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**Formation and transport of americium
pseudocolloids in aqueous systems**

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FORMATION AND TRANSPORT OF AMERICIUM PSEUDOCOLLOIDS IN
AQUEOUS SYSTEMS

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SUMMARY

The sorption of americium on colloidal quartz and montmorillonite has been studied using a batch technique. The influence of physical and chemical parameters such as storage time (6 h - 6 months), the amount of sorbent material (0.2 g, 0.4 g, 0.8 g per 20 ml solution) and the pH value (6 - 10) has been investigated.

Americium appeared to be distributed between all available surfaces in the system (particles and vessel walls). Distribution coefficients, defined as the ratio of the amount of americium per mass of colloidal matter and the concentration in the solution phase, were estimated to be of the same order of magnitude as obtained in measurements on crushed material of much larger particle sizes.

In the presence of sorbents (alumina or granite) the removal of americium from the solution was enhanced. This can be due to either the desorption of the americium from the particle phase and resorption on all available surfaces or the sorption of the whole colloidal aggregates on the sorbents.

Column experiments, with alumina or granite packing, have also been carried out in order to study the transport of americium sorbed on colloidal matter (here denoted as americium pseudocolloids). No breakthrough was observed after eluting with large volumes of aqueous phase. However, a minor fraction of the americium passed through the column without significant retention, especially under conditions with high flow rate.

CONTENTS	Page
1. INTRODUCTION	1
2. EXPERIMENTAL	1
2.1. Radionuclides and chemicals	1
2.2. Batch experiments	2
2.3. Column experiments	2
3. RESULTS	3
3.1. Removal from the solution phase	3
3.2. The centrifugable fraction	5
3.3. Batch-wise sorption studies	7
3.4. Column experiments	11
4. CONCLUSIONS	12
5. ACKNOWLEDGEMENTS	13
6. REFERENCES	13

1. INTRODUCTION

The transport of radionuclides from a geologic repository is influenced by the interaction of the dissolved trace nuclides with the various solid agents, which are present in the repository and its environments. For cationic hydrolyzed elements, like the actinides in their lower oxidation states (III and IV), the sorption on construction materials, back-fill materials and geologic materials is very high. The formation of low-sorbing complexes or the sorption of the trace nuclides on naturally occurring colloidal matter (pseudocolloids) can, however, drastically increase the mobility of the trace radionuclides. It has e.g. been observed that the tetravalent fall-out plutonium from weapons tests tends to be associated with particulates in the soil (1).

The purpose of the present work was to get quantitative information on the sorption of trivalent americium on colloidal montmorillonite and quartz, especially the effects of the presence of colloidal matter on the distribution of americium between an aqueous phase, a particulate mobile phase and stationary solid surfaces.

2. EXPERIMENTAL

2.1. Radionuclides and chemicals

The radionuclide used in the experiments was ^{241}Am (433 y). The samples were measured in a NaI well-type scintillation counter.

The colloidal solutions were prepared by stirring crushed quartz and montmorillonite, respectively, with distilled water for two weeks. After settling for about one week, a fraction of the supernatant liquid was separated from the solid material by centrifugation, and the size distribution of the colloidal particles in the liquid phase was measured by a laser technique (2). For the quartz system the average particle diameter was about 300 nm and for the montmorillonite about 525 nm (with respect to the total number of particles).

Crystalline alumina ($\alpha\text{-Al}_2\text{O}_3$; particle size of 0.090 - 0.125 mm or 0.125 - 0.250 mm) and granite from Stripa (0.090 - 0.125 mm) (3) were used as sorbent materials both in the batch and the column experiments.

2.2. Batch experiments

Batch experiments were made in order to investigate the formation of americium pseudocolloids with quartz and montmorillonite and the sorption of such colloidal particles on solid materials. The solution containing the colloidal quartz or montmorillonite was poured into 50 ml polypropylene centrifuge tubes (20 ml in each tube). Americium was added to a concentration of about 10^{-9} M. The pH was adjusted to desired value with NaOH or HClO_4 . The tubes were centrifuged, solution samples were withdrawn and then the tubes were shaken vigorously and new solution samples were taken. This procedure was repeated after various storage times. Similar experiments have been made previously in americium solutions initially free from particulate matter (4).

The sorption studies were carried out in a similar way. Solutions were made as described above. After storage for one week, solid material (alumina or granite) was added to the tubes and the distribution between the solid and solution phases was measured as a function of pH and time.

