

Heterogeneous reactions of dioctahedral smectites in illite-smectite and kaolinite-smectite mixed-layers: applications to clay materials for engineered barriers

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Abstract—The clay materials selected for use in the engineered barriers of the French nuclear waste isolation programme are mainly composed of dioctahedral smectite, either bentonite of Wyoming type or kaolinite-smectite mixed-layered minerals from the Sparnacian deposit of the Paris Basin. These dioctahedral smectites most often consist of randomly stacked layers with low and high charges. In the case of the Wyoming-type bentonite, these two differently charged layers do not react in the same way when subjected to hydrothermal alteration. Overall, the low-charge smectite layers react to form high-charge smectite layers + quartz + kaolinite. Then, fixing K ions, the high-charge smectite layers are transformed into illite-smectite mixed-layers (I/S) when the temperature conditions increase (diagenetic formations, geothermal fields or metasomatic environments). A symmetrical process is observed in natural or experimental hydrothermal conditions when the high-charge smectite layers of I/S minerals react with quartz and/or kaolinite to produce low-charge smectite layers. The chemical properties (cation exchange capacity, irreversible K fixation) of the bentonite-engineered barriers clearly depend on the low charge/high charge smectite layer proportion, which is in turn controlled by the temperature-dependent reactions in the vicinity of the waste disposal.

Although there are fewer published data on the kaolinite-smectite mixed-layered minerals (K/S), a similar low charge–high charge reaction appears to affect their smectite component. The experimental alteration of K/S leads to the formation of a low-charge beidellite with an increase in the cation-exchange capacity and in the expandability of the clay material. Thus, the properties of the engineered barrier seems to be improved after hydrothermal alteration.

INTRODUCTION

THE USE of the dioctahedral smectites (bentonites or their commercial equivalent) as backfilling materials in nuclear waste disposal options is based upon two specific properties: (1) their high swelling pressure when in contact with naturally occurring solutions (expandability), which ensures the sealing of the waste disposal site; and (2) their high absorption capacity for cations, especially for those of the transuranics and fission products, which is related to their high exchange capacity.

To retain their swelling and their cation-exchange capacities, the smectites must remain stable under the low-temperature hydrothermal conditions prevailing in the vicinity of the nuclear wastes. However, it is well known that the dioctahedral smectites are not stable in such environments and may react to form illite (non-swelling phase with low cation-exchange capacity) via intermediate I/S minerals. Moreover, dioctahedral smectites are heterogeneous phases: CICEL and MACHAJDIK (1981) have observed that K- and NH₄-dioctahedral smectites behave as

mixed-layer structures made up of three kinds of randomly stacked layers: non expandable 10-Å layers, partly expandable 14-Å layers and fully expandable 16.80-Å layers. The existence of these three kinds of layers is attributed to an inhomogeneous distribution of layer charge in the smectite structure (LAGALY and WEISS, 1976; TALIBUDEEN and GOULDING, 1983). One can expect that this layer charge heterogeneity will affect the reactivity of the smectites under hydrothermal alteration conditions. Indeed, studies of natural analogues of nuclear waste repositories (BOUCHET *et al.*, 1988a, b) show that clay materials similar to bentonites undergo complex reactions when exposed to circulating hydrothermal fluids. In particular, it appears that the high-charge smectite layers do not react in the same way as the low-charge smectite layers. Therefore, any prediction concerning the long-term behaviour of the engineered barriers will have to be supported by the accurate knowledge of these possible smectite reactions under the assumed disposal vault conditions.

Two major types of clay materials are envisaged for engineered barriers in the French nuclear waste dis-

positional programme: a Wyoming-type bentonite and a kaolinite-smectite mixed-layer mineral from a Sparnacian deposit of the Paris Basin. The objective of this paper is to review the state of knowledge about the reactivity of these two clay materials when submitted to hydrothermal alteration. Data from natural site studies and laboratory experiments are used to determine the layer charge effect on the mineral reactions produced by hot water circulation. These data are taken from studies which investigated the behaviour of high- and low-charge layers in pure smectites, illite-smectite and kaolinite-smectite mixed-layered minerals.

