde showed that formaldehyde had no additional favourable effect.

V-2. **Experimental**

V-2-1. PROCEDURE APPLIED IN THE PREPARATION OF MODIFIED PEAT

Modified peat samples have been prepared with dilute and concentrated H_2SO_4. Various factors of interest with respect to the properties of the products have been studied. In all cases moor peat was used as raw material.

V-2-1-1. *Treatment of moor peat with dilute* H_2SO_4

A known amount of the moor peat in natural form was dispersed in a solution of H_2SO_4 of known concentration. After wetting of the peat, the excess of the H_2SO_4-solution was removed by filtration in a Büchner funnel under suction. The quantity of H_2SO_4 taken up by the peat was determined by weighing and is expressed in the following always as g 100% H_2SO_4 per g peat. Subsequently the mixture was homogenized and divided into several portions each containing approximately 20 g of dry peat. These portions were put in an open beaker and heated in a stove in which varying reaction conditions were maintained. After heating, the products were weighed again and then washed with demineralized water until the reaction on H_2SO_4 in the wash water was negative.

Modified peat samples were prepared under a variety of conditions with respect to:

1. time of reaction;
2. temperature of reaction;
3. initial content of H_2SO_4 of the acid—peat mixture;
4. the presence or the absence of oxygen.

In addition some samples of modified peat were treated in a closed container through which either air or nitrogen was passed. Samples under nitrogen were prepared at a relatively short and at a rather long reaction time.

For a more extensive investigation of properties, two samples (N_B, M_B) were prepared starting with 500 g of dry peat.

V-2-1-2. *Treatment of moor peat with concentrated* H_2SO_4

Peat was wetted with the minimum amount of H_2SO_4 required for complete wetting. being 2 ml H_2SO_4 (98%) per g peat. The wetted peat consists in this case of a jelly-like black coloured paste (when wetted with dilute H_2SO_4 the particles of the peat do not clog together). The mixture ($\sim$20 g dry peat per portion) was then placed in the stove and heated during a fixed time. The product obtained is washed with demineralized water, dried in air and weighed.

In the treatment with concentrated H_2SO_4 only the effect of the time and temperature of reaction were investigated. Only one sample was prepared with an excess of H_2SO_4 over the minimum amount.

V-2-2. TESTING AND ANALYSIS OF THE SAMPLES

The samples prepared were tested for their ion exchange properties and analysed for their element composition.

In testing of the samples the following procedures have been applied.

A. *Determination of exchange capacity by titration in the presence of* $CaCl_2$

Portions of 110 mg of the modified peat (always in H-form) were dispersed in 60 ml of a 0.813 molal $CaCl_2$ solution to which different amounts of a standardized 0.1 N NaOH solution had been added. The suspensions were shaken for 24 hrs and then filtered. In the filtrate the pH was determined potentiometrically and in a few cases the free acid concentration (viz. HCl) was determined by potentiometric titration (end-pH 7) with 0.1 N NaOH. The total amount of 0.1 N NaOH consumed, represents a value for the exchange capacity of the peat. The exchange capacity found in this way is somewhat too high, because part of the NaOH is consumed by humic acids dissolved from the peat. This particularly is true at pH-values higher than about 6 and only to a limited extent at lower pH-values. Thus, this technique does not give any accurate information about the amount of calcium adsorbed by the solid material and furthermore does not indicate the selectivity between Ca en Sr adsorption. Therefore a technique described under B was also applied.

B. *Direct determination of the ion exchange capacity and the separation factor* $\alpha_{Sr/Ca}$

Portions of the peat ($\sim$100 mg) were dispersed in 50 ml of Ca-acetate solution of about 15 meq/l Ca, which contained about 5.10^{-3} μCi/l ^{85}Sr*, 50 meq/l Na-acetate as additional buffer and a known amount of 0.1 N NaOH. In most experiments this NaOH solution was diluted to 1 meq/l unless otherwise stated (Tables V-8, 9, 10 and 11). The suspensions were shaken for 24 hrs and filtered. In the filtrate the Ca-concentration, the activity of ^{85}Sr and the pH were determined. From the results obtained the exchange capacity and the separation factor were calculated.

For determining the amount of Na-ions introduced into the peat, during the test, in some cases the peat was separated quantitatively from the suspension and treated with 20 ml of a 0.1 N HCl solution. After shaking of the mixture for about 2 hrs, the peat was separated from the mixture and washed thoroughly on the filter with demineralized water. Filtrate and wash-water were combined and the volume was made up to 100 ml with demineralized water in a volumetric flask. In this solution the HCl- and the Ca-concentration were determined by titration with standardized 0.1 N NaOH and 0.0172 N EDTA respectively. The exchanged amount of Na can then be calculated from the Ca^{2}-concentration of the solution and the amount of HCl consumed in the desorption of Ca- and Na-ions from the peat.

Most of the samples were analysed for C-, H-, N-, S- and O-content. The C-, H- and N-analysis were made in two- or trifold using a Perkin-Elmer analysor Type 240.

The S-content was determined according to the method of Schöninger in duplicate ([13]). The moisture content was determined for all the samples by drying in a stove at 110°C and/or in a vacuum exsiccator over P_2O_5 to constant weight. The rest value was interpreted as being oxygen. The S-content of the samples prepared by means of dilute H_2SO_4 can be at the low side, because at that time the experimental problems of the analytical method (incomplete burning of the peat and the use of appropriate Pt-electrode in the conductrometric titration of sulphate) were not completely solved.

V-3. **Results**

All products resulting from the treatment of peat with H_2SO_4 consist of carbonized powder, containing particles which are for about 90% larger than 0.2 mm when concentrated H_2SO_4 has been used. When dilute H_2SO_4 is used, the main part (70%) of the product consists of particles smaller in size than 0.2 mm.

The latter particles are hard and, rather brittle. In general the material is moistened easily by water.

The various samples prepared are listed in Table V-1a (samples prepared with dilute

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* Specific activity of ^{85}Sr: 14,500 Ci/g.

H_2SO_4) and Table V-1 b (samples prepared with concentrated H_2SO_4) together with the condition of the preparation process.

The analytical results of the various products are summarized in Tables V-2 to V-10. Though the influence of the various process conditions are discussed below it may be said already that the H_2SO_4-treatment has a favourable effect on the specific uptake of Sr besides Ca. Moreover the treatment is accompanied by a certain loss in weight, varying between 15 and 38% by weight, depending on process conditions (see Tables VIa and V-1b).

V-3-1. TREATMENT WITH DILUTE H_2SO_4

V-3-1-1. *Effect of reaction time*

The total amount of H-ions exchanged in the titration of the product samples by means of NaOH (procedure A) has been calculated for some selected pH-values. From the results (see Fig. V-1) it follows that the capacity increases on continuation of the heating; no maximum in the exchange capacity is reached. The filtrate obtained in the titration is always completely colourless at $pH < 5.5$ and becomes slightly yellow at higher pH-values, although to a much lower extent than with natural peat and mostly not below pH 8.

The analytical results obtained according to procedure B are summarized in Table V-2, together with the results of the element analyses. In accordance with the data in Fig. V-1 an increase of the capacity is also found here with an increase in time of reaction. However, the capacity as found according to procedure B is appreciably lower than that found in the titration (procedure A). The discrepancies between both methods may be attributed to the large differences in the concentration of calcium in the solutions (compare Fig. IV-7).

Concerning the results of the element analyses the following is observed:

1. An abrupt increase of the C-content and a decrease of the O-content takes place immediately after the start of the operation, followed by a slow decrease of the C-content and an increase of the O-content on continued heating.
2. A continuous and rather strong decrease of the H-content occurs at increasing time of reacting (heating).
3. The S-content does not show a simple trend; at first an increase and later a decrease seems to occur.

V-3-1-2. *Effect of the temperature of reaction*

Testing of the samples prepared at different temperatures of reaction reveals (see Fig. V-2 and Table V-3) that the temperature has only a slight effect on the exchange capacity of the product. A maximum in the capacity seems to be reached at about 150-160°C.

Furthermore the temperature has no distinct effect on the element composition of the product; only a very slight increase of the O-content seems to take place at increasing temperature.

V-3-1-3. *Effect of the initial quantity of* H_2SO_4 *present in the peat*

The effect of the quantity of H_2SO_4 present in the peat appears to be a rather important factor with respect to the exchange capacity of the product (see Fig. V-3 and Table V-4). The results seem to indicate that a maximum capacity is reached at an initial H_2SO_4-content of the peat somewhere between 0.4 and 0.56 g 100% H_2SO_4 per g peat. In this connection it is interesting to note that attempts to prepare a modified peat at a H_2SO_4-content of 0.44 g/g did not meet with success, because of self-ignition of the peat, taking place after 4-6 hrs heating in the oven. Also one sample was lost in this way at a H_2SO_4-content of 0.56 g/g.

No distinct trend can be observed in the C-, O- and S-content of the products; the H-content decreases at increasing H_2SO_4-content of the peat.

V-3-1-4. *Effect of oxygen*

The results of the experiments given before seem to indicate that oxygen (from the air) besides oxygen from sulphuric acid takes part in the reaction. To verify this some samples were prepared in the absence of oxygen, viz. under a stream of nitrogen. These samples are referred to in the following as "N_2-samples". Reference samples were prepared simultaneously in open beakers (referred to as "air-samples"). The results are summarized in Table V-5. Significant differences between the "N_2-samples" and the "air-samples" are indeed found, namely:

1. The exchange capacity of the "N_2-samples" (viz. no. 16 and 18) is considerably lower than that of the corresponding "air-samples" (viz. no. 17 and 19).
2. The "N_2-samples have a lower O-content and a higher C- and H-content than the "air-samples".
3. Contrary to the "air-samples", the "N_2-samples" contain a substantial amount of soluble humic acids. The wash-water of the "N_2-samples" was yellow and showed a strong buffer action at pH 3-4. These effects were much less pronounced with the "air-samples". Moreover, considerably more H_2SO_4 was left behind in the "air-sample", viz. 103 ml and 301 ml 0.1 N NaOH were required for the neutralization of the wash-water of the samples 16(N_2) and 17(air) respectively.

The presence of (air-) oxygen seems to be essential for the improvement of the capacity and the stability of the material. This idea is supported by the results summarized in Table V-6. Heating in air results in a distinct increase of the capacity, even with a sample prepared under nitrogen (sample 16) from which the excess H_2SO_4 washed away (sample 22). The heating in air is always accompanied with an increase of the O-content and a decrease of the C- and H-content, especially when the heating is performed in the presence of H_2SO_4.

The treatment in an open beaker is much more effective than in a closed container using a stream of air. A considerably lower exchange capacity is obtained in the last case (see the results in Table V-7). Neutralization of the wash-water revealed that more H_2SO_4 is left behind in the peat when the treatment is performed in an open beaker than when the heating is performed in a closed container.

Sulphur-dioxide and carbon-dioxide are formed in the reaction of H_2SO_4 with peat. The quantities of these compounds were determined in the preparation of sample 16. For this purpose the N_2-gas was passed through three washing bottles placed behind the reaction vessel, which contained known amounts of standardized 1 N NaOH. Complete absorption of SO_2 was observed; the NaOH solutions were analysed for SO_2 and CO_2. About 100 mmol SO_2 and 45 mmol CO_2 were formed per 25 g peat.

The modified peat sample N_B, which has been used extensively in the sorption experiments of radionuclides (discussed in Chapter VI), was also tested according to procedure *B*. The results are summarized in Table V-8, together with the results obtained in the testing of some commercial ion exchangers.

V-3-1-5. *Effect of heating of peat in the absence of* H_2SO_4

In the light of the various results described it seemed interesting to investigate the influence of a heat treatment of peat in presence of air but in absence of H_2SO_4. Now portions of the moor peat were subjected to a heat treatment (performed in open beakers) at a temperature of 160 °C during different periods of time. The samples were tested according to procedure B.

From the results (see Table V-9) it follows that:

1. A small increase of the capacity takes place only after about 100 hrs heating.
2. The improvement of the capacity is accompanied by a slight increase of the separation factor $\alpha_{Sr/Ca}$.
3. The loss of weight increases at prolonged heating.
4. The O- and H-content decrease and the C-content increases on continued heating.

Furthermore it was observed that the filtrates of the test solutions were coloured slightly yellow. This was especially true with untreated peat and with sample V.

V-3-2. TREATMENT WITH CONCENTRATED H_2SO_4

The samples prepared with concentrated H_2SO_4 consist of mechanical stable and hard particles. This holds especially for the product obtained in the treatment with excess H_2SO_4. Such a material swells excessively when washed with water and shows a spongy form. However, during drying the material shrinks to hard particles which have lost their tendency to swell in water to a great extent. Samples prepared with the minimum amount of H_2SO_4 required for complete wetting do not show excessive swelling upon washing with demineralized water.

The effect of time and temperature of reaction on the properties of the final product have been studied. The influence of air oxygen was not investigated.

V-3-2-1. *Effect of reaction time*

Samples prepared at different reaction times were tested according to procedure B and analysed for their element composition and ash-content. The results are summarized in Table V-10. As appears from this table a product with a high exchange capacity is obtained even at a comparably short time of reaction. As was found for the samples prepared with dilute H_2SO_4, also here the exchange capacity increases with increasing time of reaction.

Concerning the elementary analyses the following may be noted:

1. As compared with the starting material the products have a considerably higher C-content and a lower H- and O-content.
2. The C-, O- and N-contents do not show a clear trend with increasing reaction time.
3. The S-content is slightly higher than in products formed with dilute sulfuric acid, but seems to decrease at increasing time of reaction. The H-content of the product also tends to decrease under continued heating.

The samples prepared with concentrated H_2SO_4 seem to have a slightly lower H-content than those prepared with dilute H_2SO_4. Moreover, contrary to the samples prepared with dilute H_2SO_4, no distinct increase of the O-content and decrease of the C-content takes place with time.

V-3-2-2. *Effect of reaction temperature*

The results of the testing and of the element analyses of the samples prepared at different temperature of reaction are summarized in Table V-11. It appears from this table that the exchange capacity of the modified peat increases on raising the temperature of the treatment. Moreover, the loss in weight increases significantly when the peat is heated at a temperature exceeding 138 °C (see Table V-1 b).

Furthermore the temperature has a distinct effect on the element composition of the product, viz.

1. The H-content decreases with increasing temperature, especially between 138 and 162 °C.

2. The S-content decreases relatively strongly with increasing temperature.
3. The O-content tends to increase at increasing temperature.

V-4. **Discussion of the results**

A heat treatment of peat in the presence of H_2SO_4 results in a product which has a strongly improved cation exchange capacity, a higher specificity for Sr relative to Ca and an improved mechanical and chemical stability.

Peat wetted with dilute H_2SO_4 looses, upon heating, at first the excess of water. Then gradually condensation, oxidation, sulfonation, and esterification reactions seem to occur under the influence of the concentrated H_2SO_4, which is left behind in the peat. The condensation reactions will lead to loss of oxygen and to dehydration under formation of C–O–C bonds. The oxidation leads to loss of hydrogen and carbonization. In the oxidation reactions new carboxylic groups may be formed, but otherwise also a certain decarboxylation occurs under the influence of H_2SO_4. According to the S-content of the modified peat samples, which is 3.3 weight percent at the maximum, sulphonic acid groups may contribute 1 meq/g to the cation exchange capacity (at a S-content of 3.3 weight percent).

In the treatment of peat with dilute H_2SO_4 the presence of air is essential in order to obtain a product with a high ion exchange capacity. Heating of peat in the absence of H_2SO_4 results in a very small improvement of the capacity. A somewhat higher increase of the capacity takes place when the peat sample has been pretreated with H_2SO_4 (sample 22, see Table V-6). An appreciable decarboxylation will probably not take place upon heating of peat in air.

Data from literature dealing with the effect of heating on coal reveal ($^{9-11}$) that decarboxylation reactions hardly occur below 170 °C. Oxidation reactions with coal already take place at a temperature of 120 °C or even lower. This results in the formation of new carboxyl-, carbonyl- and hydroxyl-groups, leading to an increase of the O-content of the material. Moreover a certain degradation of the coal takes place, resulting in formation of soluble humic acids.

The same processes probably occur in the heating of peat in air, although it results here in an increase of the C-content and in a decrease of the H- and O-content; this might be caused by the fact that peat, contrary to coal, is rich in aliphatic compounds. In the oxidation the aliphatic compounds (or the aliphatic side chains of aromatic nuclei) are attacked first.

Apparently H_2SO_4 has a promoting effect on the oxidation of peat with air-oxygen. As stated before the oxidation of peat with oxygen from the air is probably only important when dilute H_2SO_4 is used, because only in that case the area of the peat exposed to the air is large. The inducing effect of H_2SO_4 may be caused by the formation of compounds which are more sensitive to oxidation, e.g. compounds having a double bond, and hydro-sulphates. On the other side a catalytic action must probably be attributed to SO_2, because the forced removal of SO_2 results in a product of an appreciably lower capacity (see results in Table V-7).

In conclusion it may be stated that a significant improvement of the properties of peat, e.g. ion exchange capacity, selectivity, mechanical and chemical stability, can be obtained by heating peat in the presence of dilute or concentrated H_2SO_4.

Of the two techniques the use of concentrated H_2SO_4 is preferred because:

1. A much shorter time of reaction suffices for a reasonable improvement of the ion exchange properties of the material.
2. The mechanical stability of the product is better, whereas also larger particles are formed.
3. The chemical stability of the product is better (see also Chapter VI, paragraph 3.2.2) because it contains less soluble humic acids.
4. There is less chance for self ignition, since the peat wetted with concentrated H_2SO_4 consists of a compact jelly-like mass in which air-oxygen only can penetrate by diffusion.

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TABLE V-1a

Conditions of the preparations of modified peat samples (dilute H_2SO_4*)*

Sample no.	Starting material	H_2SO_4-conc. ml 98% H_2SO_4/l	H_2SO_4 content g/g peat	Reaction temp. °C	Reaction time hrs	Other reaction conditions	Weight loss %
0	H-peat	—	—	—	—	—	—
1	”	100	0.40	150	4	in open beaker	25
2	”	100	0.40	150	8	”	25
3	”	100	0.40	150	16	”	23
4	”	100	0.40	150	32	”	25
5	”	100	0.40	150	64	”	29
6	”	100	0.40	150	128	”	29
7	”	100	0.40	135	136	”	33
8	”	100	0.40	160	130	”	32
9	”	100	0.40	145	136	”	22
10	”	100	0.40	155	130	”	34
11	”	250	0.56	160	31	in beaker covered with a watchglass	33
12	”	250	0.56	160	120	in open beaker	36
13	”	250	0.56	160	64	”	36
14	”	50	0.17	160	120	”	35
15	”	95	0.25	160	120	”	38
16 (N_2)	”	150	0.62	160	96	in closed container in N_2-stream	35
17	”	150	0.62	160	96	in open beaker	33
18 (N_2)	”	200	0.48	150	8	in closed container in N_2-stream	—
19	”	200	0.48	150	8	in open beaker	—
20	19 continued*	sample 19 continued		150	119	”	—
21	18 continued*	sample 18 continued		150	119	in closed container in air	—
22	sample 16*	—	0	150	336	—	9
23	sample 16*	200	0.22	150	122	—	5
24	H-peat	200	0.48	150	126	in open beaker	—
25	”	200	0.48	150	126	in closed container in air	—
N_B	”	200	—	155	15	in open beaker	—
M_B	”	100	—	155	65	”	—

* In the formation of samples 20 and 21 excess H_2SO_4 was not removed from the starting material. Samples 22 and 23 were prepared from samples purified from excess H_2SO_4.

TABLE V-1b

Conditions of the preparation process of modified peat samples (98% H_2SO_4)
Starting material: moor peat

Sample no.	H_2SO_4-content g/g	Reaction time hrs	Reaction temperature °C	Weight loss %
A-1	3.6	1.5	156	about 28
A-2	3.6	3.0	156	—
A-3	3.6	5.5	156	about 30
A-4	3.6	7.5	156	—
A-5	3.6	23.5	156	about 30
A-6	3.6	4	94	16
A-7	3.6	4	113	14.5
A-8	3.6	4	119	17.5
A-9	3.6	4	138	17
A-10	3.6	4	162	26
A-11	3.6	4	197	31
B-1	14	7	150	27

TABLE V-2

Analysis of samples (procedure B) prepared with dilute H_2SO_4 *during different reaction times*
(150 °C, 0.40 g H_2SO_4/g peat)

Sample			Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Elements contents (% by weight on water-free samples)					
No.	Reaction time hrs	Moisture content %	meq/g water-free product			C	H	N	S	O	ash
0	untreated	10.2	1.23	0.86	6.60	53.5	4.89	0.70	0.0	37.1	3.8
1	4	4.9	1.48	1.01	6.05	62.5	4.05	0.50	1.0	29.0	2.9
2	8	5.5	1.82	1.04	6.00	—	—	—	—	—	—
3	16	5.3	1.95	1.14	5.95	60.9	2.52	0.7	2.6	30.4	2.9
4	32	7.0	2.32	1.13	5.85	60.5	1.98	—	2.2	30.1	3.5
5	64	7.5	2.53	1.18	5.80	60.0	2.00	0.8	2.65	31.7	2.8
6	128	9.7	3.01	1.17	5.73	57.0	1.70	—	1.80	35.8	3.0

TABLE V-3

Analysis of samples prepared with dilute H_2SO_4 *at different reaction temperatures*
(128-136 hrs, 0.40 g H_2SO_4/g peat)

Sample			Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Elements contents (% by weight on water-free samples)					
No.	Reaction temp. °C	Moisture content %	meq/g water free product			C	H	N	S	O	ash
0	untreated	10.2	1.23	0.86	6.60	53.5	4.89	0.7	0.0	37.1	3.8
7	135	12.9	2.80	1.10	5.85	58.8	1.51	0.6	1.15	35.0	2.9
9	145	12.6	2.98	1.18	5.75	58.8	1.47	0.8	0.55	35.9	2.5
6	150	9.6	3.01	1.17	5.75	57	1.70	—	1.80	35.8	3.0
10	155	10.5	3.16	1.21	5.75	—	—	—	—	—	—
8	160	7.2	3.16	1.17	5.70	57.8	1.36	1.10	0.55	36.0	3.2

TABLE V-4

Analysis of samples prepared with dilute H_2SO_4 *at different* H_2SO_4*-contents* (120-130 hrs, 160 °C)

Sample			Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Elements contents (% by weight on water-free samples)					
No.	H_2SO_4-content g H_2SO_4/g peat	Moisture content %	meq/g water-free product			C	H	N	S	O	ash
0	—	10.2	1.23	0.86	6.60	53.5	4.89	0.70	0.0	37.1	3.8
14	0.17	10.7	2.72	1.22	5.80	58.7	1.69	1.20	1.1	34.4	2.8
15	0.25	10.2	2.82	1.23	5.75	60.0	1.67	1.40	1.35	33.0	2.6
8	0.40	7.2	3.16	1.17	5.70	57.8	1.36	1.10	0.55	36.0	3.2
12	0.56	12.6	3.00	1.23	5.70	59.5	1.10	—	1.7	34.6	2.4

TABLE V-5

Analysis of samples prepared with dilute H_2SO_4 *under air and nitrogen*

Sample		Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Elements contents (% by weight on water-free samples)					
No.	Moisture content %	meq/g water-free product			C	H	N	S	O	ash
16 (N_2)	11.6	1.15	1.08	6.25	65.5	2.92	1.4	1.6	25.7	2.9
17	14.3	3.18	1.30	5.75	59.5	1.25	—	1.5	35.0	2.6
18 (N_2)	6.4	1.45	1.03	6.10	64.0	3.20	—	1.9	27.9	3.0
19	7.8	1.82	1.13	5.95	62.5	2.49	—	1.9	35.2	2.8
0	10.2	1.23	0.86	6.60	53.5	4.89	0.70	0.0	37.1	3.8

TABLE V-6

Analysis of samples prepared with dilute H_2SO_4 *under air and under partly air and partly nitrogen*

Sample			Exchanged amount of Ca meq/g water-free product	$\alpha_{Sr/Ca}$	pH_{equil}	Element contents (% by weight on water-free samples)					
No.	Starting material	Moisture content %				C	H	N	S	O	ash
20	19 continued in air stream during 119 hrs	7.8	2.96	1.30	5.75	59.5	1.55	1.0	1.9	33.3	2.7
19	—	7.8	1.82	1.13	5.95	62.5	2.49	—	1.90	35.2	2.8
21	18(N_2) continued in air stream during 119 hrs	7.6	2.60	1.30	5.85	62.6	2.78	0.9	2.25	28.6	2.8
18(N_2)	—	6.4	1.45	1.03	6.10	64.0	3.20	—	1.9	27.9	3.0
22	16(N_2) without H_2SO_4 (336 hrs)	3.9	2.48	1.27	5.83	60.2	1.82	—	1.29	33.8	2.8
23	16(N_2) with 0.22 g H_2SO_4/g peat (122 hrs)	4.6	2.59	1.22	5.80	60.0	1.20	—	1.35	34.0	2.7
16(N_2)	—	11.6	1.15	1.08	6.25	65.5	2.92	1.4	1.6	25.7	2.9

TABLE V-7

Analysis of samples prepared with dilute H_2SO_4 *in air in an open and in an closed container*
(120 hrs, 150 °C, 0.48 g H_2SO_4/g peat)

Sample			Exchanged amount of Ca meq/g water-free product	$\alpha_{Sr/Ca}$	pH_{equil}
No.	Condition of preparation	Moisture content %			
24	Open beaker	8.3	2.96	1.28	5.75
25	Closed container in air stream	7.0	1.64	1.18	6.05

TABLE V-8

Results of testing (procedure B) of modified peat N_B and some commercial ionexchangers

Sample		Test solution	Exchanged amount of Ca	Exchanged amount of Na	$\alpha_{Sr/Ca}$	pH_{equil}
No.	Moisture %	NaOH-conc. meq/l	meq/g water-free product	meq/g air dry product		
Imac-C-19	31.1	1	2.12	0.14	1.18	6.25
		5	3.20	0.20	0.98	9.78
		10	3.98	0.28	0.93	11.50
Amberlite IRC-75	17.8	1	3.39	0.24	0.68	5.64
		5	4.36	0.32	0.69	5.86
		10	5.92	0.51	0.64	6.33
Dowex-50	33.7	10	4.69	—	1.68	11.20
Modified peat N_B	13.9	1	2.12	—	0.94	6.02
		3	2.22	—	0.86	6.22

TABLE V-9

Results of testing (procedure B) of peat samples after heating in air at a temperature of 160 °C *during different periods and in absence of* H_2SO_4

Sample				Test solution	Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Element contents (% by weight on water-free samples)					
No.	Heating period hrs	Moisture content %	Weight loss %	NaOH-conc. meq/l	meq/g water-free product			C	H	N	S	O	ash
0	—	10.2	—	1	1.23	0.86	6.58	53.5	4.89	0.6	0.0	37.2	3.80
				3	1.47	0.74	7.35						
I	5.75	7.3	2.6	1	1.19	0.89	6.58	53.0	4.65	0.7	0.0	34.8	6.80
				3	1.45	0.73	7.27						
II	23.25	6.8	5.5	1	1.18	0.90	6.57	53.1	4.44	0.6	0.0	35.0	6.90
				3	1.44	0.75	7.09						
III	53.5	6.7	7.25	1	1.21	0.87	6.53	54.0	4.40	0.50	0.0	33.6	7.5
				3	1.44	0.76	6.99						
IV	104.25	5.8	11.9	1	1.31	0.91	6.41	54.8	4.18	0.80	0.0	32.2	8.0
				3	1.49	0.80	6.76						
V	760	5.9	17.30	1	1.97	1.01	5.96	56	3.18	0.80	0.0	31.0	9.1
				3	2.06	0.89	6.12						

TABLE V-10

Results of testing (procedure B) of peat samples prepared with concentrated H_2SO_4 *at different reaction time*

Sample			Test solution	Exchanged amount of Ca	$\alpha_{Sr/Ca}$	pH_{equil}	Element contents (% by weight on water-free samples)					
No.	Reaction time hrs	Moisture content %	NaOH-conc. meq/l	meq/g water-free product			C	H	N	S	O	ash
0	—	10.2	1	1.23	0.83	6.58	53.5	4.89	0.6	0.0	37.2	3.8
A-1	1.5	10.4	3	2.33	1.10	6.1	59.0	1.5	0.56	2.9	31.4	4.6
A-2	3.0	9.7	3	2.56	1.11	6.03	58.9	1.18	0.67	2.2	32.4	4.4
A-3	5.5	13.55	3	2.64	1.12	5.96	60.2	1.73	0.57	2.1	31.5	4.1
A-4	7.5	13.4	3	2.82	1.10	5.96	59.9	1.47	0.46	1.9	32.9	4.2
A-5	23.5	13.45	3	3.40	1.09	5.79	59.5	1.26	0.57	1.6	32.4	4.5
B-1	7	8.2	1	2.87	1.17	5.70						
			3	3.05	1.10	5.83						

TABLE V-11

Results of testing (procedure B) of peat samples prepared with concentrated H_2SO_4 *at different reaction temperatures*

Sample			Test solution	Exchanged amount of Ca	Exchanged amount of Na	$\alpha_{Sr/Ca}$	pH_{equil}	Element contents (% by weight on water-free samples)					
No.	Reaction temp. °C	Moisture content %	NaOH-conc. meq/l	meq/g water-free product	meq/g air dry product			C	H	N	S	O	ash
A-6	94	13.7	1	2.08	0.09	1.09	6.0	60.9	3.22	0.40	3.3	30.4	1.8
			5	2.50	0.16	1.02	6.72						
A-7	113	16.8	1	2.15	0.11	1.12	6.00	60.1	2.53	0.60	3.1	29.5	4.0
			5	2.66	0.18	1.06	6.65						
A-8	119	8.8	1	2.10	0.11	1.11	5.97	61.1	2.53	0.60	2.5	30.1	3.1
			5	2.46	0.18	1.05	6.61						
A-9	138	12.0	1	2.25	0.17	1.15	5.89	60.8	2.22	0.55	2.3	31.4	2.6
			5	2.64	0.18	1.06	6.55						
A-10	162	18.7	1	2.66	0.20	1.12	5.86	61.5	0.98	0.65	1.8	32.3	2.6
			5	3.05	0.24	1.05	6.49						
A-11	197	17.5	1	2.97	0.18	1.13	5.78	62.5	0.97	0.58	1.3	32.0	2.7
			5	3.31	0.26	1.06	6.34						

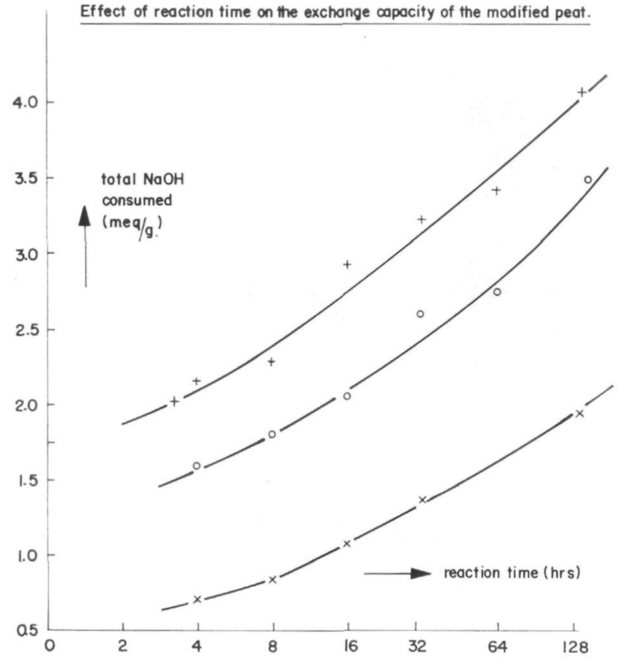

Fig. V-1 — The consumption of NaOH (procedure A) as determined at three different end-pH values;
+ end-pH 5.5 ○ end-pH 4.5 × end-pH 3.0
(Samples 1 to 6; see Table V-2).

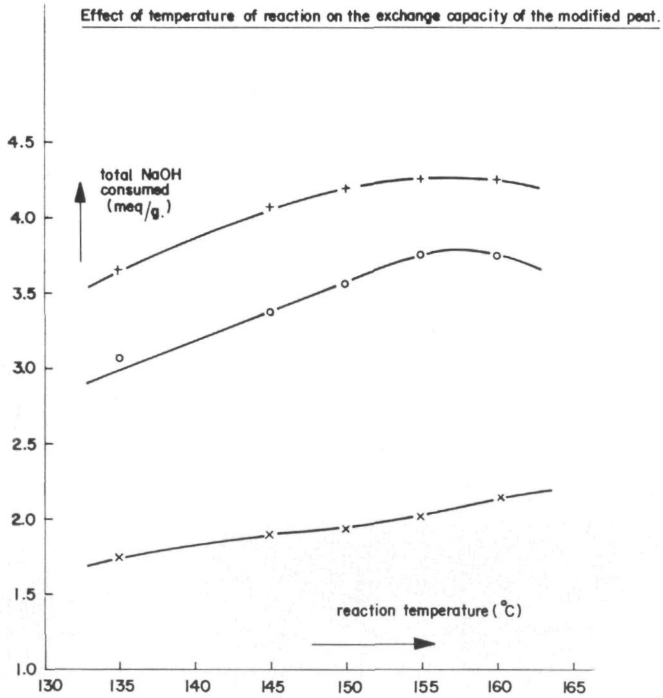

Fig. V-2 — The consumption of NaOH (procedure A) as determined at three different end-pH values;
+ end-pH 5.5 ○ end-pH 4.5 × end-pH 3.0
(Samples 7, 9, 6, 10 and 8; see Table V-3).

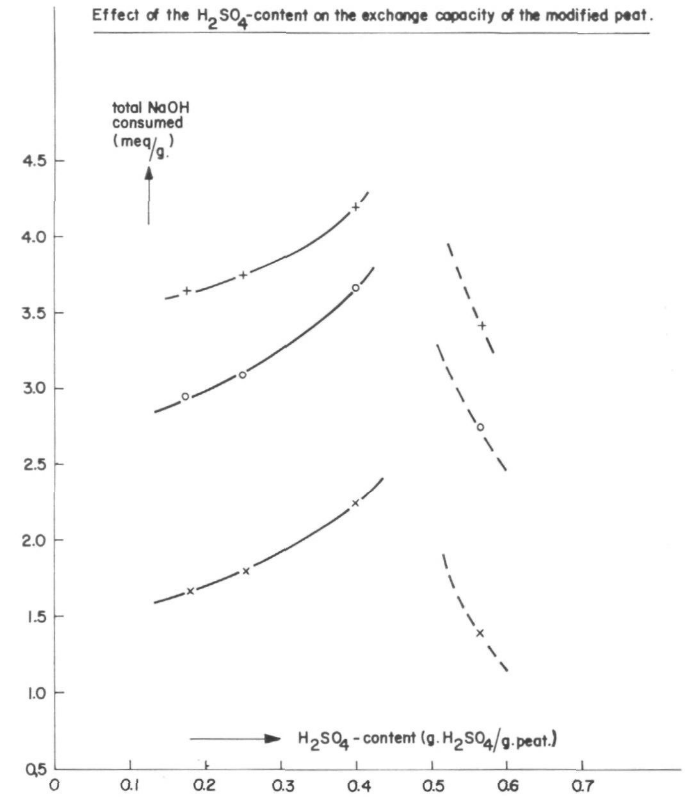

Fig. V-3 — The consumption of NaOH (procedure A) as determined at three different end-pH values;
+ end-pH 5.5 ○ end-pH 4.5 × end-pH 3.0

(Samples 14, 15, 8 and 12; See table IV-4)

VI. THE ION EXCHANGE PROPERTIES OF MODIFIED PEAT

VI-1. **Introduction**

This chapter deals with the investigation of the ion exchange properties of modified peat. In this investigation special attention was paid to the removal of various radioisotopes from water and to the dependency of the ion exchange capacity on the external conditions.

The methods used in this investigation include:

1. Potentiometric titration of the peat in solutions of various compositions with respect to nature and concentration of the competing cations. Thus information is obtained on the variation of the ion exchange capacity with pH, salt-concentration and nature of the salts present in the solution. The results are interpreted in terms of the Donnan theory*.
2. Slurry tests for establishing the ion exchange equilibria involving the relevant radioisotopes and for the measurement of the kinetics of the ion exchange process.
3. Column performance studies at various filtration velocities and with solutions containing different concentrations of Ca. Special attention has been given to the removal of radiostrontium.

VI-2. **Potentiometric titration of modified peat**

VI-2-1. PROCEDURE

A normal progressive titration, such as applied in the titration of simple acids and bases, cannot be used in the titration of peat, due to the slow establishment of equilibrium. The titration was therefore performed by means of batch experiments in which 110 mg of the peat sample in H-form was shaken for 24 hrs with 55 ml of a salt solution containing increasing concentrations of NaOH. The mixture was contained in a closed polythene bottle of 100 ml. After shaking, the pH of the mixture was determined potentiometrically by means of a Philips pH-meter type PR-9600.

In order to be able to apply the Donnan theory, the volume of the internal phase has to be known. This presents one of the main difficulties in the application of this theory, because to determine this volume a complete separation of the external and the internal solution phases is required.

To accomplish this the peat was separated from the suspension by filtration over a S& S filter 1575 under suction. In order to remove the external solution as completely as possible, suction was continued during 3 minutes after the peat on the filter looked dry. The same technique has also been used by Held and Gregor in the determination of the internal volume of synthetic ion exchangers (1).

Subsequently the peat was transferred quantitatively from the filter into a weighed container. After weighing, the container was placed either for one hour in a stove at a temperature 110 °C, or for 24 hrs in a vacuum exsiccator over P_2O_5. The loss in weight represents the quantity of water present in the peat. Both methods lead to about the same results.

Further, for the calculations, the total amount of metal ion(s) present in the peat, as well as the amount of H-ions exchanged from the peat had to be determined. This is necessary because the peat still contains a small amount of humic acids which tend to dissolve particularly at higher pH and, as appeared later on, also a small amount of H_2SO_4.

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* In the calculations the possible effects of dissolved peat have been neglected. This seemed possible because only a few percent of the modified peat was dissolved at pH 9.

The determination of the exchanged amount of H-ions ($S(1-\theta)$) was accomplished by treating the peat with 20 ml 0.100 N HCl. For this purpose the peat was either suspended in the HCl-solution or slowly percolated on the filter with this solution. After this treatment the peat was washed thoroughly with demineralized water in order to remove HCl completely from the peat. The HCl-solution and the wash-water were combined and made up to 100 ml in a volumetric flask. In 50 ml or 100 ml of this solution the HCl concentration was determined by titration with standardized 0.100 N NaOH. The amount of HCl consumed in the elution is thus obtained.

In the HCl-eluate also the concentration of other cations was determined, viz. Na-ions by flame emission spectrometric measurement and the other ions by titration with standardized 0.0572 N EDTA (e.g. Ca^{2+}, Sr^{2+}, Mn^{2+}, Co^{2+}) and/or when traced with a γ-emitting radioactive isotope, by γ-spectrometric measurement (e.g. $Sr + {}^{85}Sr$, $Co + {}^{60}Co$, $Mn + {}^{54}Mn$, $Ce + {}^{144}Ce$).

When divalent or trivalent cations were present in the peat no complete desorption of these cations could be attained with 20 ml 0.1 N HCl. Therefore the elution with 0.1 N HCl was then followed by a treatment with 1-2 ml concentrated HCl. In the eluate thus obtained the cation concentration was also determined.

The following experiments have been carried out:

1. Titration in solutions which contained various concentrations of NaCl.
2. Titration in solutions which contained various concentrations of $CaCl_2$.
3. Titration in a 1 N NaCl solution which contained 10 meq/l of Ca, Sr, Mn, Co or Ce respectively (as their chloride salts). In these experiments the peat was suspended into the solution prior to the addition of NaOH. The NaOH was added very slowly in order to prevent a precipitation of the hydroxides and/or basic salts of some of the metal ions.

When adding NaOH to the solution cerium, cobalt and manganese hydroxides will precipitate at pH 4, pH 6.8 and pH 8.6 respectively. In the procedure followed the NaOH solution was added slowly in order to prevent that these pH values are reached. Only during some experiments at higher pH the critical values may have been reached so that in these experiments part of the metal may have been precipitated as hydroxide.

VI-2-2. RESULTS

VI-2-2-1. *Titration of modified peat N_B (prepared with dilute H_2SO_4) in NaCl solutions of various concentrations*

The titration curves as determined in suspensions of various NaCl-concentrations are shown in Fig. VI-1a. Contrary to the experiments with natural peat described in Chapter IV, the pH-values were now determined in the suspensions and not in the filtrate. This was done for the reason that pH determination in the suspension lead to better reproduceable results, especially in the neutral pH-region. Moreover, the differences between $pH_{suspension}$ and $pH_{filtrate}$ appeared to be negligible at $pH < 5$. In the pH-region 6 to 7.5 the deviations between both pH-values can reach 0.3 pH-units, $pH_{filtrate}$ being mostly somewhat higher than $pH_{suspension}$. At $pH > 7.5$ again only minor differences exist between both pH-values.

As stated before, a contact time of 24 hrs was maintained in the experiments. Then equilibrium has been established completely for suspensions of $pH < 6$. At higher pH-values, however, still a slight decrease of pH takes place on continued shaking, for instance with about 0.2 to 0.4 pH-units at about pH 7 after another 3 days shaking. Since a contact time of several weeks or even months may be required for complete equilibration of alkaline suspensions, this was not persued for practical reasons.

The values for the total amount of Na^+ ($[Na]_{tot}^{pe}$) and for the amount of water present in the peat (v) plotted versus the original concentration of NaOH in the mixture are shown in

Figs. VI-1 b and VI-1 c. A relation between v and the NaCl-concentration of the solution of the type to be expected on the basis of Eq. III-5, is absent. This may be attributed to the rather poor reproducibility involved in the determination of v (compare the two experiments with solutions of 1.04 N NaCl) and the small effect found for the NaCl-concentration on v.

From the results shown in Figs. VI-1 b and VI-1 c the concentration of Na^+ in the internal solution ($[Na^+]^{II}$) can be calculated. Then, with the Na^+-concentration in the external solution ($[Na^+]^{I}$), the factor $\lambda_{Na} = [Na^+]^{II}/[Na^+]^{I}$ can be obtained. In Fig. VI-1 c the results of an experiment performed with the natural peat are also shown. Comparing these results with those of the identical experiment with modified peat shows that the swelling of the modified peat is considerably less than of the natural peat.

The internal concentration of Cl^- ($[Cl^-]^{II}$) is found from the difference between the total amount of Na^+ present in the 0.1 N HCl-eluate ($[Na^+]^{pe}_{tot}$, see Fig. VI-1 b) and the amount of HCl used for the elution. The latter quantity corresponds to the amount of Na-ions which originally neutralized the charge of the dissociated groups in the peat (before the treatment) with 0.1 N HCl. Since the contribution of the internal H^+-concentration to the dissociated amount of acid groups is very small at $pH^{I} \geqslant 3$, the amount of HCl used for the elution may be equated to $S(1-\theta)$. The values of $S(1-\theta)$ plotted versus the original NaOH concentration in the mixture, are shown in Fig. VI-2. It is evident that the determination of $[Cl^-]^{II}$ is accompanied by great uncertainties, since its concentration is extremely small (see Eq. III-13) and is found by difference of two large values.

The values of λ_{Na} and λ_{Cl} plotted versus $S(1-\theta)$ are shown in Fig. VI-2. It appears that both factors differ considerably in magnitude, λ_{Na} being higher than λ_{Cl} in most cases. A too high concentration of the co-ion relative to the concentration of the counter ion has also been observed in similar investigations performed with synthetic ion exchangers (^{2}). Here this phenomenon has been attributed to two causes. The first is the analytical error caused by retention of liquid films by the resin beads. The second cause is additional, non-Donnan-type, electrolyte sorption by impurities in the resins. In ion exchangers with inhomogeneous structure swollen regions of low cross-linking and low concentrations of fixed charges within the particles may be the main cause. Such regions exert little Donnan exclusion and thus can sorb electrolytes even from rather dilute solutions.

