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HYDROPHYSICAL PROCESSES

Interaction between Clay Minerals and Fluorine-Containing Solutions

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Abstract—The interaction between fluorine-containing solutions and natural clays is studied experimentally. Fluorine is shown to pass into solution at fluoride concentrations below certain (equilibrium) level and to be absorbed otherwise. Growing acidity of solution is found to abruptly increase the specific sorption capacity and reduce desorption of fluorides. It is shown that clay grounds, when used as a natural geochemical barrier for preventing groundwater pollution by fluorides, are effective only at pH ≤ 5.0; and the interaction of alkaline wastewater with clay will cause additional amounts of fluorides to pass into solution.

INTRODUCTION

Fluorine is a biologically active element, which, in certain amounts, is indispensable for normal vital functions of living organisms. According to hygiene and sanitary standards, the optimal concentration of fluorides in potable water is 0.7–1.5 mg/l [8]. Deviations of the fluoride concentration from these values cause tooth tissue diseases: fluorine deficiency causes caries, and its excess causes dental fluorosis. Anthropogenic environmental pollution by fluorine brings about some other pathologic changes in humans, animals, and plants. In particular, fluorides were found to affect the accumulation rate of Sr and some other metals in the bone tissue [4, 5]. Higher concentrations of F^- are supposed to facilitate the development of oncological diseases in rats [12], to disturb osmotic regulation in fish [15], and to reduce the photosynthetic capacity and biological production in plants [1, 6, 10, 13].

Water pollution by fluorides can be caused by both natural and anthropogenic processes. Thus, alkaline waters rich in bicarbonates favor F^- leaching from rocks [2]. Therefore, water with high concentrations of fluorides can form in the zones where alkaline carbonate-containing waters are in contact with fluorine-containing rocks. However, currently economic activity becomes the main cause of heavy pollution of natural waters with fluorides. Anthropogenic sources account for 58.2% of the overall F input into the global environment, and this index is even higher for the CIS countries (78%).

Soils dominated by clay minerals have high sorption capacity and frequently serve as natural geochemical barriers preventing pollutants from reaching groundwater [9, 14]. The soils also can be supposed to form an efficient sorption geochemical barrier with respect to fluorides. This effect is confirmed by the results of experiments [11], which showed that Fe and Al hydroxides, clay minerals, and different types of soils can absorb up to 0.1–3.3 mg F/g. The possibility of isomorphic replacement and the similarity of physicochemical properties of F^- and OH^- in aqueous solutions allow pH of solution to be regarded as one of the main factors to control the sorption–desorption equilibrium. However, the dependence of F^- sorption on the solution pH is poorly known; therefore, this study is an attempt to fill this gap.

EXPERIMENTAL METHODS

In our experiments, we studied two monomineral clays (kaolinite and montmorillonite) and polymineral gzhel'skaya clay, which, in addition to illite, kaolinite, microcline, quartz, and smectite, contains large amounts of hydromicas. According to X-ray phase analysis, the mineral composition of samples was as follows: kaolinite clay contained 9.6% quartz, 0.8% muscovite, 89.6% kaolinite; montmorillonite clay contained 0.6% biotite, 1.2% labradorite, 66.1% Na-montmorillonite, 32.1% amorphous phase; gzhel'skaya clay contained 23.8% illite, 1.3% hydromica, 7.1% kaolinite, 19.7% microcline, 27.2% quartz, and 20.9% smectite. The specific area of the samples of kaolinite, montmorillonite, and gzhel'skaya clays were 8.62, 112.72, and 58.06 m^2/g, repsectively.

The experiments were conducted at fixed values of solid phase–solution ratio (1:100), pH (5.0–8.8), and the initial fluoride concentration (1.8–15.1 mg/l). The level of pH in samples was maintained with the use of buffer solutions with pH 4.7, 6.2, and 8.2. The buffer solution with pH 8.2 contained 0.08 M $NaHCO_3$ and 0.01 M Na_2CO_3; the buffer solutions with pH 6.2 and 4.7 represented mixtures of 0.1 N and 0.2 N acetic acid, respectively, with 0.05 M Na_2CO_3 solution. The solutions for experiments were prepared by adding 0.5–4 ml 0.1 M NaF solution and 446–449.5 ml 0.1 M NaCl solution to 50 ml of one of the buffer solutions. NaCl solution was used as a background electrolyte to keep

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Table 1. Fluorine sorption by clays

