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The Sorption of ^{210}Pb , ^{210}Bi and ^{210}Po on Montmorillonite: A Study with Emphasis on Reversibility Aspects and on the Effect of the Radioactive Decay of Adsorbed Nuclides*

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Radionuclides / Montmorillonite / Migration / Adsorption / Desorption / Lead / Bismuth / Polonium

Summary

The influence of the ionic strength and of pH on the adsorption/desorption processes of Pb, Bi and Po on montmorillonite has been investigated. For Pb, a strong dependence of the adsorption and desorption processes on the ionic strength was observed at $\text{pH} < 7$, whereas, at higher pH values, this dependence totally disappears. The ionic medium had no influence on the sorption/desorption of both Bi and Po. For all of these nuclides, large distribution ratios (R_d) are measured. They range from 10^3 to $10^5 \text{ ml} \cdot \text{g}^{-1}$ for Pb and from 10^4 to $10^7 \text{ ml} \cdot \text{g}^{-1}$ for ^{210}Bi and ^{210}Po . When adsorption and desorption coefficients are compared, an agreement is found for both adsorption/desorption R_d 's of Pb, whereas, for Bi and Po adsorption R_d 's were several orders of magnitude lower than those obtained for desorption. The chemical activities of free Bi and Po in the liquid phase are limited by the formation of Bi and Po-colloids prior to the sorption step. This fact could explain the differences in the R_d values. While the adsorption of Pb was reversible, only very small amounts of Bi and Po could be desorbed from the montmorillonite (quasi-irreversible adsorption).

The radioactive decay of adsorbed ^{210}Pb to ^{210}Bi , which in turn decays to ^{210}Po , can lead to significant changes in the desorption behaviour of the daughter nuclides. Whereas the sorption is nearly irreversible if Bi and Po adsorb on montmorillonite from the aqueous phase, they desorb more easily if they are generated by the radioactive decay of adsorbed ^{210}Pb . The difference in the distribution coefficients R_d is approximately one order of magnitude in the case of Po, and more than 2 orders of magnitude in the case of Bi.

1. Introduction

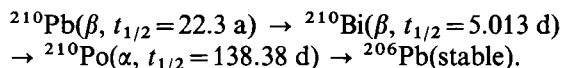
The study of the migration behaviour of radionuclides in the underground system has been emphasized for the last 20 years. For strongly sorbing radionuclides (i.e. for which the distribution coefficient R_d exceeds a value of $10^4 \text{ ml} \cdot \text{g}^{-1}$) sorption onto the non-transportable rock may enhance retardation but the sorption on colloids could have a significant influence on migration processes if the colloid concentration is sufficiently high ($> 1 \text{ ppm}$) and colloids are mobile. Things are even worse if adsorption on the colloids is irreversible and no colloid retention occurs in the

hydrogeological system. Under such conditions, the contaminated colloids could be transported over long distances [1, 2] if the colloids are enough stable. In order to assess the possible influence of colloids on the migration of radionuclides, the adsorption/desorption behaviour needs to be known. In this work, ^{210}Pb , ^{210}Bi and ^{210}Po are selected as examples of bi-, tri- and tetravalent radionuclides, respectively. Special attention must be paid to the speciation of the metal ions in the aquatic phase. The hydrolysis of lead is significant at pH larger than 6 for a total Pb concentration of 10^{-5} M [3]. For Bi, the situation is completely different. Bi^{3+} is stable only in strongly acidic medium. At pH 6, it forms a large variety of hydroxo-complexes [4]. Few data are available on the speciation of Po. Redox calculations performed with the data of Bard *et al.* [5] show that Po(IV) is the predominant redox state under oxic conditions ($P_{(\text{O}_2)} = 0.2 \text{ bar}$). However, Po^{4+} exists only in strongly acidic media. The presence of hydroxo-species (e.g. $\text{Bi}(\text{OH})_3$ and $\text{PoO}(\text{OH})_2$) suggests that Bi and Po can generate colloids in neutral or slightly acidic solutions. Furthermore, Paneth [6, 7] found that these elements form colloids under such conditions while Pb does not. Starik [8] pointed out that those colloids contain great numbers of radioactive atoms and may be formed at concentrations far below the solubility product. Lieser *et al.* [9] mentioned that the solubilities of sparingly soluble oxides or hydroxides are frequently not well defined. They depend on the composition and the pretreatment of the solid, the solubility of which is considered. Stabilized colloids may exist in water in concentrations above or below solubility limits as long as equilibria are not established.

In this work, montmorillonite was selected as clay representatives for different systems. The montmorillonites are the most important component of bentonites (65–99%), which are proposed as filling and sealing material in various repositories for nuclear waste. Furthermore, montmorillonite is a clay with a high cation exchange capacity [10]. Possible repository sites in Switzerland lie within clay (e.g. Opalinus clay) or granite formations, where groundwater colloids are composed partially of clay [11]. In order to assess the adsorption reversibility, adsorption and desorption experiments were performed.

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^{210}Bi and ^{210}Po can be sorbed on the montmorillonite by two different processes. Either they can be sorbed from solution or they can be generated by the radioactive decay of ^{210}Pb adsorbed at the particles, in the following way:

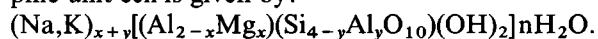


It is to be expected that the local chemical environments of Bi and Po at the clay surface may be different according to which of the two processes has taken place (caused by the different speciations of Pb, Bi and Po in solution, and by differences in the adsorptive behaviour of Pb, Bi and Po). The two adsorption processes could therefore lead to a difference in the desorption behaviour. In addition, hot chemical effects could also contribute to these differences.

2. Experimental

2.1. Montmorillonite

For these experiments, a sodium montmorillonite was used. Montmorillonites belong to the three-layer silicates and their structure is described by Hofmann *et al.* [31]. The ions in the interlayer are exchangeable and therefore the montmorillonite has the capability to swell. The general formula of the crystallographic unit cell is given by:



When Al^{3+} is replaced by Mg^{2+} in the octahedral layer, or when Si(IV) is replaced by trivalent metal ions like Al^{3+} or Fe^{3+} in the tetrahedral layers, the $(\text{Na}, \text{K})_{x+y}[(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_{4-y}\text{Al}_y\text{O}_{10})(\text{OH})_2]$ unit cell acquires a net negative charge which has to be compensated by the same amount of positive charge in the interlayer (mostly Na, Ca or K). x and y are equal to the charges in the octahedral and in the two tetrahedral layers, respectively. For montmorillonite, x is typically between 0.2 and 0.6 per $(\text{Na}, \text{K})_{x+y}[(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_{4-y}\text{Al}_y\text{O}_{10})(\text{OH})_2]$ unit, whereas y is much lower than x , with values between 0 and 0.04 [10].