The following conditions were selected for the experiments:

- pH was adjusted to a value between 6 and 10 at the start of the experiments. No corrections of the slight changes of pH with time were made.
- The initial concentration of colloidal particles was 0.32 mg/ml for the quartz systems and 2.4 mg/ml or 0.24 mg/ml for the montmorillonite systems; aqueous phase was 0.01 M NaClO_4 .
- The centrifuging speed was 6000, 10000 and 17000 rpm (corresponding to a maximum of 27000 g) and the centrifuging time 30 min.
- The amount of sorbent material was 0.2 g, 0.4 g or 0.8 g/tube (20 ml).
- The storage time was 6 h, 1 d, 1 w, 6 w and 6 months.

2.3. Column experiments

Column experiments were performed in order to study the mobility of americium pseudocolloids in contact with potential sorbents. Quartz or montmorillonite colloids containing americium were injected in columns (ca 11 cm x 4 mm HPLC steel columns) packed with alumina or granite, which was preequilibrated with a synthetic groundwater (ca 120 mg/l of dissolved solids, pH 8.2 (5)). The columns were then eluated with the same synthetic groundwater with variation of the flow-rate (0.05 ml/min or 0.5 ml/min).

The column volumes were determined by injection of a pulse of Na-22, which was assumed to pass through the column with little retention.

3. RESULTS

3.1. Removal from the solution phase

The removal of americium from the solution phase by centrifugation at 17000 rpm (27000 g) is illustrated in Figure 1.