Since the amount of Na^+ in the internal solution is determined accurately, the best and most reliable way of calculating pH^{II} is by using λ_{Na}. Eq. III-13 has been used for the calculation of the inside pH. In principle also Eq. III-17 can be used for this purpose. However, this equation cannot be used in its original form, because a fraction (β) of the added NaOH is neutralized by soluble acids present in the peat. Assuming for convenience that the soluble acids consist of HCl (in fact they are soluble humic acids and possibly a small amount of H_2SO_4), Eq. III-17 can be transformed to:

$$[H^+]^{II} = \frac{a-v}{v}[H^+]^{I}\frac{S(1-\theta)-v\,[H^+]^{II}}{ap+\beta aq-(a-v)\,[H^+]^{I}} \tag{VI-1}$$

and when $(a-v)\,[H^+]^{I} \ll ap+\beta aq$:

$$[H^+]^{II} = \frac{a-v}{v}[H^+]^{I}\frac{S(1-\theta)}{ap+\beta aq} \tag{VI-2}$$

or in logarithmic form: $$pH^{I} = -\log\frac{v}{a-v}\frac{[H^+]^{II}}{S(1-\theta)} + \log(ap+\beta aq) \tag{VI-2a}$$

At a constant value of $S(1-\theta)$ the internal pH is constant and, apart from some rather arbitrary variations in v, a linear relation with a slope -1 should hold between pH^{I} and $\log(ap)$ at not too low values of ap, e.g. exceeding 10 meq for $a = 1$ kg H_2O. As appears from Fig. VI-3 this indeed is found true.

As has been set forth in Chapter III, all titration curves must coincide when plotted on a pH^{II} versus $S(1-\theta)$ scale. As shown in Fig. VI-4 this is indeed true within certain limits. From this relationship between pH^{II} and $S(1-\theta)$ a "dissociation coefficient" can be calculated according to Eq. III-19a. However, as pointed out in Chapter III, as a rule no constant value of the dissociation coefficient is found for polymeric acids. Moreover, in the case of peat, some other complications arise in the application of Eq. III-19a, because:

1. Peat contains at least two kinds of acid groups, which do not differ sharply in acid strength, so that they cannot be differentiated in any way. Apparently at the pH where all carboxylic groups are neutralized, already part of the phenolic OH-groups are dissociated.
2. Since the phenolic acid groups are very weakly acidic, no titration end-point can be detected. Moreover, the establishment of equilibrium is extremely slow at high pH.

In practice the stronger acid groups, e.g. those which dissociate below $pH^{II}<8$ are relatively important. At this pH an appreciable part of the carboxylic groups will be dissociated, whereas the amount of dissociated phenolic OH-groups certainly still is small.

The value ot $S(1-\theta)$ at $pH^{II}=8$ can be obtained from Fig. VI-4 by extrapolation, giving about 3.25 meq/g. By means of this value of $S(1-\theta)$ an approximated dissociation relationship can be obtained. For this purpose θ is equated to zero at $pH^{II}=8$. The resulting curve, viz. the logarithm of the ratio of dissociated to undissociated acid groups versus pH^{II} is shown in Fig. VI-4a.

According to Eq. III-19a a linear relationship should exist between pH^{II} and $\log[S(1-\theta)/S\theta]$ having a slope of 1. However, the curve is linear only over a very short range of $\log[S(1-\theta)/S\theta]$, viz. from about -0.7 to about $+0.3$. Moreover the slope of the line is much higher than unity, i.e. about 3.4. In this connection it is also evident that application of the empirical modified Henderson-Hasselbalch equation (Eq. III-19b) is not meaningful.

VI-2-2-2. *Titration of modified peat N_B (prepared with dilute* H_2SO_4*) in* $CaCl_2$ *solutions of various concentrations*

The results of experiments performed with $CaCl_2$-solutions are presented in Figs. VI-5a (titration curves), VI-5b (total amount of Ca present in the peat), VI-5c (water content of the peat) and VI-5d (the exchanged amount of $H^+ = S(1-\theta)$). In accordance with the experiments carried out with NaCl solutions in the same concentration range (10-500 molal) a rather evident decrease of the water content of the peat is found at increasing $CaCl_2$-concentration of the solution. However, the water content of the peat (at higher pH) is appreciably lower when the titration is performed in solutions of $CaCl_2$ instead of NaCl. This suggests a rather high activity of the water in the internal phase (see Eq. III-5) and consequently a rather high degree of specific interaction of Ca-ions with the peat.

The values of λ_{Ca} and λ_{Cl} have been calculated according to the method used for the calculation of λ_{Na} and λ_{Cl} as described in the previous paragraph. The values of these factors plotted versus $S(1-\theta)$ are shown in Fig. VI-6. Except at low values of $S(1-\theta)$, the value of λ_{Cl} appears to be close to unity and smaller than λ_{Ca}.

The internal pH has been calculated for various values of θ from the values of λ_{Ca} (since these are most reliable) by neams of Eq. VI-3

$$\frac{[H^+]^{II}_{app}}{[H^+]^{I}} = \sqrt{\frac{(Ca^{2+})^{pe}_{tot}}{v[Ca^{2+}]^{I}}} \qquad \text{(VI-3)}$$

As appears from Fig. VI-7 approximately the same relationship is obtained between pH^{II} and $S(1-\theta)$ for the various titration experiments. However, compared with the curve of pH^{II} versus $S(1-\theta)$ for NaCl solutions (compare Fig. VI-4), a considerably lower value for pH^{II} is found in solutions containing $CaCl_2$. The main reason for this discrepancy from the point of view of Donnan theory can probably be found in the occurrence of specific interactions between Ca-ions and the peat. Then, a too low value of pH^{II} (referred to the following as $pH^{II}_{apparent}$) is calculated, because all sorbed Ca-ions have been included in the calculation of λ_{Ca}, whereas only the free Ca-ions present in phase II should have been taken into account for the calculation of this factor.

From Eq. III-6b one might deduce that the discrepancies in the pH^{II}-values could be the result of differences in the equivalent hydrated volumes of Ca- and Na-ions. However, this can be disregarded since these volumes are about equal in magnitude for Ca and Na, viz. 155 $Å^3$ and 150 $Å^3$ respectively (^{3}).

As pointed out in Chapter III the amount (X) of specifically sorbed Ca, can be calculated in principle on the basis of the dissociation relationship of the polymeric acid ($^{4, 5}$). Since this relationship cannot be presented in an algebraic form for peat, the graphical presentation in Fig. VI-4a can be used. In fact the abcis in Fig. VI-4a represents $\log [S(1-\theta)-X]/S\theta$ but X was assumed to be 0 for Na.

For Ca the same assumption cannot be made because the negative charge of the poly-ion will decrease when other than ionic interactions (for instance ion pair, covalent bond formation) occur between the metal ions and the fixed groups in the polymer (ion exchanger) deminishing the amount of available exchange sites. For interpreting the Ca-exchange data the amount of specifically bound Ca($=X$) should be estimated. This can be done by assuming that the value of X does not affect the dissociation equilibrium of the poly-basic acid groups. This means that the curve of Fig. VI-4a can be used for Ca at the same time replacing the abcis for $\log [S(1-\theta)-X]/S\theta$. The estimation of X can only be done by trial and error by using the Eq. VI-4 besides Fig. VI-4a.

$$\lambda_{Ca} = \left[\frac{(Ca^{2+})^{pe}_{tot} - X}{v[Ca^{2+}]^{I}}\right]^{\frac{1}{2}} \doteq \frac{[H^+]^{II}}{[H^+]^{I}} \qquad \text{(VI-4)}$$

In practice X-values are selected which lead to the same pH^{II} values by using both the equation and the figure.

Once the value of X is known, it is possible to calculate the equilibrium coefficient of the reaction of Ca-ions with the fixed acid groups in the peat according to Eq. VI-5 (see Eq. III-22):

$$K_c = \frac{[CaR_2]^{II}[H^+]^{II^2}}{[Ca^{2+}]^{II}[R_2H_2]} \qquad \text{(VI-5)}$$

Since

$$[CaR_2] = X/v$$

$$[H^+]^{II} = \lambda_H [H^+]^{I}$$

$$\sqrt{[Ca^{2+}]^{II}} = \lambda_{Ca}\sqrt{[Ca^{2+}]^{I}}$$

$$[H_2R_2] = \tfrac{1}{2} S\theta/v$$

$$\lambda_{Ca} = \lambda_H$$

this equation can be transformed to

$$K_c = \frac{X[H^+]^{I^2}}{\frac{1}{2}S\theta[Ca^{2+}]^{I}} \qquad \text{(VI-5a)}$$

The results of these calculations are summarized in Table VI-1. Obviously no constant value of K_c is obtained. Since pK_c increases at increasing neutralization of the peat, it may be concluded that H-ions become more and more favoured over Ca-ions in the formation of undissociated bonds. The values of pK_c plotted versus $\log [S(1-\theta)-X]/S\theta$ are further shown in Fig. VI-8, together with the dissociation relationship for NaCl solutions used as a reference. It appears that about the same relationship between pK_c and $\log [S(1-\theta)-X]/S\theta$ is obtained for the various

$CaCl_2$ experiments. This is obviously the result of the fact that, in Fig. VI-7 the various curves already coincide when no adequate correction is made for changes in λ_{Ca}.

The Eqs. VI-3 and VI-4 are related as follows:

$$\left[[H^+]^{II}_{app} \sqrt{\frac{(Ca^{2+})^{pe}_{tot} - X}{(Ca^{2+})^{pe}_{tot}}} = [H^+]^{II} \right]_{\theta = \text{constant}} \qquad \text{(VI-6)}$$

At increasing values of $(Ca^{2+})^{pe}_{tot}$, the value of X should increase in order to make the values of $|H^+|^{II}$, as calculated from Eq. VI-6 and as obtained from the reference dissociation relationship, equal. In a narrow concentration range of Ca in the external solution (e.g. 5 to 25 meq/l), X is nearly constant because $(Ca^{2+})^{pe}_{tot}$ is constant.

It further follows from Eq. VI-5 that a constant value of $S(1-\theta)$ and $(Ca^{2+})^{pe}_{tot}$ the relation between $[Ca^{2+}]^I$ and $[H^+]^I$ is given by:

$$|Ca^{2+}|^I = 1/v.\ \text{constant}\ .\ [H^+]^{I^2} \qquad \text{(VI-7)}$$

As appeared above, the water content of the peat is strongly affected by the Ca-concentration of the solution. This is particularly true for low Ca-concentrations. This can clearly be seen from Fig. VI-9, in which v has been plotted versus the square of the Ca-concentration of the starting solution.

VI-2-2-3. *Titration of modified peat* N_B *in a solution of* 1 N NaCl, *containing* 10 meq/l *of* Ca, Sr, Mn, Co *and* Ce *respectively*

When specific interactions of metal ions take place with peat, this will be reflected in a decrease of the pH relative to the situation in which such metal ions are absent. The stronger the ability of a metal ion to appear in a specific interaction the larger will be the pH-effect.

Consequently differences in the titration curves obtained in the titration of peat in solutions of 1 N NaCl containing 10 meq/l of the metal ions mentioned above, may be attributed to differences in tendency of the metal ions to interact with the peat.

As appears from Fig. VI-10a different titration curves are indeed obtained in the presence of various metals, but the differences are rather small. The sequence of the pH-effect is:

$$\text{Ce} > \text{Co} > \text{Sr} > \text{Ca} > \text{Mn} \qquad \text{at pH} < 4.5$$

$$\text{Ce} > \text{Co} > \text{Mn} > \text{Ca} > \text{Sr} \qquad \text{at pH} > 5$$

Ca-ions are preferred over Sr-ions at pH > 5, whereas at pH < 4.5 the reverse is found. The same effect is observed when Sr-ions are present in trace amounts (see Section VI-3-2-1).

Notwithstanding the apparently rather slight tendency to complex-formation of the metal ions investigated and the high concentration of NaCl in the solution, a relatively large amount of the various cations is sorbed on the peat (see Fig. VI-10b).

The total amount of Na taken up by the peat and the water content of the peat have been plotted versus the NaOH concentration of the mixture in Fig. VI-10c and Fig. VI-10d, respectively. As expected the sorption of the various metal ions replace sorbed Na in the same sequence.

Since the water content of the peat shows only minor differences in the various systems, always the same relationship has been used in the calculations of λ_{Na} and λ_{Cl}. The factor λ_{Cl} was calculated from the total amount of Na and of the metal ion (M^{m+}) present in the 0.10 N HCl-eluate and the amount of HCl consumed in the elution. The values of λ_{Na} and λ_{Cl} are shown in Fig. VI-11 in relation to $S(1-\theta)$.

As appears from Fig. VI-11 the factor λ_{Na} nearly always increases and approaches a constant value at increasing values of $S(1-\theta)$; in the experiment with Ce a slight decrease of λ_{Na} takes place. Apparently swelling effects and charge-compensation reach such a degree that a further increase of the Donnan-potential is prevented. The factor λ_{Cl} even reaches a value smaller than unity in the experiment with Ce. However, in view of the quite arbitrary character of the relationship between λ_{Cl} and $S(1-\theta)$, hardly any meaning can be attached to this factor.

The amount of the cation (X) specifically sorbed by the peat can be calculated according to the method used in the experiments with Ca-solutions, viz. by trial and error.

On the other hand, since λ_{Na} is known, X also can be calculated according to

$$\frac{[\mathrm{Na}^+]^{\mathrm{II}}}{[\mathrm{Na}^+]^{\mathrm{I}}} = \frac{[\mathrm{H}^+]^{\mathrm{II}}}{[\mathrm{H}^+]^{\mathrm{I}}} = \left[\frac{[\mathrm{M}^{m+}]^{\mathrm{II}}}{[\mathrm{M}^{m+}]^{\mathrm{I}}}\right]^{1/m} \tag{VI-8}$$

The values of X and $\mathrm{pH}^{\mathrm{II}}$ calculated according to Eq. VI-8 are summarized in Table VI-2.

It is evident that the same values of X should be obtained when calculated from the reference curve by the method of trial and error. Evidently the plots of the values of $\mathrm{pH}^{\mathrm{II}}$ versus $\log[S(1-\theta)-X]/S\theta$ from Table VI-2 should then coincide with the reference dissociation relationship (Fig. VI-4a). As appears from Fig. VI-12 this expectation is not quite fulfilled. In view of the rather arbitrary character of the assumptions underlying the calculations this is not surprising. In general the calculated curves are situated slightly higher than the reference dissociationship. This means that a lower value of X will be found when it is calculated from the reference curve. For the experiment with Ca, the X-values also have been calculated from the reference curve. The results are summarized in Table VI-3. The values of X reported in this table are indeed slightly lower than those given in Table VI-2.

The stability coefficients of the "complexes" were calculated according to Eq. VI-4 (for divalent ions) and Eq. VI-9 (for trivalent ions)

$$K_c' = \frac{[\mathrm{MR}_3][\mathrm{H}^+]^{\mathrm{II}^3}}{[\mathrm{M}^{3+}]^{\mathrm{II}}[\mathrm{H}_3\mathrm{R}_3]} \tag{VI-9}$$

The values of the stability coefficients are summarized in the last column of Table VI-2 and of Table VI-3. Again an increase of pK_c at increasing neutralization of the peat is observed.

A comparison of the pK_c-values for Ca from Table VI-2 and Table VI-3 with those in Fig. VI-8 indicates that complexes with a somewhat higher stability exist when NaCl is present in the mixture.

VI-3. The sorption of radionuclides by modified peat

VI-3-1. INTRODUCTION

As has been said before, in a radioactive contamination of water extremely small quantities of radioelements are involved. Since they occur in the water mostly besides a large excess of inactive ions, sorbents are required for the decontamination of the water which exert a pronounced specificity in the binding of radionuclides.

Before an application of modified peat for water decontamination can be considered, appropriate information should be obtained about this specificity.

As a consequence experiments were carried out with solutions of various compositions, containing inactive salt(s) and contaminating radionuclide. The sorption of the following radionuclides has been investigated: ^{85}Sr, ^{60}Co, ^{54}Mn, ^{137}Cs, ^{144}Ce and ^{106}Ru. All experiments described in this section concern slurry tests. Unless specified otherwise the experiments were carried out in the same manner as described in Chapter IV-1.

VI.3.2. RESULTS

VI-3-2-1. *The sorption of radiostrontium*

The sorption of radiostrontium was investigated as a function of pH with solutions containing Ca, Mg, Co and Mn as competing cations. In all experiments modified peat N_B in H-form was applied as sorbent.

The sorption of ^{85}Sr *from solutions containing* Ca *as competing cation*

As already observed in the testing of the modified peat species, the treatment of peat with sulphuric acid is accompanied by a rather important improvement of the separation factor $\alpha_{Sr/Ca}$. How far and to what extent this separation factor depends on pH- and Ca-concentration has been investigated in a series of experiments of which the results are shown in Fig. VI-13. In this figure the relative concentrations of ^{85}Sr and of Ca have been plotted versus the end-pH of the mixture. Up to pH^I 5 to 7.5, depending on the Ca-concentration of the solution, strontium is preferred over calcium. Separation factors and amounts of exchanged Ca, $(Ca)_{pe}$, calculated from the data in Fig. VI-13 are summarized in Table VI-4.

The exchanged amount of Ca is determined by the pH and Ca-concentration of the solution. The value of $((Ca)_{pe})$ approaches the actual effective exchange capacity of the peat at high Ca-concentration in the starting solution. For Ca-concentration lower than approximately 5 meq/l this is only true for the neutral and acid pH^I region. Under these various circumstances the number of sites occupied by Na becomes relatively small.

In accordance with the results obtained with natural peat (compare Table IV-3) the separation factor $\alpha_{Sr/Ca}$ tends to decrease with increasing Ca-concentration of the solution and with increasing pH^I. However, the modified peat exerts a higher selectivity towards Sr than the natural peat.

The sorption of ^{85}Sr *from solutions containing* Ca *and* Mg *as competing cations*

Since Ca and Mg are frequently present simultaneously in water, some information is also required about the ion exchange equilibria of both ions in mixtures as well as about their influence on the sorption of ^{85}Sr.

Experiments were carried out with solutions containing always 10 meq/l of Ca + Mg with various Ca/Mg ratios, 5.10^{-3} μCi/ml ^{85}Sr* and various amounts of 0.1 meq/l NaOH. The procedure applied in these experiments is the same as in previous experiments, except that the NaOH solution was added after the peat was immersed in the solution. A contact time of about 18 hrs was maintained. The filtrate was analysed for the sum of Ca + Mg (by titration with 0.035 N EDTA), for Ca separately (by flame emission spectrometry) and for the ^{85}Sr-activity. The pH of the filtrate was determined potentiometrically.

The results are shown in Table VI-5 and in Figs. VI-14a and VI-14b where the relative concentrations of ^{85}Sr and of Ca respectively are shown versus the end pH of the solution and in Fig. VI-15, where the relative concentration of Ca + Mg is given versus the end-pH of the solution. From these data the equivalent fraction of Ca in the solution (X_{Ca}) and in the peat (Y_{Ca}) have been calculated at some interpolated values of pH^I. The relationship between X_{Ca} and Y_{Ca} for the various mixtures of Ca and Mg is shown graphically in Fig. VI-16, together with some theoretical curves calculated for a number of selectivity coefficients $K_{Ca/Mg}$ assuming that these are constants. As to be expected the ion exchange equilibrium between Ca and Mg on peat cannot be described with a constant selectivity coefficient. In fact this coefficient seems to change in a range between 10 and 40. Moreover, the practical curve seems to hold for various pH-values, indicating that the effect of pH on the sorption of Ca and Mg is about the same.

The exchanged amount of Ca + Mg at any selected pH^I is not constant (comp. Table VI-5) but depends somewhat on the ratio of Ca and Mg in the mixture, i.e. the higher the relative

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* Specific activity of ^{85}Sr: 14,500 Ci/g

concentration of Ca in the solution, the higher is the sorbed amount of Ca + Mg. This effect must be attributed to the fact that Ca-ions are preferred by the peat over Mg-ions. As a consequence titration curves obtained in solutions with different ratios of Mg and Ca do not coincide, but are situated slightly higher when the ratio Mg/Ca in the solution is higher. The preference of peat for Ca relative to Mg probably must be mainly attributed to a stronger bond strength for Ca-ions because the effect of the difference in the equivalent hydrated volumes of Ca^{2+} (155 $Å^3$) and Mg^{2+} (180 $Å^3$) on the selectivity coefficient $K_{Ca/Mg}$ can only be small. Taking for the swelling pressure successively a value of 300 atm., 150 atm. and 75 atm., the following values of $K_{Ca/Mg}$ were calculated by means of Eq. III-7a viz. 2.1, 1.44 and 1.21, respectively. This illustrates the greater bond-strength of Ca.

Concerning the affinity of peat for strontium relative to calcium, about the same picture is obtained as in the experiments where calcium is the only competing cation (compare Fig. VI-14 and Fig. VI-13).

The sorption of ^{85}Sr *from solutions containing* Ca, Mn *or* Co *as competing cation*

In section VI-2-2-3 it was observed that the preference of peat towards cations decreases in the sequence:

$$\text{Ce} > \text{Co} > \text{Mn} > \text{Ca} > \text{Sr} \qquad \text{at pH}^{\text{I}} > 5$$

$$\text{Ce} > \text{Co} > \text{Sr} > \text{Ca} > \text{Mn} \qquad \text{at pH}^{\text{I}} < 4.5$$

In view of that it seems reasonable to expect on first sight that the competing action of Co and Mn in the sorption of radiostrontium should exceed that of Ca, at least at pH above 5. However, the contrary appears to be true. This was observed in experiments performed with ^{85}Sr-solutions, which contained Co, Mn or Ca as competing cations, and which were carried out with a mixture of the modified peat species 6, 8 and 10 as sorbent. In these experiments the peat (110 mg) was immersed into the solution (50 ml) prior to the addition of the NaOH-solution. After NaOH addition the volume was made up to 55 ml with demineralized water. The mixtures were shaken for 24 hrs. The peat was then separated quantitatively from the mixture by filtration. In the filtrate the pH, the ^{85}Sr-activity and the concentration of the competing cation were determined (by EDTA-titration).

Subsequently the peat was suspended in 20 ml 0.05 N HCl, the mixture was shaken for 24 hrs and then filtered. Hereupon the peat on the filter was washed with demineralized water. Filtrate and wash-water were combined and made up with demineralized water to 100 ml in a volumetric flask. In this solution the activity, the cation concentration and the excess of HCl were determined.

Finally the peat was treated once again with 1-2 ml concentrated HCl. The eluate obtained was diluted to 25 ml and the ^{85}Sr-activity of the solution was determined.

Quite contrary to the expectations a considerably higher sorption of ^{85}Sr is observed in the sorption experiments from solutions which contain Co and Mn as competing ion than from solutions in which Ca is present as the competing cation (see Fig. VI-17a). This is the more surprising since the amount of Co and Mn sorbed by the peat, exceeds that of Ca considerably (see Fig. VI-17b).

Although at pH > 4.5 some hydrolysis of Co^{2+} and Mn^{2+} may have occurred this certainly cannot only account for the high sorption of ^{85}Sr, because already at low pH a much better sorption of ^{85}Sr takes place. Obviously the peat contains some groups or arrangements of groups which are, in presence of Co and Mn, quite active for Sr. As a result the selectivity of Sr uptake relative to that of Mn and Co is higher than with respect to Ca (comp. Table VI-6).

The higher capacity of the peat species for Co and Mn indicates that an increasing amount of weakly acid groups participate in the binding of these ions.

From the results of the desorption it follows (see Figs. VI-17c, VI-17d and VI-17e):

1. When using 0.05 N HCl an appreciably higher desorption of ^{85}Sr takes place when Ca is the competing cation instead of Co or Mn.
2. Even after treatment of the peat with concentrated HCl, no complete desorption of ^{85}Sr is attained when Co^{2+} and Mn^{2+} are present as competing cations.
3. Smaller amounts of Co and Mn are desorbed with 0.05 N HCl as compared with Ca.

Apparently, in systems with Co and Mn as competing cations, ^{85}Sr is sorbed preferentially on strong acid groups. The Co^{2+} and Mn^{2+} probably involve weak acid groups, leaving some strong acid groups available for the interaction with ^{85}Sr. Since also a larger quantity of Co and Mn are sorbed and the desorption of these species with 0.05 N HCl is relatively small specific interactions between these elements and peat may be assumed important.

VI-3-2-2. *The sorption of radiocobalt*

In the sorption of radiocobalt on natural peat it was observed that a sharp decrease in the removal of this nuclide takes place when the pH of the mixture becomes higher than 6-7. This was attributed to the presence of soluble humic acids in the peat (see Chapter IV-2-2).

Since the modified peat contains soluble humic acids to a considerably lesser extend, it is reasonable to expect an appreciably higher efficiency of this material for the removal of ^{60}Co from alkaline solutions. This should hold all the more, when the soluble humic acids still present in the material are removed, before the peat is dispersed in the solution of ^{60}Co. For this purpose the modified peat (sample N_B) was pretreated by suspending it in a solution of NaOH during about 15 minutes (end-pH of the mixture was 11.4), followed by a treatment with 0.1 N HCl (in order to transfer it to H-form) and washing with demineralized water until the wash-water was free of Cl^-.

The sorption of ^{60}Co has been investigated with the pretreated sample N_B, with the untreated sample N_B and finally with a modified peat sample A-3 (compare Table V-1 b) prepared with concentrated H_2SO_4. The results of these experiments are presented in Fig. VI-18 (for sample N_B) and Fig. VI-19 (for sample A-3).

It appears from these results:

1. A slight decrease in the sorption capacity for ^{60}Co takes place with increasing pH in alkaline region, particularly at low concentrations of Ca in the solution. This effect is much smaller with sample A-3 as compared with the pretreated and the untreated sample N_B; moreover the latter two samples behave about identically in the sorption of ^{60}Co. Apparently the soluble humic acids have been incompletely removed in the treatment with NaOH; with both samples N_B a slightly yellow filtrate is obtained when the end-pH of the mixture exceeds a value of 10. With sample A-3 the filtrate is almost colourless even at $pH > 10.7$. $KMnO_4$-values were determined only in the experiments with untreated peat N_B; high values were found at $pH > 10$, viz. 200 mg/l $KMnO_4$ and higher. In solutions of lower pH the $KMnO_4$-value of the solution is considerably lower, viz. being 40 mg/l at $pH = 9$, 20 mg/l at $pH = 7.6$ and < 10 mg/l at $pH < 6$.
2. In acid solutions the competing action of Ca-ions becomes apparent.

Separation factors and exchange capacities were calculated from the data in Figs. VI-18 and VI-19. The results are summarized in Table VI-7 and can be compared with those found for normal peat (Table IV-8). Also here the separation factor reaches a maximum at a certain pH, depending on the Ca-concentration of the solution and on the peat sample used. The decrease of $\alpha_{Co/Ca}$ at higher pH must be apparent and will be related to the increasing dissolution of humic acids which leads to an increasing formation of soluble Co-complexes. The similarity of the

$\alpha_{Co/Ca}$ data for N_B with and without NaOH treatment confirms the fact that they produce comparable amounts of dissolved humic acids.

When compared with similar experiments with normal peat (see Figs. IV-14a and b) the optimum pH of Co-removal is found slightly higher (5.75 for modified peat and 5.25 for normal peat). However, the modified peat is much more effective for Co-removal than normal peat at higher pH-values. This evidently can be attributed to the higher solubility of humic acids in the natural peat (compare $KMnO_4$-values in Fig. IV-14b, with those measured for the modified peat).

It is obvious that sample A-3 contains considerably less soluble humic acids than the samples N_B (pretreated and untreated); at high pH a much better sorption with sample A-3 is obtained.

The exchange capacity of sample A-3 is about 5 times that of the natural peat at pH 3.5, and about 3-3.5 times that of the natural peat (see Table IV-2) at pH 6.5. The exchange capacity of the sample N_B appears to be considerably higher than was found in other experiments performed with this sample, viz. the experiments concerning the sorption of ^{85}Sr (although performed in the presence of 5 meq/l Na (see Paragraph VI-3-2-1)) and of ^{144}Ce (see Paragraph VI-3-2-5), which were carried out respectively about 12 and 2 months earlier. The reason for this is unknown, because the same chemicals (pro-analyse quality) were used and the experiments were carried out in the same manner. The only available explanation is a sensitivity of the modified peat for oxidation also during standing and not only during preparation as was already observed (compare Paragraph V-3-1-4).

VI-3-2-3. *The sorption of radiocesium*

In view of the low affinity of peat for Na relative to Ca, a high sorption of ^{137}Cs on modified peat will presumably not take place, unless the concentration of competing cations, especially of the higher valency cations in the solution is very small.

Experiments were carried out with ^{137}Cs-solutions containing different concentrations of Ca, using modified peat N_B and natural moor peat as sorbent. The results of these experiments are presented in Fig. VI-20. The amount of radiocesium removed, increases with decreasing Ca-concentration of the solution. However, even at a low Ca-concentration in the solution (viz. 1.55 meq/l) at $pH = 8\text{-}9$, only about 60-70% of the cesium is removed by using modified peat N_B as sorbent. Nevertheless this is considerably more than can be attained with the natural peat under the same conditions, viz. being 20-30%.

Evidently a batch process is quite unsuitable for removing ^{137}Cs from aqueous solutions. By applying modified peat in columns a reasonable amount of cesium can be removed. However, break-through of ^{137}Cs will occur considerably earlier than break-through of hardness.

VI-3-2-4. *The sorption of radiomanganese*

In addition to the experiments with natural peat (see Chapter IV-2-3) some experiments were carried out with modified peat, viz. with sample M_B (see Table V-1 a). Carrier free solutions of ^{54}Mn (about 5.10^{-3} μCi/ml) containing different concentrations of Ca were used.

The results are shown in Fig. VI-21. Radiomanganese can be removed by means of a batch process almost completely when the pH of the mixture is fixed on a level of about 9 to 10. At higher pH-values the sorption is somewhat less, which will mainly be the result of the dissolution of soluble humic acids from the species. Compared with the experiment with natural peat (see Fig. IV-19) the effect is much less significant for peat M_B.

From the data shown in Fig. VI-21 the separation factor $\alpha_{Mn/Ca}$ and the exchange capacity of the peat have been calculated. The results are summarized in Table VI-7.

The separation factor $\alpha_{Mn/Ca}$ increases strongly with increasing pH of the solution from

3 to 8 and is smaller than $\alpha_{Co/Ca}$. At low pH the peat exerts a slight preference for Ca relative to Mn. This is in accordance with the results obtained with macro amounts of manganese (see Paragraph VI-2-2-3).

VI-3-2-5. *The sorption of radiocerium*

Of the rare earth elements only the sorption of cerium has been investigated. Since the rare earth elements are very similar in chemical properties, the results obtained with cerium may be considered representative for the whole class of these elements. This includes also the elements scandium and yttrium, which are not rare earth elements, but are very similar in their chemical behaviour.

The rare earth elements exist under normal conditions in aqueous solutions only as their trivalent ions. Upon raising the pH of the solution the hydroxides of these elements precipitate, unless the concentration is extremely small (solubility of $Ce(OH)_3 = 4.0 \times 10^{-6}$ mol/l).

Experiments have been carried out with solutions of ^{144}Ce containing $1.1 . 10^{-6}$ g Ce/l and different concentrations of Ca, using modified peat N_B as sorbent. In addition also an experiment was carried out with the natural moor peat in H-form. The results, are shown in Fig. VI-22. Almost a complete removal of ^{144}Ce is attained, when the pH of the mixture is maintained at a level 4.5 to 6.5. Even at low pH the main part of ^{144}Ce is removed from the solution, viz. 80-95% at $pH^I = 3$ depending on the Ca-concentration of the solution. However, when the pH of the mixture exceeds a value of 6.5 a slightly diminished sorption of ^{144}Ce on modified peat is observed. As expected, the decrease in the sorption on the natural peat at $pH^I > 6.5$ is much more pronounced as a result of increased dissolution of peat.

In addition to the above experiment with moor peat in H-form, the sorption of ^{144}Ce to various amounts of moor peat in the Ca-form from a solution of ^{144}Ce (pH ca. 3.5) containing additional $CaCl_2$, Na_2SO_4 and NaCl was investigated. The results of the experiment are summarized in Table VI-8.

As appears from this Table, already a very small amount of the peat removes the main part of ^{144}Ce from the solution at low pH.

VI-3-2-6. *The sorption of radioruthenium*

The chemical behaviour of ruthenium in aqueous solutions and consequently towards sorption processes, chemical treatment etc. is extremely complex, since the element can exist in all valency states from zero to eight. Anionic, cationic, uncharged, insoluble, colloidal and complex forms of ruthenium can all exist, depending on the composition of the solution and other conditions (6).

In acid solutions ruthenium exists in the lower valency states (-I, -II, -III and -IV) and reportedly resembles bivalent and trivalent iron. In alkaline solutions the element is found in its higher valency states and behaves somewhat like manganese.

There are relatively few stable ruthenium compounds, because of the ease in which this element changes valency states. The compounds of Ru^{II} and Ru^{III} are most frequently occurring and stable.

Of the trivalent form of ruthenium numerous complexes are known, for instance halide, amine and nitro- and oxalato complexes. In fact the simple compound $RuCl_3$ is found in aqueous solutions in undissociated form. Moreover various anionic chloride complexes from $M(RuCl_4)$ to $M_4(RuCl_7)$ can occur. Addition of alkali to a solution of the easily hydrolizing $RuCl_3$ results in the formation of the insoluble $Ru(OH)_3$. Hexamines of Ru are the final products of the action of ammonia on $RuCl_3$. These compounds are resistant to acids (in the cold) but are very sensitive towards alkalies.

The compounds of Ru^{IV}, including the complex salts, are less frequently occurring than of Ru^{III}. The chloride exists as $RuCl_4 . 5H_2O$ and $RuOHCl_3$, of which especially $RuOHCl_3$ is very soluble in water.

A special class of compounds of ruthenium are those of nitroso-ruthenium. These compounds are formed when ruthenium salts are treated with moderately strong nitric acid, such as applied in the dissolution and purification of used reactor fuel. Therefore, the sorption behaviour of these complexes is specially important as low activity waste of fuel reprocessing plants will contain relatively high amounts of radioruthenium in the form of these complexes. Numerous simple and complex compounds of nitroso-ruthenium are known, e.g. ruthenium-nitroso-trichloride ($RuNOCl_3 . 5H_2O$) tetra-amine-nitroso compounds ($RuNO(Am)_4OHX_2$) etc.

N. M. Sinitsyn and F. Ya. Rovinskii (^{7}) have made a rather extensive study of the sorption of ruthenium from solutions in which the element was present as nitroso-nitrato complexes ($RuNO(NO_3)_x(OH)_y(H_2O)_z$), nitroso-chloro complexes ($RuNOCl_x(OH)_y(H_2O)_z$) and as ruthenium chloro complexes ($RuCl_x(OH)_y(H_2O)_z$). Solutions of the hydrolized and unhydrolized forms of these compounds were used. The sorption was studied on five different natural materials, viz. sand, clay, soil, peat and mud. Most of the sorption experiments were performed at pH 2.

Regardless of the nature of the sorbent it was found that maximum sorption of ruthenium occurred from a solution of the nitroso-nitrato complexes. The sorption of ruthenium from solutions containing the element as nitroso-chloro and as chloro-complex was considerably lower. The sorption of the chloro complexes also differs appreciably from that of the nitroso-chloro complexes. Moreover it was observed that the hydrolized compounds were removed from the solution substantially better than of the unhydrolized compounds. Furthermore it was shown that peat was the most effective sorbent.

Experiments carried out

Since an extensive study of the sorption of ruthenium on peat falls beyond the scope of this study only a few investigations were carried out. Most experiments were performed with solutions of ruthenium as tri- and tetra-chloride and/or partly as hydrolized chloride. A few experiments with hexamine were also carried out.

The experiments were performed in the same manner as before, except that the sorbent (modified peat N_B in H-form) was brought into the polythene bottle prior to the solution of ^{106}Ru (carrier free), in order to reduce wall adsorption of ruthenium. Blank experiments, in which solutions of ^{106}Ru of different pH were shaken in the absence of peat, showed that 85% or more of ^{106}Ru is removed from the solution by wall-adsorption when the pH of the solution is higher than 5.5. The wall-adsorption is substantially lower, when the pH of the solution is lower than 5.5, viz. being about 10% at pH 5 and only 0-5% at pH 4. By bringing the peat into the bottle prior to the ^{106}Ru solution, wall adsorption is greatly prevented due to the pH-decrease which takes place as a result of the exchange of H^+ for Ca^{2+}. The pH of the added chloride and hexamine solution were 3.9 and 6 respectively. The final pH was adjusted after mixing peat and Ru-solution.

Besides the activity of the filtrate, in most cases the activity present in the peat was also determined to confirm that no wall effect has taken place. For this purpose the peat was transferred quantitatively into a counting tube followed by addition of 4 ml concentrated HNO_3 by which peat is nearly completely decomposed.

Since the activity of the filtrate was also determined in 4 ml samples, the activity measurements of the peat and of the filtrate are directly comparable.

The experimental solutions were always prepared directly before the experiment by dilution (400 times) of a concentrated ^{106}Ru-stock solution, which contained 2 μCi/ml ^{106}Ru and was 0.05 N in HCl. For the experiment with hexamine complex the ^{106}Ru-stock solution was treated with excess concentrated NH_4OH, viz. 4 ml NH_4OH/ml ^{106}Ru-solution, prior to dilution. After dilution the solution was neutralized with HCl to pH 6.

Results

The results are shown in Fig. VI-23, giving $(C/C_0)_{^{106}Ru}$ as a function of pH^I. The measurement of the activity of the peat confirmed that practically all the activity removed from the solution was present in the peat, i.e. 100% at $pH^I < 5$ and 90-100% at $pH^I > 5$.

Concerning the results shown in Fig. VI-23 the following may be noted:

1. The Ca-concentration of the solution seems to have no distinct effect on the sorption of ruthenium, even not at low pH^I.
2. Contrary to the sorption of ^{60}Co, ^{54}Mn and ^{144}Ce, a decrease of sorption of ^{106}Ru at pH^I-values higher than 9 cannot be observed. Apparently ruthenium is not associated with soluble humic acids or, possibly, the solubility of the humic acids is considerably decreased because of their association with ruthenium.
3. Any differences in the sorption of ruthenium from solutions in which the element is present as its chloride (or hydrolized chloride) or as its hexamine complex, cannot be observed.

Apparently ruthenium is sorbed on peat by some mechanism different from ion exchange. Since the element forms easily complexes, its particular behaviour may be attributed to the formation of compounds with peat which are poorly dissociated if at all. In view of the tendency of the Ru-compounds to be adsorbed by the wall of the plastic bottles it seems possible that a similar surface-adsorption process takes place with the peat.

Once the ruthenium is sorbed on the peat it is not easily desorbed as appears from the fact that adsorption is still strong at high pH. This is confirmed by some desorption experiments, using 20 ml 0.1 N HCl and portions of peat N_B (55 mg) to which at different pH-values ^{106}Ru had been sorbed from a solution of its chlorides. After overnight shaking of the mixture only 5-8% of the ruthenium was found to be desorbed. This also indicates that the element is present in the peat in some insoluble or unexchangeable form.

VI-4. **Rate of ion exchange on modified peat**

In judging the applicability of modified peat as an ion exchanger the rate of the ion exchange reaction has to be investigated. This was done by measuring the exchange of tracers of a counter ion in the presence of a large excess of the same or an other ion, because mathematical equations developed for this type of exchange can be used for analysing the results (Compare III-3). In these experiments a sieve fraction of 40-60 mesh of modified peat N_B was used. Examination of a representative sample of the peat under the microscope learned that the material consists of irregularly shaped solid objects with jagged edges. The mean diameter d_p (defined as $\Sigma nd^3/\Sigma nd^2 = d_p$, where d is the diameter of a circle with the same projected area as the particle and n is the number of particles which have such an area) was estimated to be about 0.27 mm.

VI-4-1. EXPERIMENTAL

A known amount of the H-form of the peat was suspended in 250 ml of a solution of $CaCl_2$ to which a specific amount of NaOH had been added. The mixture was shaken for 48 hrs and then 1 ml of a solution of ^{85}Sr (1.25 μCi/ml) was rapidly added to the well stirred mixture. Directly after the addition and after different time intervals, samples of 4 ml were withdrawn from the mixture by a wide jet pipet. The samples were filtered immediately and the filtrates were stored for activity measurement. The activity of the filtrates was determined in aliquots of 3 ml.

After the activity of the filtrate reached a constant value the whole suspension was filtered. The filtrate was titrated with EDTA for determination of its Ca-concentration. The peat, including the portions filtered in sampling, was treated with 5N HCl in order to remove Sr from it. The eluate and the filtrate were combined and made up to a certain end-volume in a volumetric flask. The activity of the suspension at zero time (i.e. at the moment of the addition of ^{85}Sr to the mixture) can then be calculated accurately from the activity of the latter solution.

Experiments were carried out with solutions of $CaCl_2$ of various concentrations, containing different amounts of NaOH. In addition also an experiment was carried out with a solution of $SrCl_2$. In all experiments a peat concentration of 2000 ppm was used.

VI-4-2. RESULTS

The results of the experiments are presented graphically in Fig. VI-24, in which the fractional attainment of equilibrium y is shown as a function of the root of the time of contact. The end-values of the Ca- and the water content of the peat, the concentration of Ca and ^{85}Sr in the supernatant liquid and the end-pH of the solution are summarized in Table VI-9, together with the values of the distribution coefficient and of the separation factor calculated from these data for the equilibrium situation.

In accordance with theory (Eq. III-30) the logarithm of $(1-y)$ has been plotted in Fig. VI-25 versus the factor $^{kt}/K_d' r_0$, which has been calculated by using for k a value corresponding to a film thickness $\delta = 5.10^{-3}$ cm. Some theoretical curves as calculated with Eq. III-30 are also shown in Fig. III-25. A comparison shows that the experimental curves deviate strongly from the theoretical curves. The rate of the ion exchange process on peat is in the beginning considerably faster than calculated from Eq. III-30. This discrepancy between theory and experiment may be attributed to the fact that the particles are not uniform in size. Moreover, the shape of the particles deviates strongly from a spherical geometry.

A further examination of the results in Fig. VI-25 shows that:

1. The rate of exchange of ^{85}Sr is considerably lower in systems containing Ca as compared to systems which contain only Sr. This has to be attributed to a slower exchange reaction between ^{85}Sr and Ca as compared to that between ^{85}Sr and Sr, because the diffusion coefficients of Sr- and Ca-ions are almost equal in magnitude i.e. $\mathbb{D}_{Sr} = 1.24.10^{-5}$ cm^2/sec and $\mathbb{D}_{Ca} = 1.21.10^{-5}$ cm^2/sec).
2. The various curves obtained for different solutions of $CaCl_2$ coincide for $^{kt}/K_d' r_0 < 0.95$. At higher values of this factor the rate of exchange is somewhat lower in acid solutions than in neutral solutions. The explanation may be found in the exchange reaction between part of the ^{85}Sr and the undissociated protons from the peat which is relatively slow as compared to the exchange with Ca from the peat. In this respect it has to be remembered that at these low pH-values the peat shows a pronounced selectivity for Sr.

VI-5. **Column experiments**

VI-5-1. EXPERIMENTAL

In addition to the experiments discussed in the previous paragraph, some column experiments were carried out. Break-through curves at different flow rates were determined for ^{85}Sr when using solutions with different concentrations of $CaCl_2$, and for ^{60}Co when using a solution containing 13.2 meq/l Ca. All experiments were carried out with the Ca-form of modified peat N_B (40-60 mesh fraction) and with solutions of pH 6.1.

The arrangement used in these experiments was the same as that used in the experiments with the natural peat, except that a dose pump was used instead of a centrifugal pump. The column (of diameter 1.5 cm) was filled with 3.72 g air-dry peat to a height of 8 cm.

After each experiment the peat was regenerated with an 1 molar solution of $CaCl_2$ of pH 6.1. After the last experiment (measurement of ^{60}Co break-through) the peat was removed from the column and its water content (in the way described in paragraph VI-2-1) and Ca-content (by elution of the material with 2N HCl and titration of the eluate with EDTA) were determined. These quantities were found to be 0.80 g H_2O/g peat and 2.26 meq/g peat (air-dry) respectively.