PRESENT KNOWLEDGE

Solid solution in dioctahedral smectites

The chemical compositions of the dioctahedral smectites are complex because of variable Al for Si substitution in the tetrahedral layer and divalent for trivalent cations substitution in the octahedral layer. As a consequence, the 2/1 layer charge varies between low-charge and high-charge domains. Montmorillonites and beidellites are distinguished respectively by their 10-Å collapsing or 17-Å swelling properties after neutralization of the octahedral charges with Li (GREENE-KELLY, 1955; BYSTRÖM-BRUSEWITZ, 1976; MALLA and DOUGLAS, 1987b). The low-charge and high-charge smectite layers are distinguished, respectively, by their swelling or collapsing capacities after saturation of their interlayer sites with K (SCHULTZ, 1969; CICELO and MACHAJDIK, 1981; MALLA and DOUGLAS, 1987a, b).

The chemical analyses of dioctahedral smectites reported in this paper were selected from a literature review using the following procedure: chemical analyses are calculated into structural formulae on the basis of an $O_{10}(OH)_2$ anion content and any octahedral occupancy >2.09 atoms or interlayer charge >0.66 (upper limit for the expandable phases; CALLE and SUQUET, 1988) disqualified an analysis from use. A chemiographic analysis of these dioctahedral minerals can be used to study the layer charge effect: the $M^+ - 4Si - R^{2+}$ system (MEUNIER and VELDE, 1989) separates beidellite from montmorillonite and illite: $M^+ = K + Na + 2Ca$; $4Si =$ number of Si divided by the four tetrahedral sites; $R^{2+} = Fe^{2+} + Mg + Mn$. A dioctahedral smectite for which chemical analysis (on $O_{10}(OH)_2$ anion content) and expandability property after Ca- (or Na) and K-saturation have been determined will be represented by a point in these coordinates. Four zones in the region of the solid solution in dioctahedral smectites can thus be defined from the following limits: a charge of 0.43 separates the high-charge region from the low-charge region; the boundary between the beidellite and montmorillonite regions is attained when the percentage of tetrahedral substitution is 50% of the total charge of

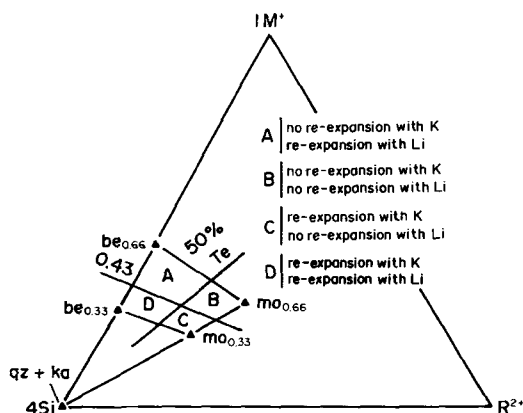


FIG. 1. Chemical composition domains of high-charge beidellites (A), high-charge montmorillonites (B), low-charge montmorillonites (C) and low-charge beidellites (D). The definition of these domains is discussed in the text. qz = quartz; ka = kaolinite; 50% Te = 50% of the total charge of the layer in the tetrahedral layer; 0.43 is boundary between the low- and high-charge domains; the $be_{0.33}-be_{0.66}$ composition line defines the theoretical low- and high-charge beidellite end members; $mo_{0.33}-mo_{0.66}$ is the composition line for the theoretical low- and high-charge montmorillonite end members.

the 2/1 layer (Fig. 1). The selected compositions are thus distributed between the following four poles: low-charge montmorillonite ($mo_{0.33}$); high-charge montmorillonite ($mo_{0.66}$); low-charge beidellite ($be_{0.33}$) and high-charge beidellite ($be_{0.66}$). These four types of smectite layers can, theoretically, be a part of the structure of mixed-layered minerals such as illite-smectite and kaolinite-smectite.

This $M^+ - 4Si - R^{2+}$ diagram can be used to represent the evolution of the layer charge and the change in the beidellite-montmorillonite series. Then, mineral reactions can be interpreted by the classical geometrical laws which are commonly applied in phase diagrams (see metamorphism studies, for example). This method is applied here to interpret the relations between low-charge and high-charge smectite layers which were evidenced in previous studies concerning illite-smectite (JENNINGS and THOMPSON, 1987; BOUCHET *et al.*, 1988b) and kaolinite-smectite mixed-layered minerals (PROUST *et al.*, 1990a, b).