The cation exchange capacity of the sample used is $7.64 \times 10^{-4} \text{ eq} \cdot \text{g}^{-1}$ and its specific surface is $31.8 \text{ m}^2 \cdot \text{g}^{-1}$ (N_2 -BET) [12]. In this study, the inventories of all sorbing nuclides were several orders of magnitude lower than the cation exchange capacity.

The colloid and particle size distribution was determined by ultrafiltration and subsequent scanning electron microscope analysis. The montmorillonite particle size ranges from 40 to 6000 nm. Table 1 gives the normalized size distribution. When the values of Table 1 are used to calculate the specific surface of hypothetically spherical particles, a value of $6 \text{ m}^2 \cdot \text{g}^{-1}$ results, which is significantly lower than the value obtained by the BET-method. The difference can be explained by the fact that the particles are not spheres with a smooth surface, but are mostly flat and have very rough surfaces.

The filtration cut-off selected for this study was 30 nm. It was sufficient to collect all significant fractions of colloids for which normal mass distribution shows a maximum around 2000 nm and a maximum for the normal surface distribution around 300 nm.

A stock suspension of 2000 ppm was prepared in suprapure Milli-Q water. The suspension was treated for some minutes in an ultrasonic bath prior to being used in the adsorption and desorption experiments.

2.2. Radionuclides and analytical tests

The solution of ^{210}Pb was delivered by the Physikalisch-Technische Bundesanstalt in Braunschweig (Germany). The concentrations in this solution were 0.5 M HNO_3 , $9.1 \times 10^{-5} \text{ M Pb(NO}_3)_3$, $7.6 \times 10^{-5} \text{ M Bi(NO}_3)_3$, $2.37 \times 10^{-6} \text{ M }^{210}\text{Pb}$. The ^{210}Pb activity in this solution was 1.407 MBq per gram of solution. ^{210}Bi and ^{210}Po were in secular equilibrium with ^{210}Pb .

Due to the short half-lives of Bi and Po, their activities are subject to change during the course of an experiment (2–3 weeks), which must be corrected for. The activity of ^{210}Bi depends on both the activity of ^{210}Bi at the time $t=0$ and on the activity of its parent nuclide ^{210}Pb , according to the following equation:

$$\begin{aligned} A(^{210}\text{Bi}, t) &= A(^{210}\text{Pb}, t=0) * (1 - e^{-\lambda_2 t}) \\ &+ A(^{210}\text{Bi}, t=0) * e^{-\lambda_2 t} \end{aligned}$$

where $A(^{210}\text{Bi}, t)$ is the activity of ^{210}Bi at time t , λ_2 is the decay constant of ^{210}Bi and $A(^{210}\text{Pb}, t=0)$ and $A(^{210}\text{Bi}, t=0)$ are the activities of ^{210}Pb and ^{210}Bi at the time $t=0$, respectively. Since the half-life of ^{210}Pb (22.3 a) is much longer than the experimental work time, losses caused by radioactive decay are negligible.

The activity of ^{210}Po as a function of time can be calculated by a similar equation. Because the half-life of ^{210}Bi is much shorter than the half-lives of ^{210}Pb and of ^{210}Po , the following simplification can be used: although the decay of ^{210}Pb to ^{210}Po proceeds through the intermediate product ^{210}Bi , in the kinetic equation it can be treated as if the decay of ^{210}Pb proceeded directly to ^{210}Po . Therefore, the time dependence of the ^{210}Po activity can be described by the following equation:

$$\begin{aligned} A(^{210}\text{Po}, t) &= A(^{210}\text{Pb}, t=0) * (1 - e^{-\lambda_3 t}) \\ &+ A(^{210}\text{Po}, t=0) * e^{-\lambda_3 t} \end{aligned}$$

where $A(^{210}\text{Po}, t)$ is the activity of ^{210}Po at time t , λ_3 is the decay constant of ^{210}Po . $A(^{210}\text{Pb}, t=0)$ and $A(^{210}\text{Po}, t=0)$ are the activities of ^{210}Pb and ^{210}Po at the time $t=0$, respectively. During the desorption experiments, corrections were made for the activities of ^{210}Bi and ^{210}Po in both the liquid and the solid phases.

The activities of ^{210}Pb , ^{210}Bi and ^{210}Po were determined with a Packard liquid scintillation unit. In the liquid scintillation spectrum, the individual spectra of the studied nuclides overlap; however, selection of the

Table 1. The normal distributions (relative distributions of number, mass and surface) of montmorillonite, determined by SEM analysis

Conditions: [coll]=1 ppm, volume=2 ml, φ colloidal particle size, s_{coll}: colloid surface per liter solution.

φ nm	d[coll]/dφ pt · l ⁻¹ · nm ⁻¹	d[coll]/dφ ppt · nm ⁻¹	ds _{coll} /dφ nm ² · l ⁻¹ · nm ⁻¹
0 – 40	—	—	—
40 – 100	7.8 × 10 ⁷	2.8 × 10 ¹	1.2 × 10 ¹²
100 – 200	2.4 × 10 ⁷	8.4 × 10 ¹	1.7 × 10 ¹²
200 – 400	1.6 × 10 ⁷	4.4 × 10 ²	4.4 × 10 ¹²
400 – 1000	1.4 × 10 ⁶	4.9 × 10 ²	2.1 × 10 ¹²
1000 – 2000	2.3 × 10 ⁵	8.1 × 10 ²	1.6 × 10 ¹²
2000 – 4000	3.1 × 10 ⁴	8.7 × 10 ²	8.7 × 10 ¹¹
4000 – 6000	5.0 × 10 ³	6.6 × 10 ²	4.0 × 10 ¹¹