VI-5-2. RESULTS

The break-through curves determined for ^{85}Sr and ^{60}Co are shown in Figs. VI-26, VI-27 and Fig. VI-28 (solid curve) respectively. In these figures the relative concentration (x) of the radionuclides has been plotted versus the factor $\varepsilon(v_f t - z)/K_d'(1-\varepsilon)z$, (Compare paragraph II-4). The latter factor has been equated to 1 at 50% break-through in all cases. The values of the effluent at 50% break-through (V_{50}) are summarized in Table VI-10 together with the distribution and selectivity coefficients. The distribution coefficients were calculated from $\varepsilon(v_f t - z)/K_d'(1-\varepsilon)z = 1$, using $\varepsilon = 0.526$ (calculated on the basis of a wet volume of the peat of 1.60 ml/g air-dry peat). Selectivity coefficients ($K_{Sr/Ca} = \alpha^2_{Sr/Ca}$) were calculated from the K_d'-values on the basis of $K_{Sr/Ca} = 1$ at $(Ca)_0 = 8.22$ meq/l (which must be approximately true at pH 6.1 according to the data reported in Table VI-5), and of a constant Ca-content of the peat, i.e. 1.42 meq/ml peat (or 2.20 meq/g). This latter value represents the mean value of the Ca-content of the peat as calculated from the K_d'-values at $(Ca)_0 = 8.22$ meq/l by taking $K_{Sr/Ca} = 1$. The selectivity coefficients thus obtained (see Table VI-10) increase in magnitude at decreasing Ca-concentration of the solution. This was also observed in slurry experiments (compare paragraph VI-3-2-1). The effect observed here will in fact be even more pronounced because the Ca-content of the peat decreases at decreasing Ca-concentration of the solution (compare Table VI-4).

The selectivity coefficient for Co, $K_{Co/Ca}$, has been calculated in the identical way from the observed distribution coefficient and the Ca-content of the peat (2.26 meq/g). The value of 394 calculated for $K_{Co/Ca}$, appears to be considerably lower than the value of 2500 found previously in the slurry experiments (see Table VI-6). This discrepancy probably must be attributed to the fact that in the slurry experiments the pH of the suspension temporary attained a rather high value at the moment directly after the addition of the NaOH-solution. This results in a rapid and high sorption of ^{60}Co, which—as we have seen—is not easily reversed. Thus after the establishment of the pH-equilibrium still a high value of $K_{Co/Ca}$ will be found.

In column experiments the partial mass transfer coefficient k, can be calculated approximately by means of Eq. III-38 or Eq. III-39 depending on the magnitude of the Reynolds number. It is evident that only a very rough approximation of the actual value of k can be obtained, because the particles differ widely from spheres. To account for the form of the particles arbitrarily a value of 2.5 for the form-factor γ has been choosen. The values calculated for Re_p on this basis appear to be smaller than unity (see Table VI-11). For the calculation of k therefore Eq. III-39 has been used; the results are also given in Table VI-11.

The number of transfer units N' calculated from k ($N' = k\bar{S}z/v_0$) appears to be rather high (see Table VI-11).

Comparison of the break-through curves at $N' = 40$ with numerical solutions of Eq. III-40 at $N' = 40$ which are reported in literature ([8]) shows that the factor $kd_p/\mathrm{ID}K_d' \simeq 5$. This indicates that (see Chapter III-3) mass transfer in the particle and in the solution are about of equal importance.

By fitting the experimental curves with the theoretical curves of Schumann (see Fig. VI-28), the number of mass transfer units (N) based on an overall mass transfer coefficient could also be determined (see the last column of Table VI-11). The values of N are about a factor two lower than the values of N'. The height of a transfer unit is found to be about 2 mm at a flow rate of 102 cm/hr. This quantity was about 5 mm in comparable experiments with the natural peat (see Chapter IV paragraph 2-1-2).

In conclusion it may be stated that modified peat is quite suitable for application in columns. The exchange capacity of the material is effectively used and a flow rate of 250 ml/hr can easily be maintained.

VI-6. **Discussion of the results**

In heating of peat in the presence of H_2SO_4 an excellent cation exchanger is obtained. The product has a pronounced specificity for the higher valency cations, especially those of the rare earth and the transition elements. As true for natural peat, the present material strongly prefers earth alkaline ions over alkaline ions.

The specificity of peat and of modified peat may be attributed to specific interactions between the metal ions concerned and the fixed groups present in the material, e.g. the formation of ion-pairs and/or covalent bonds. Covalent bonds are predominantly formed in the sorption of the transition metal ions, but according to Van Dijk (9) even the interaction between peat humic acids and alkaline earth ions is not of a purely electrostatic nature.

The occurrence of specific interactions can be deduced from the results obtained in the titration of modified peat (see Paragraph VI-2). The presence of different cations leads to different decreases in pH. According to the chemistry of metal chelate compounds this pH-fall is an indication for the occurrence of specific interactions; complex stability constants could be calculated from it.

An attempt was made to interprete the titration data quantitatively on the basis of the Donnan theory. Assuming that the activity coefficients for Na-ions in the internal and the external solutions are equal in magnitude, the titration curves as determined in solutions containing different concentrations of NaCl can be brought to coincidence if $\mathrm{pH}^{\mathrm{II}}$ is plotted as a function of $S(1-\theta)$. The values of $\mathrm{pH}^{\mathrm{II}}$ were calculated by means of the Donnan theory. The Donnan theory apparently gives a reasonable description of the titration behaviour of the modified peat.

Assuming that in the interaction between peat and metal ions only acid groups participate which dissociate at $\mathrm{pH}^{\mathrm{II}} \leqslant 8$, a relationship between $\mathrm{pH}^{\mathrm{II}}$ and $\log S(1-\theta)$ can easily be obtained. This relationship has been used as the basis for the calculation of the "stability coefficients" of the complexes (or chelates) of the metal ions with the peat. The amount of the metal ion involved in the specific interaction (X) was calculated by means of a method of trial and error from the pH-effect (i.e. experiments with Ca-solutions), and/or via the values of λ_{Na}.

The calculated stability coefficients were not constant, but were found to decrease at increasing values of $\log S(1-\theta)/S\theta$, indicating that at low H-occupation of the peat the affinity of the material for protons becomes increasingly higher relative to that for metal ions. However, because of the rather extreme assumptions made, it is not clear to what extent the calculated stability coefficients can be trusted.

Apart from that it is evident that the bond strength between peat and metal ions decreases in the sequence:

$$\mathrm{Ce} > \mathrm{Co} > \mathrm{Mn} > \mathrm{Ca} > \mathrm{Sr} > \mathrm{Mg} \qquad \mathrm{pH} > 5$$

$$\mathrm{Ce} > \mathrm{Co} > \mathrm{Sr} > \mathrm{Ca} > \mathrm{Mn} \qquad \text{at pH} < 4.$$

These series deviate rather much from that of Irving and Williams. Apparently the specificity of peat for metal ions cannot merely be attributed to the formation of complexes and/or chelates.

A peculiar effect was observed in the sorption of radiostrontium from solutions which contain Ca, Co or Mn as competing cation (in about the same concentration). Quite contrary to the expectations the competing action of these cations increases in the sequence

$$Co < Mn < Ca$$

This effect is the more peculiar because the quantity of these ions sorbed on the peat decreases in this sequence. It further was observed in these experiments that a comparably low desorption of ^{85}Sr takes place in 0.05 N HCl, when Co and Mn are the competing cations instead of Ca. These observations indicate that ^{85}Sr as well as Ca are preferentially sorbed by the more acidic groups in the presence of Co and Mn which seem to be preferentially bound by the weakly acidic groups.

The observations find some support in literature data describing the exchange of Li^+ by divalent metal-ions (M^{2+}) on a sulphonic acid cation exchanger (10). Here it was found that the selectivity coefficient K_{M^{2+}/Li^+} increases in the sequence:

$$Mg < Zn < Co < Cu < Ca < Sr < Pb < Ba$$

Since the modified peat undoubtedly contains a certain amount of sulphonic acid groups, these groups may be responsible for the small competing action of Co and Mn.

Radioruthenium, present in the solution as its III- and IV-valent chloro-complexes can be effectively removed with peat. The ruthenium is sorbed in some un-exchangeable form; Ca-ions do not have any distinct effect on the sorption of ruthenium, not even in the acid pH-region where the element is sorbed relatively poorly. There are some indications that the removal of Ru is not the result of ion exchange but of surface adsorption. Probably also other chemical forms of the element, such as its nitroso-chloro and nitroso-nitrato complexes, can be removed effectively by peat and modified peat. According to data reported in the literature (11) peat is also an effective sorbent for element such as Ra and U.

The sorption of radiocesium by modified peat is strongly affected by other cations present in the solution. However, this radionuclide can be removed in a still reasonably effective way from solutions which do not contain large quantities of dissolved salts.

The sorption of radioiodine on modified peat has not been investigated but an appreciable sorption of this radionuclide will certainly not take place.

Modified peat represents a material which is eminently suitable for the application in decontamination of water containing radioactive compounds, whatever the source of the water may be. The modified peat is superior in properties to the natural peat. This holds particularly for the stability against alkalies, the exchange capacity, and the mechanical and swelling properties (water adsorption). Its content of soluble humic acids is considerably lower as compared to that of the natural peat, especially when concentrated H_2SO_4 is applied in the treatment. Moreover, the rate of exchange on this material was found to be high.

As a result the material may be used at pH-values between 7-9 or even higher, dependent on the conditions of the preparation. An ion exchange capacity of 2.5 to 5 meq/g can easily be realized.

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TABLE VI-1

Calculation of specific functions (X and K_c) for Ca-exchange *by modified peat* N_B

NaOH meq/kg	v g.H_2O per g peat	X meq/g	$S(1-\theta)-X$ meq/g	$S\theta$ meq/g	Ca_{peat} meq/g	λ_{Ca}	pH^{II}	$\log\left[\frac{S(1-\theta)-X}{S\theta}\right]$	pK_c
$Ca_0 = 9.72$ meq/kg									
0.0	0.45	0.08	0.28	2.88	0.36	8.4	2.29	−1.0	2.63
0.5	0.50	0.08	0.36	2.81	0.44	9.0	2.50	−0.88	3.10
1.5	0.57	0.14	0.55	2.55	0.69	10.8	3.06	−0.66	4.04
2.5	0.64	0.31	0.75	2.18	1.06	12.4	3.74	−0.455	5.09
3.5	0.72	0.60	0.94	1.70	1.54	14.1	4.41	−0.25	6.09
4.5	0.79	0.82	1.17	1.25	2.00	16.0	5.16	−0.03	7.41
5.5	0.87	1.16	1.25	0.84	2.41	17.1	5.72	+0.17	8.25
$Ca_0 = 50$ meq/kg									
0.5	0.46	0.08	0.44	2.73	0.55	4.51	2.67	−0.795	3.58
1.5	0.50	0.14	0.60	2.50	0.80	5.12	3.16	−0.62	4.39
2.5	0.57	0.33	0.80	2.12	1.16	5.38	3.82	−0.42	5.32
3.5	0.63	0.59	0.98	1.67	1.62	5.70	4.49	−0.23	6.34
4.5	0.70	0.87	1.18	1.19	2.06	5.80	5.28	0.00	7.40
5.5	0.77	1.12	1.26	0.87	2.45	5.88	5.79	+0.16	8.41
$Ca_0 = 250$ meq/kg									
0.5	0.45	0.07	0.49	2.68	0.65	2.24	2.85	−0.73	4.09
1.5	0.47	0.19	0.62	2.43	0.90	2.45	3.28	−0.59	4.54
2.5	0.52	0.39	0.88	2.06	1.27	2.62	3.86	−0.515	5.38
3.5	0.57	0.65	0.98	1.61	1.72	2.74	4.56	−0.215	6.48
4.5	0.64	0.89	1.17	1.18	2.15	2.78	5.29	0.00	7.71
5.5	0.71	1.18	1.27	0.79	2.56	2.78	5.94	+0.20	8.68
$Ca_0 = 833$ meq/kg									
0.5	0.45	0.13	0.50	2.61	0.92	1.46	2.91	−0.715	4.07
1.5	0.46	0.21	0.64	2.39	1.17	1.58	3.33	−0.57	4.73
2.5	0.50	0.48	0.77	1.99	1.61	1.65	3.85	−0.41	5.36
3.5	0.53	0.73	0.93	1.57	2.01	1.73	4.51	−0.23	6.45
4.5	0.57	1.00	1.10	1.15	2.47	1.75	5.21	−0.02	7.59
5.5	0.63	1.32	1.15	0.77	2.88	1.73	5.81	+0.17	8.48

TABLE VI-2

Calculation of specific functions (X and K_c) for metal-exchange by modified peat N_B using λ-values

NaOH meq/kg	λ_{Na}	pH^{II}	$[M^{m+}]^{I}$ meq/kg	$[M^{m+}]_{peat_{tot.}}$ meq/kg	X/v meq/kg	$\log\left[\frac{S(1-\theta)-X}{S\theta}\right]$	pK_c
Ca^{2+}: $(Ca)_0 = 10.16$ meq/kg							
0	1.75	2.74	10.04	150	119	−0.77	2.43
1	2.22	3.15	10.00	195	146	−0.63	3.34
2	2.57	3.87	9.78	338	273	−0.43	4.53
3	2.85	4.65	9.66	590	511	−0.23	5.65
4	2.99	5.35	9.15	875	792	−0.05	6.88
5	3.14	6.01	8.70	1135	1048	+0.14	7.85
Sr^{2+}: $(Sr)_0 = 10.19$ meq/kg							
0	2.09	2.65	9.97	274	230	−0.81	2.12
1	2.11	3.14	9.91	336	291	−0.68	2.95
2	2.38	3.88	9.81	420	364	−0.46	4.28
3	2.88	4.70	9.56	620	531	−0.23	5.71
4	3.14	5.40	9.22	840	749	−0.04	6.97
5	3.26	6.04	9.03	980	884	+0.14	7.99
Mn^{2+}: $(Mn)_0 = 10.02$ meq/kg							
0	1.85	2.71	10.10	125	90	−0.76	2.55
1	2.04	3.16	10.07	152	110	−0.63	3.39
2	2.31	3.89	9.94	294	241	−0.41	4.52
3	2.56	4.73	9.56	627	564	−0.24	5.82
4	2.63	5.36	8.87	1158	1096	−0.12	6.58
5	2.64	5.97	8.20	1550	1493	+0.05	7.44
Co^{2+}: $(Co)_0 = 10.08$ meq/kg							
0	1.88	2.64	9.95	160	125	−0.74	2.31
1	1.98	3.10	9.69	470	432	−0.73	2.65
2	2.04	3.70	9.32	840	803	−0.55	3.67
3	2.25	4.50	8.87	1190	1155	−0.36	4.85
4	2.32	5.13	8.38	1480	1435	−0.17	5.85
5	2.40	5.67	7.82	1760	1715	+0.02	6.65
Ce^{3+}: $(Ce)_0 = 9.90$ meq/kg							
0	1.63	2.66	9.51	490	449	−0.84	1.37
1	1.74	3.00	9.19	855	806	−0.86	2.10
2	1.67	3.51	8.57	1460	1419	−0.76	3.20
3	1.62	4.04	7.72	2140	2107	−0.70	4.40
4	1.53	4.50	6.85	2660	2575	−0.54	5.41
5	1.55	4.78	5.93	3100	3077	−0.36	5.81

TABLE VI-3

Calculation of specific functions (X and K_c) for Ca-*exchange by modified peat* N_B, *according to the method based on the reference dissociation relationship*

NaOH meq/kg	v g H_2O/g	X/v meq/kg	$[Ca^{2+}]_{peat_{tot.}}$ meq/kg	pH^{II}	$\log\left[\frac{S(1-\theta)-X}{S\theta}\right]$	pK_c
0	0.40	125	150	2.72	−0.78	2.72
1	0.41	145	195	3.13	−0.63	3.61
2	0.45	275	338	3.84	−0.43	4.81
3	0.51	440	590	4.51	−0.22	6.11
4	0.57	690	875	5.18	−0.03	7.19
5	0.64	900	1135	5.80	+0.18	8.23

TABLE VI-4

Separation factors ($\alpha_{Sr/Ca}$) *and amounts of exchanged* Ca, $(Ca)_{pe}$, *as calculated at various* pH^I-*values*

(Ca) meq/l	$pH^I = 3.5$		$pH^I = 4.25$		$pH^I = 5.0$		$pH^I = 6.0$		$pH^I = 8.0$	
	$\alpha_{Sr/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Sr/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Sr/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Sr/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Sr/Ca}$	$(Ca)_{pe}$ meq/g
15.09	1.95	0.44	1.40	0.82	1.16	1.19	1.0	1.80	0.835	3.21
10.18	1.83	0.45	1.38	0.80	1.16	1.18	1.02	1.74	0.865	3.07
7.87	1.80	0.43	1.52	0.71	1.34	1.05	1.15	1.58	1.08	2.85
4.31	2.17	0.31	1.62	0.58	1.33	0.95	1.18	1.48	1.00	2.12
1.08	1.80	0.21	1.50	0.35	1.30	0.46	—	1.07	—	—

TABLE VI-5

Composition of the starting solution		NaOH = 0 meq/l		NaOH = 2 meq/l		NaOH = 5 meq/l		NaOH = 8 meq/l	
Ca meq/l	Mg meq/l	pH^I	$(Ca+Mg)_{pe}$ meq/g	pH^I	$(Ca+Mg)_{pe}$ meq/g	pH^I	$(Ca+Mg)_{pe}$ meq/g	pH^I	$(Ca+Mg)_{pe}$ meq/g
10.19	0.0	3.22	0.38	4.65	0.97	6.80	2.27	8.40	3.42
7.63	2.5	3.22	0.36	4.70	0.97	6.88	2.27	8.48	3.42
5.09	5.0	3.24	0.35	4.75	0.95	6.95	2.27	8.55	3.42
2.54	7.5	3.28	0.34	4.80	0.95	7.00	2.27	8.65	3.42
0.0	10.0	3.32	0.32	4.90	0.93	7.10	2.27	8.75	3.42

TABLE VI-6

Separation factors $\alpha_{Co/Ca}$ *and exchange capacities* $(Ca)_{pe}$ *at definite* pH-*values*

	Modified peat N_B, pretreated with NaOH						Modified peat N_B		Modified peat A-3			
	$(Ca)_0 =$ 18.38 meq/l		$(Ca)_0 =$ 9.20 meq/l		$(Ca)_0 =$ 4.53 meq/l		$(Ca)_0 =$ 4.53 meq/l		$(Ca)_0 =$ 18.31 meq/l		$(Ca)_0 =$ 4.45 meq/l	
pH	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Co/Ca}$	$(Ca)_{pe}$ meq/g
3.5	5.05	0.81	5.75	0.69	5.6	0.64	5.15	0.59	11.–	1.70	9.7	1.—
4.25	15.0	1.19	12.9	1.06	9.5	1.03	9.0	0.94	25.3	2.16	19.7	1.51
5.00	29.4	1.67	21.2	1.55	16.0	1.43	14.0	1.38	51.5	2.60	45.5	1.89
5.75	51.5	2.17	34.2	2.02	17.2	1.84	17.5	1.80	110.–	3.02	77.–	2.21
6.50	64.0	2.63	33.0	2.50	12.3	2.26	12.5	2.20	176.–	3.32	69.–	2.51
7.25	70.0	3.12	26.0	2.99	6.2	2.83	6.2	2.81	247.–	3.84	62.–	2.97
8.00	71.5	3.86	20.3	3.72	2.0	3.72	2.0	3.70	344.–	4.85	23.–	3.63

TABLE VI-7

Separation factors $\alpha_{Mn/Ca}$ *and exchange capacities* $(Ca)_{pe}$ *as calculated at some selected* pH-*values*

$(Ca)_0$ meq/l	$pH^I = 3.5$		$pH^I = 4.25$		$pH^I = 5.0$		$pH^I = 6.0$		$pH^I = 8.0$	
	$\alpha_{Mn/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Mn/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Mn/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Mn/Ca}$	$(Ca)_{pe}$ meq/g	$\alpha_{Mn/Ca}$	$(Ca)_{pe}$ meq/g
17.8	0.71	0.84	1.19	1.34	1.83	1.85	4.0	2.58	26.8	4.32
9.28	0.75	0.69	1.18	1.14	1.92	1.65	3.8	2.46	12.0	4.06
4.80	0.60	0.60	0.94	1.03	1.66	1.52	3.8	2.02	10.5	2.58

TABLE VI-8

Effect of the concentration of moor peat (in Ca-form) on the amount of ^{144}Ce *removed from the solution (composed of* 5 meq/l $CaCl_2$, 2.5 meq/l NaCl *and* 2.5 meq/l Na_2SO_4)

Peat concentration (ppm)	996	402	202	110	26	10
$(C/C_0)_{Ce144}$ (%)	0.42	1.08	1.64	3.34	11.41	26.45
End-pH	4.98	4.67	4.24	4.02	3.80	3.66
K_d^* (ml/g)	234.10^3	229.10^3	298.10^3	263.10^3	300.10^3	278.10^3

TABLE VI-9

Kinetic experiments of the ion exchange on modified peat N_B
($\mathbb{D}_{Sr} = 1.24.10^{-5}$ cm^2/sec, $\varepsilon = 5.10^{-3}$ cm, $k = \mathbb{D}/\varepsilon = 2.28.10^{-3}$ cm/sec)

		At equilibrium								
$(Ca)_0$	$(Sr)_0$	pH^I	$(Ca)^I$	$(Sr)^I$	$(Ca)_{pe}$	$(Sr)_{pe}$	v	$(C/C_0)_{Sr85}$	K_d'	$\alpha_{Sr/Ca}$
Solution meq/l			meq/l		meq/g		g H_2O/g peat	%	ml/ml	
20.8	—	7.5	13.78	—	3.15	—	0.90	68.5	121	0.90
9.35	—	5.9	5.09	—	2.13	—	0.75	55.1	232	0.98
4.29	—	4.4	2.17	—	1.06	—	0.70	44.5	367	1.28
—	8.35	6.3	—	3.94	—	2.20	0.80	47.2	311	—

TABLE VI-10

Values of V_{50} *and* K_d^l, $K_{Sr/Ca}$ *and* $K_{Co/Ca}$ *as obtained from the results of the column experiments*

$(Ca)_0$ meq/l	Flow rate cm/hr	$V_{50} = F_c \varepsilon (v_f t - z)$ ml	K_d^l ml/ml	$K^*_{Sr/Ca}$	$K_{Co/Ca}$
8.22	636	960	143	1.0	—
8.22	255	995	148	1.0	—
8.22	102	970	145	1.0	—
4.14	636	2010	300	1.08	—
4.14	255	2050	306	1.12	—
1.0	255	8980	1340	1.35	—
13.20	442	12000	1790	—	392

* On the basis $K_{Sr/Ca} = 1$ at $(Ca)_0 = 8.22$ meq/l and pH = 6.1.

TABLE VI-11

The values of Re_p, k, $N'(=k\bar{S}z/v_0)$ *and* $N(=K\bar{S}z/v_0)$ *for column experiments shown in Fig. VI-26*
($\mathrm{Sc}_{\mathrm{Sr}} = 807$, $\mathbb{D}_{\mathrm{Sr}} = 1.24 . 10^{-5}$ cm^2/sec, $\mathrm{Sc}_{\mathrm{Co}} = 1260$, $\mathbb{D}_{\mathrm{Co}} \simeq 0.85 . 10^{-5}$ cm^2/sec)

v_0		Re_p	k cm/sec	$N' = k\bar{S}z/v_0$	$N = K\bar{S}z/v_0$
cm/hr	cm/sec				
Experiments with ^{85}Sr					
636	0.177	0.39	$3.43 . 10^{-3}$	40	20
255	0.071	0.16	$2.93 . 10^{-3}$	87	30
102	0.0284	0.064	$1.72 . 10^{-3}$	128	40
Experiments with ^{60}Co					
442	0.125	0.29	$2.76 . 10^{-3}$	47	20

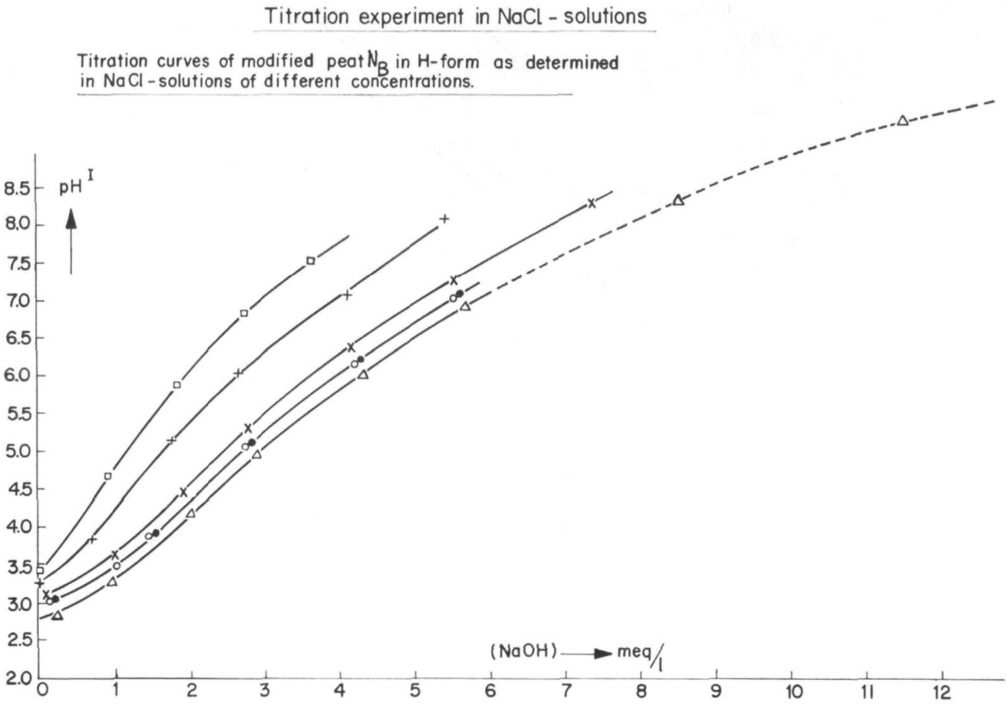


Fig. VI-1 a

Sorbent: 2000 ppm modified peat N_B
Contact time: 24 hrs
Solution:

- □ $9.1 . 10^{-3}$ molal NaCl
- \+ $50 . 10^{-3}$ molal NaCl
- × 0.504 molal NaCl
- ○ ● 1.04 molal NaCl (experiments performed at different date)
- △ 2.08 molal NaCl

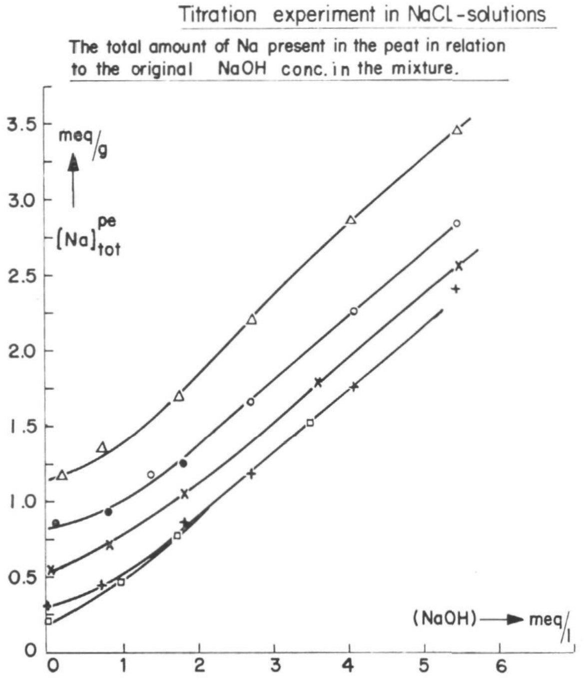


Fig. VI-1 b — See subscription Fig. VI-1a

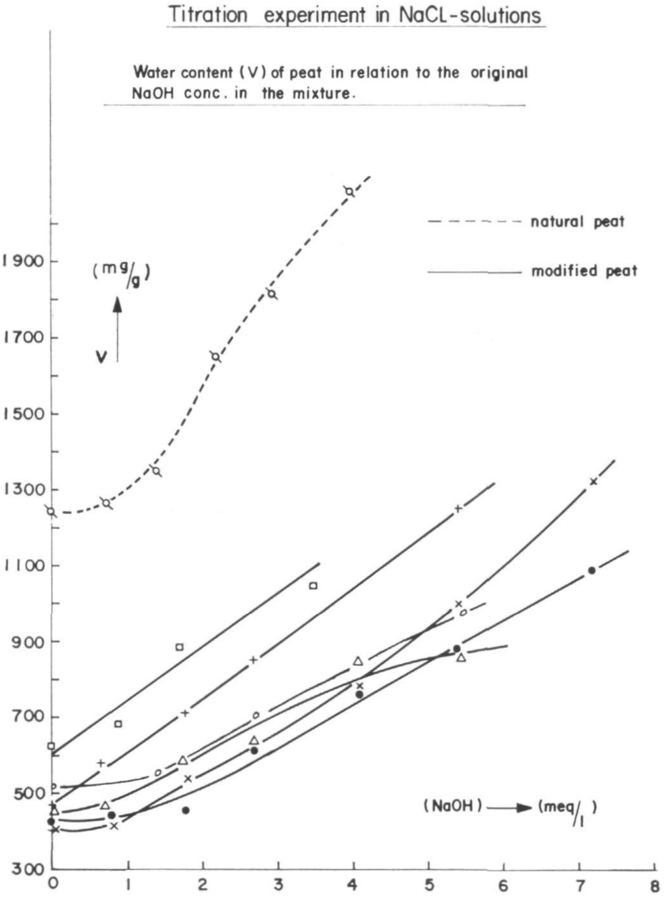


Fig. VI-1 c — See subscription Fig. VI-1a

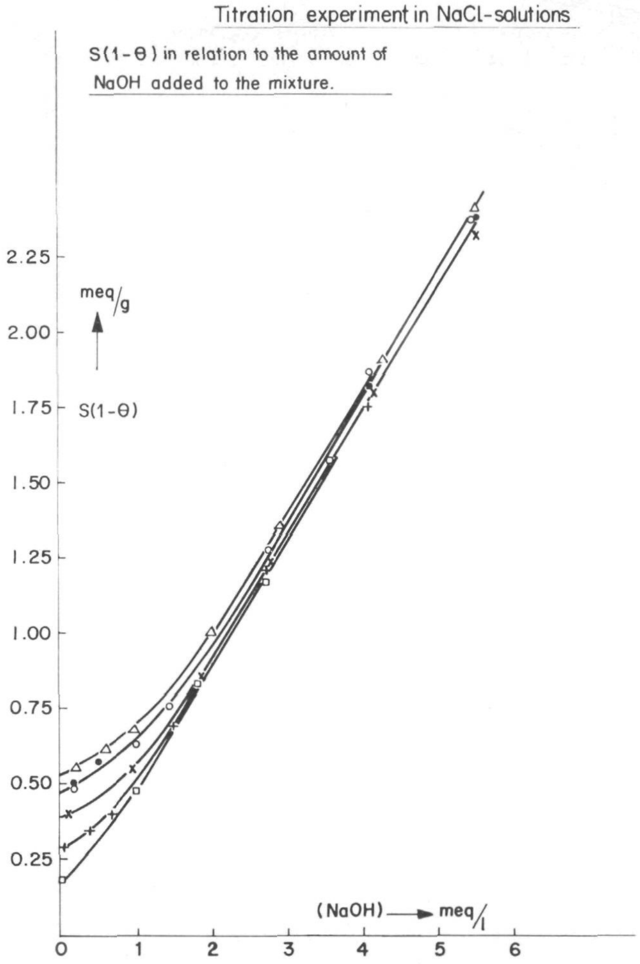


Fig. VI-1 d — See subscription Fig. VI-1a

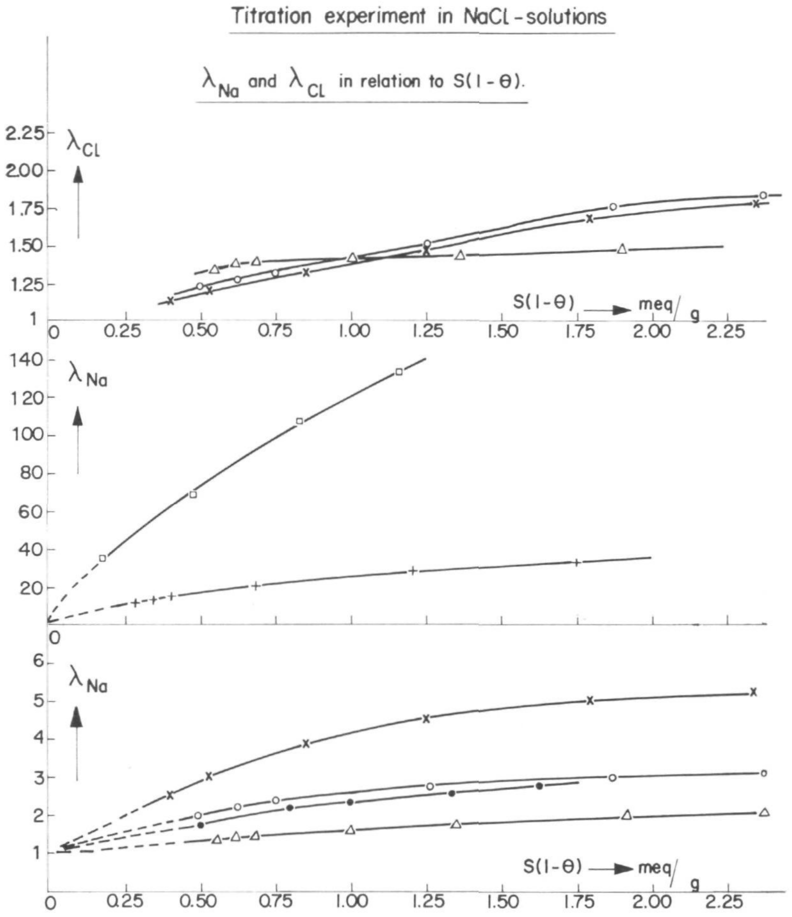


Fig. VI-2 — See subscription Fig. VI-1a.

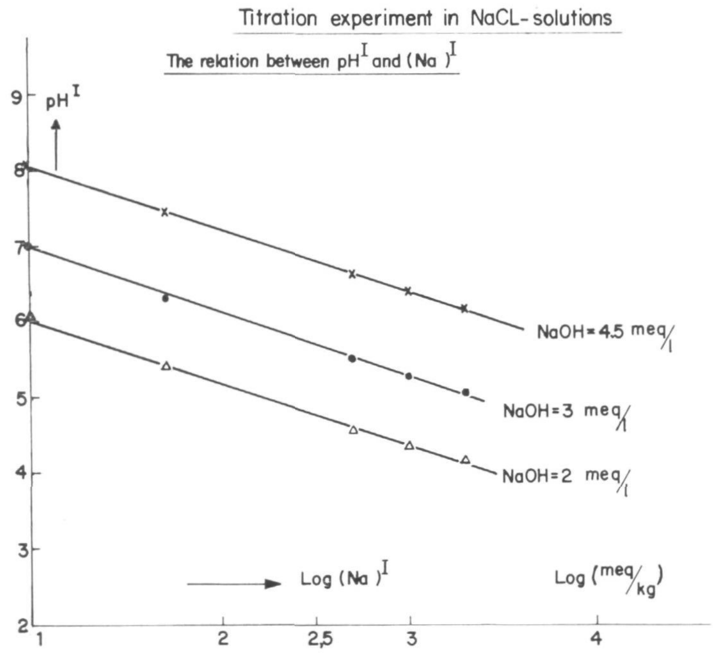


Fig. VI-3 — See subscription Fig. VI-1a

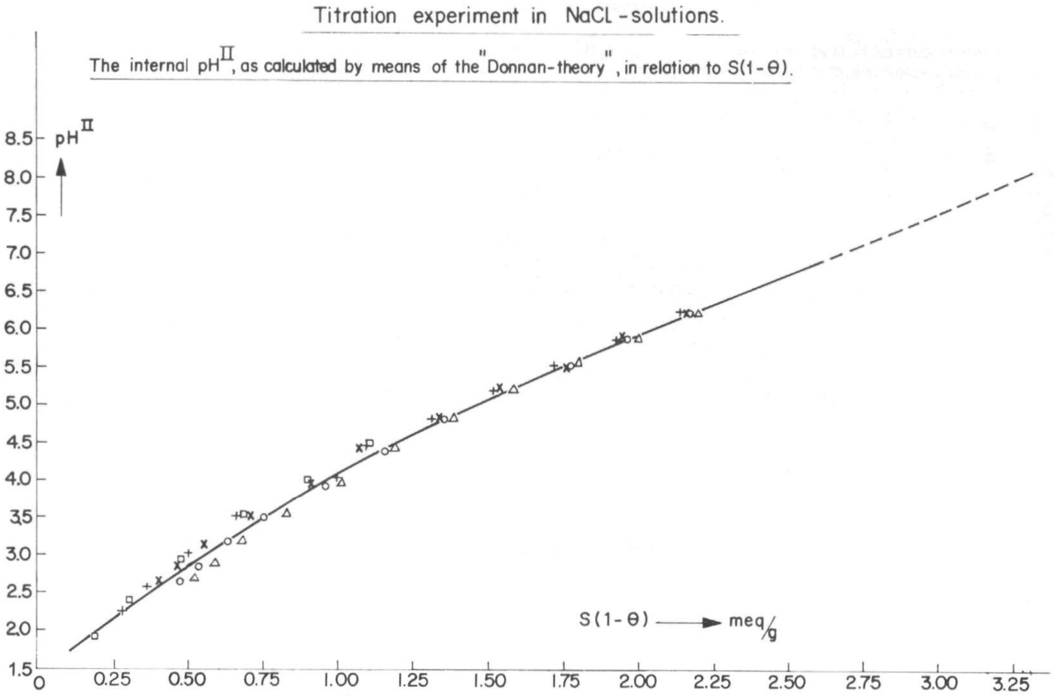


Fig. VI-4 — See subscription Fig. VI-1a

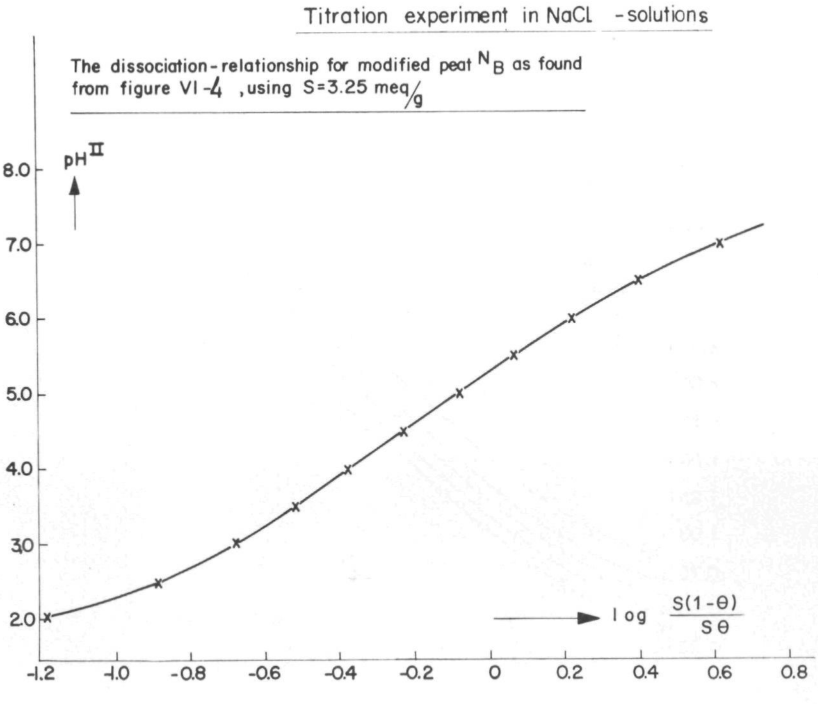


Fig. VI-4a — See subscription Fig. VI-1a

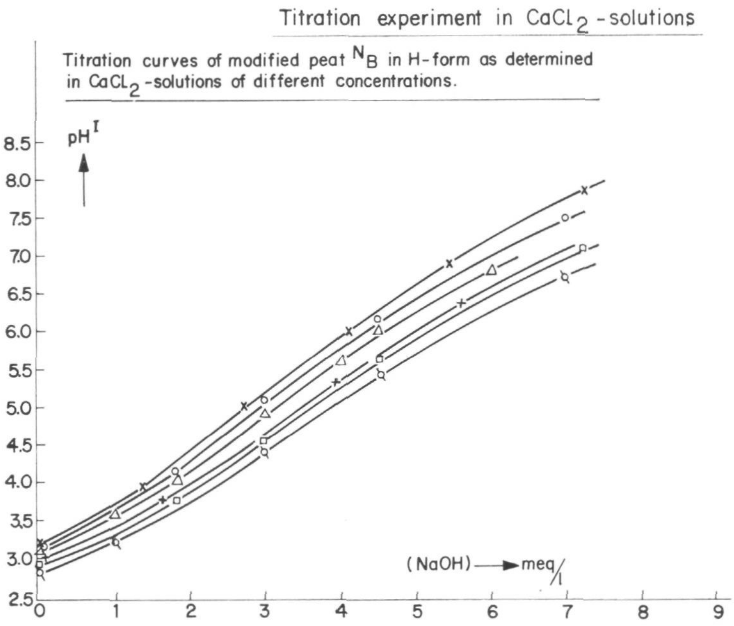


Fig. VI-5a

Sorbent: 2000 ppm modified peat N_B
Contact time: 24 hrs
Solution:

×	$4.86 . 10^{-3}$	molal $CaCl_2$
○	$12.5 . 10^{-3}$	molal $CaCl_2$
△	$25 \ . 10^{-3}$	molal $CaCl_2$
+	0.125	molal $CaCl_2$
□	0.252	molal $CaCl_2$
ϕ	0.421	molal $CaCl_2$