The illite-smectite mixed-layers

The illite-smectite mixed-layers appear in different types of geological environments; sedimentary diagenetic successions (PERRY and HOWER, 1970; WEAVER and BECK, 1971; HOWER *et al.*, 1976; RETTKE, 1976; BOLES and FRANKS, 1979), geothermal fields (STEINER, 1968; McDOWELL and ELDERS, 1980; INOUE *et al.*, 1978; HORTON, 1985; JENNINGS and THOMPSON, 1987), metamorphic environments (NADEAU and REYNOLDS, 1981; PYTTE, 1982; HUNZIKER *et al.*, 1986), and bentonite deposits (ESLINGER *et al.*, 1979; HUFF and TURKMENOGU, 1981; NADEAU

and BAIN, 1986; SRODON *et al.*, 1986; BRUSEWITZ, 1986). VELDE and BRUSEWITZ (1986) showed that the smectitic component of the illite-smectite mixed-layer is always a montmorillonite (no tetrahedral Al for Si substitution) with a constant layer charge in a given geological environment. The illite-beidellite mixed-layers are much rarer and are, indeed, practically always found in rectorite (VELDE, 1985).

Referring to the $M^+ - 4Si - R^{2+}$ system, illite-smectite mixed-layers from the same geological environment are chemically distributed along tie-lines joining a unique illite pole to a unique montmorillonite with a composition located between the low-charge ($mo_{0.33}$) and the high-charge ($mo_{0.66}$) end members (Fig. 2). Thus, in spite of crystallographic evidence for the existence of two differently charged layers, montmorillonites seem to behave as complete solid solutions in chemical reactions. This contradiction between physical and chemical properties leads to the fundamental question: what is a phase? As far as this study is concerned, the montmorillonite species will be considered as a solid solution which can be depicted by the low-charge to high-charge layer ratio, just as the plagioclase series is depicted by the albite to anorthite ratio.

The kaolinite-smectite mixed-layers

The kaolinite-smectite mixed-layers which are less widely distributed in geological environments than the illite-smectite mixed-layers, were discovered in the acid hydrothermal alterations of volcanic rock by SUDO and HAYASHI (1956). From that time, they have been reported in other hydrothermal systems (WIE-

WIORA, 1971) and in some Tertiary sedimentary units of the Yucatan (SCHULTZ *et al.*, 1971) and of the Paris Basin (BRINDLEY *et al.*, 1983). It appears that these mixed-layered minerals are formed by the alteration of pre-existing smectites (ALTSCHULER *et al.*, 1963; SRODON, 1980; THIRY, 1981).

The plastic clay formations of Sparnacian age, exploited in the Paris Basin, are made up of kaolinite-smectite mixed-layered minerals with a wide range of smectite proportion; from 0 to 100% according to BRINDLEY *et al.* (1983). The mixed-layered minerals studied for the engineered barriers have the following composition: 50% kaolinite, 35% high-charge smectite and 15% low-charge smectite (PROUST *et al.*, 1990a, b).

HYDROTHERMAL ALTERATION OF WYOMING-TYPE BENTONITES

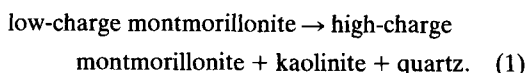
Formation of illite-montmorillonite mixed-layers

The bentonite deposits are formed by alteration of volcanic ash in water and are mostly made up of highly expandable illite-smectite mixed-layers (PEVEAR *et al.*, 1980; KONTA, 1986). The amount of the illite layer increases when physicochemical conditions change; increase in temperature or in K chemical potential (PEVEAR *et al.*, 1980; PYTTE, 1982; SRODON *et al.*, 1986; VELDE and BRUSEWITZ, 1982). The chemical compositions of the highly expandable illite-smectite mixed-layers of Cretaceous age (NADEAU and BAIN, 1986; ESLINGER *et al.*, 1979) are widely scattered when plotted in the $M^+ - 4Si - R^{2+}$ system. On the contrary, the chemical compositions of older deposits (Cambrian to Carboniferous) are aligned between the high-charge illite pole and a montmorillonite pole located between the $mo_{0.33}$ and $mo_{0.66}$ poles (Fig. 2). Such a regular distribution of compositions in the older deposits implies the existence of two successive mineral reactions:

Reaction No. 1: formation of 100% montmorillonite crystals, composed of low-charge and high-charge layers in different proportions, from the smectite produced by the alteration of volcanic glass.

Reaction No. 2: progressive formation of illite-montmorillonite mixed-layers with increasing illite content.