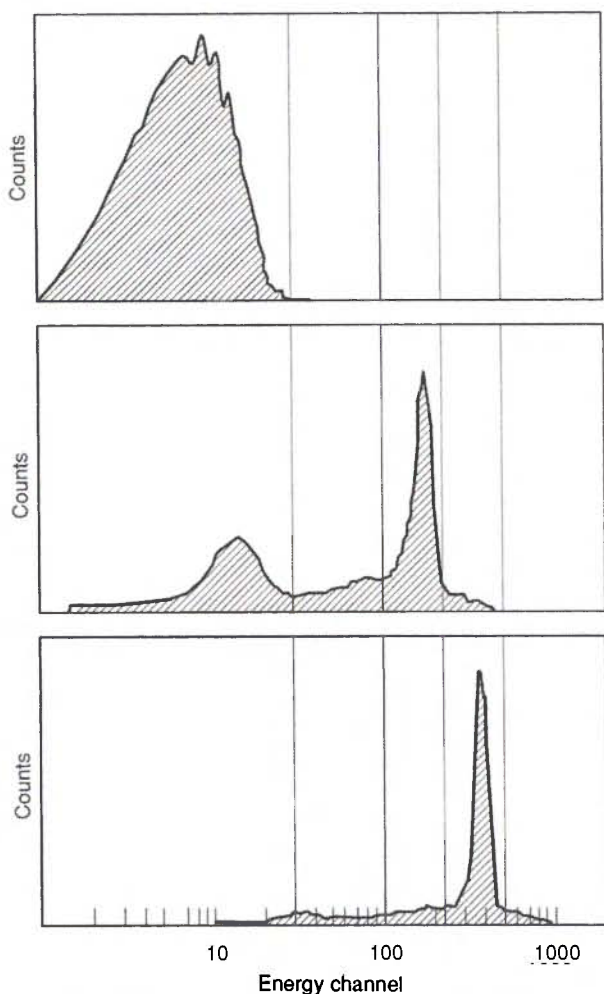


Fig. 1. Liquid scintillation spectra of ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po. a. spectrum of ²¹⁰Pb (245 Bq) without decay nuclides, b. spectrum of the mixture: ²¹⁰Pb (1.5 KBq), ²¹⁰Bi (1.3 KBq) and ²¹⁰Po (1.2 KBq), c. spectrum of ²¹⁰Po (7.1 KBq) alone. Conditions: 4 ml cocktail. a and b: 50% instagel and 50% solution. The calculation of the different activities is possible by counting the nuclides with 4 energy channel windows (i.e. 0 – 30 for ²¹⁰Pb and 0.15 ²¹⁰Bi, 30 – 100 for 0.35 of ²¹⁰Bi activity, 100 – 220 for ²¹⁰Po and 0.35 of ²¹⁰Bi and 220 – 500 for 0.15 of ²¹⁰Bi). c 95% instagel and 5% solution. No significant quenching effect was observed for the solutions used in this study, peaks are only shifted when changing cocktail proportions (5 to 50% solution).

energy windows allows determination of the individual nuclide activities (Figure 1).

The Milli-Q water, a diluted suspension of montmorillonite (10 ppm) and the filtrate of the stock suspension (2000 ppm) were tested by inductively coupled plasma mass spectroscopy (ICP-MS) for contamination by natural ²⁰⁹Bi. There was no evidence of any contamination above the detection limit (<25 ppt, corresponding to a concentration of 1.2 × 10⁻¹⁰ M ²⁰⁹Bi). For Pb, no contamination greater than the detection limit (2 × 10⁻¹⁰ M) was found. Activities of ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po in the blank samples were below the detection limit of 5 counts per minute per ml solution.

A distribution coefficient *R_d* can be defined as follows:

$$R_d = \frac{[Me_{(s)}]}{[Me_{(l)}] \cdot [coll]} \quad (\text{ml} \cdot \text{g}^{-1})$$

[Me_(s)] (M) is the partial concentration of the nuclide adsorbed on the colloidal particles, [Me_(l)] (M) is the concentration of the free nuclide in solution and [coll] (g · ml⁻¹) is the concentration of the colloidal particles.

2.3. Adsorption experiments

Adsorption experiments were performed at the pH values 5, 6 and 7, each of them at five different ionic strengths: 0.01, 0.02, 0.05, 0.1 and 0.2 M NaClO₄. For the adjustment of the pH, the following buffers were used: pH 5: Acetic acid/Na-acetate, pH 6: 2-Morpholinoethane-sulfonic acid (MES, pK=6.2) and pH 7: (N-N-Bis(2-Hydroxyethyl)-2-aminoethane-sulfonic acid) (BES, 99+%, pK=7.2). The total concentrations of these buffers were 0.01 M during the experiments and pH changes were less than 0.1. Additional tests (performed by the Schubert complexation method [13]) showed that, under the actual experimental conditions, complexation of Pb by the buffer substances in solution could affect the distribution coefficient *R_d* by a factor 2 in the worst case. Due to strong hydrolysis of Bi and Po, the effect exerted by the buffers is expected to be less pronounced than in the case of Pb. The presence of the buffers may affect the speciations in solution. However, the complexation constants of the buffers are several orders of magnitude lower than the hydrolysis constants. For these nuclides the Schubert method was also applied but no significant difference could be observed between activities with and without buffer (as potential complexant). Before the experiments, the montmorillonite suspen-

sions were conditioned for the planned pH values and ionic media. The sorption was performed in 50 ml polyethylene centrifuge tubes. 25 ml suspensions were spiked with ^{210}Pb to yield the following total concentrations: at pH 5: $[^{210}\text{Pb}] = 2.04 \times 10^{-11} \text{ M}$, $[\text{Pb}_{(\text{tot})}] = 7.74 \times 10^{-10} \text{ M}$, at pH 6 and 7: $[^{210}\text{Pb}] = 8.16 \times 10^{-11} \text{ M}$, $[\text{Pb}_{(\text{tot})}] = 3.10 \times 10^{-9} \text{ M}$. All experiments were run twice. Double blank experiments without montmorillonite were carried out under all different conditions. During the equilibration phase, the suspensions and the blanks were shaken for 24 hours. Next, the samples were centrifuged for 30 minutes at 10,000 rpm (equivalent to 11,000 g), before 2 ml of the supernatant solution were analyzed by liquid scintillation. Tests performed with laser beam showed that virtually all the colloidal particles had been removed from the solution during the centrifugation process. The amount of nuclide adsorbed on the montmorillonite can be calculated as the difference between the sample and its corresponding blank. Corrections were made for the losses caused by adsorption on the walls; it was assumed that the losses were proportional to the concentration of the free metal in the solution.

2.4. Desorption experiments

Two series of experiments were performed. In the first, Pb, Bi and Po were adsorbed simultaneously from solution, by spiking the diluted stock solution of the nuclides, which contained ^{210}Pb , ^{210}Bi and ^{210}Po in secular equilibrium and inactive carrier Pb and ^{209}Bi . In the second series of experiments, parts of the nuclide stock solution were depleted of the daughter nuclides ^{210}Bi and ^{210}Po and of ^{209}Bi . The same total concentrations of Pb were used in both series, while, in the second series, the initial concentrations of Bi and Po were kept about 2 orders of magnitude lower than in the first. In the first series of experiments, the desorption was performed shortly after the adsorption step (1 day), in order to obtain informations about the desorptive behaviour of those fractions of Bi and Po which had adsorbed from the solution and in order to avoid "contamination" by ^{210}Bi and ^{210}Po which are being generated by adsorbed ^{210}Pb . In the second series, the montmorillonite particles were collected on a filter membrane shortly after the adsorption step. The membranes with the particles were dried and kept for about 3 months, in order to ensure that a high percentage of the ^{210}Bi and ^{210}Po sorbed on the particles had been generated by the decay of adsorbed ^{210}Pb . The desorption results were then compared for the two series.