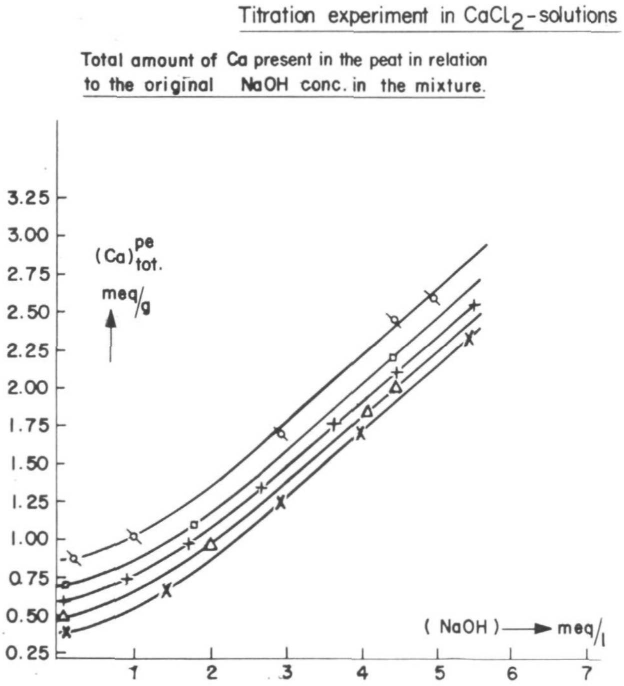


Fig. VI-5b — See subscription Fig. VI-5a

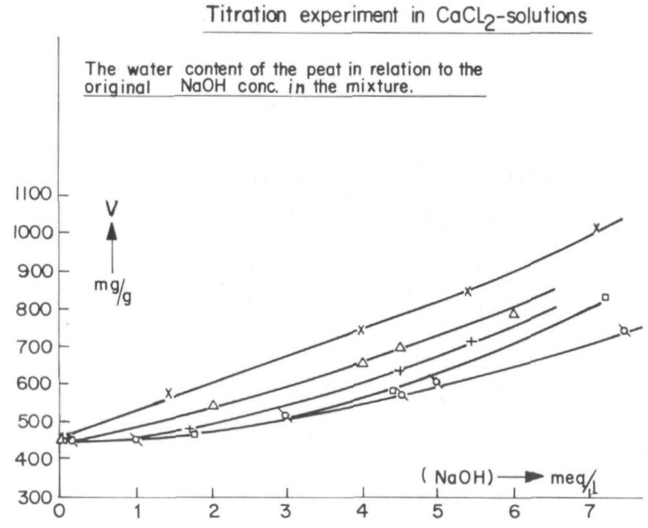


Fig. VI-5c — See subscription Fig. VI-5a

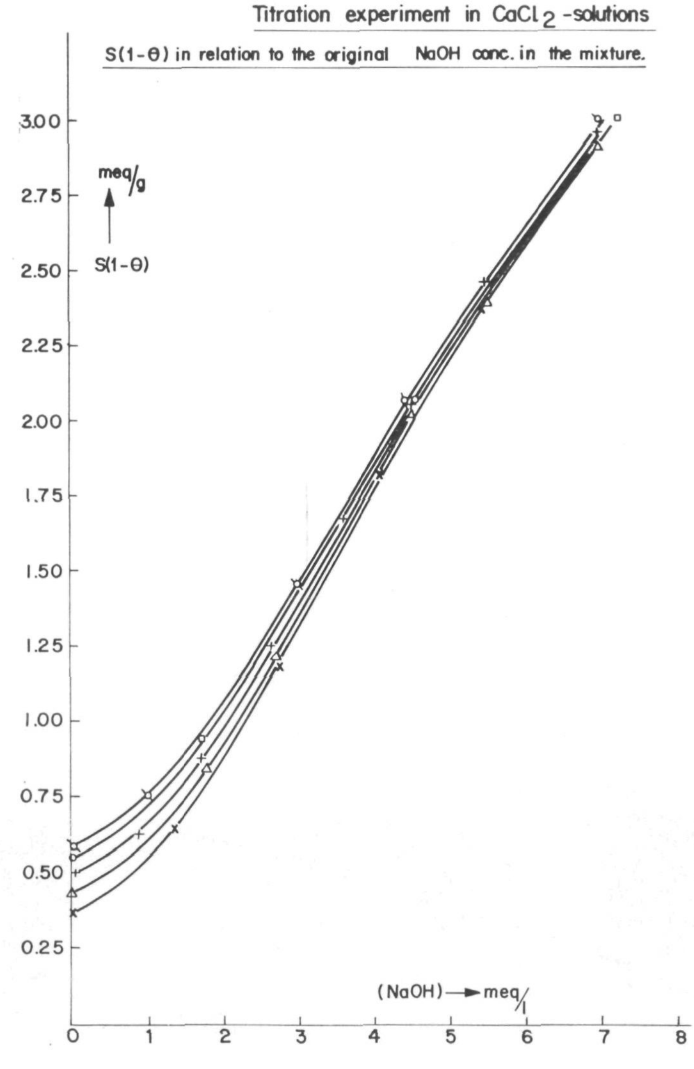


Fig. VI-5d — See subscription Fig. VI-5a

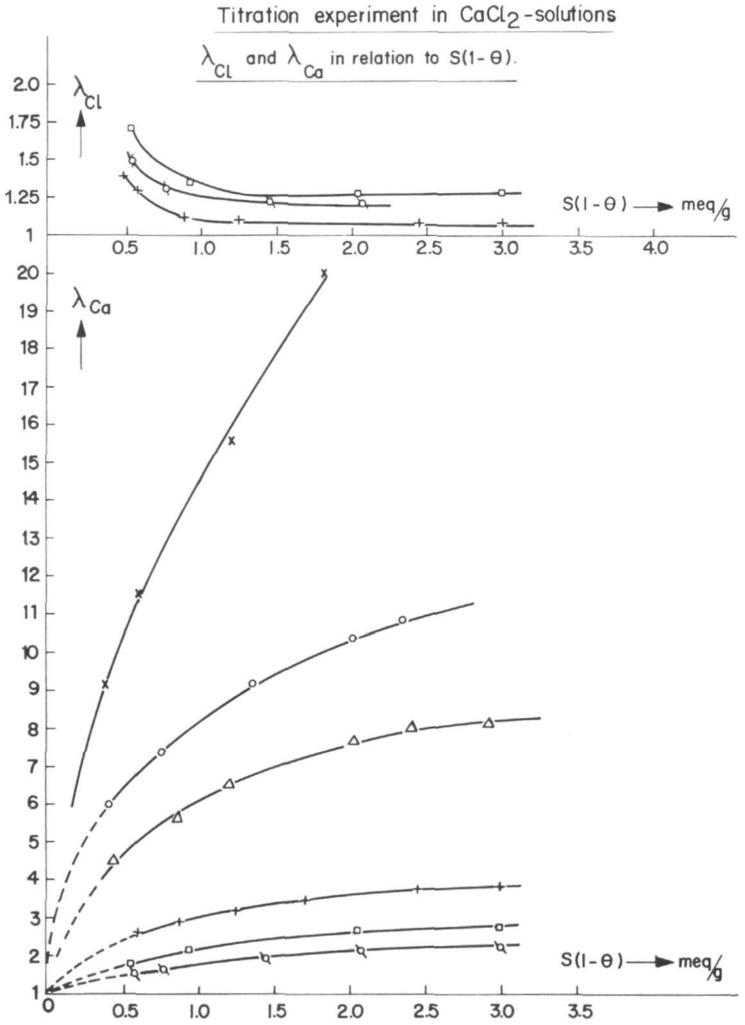


Fig. VI-6 — See subscription
Fig. VI-5a

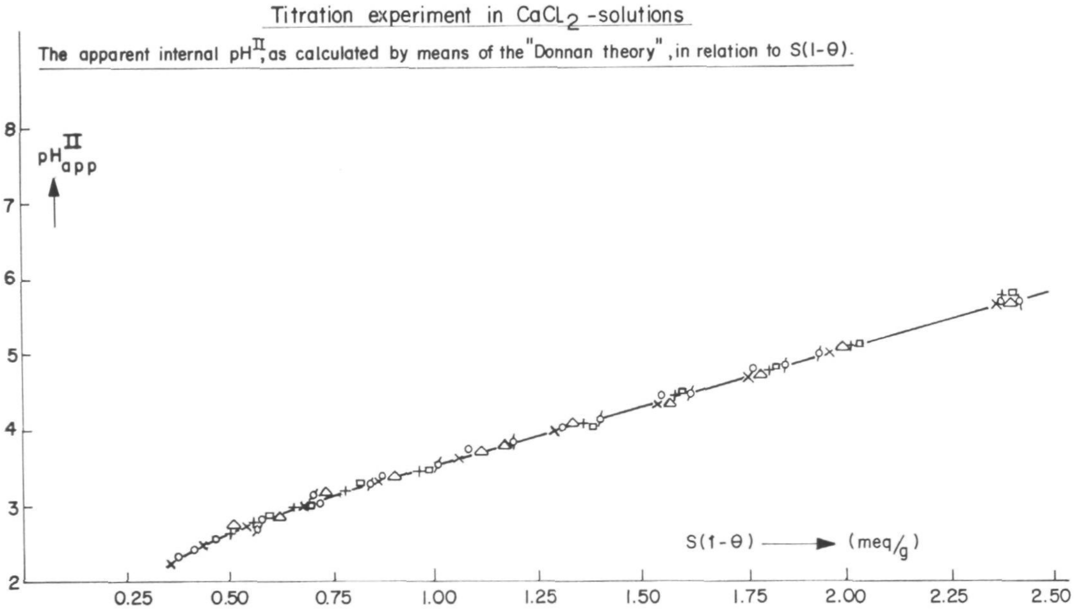


Fig. VI-7 — See subscription Fig. VI-5a

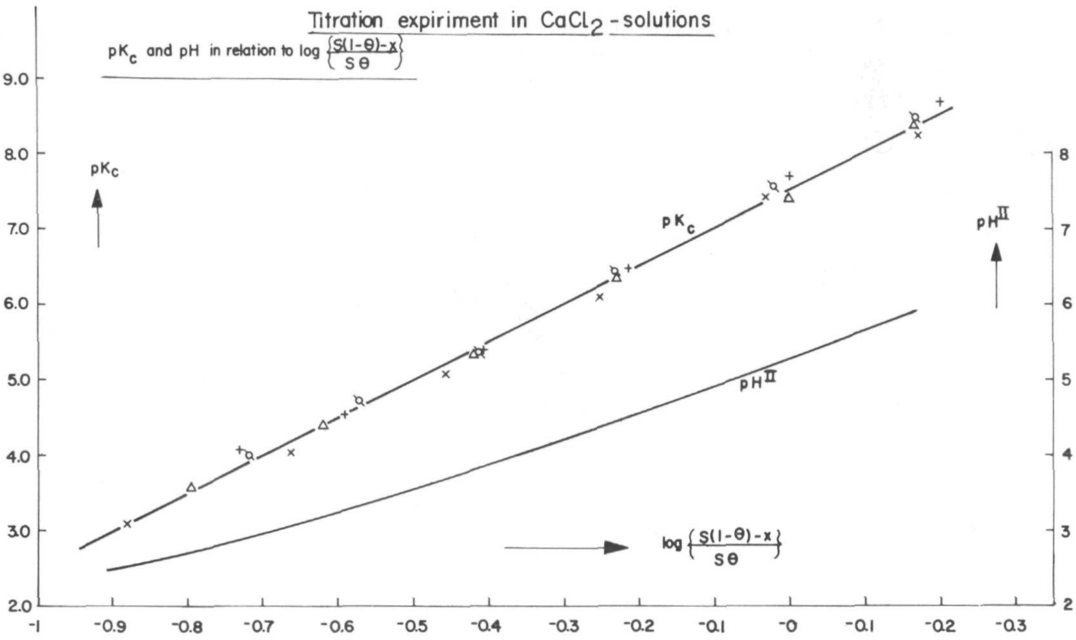


Fig. VI-8 — See subscription Fig. VI-5a

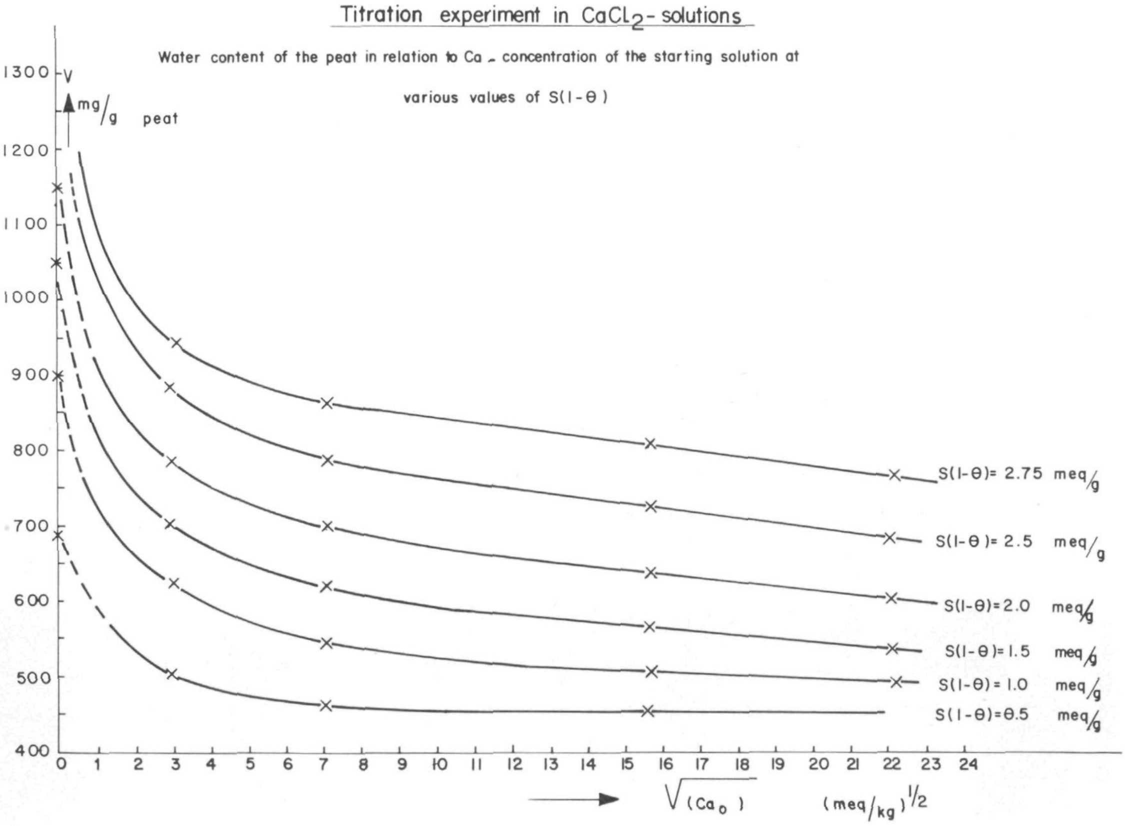


Fig. IV-9 — See subscription Fig.VI-5a

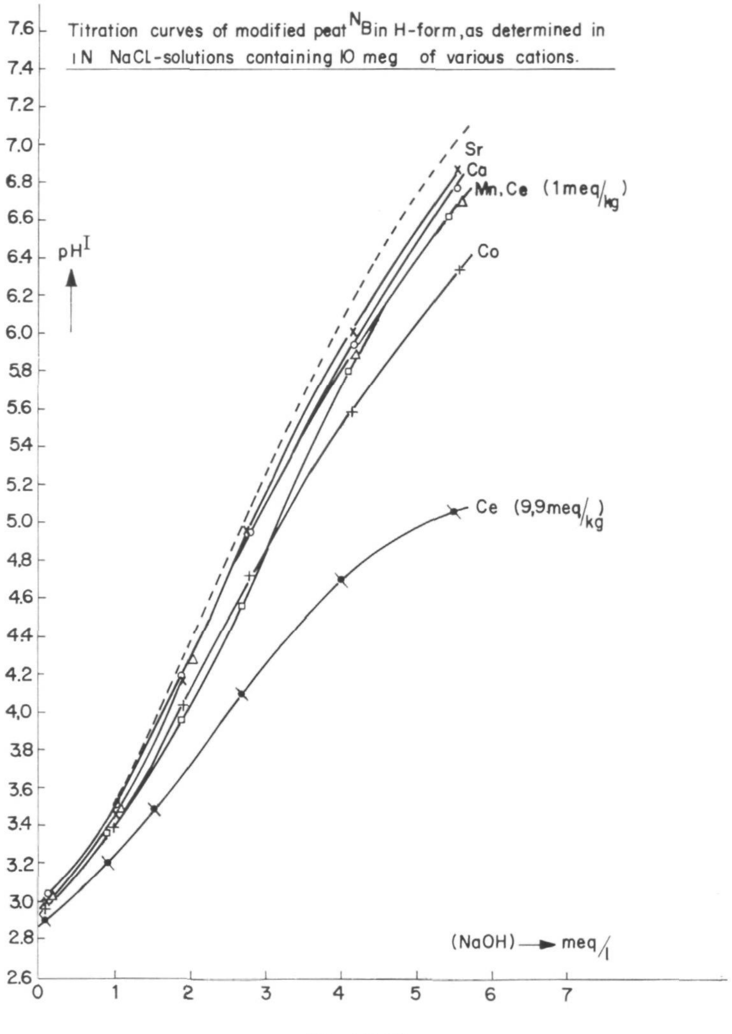


Fig. VI-10a

Sorbent: 2000 ppm modified peat N_B
Contact time: 24 hrs
Solution: ○ $10.16 . 10^{-3}$ molal $CaCl_2$
× $10.19 . 10^{-3}$ molal $SrCl_2$ $+5 . 10^{-3}$ μCi ^{85}Sr/ml
△ $10.20 . 10^{-3}$ molal $MnCl_2$ $+5 . 10^{-3}$ μCi ^{54}Mn/ml
+ $10.08 . 10^{-3}$ molal $CoCl_2$ $+5 . 10^{-3}$ μCi ^{60}Co/ml
● $9.90 . 10^{-3}$ molal $CeCl_3$ $+5 . 10^{-3}$ μCi ^{144}Ce/ml
□ $1.0 \; . 10^{-3}$ molal $CeCl_3$ $+5 . 10^{-3}$ μCi ^{144}Ce/ml
All solutions are 1.04 molal in NaCl.

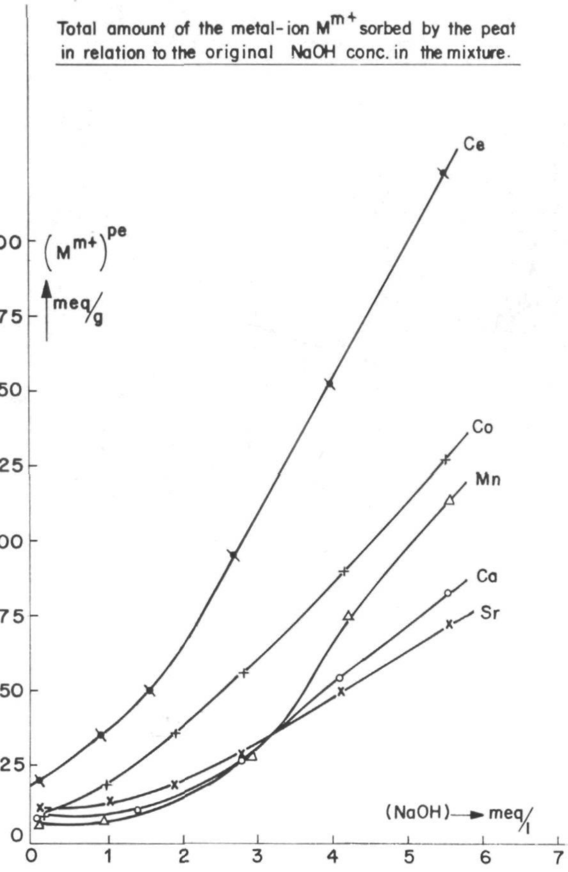


Fig. VI-10b — See subscription Fig. VI-10a

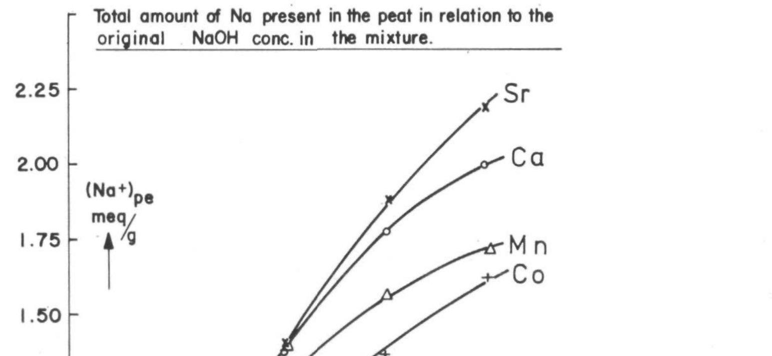


Fig. VI-10c — See subscription Fig. VI-10a

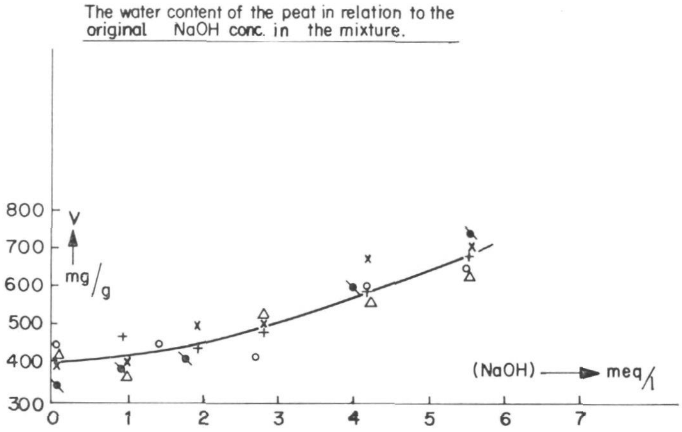


Fig. VI-10d — See subscription Fig. VI-10a

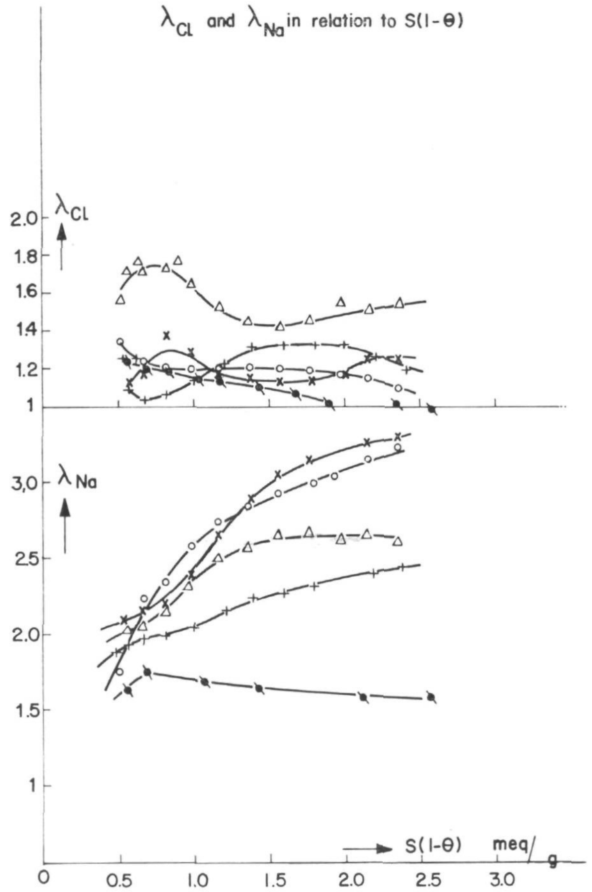


Fig. VI-11 — See subscription Fig. VI-10a

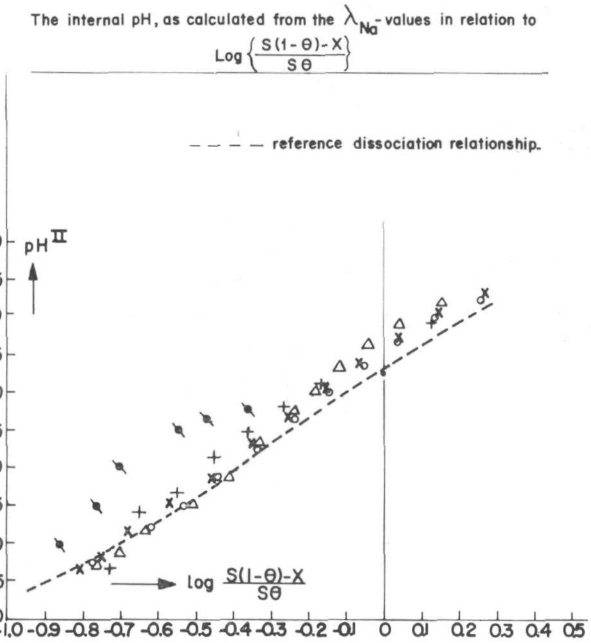


Fig. VI-12 — See subscription Fig. VI-10a

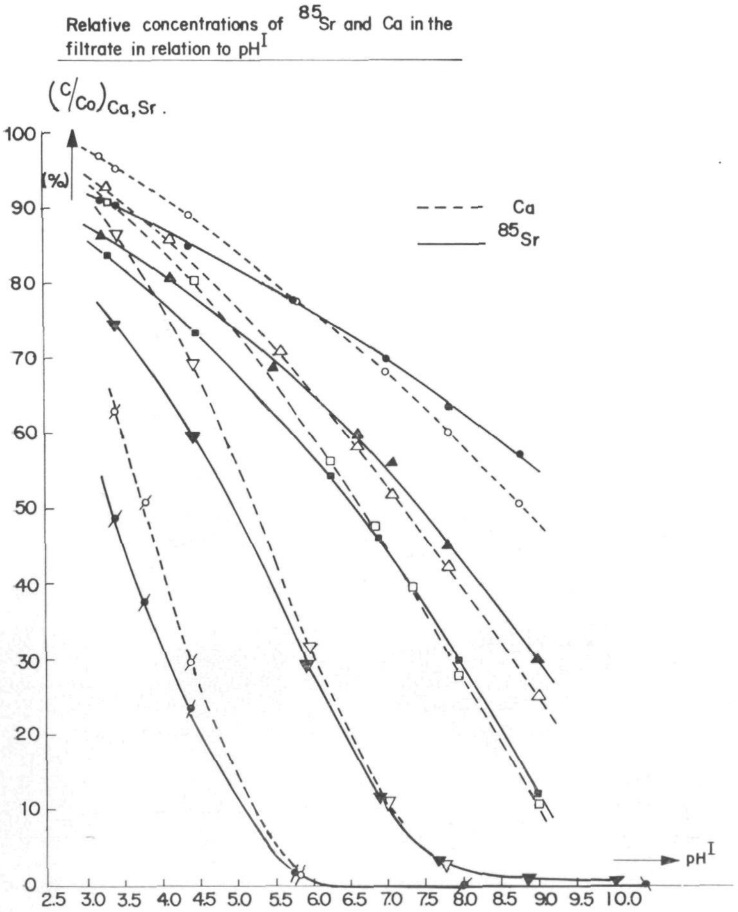


Fig. VI-13

Sorbent: 2000 ppm modified peat N_B
Contact time: 24 hrs
Solution:

○	●	15.09 meq $CaCl_2$/l
△	▲	10.18 meq $CaCl_2$/l
□	■	7.87 meq $CaCl_2$/l
△	▲	4.31 meq $CaCl_2$/l
⟠	♦	1.08 meq $CaCl_2$/l

All solutions contained 5.10^{-3} $\mu Ci\,^{85}Sr$/ml.

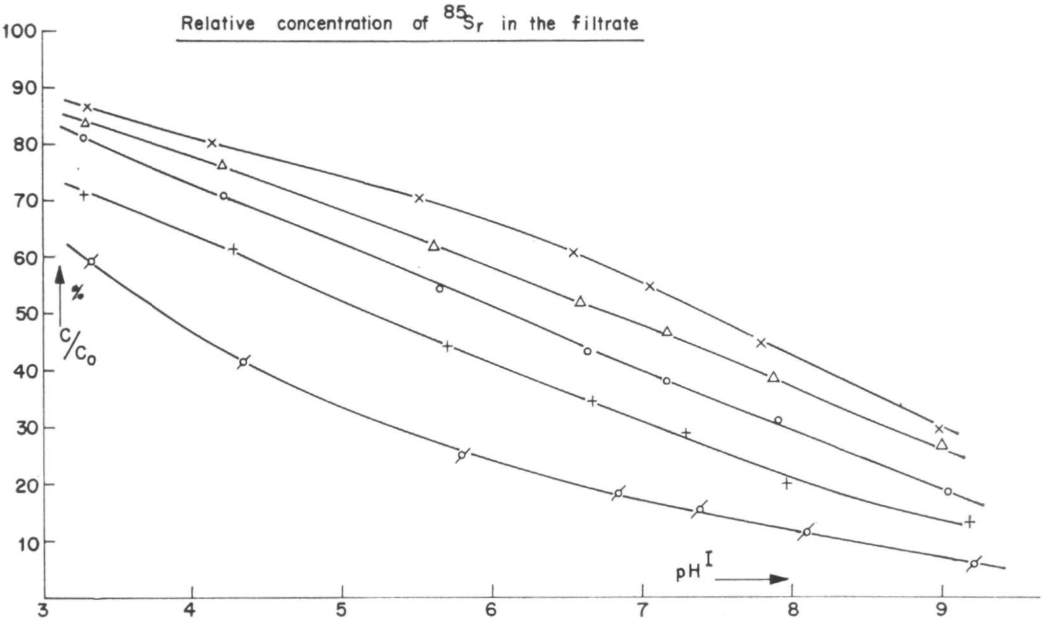


Fig. VI-14a

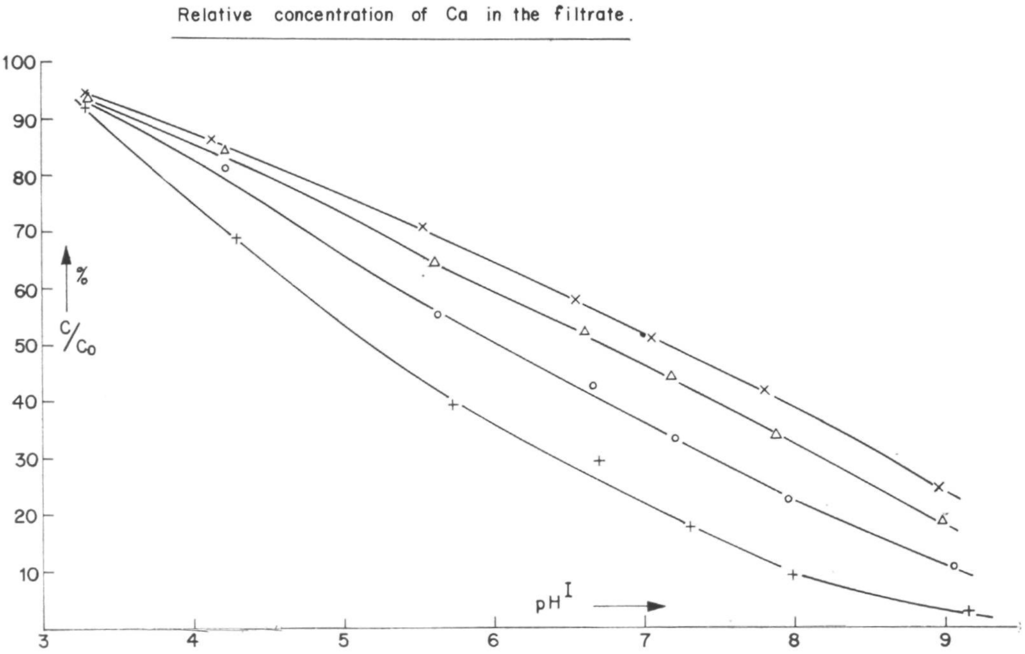


Fig. VI-14b

Fig. VI-14

Sorbent: 2000 ppm modified peat N_B

Contact time: approximately 18 hrs

Solution: × 10.19 meq $CaCl_2$/l

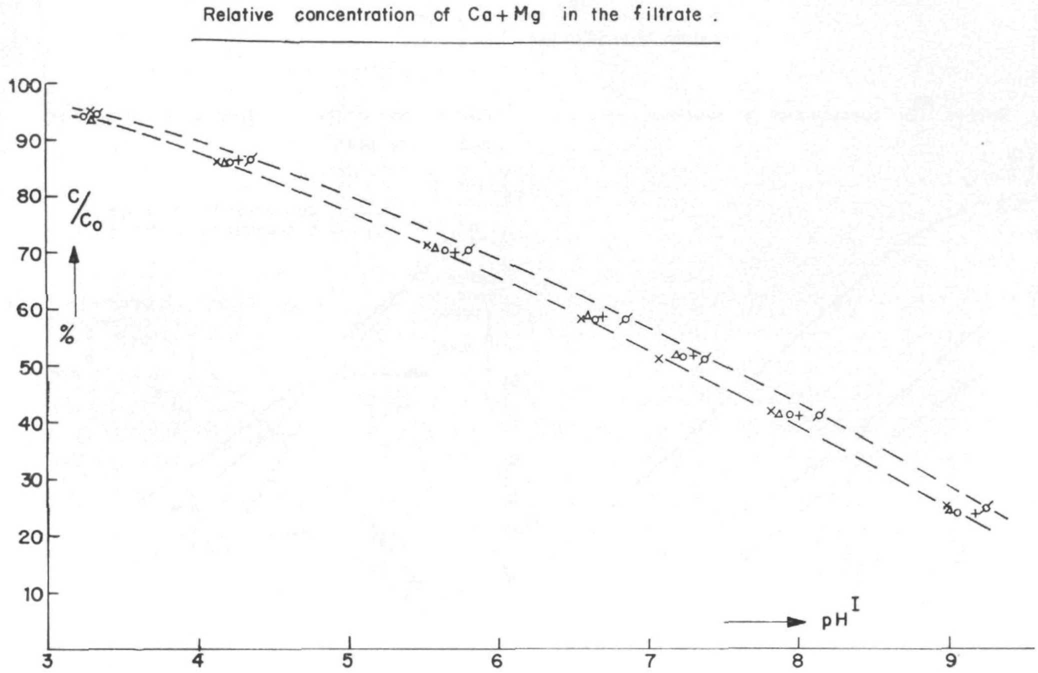
△ 7.63 meq $CaCl_2$/l + 2.5 meq $MgCl_2$/l

○ 5.09 meq $CaCl_2$/l + 5.0 meq $MgCl_2$/l

\+ 2.54 meq $CaCl_2$/l + 7.5 meq $MgCl_2$/l

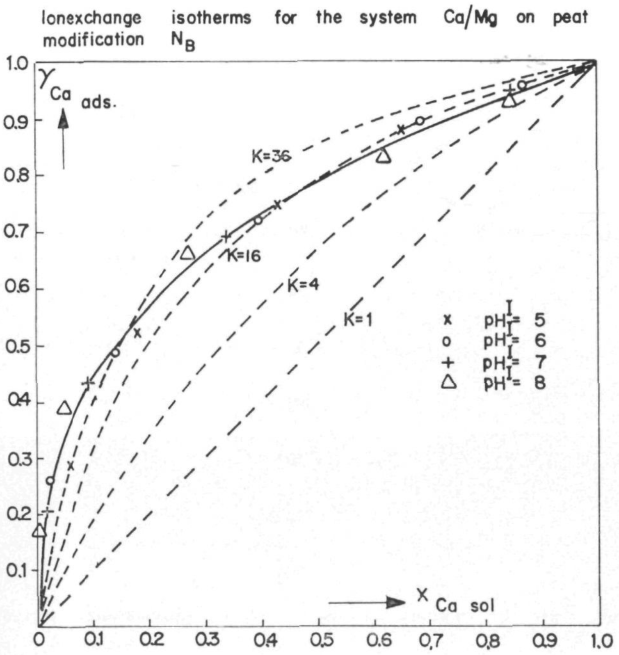
ϕ 10.0 meq $MgCl_2$/l

All solutions contained 5.10^{-3} μCi^{85}Sr/ml.



Relative concentration of Ca+Mg in the filtrate.

Fig. VI-15 — See subscription Fig. VI-14.



Ionexchange isotherms for the system Ca/Mg on peat modification N_B

Fig. VI-16

The sorption of ^{85}Sr and of the competing cations by modified peat.

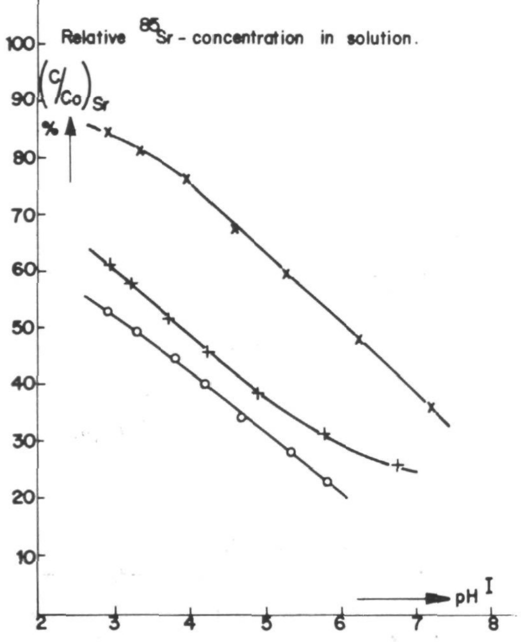


Fig. VI-17a

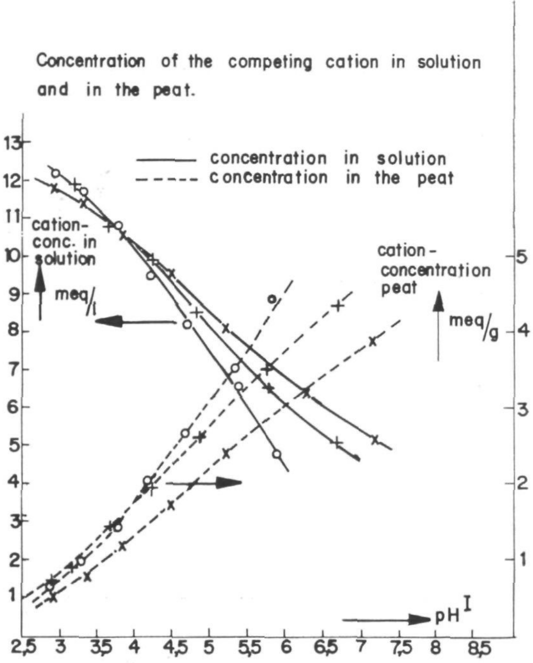


Fig. VI-17b

Desorption of ^{85}Sr from the peat by HCl - solutions.

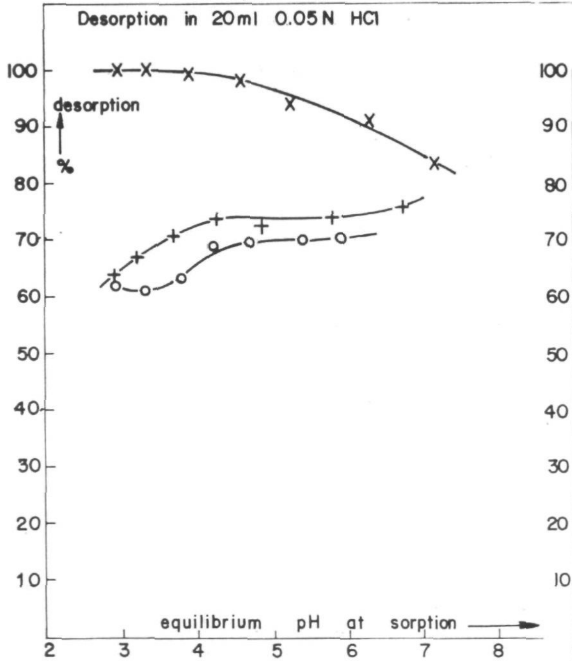


Fig. VI-17c

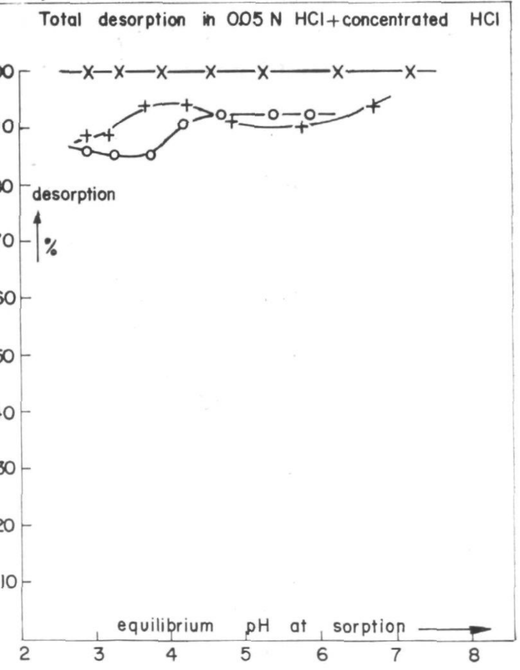


Fig. VI-17d

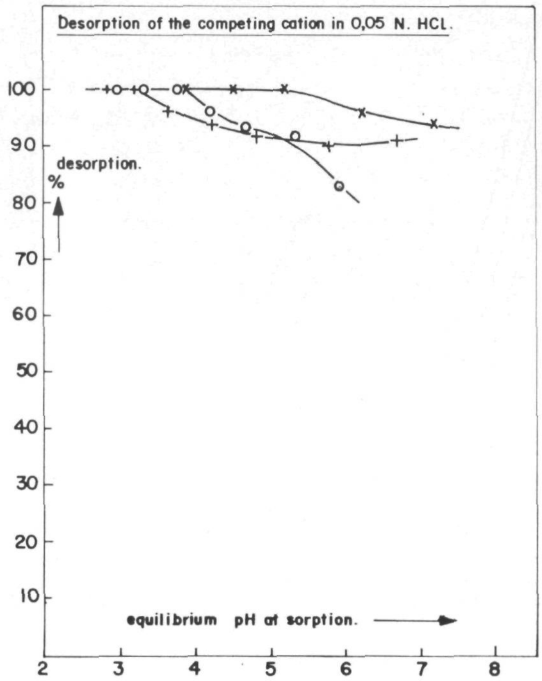


Fig. VI-17e

Fig. VI-17
Sorbent: 2000 ppm modified peat (mixture of samples 6, 8 and 10)
Contact time: 24 hrs
Solution: × 13.20 meq $CaCl_2$/l –
+ 13.71 meq $CoCl_2$/l – All solutions contained 5.10^{-3} μCi ^{85}Sr/ml.
○ 13.49 meq $MnCl_2$/l–

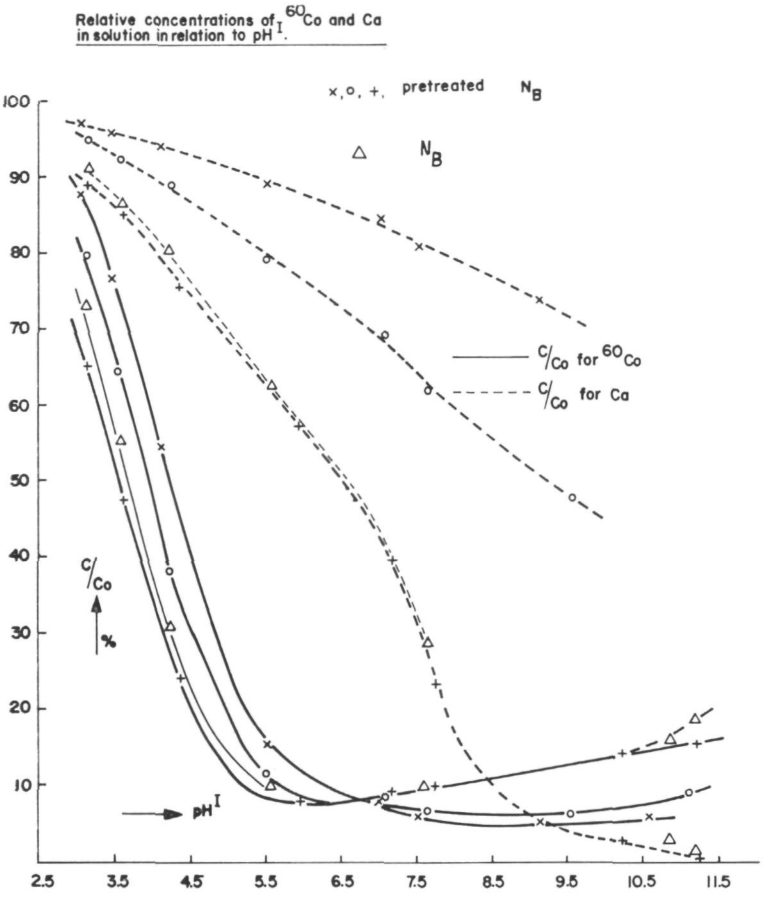


Fig. VI-18

Sorbent: 1000 ppm modified peat N_B

Contact time: 24 hrs

Solution:

× 18.38 meq $CaCl_2$/l

○ 9.20 meq $CaCl_2$/l

+ △ 4.53 meq $CaCl_2$/l

All solutions contained

$5\ 10^{-3}$ μCi^{60}Co/ml.

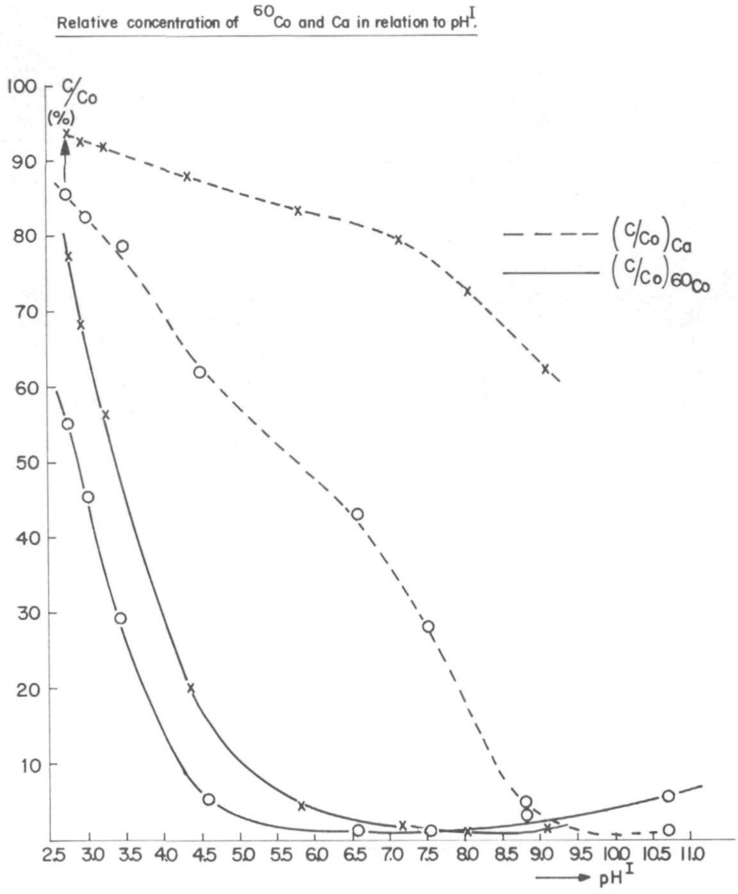


Fig. VI-19

Sorbent: 1000 ppm modified peat A-3

Contact time: 24 hrs

Solution: × 18.31 meq $CaCl_2$/l

○ 4.45 meq $CaCl_2$/l

Both the solutions contained 5.10^{-3} μCi ^{60}Co/ml.