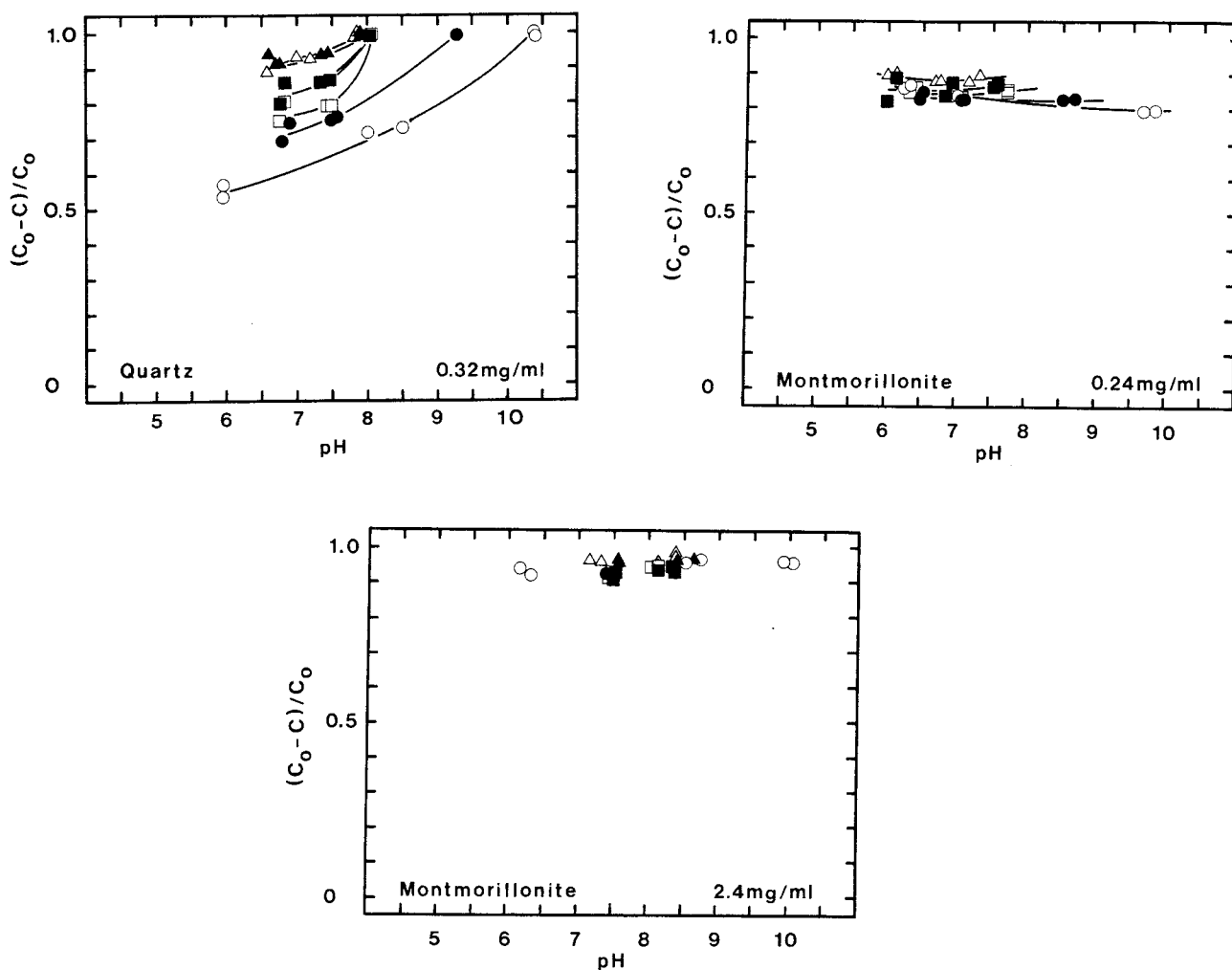


Fig. 1. Removal of americium from pseudocolloid solutions of quartz and montmorillonite after centrifugation (17000 rpm, 30 min) and after various storage times.

○ = at the start, ● = 6 h, □ = 1 d, ■ = 1 w, △ = 6 w, ▲ = 6 months.

For the quartz system, more than 50% of the added americium was immediately removed from the solution (centrifugation and sampling directly after the addition of the americium stock solution). The removable fraction increased with time and reached a maximum of 90 - 100% after 6 w. Further storing (up to 6 months) did not change this removal. There was also a change in pH during the first day, giving a pH-range of 6.5 - 8, which was essentially constant from 1 day to 6 months.

For the montmorillonite system there were two initial concentrations of the colloidal particles. At the low concentration, 0.24 mg/ml, the removable fraction was 80 - 90% already at the start. This fraction did not change significantly with time. Neither for the high concentration system (2.4 mg/ml) was there any change in the removal after the first hours. The removal was, however, somewhat higher (up to 95%) for this system. The pH value was changing to its final range within 1 day, even for the montmorillonite solutions, but these pH-ranges were somewhat different for the two concentrations. At the high concentration the range was between pH 7 and 8.5 and at the low concentration between pH 6 and 7.5.

The removal of activity from the solution phase was more rapid than in a system free from particles (4). Also the fact that the removal was mostly independent of pH, which was not the case in the absence of particles, indicates an association to centrifugable particles and not only sorption on the vessel walls. However, also in the absence of any initially added particle fraction between 50 and 90% of the americium was removed from the solution after 6 months of storage, primarily due to sorption on the vessel walls (4).

Figure 2 shows the removal of americium at different centrifugation speeds. In the quartz system there was no significant difference between the various centrifugation speeds, which indicates that the activity was associated with predominantly large particles. So there seems not to be any larger variation in particle sizes in the original colloidal quartz solution. Neither was there any drastic change in size during the experimental time. However, for the montmorillonite system there appeared to be a significant difference in the removal of americium for various centrifugation speeds. This indicates a larger size distribution in the original colloidal montmorillonite solution. The difference between the various centrifugation speeds decreased with increasing storage time, indicating an increase of the particle size with time.