In experimental closed systems, reaction No. 1 leads to the formation of high-charge montmorillonitic layers, quartz and, in some cases, of kaolinite at the expense of the original smectite (HOWARD and ROY, 1985; WHITNEY and NORTHROP, 1988). This reaction can be formally expressed as:



The product is a pure montmorillonite with a bulk

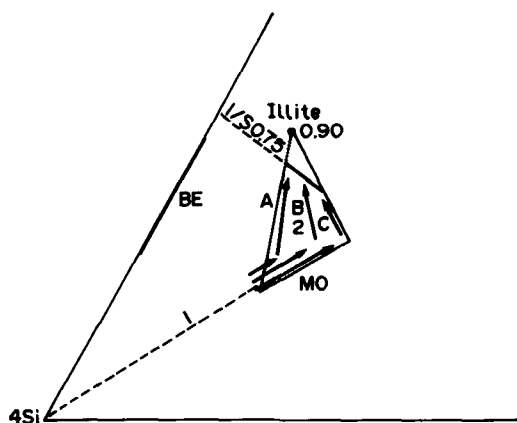
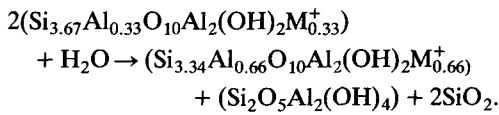


FIG. 2. Formation of a series of illite-smectite mixed-layers in bentonite deposits (MEUNIER and VELDE, 1989). A: Carboniferous, from Poland; B: Silurian, from Great Britain; C: Silurian and Ordovician, from Sweden and the U.S.A. 1: Formation of pure montmorillonite with variable charge (reaction No. 1 in the text); 2: formation of illite-montmorillonite mixed-layer (reaction No. 2 in the text). Illite_{0.90}: high-charge illite; I/S_{0.75}: illite-smectite mixed-layer with a charge of 0.75 (0% expandability on XRD); MO and BE: theoretical compositions of montmorillonites and beidellites.

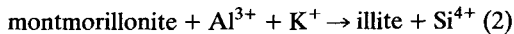
interlayer charge between 0.33 and 0.66. Assuming that the compositions of low-charge and high-charge montmorillonite are those of the end members, the above reaction can be written in the following way:



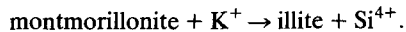
This reaction is more complex in natural environments because other mineral phases are altered. In addition to the smectite, volcanic glass, micas and feldspars components contribute to the reaction when temperature conditions increase: biotites are chloritized while remaining glass and alkaline feldspars dissolved. Nevertheless, the reaction is globally identical to the experimental one because the formation of quartz and, in some cases, kaolinite is observed (PEVEAR *et al.*, 1980).

After completion of reaction No. 1, the illite-smectite mixed-layers crystallize. The chemical composition of the smectite component (formed by reaction No. 1) remains constant, as indicated by the distribution of illite-smectite mixed-layers compositions on the illite to montmorillonite tie lines (MEUNIER and VELDE, 1989). Thus, the formation of illite-smectite mixed-layer from a montmorillonite precursor can be controlled by the two following mechanisms:

mechanism 1 (HOWER *et al.*, 1976):



mechanism 2 (BOLES and FRANKS, 1979):



The progressive increase in the number of illite layers in illite-smectite mixed-layers should no longer be considered as a layer to layer transformation mechanism (HOWER *et al.*, 1976; BETHKE and ALTANER, 1986; BETHKE *et al.*, 1986) but as a crystalline growth process. In fact, the analysis of mixed-layer particle size has shown that their statistical distribution is governed by an Ostwald ripening-like process (INOUE *et al.*, 1988; EBERL and SRODON, 1988; EBERL *et al.*, 1990). Decomposition of X-ray diffraction curves and analyses of crystal morphology of illite-smectite mixed-layers from a diagenetic series show that two populations of particles grow simultaneously: illite-smectite mixed-layer laths and illite hexagons (LANSON and CHAMPION, 1991). Illite behaves as a phase different from illite-smectite mixed-layers with a particular chemical composition (MEUNIER and VELDE, 1989).