The first suspension was prepared with the following concentrations: $[\text{Mont}] = 1000 \text{ ppm}$, $[^{210}\text{Pb}] = 1.0 \times 10^{-9} \text{ M}$, $[\text{Pb}_{(\text{tot})}] = 3.9 \times 10^{-8} \text{ M}$, $[\text{Bi}_{(\text{tot})}] = 3.2 \times 10^{-8} \text{ M}$ and $[\text{Po}] = 1.65 \times 10^{-11} \text{ M}$. The suspension was equilibrated for about 1 month to reach sorption equilibrium. However, additional experiments showed that changes were minor after an equilibration time of 24 hours. Aliquots of 20 ml were then filtered using 30 nm Nucleopore membranes. After each desorption (resuspension) step, the nuclide activities were measured in both the filtered and the particle suspension solutions. Due to the large particle concentration, losses by sorption on the cell walls was limited to about 10% for Pb and about 40% for both Bi and Po over the series of experiments. Sorption on the hydrophobic membranes were within a few percent of the total inventories, corrections were made in the mass balances of each nuclide. The montmorillonite particles were resuspended from the filter membranes in 20 ml solutions of various ionic media, (NaClO_4 0.2 mM, 2 mM and 0.1 M). After an equilibration phase of at least 24 hours, the suspensions were filtered again. This filtration/resuspension step was repeated seven times. Before and after each filtration, aliquots of the suspensions and of the filtrates were analyzed by liquid scintillation. This treatment allows the computation of the distribution coefficient for each desorption step.

The second series of experiments was performed on suspensions with lower Bi and Po concentrations. Therefore, parts of the stock ^{210}Pb solution (in which the daughters ^{210}Bi and ^{210}Po are in secular equilibrium and which contains also inactive ^{209}Bi)

have been Bi- and Po-depleted. By this procedure, the initial concentrations of Bi and Po could be reduced to about 2% of their original values. By using the ^{210}Pb stock solution depleted of Bi and ^{210}Po , the following total concentrations were attained in this series: $[^{210}\text{Pb}] = 1.0 \times 10^{-9} \text{ M}$, $[\text{Pb}_{(\text{tot})}] = 3.9 \times 10^{-8} \text{ M}$, $[\text{Bi}_{(\text{tot})}] = 6.4 \times 10^{-10} \text{ M}$ and $[\text{Po}] = 3.2 \times 10^{-13} \text{ M}$.

In both series of experiments, the pH was 5.8 ± 0.2 . The desorption measurements were performed without any addition of buffer.

3. Results and discussion

3.1. Element speciation

The hydrolysis behaviour of lead for a concentration of 10^{-5} M is described in the literature [3]. For $\text{pH} < 6$, Pb is not hydrolyzed and no hydroxo-complexes are expected. Hydrolysis starts above pH 6: the dominating species are $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2$ below pH 11. Polynuclear complexes, such as $\text{Pb}_3(\text{OH})_4^{4+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$, are only relevant at much higher Pb concentrations than those used in this study (about 10^{-9} M) [4].

For Bi^{3+} , the situation is different. At pH 6 it forms a large variety of hydroxo-complexes, such as: $\text{Bi}(\text{OH})^{2+}$, $\text{Bi}(\text{OH})_2^+$, $\text{Bi}(\text{OH})_3$, $\text{Bi}(\text{OH})_4^-$, $\text{Bi}_6(\text{OH})_{12}^{6+}$, $\text{Bi}_9(\text{OH})_{20}^{7+}$, $\text{Bi}_9(\text{OH})_{21}^{6+}$ and $\text{Bi}_9(\text{OH})_{22}^{5+}$. Equilibrium calculations showed that, under the experimental conditions of this study ($[\text{Bi}_{(\text{tot})}] = 3.2 \times 10^{-8} \text{ M}$), only $\text{Bi}(\text{OH})_3$ (about 99.9%) and $\text{Bi}(\text{OH})^{2+}$ (about 0.05%) should be present, whereas the concentration of free Bi^{3+} is approximately $5 \times 10^{-16} \text{ M}$ [3].

Redox calculations performed with the data of Bard *et al.* [5] show that $\text{Po}(\text{IV})$ is the predominant redox state under oxic conditions ($P_{(\text{O}_2)} = 0.2 \text{ bar}$). However, Po^{4+} exists only in strongly acidic media. In slightly acidic or neutral media, $\text{PoO}(\text{OH})^+$, $\text{PoO}(\text{OH})_2$ and PoO_2 prevail, whereas, in alkaline media, PoO_3^{2-} predominates. The presence of the hydroxo-species $\text{Bi}(\text{OH})_3$ and $\text{PoO}(\text{OH})_2$ suggests that Bi and Po can easily be associated with colloids or active surfaces.

The properties of colloids and the problem of solubility of trace elements have been discussed by several authors, and the real situation can be more complicated than simple equilibrium calculations might suggest. Paneth [6, 7] found that colloids can be formed in concentration ranges considerably below the concentration limits given by the solubility product, and Zsigmondy [28] suggested that the radionuclides might be associated with impurities. According to Haissinsky [29, 30], solutions of radionuclides present in trace concentrations (10^{-6} M or lower) can not be considered in the normal terms of solubility and solubility products, but are rather polydispersed systems which are not in thermodynamic equilibrium and which contain colloidal particles of variable dimensions in addition to simple and complex ions. Furthermore, he concluded that the solubility will vary with the method of preparation and other parameters. During the sorption experiments, locally higher concentrations (which occur prior to uniform dilution in

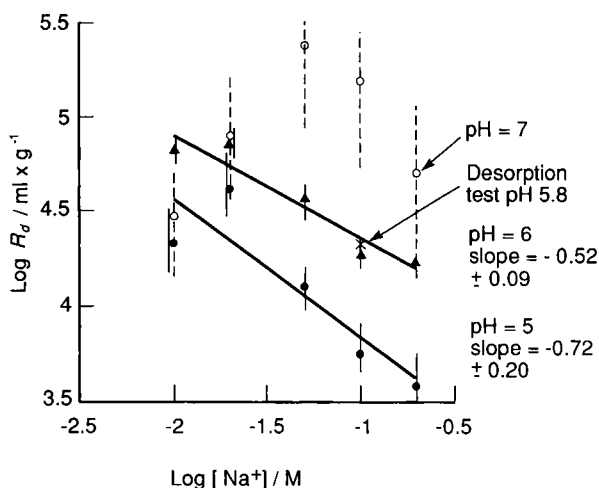


Fig. 2. Distribution coefficient R_d for the sorption of Pb on montmorillonite as a function of $[\text{Na}^+]$ and the pH. The desorption result performed under comparable conditions is added for comparison. Condition: $[\text{Pb}_{(\text{tot})}] = 1.5 \times 10^{-10}$ M. Error bars are given for pH 7 (dashed lines) and for pH 5 and 6 (solid lines).

the true solution) can therefore lead to the formation of such colloids prior to sorption onto montmorillonite particles.