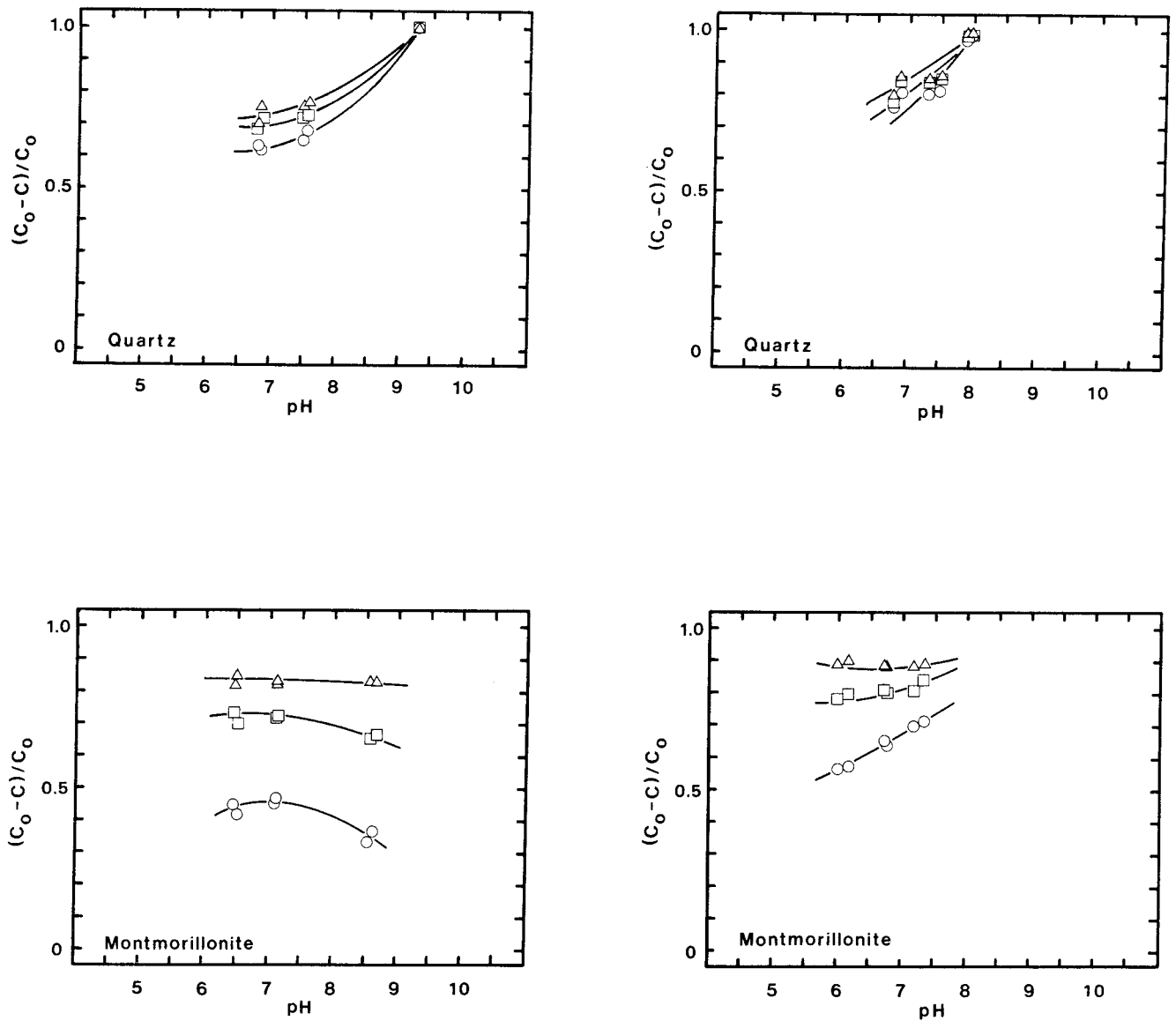


Fig. 2. Removal of americium from pseudocolloid solutions of quartz and montmorillonite after centrifugation at various speeds.

○ 6000 rpm, □ 10000 rpm, △ 17000 rpm,
(6 h, left and 6 w right)

3.2. The centrifugable fraction

A comparison of the removable fractions after centrifugation and after vigorous shaking gives some indication of the proportions of the americium that was sorbed on the added particles and on the vessel walls, Figure 3.