F^-, mg/l*	Γ, mg F/g	pH
Kaolinite clay		
1.79/0.59	0.120	5.02 ± 0.10
3.73/0.82	0.291	
7.34/2.01	0.533	
10.92/3.79	0.713	
15.14/4.65	1.049	
1.83/1.71	0.012	8.04 ± 0.15
3.71/3.38	0.033	
7.20/6.64	0.056	
11.09/10.56	0.053	
15.12/14.12	0.100	
1.86/1.98	–0.012	8.76 ± 0.12
3.71/3.77	–0.006	
7.28/7.14	0.014	
11.04/10.91	0.013	
15.12/14.70	0.042	
Montmorillonite clay		
1.79/0.21	0.158	4.99 ± 0.12
3.73/0.33	0.340	
7.34/0.76	0.658	
10.92/1.09	0.983	
15.14/3.40	1.174	
1.83/2.21	–0.038	7.96 ± 0.08
3.71/3.26	0.045	
7.20/6.52	0.068	
11.09/10.26	0.083	
15.12/13.95	0.117	
1.86/2.42	–0.056	7.96 ± 0.08
3.71/4.16	–0.045	
7.28/7.46	–0.018	
11.04/11.26	–0.022	
15.12/15.00	0.012	
Gzhel'skaya clay		
1.79/1.69	0.010	5.42 ± 0.30
3.73/3.64	0.009	
7.34/6.89	0.045	
10.92/10.42	0.050	
15.14/13.93	0.121	
1.83/1.83	0.0	8.43 ± 0.13
3.71/3.80	–0.009	
7.20/7.14	0.006	
11.09/10.91	0.018	
15.12/14.58	0.054	
1.86/2.12	–0.026	8.85 ± 0.05
3.71/3.90	–0.019	
7.28/7.37	–0.009	
15.12/15.18	–0.006	

* The first and second numbers correspond to the initial and final F^- concentrations, respectively.

the ionic strength constant (I = 0.1). Since the natural clay minerals contain F^-, additional experiments were conducted to study the effect of solution pH on fluorides release from clay.

Weighted samples of clays (1 g) were put into cone flasks, and 100 ml of solution with 0–15.1 mg/l of fluorides were poured into each flask. Kinetic experiments showed that the sorption equilibrium was attained within 6–7 days. This result is in agreement with data in [11], where the sorption equilibrium between fluorine-containing solution and clay minerals also was found to attain within a short time. The samples were agitated every day for two months and next filtered through a dense paper filter. The filtrate was analyzed for pH and the concentration of fluorine using potentiometric techniques with a glass hydrogen and fluorine ion-selective electrodes [7]. The accuracy in determining solution pH and fluoride concentration amounted to ±0.005 and ±1 rel. %, respectively.

RESULTS AND DISCUSSION

The results of experiments are given in Table 1. As seen from the figure, the dependence of the specific sorption of fluorides on their equilibrium concentration in solution is linear

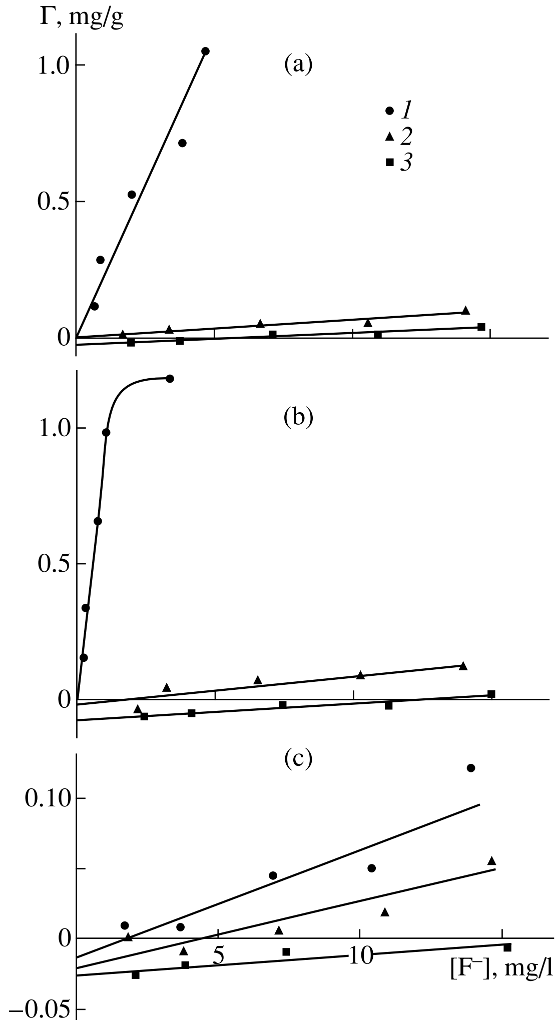
$$\Gamma = k[F^-] + b, \tag{1}$$

where Γ, mg F/g, is the specific sorption of fluorides; $[F^-]$, mg/l, is the concentration of fluorides in the equilibrium solution; k and b are proportionality factors. This equation describes the experimental data with a correlation coefficient of r = 0.88–0.99 (Table 2). As the solution acidity grows, Γ abruptly increases in all the clay samples: at a decrease in pH from 8.8 to 5.0, the value of k in (1) increases by 50, 180, and 6 times for kaolinite, montmorillonite, and gzhel'skaya clays, respectively (Table 2).

The largest sorption capacity with respect to fluorides is typical of montmorillonite clay (k = 0.89 at pH 5.0). Kaolinite clay exhibits somewhat lower fluoride sorption (k = 0.20 at pH 5.0). Gzhel'skaya clay is the least efficient sorbent, because it has k = 0.0086 at pH 5.4, which is about two orders of magnitude lower than that of montmorillonite clay.