3.2. Sorption experiments

The sorption of different metals on clay minerals has been reported in the literature [14]. Comans *et al.* [15] have tested the reversibility of the Cs sorption on illite. Besides a fast and reversible sorption on the outer layers, they noticed a slow migration of the Cs to energetically favourable interlayer sites, from which it is not easily released. Mahoney *et al.* [16] found that the sorption of Sr on montmorillonite was dependent on the ionic strength, at pH 5 and 7. The slope ($\log R_d$ vs. $\log[\text{Na}^+]$) is about -2 for both pH values. This behaviour is characteristic of a bivalent/monovalent ion exchange mechanism, indicating that this is the predominant uptake mechanism. For nickel, similar behaviour was found at pH 5. However, at pH 7 the value of the slope ($\log R_d$ vs. $\log[\text{Na}^+]$) changed to -1 [17]. This can be explained by the hydrolysis of Ni, above pH 7. The NiOH^+ complexes can react specifically with the lateral $>\text{Al-OH}$ sites of the montmorillonite. According to Dalang [18], electrostatic effects become less important for the sorption reactions of heavy metals as their tendency to hydrolyse increases. It is known that the hydroxo-complexes of many heavy metals adsorb more strongly at oxide surfaces than the unhydrolysed metal ions. Consequently, a pure ion-exchange model is not applicable for the description of such reactions, and special chemical interactions between the reacting heavy metal and the surface hydroxo groups have to be considered.

In this study, three heavy metals showing moderate (Pb) and very strong (Bi and Po) tendency to hydrolyse are under examination.

The sorption of Pb on montmorillonite is illustrated in Figure 2. At pH 5, the distribution coefficient is dependent on the ionic strength ($\log R_d$ vs. $\log[\text{Na}^+] = -0.72$). At pH 6, this dependence is less pronounced, and at pH 7, it disappears totally, within experimental error. This behaviour is caused by different sorption mechanisms at higher pH values. Whereas, at pH values below 6, Pb^{2+} is the most abundant species, hydroxo-complexes are formed at higher pH. O'Connor and Kester [19] have found similar behaviour for the adsorption of Cu and Co on illite. At lower pH values, the metal ions are predominantly sorbed by ion exchange, whereas, at pH values higher than 7, specific covalent reaction with surface OH-groups prevails. In the case of Pb, the slope in the diagram $\log R_d$ vs. $\log[\text{Na}^+]$ is greater than -2 , as would be expected for a pure ion exchange reaction. For Co(II) adsorption on montmorillonite, similar behaviour has been observed by Serne *et al.* [14]. Stumm *et al.* [20] found that Pb adsorbs specifically on aluminum oxide (covalent bonding). Sigg [21] compared the adsorption of Pb on silica and on aluminum oxide. Under identical conditions, the sorption coefficient on aluminum oxide was about one order of magnitude larger than on silica. The capability of surface hydroxyl groups to specific (or covalent) complexes with sorbents has been related to the degree of covalency in the chemical bond between the surface center and the hydroxyl group, i.e. of the bond $>\text{S-OH}$. Forbes *et al.* [22] postulated that a high degree of covalency of the bond $>\text{S-OH}$ generally hinders the specific reaction of a particular metal ion Me to form $>\text{S-O-Me}$. This can be explained by the fact that the basicity of the hydroxyl group is reduced when the bond $>\text{S-OH}$ has a higher degree of covalency. Therefore, the possibility to interact with is reduced. The bond $>\text{Si-OH}$ is more covalent than the bond $>\text{Al-OH}$, therefore the surface complexation of Pb is stronger with $>\text{Al-OH}$ than with $>\text{Si-OH}$. On the montmorillonite, stronger covalent bonding is to be expected with the lateral $>\text{Al-OH}$ -sites, whereas, on the $>\text{Si-OH}$ -groups of the surface layer, nonspecific ionic interaction prevails (dependent on the ionic strength). Experimental results support these theoretical considerations. The capability of a metal to associate specifically to a metal oxide surface depends on its capability to form moderately strong covalent bounds to the surface hydroxyl groups. According to Schindler and Stumm [23], the capability to form specific surface hydroxo-complexes correlates with the hydrolysis constant in solution. If the bond Me-OH is too weak, then the metal is not capable of forming covalent surface complexes (e.g. alkali metals). When, however, the bond Me-OH is too strong, a specific interaction, i.e. a reaction with the surface hydroxyl groups, is hindered because then the metal ion is not capable of exchanging its coordinated ligands by the surface hydroxyl group. Metals like Pb, Cd, Zn and Cu can meet the requirements for strong specific surface interaction with surface hydroxyl

Table 2. Distribution coefficients of Pb, Bi and Po on montmorillonite, obtained from sorption experiments.

Error ranges have been calculated based on the reproducibility of duplicate experiments and by estimation of systematic errors. Conditions: $T = 20^\circ\text{C}$, $[\text{coll}] = 800 \text{ ppm}$

Element:		Pb		
Ionic strength $\text{eq} \cdot \text{l}^{-1}$	pH 5	$\log R_d / \text{ml} \cdot \text{g}^{-1}$		pH 7
		pH 6		
0.01	4.3 ± 0.2	4.8 ± 0.2		4.5 ± 0.4
0.02	4.6 ± 0.1	4.8 ± 0.2		4.9 ± 0.2
0.05	4.1 ± 0.1	4.6 ± 0.1		5.4 ± 0.4
0.1	3.8 ± 0.1	4.3 ± 0.2		5.2 ± 0.2
0.2	3.6 ± 0.1	4.2 ± 0.1		4.7 ± 0.3

Element:		Bi		
Ionic strength $\text{eq} \cdot \text{l}^{-1}$	pH 5	$\log R_d / \text{ml} \cdot \text{g}^{-1}$		pH 7
		pH 6		
0.01	3.4 ± 1.0	4.1 ± 1.0		4.5 ± 1.0
0.02	3.5 ± 1.0	4.1 ± 1.0		4.7 ± 1.0
0.05	3.4 ± 1.0	4.4 ± 1.0		4.7 ± 1.0
0.1	3.5 ± 1.0	4.3 ± 1.0		4.7 ± 1.0
0.2	3.5 ± 1.0	4.4 ± 1.0		4.7 ± 1.0

Element:		Po		
Ionic strength $\text{eq} \cdot \text{l}^{-1}$	pH 5	$\log R_d / \text{ml} \cdot \text{g}^{-1}$		pH 7
		pH 6		
0.01	—	3.2 ± 1.0		3.2 ± 1.0
0.02	—	3.1 ± 1.0		3.2 ± 1.0
0.05	—	3.4 ± 1.0		3.1 ± 1.0
0.1	—	3.3 ± 1.0		3.2 ± 1.0
0.2	—	3.5 ± 1.0		3.2 ± 1.0

groups. Therefore, one can expect that, especially at low total concentrations, Pb can react specifically with lateral $> \text{Al}-\text{OH}$ groups on the montmorillonite. Generally, the tendency towards a nonspecific (ion exchange) mechanism increases with the total concentration of the metal [24]. In these tests the concentration of sorbing element was always smaller than the concentration of superficial sites obtained on the basis of the size distribution.