The alteration of illite-montmorillonite mixed-layers

It is important to know if the reactions described above, by which the smectites are transformed to illite-montmorillonite mixed-layers, constitute a re-

Table 1. Chemical compositions of clays from natural hydrothermal alteration sites (expressed on $\text{O}_{10}(\text{OH})_2$ anion content). Trois Ilets site, Martinique (BOUCHET *et al.*, 1988b): 1 and 4 are the clay deposits in the veins, 2 and 5 are the altered wall rock, 3 is the clay fraction of unaltered rock. Colorado River delta (JENNINGS and THOMPSON, 1987): fraction $<0.1 \mu\text{m}$ for the following temperatures: 1: 39°C, 2: 48°C, 3: 68°C

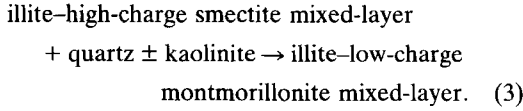
	Les Trois Ilets (Martinique)					Colorado River		
	1	2	3	4	5	1	2	3
Si ^{iv}	3.71	3.61	3.55	3.81	3.61	3.52	3.77	3.78
Al ^{iv}	0.29	0.39	0.45	0.19	0.39	0.48	0.23	0.22
Al ^{vi}	1.52	1.32	1.38	1.43	1.45	1.27	1.35	1.37
Fe ³⁺	0.25	0.46	0.31	0.19	0.35	0.51	0.39	0.36
Mg	0.28	0.29	0.36	0.40	0.27	0.31	0.34	0.36
Ti	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.01
Ca	0.08	0.02	0.13	0.08	0.12	0.00	0.00	0.00
Na	0.04	0.14	0.20	0.19	0.15	0.17	0.10	0.06
K	0.17	0.12	0.08	0.08	0.05	0.24	0.22	0.23

versible process. In other words, can such mixed-layered minerals be recrystallized to another mixed-layer phase with a higher percentage of montmorillonite or even into a new smectite? Two recent studies allow this problem to be dealt with: the alteration of the clay formation at Trois Ilets in Martinique (BOUCHET *et al.*, 1988b) and the sequence of illite-smectite mixed-layers of the Colorado River delta (JENNINGS and THOMPSON, 1987). In the first site, hydrothermal veins crosscut an argillized lava which is mainly composed of a random illite-smectite mixed-layer. The high-charge layer proportion in the smectite component of the mixed-layer diminishes toward the vein while the low-charge smectite and the illite layer proportions increase. The chemical compositions of the mixed-layer minerals are given in Table 1.

The sediment in the Colorado River delta was originally composed of a mixture of detrital minerals including illite-smectite mixed-layers with different degrees of expandability, discrete illite and kaolinite. It was progressively transformed to a pure smectite when the temperature increased from 39 to 68°C (Table 1). Unfortunately, there is no means of knowing if illite and kaolinite were neofomed during this process.

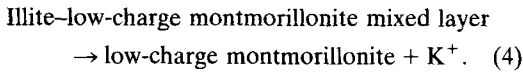
When plotted in the $\text{M}^+ - 4\text{Si} - \text{R}^{2+}$ system (Fig. 3), the compositions of the smectites produced in both cases are very close to the low-charge montmorillonite end member ($\text{mo}_{0.33}$). The reaction takes place in the presence of quartz plus kaolinite and these two phases are found in the Trois Ilets and the Colorado River delta sediments. Two reactions are detectable in the Trois Ilets site. Indeed, the compositions of the clay minerals in the altered rock are on the line joining the quartz (\pm kaolinite) pole to the composition of the clay minerals in the unaltered rock (Fig. 3). This means that the first reaction to occur (reaction No. 3), produces an illite- $\text{mo}_{0.33}$ mixed-layer at

the expense of the illite-high charge smectite mixed-layer which is consumed with quartz and kaolinite:



In spite of the fact that we do not know the contribution of the coarse fraction components, such as feldspars and carbonates, in this reaction, it appears that a brief period of hydrothermal alteration does not increase the amount of illite in illite-smectite mixed-layers, as classically admitted, but modifies the composition of the expandable layers.

The compositions of the clay minerals in altered rock and vein deposits are on the illite to low-charge montmorillonite tie line (Fig. 3). This means that the second reaction to occur (reaction No. 4) produces 100% expandable low-charge montmorillonite at the expense of the illite-mo_{0.33} mixed-layer in the Trois Ilets series:



In a closed chemical system, the geometric relations between clay phases depicted in Fig. 3 imply that reaction No. 4 must produce illite with the low-charge montmorillonite. It is more probable that chemical systems in hydrothermal environments are open; thus, dissolved ions (mainly K⁺) are leached out of the altered rock and illite cannot form.