Table 2. Parameters of equations (1) and (2)

Clay	pH	k	b	$[F_0^-]$, mg/l	r
Kaolinite	5.02	0.197	0.074	0	0.97
"	8.04	0.0060	0.007	0	0.94
"	8.76	0.0039	–0.020	5.13	0.96
Montmorillonite	4.99	0.894	0.0003	0	0.99
"	7.96	0.0104	–0.020	1.92	0.88
"	8.70	0.0049	–0.065	13.26	0.95
Gzhel'skaya	5.42	0.0086	–0.016	1.86	0.94
"	8.43	0.0043	–0.019	4.42	0.91
"	8.85	0.0014	–0.025	17.86	0.89



Specific sorption on natural clays versus equilibrium concentration of F^- in solution. (a) Kaolinite clay, (*1–3*) pH 5.02 ± 0.10, 8.04 ± 0.15, and 8.76 ± 0.12, respectively. (b) Montmorillonite clay, (*1–3*) pH 4.99 ± 0.12, 7.96 ± 0.08, and 8.70 ± 0.04, respectively. (c) Gzhel'skaya clay, (*1–3*) pH 5.42 ± 0.30, 8.43 ± 0.13, and 8.85 ± 0.05, respectively.

Since the natural clay samples contain F^-, their interaction with aqueous solutions low in fluorides can be accompanied by F^- release from the clays. As shown by experiments (Table 3), the amount of fluorides released into solution nonlinearly increases with pH. As to the rate of fluoride release, the examined samples can be ranked in the same order as they were for sorption: montmorillonite clay > kaolinite clay > gzhel'skaya clay (the release of fluorides at pH 5.0 amounts to 0.060, 0.040, and 0.019 mg/g, respectively).

Table 3. The effect of pH on the release of fluorides by clays

Clay	pH	F^-, mg/l	*D*, mg F/l
Kaolinite	5.02	0.037	0.004
	8.04	0.203	0.020
	8.76	0.402	0.040
Montmorillonite	4.99	0.023	0.002
	7.96	0.052	0.005
	8.70	0.602	0.060
Gzhel'skaya	5.42	0.047	0.005
	8.43	0.118	0.012
	8.85	0.194	0.019

The parameters of sorption–desorption equilibrium can be determined from the plots of fluoride specific sorption at different pH versus the equilibrium F^- concentration in solution (figure). The concentrations of fluorides, determined by the coordinates of these plots crossing the abscissa axis ($[F_0^-]$), correspond to the equilibrium conditions. At concentrations below or above $[F_0^-]$, either release of fluorides from clay or their absorption will take place. Since the experimental data can be adequately described by formula (1), the equilibrium concentration of fluorides at $\Gamma = 0$ can be easily found from the relationship between the proportionality factors *b* and *k* in this formula:

$$[F_0^-] = -b/k. \tag{2}$$

As seen from Table 2, the increase in $[F_0^-]$ with pH is nonlinear for all the clay samples under consideration. This agrees with the results of experiments aimed at studying the effect of pH on the release of fluorides by clays into solution originally containing no $[F^-]$. These experiments established a nonlinear increase in fluorides desorption from clays *D* with growing pH (Table 3).

The lowest equilibrium fluorides concentrations, at which the sorption begins, are typical of kaolinite clay. In alkaline environment, the release of fluorides into solution is significant ($[F_0^-]$ = 5.1 mg/l at pH 8.8), whereas at pH < 8, the effect of desorption processes can be neglected. The desorption of fluorides from montmorillonite clay at pH 5.0 also is negligible; however, in alkaline environment, the rate of fluoride release into solution increases more rapidly (the fluoride equilibrium concentration increases from 1.9 to 13.3 mg/l with pH growing from 8.0 to 8.7). As distinct from kaolinite and montmorillonite clays, the desorption of fluorides from gzhel'skaya clay takes place even in acid environment: at pH 5.4 $[F_0^-]$ = 1.9 mg/l, and at pH 8.8 $[F_0^-]$ = 17.9 mg/l (Table 2).

Therefore, the use of clays as a natural geochemical barrier for protecting groundwater against fluoride pollution can be efficient only when wastewater pH does not exceed 5.0 or when its interaction with soil reduces pH to this value. Wastewater with alkaline properties, when interacting with clays, will cause additional release of fluorides into solution.

CONCLUSION

The interaction of clays with fluorine-containing aqueous solutions can cause either decrease or increase in the dissolved fluoride concentrations. When the concentration of fluorides drops below certain (equilibrium) value, fluorides will pass from clays into solution. In the case where fluoride concentration exceeds the equilibrium value, fluoride sorption begins, which reduces the fluoride content of solution. In accordance with the rates of fluoride release and sorption, the examined samples can be ranked as follows: montmorillonite clay > kaolinite clay > gzhel'skaya (hydromicaceous) clay.

The use of clays as a natural geochemical barrier for preventing groundwater pollution by fluorides is efficient only when the wastewater pH either is originally low enough or its interaction with clay reduces pH to 5.0. In the case of alkaline wastewater discharge, one should take into account that additional amounts of fluorides can enter the solution from clay minerals.

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