The sorption of Bi is independent of the ionic medium, there is, however, a slight dependence on pH (Table 2). This can be explained by the speciation of Bi, which, under the actual conditions (i.e. at pH 5 to 7), exists mostly in form of the $\text{Bi}(\text{OH})_3$ species (see discussion in 3.1.). Strong specific reaction on the lateral $> \text{Al}-\text{OH}$ -sites is to be expected (see above discussion about the association of metal ions on the clay surface).

In the case of Po, the situation is complicated by hydrolysis in solution and formation of colloids, which might stick strongly on the wall of the tubes. In the case of pH 5, it was not possible to determine a distribution coefficient because the error ranges were too large.

Table 3. Desorption of Pb, Bi and Po from montmorillonite, for $\text{pH} = 5.8 \pm 0.2$, $[\text{coll}] = 1000 \text{ ppm}$ and $I = 0.1 \text{ eq} \cdot \text{l}^{-1}$ (NaClO_4), $T = 20^\circ\text{C}$

[Pb(l)] M	[Bi(tot)] M	$\log R_d$ (Pb) $\text{ml} \cdot \text{g}^{-1}$
10^{-8}	$3 \cdot 10^{-8}$	3.1 ± 0.1
10^{-8}	$6 \cdot 10^{-10}$	3.4 ± 0.1
10^{-9}	$3 \cdot 10^{-8}$	3.7 ± 0.1
10^{-9}	$6 \cdot 10^{-10}$	3.9 ± 0.1

Comparison between ^{210}Bi and ^{209}Bi , ^{209}Bi sorbes from the solution, ^{210}Bi is generated by the decay of sorbed ^{210}Pb . The distribution coefficient is evaluated for different concentrations of free ^{210}Bi

$^{210}\text{Bi}(\text{l})$ M	[Bi(tot)] M	$\log R_d$ (^{210}Bi) $\text{ml} \cdot \text{g}^{-1}$	$\log R_d$ (^{209}Bi) $\text{ml} \cdot \text{g}^{-1}$
10^{-15}	$3 \cdot 10^{-8}$	5.3 ± 0.2	> 10
10^{-15}	$6 \cdot 10^{-10}$	5.3 ± 0.2	> 10
10^{-16}	$3 \cdot 10^{-8}$	6.1 ± 0.2	> 10
10^{-16}	$6 \cdot 10^{-10}$	6.3 ± 0.2	> 10

Desorption of ^{210}Po : the R_d values are listed for Po which has sorbed from the solution (S) and for Po generated by the decay of sorbed ^{210}Pb and ^{210}Bi , respectively (D)

$^{210}\text{Po}(\text{l})$ M	$\log R_d$ (S) $\text{ml} \cdot \text{g}^{-1}$	$\log R_d$ (D) $\text{ml} \cdot \text{g}^{-1}$
10^{-15}	—	6.3 ± 0.2
10^{-14}	6.0 ± 0.2	5.3 ± 0.2
10^{-13}	5.2 ± 0.2	—

This could be due to the fact that Po can form colloids in the liquid phase by sorbing onto particulate impurities, which, at higher ionic strength, show increasing tendency to coagulate and therefore to be eliminated from the liquid phase by the centrifugation process. After an increase of the total concentration of Po, semiquantitative results could be obtained in the case of pH 6 and 7 (Table 2). Between these two pH values, R_d values do not change drastically. Ionic strength does not affect the distribution of Po. As is the case for Bi, the sorption mechanism of Po can be described as strong specific surface complexation, predominantly on the lateral $> \text{Al}-\text{OH}$ -groups. However, if larger conglomerates and polynuclear hydroxo complexes were formed in the liquid phase, strong sorption could occur also on the surface layer ($> \text{Si}-\text{O}$ -groups): Matijevic [25, 26] postulates that the high charges of such polynuclear species enables them to associate strongly on oxide surfaces. The sorption results of Pb, Bi and Po with montmorillonite are summarized in Table 2.

3.3. Desorption experiments

The desorption of Pb (Table 3) is dependent on the ionic strength, as it is the case for the sorption experi-

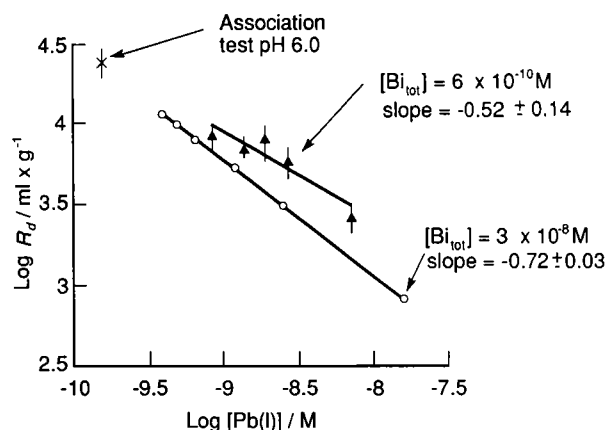


Fig. 3. The distribution coefficient R_d of Pb as a function of the free Pb concentration in solution, derived from desorption tests. The desorption of Pb is compared at two different total concentrations of Bi. For comparison, the result of the sorption experiment is shown, performed at a total bismuth concentration of $3 \cdot 10^{-8}$ M. Conditions: pH 6, ionic strength 0.1 M.

ments. Figure 3 shows $\log R_d$ as a function of the concentration of free lead in solution, $[\text{Pb}(l)]$. The slope of the line $\log R_d$ vs. $\log[\text{Pb}(l)]$ is between -0.5 and -0.7 . The distribution coefficient depends strongly on the surface concentration of Pb, i.e. there are sites of largely different qualities. Pb can react specifically on the lateral $>\text{Al}-\text{OH}$ -sites, which are the most reactive ones. Furthermore, Pb can also sorb nonspecifically at the surface (loaded $>\text{Si}-\text{OH}$ -sites) at $\text{pH} < 7$, mainly with the net negative charge of the three-layer unit cells of the clay. From the latter sites, the Pb is released more easily and the desorption of this fraction is strongly dependent on the ionic medium.

When the distribution coefficients measured in the sorption experiments are compared with those obtained in the desorption tests under the same conditions, they are equal within experimental error. Therefore, the sorption of Pb can be considered to be mostly reversible (see Figures 2 and 3).

The desorption of Pb from montmorillonite was enhanced by higher Bi-concentrations (Figure 3). Bi shows a much stronger tendency to remain sorbed than Pb, it shows strong specific sorption (see text above), thus competing with Pb for the most reactive surface sites.