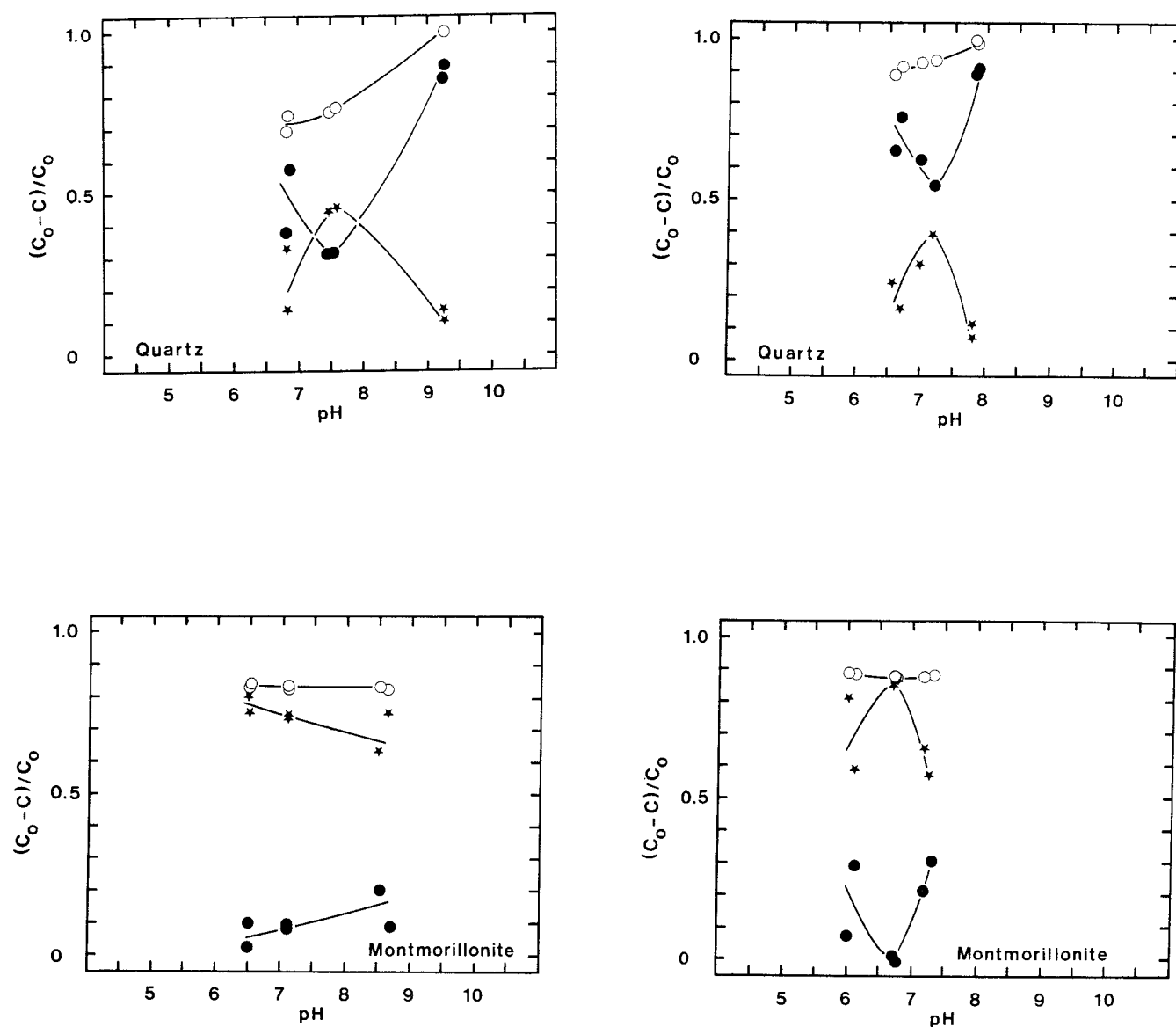


Fig. 3. The centrifugable americium pseudocolloid fraction after various storage times (6 h, left and 6 w, right)

- after centrifugation, 17000 rpm
- after shaking
- ★ centrifugable fraction

After 6 h about 10 - 40% of the americium was associated with particles in the quartz system, with the maximum around pH 7.5. Although the total amount of americium that was removed from the solution increased with time (up to 6 w), the particle fraction appeared to be constant. This indicates that also sorption on the vessel walls is of importance just as was observed previously (4).

In the montmorillonite system about 60 - 80% of the americium seemed to be associated with the particle fraction. Apparently, the sorption on the particle phase dominates over the sorption on the vessel walls.

Both quartz and montmorillonite would have a negative lattice charge in the present pH-range (6-8). Thus, since americium exists mostly as cationic species in the corresponding solutions (9), the observed sorption is reasonable, considering the charge distribution. An estimation of the total surface provided by the added quartz and montmorillonite aggregates (assuming spherical particles defined by the average diameter) indicates, that the particle surfaces in both systems are of the same order of magnitude. These total surfaces are at least one order of magnitude larger than the surface provided by the vessel wall. Thus, the sorption on the particles can be expected to dominate in the system, although the sorption on the vessel can not be neglected (cf. ref 4).

From the calculated americium fraction associated with particles, Figure 3, a formal distribution coefficient can be calculated, defined as (concentration in particle phase)/(concentration in solution). For the quartz and montmorillonite systems values in the range 0.2 - 0.4 m³/kg and 6 - 16 m³/kg respectively, are obtained. These values are in fair agreement with data from batch-wise studies for pure mineral-groundwater systems in the corresponding pH-ranges (6).

3.3. Batch-wise sorption studies

The removal of americium from colloidal quartz and montmorillonite solutions in contact with alumina and granite was studied.

For the quartz system, the removal seemed to be more rapid in the presence of a macroscopic sorbent than in the absence of such a solid, and the maximum removal reached almost 100% after 6 w storage time. Also for the montmorillonite system the removal was rapid and the maximum removal was about 95%, which was higher than for the system without sorbent (Figure 4).