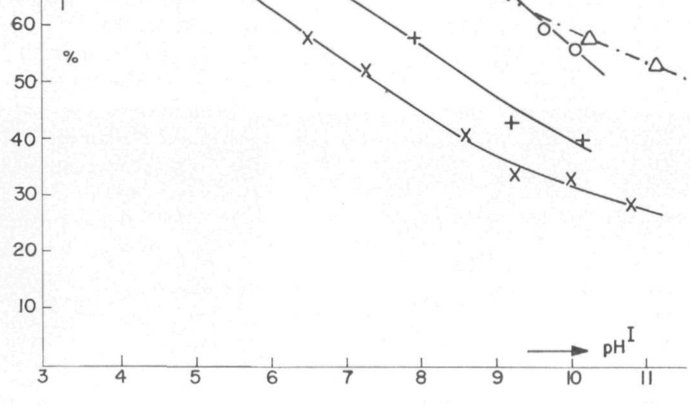


Fig. VI-20

Sorbent: 1820 ppm modified peat N_B

1820 ppm moor peat

Contact time: 24 hrs

Solution: ○ 5 meq $CaCl_2$/l

\+ 2.44 meq $CaCl_2$/l

△ × 1.55 meq $CaCl_2$/l

All solutions contained 5.10^{-3} μCi ^{137}Cs/ml.

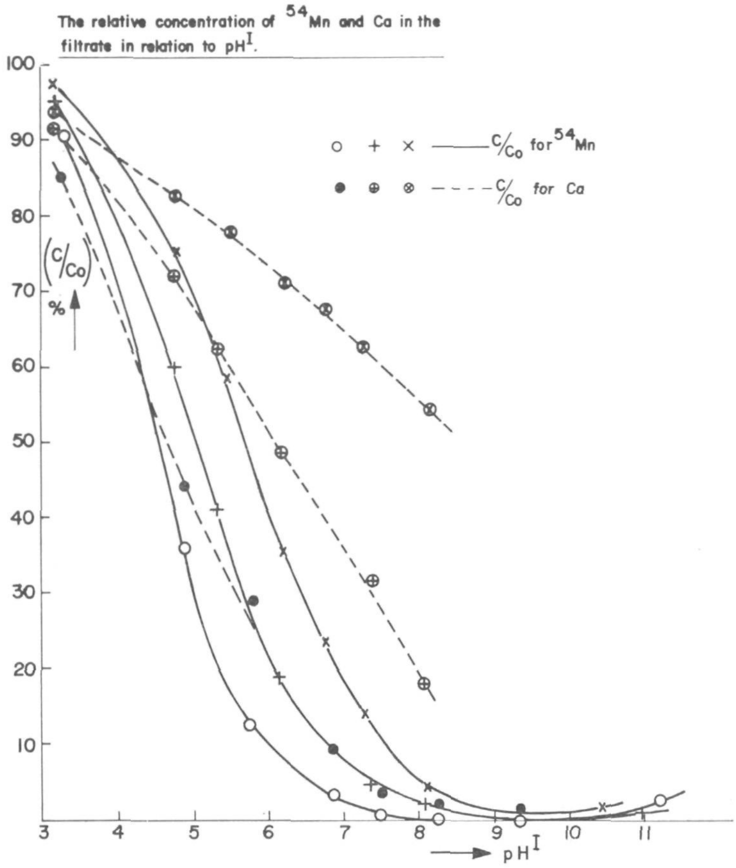


Fig. VI-21

Sorbent: 1820 ppm modified peat N_B

Contact time: approximately 24 hrs

× ⊗ 17.88 meq $CaCl_2$/l

+ ⊕ 9.28 emq $CaCl_2$/l

○ ● 4.80 meq $CaCl_2$/l

All solutions contained

5.10^{-3} μCi ^{54}Mn/ml

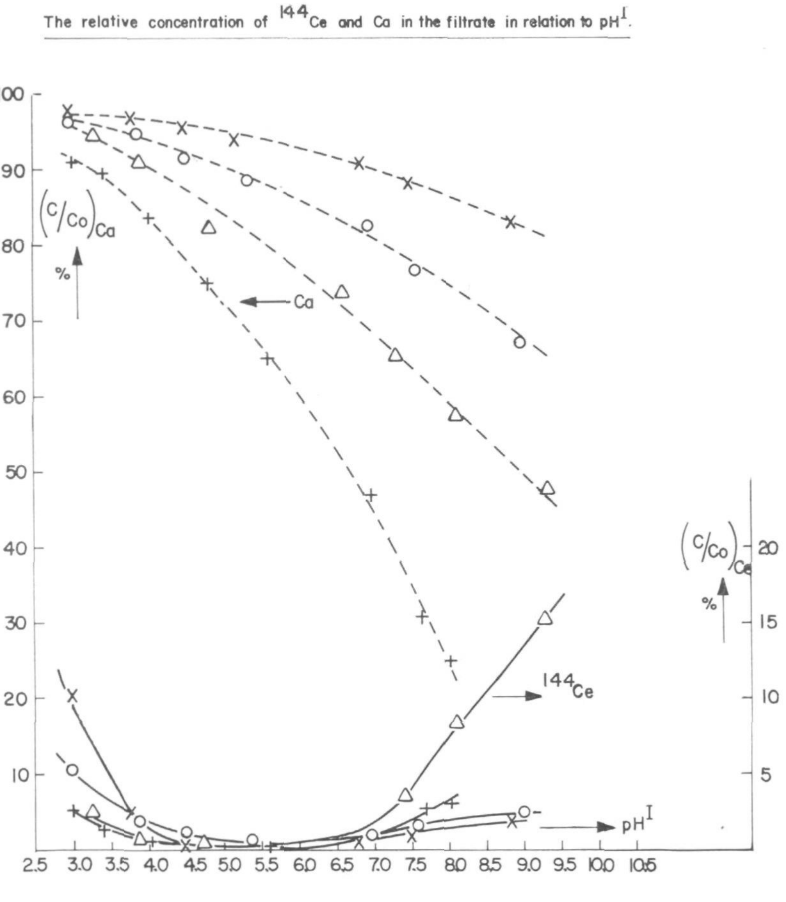


Fig. VI-22

Sorbent:

1000 ppm modified peat N_B (×, ○, +)

1000 ppm moor peat (△)

Contact time: 24 hrs

Solution:

× 27.32 meq $CaCl_2$/l

○ 13.61 meq $CaCl_2$/l

△ + 4.51 meq $CaCl_2$/l

All solutions contained

5.10^{-3} μCi ^{144}Ce/ml.

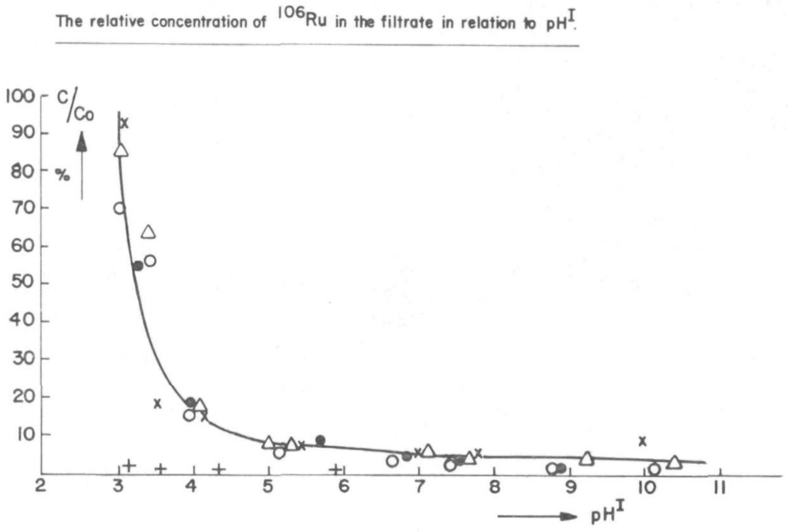

The relative concentration of ^{106}Ru in the filtrate in relation to pH^I.

Fig. VI-23

Sorbent: 1000 ppm modified peat N_B
Contact time: 24 hrs
Solution: ● ○ 13.5 meq $CaCl_2$/l, pH_0 3.9, 5.10^{-3} μCi $^{106}Ru^{III,IV}$ml as chloride
△ 9.0 meq $CaCl_2$/l, pH_0 3.9, 5.10^{-3} μCi $^{106}Ru^{III,IV}$ml as chloride
× 4.54 meq $CaCl_2$/l, pH_0 3.9, 5.10^{-3} μCi $^{106}Ru^{III,IV}$ml as chloride
+ 13.5 meq $CaCl_2$/l, pH_0 6.0, 5.10^{-3} μCi $^{106}Ru^{III,IV}$ml partly as hexamine.

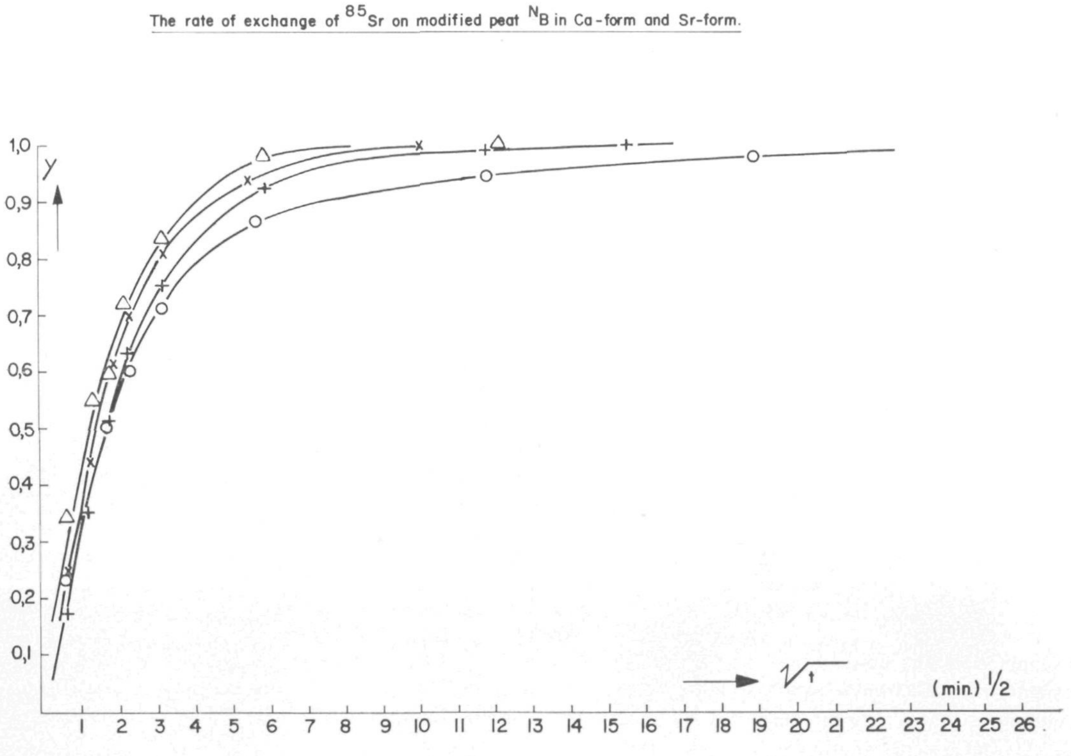

The rate of exchange of ^{85}Sr on modified peat ^{N}B in Ca-form and Sr-form.

Fig. VI-24

Sorbent: 2000 ppm modified peat N_B (mean particle size 0.27 mm)

Solution: △ 20.08 meq $CaCl_2$/l, pH^I 7.5	○ 4.29 meq $CaCl_2$/l, pH^I 4.4
+ 9.35 meq $CaCl_2$/l, pH^I 6.2	× 8.35 meq $SrCl_2$/l, pH^I 6.2.

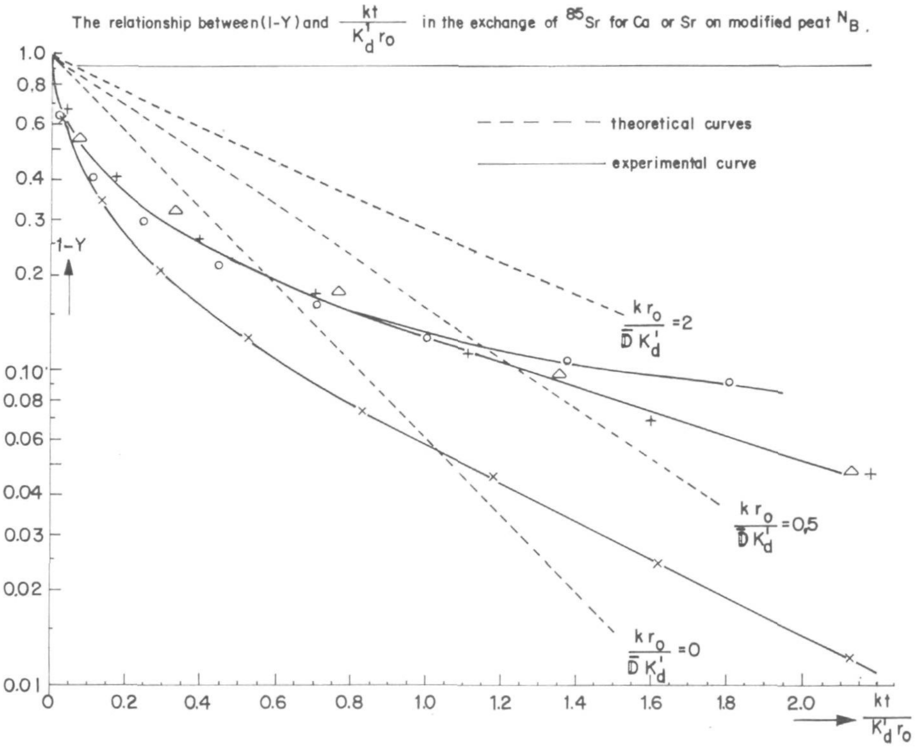


Fig. VI-25 — See subscription Fig. VI-24.

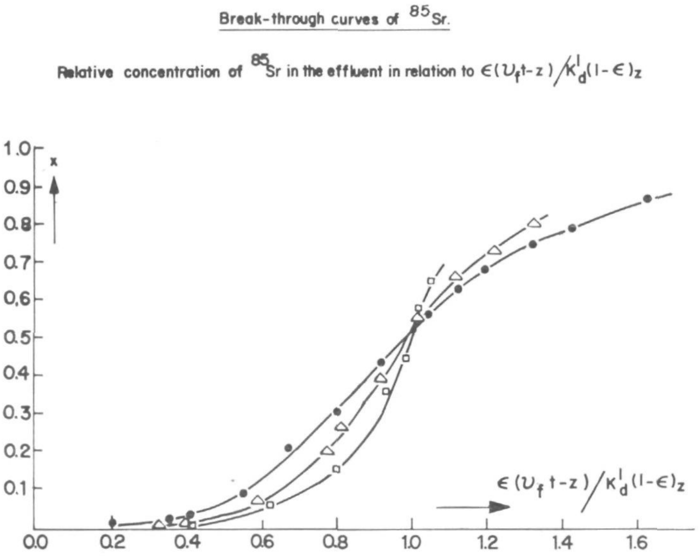


Fig. VI-26

Column diameter: 1.5 cm

Column height: 8.0 cm

Amount of peat: 3.72 g modified peat N_B (mean particle size 0.27 mm) in Ca-form.

$CaCl_2$-conc. solution	Flow rate v_0
● 8.22 meq/l	636 cm/hr
△ 8.22 meq/l	255 cm/hr
□ 8.22 meq/l	102 cm/hr

All solutions contained $5 . 10^{-3}$ μCi ^{85}Sr/ml.

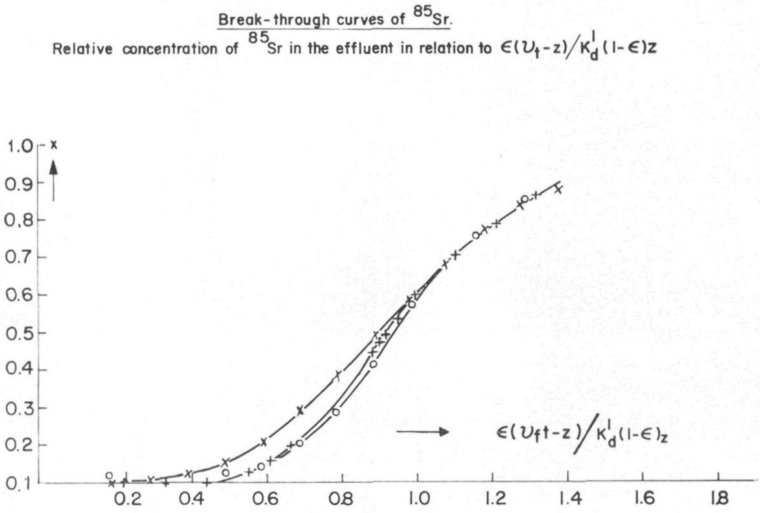


Fig. VI-27

Column diameter: 1.5 cm

Column height: 8.0 cm

Amount of peat: 3.72 g modified peat N_B in Ca-form (mean particle size 0.27 mm).

$CaCl_2$-conc. solution	Flow rate v_0
+ 4.14 meq/l	255 cm/hr
× 4.14 meq/l	636 cm/hr
○ 1.04 meq/l	255 cm/hr

All solutions contained 5.10^{-3} μCi ^{85}Sr/ml.

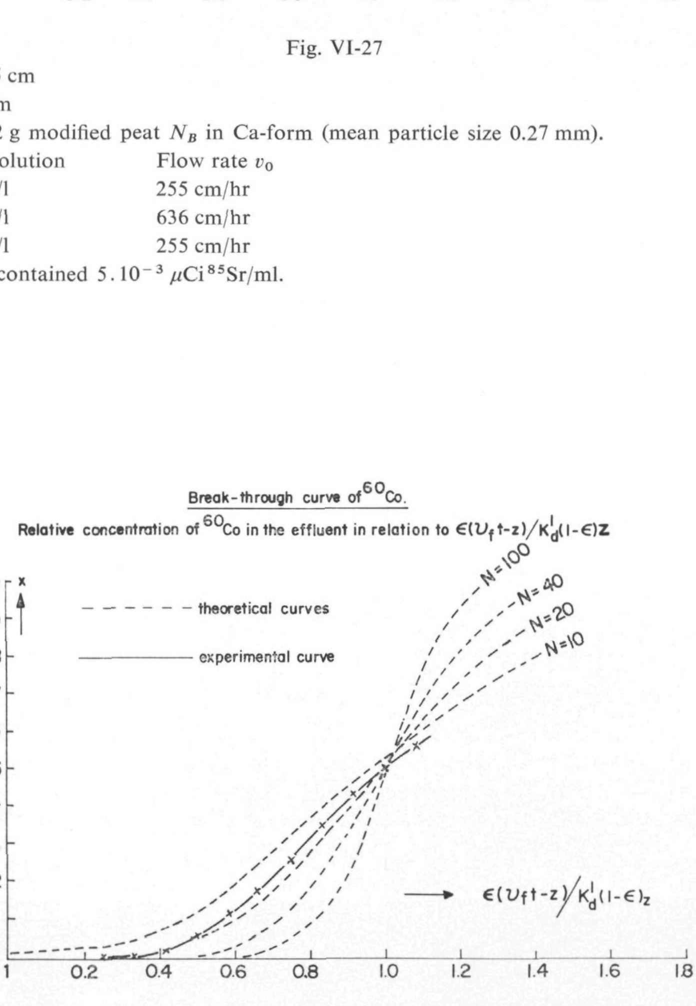


Fig. VI-28

Column diameter: 1.5 cm

Column height: 8.0 cm

Amount of peat: 3.72 modified peat N_B in Ca-form (mean particle size 0.27 mm).

Solution: 13.20 meq $CaCl_2$/l, 5.10^{-3} μCi ^{60}Co/ml (×)

Flow rate: v_0: 442 cm/hr.

VII. THE REMOVAL OF RADIOIODINE

VII-1. **Introduction**

Conventional water treatment processes, such as coagulation and sand-filtration, are not effective in the removal of radioiodine. Although an improvement can be achieved by adding (e.g. prior to or simultaneously with coagulation) specific reagents, such as $AgNO_3$ (1–3), AgCl (5), $CuSO_4$ (1), $CuSO_4+Na_2SO_3$ (4) or activated carbon (1, 2, 5) even then it is questionable whether the radioiodine is sufficiently removed.

The decontamination of solutions containing radioiodine represents a complex problem, because different chemical forms can occur simultaneously in the same solution, some of which change easily into each other. As a consequence a general technique such as physical adsorption to materials with high specific surface areas, such as active carbon, might have special attractions relative to chemical reagents which show a specific chemical action to only one of the chemical forms. Still one can expect that a sorbent which is effective in the removal of some specific chemical form of the iodine may be much less effective or even inert with respect to the removal of other forms of the element.

With respect to active carbon or other common sorbents, little information is available about the sorption of iodine compounds.

Elementary iodine seems to be sorbed rather well on activated carbon (6, 12, 13, 16, 17). However, it is questionable, how far the various literature data are reliable, because part of the iodine is converted into hydro-iodic acid in presence of carbon (6, 18). This amount is not determined in the supernatant liquid as iodine and may thus easily be accounted for as being sorbed. Nevertheless it may be accepted that sorption of iodine (I_2) takes place on carbon. This seems to occur partly in irreversible form (12, 19). The amount adsorbed depends on a large number of factors, such as the type of the carbon (conditions of the preparation) I_2- and I^--concentration, solvent, pH etc.

With respect to the sorption of electrolytes on carbon the temperature at which the carbon has been activated seems to be important. When the activation is performed at temperatures above 850 °C a product is obtained which sorbs acids; carbons activated at 300-500 °C sorb bases (6 – 12). In the intermediate temperature range a product with amphoteric properties seems to be formed (7, 9). The mechanism of the sorption is still obscure; the presence of oxygen, carbon oxides (7, 8, 11, 12) as well as hydrogen (7, 10) has been mentioned as being important.

Very little information is available about the sorption of iodine compounds on charcoal. Using a pure sugar charcoal, Kolthoff (13) and Miller (14) investigated the sorption of various acids from 0.1 N solutions.

The following sequence of decreasing sorption was established:

$$HCNS > HI > HNO_3 > HIO_3 > HCl > HClO_4 > H_2SO_4 \ (^{13}).$$

Contrary to these results Dubinin (15) observed a better sorption of HIO_3 as compared with HI.

In a few publications it has been mentioned that iodine and/or iodine compounds are sorbed to some extent on *peat*. According to Burkat (20) elementary iodine is bound to peat partly chemically (i.e. about 75%) and partly physically (about 25%). However, any sorption of iodide ions on peat was not observed by this author. On the other hand Shilow (21) found a certain sorption of HI, HIO_3 and other acids on peat. The following sequence of decreasing sorption was established: $HI > HIO_3 > HClO_4 > HClO_3 > HIO_4$. Nevertheless according to Szilagyi (22) peat seems to be rather ineffective for the removal of radioiodine from carrier-free aqueous solutions.

As mentioned above the difficulties involved in the removal of radioiodine from aqueous solutions must be attributed mainly to the complicated chemical behaviour of the element also with respect to coal (24, 25). Various chemical forms can occur simultaneously in the same solution, depending on the pH, concentration and the presence of oxidizing or reducing substances ($^{23-25}$).

Elementary iodine is liable to hydrolysis in an aqueous environment. In neutral and in acid media, iodide and hypoiodite are formed according to the fast reaction:

$$I_2+H_2O=HIO+H^++I^- \tag{1}$$

equilibrium constant $K_1=4.6.10^{-13}$ (^{26}) at room temperature. In alkaline solutions the hypoiodite is not stable and iodate is formed according to the overall reaction:

$$3I_2+3H_2O = 6H^++5I^-+IO_3^- \tag{2}$$

equilibrium constant $K_2=2.8.10^{-47}$, at room temperature.

The mechanism of the formation of iodate is complicated. It is formed directly when the ratio $[OH^-]/[I_2]$ is small. Under these conditions the rate of the reaction is proportional to $[OH^-]$ and $[I^-]^{-1}$ and is very small when $[OH^-]/[I^-] \ll 1$. At large values of the ratio $[OH^-]/[I_2]$ the reaction takes place via the intermediate formation of IO^- and then the oxidation of IO^- to $IO_3{}^-$ is rate-determining.

Iodide solutions are liable to oxidation by air. Iodine, hypoiodite or iodate are formed, depending on the pH of the solution. In neutral and alkaline media the reaction proceeds only slowly in the presence of light. In acid solutions the reaction is faster and proceeds also in the dark. Under the latter circumstances the reaction is catalysed by I_2, by heavy metal ions such as Cu^{2+} and Fe^{2+}, and by HNO_2. According to investigations of Behrens (^{35}) $^{131}I^-$ added to surface water and rain water as carrier free ^{131}I (or in the presence of an extremely small amount of carrier) is gradually converted into iodate, periodate and some unidentified compounds. Such transformations were not observed in deep groundwater.

Iodine and iodide are oxidized to iodate with excess of chlorine (or HClO*) ($^{27,\,33}$). In weakly acid and alkaline solutions this reaction proceeds through the intermediate formation of HIO. The further oxidation of HIO is rate determining in the overall reaction ($^{33,\,34}$).

Iodate is formed in neutral media from HIO according to the following reactions:

$$HIO+I^-+H^+ = I_2+H_2O \tag{3a}$$

$$2HClO+I_2+2e = 2HIO+2Cl^- \tag{3b}$$

$$2HClO+HIO = IO_3^-+3H^++2Cl^- \tag{3c}$$

Reaction (3a) is relatively slow, whereas reactions (3b) and (3c) are fast.

In alkaline media iodate is also formed through reaction (3d):

$$3HIO = IO_3^-+2I^-+3H^+ \ (K=2{,}88.10^{-10}) \tag{3d}$$

which is relatively slow.

In strongly alkaline media iodate is oxidized to periodate by ClO^-.

In acid solutions the preliminary formed I_2 is oxidized by Cl_2 (or HClO) quantitatively in $IO_3{}^-$ through the reaction:

$$I_2+5Cl_2+6H_2O = 2IO_3^-+10Cl^-+12H^+$$

The equilibrium constant of this reaction is unknown.

In the presence of oxidizable organic substances (i.e. humic acids etc.) and charcoal an excess of chlorine is required to complete the oxidation of iodide (^{28}). Certain types of carbon seem to affect various equilibria of iodine (^{36}), i.e. the hydrolysis of I_2 (reaction (1)) as it reduces HIO through the reaction $2HIO+C=CO_2+2HI$, and the oxidation of I^- by $IO_3{}^-$ (reverse of

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* Chlorine hydrolyses in water according to the reaction $Cl_2+H_2O=HOCl+Cl^-+H^+$, with an equilibrium constant 3.10^{-4} (15 °C). The dissociation equilibrium constant of HOCl is $3.3.10^{-8}$ (20 °C).

reaction (2)), because of preferential sorption of HI. An excess of chlorine may also be required when ammonium salts are present in the solution which is normal for surface water to an extent of a few ppm. The ammonium ion reacts with chlorine (or hypochlorite) under the formation of chloramines, nitrogen trichloride, nitrogen and/or nitrate to extents which depend on conditions. The formation of the higher substituted derivatives is favoured at higher acidities and at increased ratios of chlorine to ammonia. Below pH 4.5 mainly NCl_3 is formed, while at $pH > 7$ the main reaction product is NH_2Cl. The reactions are catalysed by H^+ and CH_3COOH ([29-31]).

It is evident that the sorption of iodine on either carbon or peat will depend on a large number of factors. The mechanism of the sorption will undoubtedly be extremely complicated, the more so since the distribution of iodine over the various chemical species may be quite different at very low concentrations ([32]). Therefore the object of the present investigation is to obtain a rough impression on the usefulness of carbon and peat for the removal of radioiodine from aqueous solutions rather than to make an extensive study of the mechanism of the sorption.

VII-2. **Experimental**

The sorption of radioiodine on activated carbon and on peat has been investigated by means of slurry experiments. Solutions of ^{131}I as iodide, iodine and iodate and different amounts of carrier were used. In accordance with the composition of most surface waters, ions such as Ca^{2+}, Na^+, NH_4^+ and Cl^- were added to these solutions. The experimental solutions were always freshly prepared from a concentrated $Na^{131}I$ stock solution, which was kept at a pH 8-9 and stored in the dark in order to prevent oxidation of the iodide.

The experiments with carbon were carried out with a product of standard quality obtained from Fluka AG-Buchs SG and designated by 50417 (now supplied under number 5120). No additional information about the raw material, the conditions of preparation, analysis etc. could be obtained from the supplier. A tritration of the carbon (performed by shaking fresh quantities of the material with solutions containing known amounts of standardized NaOH or HCl) showed that H^+-ions or OH^--ions are sorbed depending on the pH of the solutions (see Table VII-1).

The sorption of ^{131}I to carbon and peat was studied in the absence and in the presence of chlorine. Experiments with peat were carried out with moor peat in Ca- and H-form.

The procedure applied in these experiments was about the same as in the previous experiments concerning the sorption of cationic radionuclides on peat (see Chapter IV and VI). In the experiments with peat, suspensions of 400 mg in 200 ml solution were used. The mixtures were shaken and after different time intervals samples of about 10 ml were withdrawn and filtered. The supernate solution was analysed for ^{131}I-concentration by γ-counting. After measurement of the activity and pH, the filtrate and the filtered peat were brought back into the mixture. The same procedure was also applied in the experiments with carbon in the absence of chlorine. In the other experiments with carbon separate suspensions of 50 ml containing 50 mg of carbon were prepared and shaken during a fixed period of time and then filtered completely. Subsequently the activity and the pH of the filtrate were determined. In some cases also the pH of the solution, directly after the addition of chlorine (and before the addition of the carbon) was measured (pH_{Cl_2}).

The chlorine was added as a dilute aqueous solution, which was prepared always freshly from a concentrated Cl_2-stock solution. All experiments were performed in polythene bottles.

VII-3. **Results**

VII-3-1. ACTIVATED CARBON AS SORBENT

Experiments carried out with freshly prepared solutions of carrier free $Na^{131}I$ in which the carbon was in continuous contact with the solution, show (see Fig. VII-1) that an appreciable sorption of iodine takes place only in acid solutions. However, the rate of the sorption is very small. In addition to the above experiments the sorption was also determined in relation to the age of a $Na^{131}I$ solution which was stored under daylight. For this purpose after different time intervals aliquots of the above mentioned starting solution where shaken during 30 minutes with fresh portions of the carbon (50 mg carbon per 50 ml solution). The results of these experiments are summarized in Table VII-2.

Apparently an alteration takes place in the carrier-free solution which improves the sorption of the iodine. Other experiments show that this alteration is the rate determining step in the sorption. This transformation could be an oxidation to elementary iodine or hypoiodite. According to the equilibrium constant of the reaction of free iodine with water (reaction 1) applied to a total iodine concentration of 7.10^{-12} g mol/l (based on a specific activity of 5000 Ci/g iodine and a ^{131}I-concentration of 5.10^{-3} μCi/ml) more than 98% of the iodine formed should be transformed into iodine and hypoiodite at pH-values of 3 and higher. Therefore HIO is the only oxidation product available and thus HIO is better sorbed than I^- at $pH > 2.9$. Since it is impossible to estimate the amount of hypoiodite formed, a certain sorption of iodide at low pH cannot be excluded. The time effect of contact with carbon is mainly the result of the oxidation described but may to a minor extent also be related to some reaction between carbon and the iodine compound involved.

The decreased sorption at high pH is explained by the decreased sorption of iodide under these circumstances as a result of strong competition by OH^--ions. Moreover, no HIO will have been formed as a result of decreased oxidation rate. (Compare Table VII-2 at pH 8.5.)

In order to obtain some additional information about the processes involved in the sorption on this type of carbon some experiments were carried out with solutions of $Na^{131}I$ containing a small amount of carrier, which was added either as I_2 or as I^-. As the exchange reaction between I_2, HIO and I^- is very fast, the radioiodine will always be distributed over the iodine, iodide and hypoiodite present.

The results of the experiments are shown in Figs. VII-2 and VII-3 respectively. The highest sorption takes again place from solutions at low pH. However considerably less iodine is removed from solutions to which free iodine was added than from solutions made by addition of iodide as carrier.

In order to be able to make appropriate conclusions some information is necessary about the equilibrium concentrations of the various iodine compounds under the conditions of the experiments. In Table VII-3 the percentage of free iodine which is hydrolized as calculated from the equilibrium constant of reaction (1) is presented for various pH-values.

It is clear that below pH 4 nearly all iodine is present in the elemental form. Therefore Fig. VII-2 indicates that the sorption capacity of the present carbon for free iodine at this concentration is rather poor and also depends on pH. (Compare data at pH_e 2.4 and 4.1.)

At pH_e 7.0 about 90% of the iodine will be present in the solution as HIO and I^-. Nevertheless little difference is found in the removal of ^{131}I from a solution of pH_e 4.1 and pH_e 7.0. As the sorption of I^- is small at this pH (compare Fig. VII-1) it may be concluded that at pH 7 HIO* is sorbed to the same extent as free iodine at pH 4.

At high pH_e (11.6) the sorption of iodine is extremely low. Under equilibrium conditions the iodine at this pH is merely present in the form of I^- and IO_3^-. However, because of a slow rate of reaction (3a) some HIO may still be present. The total concentration of iodine in the various forms is only 10^{-6} g mol/l, which is very small as compared to the OH^--ion concentration (4.10^{-3} at pH 11.6). Therefore a very strong competition will take place leading to a

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* HIO is a very weak acid, having a dissociation constant 3.10^{-13} at 25 °C ([37]). Hence at $pH < 11$ practically none of the HIO dissociates. For HIO_3 (dissociation constant = $1.67.10^{-7}$) 100% is dissociated at pH 11.

strong negative surface charge of the carbon and thus to a decreased sorption of all iodine containing free anions.

As in the experimental solution the concentration of iodate was not known, it was interesting to measure the sorption behaviour of iodate separately. A carrier free iodate ($^{131}IO_3$) solution was prepared from an iodide solution by oxidation with chlorine in the presence of nitric acid (pH 1). After removal of excess chlorine by boiling, the solution was diluted fifty times leading to a nitrate concentration of 2 meq/l. The ion strength of the solution was made comparable to that used in the experiments of Fig. VII-1 by adding 5 meq $CaCl_2$/l. The results shown in Table VII-4 indicate that iodate ions are not well adsorbed by the carbon.

When looking again to Fig. VII-2 it can also be concluded that again the sorption proceeds very slowly in all experiments. As this cannot be attributed to a slow transport process, it seems that some slow chemical transformation occurs. As the chemical reactions in the liquid at $pH<7$ are fast, a slow reaction with the carbon seems most likely.

In the experiments with NaI-carrier solutions the results obtained are somewhat comparable to those found with carrier-free $^{131}I^-$ solutions (Fig. VII-1). In both experiments sorption is better at low pH. Again, Fig. VII-3 indicates an important time effect. This effect is so strong that in the first 30 minutes only a minor sorption is found also at low pH. From Table VII-2 it is clear that a contact time of 30 minutes is enough to establish near sorption equilibrium. Therefore, the results observed with carrier-iodide must be the result of some slow reaction. If this reaction takes place in the liquid (not investigated here) — as was found for the experiments with tracer amounts of iodide — again oxidation to HIO seems to be the most likely explanation. However, at pH 4 the amount of HIO can only be small (compare Table VII-3) and thus the strong adsorption indicated in Fig. VII-3 for this pH can only be explained by assuming that HIO is selectively removed from the solution.

The experiments described so far indicate that optimum removal of iodine from neutral solutions can be expected if the iodine is present in the form of HIO. A mild oxidation of iodide or iodine to hypoiodite prior to or simultaneously with the addition of the carbon was therefore expected to have a favourable effect on iodine removal.

In view of that *the addition of chlorine*, a chemical in common use for drinking water desinfection, has been investigated.

Chlorine indeed brings about a pronounced improvement of the sorption of ^{131}I from a carrier-free solution by carbon at $pH>5$. The sorption depends on a large number of factors. This will be discussed together with the experimental results.

The pH and the composition of the solution have a pronounced effect. This is clearly illustrated in Figs. VII-4 and VII-5, which show the results of experiments carried out without and with NH_4^+ and CH_3COO^- containing solution. The solutions also contain various amounts of NaOH and HCl to adjust the pH. The chlorine was added in all these experiments 5 minutes before the addition of carbon (time interval between the addition of Cl_2 and carbon is indicated as Δt_i).

The pH before and after addition of carbon are indicated as pH_{Cl_2} and pH_e respectively. Their relationship is given in Fig. VII-6. From the results in Figs. VII-4 and VII-5 it appears:

1. Contrary to the experiments without chlorine the sorption of ^{131}I from a NH_4^+ and acetate free solution increases with increasing pH. Moreover, the sorption effects observed are relatively low.
2. The presence of NH_4^+ and CH_3COO^--ions results in a good sorption of ^{131}I at $pH>4.5$ but not in the region 10 to 11.

The results clearly indicate the extremely complex character of the processes involved. This is conceivable because the iodide is brought in the presence of an oxidation agent (chlorine) but also in the presence of materials (carbon, acetate, NH_3) which can be oxidited or otherwise react with chlorine and iodine. Insufficient data are available to explain the effects observed. Moreover, the time factor is very important as can be seen from Figs. VII-7, 8, 9 and 10. In the absence of NH_4^+ the sorption decreases at increased Δt_i. This effect is more pronounced the higher is the chlorine dose used. In the presence of $NH_4{}^+$ the sorption seems to be almost independent of Δt_i for chlorine concentrations up to 24 ppm.

In the experiments discussed so far the chlorine was always added prior to the carbon. However, the reversed procedure sometimes is more effective. This is particularly true when the pH of the solution after the addition of chlorine (pH_{Cl_2}) would fall below the critical value of $pH_{Cl_2} = 4.5$ (see Fig. VII-4 and Fig. VII-5). Such a sharp decrease of the pH can be prevented to some extent when the carbon is added first, because this material removes protons from acid solutions (see Fig. VII-6). In a single experiment performed with a neutral $CaCl_2$–$Na^{131}I$ solution and with a Cl_2-dose of 4 ppm it appeared that no ^{131}I is removed from the solution, when first chlorine is added ($pH_{Cl_2} < 4.5$), whereas 67% of the iodine is sorbed when the reversed procedure is applied. In the latter event the pH of the mixture is 6.9 which is not much different from the pH_e to be obtained in the normal procedure. Obviously a low intermediate pH causes a specific chemical reaction which is irreversible.

A comparable conclusion can be made from Fig. VII-12 which forms a cross section of the three dimensional space defined by the axes C/C_0, pH_{Cl_2} and Cl_2 concentration. This cross section is perpendicular to that given in Fig. VII-4. In Fig. VII-12 a maximum adsorption is found for every value of pH_0 at a specific chlorine dose. Zero adsorption can again be obtained with higher amounts of chlorine. This is found when starting at lower pH_0 values (8.0, 8.8). Here the critical pH_{Cl_2} value for that amount of chlorine is probably passed; this is not necessarily always situated at 4.5. In Fig. VII-12 no data are given for the pH_{Cl_2} range between 5.0 and 10.35 (pH_0 between 8.8 and 10.35), where the sorption is a very irregular function of pH_{Cl_2} (see Fig. VII-4). Therefore, it is difficult to predict the corresponding curves in Fig. VII-12 for this pH-range. For $pH_{Cl_2} > 10.35$ (max. in Fig. VII-4) the influence of more chlorine is clear again because addition of chlorine will decrease pH_{Cl_2} and thus also the sorption. Now, it was found that in that high pH-region an addition of carbon followed by chlorine can also be beneficial for the iodine uptake. Here the normal procedure will not lead to a $pH_{Cl_2} < 4.5$. This indicates that the irreversible chemical reaction does not only occur at pH 4.5. From Fig. VII-11 it appears that the reversed procedure is not beneficial at all chlorine concentrations. From this discussion it will at the same time be clear that the data obtained by adding chlorine after carbon will not coincide with those obtained when chlorine is added first.

As it was found in Figs. VII-7–VII-9 that the chlorine concentration has no effect on iodine sorption when the liquid contains acetate ions it is obvious that with such solutions graphs will be obtained which are different from VII-11 and VII-12 for neutral solutions, as a result of the strong buffer capacity of acetate in the pH-region 4-6.

In addition to the experiments with carrier free solutions of ^{131}I, some experiments were also carried out with solutions to which a small amount of I^- (viz. 0.10 ppm) or I_2 (viz. 0.127 ppm) were added. With neutral solutions here also an optimum Cl_2-concentration (-range) is found, but in solutions of high pH chlorine addition is always beneficial up to 8 ppm (see Figs. VII-13 and VII-14). The results given in Fig. VII-13 show that for pH_{Cl_2} approximately 10 a relatively low sorption of iodine is obtained when compared to pH_{Cl_2} values which are lower and higher. Obviously, here a similar relationship between C/C_0 and pH_{Cl_2} is found as is shown to be valid for carrier free solutions in Fig. VII-4.

In the experiments discussed so far a contact time (t_c) of 30 minutes was always maintained. This value has been chosen since it leads to a maximum sorption of the iodine. At longer contact times a small but distinct desorption takes place (compare Fig. VII-15). These effects are not resulting from a slow establishment of sorption equilibria as can be seen from sorption values found at small contact times. For practical application relatively short contact times are attractive.

Desorption experiments

Desorption experiments were performed in order to obtain some insight in the type of the interaction between iodine and carbon. For this purpose carrier-free ^{131}I was sorbed on a number of carbon samples under always identical conditions, viz. $\Delta t_i = 5$ min., $t_c = 30$ min. and a Cl_2-dose of 2 ppm from a $CaCl_2$-$Na^{131}I$ solution containing 4 ppm NH_4^+. The carbon was separated quantitatively from the suspension by filtration, washed with water and then suspended in a desorption solution of chosen composition. The extent of desorption, obtained in these solutions after two different periods of contact, was determined by γ-activity measurement in aliquots of the supernatant. The results are summarized in Table VII-5. From these it follows:

1. A small but distinct desorption takes place in solutions of $CaCl_2$.
2. The presence of chlorine in the solution results in a relatively small increase of the desorption in neutral and alkaline solutions, whereas in acid solutions more ^{131}I is desorbed.
3. A considerable desorption takes place when I^- and/or I_2 are present in the solution. This is not so when a comparable amount of iodate is present in the solution.

The results show that the main part of the ^{131}I is attached to the carbon in such a way, that isotopic exchange between I^-, I_2 and HIO occurs only very slowly. Since it is known tha isotopic exchange reactions between I^-, I_2 and HIO takes place almost instantaneously, and that isotopic exchange between I^-, I_2, HIO on the one hand and IO_3^- on the other hand is extremely slow in neutral and alkaline media (half life of the reaction is 26 years in neutral solutions), it may be concluded that iodine is not bound to carbon in a form of simple physical adsorption.

VII-3-2. PEAT AS SORBENT

In view of literature data an appreciable uptake of ^{131}I by peat is unlikely. The results of some experiments performed with carrier-free solutions of $Na^{131}I$ using the Ca-form of moor peat show indeed that peat is not an effective sorbent for iodine (see Fig. VII-16). However, a considerable improvement of the sorption of radioiodine on peat can be achieved also here, by adding a small amount of chlorine to the mixture. Results of preliminary experiments, which will not be discussed in detail, showed that:

1. the sequence of the addition Cl_2 and peat does not have any influence on the ultimate sorption of iodine;
2. NH_4^+-ions have no effect on the sorption.