As is the case for sorption, the desorption of Bi from montmorillonite is independent of the ionic medium. Because the half-life of ^{210}Bi is very short (5.013 d), it can be assumed that, in both series of experiments, most of the ^{210}Bi is generated by the decay of sorbed ^{210}Pb , whereas the inactive ^{209}Bi sorbs with the colloidal particles from the solution. In Figure 4, the desorption of Bi from montmorillonite is compared for different initial concentrations of ^{209}Bi , the other conditions being identical. The slope $\log R_d$ vs. $\log[\text{Bi}(l)]$ is equal to -1 . This means that R_d is proportional to the inverse of $[\text{Bi}(l)]$, indicating that the fraction of sorbed $[\text{Bi}(s)]$ is virtually constant over

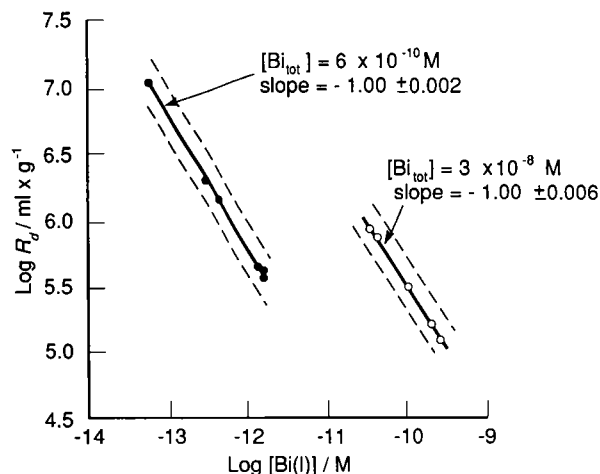


Fig. 4. The desorption of Bi from montmorillonite, for different total concentrations of Bi. Initial concentrations of ^{210}Pb , ^{210}Bi and all other experimental conditions were identical for the two series of experiments: pH 6, ionic strength 0.1 M NaClO_4 , $[\text{Pb}_{\text{tot}}] = 3.9 \cdot 10^{-8}$ M, $[\text{coll}] = 1000$ ppm. Calculations of the R_d values are performed under the assumption that no isotopic effects occur during the desorption reaction, i.e. that the ratio $^{210}\text{Bi}/^{209}\text{Bi}$ is identical in all phases. Error ranges were determined by worst case assessment of systematical error in the experiments (dashed lines).

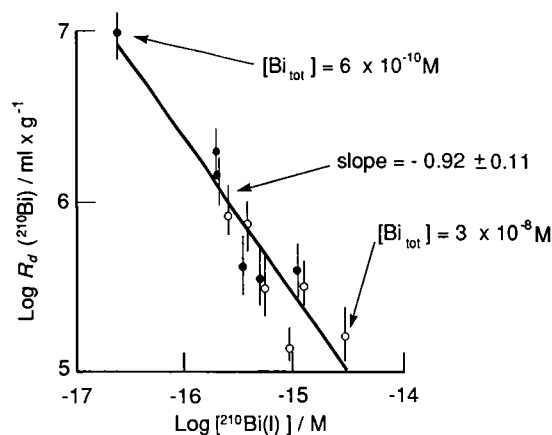


Fig. 5. The desorption of ^{210}Bi from montmorillonite for two different initial total concentrations of bismuth. The effect of changes in the concentration of inactive ^{209}Bi on the desorption of the active ^{210}Bi is illustrated (series with $[\text{Bi}_{\text{tot}}] = 6 \cdot 10^{-10}$ M: filled circles symbols, series with $[\text{Bi}_{\text{tot}}] = 3 \cdot 10^{-8}$ M: circles).

the experimental period, i.e. that only a very small fraction of the total Bi is desorbed from the montmorillonite particles. In this Figure, it is assumed that no isotopic effects occur during the desorption process, i.e. that the ratio $^{210}\text{Bi}/^{209}\text{Bi}$ in the desorbing fraction is the same as in the sorbed fraction. Calculations based on this assumption lead to large differences in the distribution coefficients for the two Bi isotopes, indicating that such an approach is not correct. If the desorption of ^{210}Bi is examined (see Figure 5), the value of the slope $\log R_d$ vs. $\log[^{210}\text{Bi}(l)]$ is -0.92 , which is still close to -1 . This means that only a small fraction of the ^{210}Bi is desorbed. Furthermore,

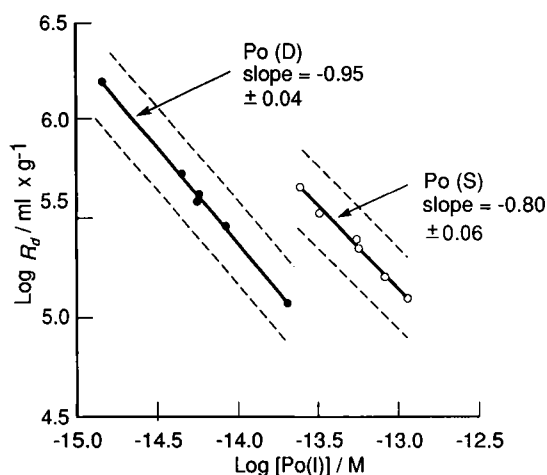


Fig. 6. The desorption of ^{210}Po from montmorillonite. In the first case, the ^{210}Po was sorbed onto the particles from the solution (curve with the label Po(S)), whereas, in the second case, the ^{210}Po was generated by the decay of ^{210}Pb labelled montmorillonite (curve called Po(D)). The initial concentrations of ^{210}Po were: 1.65×10^{-11} M for the experiment Po(S) and 2.8×10^{-12} M for the series Po(D).

Figure 5 shows that the desorption of ^{210}Bi is independent of the initial concentration of sorbed ^{209}Bi . Estimative model calculations show that the distribution coefficient for ^{209}Bi must be several orders of magnitude higher than for ^{210}Bi : $\log R_d(^{209}\text{Bi})$ yields values between 10 and 11 in the case of $[\text{Bi}_{\text{tot}}] = 6 \times 10^{-10}$ M. These values indicate that the sorption of ^{209}Bi (and, therefore, the association of all Bi sorbing from the solution) is virtually irreversible. This fraction of Bi undergoes strong specific sorption at the surface, most likely through hydroxyl-groups (the sorbing species, under the actual conditions, is mostly $\text{Bi}(\text{OH})_3$). Schindler and Stumm [23] found that the capability of a metal ion to react specifically with surface hydroxyl groups correlates with its hydrolysis constant in solution. Therefore, Bi and Po can form covalent surface complexes of higher stability than Pb. If Bi and Po sorb onto montmorillonite from the solution, they occupy the most reactive lateral sites, from which they are not easily released. Pb forms less stable covalent surface complexes, furthermore, Pb reacts partly by ionic interaction with the surface layer. When a ^{210}Pb which is sorbed onto a colloidal particle decays to ^{210}Bi (and, later, to ^{210}Po), the daughter nuclides find themselves on less reactive sites (from which they are more easily released) than the fractions of Bi and Po which sorbed directly from the solution.