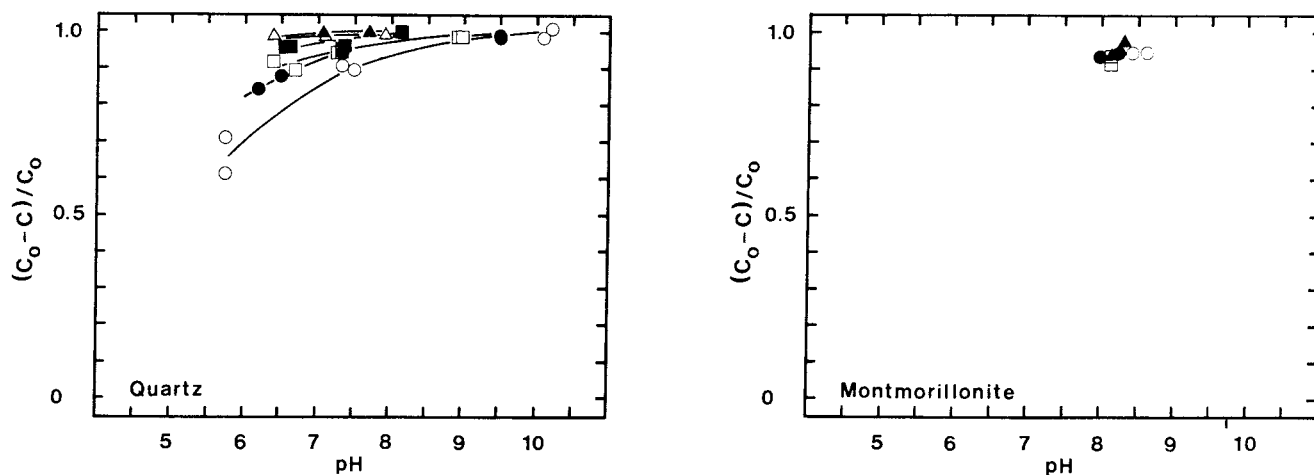


Fig. 4. The removal of americium from pseudocolloid solutions in presence of alumina (10 g/l, 0.090 - 0.125 mm, 17000 rpm) after various storage times.

○ at the start, ● 6 h, □ 1 d, ■ 1 w, △ 6 w, ▲ 6 months

Figure 5 shows that the sorption behaviour was very similar in the alumina and granite systems. No significant differences between the two sorbents could be noticed. Neither had the particle size (0.090 - 0.125 or 0.125 - 0.250 mm) any observable influence on the removal.

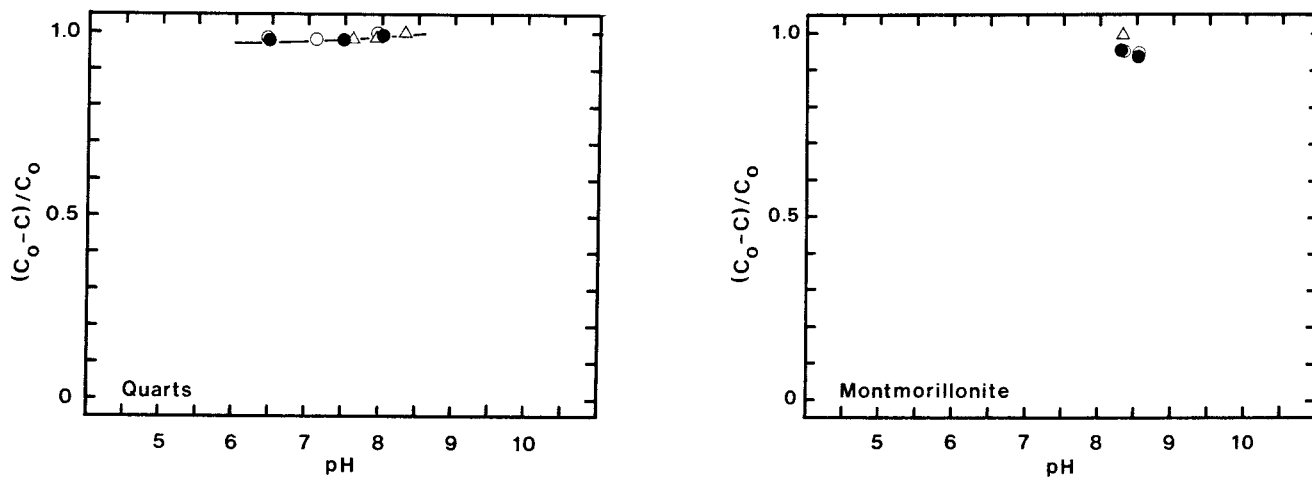


Fig. 5. The removal of americium from pseudocolloid solutions in presence of solid sorbents (10 g/l, 17000 rpm) after 6 w storage time.

○ Al_2O_3 , 0.090 - 0.125 mm; ● Al_2O_3 , 0.125 - 0.25 mm;
 △ Stripa granite, 0.090 - 0.125 mm.

The removal of americium both before and after centrifuging at 17000 rpm at various storage times are illustrated in Figure 6.