In all the experiments discussed below the chlorine has been added one minute before the addition of the peat.

The effect of the pH on the sorption of ^{131}I (starting with carrier-free solutions of $Na^{131}I$) has been investigated using moor peat in Ca- and H-form as sorbent. The results are shown in Figs. VII-17 and VII-18 respectively. Remarkable differences in the sorption of ^{131}I in the pH range 4 to 7 between both forms of the peat are found at larger contact times. The reason for the different behaviour of both forms of peat is obscure, because apart from the cation occupation, the materials are identical. At low pH the peats behave more identically probably because then the Ca-peat has replaced its calcium almost completely by protons. From the point of view of application to drinking water purification the moderate sorption in the near-neutral pH range seems to have more practical advantages than the high sorption at low pH though much longer contact times are necessary.

Less ^{131}I is removed from solutions which contain an additional amount of iodine carrier either added as I_2 or I^-. Even a certain desorption is found to occur at pH values below 4 and after prolonged contact times. This effect is already found with iodide carrier after 25 hours but with iodine carrier only after 50 hrs.

The effect of the Cl_2-concentration was investigated with carrier-free solutions of $Na^{131}I$

of high and low pH using the Ca-form of the peat as sorbent. The results (see Table VII-6) indicate that in acid solutions an increase of iodine sorption occurs with increasing Cl_2-concentration only below 5 ppm of Cl_2. In alkaline solutions an improved sorption is also observed above Cl_2-doses of 5 ppm.

From the experiments described so far it is obvious that an addition of chlorine is necessary in order to achieve a reasonable sorption of ^{131}I from solutions of $Na^{131}I$. Since the iodide is oxidized to iodate by chlorine with a high rate in acid media and because a maximum sorption of ^{131}I occurs under these circumstances, it might be concluded that the iodine is sorbed in the form of the iodate. In view of this some sorption experiments were carried out with a 0.002 molar solution of iodate, labeled with $^{131}IO_3^-$. In these experiments no chlorine was added to the mixture.

As shown from the results (see Table VII-7) iodate is indeed sorbed reasonably well on peat from acid solutions. The removal of the iodate from the solution was determined in these experiments by γ-counting as well as by iodometric titration of the supernatant solution. The percentage sorption obtained by the latter method were always found slightly higher than those obtained from the activity measurements. These discrepancies probably may be attributed to the consumption of some iodate for the oxidation of dissolved humic acids by IO_3^- after the acidification of the solution with 0.3 N H_2SO_4, which is required for the iodometric titration of the iodate.

Finally some desorption experiments were carried out. For this purpose ^{131}I was sorbed on a number of peat samples (in H-form) from a carrier-free solution of $Na^{131}I$ of pH 2.0 using a dose of chlorine of 6 ppm. These peat samples were brought into contact with solutions of various compositions. The desorption brought about was followed by γ-counting of samples of the supernatant solution.

The results of these experiments are summarized in Table VII-8 and are shown further in Fig. VII-21.

Apparently a significant desorption by water takes place only in alkaline media which is in accordance with data in Fig. VII-18. However, this desorption certainly may not be attributed exclusively to desorption as a significant amount of peat dissolves at pH 11.

The results in Fig. VII-21 show the effect of the presence of iodide, iodine and iodate in the treating solution. It appears that the desorption rates obtained in solutions of I_2 and I^- are almost the same. However, the initial desorption in a weakly alkaline solution is considerably faster than that in acid solutions. This fast desorption is probably mainly the result of a fast peptisation of humic acids, which takes place to a considerable extent because the peat is in H-form and the alkaline solution in which the peat is suspended does not contain any Ca^{2+} or other divalent ions which reduce the solubility of the humic acids.

The various data are not in contradiction with the assumption that iodine is sorbed to peat in the form of iodate. The isotopic exchange with iodide and iodine is slow at high pH (halflife 26 years) and considerably faster (halflife 280 hrs) in acid media. Desorption rates found for iodine and iodide solutions at pH 3.1 show half-life values of approximately 300 hrs. The slow desorption found for iodate solutions may be attributed to the slow desorption rates of iodate (compare Table VII-7).

VII-4. **Discussion of the results**

VII-4-1. ACTIVATED CHARCOAL AS SORBENT

In the absence of chlorine an appreciable sorption of ^{131}I from carrier-free iodide solutions is possible only at pH-values below 7. The sorption process is slow and seems to be connected with some change in the chemical form of the iodide, presumably an oxidation under the influence of air and light. A strongly decreased sorption, but a comparable influence of pH, is obtained in the presence of I_2 as carrier. With I^- as carrier the results are very similar as compared with carrier-free solutions. In the presence of chlorine (2 to 8 ppm) an appreciably better and faster removal of ^{131}I can be obtained. However, a number of factors are important, i.e.

1. The presence of NH_4^+ and acetate-ions as activators. These ions can improve the sorption considerably.
2. The sequence of the addition of chlorine and carbon. When chlorine is added first, the time interval between the addition of chlorine and charcoal can be important. Some irreversible reactions between the various components seem to take place.
3. The pH of the medium. In the absence of NH_4^+ and acetate a higher sorption takes place at increasing pH. In the presence of NH_4^+ and acetate the sorption of iodine is maximum between pH_{Cl_2} 4.5 and 8.
   In no case any iodine is sorbed when pH_{Cl_2} is lower than 4.5.
4. The chlorine concentration. This effect is strongly related to the complex dependency of the sorption from pH_{Cl_2} (Figs. VII-4 and VII-5). For every pH_0 of the starting solution a maximum sorption is found for a specific chlorine dose. High amounts of chlorine can lead to zero iodine sorption when starting at relatively low pH_0 values. This can be attributed to a decrease of pH_{Cl_2} below approximately 4.5. The presence of small amounts of carrier has little influence. In the presence of acetate the solution is buffered so that no chlorine concentration effect is found.
5. Time of contact between solution and carbon. Optimum results are obtained at a contact time of about 30 minutes.

The results indicate that a reasonable removal of ^{131}I can be achieved with the charcoal sample investigated, provided the carbon is present in excess, chlorine is added to the solution and the conditions are scrupulously controlled. The sorption process seems to be rather complicated and involves various reactions of iodine compounds, carbon and chlorine. The iodine is probably bound as a result of a chemical reaction of some intermediate product with the carbon. In view of the wide variation in the properties of the various commercially available carbons considerable differences may exist between the various carbon species in their ability to sorb iodine and/or iodine compounds. The results obtained here will therefore not be representative for other carbon species. An extensive investigation of the properties of every new material with respect to the sorption of iodine will therefore be necessary.

VII-4-2. PEAT AS SORBENT

In the absence of chlorine some sorption of ^{131}I from carrier-free iodide solutions only takes place at $pH < 3$.

The sorption of ^{131}I on peat can be improved considerably by adding a small amount of chlorine (viz. about 5 ppm) to the solution, although even then a long contact time is required (viz. 10-20 hrs). Under these circumstances an appreciable sorption of ^{131}I only takes place at low pH, viz. below pH 4. With the Ca-form of the peat a considerable part of ^{131}I can also be removed from neutral solutions, but then much longer contact times are required, viz. ~50 hrs. With the H-form of the peat a much smaller sorption of ^{131}I is obtained in neutral solutions.

In contrast to the results obtained with carbon the presence of NH_4^+, the sequence of the addition of chlorine and peat and the time interval between the addition of chlorine and peat appeared not to be important. Some indications are found that in the presence of chlorine iodine is bound to peat in the form of iodate.

Since the peat in fact removes ^{131}I only effectively from solutions of low pH, it is evident that it cannot be considered as an attractive sorbent in the removal of radioiodine from drinking water.

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TABLE VII-1

Sorption of OH^- *and* H^+ *by activated carbon as determined by titration of the material in water and in a* $CaCl_2$*-solution of* 100 meq/l

pH_e	Titration in water		Titration in a 100 meq/l $CaCl_2$-solution	
	OH^- sorbed	H^+ sorbed	OH^- sorbed	H^+ sorbed
	meq/g		meq/g	
3.0	—	1.95	—	1.88
4.0	—	1.69	—	1.60
5.0	—	1.30	—	1.10
6.0	—	0.78	—	0.38
7.0	—	0.36	0.21	—
8.0	0.06	—	0.56	—
9.0	0.32	—	0.85	—
10.0	0.54	—	1.17	—
11.0	0.75	—		

TABLE VII-2

Removal of ^{131}I *in % from solutions of* $Na^{131}I$ *of increasing age* (1000 ppm *carbon, contact time* 30 min)

Age of the solution	5 hrs	10 hrs	20 hrs	50 hrs
pH of the solution 8.5	4.1	3.5	5.2	6.0
pH of the solution 2.9	35	43.5	51.0	65.0

TABLE VII-3

Percentage of I_2 *hydrolized in a* 10^{-6} *molar* I_2*-solution*

pH	2.4	4	5	6	7
% hydrolized	1.5	8	26	60	90

TABLE VII-4

Sorption of $^{131}IO_3^-$ *from almost carrier-free solutions of* $^{131}IO_3^-$ *by activated carbon at various* pH*-values* (1000 ppm *carbon, contact-time* 30 min.)

pH_e	1.9	2.75	4.9	6.8	10.9
% ^{131}I removed	15	6	2	0.6	0

TABLE VII-5

Desorption of ^{131}I *from carbon (spec. act.* 4 μCi/g) *by solutions of various composition (basic composition of the desorption solution:* 5 meq/l $CaCl_2 + 4$ ppm NH_4^+)

Additional compound present in the desorption solution		Desorption after 30 min		Desorption after 19 hrs	
	pH_0	%	pH_e	%	pH_e
—	7.2	3.5	7.7	8.2	7.1
2 ppm Cl_2	4.8	5.1	6.8	10.1	7.0
2 ppm Cl_2	11.1	6.6	10.7	11.9	10.4
2 ppm Cl_2	2.0	10.1	2.1	18.5	2.2
1 ppm I^-	7.0	17.4	7.0	28.6	7.1
1 ppm iodine as IO_3^-	7.0	4.8	7.1	12.9	7.1
0.1 ppm I_2	7.0	6.4	7.3	17.1	7.0
0.5 ppm I_2	7.0	7.9	7.0	19.8	7.0
0.1 ppm I_2	7.7	27	7.0	33.4	7.0
1.0 ppm I_2	11.8	18.2	11.8	26.8	11.8
1 ppm $I_2 + 2$ ppm Cl_2	4.7	20.0	6.7	38.4	7.2

TABLE VII-6

Influence of the Cl_2*-concentration on the sorption of* ^{131}I *from a carrier free solution of* $Na^{131}I$ (2000 ppm *moor peat in* Ca-*form*)

Dose of Cl_2 (ppm)	$pH_e = 3$				$pH_e = 9.5$			
	0	1	5	10	0	1	5	10
Time of contact 10 hrs	12%	64%	84%	84%	6%	11%	13%	17%
Time of contact 50 hrs	17%	67%	84%	84%	6%	10%	12%	15%

TABLE VII-7

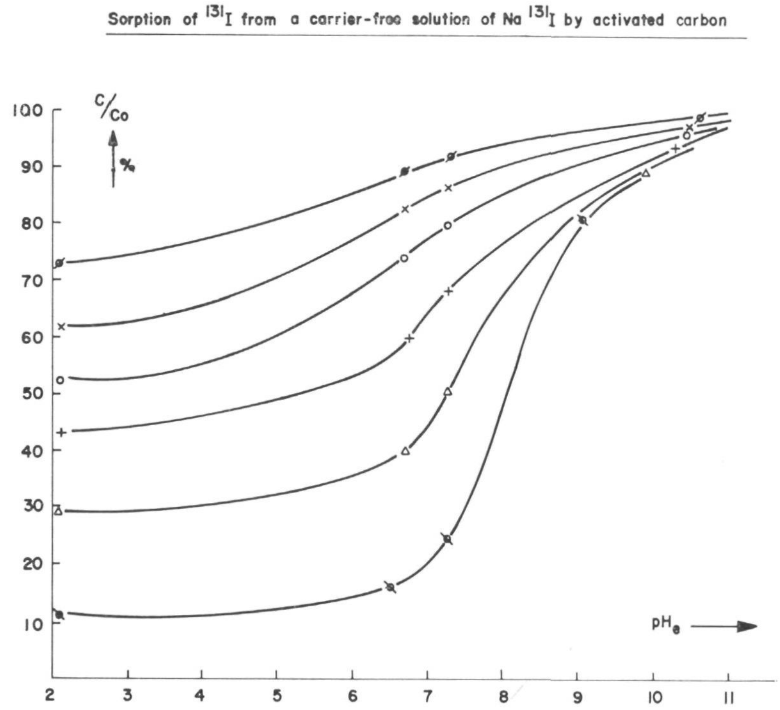
The sorption of iodate by moor peat in Ca-*form from a* 0.002 *molar solution of* IO_3^-

Contact time hrs	Peat-concentration (ppm)	pH_e	Percentage of the iodate sorbed	
			From γ-activity measurement	From iodometric titration
0.26	10,000	1.8	16.3	16.7
2.40	10,000	1.9	29.2	33.0
66	10,000	2.0	75.4	77.9
66	5,000	1.9	49.2	51.6
66	10,000	3.8	42.4	49.3
66	10,000	7.5	4.7	10.4

TABLE VII-8

Desorption of ^{131}I *from* H-*peat by water and dilute solutions of* NaOH *and* HCl

% ^{131}I sorbed	Solution used in the desorption	% desorption relative to the original ^{131}I-content of the peat					
		Contact time (hrs)	%	pH_e	Contact time (hrs)	%	pH_e
88	water neutral	4.5	4.15	5.0	24.5	6.6	5.0
87.8	water pH 2.2	4.5	3.10	2.5	24.2	3.8	2.7
88.9	water pH 11.5	1.16	42.4	11	22.0	50	11



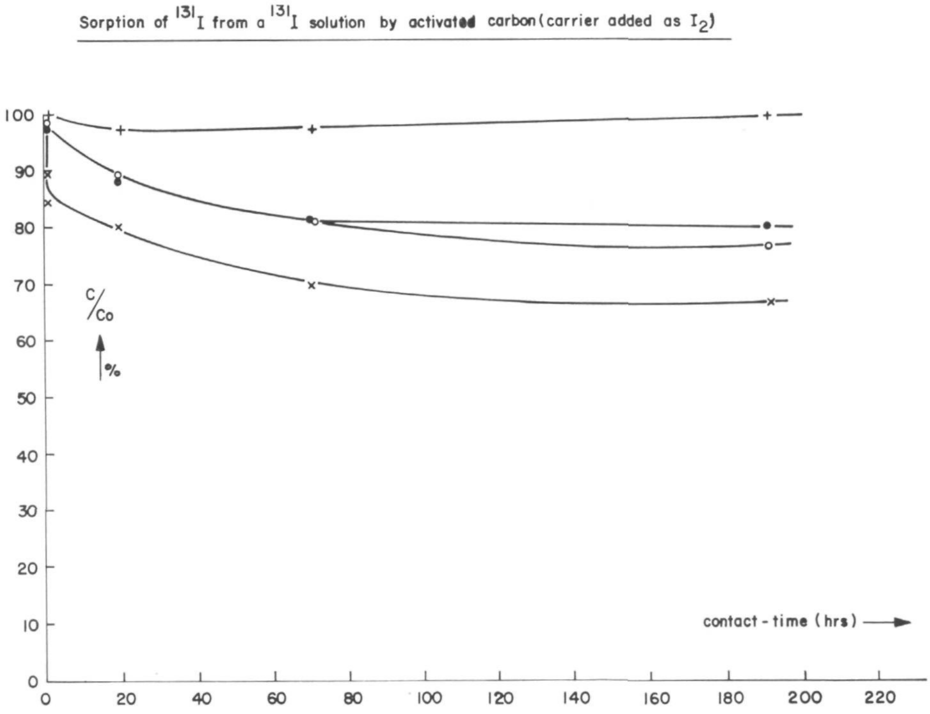
Sorption of ^{131}I from a carrier-free solution of Na ^{131}I by activated carbon

Fig. VII-1

Carbon concentration: 1000 ppm

Starting solution: 5 meq $CaCl_2$/l; 5.10^{-3} μCi carrier free ^{131}I/ml (as NaI)

Contact time: ø 2 hrs × 5 hrs ○ 10 hrs + 20 hrs △ 50 hrs ⊘ 150 hrs



Sorption of ^{131}I from a ^{131}I solution by activated carbon (carrier added as I_2)

Fig. VII-2

Carbon concentration: 1000 ppm

Starting solution: 5.10^{-3} μCi ^{131}I/ml; 0.13 ppm I_2; 4 ppm NH_4^+; 5 meq $CaCl_2$/l

+ pH_0 11.7; pH_e 11.6 ○ pH_0 7.5; pH_e 7.0 ● pH_0 3.0; pH_e 4.1 × pH_0 2.2; pH_e 2.4

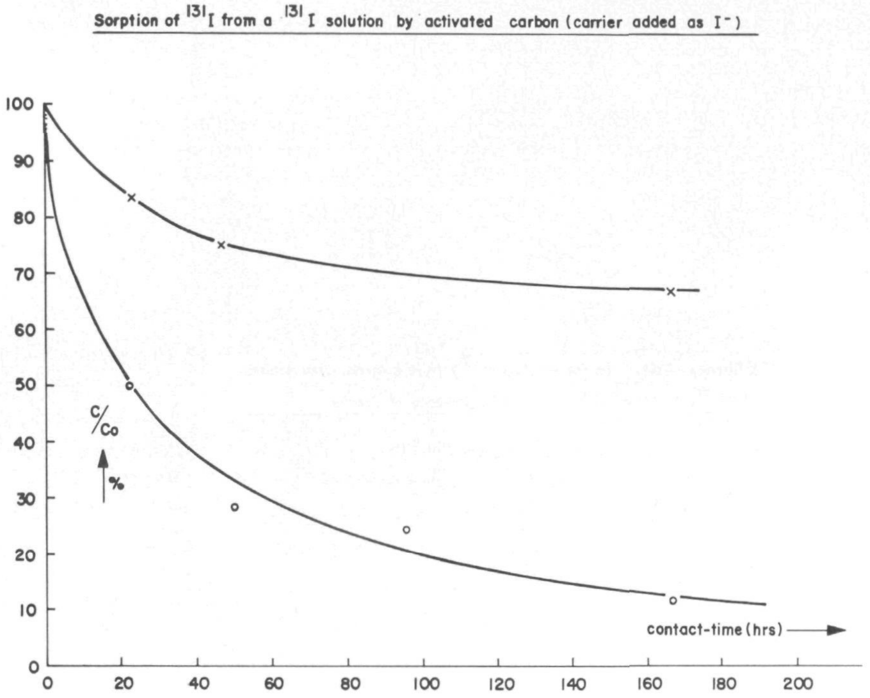


Fig. VII-3

Carbon concentration: 1000 ppm — Starting solution: 5.10^{-3} μCi ^{131}I/ml; 0.1 ppm I^-; 4 ppm NH_4^+; 5 meq $CaCl_2$/l × pH_0 7.5; pH_e 7.0 ○ pH_0 2.3; pH_e 4.1

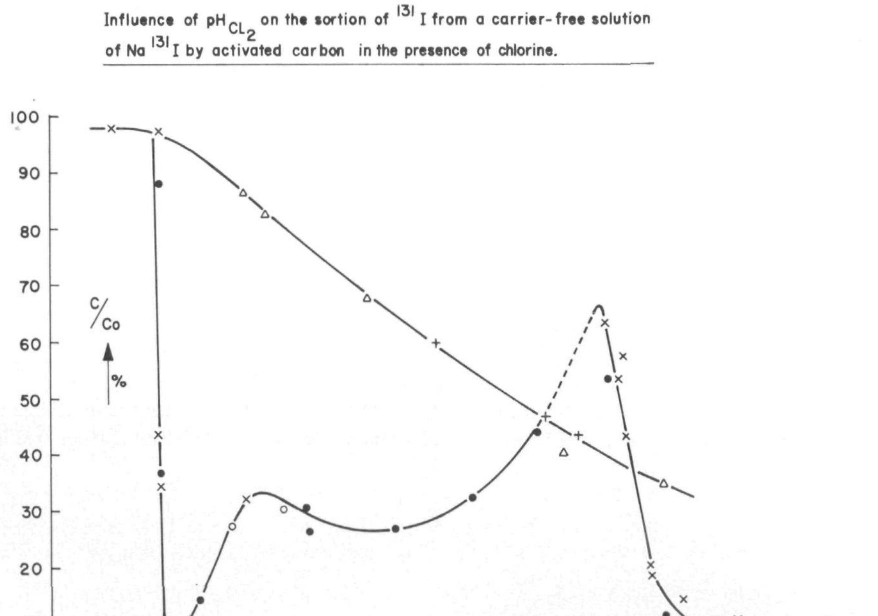


Fig. VII-4

Carbon concentration: 1000 ppm — Chlorine concentration: 2.2 ppm

Δt_i: 5 min — Contact time: 30 min

Starting solution: △ + 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)

● ○ × 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI); 4 ppm NH_4^+

Experiments were performed at various dates.

Influence of pH_{Cl_2} on the sorption of ^{131}I from a carrier-free solution of $Na^{131}I$ by activated carbon in the presence of chlorine.

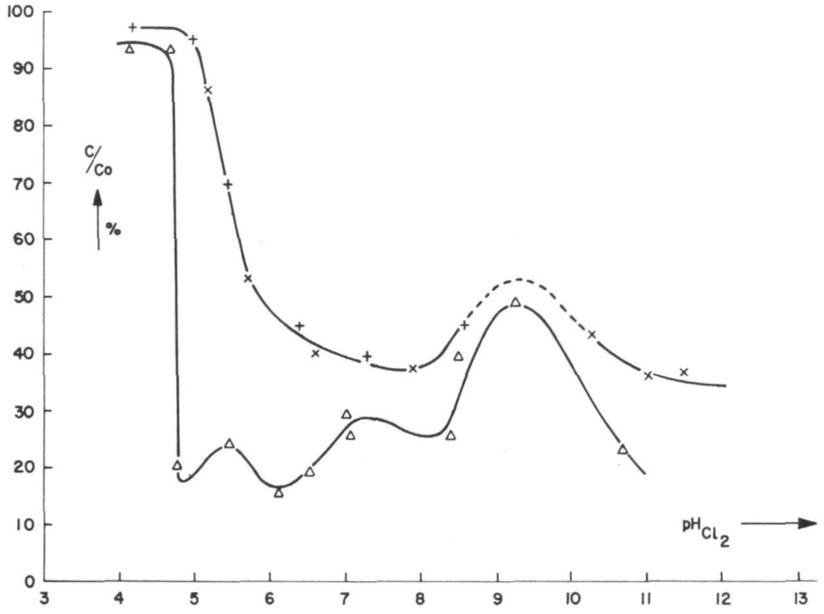


Fig. VII-5

Carbon concentration: 1000 ppm
Chlorine concentration: 2.2 ppm
$\triangle t_i$: 5 min
Contact time: 30 min
Starting solution: + × 5 meq $CaCl_2$/l; 0.5 meq $Ca(CH_3COO)_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)
△ 5 meq $CaCl_2$/l; 0.5 meq $Ca(CH_3COO)_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI); 4 ppm NH_4^+.

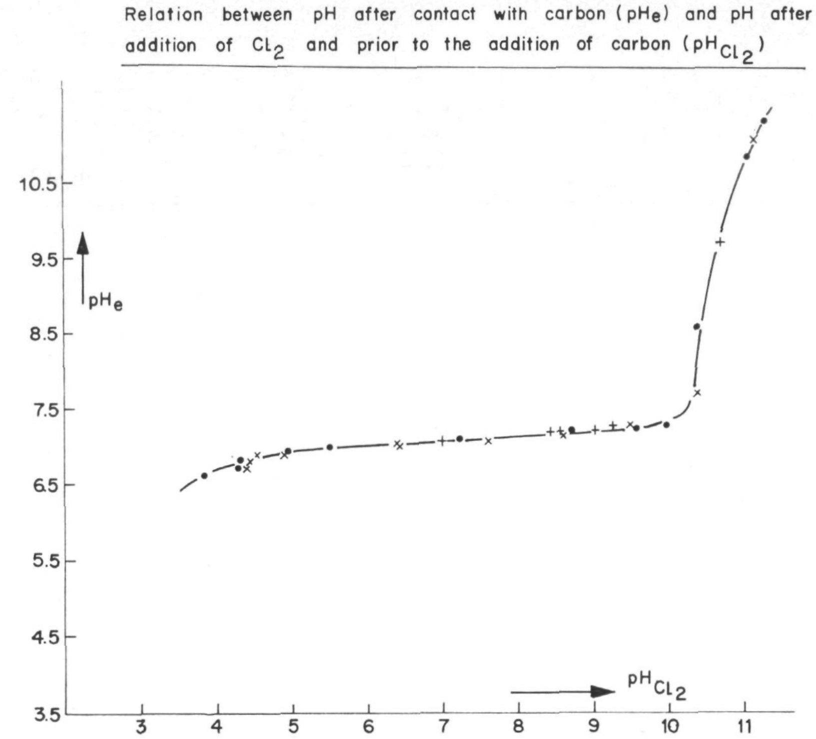


Fig. VII-6

Carbon concentration: 1000 ppm — $\triangle t_i$: 5 min; contact time: 30 min

● solution containing 5 meq $CaCl_2$/l

× solution containing 5 meq $CaCl_2$/l and 4 ppm NH_4^+

\+ solution containing 5 meq $CaCl_2$/l, 0.5 meq $Ca(CH_3COO)_2$/l.

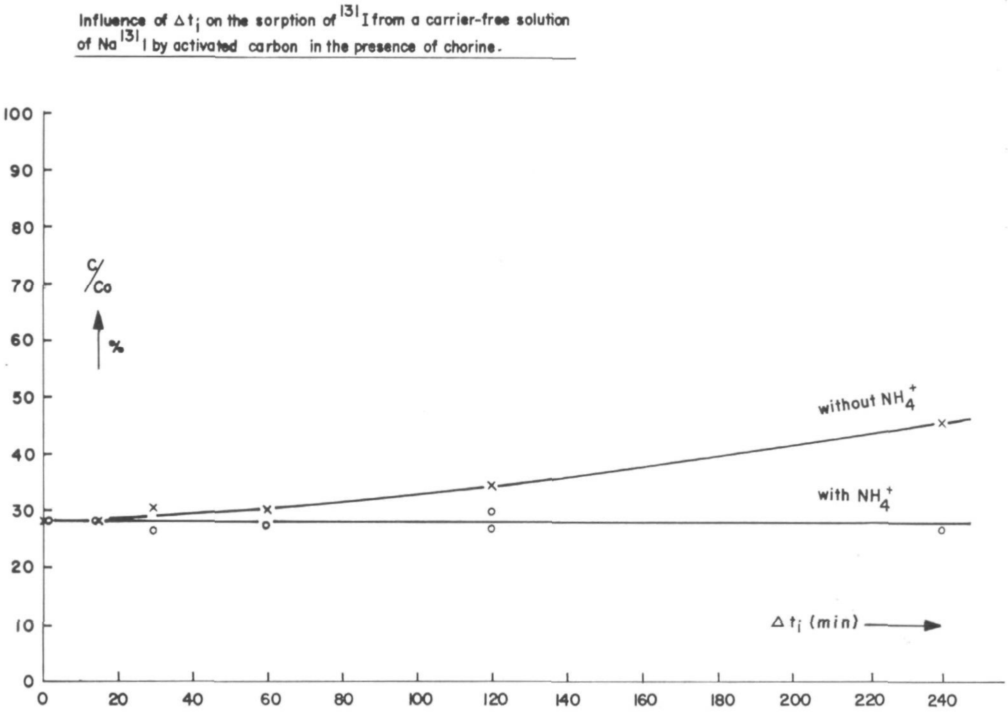


Fig. VII-7

Carbon concentration: 1000 ppm — Contact time: 30 min — Chlorine concentration: 1 ppm
Starting solution: 5 meq $Ca(CH_3COO)_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI), pH_0 6.5 - 7.0
× without NH_4^+ ○ with 4 ppm NH_4^+

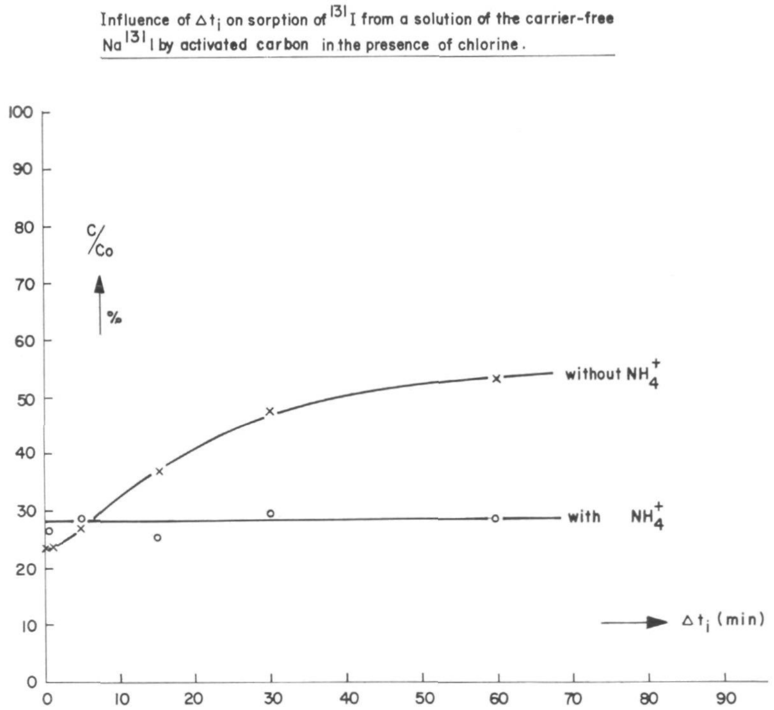


Fig. VII-8

Carbon concentration: 1000 ppm — Contact time: 30 min — Chlorine concentration: 6 ppm
Starting solution: 5 meq $Ca(CH_3COO)_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI), pH_0 6.5 - 7.0
× without NH_4^+ ○ with 4 ppm NH_4^+

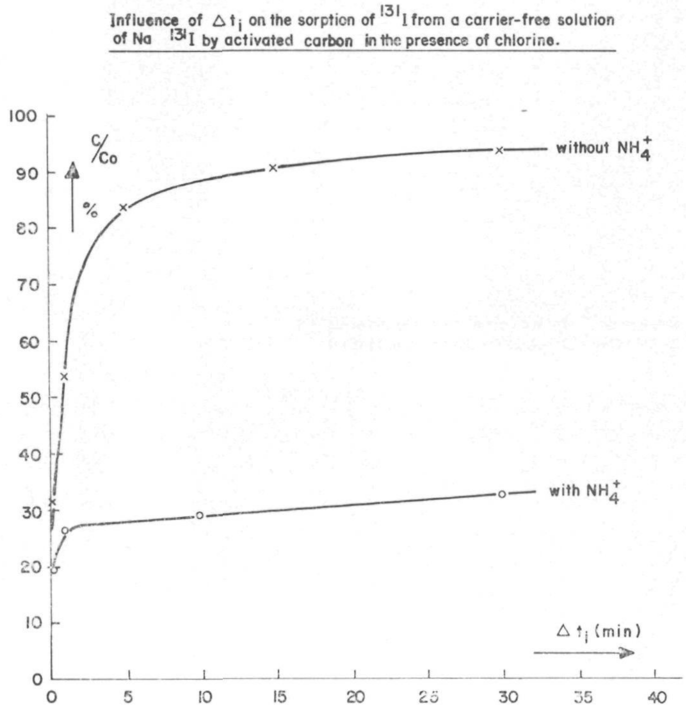


Fig. VII-9

Carbon concentration: 1000 ppm — Contact time: 30 min — Chlorine concentration: 24 ppm
Starting solution: 5 meq $Ca(CH_3COO)_2/l$; 5.10^{-3} μCi $^{131}I/ml$ (carrier free as NaI), pH_0 6.5 - 7.0
× without NH_4^+ ○ with 4 ppm NH_4^+

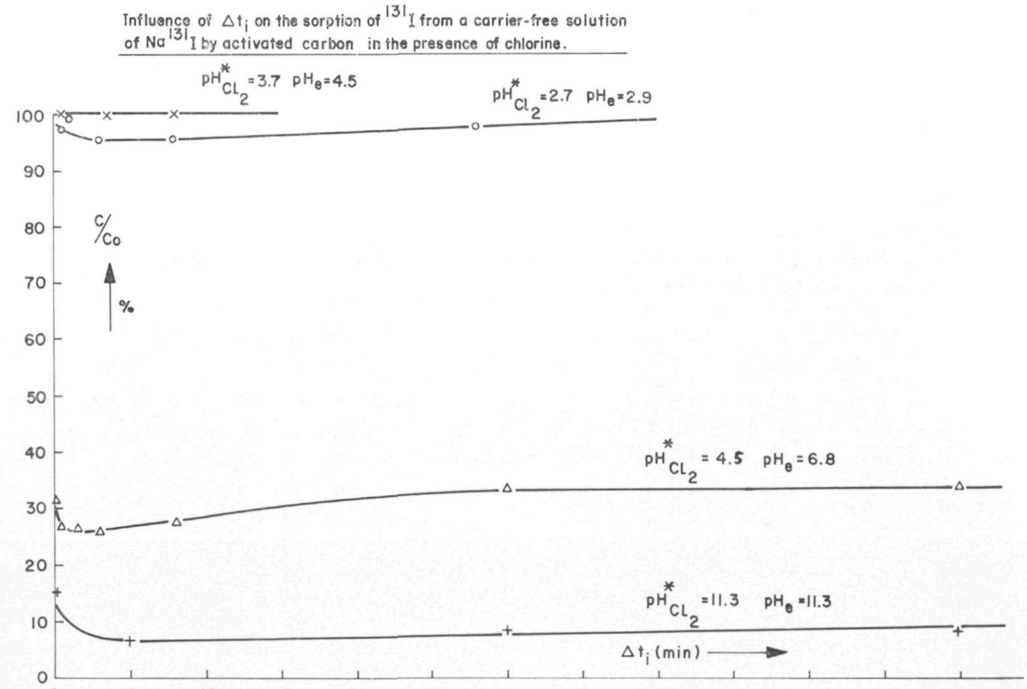


Fig. VII-10

Carbon concentration: 1000 ppm — Contact time: 30 min — Chlorine concentration: 1 ppm
Starting solution: 5 meq $CaCl_2/l$; 4 ppm NH_4^+; 5.10^{-3} μCi $^{131}I/ml$ (carrier free as NaI); various pH_0 values.

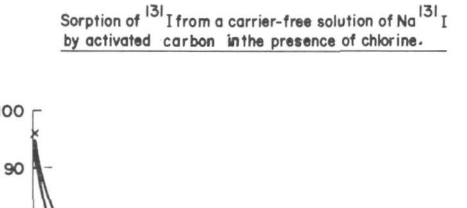


Fig. VII-11

Carbon concentration: 1000 ppm

Contact time: 30 min

Starting solution: 5 meq $CaCl_2$/l; 4 ppm NH_4^+; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI), pH_0 10.6

- ○ carbon added 5 min after chlorine
- × chlorine added 1 min after carbon.

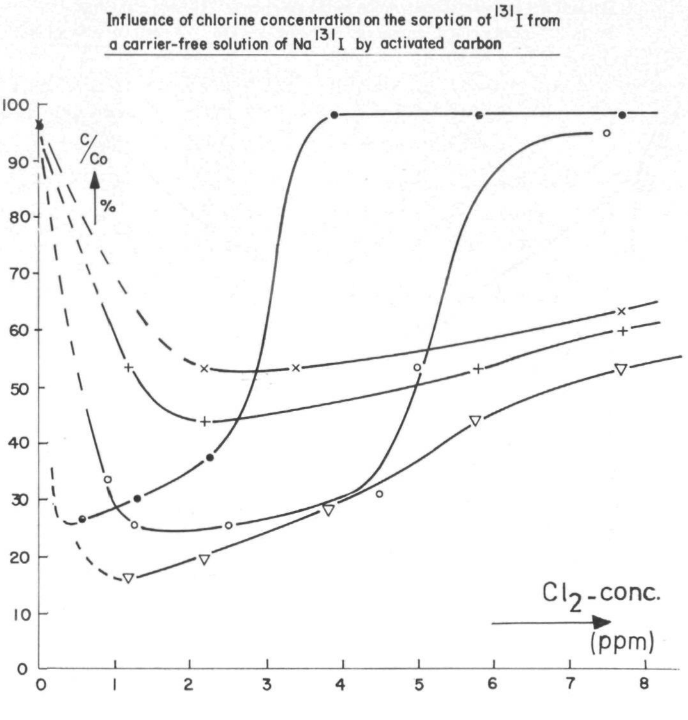


Fig. VII-12

Carbon concentration: 1000 ppm

Contact time: 30 min

$\triangle t_l$: 5 min

Starting solution: 5 meq $CaCl_2$/l; 4 ppm NH_4^+; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)

- ● pH_0 8.0 ; pH_e 6.8 - 6.6; $pH_{Cl_2}^*$ 4.5 - 3.9
- ○ pH_0 8.8 ; pH_e 6.9 - 6.5; $pH_{Cl_2}^*$ 5.0 - 3.7
- × pH_0 10.35; pH_e 8.1 - 7.5; $pH_{Cl_2}^*$ 10.35 - 10.15
- \+ pH_0 10.7 ; pH_e 9.4 - 7.7; $pH_{Cl_2}^*$ 10.65 - 10.25
- ▽ pH_0 10.95; pH_e 10.7; $pH_{Cl_2}^*$ 10.9

Influence of chlorine concentration on the sorption of ^{131}I from a solution of $Na^{131}I$ containing I^--carrier by activated carbon at various pH-values.

Fig. VII-13

Carbon concentration: 1000 ppm

Contact time: 30 min

$\triangle t_t$: 10 min

Starting solution: 5 meq $CaCl_2$/l; 4 ppm NH_4^+; 5.10^{-3} μCi ^{131}I/ml; 0.1 ppm I^-

- × pH_0 11.5; pH_e 11.5 - 11.4; $pH_{Cl_2}^*$ 11.5 - 11.4
- △ pH_0 10.25; pH_e 7.5 - 7.4; $pH_{Cl_2}^*$ 10.15 - 10.0
- \+ pH_0 9.5 ; pH_e 7.2 - 6.8; $pH_{Cl_2}^*$ 9.0 - 4.5
- ● pH_0 7.0 ; pH_e 6.8 - 6.6; $pH_{Cl_2}^*$ 4.5 - 3.8

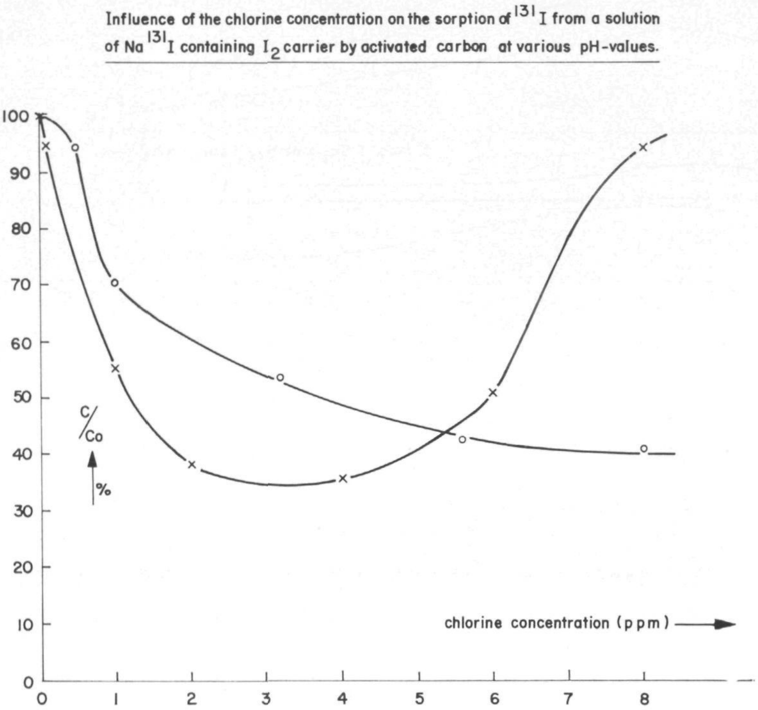

Influence of the chlorine concentration on the sorption of ^{131}I from a solution of $Na^{131}I$ containing I_2 carrier by activated carbon at various pH-values.

Fig. VII-14

Carbon concentration: 1000 ppm
Contact time: 30 min
$\triangle t_i$: 10 min
Starting solution: 5 meq $CaCl_2$/l; 4 ppm NH_4^+; 5.10^{-3} μCi ^{131}I/ml; 0.125 ppm I_2
× pH_0 8.7; pH_e 7.1 - 6.8; $pH_{Cl_2}^*$ 7.5 - 4.5
○ pH_0 11.0; pH_e 10.7 - 10.6; $pH_{Cl_2}^*$ 11.0 - 10.95

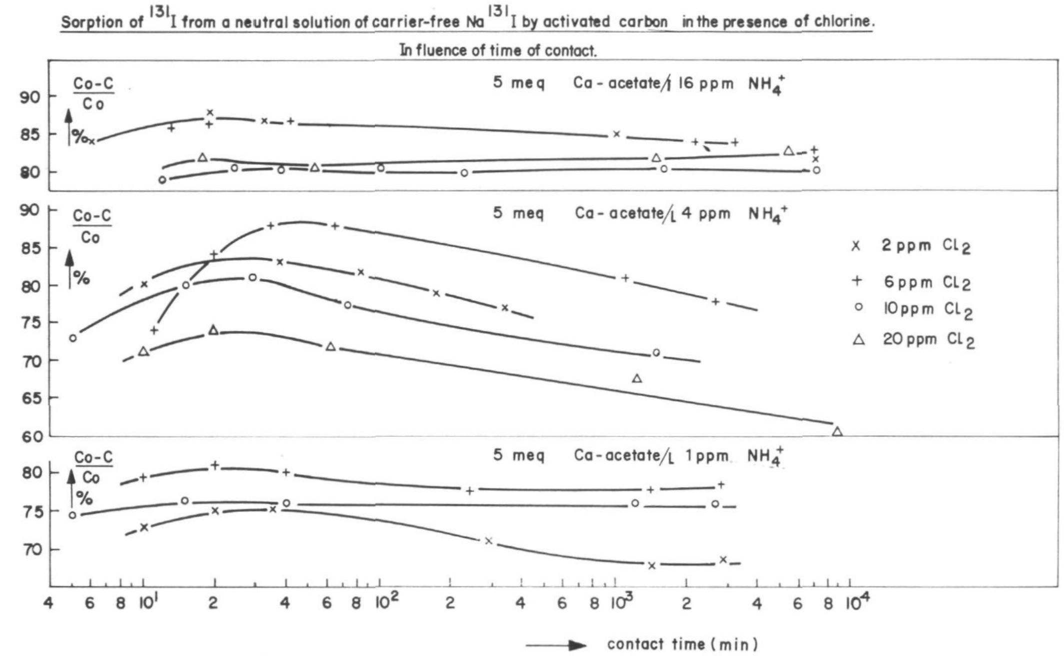


Fig. VII-15

Carbon concentration: 1000 ppm — Δt_i: 10 - 20 sec

Starting solution: 5 meq Ca(CH$_3$COO)$_2$/l; various concentrations NH_4^+; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI); pH$_e$ 5 - 6

Chlorine concentration: × 2 ppm + 6 ppm ○ 10 ppm △ 20 ppm

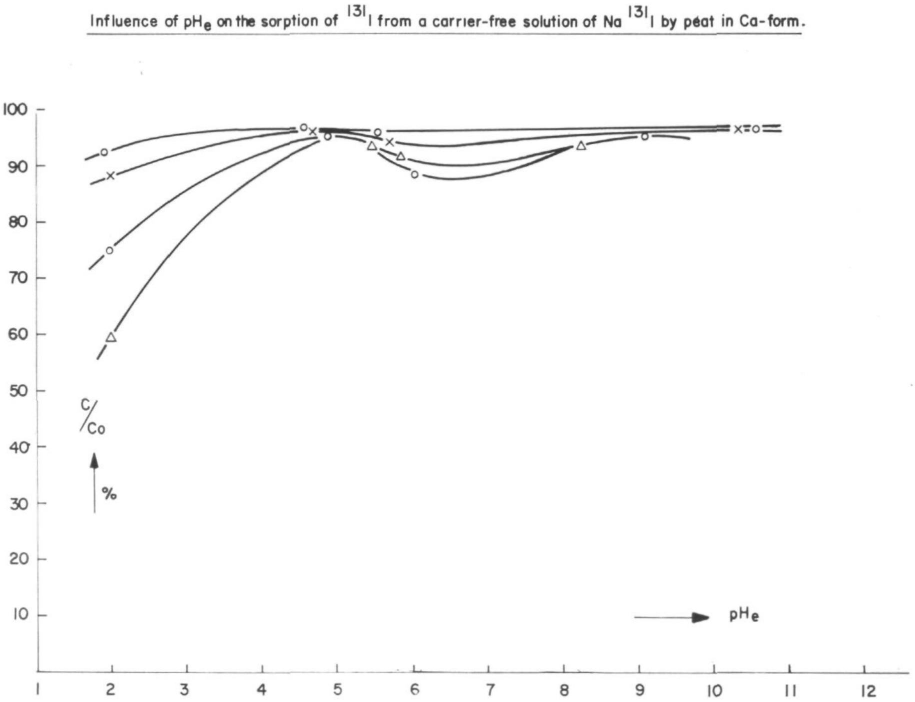


Fig. VII-16

Peat concentration: 2000 ppm moor peat in Ca-form

Starting solution: 5 meq CaCl$_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)

Contact time: ○ 2 hrs × 5 hrs ● 20 hrs △ 45 hrs

Influence of pH_e on the sorption of ^{131}I from a carrier-free solution of $Na^{131}I$ by Ca-peat in the presence of chlorine at various times of contact.