A similar effect can be measured for ^{210}Po . In this case, the situation is less complicated because ^{210}Po is isotopically pure. Due to the convenient half-life, it is possible to compare a fraction of ^{210}Po which has mainly been sorbed from the solution with another fraction of ^{210}Po which has been generated by the decay of sorbed ^{210}Pb . The results of these desorption tests are shown in Figure 6. For ^{210}Po , they show a difference in the distribution coefficients which equals

about one order of magnitude. Compared with Bi, the effect is less pronounced but still significant. In order to explain this behaviour, similar reasons can be mentioned as in the case of Bi. The large difference in the desorption behaviour of the two different fractions of Po can be explained by the differences in the sorption behaviour of Pb on one side and of Bi, Po on the other side. Hot chemical effects are also likely to contribute to this effect, the maximum energy of the β particles of ^{210}Pb and ^{210}Bi being 60 keV and 1.2 MeV, respectively. Such energies are high enough to break chemical bonds. The slope $\log R_d$ vs. $\log [^{210}\text{Po}(\text{l})]$ is between -0.80 and -0.95 , indicating that a small fraction of the total ^{210}Po can be desorbed in both cases (see Figure 6).

All data of the desorption of Pb, Bi and Po from montmorillonite are listed in Table 3.

3.4. Comparison between sorption and desorption experiments

When the data obtained for the sorption and the desorption processes are compared, useful information about the reversibility can be deduced.

In the case of Pb, the R_d values obtained for the sorption and the desorption processes show good agreement even at very low total concentrations, thus indicating good reversibility (Figures 2 and 3).

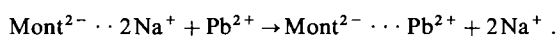
In the case of Bi and Po, the situation is complicated by the fact that both these elements can form colloids in the liquid phase (see introduction and discussion in 3.1.). As postulated by Lieser *et al.* [9], the solubilities of sparingly soluble oxides or hydroxides depend frequently on the composition and the pre-treatment of the solid, the solubility of which is considered. In the sorption experiments, relatively high local concentrations of Bi and Po are present in the solution prior to uniform dilution and prior to the sorption step, thus favouring the formation of polynuclear complexes and/or the sorption on colloidal impurities in solution (see discussion in 3.1.). Such colloids can be stabilized in solution and persist over long time scales. In the desorption experiments, the concentrations of Bi and Po in the true solution are several orders of magnitude lower than in the sorption experiments, therefore, the formation of such colloids of hydroxo-polymer of Bi and Po in solution is unlikely. Actually, the R_d values for the desorption process are several orders of magnitude higher than for the sorption process (Tables 2 and 3). In addition, experiments showed that the sorption is quasi irreversible if Bi and Po sorb from the solution.

Different R_d values are obtained for the sorption and the desorption processes; either this indicates an irreversible or quasi-irreversible sorption process, or the equilibration is much slower than in the case of Pb. In some of the cases, the equilibration times were prolonged from 1 to 5 days, without any significant change. Therefore, the second possibility seems less probable.

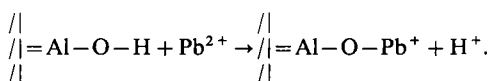
Whereas the sorption of Pb is mostly reversible and dependent on the ionic strength, the sorption of Bi and Po is quasi irreversible and independent of the ionic strength. Bi and Po have a higher tendency to form very stable covalent surface complexes than Pb. Therefore, one can expect that Bi and Po can occupy the most reactive sites at the surface, whereas Pb finds itself on less reactive sites. If a sorbed ^{210}Pb decays to ^{210}Bi , it occupies a site which previously would not have been selected by sorbing Bi or Po, but which had been occupied by Pb. Hot chemical effects could also contribute to this behaviour because the β -particle energies of ^{210}Pb and ^{210}Bi are sufficiently high to cause cleavage of chemical bonds and, thus, desorption of the daughter nuclides from their sites. Therefore, these fractions may get desorbed from the colloidal particles more easily than Bi and Po which had been able to select "their own" reaction sites by sorbing from the solution.

The reaction mechanism suggested from this study are summarized as follows:

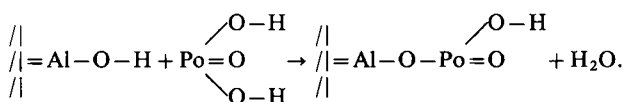
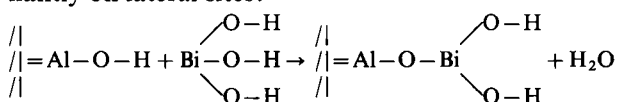
Nonspecific ionic exchange at the surface layer:



Specific surface complexation on lateral sites:



Specific surface complexation of Bi and Po, predominantly on lateral sites:



As additional proof that such mechanisms are taking place, experiments such as those performed by Dran *et al.* [27] using ion beam analysis on the samples after sorption or desorption should be carried out. However, these tests are realized with macroscopic rock samples and not yet with colloidal particles.

4. Conclusions

For both sorption and desorption experiment series mostly carried out with sorbent concentrations smaller than the sorption capacity (surface site) of the montmorillonite material, the following can be concluded:

The sorption of Pb on montmorillonite is dependent on the ionic strength at low pH; this dependence disappears at pH higher than 7. The sorption at lower pH values proceeds partly by an ion exchange mechanism; at higher pH, specific sorption becomes more dominant.

The sorption of Pb is reversible. Distribution coefficients measured in sorption experiments show good agreement with those obtained in desorption tests.

The desorption of Pb is affected by the concentration of total Bi, even when the concentration of the latter is lower. Bi can react strongly with lateral $>\text{Al}-\text{OH}$ -sites, thus forcing Pb to occupy less favourable sites, from which the dissociation is easier.

Both Bi and Po sorptions are independent of the ionic strength and are thus dominated by strong specific (covalent) interaction with the clay surface. In both cases, the interpretation of the process is complicated by the fact that Bi and Po may form colloids in solution.

The sorption of Bi and Po is quasi-irreversible for the species sorbing from the aqueous phase, whereas, for ^{210}Bi and ^{210}Po generated by the decay of sorbed ^{210}Pb , the desorption is significantly facilitated. It yields R_d 's 2 to 3 orders of magnitude smaller for ^{210}Bi and approximately 1 order of magnitude smaller for ^{210}Po . Such effects reduce irreversibility of the sorption, reducing therefore the hazard of nuclide transport by colloids.

Generally, it can be said that radioactive decay processes significantly affect the distribution of radionuclides between the solid and the liquid phase. The partial release of nuclides which, in pure chemical terms, are irreversibly sorbed with the colloids, can be relevant also for long-lived nuclides, because their activities in the "true" water phase can be largely enhanced. Therefore, subsequent sorption on geologically stable formations and retention are favoured.

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