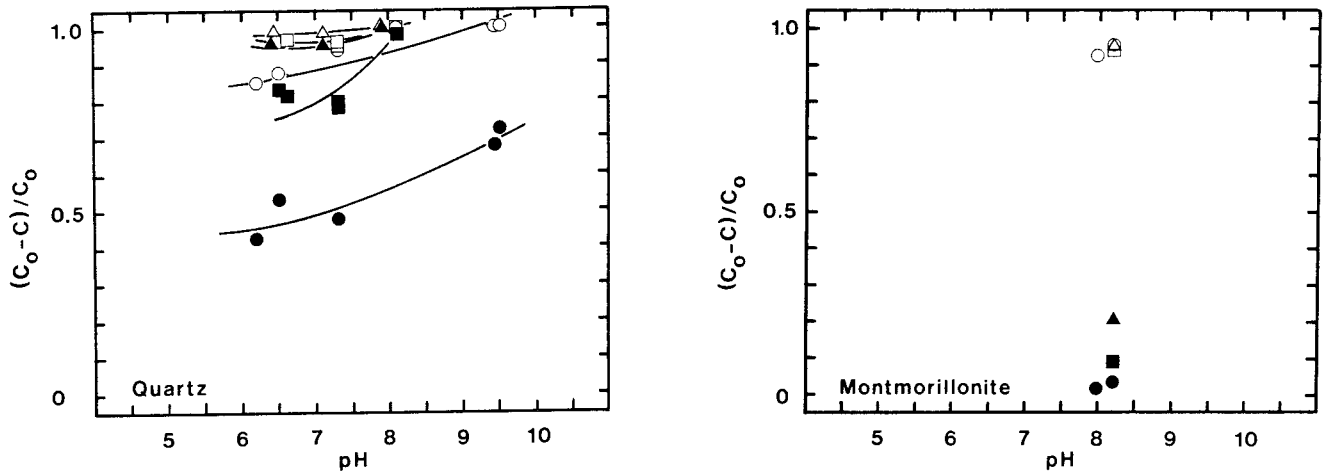


Fig. 6. The removal of americium from pseudocolloid solutions in presence of alumina (10 g/l, 0.090 - 0.125 mm) after various storage times and before and after centrifuging at 17000 rpm.

● 6 h, before; ○ 6 h, after; ■ 1 w, before; □ 1 w, after;
▲ 6 w, before; △ 6 w, after.

For quartz there was a significant difference after 6 h but this difference decreased with the storage time and after 6 w it was very small. For the montmorillonite system this difference was much greater than for the quartz system, indicating that most of the activity is associated to centrifugable particles.

The amount of sorbent had no influence on the removal of americium from the solutions, as illustrated in Figure 7.

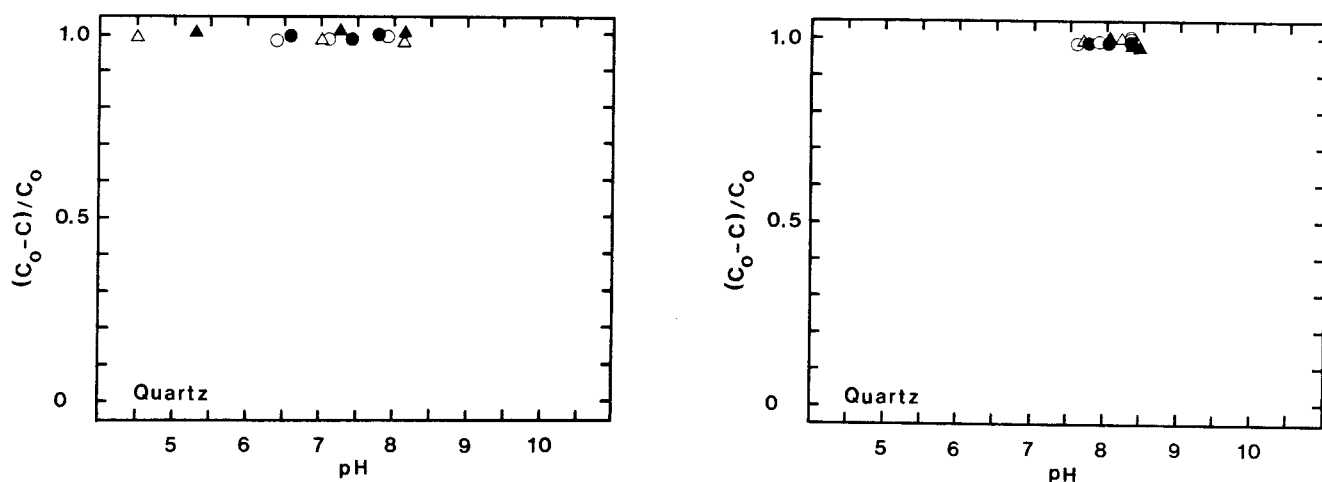


Fig. 7. The removal of americium from pseudocolloid solutions in presence of various amounts of solid sorbents after 6 w storage time and centrifuging at 17000 rpm. (Al_2O_3 , 0.090 - 0.125 mm, left and Stripa granite 0.090 - 0.125 mm, right)