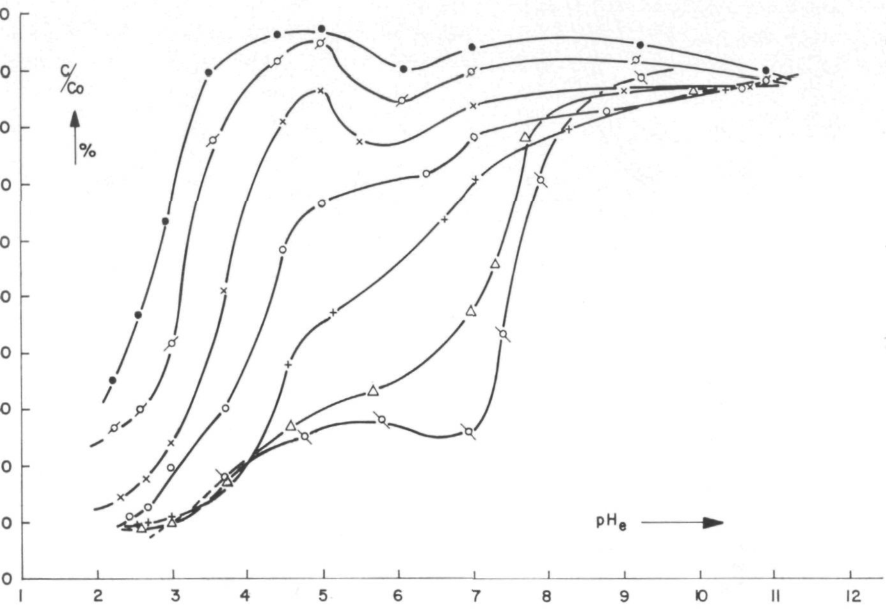


Fig. VII-17

Peat concentration: 2000 ppm moor peat in Ca-form

Starting solution: 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)

Chlorine concentration: 6 ppm

$\triangle t_i$: 1 min

Contact time:		
	●	0.5 hr
	⌀	2 hrs
	×	5 hrs
	○	10 hrs
	+	20 hrs
	△	50 hrs
	⍉	120 hrs

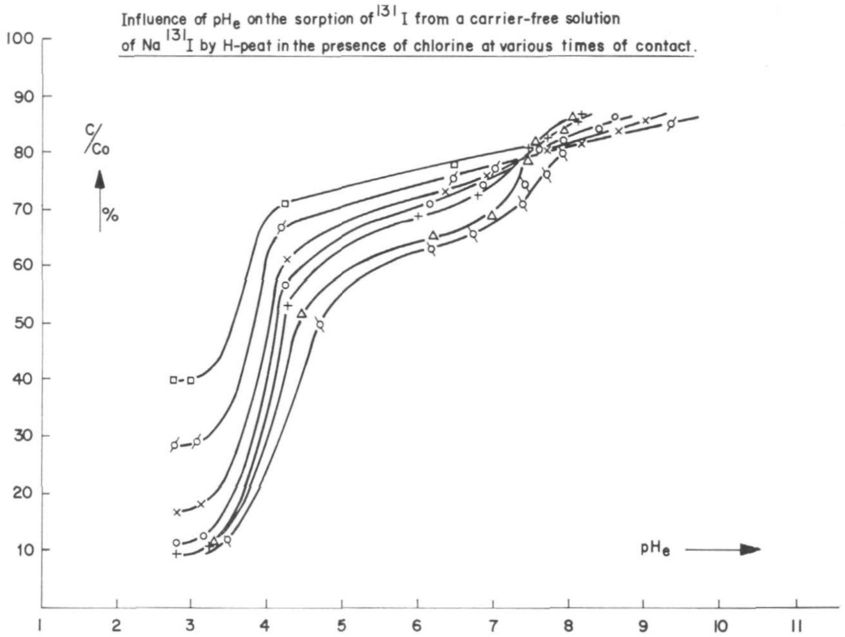


Fig. VII-18

Peat concentration: 2000 ppm moor peat in H-form

Starting solution: 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml (carrier free as NaI)

Chlorine concentration: 6 ppm — Δt_i: 1 min

Contact time:							
□	0.5 hr	ø	2 hrs	×	5 hrs	○	10 hrs
+	20 hrs	△	50 hrs	ϙ	120 hrs		

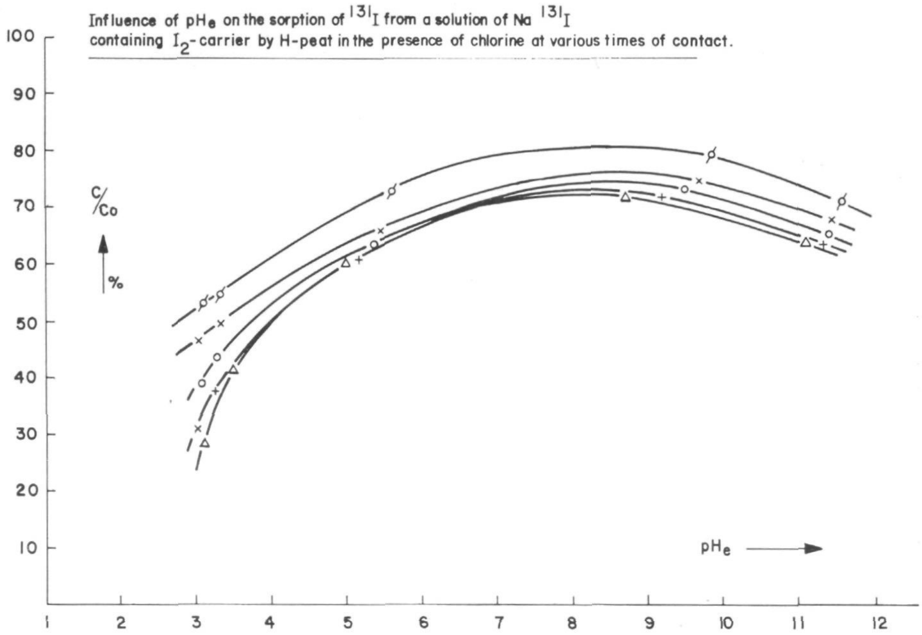


Fig. VII-19

Peat concentration: 2000 ppm moor peat in H-form

Starting solution: 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml; 0.1 ppm I_2 — Chlorine concentration: 4.8 ppm

Δt_i: 1 min

Contact time: ø 2 hrs × 5 hrs ○ 10 hrs + 20 hrs △ 50 hrs

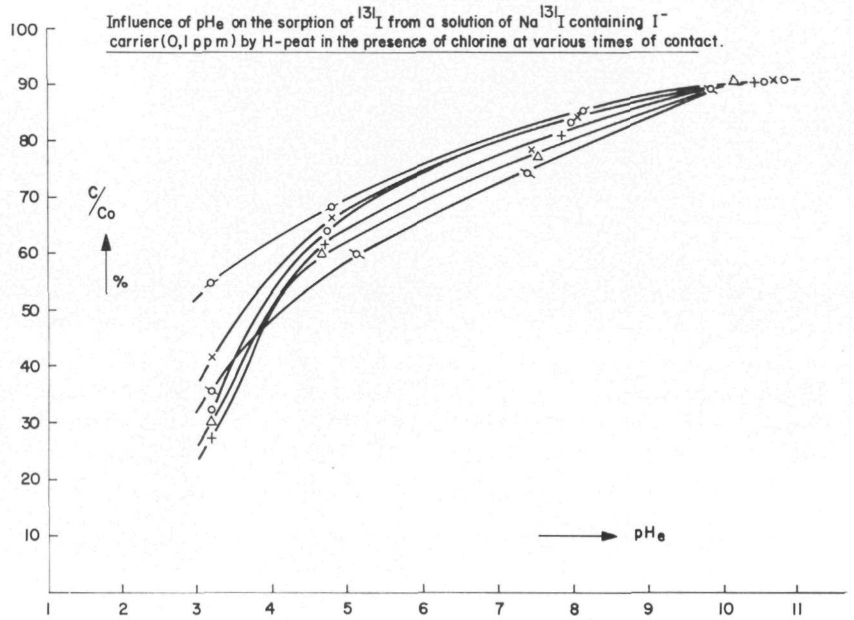


Fig. VII-20

Peat concentration: 2000 ppm moor peat in H-form

Starting solution: 5 meq $CaCl_2$/l; 5.10^{-3} μCi ^{131}I/ml; 0.1 ppm I^- — Chlorine concentration: 4.8 ppm

Δt_i: 1 min

Contact time: ø 2 hrs × 5 hrs ○ 10 hrs + 20 hrs △ 50 hrs ϙ 120 hrs

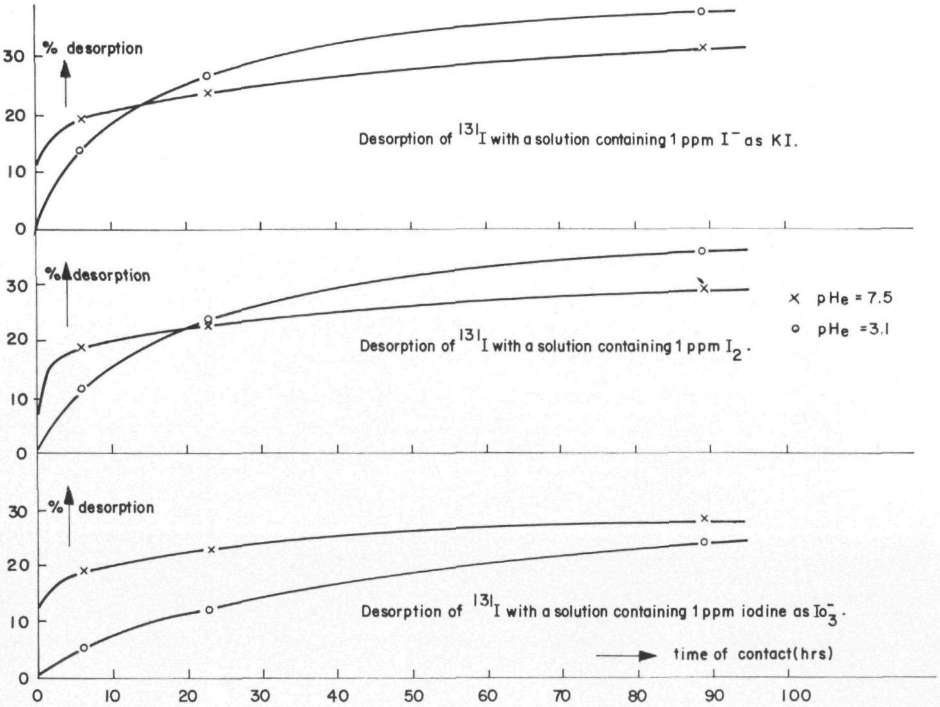


Fig. VII-21 — Percentage desorption achieved at pH_e 3.1 and 7.5 with solutions containing 1 ppm iodine as I^-, I_2 and IO_3^-. ^{131}I was sorbed to the peat beforehand by contacting it (i.e. moor peat in H-form) with a carrier free solution of ^{131}I (5.10^{-3} μCi/ml) at pH 2.0 in the presence of 6 ppm Cl_2.

VIII. THE SORPTION OF RADIONUCLIDES BY CLAY AND RIVERSILT

VIII-1. **Introduction**

It appears from data reported in the literature (see Chapter II-2-3) that soils which contain illite and/or vermiculite as main clay-minerals show an increased sorption of cesium-ions. This is not found for synthetic and natural organic ion exchangers, because these materials show a preference for ions of higher valence. As a consequence illitic clays have been applied already since many years in the treatment of radioactive wastes for the removal of ^{137}Cs. Moreover the application of clays has been suggested for the decontamination of drinking water in case of an emergency situation.

Since illite is the main clay mineral present in most of the Dutch clay-soils (^{1}) it is likely that a rather efficient removal of radiocesium can be achieved with these soils. Therefore some clay samples of Dutch origin have been investigated in this respect. Clay samples have been collected from different locations in the country. Distinction has been made between natural clays of two different origins, i.e. river clay and marine clay. A distinct difference in the efficiency of the sorption of ^{137}Cs may exist between these two types of soils, merely by the fact that the marine clay soil has been in prolonged contact with water with an appreciable potassium content (^{2}). Data about the clay samples are summarized in Table VIII-1.

In addition to the sorption of ^{137}Cs, the sorption of some other radionuclides has also been investigated, viz. of ^{90}Sr, ^{90}Y and of ^{60}Co.

Furthermore some experiments were carried out with silt samples from the river Rhine. Only a few of such experiments have been carried out, since extensive investigations concerning the sorption of radionuclides on this material were made already elsewhere (^{3,4}). The silt samples were obtained at the filtering and pumping station of the drinking water production company of the Hague at Bergambacht. Here river water passes sedimentation basins and filters before it is pumped via a pipeline to the infiltration areas north of the Hague. In the two stages of the pretreatment at Bergambacht approximately 50% of the suspended matter is removed from the water. The silt sample used in this investigation was collected from the filters. It was dried and homogenized (by grinding in a mortar) in the laboratory.

VIII-2. **Experimental**

The sorption of the various radionuclides was determined by means of slurry experiments. The experiments were performed in the same way as described for peat in the preceding Chapters. The clay was separated from the mixture by filtration over a millipore filter S & S 1119. Other details concerning the performance of the experiments will be given in the next paragraph.

VIII-3. **Results**

VIII-3-1. EXPERIMENTS WITH CLAY SAMPLES

Exchange Capacity

The exchange capacity of a clay sample was determined by shaking 1 g of the clay with 50 ml of a 0.02 molar solution of traced (^{137}Cs)$CsNO_3$ of pH 3.3 and also with 50 ml of a 0.012 molar solution of traced (^{85}Sr) $Sr(CH_3COO)_2$ of pH 7.8. The mixtures were shaken during approximately 15 hrs. The exchange capacity has been calculated from the loss of activity from the solution. The results are summarized in Table VIII-2 together with the results of some other analyses. The determination of the cation-value is performed by percolating a mixture of the soil and quartz sand successively with a calcium acetate solution of pH 8.2, a calcium acetate solution of pH 6.5, demineralized water and a NaCl-solution. From the titration of the first percolate with standardized NaOH the H-occupation can be calculated .The cation-value can be calculated from the Ca-content and CO_3''-content of the NaCl-percolate.

The cation occupation is obtained by percolating two samples of soil and quartz sand mixtures with either a NaCl- or an NH_4NO_3-solution. In the NaCl percolate the concentration of Ca, Mg and CO_3'' are determined (giving the Ca and Mg occupation) whereas in the NH_4NO_3-percolate the concentration of Na and K (giving the K and Na occupation) was analysed.

The sum of $Na+K+Mg+Ca+H$ in meq/g must correspond approximately with the cation value of the soil.

The organic matter content is obtained by glowing the soil in an oven at 800-1000 °C. The moisture content has been determined by drying to constant weight in a stove at 110 °C.

As appears from Table VIII-2 considerable differences are found between the cation values at the one hand and the exchanged amounts of Sr and Cs at the other hand for each type of clay. The main reason for this has to be sought in the fact that in the determination of the cation value molar solutions of calcium acetate and sodium chloride were used, whereas the exchanged amounts of Sr and Cs were obtained by using 0.012 and 0.02 molar solutions respectively. Moreover, in the determinations of the exchanged amount of Sr and Cs a slurry technique was applied (i,e. ions removed from the clay remain in the system) whereas the cation value was determined by a percolation technique.

The extra-ordinary high amount of exchanged Sr found for reed-clay 70/90 may be attributed to the precipitation of some salt of strontium.

It further appears from the table that considerable differences are found in the exchanged amounts of Cs at the one hand and Sr at the other hand for reed clay 40/50. The higher value found for Sr can be explained from the fact that the end-pH of the solution was higher in the Sr-experiment as compared with the Cs-experiment. Moreover, the relatively high organic matter content of these samples may, to some extent, also contribute to the higher capacity for strontium.

The efficiency of the clay samples towards the removal of radiocesium

In order to get an idea of the relative selectivity of the clay samples for cesium, some preliminary experiments were carried out with carrier free solutions of ^{137}Cs, to which different competing cations had been added. The pH of the solutions was 3.5 in all experiments. The results are summarized in Table VIII-3.

From the results in Table VIII-3 it follows:

1. River clay samples are considerably more effective in the removal of ^{137}Cs than the marine clay samples. The relatively poor removal obtained with the latter clay samples probably may be attributed to their prolonged contact with sea water. Moreover the high organic matter content of these samples, may be detrimental with respect to Cs-uptake.
2. K-ions show a severe detrimental effect on the sorption of ^{137}Cs. This is in agreement with data reported in the literature (see Chapter II-2-3).
3. The competing action of Na- and Ca-ions on the sorption of ^{137}Cs is small. With A-clay even an improved sorption of ^{137}Cs is found when Ca-ions are present in the solution.

The last may probably be attributed to a more complete separation of colloidal clay particles which was observed here, contrary to the experiment carried out with a pure ^{137}Cs-solution. Therefore the absolute values in Table VIII-3 have less significance than the comparisons.

The effect of cations has been investigated in more detail with A-*clay*

It is obvious that Cs-ions themselves will have a strong effect on the sorption of ^{137}Cs. The results of experiments carried out with solutions containing different concentrations of the element indicate that especially in the lower concentration range the removal of radiocesium strongly decreases (see Table VIII-4).

The competing action of K, Ca and Mg on the sorption of ^{137}Cs can be deduced from the results shown in Fig. VIII-1. Furthermore the effect of K on the sorption of ^{137}Cs using different clay concentrations is shown in Fig. VIII-2.

A comparison of the results in Table VIII-4 and in Figs. VIII-1 and VIII-2 shows that the competing action of the cations increases in the sequence: $Ca < Mg < K < Cs$.

Time effect in the sorption of ^{137}Cs *on* A-*clay**

A remarkable irregularity was observed in the kinetics of the sorption of ^{137}Cs on A-clay as appears clearly from results of experiments carried out at different contact times (see Fig. VIII-3) using untreated air-dry A-clay and H_2O_2-pretreated air-dry A-clay as sorbent. The pretreatment of the clay consisted of warming the clay with 30% H_2O_2 (i.e. 50 ml H_2O_2 per 2 g clay) on a water bath at 70-80 °C for 3-4 hrs. By this treatment the organic matter present in the clay is removed ([5]).

As follows from Fig. VIII-3 an equilibrium situation has apparently been established after approximately 4 hrs shaking. The ^{137}Cs concentration remains unchanged the next 40-44 hrs, but then again a sudden decrease in the Cs-concentration of the solution takes place. This phenomenon is reproduceable and independent of the mechanical way of mixing. Moreover, it is shown by the untreated and pretreated clay in exactly identical way, except that the sorption of Cs is slightly higher on H_2O_2-pretreated clay. Apparently the presence of organic matter in the clay inhibits the uptake of cesium; according to literature ([10]) this holds also with respect to the uptake of K by illites.

In order to obtain some additional information about the time effect observed in the sorption of cesium on A-clay some experiments were carried out with the clay after it had been subjected to a pretreatment with either demineralized water or a K-solution. In the pretreatment with water 5 mg of the clay was immersed in 10 ml water and shaken in a polythene bottle for a definite period of time; then 40 ml of K and ^{137}Cs containing solution was added to the mixture, giving a final concentration of 10^{-2} ppm Cs, 10^{-2} μCi/ml ^{137}Cs and 100 ppm K in the mixture, and shaking was continued. In the pretreatment with the K-solution 5 mg of the clay was immersed in 35 ml of 143 ppm K-solution; after shaking the mixture was made up to 50 ml by adding the tracered Cs-solution, leading to the same concentrations for the various constituents as specified above. In both types of experiments different pretreatment and contact periods were applied.

The results of these experiments have been summarized in Tables VIII-5a and VIII-5b. From the data shown in these tables it can be deduced that:

1. The time effect in the uptake of cesium disappears after applying a pretreatment period of 1.5-5 hrs with demineralized water and after approximately 4 hrs when the clay is pretreated with a K-solution.
2. Both pretreatment methods result in a substantial decrease of the sorption of cesium.

The explanation of these phenomena probably has to be sought in structural changes of the clay lattice. For this reason attention should be given to the properties of K-fixing illites and to factors which influence the uptake of K in such illites. According to Bolt, Sumner, and

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* Work carried out by J. A. Goverde.

Kamphorst (7) and van Schouwenburg and Schuffelen (8) three different types of exchange sites should be distinguished in illites:

1. *Outer planar surface sites*, which do not exert any high specificity for K-ions. The rate of exchange on these sites is fairly rapid.
2. *Interlattice positions near the edges of the particles*. These sites are highly specific for K-ions and some other ions such as NH_4^+, Cs^+ and Rb^+. The rate of exchange on these sites is still rapid as was found in tracer studies (using ^{42}K) in pre-equilibrated systems involving dilute K-solutions (appr. 10^{-4} mol/l); in practice the exchange is virtually completed within a few hours (9). The ease of release of K-ions from these sites depends on the nature of the replacing cation. Ammonium ions are rather effective for a fast exchange of a definite and limited quantity of K. Sodium and calcium are much less effective, although no definite end-point can be detected upon repeated extractions with 0.5 solutions of the replacing cations. Bolt *et al.* (9), observed that the effectiveness of an extraction of K from illite-clay with a 0.5 N NH_4^+-solution can be greatly enhanced by a repeated pretreatment of the clay with 0.5 N $CaCl_2$-solution. Bolt interpreted this effect as originating from a subsequent breakdown of the already opened lattice, resulting in a release of K-ions from edge inter-lattice positions.
3. *Inter-lattice positions*, away from the edges of the clay particles. These sites are occupied mainly by K-ions and are highly specific for these ions. Ion exchange on these sites is governed by a solid state diffusion process, which is extremely slow. This was shown in tracer studies in dilute pre-equilibrated systems using ^{40}K as tracer (12). The inter-lattice K is therefore barely accessible for exchange against other ions, even at 0.5 N concentrations.

As mentioned above Cs-ions are bound by illites also in a nearly irreversible way. As a matter of fact Cs-ions are even preferred over K-ions, due to the fact that they fit more closely into the hexagonal perforations between the layers of two successive structure units than do K-ions.

The A-clay is a strongly K-fixing illite (10), probably mainly as a result of extensive agricultural use over many centuries involving exchange of K against H-ions under wet conditions and the subsequent uptake of Ca-ions over long periods of time. As the amount of exchangeable Ca in A-clay is high (compare Table VIII-2) part of the inter-lattice positions are presumably better accessible for cation exchange as a result of a wedge action of Ca-ions occupying edge-inter-lattice exchange sites; such an effect of Ca is very likely, since as we have seen above, an extraction of K-ions from illite is greatly enhanced by pretreating it with 0.5 N $CaCl_2$-solutions. As a result of the highly open character of the lattice near to the edges of the particles the Cs–K solution can penetrate rapidly and relatively deep between the sheets of the lattice. As a result Ca-ions are replaced rapidly by Cs and K ions and, consequently the lattice will collapse. Here it should be remembered that, while the clay will collapse both with K and Cs ions, the latter ions are still preferred, as they are smaller in size than K ions. Thus the "two-step" kinetics o the observed reaction probably can be explained as:

a) Initial collapse with a relative excess of K because the Cs ions necessary to satisfy the preference for Cs are not yet available at the location where collapse is starting. As can be deduced from the results in Fig. VIII-3 and the data given in Table VIII-2, already in the first rapid exchange Cs ions are preferred strongly over K-ions, i.e. 40% Cs is removed and only approximately 1.5% K, as can be estimated from the available exchange capacity of the clay (0.04 meq/100 mg clay) and the K concentration of the starting solution (2.5 meq/l).
b) Subsequent redistribution of K and Cs inside the K-collapsed lattice, where Cs tends to accumulate in "pitches" which then collapse even further than with K.
c) In turn the formation of Cs-islands tends to enhance the preference for Cs, thus the difference in chemical potential of Cs ions around the "pitches" and in solution increases, leading to a temporary increase in the rate of exchange of K against Cs from the solution. Ultimately a

new equilibrium situation will be established between solution and the clay lattice with the Cs-islands.

Another possible reason, though even more hypothetical, for the two-step kinetics might be the appearance of severe stresses within the lattice near the edges of the particles, as a result of the formation of Cs-islands formed during and/or immediately after the initial uptake. These Cs-islands presumably have a higher degree of contraction than the surrounding K-collapsed lattice. As a result of rearrangements of Cs and K ions within and in the direct vicinity of these islands the stresses within the lattice may steadily increase, ultimately leading to a sudden, temporary and local opening of the lattice.

It is evident that a KCl pretreatment of the clay must result in a lower removal of Cs; dependent on the duration of the pretreatment the lattice will already be collapsed to a greater or smaller extent when the clay is brought in contact with the Cs solution; in first instance the accessibility of the positions farthest away from the edges will diminish by the pretreatment.

A pretreatment with demineralized water apparently also results in a partial collapse of the lattice; probably some Ca-ions, which acted in the untreated clay as wedge between the layers of the lattice, are leached from the clay and replaced by the much smaller $H_3O^+_-$ ion.

Effect of the pH *on the sorption of* ^{90}Sr, ^{90}Y, ^{137}Cs *and* ^{60}Co

The results of experiments performed at different pH with solutions of ^{60}Co, ^{137}Cs and ^{90}Sr$+^{90}$Y respectively and with the A-clay as sorbent are shown in Fig. VIII-4. The sorption of ^{90}Sr and its daughter ^{90}Y were determined by β-activity measurement of aliquots of the filtrate in a liquid Geiger Müller counter after different periods of time following on the separation of the clay from the mixture.

It appears that the sorption of ^{90}Y and ^{137}Cs remains practically unaffected by the H^+-concentration of the solution in the pH-range investigated. This evidently is not valid for ^{90}Sr and ^{60}Co; the sorption of both these ions strongly decreases at $pH<6.5$.

The effect of Ca-*ions on the sorption of* ^{90}Sr, ^{90}Y *and* ^{60}Co *by* A-*clay*

The results of experiments performed with solutions of different concentrations of Ca and with A-clay as sorbent are summarized in Table VIII-6.

As expected, the sorption of ^{90}Sr is decreased significantly by Ca-ions. The same influence of Ca is found in the sorption of ^{60}Co, although to a lower extent. On the other hand Ca-ions do not show any detrimental effect on the sorption of ^{90}Y.

VIII-3-2. Experiments with silt samples

Only a few experiments were carried out with the silt-samples from the river Rhine, because comparable investigations have already been carried out by others ($^{3,\,4}$).

As in the experiments with A-clay the effect of contact time on the sorption of ^{137}Cs has been investigated*. For this purpose a solution of ^{137}Cs containing 100 ppm K was shaken during different periods of time with 100 ppm of the silt.

The behaviour of the silt towards the sorption of ^{137}Cs appears to be different from that of the A-clay. First of all the sorption of ^{137}Cs on silt is appreciably lower as compared to that on the A-clay; only 17% of the cesium is removed from the solution with silt, whereas the A-clay removed 40-50% under identical conditions (see Fig. VIII-3). Furthermore the sorption is indepen-

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* Work carried out by J. A. Goverde.

dent on the contact time after the initial fast uptake; at all contact times investigated between 20 and 140 hrs always the same amount of ^{137}Cs was removed from the solution, viz. 17%. This percentage corresponds to a distribution coefficient of about 2000 ml/g, which certainly is not low. Moreover with river water this factor will undoubtedly be higher because the K-concentration of the river water (Rhine) is appreciably lower than of the solutions used in these experiments. In this connection the extremely low values for this factor as found for bottom sediments in the investigation of EURATOM (^{3}), viz. 33 ml/g, seems incomprehensible at first sight. However, a closer examination of these data shows that the sorption was determined in the presence of an incomparably high concentration of inactive cesium, i.e. 1 meq/l. Actually the Cs-concentration of river water does not exceed a value of 10^{-3} ppm, so that certainly much higher values of the distribution coefficient will exist in the river system than those suggested in the concerning investigation of EURATOM. At the other hand high values, e.g. exceeding 10 000 ml/g are unlikely for bottom sediments, because the main part of this material consists of sand. This is confirmed by the results of Block and Schneider (^{4}), who found with bottom sediments a distribution coefficient ranging from 670 to 2400.

In addition, experiments have also been carried out with silt, which had been pretreated with 100 ppm solution of K. These experiments were performed in exactly the same way as described for the A-clay (Table VIII-5b).

Contrary to the results obtained with the A-clay, any decrease in the sorption of ^{137}Cs on the silt could not be detected. Obviously this material is already greatly adapted to the presence of K-ions in the solution (i.e. lattice is closed).

Finally some sorption experiments were carried out with a carrier-free solution of ^{60}Co, containing 5 meq/l Ca. Different doses of silt were added to the solution, viz. ranging from 20 to 100 ppm. The mixtures were shaken for a period of 24 hrs and then treated further in the usual way. The results are summarized in Table VIII-7.

It follows from these results that a considerable part of ^{60}Co released into the river will associate with suspended matter.

VIII-4. **Discussion of the results**

Ammerzoden clay shows a pronounced selectivity for cesium ions and is therefore, amongst other Dutch river clay deposits (^{11}), quite suitable for application in the decontamination of drinking water. The two marine clay species investigated in this study appeared to be much less effective in this respect. However various old (and weathered) marine sediments found in Dutch soil show also an appreciable K-fixing capacity (^{10,11}).

The sorption of ^{137}Cs is mainly affected by K-ions and of course by Cs-ions themselves. As a consequence the dose of the clay required for a sufficient decontamination of drinking water is determined predominantly by the concentration of these ions in the water. When the K-concentration of the water is 10 ppm and its Cs-concentration is 0.01 ppm, which is already quite high for surface water (^{6}) a reasonable decontamination (viz. about 76%) can be achieved with 100 ppm A-clay. The best way of applying the clay is in combination with chemical coagulation, because then colloidal clay particles are removed effectively.

Structural effects are probably involved in the sorption of cesium on A-clay; a suddenly renewed sorption of ^{137}Cs occurs on this clay after it has been shaken for about 44 hrs with the solution. However, this effect is absent when the clay has been brought into contact beforehand with demineralized water or a solution of K. Apparently in a pretreatment of the clay with water or a K-solution, the clay lattice is collapsed to such a degree that potential exchange sites for Cs-ions inside the clay particles are not accessible anymore.

The A-clay is also effective in the removal of other radionuclides such as ^{90}Y (and probably also of the rare earth elements) and ^{60}Co and probably of the other transition elements. In the sorption of ^{60}Co the pH of the mixture must be 7 or higher. Moreover Ca-ions must not be present in a high concentration. The sorption of radiostrontium is very small when the solution contains more than 2 meq/l Ca.

Suspended inorganic matter in the river Rhine shows a rather high selectivity for cesium; a appreciably higher selectivity for Cs is found for old river clay deposits from which part of the potassium is leached by weathering and extensive agricultural use over many centuries. The relatively low selectivity of suspended matter may probably be attributed also to the relatively high concentration of K in the water of the river Rhine to-day. Nevertheless even at present its distribution coefficient for ^{137}Cs is 2000 or more.

The material also exerts a high affinity for cobalt; for carrier-free solutions of ^{60}Co a distribution coefficient of 70 000 has been found.

It is therefore obvious that suspended matter in the water of the river Rhine will play a predominant part in the transport of radioactive elements released to it. This will especially be true for the radionuclides of the transition elements, of the rare earth elements and for radiocesium. As a consequence in the production of drinking water one has to take care that a complete removal of the suspended matter is realized. As a rule this will not provide any severe problems.

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TABLE VIII-1

Clay samples investigated in the sorption of radionuclides*

Clay sample	Source of the sample	Remarks
A-clay	Ammerzoden (Betuwe)	River clay
D-clay	Eiland van Dordrecht	Tide clay
Reed-clay 40/50	Polder Zevenhuizen	Marine clay containing reed rests
Reed-clay 70/90	Polder Zevenhuizen	Marine clay containing reed rests

* The samples were obtained in kind co-operation with the "Instituut voor Bodemkartering" at Alphen aan de Rijn, and the "Laboratorium van Chemische Bodemkunde" at Ede.

TABLE VIII-2

Analyses of clay-samples

Sample	Moisture content %	Org. matter(1) content %	Cation occupation (1)					Cation(1) value	Exchanged amount of Sr and Cs			
									For Sr		For Cs	
			Na	K	Mg	Ca	H		meq/g	end-pH	meq/g	end-pH
			meq/g									
Reed-clay 40/50	4	17.1	0.085	0.011	0.018	0.018	0.349	0.419	0.28	5.6	0.12	3.5
Reed-clay 70/90	5	16.4	0.003	0.002	0.022	0.259	0.956(2)	0.347	0.55	5.2	0.11	3.2
A-clay	4.4	6.5	0.006	0.005	0.020	0.340	0.020	0.403	0.28	7.35	0.33	7.0
D-clay	6.0	7.5	0.006	0.005	0.015	0.324	0.015	0.333	0.20	7.50	0.21	7.3

(1) Analyses carried out according to standard methods by Bedrijfslaboratorium voor Grond- en Gewasonderzoek at Oosterbeek.

(2) Contains Fe.

TABLE VIII-3

The sorption of ^{137}Cs *in per cent from carrier free solutions containing competing cations* (100 ppm *clay, contact time* 20 hrs)

Clay sample	A-clay	D-clay	Reed-clay 40/50	Reed-clay 70/90
Composition of the solution	Percentage removal of ^{137}Cs			
No competing ions	84	95	56	61
7 meq/l Na	82	95	51	55
1 meq/l K	62	47	5	20
7.5 meq/l Ca	90	70	47	60

TABLE VIII-4

The effect of Cs-*concentration on the sorption of* ^{137}Cs *by A-clay* (*solution:* 10 ppm K, 10^{-2} μCi/ml ^{137}Cs *and various* Cs-*concentrations; clay concentration:* 1000 ppm; *contact time: approximately* 20 hrs)

Cs-concentration (ppm)	10^{-4}	1	10	20
^{137}Cs removed (%)	96	72	61	45
K_d^* (ml/g)	24,000	2,600	1,560	820

TABLE VIII-5a

Effect of a pretreatment of A-clay with demineralized water on the sorption of ^{137}Cs (^{137}Cs-*solution:* 100 ppm K, 10^{-2} ppm Cs, 10^{-2} μCi ^{137}Cs/ml; *clay concentration:* 100 ppm)

Contact time pretreatment hrs	Contact time sorption hrs	Relative concentration of ^{137}Cs in the supernatant %
124	23	65
124	46	63
124	52	63
124	71	62
5	19	62.5
1.5	70	57
1.5	75	56
1.5	22	61

TABLE VIII-5b

Effect of a pretreatment of A-clay with a 143 ppm K-*solution on the sorption of* ^{137}Cs (^{137}Cs-*solution:* 100 ppm K, 10^{-2} ppm Cs, 10^{-2} μCi ^{137}Cs/ml; *clay concentration:* 100 ppm)

Contact time pretreatment hrs	Contact time sorption hrs	Relative concentration of ^{137}Cs in the supernatant %
124	70	71
124	46	71.5
124	22	70.5
100	22	72
65	24	71.5
21	71	70.5
20	21	71
4	20	71
1	113	61.5
1	17	67
0.5	168	60.5
0.5	18	64.5
0.166	138	59.5
0.166	18	63

TABLE VIII-6

The effect of Ca-*ions on the sorption of* ^{90}Y, ^{90}Sr *and* ^{60}Co *by A-clay from* 5.10^{-3} μCi/ml *carrier free solutions* (*end*-pH *of the solution:* 6.3 - 6.8)

Ca-concentration (meq/l)	0	1.0	2.0	3.0	5.0	10.0
% ^{90}Sr sorbed (1200 ppm clay)	78	23	9.5	5.0	2.3	1.3
% ^{60}Co sorbed (440 ppm clay)	91	76	70	67	62	59
% ^{90}Y sorbed (800 ppm clay)	97	98		98		98

TABLE VIII-7

The sorption of ^{60}Co *by river silt* (*end*-pH *of the mixture* 6.8 - 7.0) *from a* 5.10^{-3} μCi/ml *carrier free solution containing* 5 meq Ca/l

Silt concentration (ppm)	18	60	81	102
Percentage ^{60}Co removed	66	82	86	87.5
K_d^* (ml/g)	108,000	76,000	76,000	69,000

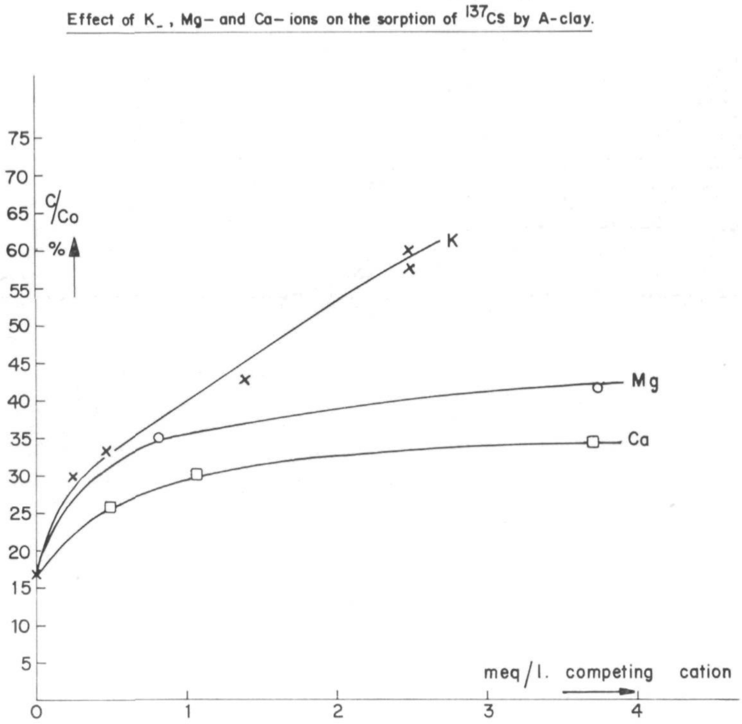

Fig. VIII-1

Clay concentration: 100 ppm A-clay — Contact time: 17 hrs

Starting solution: 5.10^{-3} μCi ^{137}Cs; 0.01 ppm Cs; various concentrations K, Mg and Ca.

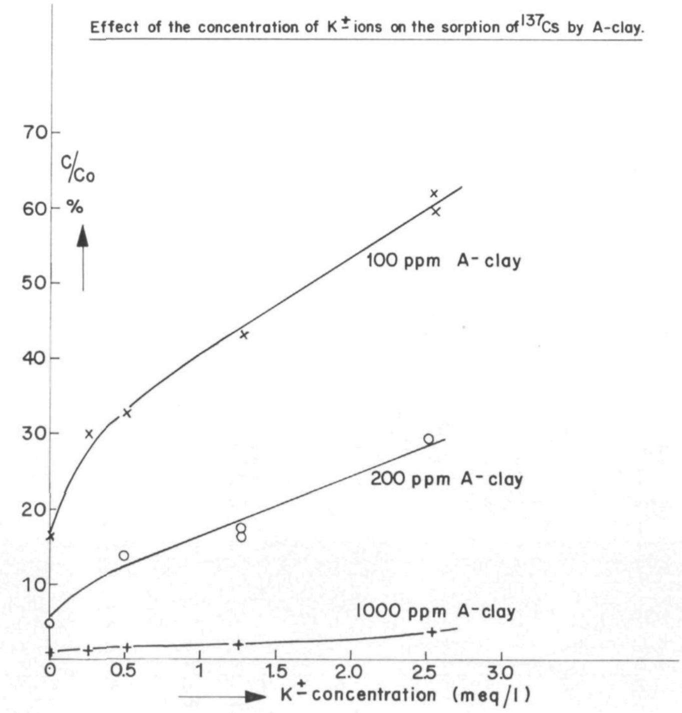

Fig. VIII-2

Starting solution: 5.10^{-3} μCi ^{137}Cs/ml; 0.01 ppm Cs; various concentrations of K — Contact time: 17 hrs

Clay concentration: 100, 200 and 1000 ppm A-clay.

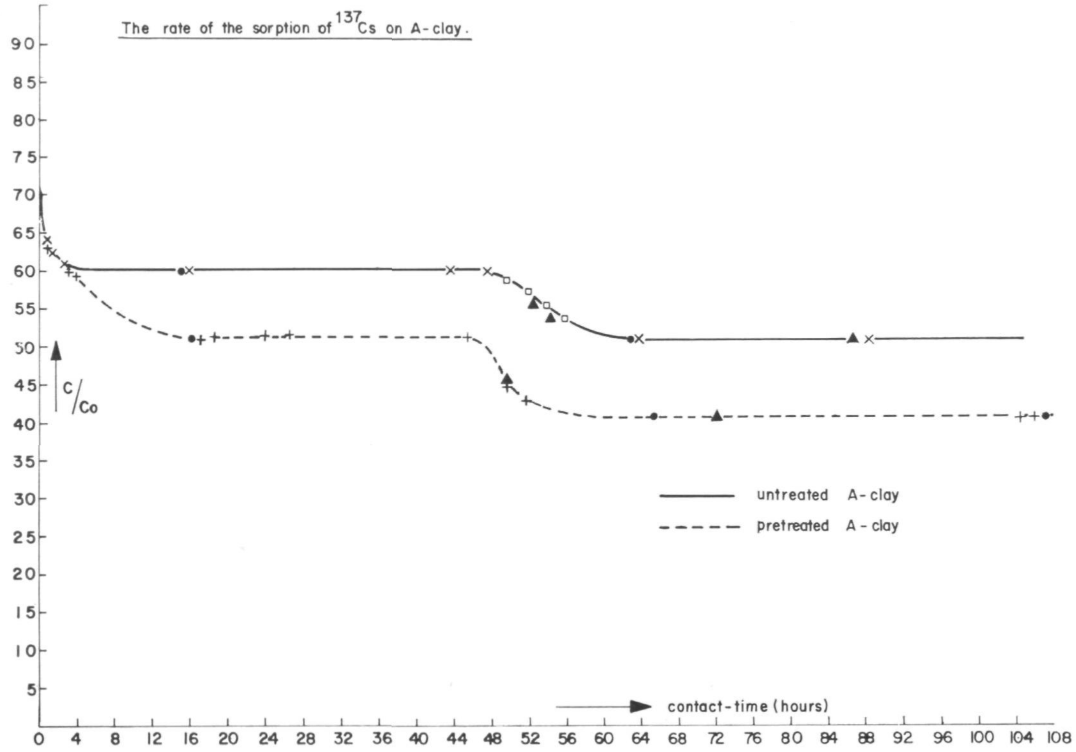

Fig. VIII-3

Clay concentration: 100 ppm A-clay — Starting solution: 5.10^{-3} μCi ^{137}Cs/ml; 0.01 ppm Cs; 100 ppm K

× + □ shaking experiments ▲ ● stirring experiments

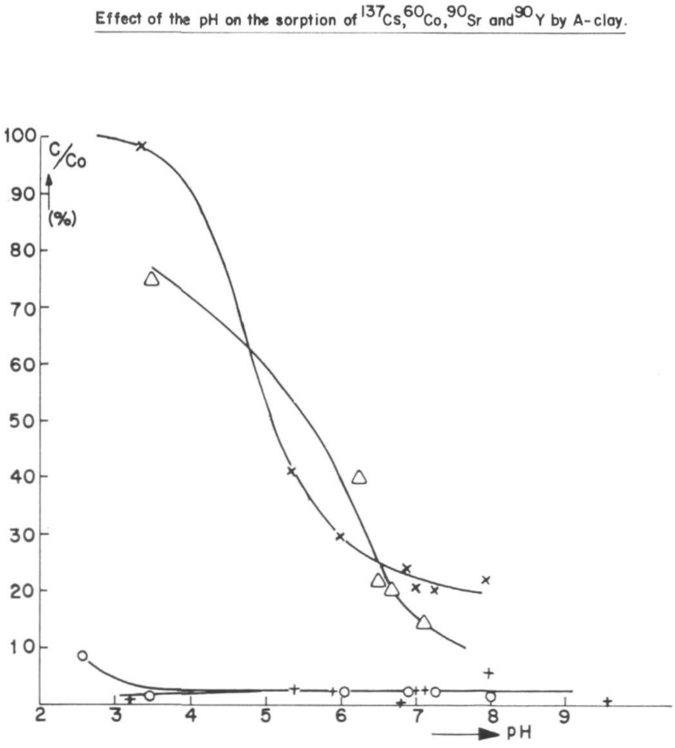

Fig. VIII-4

Starting solution: carrier free solutions of ^{90}Sr, ^{137}Cs, ^{90}Y and ^{60}Co

△ ^{90}Sr, 1200 ppm A-clay × ^{60}Co, 250 ppm A-clay + ^{90}Y, 1200 ppm A-clay ○ ^{137}Cs,1000 ppm A-clay

IX. FINAL DISCUSSION

A real emergency situation concerning a radioactive contamination of water supplies for drinking water *seems* only possible in the event of a nuclear war, in which an excessive and uncontrolled use is made of nuclear weapons or in which nuclear installations are destroyed by conventional explosives.

As set forth in Chapter II, no serious contamination of water supplies will arise from the peaceful uses of atomic energy, provided that the regulations for discharge of radioactive wastes in surface waters are closely followed. Techniques are available to limit the contamination of surface waters by such wastes to any desired level, except possibly in the case of tritium, which radionuclide is released in appreciable quantities in fuel reprocessing plants but also in the normal operation of nuclear reactors. Although tritium is generally considered to be one of the least hazardous radioisotopes, its long half-life (12 years) means that it will accumulate over a relatively long period of time. A hazardous contamination of water supplies as a result of accidental spillage of radioactivity will always be *temporary and local*. Moreover, only relatively small quantities of radioactivity are *probably* involved.

The danger of a severe contamination is probably greatest in the event of a nuclear war. However, then it is difficult to predict the degree of contamination of water and food supplies by radioactive fall-out. This is especially true because incidental factors such as meteorological conditions, degree of destruction of public facilities may play an important role apart from the concentration of nuclear bombing which is a matter of military tactics.

Concerning the production of safe drinking water under such circumstances it may be mentioned that, apart from the scientific and technical know-how involved in the decontamination of the water, one will probably have to deal with other severe problems, related with the degree of disorganisation of society, e.g.: difficulties in the production of drinking water, because of lack of skilled personnel, lack of energy and lack of equipment and difficulties in the distribution of drinking water.

As mentioned in Chapter II the severest contamination will occur in rain water and in surface water, although to a lower extent in surface water. As a rule ground water will be safeguarded reasonably well from a radioactive contamination, provided an artificial supply of contaminated surface water by means of infiltration is avoided. Consequently, the first action which has to be taken in case of an emergency situation implies a switch over to ground water use for consumption water production without applying infiltration of contaminated surface water. As the amount of ground water available per head of the population is limited, the ground water should be reserved exclusively for consumption purposes. Provisions are then required to distribute drinking water and industrial water via a separate stringent system, i.e. drinking water via a "milkman system". Such a system certainly must become operative when ground water resources are not available at all. Under the latter circumstances one depends exclusively on the use of surface water as raw material for the production of drinking water and a decontamination procedure must be applied. Radionuclides of primary concern which have to be removed are: ^{131}I, ^{90}Sr, ^{89}Sr, ^{137}Cs, ^{106}Ru, ^{103}Ru, ^{140}Ba, ^{144}Ce a.o. Since ^{131}I and ^{140}Ba are present only during a relatively short period of time after the nuclear explosion(s), the removal of these nuclides has to be considered when there is no possibility for storing water long enough to allow these isotopes to decay. In these exceptional events ^{131}I represents the most hazardous radioisotope (see Chapter II-1), the more so as it is difficult to remove.

As stated above the hazard for a contamination with ^{131}I is only relevant when the contamination is of recent date. Consequently the problem of purification of the drinking water with ^{131}I can be solved easily when infiltration areas or reservoirs are available in which the water has a residence time of 100 days or more, so that the iodine activity can be reduced 4000 times by its own decay. Such a residence time may be available in a continuous flow reservoir if plug flow occurs and the contribution of iodine containing rain water to the reservoir is negligible.

As to the removal of radioactive isotopes from surface water, knowledge is required about the chemical, physical and biochemical behaviour of radionuclides in the aquatic environment. This is not only important for the production of drinking water, but also for other down-stream uses of the water, such as irrigation, swimming, boating and the use of the water as natural habitat of fish and wild life. Evidently the residence time of the radionuclides in the river-system is important in this respect. Furthermore it is important to have a clear insight about the ultimate distribution of the radioactive compounds in the biosphere.

In this respect it may be mentioned that dissolved radioactive compounds move downstream with the same velocity as the river water. Radioisotopes which occur in the river water almost exclusively in soluble form are those of strontium and iodine. Since the extent to which they are removed in conventional water treatment processes (coagulation, sedimentation, filtration) is by no means complete, the discharge of these radionuclides must be avoided as far as possible. Other radionuclides, such as cesium, cobalt, ruthenium etc. will be present in the water partly in soluble (e.g. ionic, complexed or colloidal) or suspended form dependent on the concentration of humic acids, of the amount of carrier, on the quantity and nature of the suspended matter, on the pH and on the amount and nature of dissolved salts in the water. With respect to the removal of these radionuclides by conventional water treatment processes, problems may arise in the removal of radioisotopes associated with humic acids. As far as the radioactivity is associated with particulate material it may be assumed that the role of coarser particles present in the river system in the accumulation and retention of radioactive compounds is negligible. For particles smaller than about 0.1 mm the residence time in the river system will be small. However, a considerable accumulation of the finer particles will take place by sedimentation in lakes, reservoirs or other places where the flow is slackened, e.g. in the river delta. Since in the drinking water treatment processes no difficulties are encountered in removing suspended matter, therefore, the discharge of radioisotopes which associate easily with suspended particles is limited by the function of stagnant waters in which the particles accumulate. It is evident that an accumulation of particulate associated radioactive compounds in raw water storage reservoirs for drinking water production can frequently be prevented to a great extent by applying a prefiltration of the water at the entrance of the reservoir. This as a rule is not possible for stagnant natural waters.

Radioisotopes which associate easily with suspended matter are: ^{60}Co, ^{95}Zr, ^{144}Ce, ^{90}Y, ^{137}Cs, ^{106}Ru, etc. Moreover, the interaction is frequently strong so that an appreciable desorption can take place only at a severe change of the external conditions in the aqueous environment. Nevertheless part of the accumulated radioisotopes may reach the population via bottom- and aquatic organisms. Aquatic organisms may accumulate dissolved radioisotopes to a considerable extent, especially those of Zn, P and Co.

For the purification of drinking water from other radionuclides a number of methods or combination of methods can be applied.

Flocculation, *filtration* and *sedimentation* are effective in the removal of particulate associated radioactive compounds and of 3-, 4- and 5-valent radionuclides. However, a complete removal of the radioactive compounds cannot be achieved by means of this method. The removal of the lower valency cations (Cs, Sr, Ba) and of anionic radionuclides particularly is insufficient.

Soda softening. Radiostrontium and many other cationic radionuclides can be removed to a considerable extent from aqueous solutions by co-precipitation with $CaCO_3$. However, a sufficient removal of radiostrontium can be achieved only when a large excess of soda and/or a repeated precipitation of $CaCO_3$ is applied.

Nevertheless the soda softening process can always be applied profitably in the decontamination of drinking water, e.g. for the lowering of the Ca-content of the water.

Moreover, results of preliminary experiments concerning the co-precipitation of radiostrontium with $CaCO_3$ indicated that the efficiency of the process with respect to the removal of radiostrontium can be improved considerably, provided that the process is performed in an appropriate way. However, since the information available is still rather meager, a further discussion of the results at this stage would be premature.

Distillation, *electro-dialysis*, etc. An effective decontamination of drinking water can be achieved by means of distillation and electro-dialysis. These techniques can be considered for the decontamination of relatively small quantities of water when appropriate apparatus is available and, needless to mention, energy.

Ion exchange. In principle all cationic and anionic radionuclides present in dissolved form in the water can be removed completely by means of ion exchange. However, the application of ion exchange in the decontamination of water is attractive only when the salt content of the water is low, because then relatively large amounts of water can be treated before exhaustion of the ion exchanger. Such a situation is only found in the purification of cistern water.

For surface water which frequently contains a relatively high concentration of Ca-salts ion exchangers show a decreased capacity for radionuclides. In order to make efficient use of the ion exchange capacity, ions with a severe competitive action, such as Ca-ions in the removal of radiostrontium, have to be removed before ion exchange is applied. For Ca this can be achieved by means of lime soda softening. Moreover, part of the radiostrontium and of other radionuclides will then be co-precipitated with the $CaCO_3$ formed.

In principle all ion exchange materials with a reasonable capacity and selectivity can be applied, viz. synthetic as well as natural, organic as well as mineral ion exchangers. The relatively high price of synthetic ion exchangers might prove objectionable for their application in the decontamination of drinking water, although as a rule these materials are superior in properties as compared with their natural counterparts. However, economical considerations, normally important, may be disregarded for obvious reasons in an event as considered here. Therefore, if possible, these materials should be applied when they are available, for instance in industrial desalting plants.

In view of the high price of synthetic ion exchangers and their limited availability when an emergency situation might occur, it seemed worthwhile to investigate the practical applicability of some natural occuring materials, such as peat and clay. These materials are cheap and available in large quantities. Moreover they frequently show a reasonable exchange capacity and for a pronounced selectivity for various cations. Therefore the work described in this study is concerned mainly with an investigation of the ion exchange behaviour of peat and clay, the preparation of a chemically modified peat with superior properties and a study of the ion exchange behaviour of modified peat. In addition an investigation was made of the applicability of an activated carbon species and of peat for the removal of radioiodine.

Clay as decontaminant

Dutch river clay deposits, such as Ammerzoden clay, have a high specificity for cesium ions. This material therefore can be used advantageously in the decontamination of water contaminated with radiocesium. The dose of the clay required for a sufficient decontamination for cesium depends on the concentration of K- and inactive Cs-ions in the water.

In surface water containing 10 ppm K and less than 10^{-2} ppm Cs (e.g. Rhine water) a decontamination of at least 91.5 can be achieved by using 300 ppm A-clay when the clay is added in one dose. This means that about 99% of ^{137}Cs can be removed when the same quantity of the clay is added in three doses. Unfortunately clay can not be applied in column operation but has to be used in dispersed form.

Natural peat as decontaminant

As was shown in Chapter IV peat has a pronounced specificity for the higher valency cationic radionuclides. It can therefore be used advantageously in the decontamination of surface water for the production of drinking water. However, the application of natural peat in drinking water plants can only be considered as practical when the untreated water does not contain appreciable quantities of dissolved salts. For untreated surface water the decontamination capacity is limited by the calcium present leading to the use (and transport) of excessive quantities of peat.

For the decontamination of water of a rather high Ca-content, e.g. 3-5 meq/l, the application of peat in its natural place would be more attractive. However, before such an application can be considered, further investigations are required to provide answers on the following questions:

1. Whether an infiltration and recovery technique can be applied with natural peat layers.
2. Whether the contact between peat mass and the infiltered water will be sufficient for purification.

Anyhow, it is clear that ground water originating from peaty soils will largely be freed from radioactivity but may need an extra treatment for lowering the organic matter content (taste, odour, colour) .

For domestic purposes, for instance in the decontamination of cistern water, a filter filled with a mixture of clay, sand and peat can be used, provided the concentration of ^{131}I in the water is low. Synthetic cation and anion exchangers can also be applied in that case.

Chemically modified peat as decontaminant

As appeared from the results discussed in Chapter V and VI an excellent cation exchanger can be prepared from natural peat by treating it at elevated temperatures in the presence of either dilute or concentrated sulphuric acid. The product obtained in this treatment has superior properties over the untreated peat in various respects, i.e. the cation exchange capacity, the selectivity for strontium relative to calcium, the chemical stability, swelling and the mechanical stability. As found for natural peat, the modified peat exerts a pronounced specificity for the higher valency cations, especially for the cations of the transition elements and of the rare earth elements and for cationic Ru-complexes. According to literature data this is also true for cations of elements like Ra and U. Compared with the alkaline elements also the alkaline earth elements are sorbed with a high specificity.

However, within the last group a rather strong competitive action exists between the various species. The sorption of strontium is strongly affected by Ca-ions; in practice the break-through of radiostrontium will almost coincide with hardness (Ca) break-through. Because of the slightly higher selectivity of modified peat for strontium relative to calcium up to pH 6.5-7, hardness break-through will take place slightly earlier than the break-through of radiostrontium. The effect of magnesium on the sorption of strontium is considerably smaller than that of calcium.

Modified peat therefore is eminently suitable for application in the decontamination of radioactively contaminated water, either for the production of drinking water or for the treatment of radioactive waste solutions.

Carbon as decontaminant for iodine

If contamination of the raw water with ^{131}I cannot be avoided in any way, an additional treatment of the water is required for the elimination of this radioisotope. For this purpose activated carbon $+Cl_2$, (if necessary combined with the addition of a silver-salt) can be applied. As was shown in Chapter VII a rather large proportion of ^{131}I can be removed by this method, provided that the properties of the carbon, with respect to the sorption of iodine are well known and the conditions of the treatment are scrupulously controlled.

The techniques described in this study can be used either for purification of contaminated surface water and/or rain water, and for the purification of low level radiactive wastes prior to discharge into surface water.

X. SAMENVATTING

Van een werkelijke noodtoestand betreffende een radioactieve besmetting van zoet watervoorraden *lijkt* in feite slechts mogelijk in geval van een nucleaire oorlog, waarin op grote schaal nucleaire wapens tot ontploffing worden gebracht en/of nucleaire installaties worden vernietigd.

De kans op een ernstige radioactieve besmetting van watervoorraden als gevolg van het vreedzaam gebruik van kernenergie is zeer gering, mits althans bij de lozing van radioactieve afvalstoffen in de omgeving de hiervoor geldende voorschriften nauwgezet worden nageleefd. Met behulp van de thans beschikbare technieken kunnen, met uitzonderin van o.a. tritium, radioactieve bestanddelen uit radioactief afvalwater tot ieder gewenst niveau worden verwijderd. Hoewel tritium algemeen beschouwd wordt als een van de minst gevaarlijke radioisotopen, kan het tengevolge van de betrekkelijk lange halfwaarde tijd (12 jaar) over een lange periode in de omgeving ophopen. Daar het bij de normale operatie van kernreactoren alsmede ook bij de opwerking van splijtstof in aanzienlijke hoeveelheden vrijkomt, kan dit isotoop mogelijk op de duur aanleiding geven tot problemen. De kans op besmetting tengevolge van ongelukken in nucleaire installaties of tijdens het transport van radioactiviteit is uiterst gering; bovendien zullen dergelijke besmettingen van *plaatselijke* en *tijdelijke* aard zijn, terwijl er waarschijnlijk slechts *betrekkelijk* kleine hoeveelheden radioactiviteit bij vrijkomen.

Het gevaar op een ernstige radioactieve besmetting is waarschijnlijk het grootst in geval van een nucleaire oorlog. Het is echter zeer moeilijk een voorspelling te maken van de mate waarin water en voedselvoorraden door radioactieve fallout besmet kunnen worden. Diverse moeilijk of in het geheel niet te bepalen faktoren spelen hierbij een rol, zoals meteorologische condities, vernietiging van publieke werken, militaire overwegingen, etc.

Wat betreft de produktie van veilig drinkwater onder dergelijke omstandigheden zal men, afgezien van de wetenschappelijke en technische kennis aangaande de decontaminering van het water, zeer waarschijnlijk met tal van andere ernstige problemen worden geconfronteerd, zoals: moeilijkheden in de produktie van drinkwater als gevolg van gebrek aan ervaren personeel, gebrek aan energie en apparatuur, en moeilijkheden in de distributie van het water.

Zoals in Hoofdstuk II is uiteengezet zal de sterkste besmetting optreden in regenwater en, zij het in mindere mate, in oppervlaktewater. Mits infiltratie van besmet oppervlaktewater achterwege wordt gelaten is de kans op een sterke besmetting van grondwater erg klein. Het is derhalve duidelijk dat in geval van een noodsituatie direct overgeschakeld moet worden op het gebruik van grondwater voor de produktie van drinkwater; suppletie van het grondwater met besmet oppervlaktewater moet uiteraard achterwege blijven. Daar de hoeveelheden beschikbaar grondwater vaak zeer beperkt zijn, is het wenselijk het hieruit geproduceerde drinkwater uitsluitend voor consumptiedoeleinden te gebruiken. Het "consumptiewater" zal hiertoe via een afzonderlijk systeem moeten worden gedistribueerd, b.v. via melkboer of kruidenier. Dit is zeker noodzakelijk indien in het geheel niet beschikt kan worden over grondwater. In dat geval is men volledig aangewezen op het gebruik van oppervlaktewater voor de bereiding van drinkwater en zal een decontamineringsmethode moeten worden toegepast. De belangrijkste radioisotopen die verwijderd zullen moeten worden zijn: ^{131}J, ^{90}Sr, ^{89}Sr, ^{137}Cs, ^{106}Ru, ^{103}Ru, ^{140}Ba, ^{144}Ce e.d. Daar ^{131}J en ^{140}Ba alleen gedurende een betrekkelijk korte periode na de kernexplosie(s) aanwezig zijn, behoeft met deze isotopen alleen rekening te worden gehouden indien het onmogelijk is het water zo lang op te slaan dat ze door radioactief verval in voldoende mate zullen zijn verdwenen. In dat geval is ^{131}J het gevaarlijkste radioisotoop, temeer daar het moeilijk is te verwijderen. Het probleem van een besmetting van drinkwater met ^{131}J kan echter eenvoudig worden opgelost indien infiltratiegebieden of spaarbekkens beschikbaar zijn, waarin het water gedurende een periode van 100 dagen of meer kan worden opgeslagen; de concentratie van ^{131}J kan dan door radioactief verval met een faktor 4000 afnemen. Een dergelijke verblijftijd is bij continu doorstroomde reservoirs mogelijk indien hierin sprake is van een propstroming en de bijdrage van met ^{131}J besmet regenwater aan de suppletie van het reservoir zeer klein is.

Voor wat betreft de verwijdering van radioactieve isotopen uit oppervlaktewater is het noodzakelijk een goed inzicht te hebben in het chemisch, fysisch en biochemisch gedrag van de radioactieve isotopen in het oppervlaktewater. Dit is niet alleen van belang ten aanzien van de produktie van drinkwater, maar met name ook voor het gebruik dat stroomafwaarts van het water wordt gemaakt, b.v. voor irrigatie, recreatie e.d. Het is duidelijk dat de verblijftijd van de radioisotopen in het riviersysteem in dit opzicht belangrijk is. Het is voorts belangrijk een duidelijk inzicht te hebben in de uiteindelijke distributie van radioisotopen in de biosfeer.

Wat dit betreft kan worden gesteld dat opgeloste radioactieve verbindingen met dezelfde snelheid stroomafwaarts zullen bewegen als het rivierwater. Radioisotopen die vrijwel volledig in opgeloste vorm in het rivierwater zullen worden aangetroffen zijn die van strontium en jodium. Daar deze isotopen met behulp van conventionele drinkwaterzuiveringsprocessen (coagulatie, filtratie e.d.) zeer onvolledig worden verwijderd is het duidelijk dat de lozing hiervan zoveel mogelijk moet worden vermeden. Radioisotopen van ceasium, cobalt, ruthenium e.a. zullen in het water gedeeltelijk in opgeloste (ionogeen, gecomplexeerd of colloidaal) of gesuspendeerde vorm voorkomen, een en ander afhankelijk van de concentratie aan humuszuren, hoeveelheid inaktieve drager, aard en hoeveelheid van gesuspendeerd materiaal, van de pH van het water en van de aard en concentratie van in het water opgeloste zouten. Met conventionele zuiveringsmethoden zullen de radioisotopen die geassocieerd zijn met humuszuren waarschijnlijk slecht worden verwijderd. Wat betreft de radioactiviteit die is geadsorbeerd aan vaste deeltjes kan worden gesteld dat de bijdrage van de grovere deeltjes aan de ophoping en retentie van radioisotopen in het riviersysteem verwaarloosbaar klein zal zijn. Voor deeltjes kleiner dan ca. 0.1 mm zal de verblijftijd in het riviersysteem klein zijn. Hier staat echter tegenover dat tengevolge van bezinking een aanzienlijke accumulatie van dergelijke deeltjes plaats kan vinden in meren, reservoirs of andere plaatsen waar de stoomsnelheid laag is. De lozing van radioactieve isotopen, die gemakkelijk worden geadsorbeerd op gesuspendeerde deeltjes, wordt in verband hiermee bepaald door de funktie die plaatsen met een lage stroomsnelheid in het riviersysteem hebben. Het is duidelijk dat een ophoping van radioactieve isotopen, die zijn geadsorbeerd op gesuspendeerde deeltjes, in spaarbekkens al grotendeels kan worden voorkomen door bij de inlaat van het spaarbekken een voor-filtratie toe te passen. Zoiets is in de regel niet mogelijk bij natuurlijk stilstaand water.

Radioisotopen die gemakkelijk worden geadsorbeerd op gesuspendeerde deeltjes zijn o.a. ^{60}Co, ^{95}Zr, ^{144}Ce, ^{90}Y, ^{137}Cs en ^{106}Ru. De binding van deze isotopen aan de gesuspendeerde deeltjes is bovendien dikwijls zo sterk dat een aanzienlijke desorptie alleen plaats zal vinden bij een sterke verandering van de uitwendige omstandigheden in het waterige milieu. Niettemin kan een deel van de opgehoopte radioisotopen mens en dier bereiken via bodem en waterorganismen. Sommige waterorganismen accumuleren opgeloste isotopen, met name die van Zn, P en Co in aanzienlijke mate.

Voor de verwijdering van radioisotopen uit drinkwater kunnen een aantal methoden of combinatie van methoden worden toegepast.

Vlokking, filtratie en sedimentatie zijn effectief ten aanzien van de verwijdering van 3-, 4- en 5-waardige isotopen, alsmede voor gesuspendeerde deeltjes waaraan radioactieve isotopen zijn geadsorbeerd. De verwijdering van 1- en 2-waardige kationogene radioisotopen en van radioisotopen die als anion in water voorkomen is met behulp van deze methoden zeer onvolledig.

Soda-ontharding. Strontium en vele andere kationogene radioisotopen kunnen door middel van co-precipitatie met $CaCO_3$ tamelijk goed uit water worden verwijderd. Strontium kan echter alleen in voldoende mate worden verwijderd indien een grote overmaat soda wordt gebruikt en/of een meermalige precipitatie van $CaCO_3$ wordt toegepast. Desalniettemin is de inschakeling van een (soda)-ontharding voor de decontaminering van water altijd nuttig, al was het alleen maar voor het verlagen van het calciumgehalte van het water. Bovendien is uit oriënterende experimenten betreffende de co-precipitatie van radiostrontium met $CaCO_3$ gebleken dat waarschijnlijk een aanzienlijk betere verwijdering van strontium door middel van soda-ontharding mogelijk is. Daar dit onderzoek nog in de aanvangsfase verkeert zal op de resultaten hier verder niet worden ingegaan.

Destillatie, electro-dialyse e.d. Door middel van destillatie en electro-dialyse kan drinkwater goed worden gedecontamineerd. Deze methoden zouden voor de zuivering van kleine hoeveelheden water eventueel kunnen worden toegepast.

Ionenuitwisseling. In principe kunnen alle opgeloste kationogene en anionogene radioisotopen met behulp van ionenuitwisseling volledig uit water worden verwijderd. De toepassing van ionenuitwisseling voor de decontaminatie van radioactief besmet water is echter alleen interessant indien het zoutgehalte van het water laag is, daar alleen dan een grote hoeveelheid water kan worden gezuiverd. Een dergelijke situatie doet zich voor bij de zuivering van regenwater.

Voor oppervlaktewater, waarin dikwijls een betrekkelijk hoge concentratie aan zouten is opgelost, kan het gebruik van ionenuitwisseling alleen worden overwogen indien van te voren de concentratie aan competerende ionen (zoals calcium voor strontium) middels een of andere bewerking sterk is verlaagd. Voor wat betreft calcium zou hiervoor een kalk-soda-ontharding kunnen worden toegepast.

In principe kunnen alle ionenwisselaars met een redelijk hoge uitwisselingscapaciteit en selectiviteit worden gebruikt, natuurlijke zowel als synthetische en organische zowel als anorganische. Hoewel synthetische ionenuitwisselaars in de regel superieur in eigenschappen zijn vergeleken met natuurlijke ionenwisselaars, zal mogelijk de betrekkelijk hoge prijs van deze materialen de toepassing ervan bij de decontaminering van drinkwater kunnen verhinderen. Het is echter waarschijnlijk dat in dergelijke noodsituaties financiële overwegingen van ondergeschikt belang zijn. Voor zover voorradig, b.v. in industriele ontzoutingsinstallaties, dienen deze materialen bij de zuivering van drinkwater te worden ingeschakeld.

Met het oog op de prijs van synthetische ionenwisselaars en het feit dat ze in geval van een noodsituatie waarschijnlijk slechts op zeer beperkte schaal voorradig zijn, leek het nuttig de toepassingsmogelijkheden van een aantal natuurlijke ionenwisselaars voor de decontaminering van radioactief besmet water te bestuderen. Materialen als veen en klei zijn goedkoop, in grote hoeveelheden voorradig, bezitten een redelijke uitwisselingscapaciteit en vertonen bovendien voor bepaalde radioisotopen een hoge selectiviteit. De in dit rapport beschreven onderzoekingen betreffen derhalve de bestudering van de ionenuitwisselingseigenschappen van klei en veen, en de bereiding van een chemisch gemodificeerd veen met superieure ionenuitwisselingseigenschappen. Bovendien is een onderzoek gedaan naar de toepasbaarheid van actieve kool en veen voor de verwijdering van radioactief jodium.

De toepassing van klei

Sommige Nederlandse rivierkleiafzettingen, zoals Ammerzoden klei, blijken zeer selectief voor ceasium ionen te zijn. Een materiaal als Ammerzoden klei kan dan ook zeer goed worden gebruikt voor de zuivering van ^{137}Cs-houdend water. De hoeveelheid klei die voor het verkrijgen van een voldoende zuivering moet worden toegevoegd, wordt bepaald door de concentratie aan kalium en inactief ceasium in het water. In oppervlaktewater met 10 ppm kalium en minder dan 10^{-2} ppm ceasium wordt minimaal 91,5% van het ceasium verwijderd bij gebruik van 300 ppm klei in één dosis. Wanneer dezelfde portie klei toegevoegd wordt in drie doses van 100 ppm kan zelfs 99% van het ceasium worden verwijderd. Jammer genoeg is klei niet geschikt voor gebruik in kolommen, zodat men op een ladingsgewijze toepassing is aangewezen.

De toepassing van natuurlijke veen

Natuurlijk veen bezit een uitgesproken selectiviteit voor meerwaardige kationen, in het bijzonder voor de overgangs- en de zeldzame aardelementen. Aardalkali elementen worden t.o.v. de alkali elementen met een sterke voorkeur gebonden, maar binnen deze groep beinvloeden deze elementen elkaars sorptie vrij sterk. Dit is met name het geval t.a.v. de sorptie van strontium en calcium; bij lage pH (<4) bezit veen een lichte voorkeur voor strontium maar bij hoge pH wordt calcium geprefereerd. Vanwege de sterke voorkeur van veen voor meerwaardige kationen is het in principe zeer goed bruikbaar voor decontaminering van radioactief besmet water. Toepassing van veen in drinkwaterzuiveringsinstallaties is echter voor de praktijk alleen mogelijk indien het zoutgehalte van het besmette water laag is. Voor onbehandeld oppervlaktewater is vanwege het hoge calciumgehalte de zuiveringscapaciteit zeer beperkt, zodat zeer grote hoeveelheden veen gebruikt (en getransporteerd) zouden moeten worden.

Voor de zuivering van water met een hoog calciumgehalte (3-5 meq/l) lijkt een toepassing van veen op haar natuurlijke plaats veel aantrekkelijker. Alvorens een dergelijke toepassing echter kan worden overwogen is het noodzakelijk dat op de volgende vragen een antwoord wordt gegeven:

1. Is een infiltratietechniek bij veengrond praktisch uitvoerbaar.
2. Is er voldoende contact tussen geinfiltreerd water en de veenmassa om het gewenste zuiveringseffect te verkrijgen.

Wat betreft grondwater afkomstig uit veengrond mag worden gesteld dat hierin vrijwel geen radioactiviteit voor zal komen; voor dergelijk water is waarschijnlijk alleen een extra behandeling nodig voor het verlagen van het organische stofgehalte, een en ander in verband met kleur, smaak en geur.

Voor huishoudelijk gebruik, b.v. voor de decontaminering van regenwater zou een filter gevuld met een mengsel van klei, veen en zand kunnen worden gebruikt, mits althans de concentratie van ^{131}J in het water gering is. Voor dit doel kunnen synthetische kationen en anionenwisselaars eveneens worden gebruikt.

De toepassing van chemisch gemodificeerde veen

Zoals is gebleken bij de bespreking van de resultaten in hoofdstuk V en VI kan uit veen een uitstekende kationenwisselaar worden bereid door het bij verhoogde temperatuur in aanwezigheid van verdund of geconcentreerd zwavelzuur te behandelen. Het hierbij verkregen produkt heeft vergeleken met natuurlijk veen aanzienlijke betere eigenschappen, n.l. wat betreft kationenuitwisselingscapaciteit, de selectiviteit voor strontium t.o.v. calcium, chemische en mechanische stabiliteit en zwellingseigenschappen. Evenals natuurlijk veen bezit het gemodificeerde veen in de binding van kationen een sterke voorkeur voor meerwaardige kationen, in het bijzonder voor die van de overgangselementen en de zeldzame aardelementen. Kationogene rutheniumcomplexen worden eveneens zeer goed gebonden. Afgaande op literatuurgegevens mag worden aangenomen dat dit ook het geval is voor elementen als Ra en U. Vergeleken met alkali-elementen worden aardalkali-elementen zeer selectief gebonden.

Evenals bij het natuurlijk veen, bestaat er binnen de groep van de aardalkali-elementen een sterke competerende werking. Zo wordt de sorptie van strontium sterk beinvloed door Ca-ionen; in de praktijk zal de doorbraak van strontium ongeveer samenvallen met die van calcium. Vanwege de geringe voorkeur die gemodificeerde veen tot pH 6,5-7,0 bezit voor strontium t.o.v. calcium, zal de doorbraak van de hardheid iets eerder plaatsvinden dan die van strontium. De competerende werking van Mg op de sorptie van strontium is aanzienlijk kleiner dan van Ca.

Gemodificeerd veen mag derhalve worden beschouwd als een produkt dat zeer geschikt kan worden toegepast bij de zuivering van radioactief besmet water, t.w. zowel voor de produktie van drinkwater als voor de behandeling van radioactief afvalwater.

De toepassing van actieve kool voor de verwijdering van jodium

Indien de aanwezigheid van ^{131}J in het ruwe water niet is te voorkomen, is voor de verwijdering van dit radioisotoop een extra behandeling noodzakelijk. Hiervoor kan actieve kool $+Cl_2$ (eventueel gecombineerd met de toevoeging van een zilverhout) worden gebruikt. Zoals in hoofdstuk VII is gebleken kan met behulp van deze methode, mits althans de sorptie-eigenschappen van de kool voor jodium goed bekend zijn en de condities waaronder de behandeling wordt uitgevoerd goed in de hand worden gehouden, een goede verwijdering van het jodium worden verkregen.

De in dit proefschrift beschreven technieken kunnen worden toegepast voor de behandeling van laag actief radioactief afvalwater voordat dit in oppervlaktewater wordt geloosd en tevens, indien noodzakelijk, worden toegepast bij de zuivering van radioactief besmet oppervlakte- of regenwater ten behoeve van de produktie van drinkwater.

LIST OF SYMBOLS

a	amount water per weight quantity peat; (kg/kg); valency of ion A^{a+}
a_i	activity of species i (mole/l);
b	valency of ion B^{b+};
C_i^{∞}	equilibrium concentration of species i in solution (meq/l);
C_0	concentration of sorbed compound in starting solution (meq/l);
C_t	total concentration in solution (meq/l);
d	diameter of circle with same projected area as the particle (cm);
d_p	mean particle size (cm);
$\mathbb{D}$	diffusion coefficient in solution (cm^2/sec);
$\overline{\mathbb{D}}$	diffusion coefficient in particle (cm^2/sec);
E_{Donnan}	Donnan potential (volt);
f_i	activity coefficient;
F	Faraday constant (coulomb/mole);
F_c	cross section area (cm^2);
G	free energy (erg);
k	partial mass transfer coefficient in solution (cm/sec);
k_p	partial mass transfer coefficient in particle (cm/sec);
K	overall mass transfer coefficient (cm/sec);
K_a	dissociation constant;
K_b	complex constant (Eq. III-20);
K_c	modified complex constant (Eq. III-21);
K_d	distribution coefficient based on equivalent fractions;
K_d'	distribution coefficient based on volume (cm^3/cm^3);
K_d^*	distribution coefficient based on volume and weight (cm^3/g);

K_m	empirical factor of Henderson-Hasselbalch equation;
$K_{A/B}$	selectivity coefficient concerning ion exchange between ions A^{a+} and B^{b+};
m_i	molality species i (mole/kg);
M_i	molecular weight;
n	empirical factor in Henderson-Hasselbalch equation;
N	number of transfer units $(K\bar{S}z/v_0)$;
p	molality of NaCl in starting solution (mole/kg);
P	pressure (atm.);
q	molality of NaOH in starting solution (mole/kg);
q_i	concentration of species i in ion exchanger (meq/cm^3);
q_i^∞	equilibrium concentration of species i in ion exchanger (F meq/cm^3);
Q	total concentration of cations in ion exchanger (meq/cm^3);
r	radial space coordinate (cm);
r_0	radius of ion exchanger particles (cm);
Re_p	Reynolds number $v_0 d_p/(1-\varepsilon)\gamma\nu$;
s	concentration $CaCl_2$ in starting solution (meq/kg);
S	total amount of sites being capable to exchange ions (meq/g);
$\bar{S}$	specific surface area ion exchanger $(6(1-\varepsilon)/d_p$ (cm^3/cm^2);
Sh	Sherwood number $2kr_0/\mathbb{D}$;
Sc	Schmidt number $(\nu/\mathbb{D})$;
v	amount of water present in the ion exchanger (g/g air-dry);
v_f	flow velocity in the packed bed (cm/sec);
v_i	partial molar volume species i (cm^3/mole);
v_0	flow velocity in empty column (cm/sec);
V	volume (cm^3);
V_b	volume of wet peat (cm^3/g air-dry);
V_e	equivalent volume ion exchanger (cm^3/eq. weight);
x	dimensionless concentration (C_i/C_i^∞);
x_w	dimensionless concentration at the interface;
X	amount of cation specifically sorbed (meq/g);
X_i	equivalent concentration of species i in solution;
y	dimensionless concentration in the particle (q_i/q_i^∞);
Y_i	equivalent concentration of species i in ion exchanger;
z	column height (cm);
z_i	valency of species i;
α_{AB}	separation factor (Eq. III-8);
β	fraction of alkali used in the neutralization of peat;
γ	form factor of particles (external surface area $=\frac{1}{4}\pi d^2\gamma$);
δ	thickness laminar film (cm);
ε	porosity bed;
ϕ	osmotic coefficient;
λ	Donnan distribution factor;
η	dimensionless concentration in ion exchanger;
η_i	electrochemical potential of species i (erg/mole);
μ_i	chemical potential of species i (erg/mole);
ν	kinematic viscosity (stoke);
ν_{AY}	number of particles formed in the dissociation of AY;
π	swelling pressure (atm.);
ψ	electric potential (volt);
θ	fraction of sites occupied with a proton;
ζ	solution capacity parameter.

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STELLINGEN

Gatze Lettinga
december 1972.

1.

Het is wenselijk bij de bestudering van de verontreiniging van het milieu door zware metalen meer aandacht te besteden aan de te verwachten belangrijke rol welke in het milieu aanwezige organische stoffen hierbij spelen.

2.

A.I.Berdnikov en medewerkers gaan in hun studie aangaande de sorptie van cobalt aan veen ten onrechte geheel voorbij aan de rol welke in het veen aanwezige oplosbare humuszuren spelen.

A.I.Berdnikov, V.F.Oreshko, V.Przhbyl'skii, Radiokhimiya, 4, 499,1962; 5, 390, 1963; 7, 494,1965.

3.

De concentratiefaktoren van radioisotopen aan rivierslik, zoals die zijn bepaald in modelproeven beschreven in het EURATOM-rapport EUR-3741f, zijn geenzins representatief voor de mate van concentrering van radioisotopen aan het slik, zoals die in het riviersysteem onder natuurlijke omstandigheden zal optreden.

"ETUDE GENERAL DE LA RADIOACTIVITE DU BASSIN DU RHIN", EUR-3741f,1968.

4.

De conclusie van Buzzell en Sawyer ten aanzien van de noodzaak tot verdere evaluatie van de titratiemethode voor de bepaling van vluchtige vetzuren volgens Diallo en Albertson, is door McGhee ten onrechte in negatieve zin geinterpreteerd.

F.J.McGhee, Water Sew.Works, 162, 1968.
J.C.Buzzell, C.N.Sawyer, J.Water Poll.Control Fed.,35, 205,1963.
R.Dilallo, O.E.Albertson, J.Water Poll.Control Fed.,33,356,1961.

5.

In de "relatieve rate factor" geintroduceerd door Weber c.s. voor de beschrijving van adsorptieverschijnselen aan aktieve kool wordt onvoldoende rekening gehouden met de theorie van de adsorptiekinetiek, waarbij sprake is van een correlatie met de relatieve concentratie t.o.v. de evenwichtstoestand. Als gevolg daarvan worden onjuiste conclusies getrokken over de mate waarin en de wijze waarop de snelheid van adsorptie door een aantal van de door hen onderzochte parameters worden beïnvloed.

W.J.Weber, J.C.Morris, AWTR-16,1966.
W.J.Weber, in "Principles and Applications of Water Chemistry" S.D.Faust, J.V.Hunter, New York, 1967.

6.

De verklaring voor het door Wille waargenomen "kolomeffekt", inhoudende het bereiken van een hogere beladingsgraad van a-kool met fenol in kolomexperimenten in vergelijking met ladingsgewijs uitgevoerde experimenten, moet worden gezocht in het feit, dat in de ladingsgewijs uitgevoerde experimenten zich geen volledig evenwicht heeft ingesteld en in de kolom chemische en microbiologische omzettingen van het adsorbaat plaatsvinden.

H.Wille, proefschrift, Karlsruhe, 1971.

7.

De door Middlebrooks c.s. gesuggereerde doelmatigheid van de door hen voorgestelde methode voor de verwijdering van radioisotopen uit water door middel van klei is twijfelachtig, omdat onvoldoende rekening wordt gehouden met de aanwezigheid van concurrerende ionen.

E.J.Middlebrooks, W.A.Goldsmith, J.Amer.Water Works Ass.,58,1052,1966.
E.J.Middlebrooks, C.L.Sumrall, J.Amer.Water Works Ass.,60,485,1968.

8.

De bewering van Jellinek en medewerkers, dat met polygalacturonzuur en andere natuurlijke polyelektrolyten effektief - en in vergelijking met ionenuitwisseling voor de praktijk zelfs op eenvoudiger wijze - zware metaalionen uit verontreinigd afvalwater kunnen worden verwijderd en teruggewonnen, is aanvechtbaar.

H.H.Jellinek, S.P.Sangal,Water Research, 6,305,1972;
H.H.Jellinek, M.D.Luh, J.Polymer Sci.,A-1,7,2445,1969.

9.

Met het oog op de belangrijke principiële voordelen welke een anaeroob biologische zuivering van afvalwater biedt boven overeenkomstige aerobe methoden, met name inzake de mogelijke conservering van materiaal en energie, verdient het aanbeveling het onderzoek op dit terrein - zowel in fundamenteel als toegepast opzicht - krachtiger ter hand te nemen.

10.

Tegen de door Block en Schneider toegepaste onderzoekmethodiek en gegeven interpretaties van resultaten aangaande de te verwachten retentie van geloosde radioisotopen in de Rijn, zijn enige ernstige bedenkingen in te brengen.

W.Block, H.Schneider, Gas Wasserfach, 108,1249,1967;109,1178,1410,1968,110,647, 1969.

11.

Het verdient aanbeveling om de wetenschappelijke onderzoekingen verricht aan universiteiten en hogescholen - die nog niet voor publikatie in aanmerking komen frequent in de vorm van samenvattingen bekend te maken. Dit is van belang voor een goede informatie van de maatschappij en van andere onderzoekers in het bijzonder.

12.

De bewering van Clark en Speece dat bij de methaangisting van azijnzuur, diverse op elkaar volgende en gelijke pH-verlagingen eenzelfde mate van remming teweeg brengen, wordt door de hen gepresenteerde resultaten niet bevestigd.

R.H.Clark, R.E.Speece,paper 5th Intern.Water Poll.Res.Conf.,1971.

13.

Belangrijke technisch maatschappelijke projekten te financieren uit gemeenschapsgelden verlangen, meer dan tot nu toe is gebeurd, een degelijke wetenschappelijk technische evaluatie gebaseerd op onderzoek en eveneens een bestudering van de motieven, resultaten, adviezen en technische uitvoeringsvorm door onafhankelijk objektieve deskundigen. Een uiterst nuttige en zinvolle taak ligt hier voor universiteiten en hogescholen, onder meer in het kader van de aan deze instellingen door de Wet toebedachte taak aandacht te besteden aan de bevordering van maatschappelijke verantwoordelijkheidsbesef, en een organisatie als TNO, krachtens de haar bij de Wet van 30 oktober 1930 gegeven taakstelling.

14.

Voor het scheppen van een prettige werksituatie zou de invoering van een "tweerichtings personeelsbeoordelings systeem" - waarin met betrekking tot het te beoordelen personeelslid evenveel waarde wordt toegekend aan het oordeel van zijn/haar ondergeschikten als aan dat van zijn/haar superieuren - van groot nut kunnen zijn.

15.

Gezien de immer slinkende tijd welke vele hoogleraren, als gevolg van hun steeds groeiende belasting met meer of minder noodzakelijke zaken van zeer verschillende aard, beschikbaar hebben voor de begeleiding van hun promovendi en voor de beoordeling van het uiteindelijke resultaat van hun werkzaamheden, is het gewenst dat de mogelijkheid wordt gecreëerd dat ervaren en competente wetenschappelijke medewerkers als begeleider en promotor op kunnen treden. Hiermee kan worden bevorderd dat een promotie binnen aanvaardbare tijd zijn beslag krijgt, dat er tijdens de werkzaamheden regelmatig meer intensief overleg plaatsvindt en dat in het laboratorium aanwezig wetenschappelijk talent zich beter kan ontplooien.

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