○ 10 g/l, ● 10 g/l + 10 g/l after 1 w, △ 20 g/l, ▲ 40 g/l

A desorption of americium from the particle phase (quartz or montmorillonite) and distribution on all available surfaces (particles phase plus sorbent phase) could explain the observed behaviour. The time for such a new distribution appears to be of the order of several weeks. The somewhat lower final value in the alumina-montmorillonite system in comparison with the alumina-quartz system would be expected, considering the much higher sorption on montmorillonite than on alumina and therefore certain preference for montmorillonite in the montmorillonite-alumina mixture.

Evidently, the surfaces provided by 0.2 g of solid sorbent are large enough that no loading effects can be observed. Any effects of particle size or amount of sorbent in the system should therefore have been studied at much lower sorbent/volume ratios.

The observed removal of americium from the solution phase can be due to two different mechanisms:

- The americium is partly desorbed from the particle phase and redistributed on all available surfaces (particles plus sorbent) in the system.
- The whole colloidal aggregates (quartz or montmorillonite) are sorbed on the solid.

Possibly both processes are occurring. At least alumina would have a positive surface charge in the pH-range of the experiment (7,8) which would attract the negatively charged colloidal aggregates. The exact mechanism can, however, not be concluded from the present data.

3.4. Column experiments

The results from the column experiments are summarized in Table I.

Table I. Mobility of americium pseudocolloids in columns packed with alumina or granite.

Sorbent ^a	Colloidal ^b carrier	Initial pH	Flow rate ml/min	Eluation ^c %	Max. volume ^d
a	Qz	6	0.05	0.2	120
a	Qz	6	0.5	0.3	25
a	Qz	8	0.05	0.5	95 ^e
a	Qz	8	0.5	6.0	200
a	Mo	8	0.05	0	90
a	Mo	8	0.5	6.2	250
b	Qz	8	0.05	0	150
b	Mo	8	0.05	0.2	350
b	Mo	8	0.5	4.4	120
c	Qz	8	0.05	0	140
c	Qz	8	0.5	0.3	220
c	Mo	8	0.05	0.1	380
c	Mo	8	0.5	3.2	210

^a a = Al₂O₃, 0.090 - 0.125 mm; b = Al₂O₃, 0.125 - 0.250 mm; c = Stripa granite, 0.090 - 0.125 mm

^b Qz = quartz, Mo = montmorillonite

^c Fraction passing through the column (average of two runs) with little retention (calibration with Na-22); 0 indicates no significant activity above background

^d Maximum volume (number of column volumes) that passed through the column (without break-through in any case)

^e Ca 880 column volumes in one column with the dimensions 23 cm x 4 mm.

In all of the experiments with the high flow rate (0.5 ml/min) and in some of the systems with the low flow rate (0.05 ml/min) a minor fraction of the americium passed through the column without significant retention. Evidently the short contact time during especially the high flow rate (a few minutes) is not sufficient for the establishment of a new sorption equilibrium between americium, quartz or montmorillonite particles and column filling. No break-through was observed in any of the systems (after elution with up to 880 column volumes). No significant differences in performance between the various column filling materials could be observed under the present experimental conditions.

4. CONCLUSIONS

Americium appeared to be sorbed on quartz and montmorillonite particles of colloidal size. The apparent distribution coefficients related to the distribution between the particle phase and solution was similar to values obtained with crushed minerals of much larger particle size. Evidently, the americium was distributed over all available surfaces (on particulates as well as vessel walls).

The removal of americium was more rapid and enhanced in the presence of a sorbent (alumina or granite) with macroscopic surfaces. However, the mechanism for the americium distribution (desorption from the particle phase and resorption on all available surfaces or sorption of the whole colloidal quartz or montmorillonite carriers on the sorbent) could not be concluded.

A minor fraction of pseudocolloidal americium passed through a column with alumina or granite with little sorption. Slow kinetics for the desorption-resorption process is a possible reason for the existence of this mobile fraction (very short hold-up time in the column). No break-through was observed after up to 880 column volumes of eluate solution.

A sorption of americium on all exposed surfaces (particles as well as the surfaces and pores of water-carrying fissures etc) would be expected under the conditions in a geologic repository. Formation of a highly mobile, non-sorbing particle fraction does not appear probable.

5. ACKNOWLEDGEMENT

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