Reaction Nos 3 and 4 occur under low temperature conditions (<100°C). In the Trois Ilets series, reaction No. 3 is the first to operate (farthest altered wall-rock) whereas reaction No. 4 occurs in the vein. This succession is not so obvious in the Colorado River

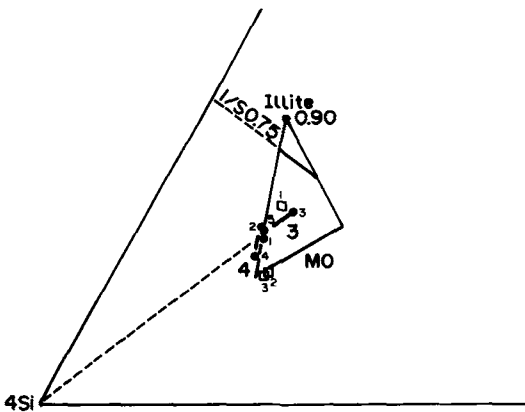


FIG. 3. Hydrothermal alteration of illite-smectite mixed-layers in natural environments. Full circles: Les Trois Ilets, Martinique (BOUCHET *et al.*, 1988b); squares: Colorado River delta (JENNINGS and THOMPSON, 1987). Small-sized numbers refer to the analysis numbers in Table 1. 3: Formation of an illite-low-charge smectite mixed-layer (reaction No. 3 in the text); 4: formation of pure low-charge montmorillonite (reaction No. 4 in the text). MO = theoretical compositions of montmorillonites.

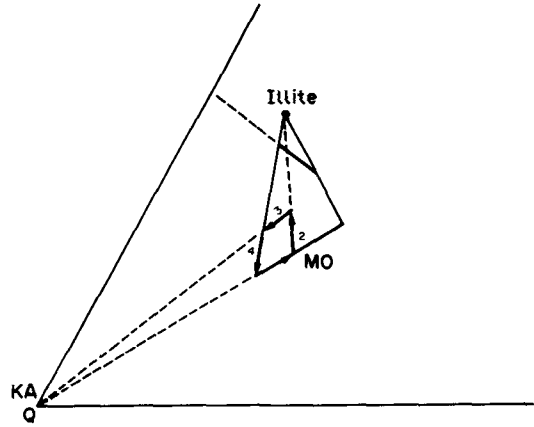


FIG. 4. Representation of the phase relations which control clay mineral reactions when the time \times temperature ($t \times T$) variable is weak (reaction Nos 3 and 4) and high (reaction Nos 1 and 2); KA = kaolinite; Q = quartz; MO = theoretical compositions of montmorillonites. See text for detailed explanation of the reactions.

delta series because there are only three samples. Nevertheless, as the starting and end points are similar to those of the Trois Ilets series, it is possible that reaction Nos 3 and 4 may occur in the same order.

In both cases, the expandability of the starting clay material increases when transformed by short time hydrothermal alteration when temperature conditions are not >100°C. The crystallization and alteration mechanisms of illite-smectite mixed-layers appear to be controlled by a cyclic set of reactions: reaction paths 3 and 4 are symmetrical to reaction paths 1 and 2 (Fig. 4). The crystallization (reaction No. 2) or the dissolution (reaction No. 4) of illite-smectite mixed-layers is controlled by the single illite composition (MEUNIER and VELDE, 1989; ROSENBERG *et al.*, 1985). The crystallization (reaction No. 1) or the dissolution (reaction No. 3) of high-charge montmorillonite layers is controlled by the presence of quartz and/or kaolinite.

The four reactions are all activated by a temperature increase. Nevertheless, the time \times temperature ($t \times T$) conditions are not identical for reaction Nos 3 and 4 (low temperature domain; short time) and reaction Nos 1 and 2 (higher temperature domain; longer time). If the $t \times T$ variable is the active parameter, the stable phase must be the low-charge montmorillonite when $t \times T$ is weak. This is the case in surface conditions where this phase crystallizes in soils and sediments.

Application to engineered barriers

The Wyoming-type bentonite is mainly composed of a low-charge montmorillonite. Experimental as well as natural alteration indicate that it will be transformed first into high-charge montmorillonite

by interaction with hot water. In spite of the fact that the expandability is not affected by this reaction, the exchange capacity decreases. High-charge layers are more reactive and produce illite if K is available in the circulating solutions.

HYDROTHERMAL ALTERATION OF KAOLINITE-SMECTITE MIXED-LAYERS

Experimental results

The mixed-layer taken from the Sparnacian clays of the Paris Basin consist of randomly stacked kaolinite, low- and high-charge smectite layers; it was experimentally altered in deionized water and in a 0.43 M CaCl₂ solution. It was observed that nearly all the high-charge smectite layers, the free kaolinite (5%) and quartz disappeared while a low-charge smectite was formed (PROUST *et al.*, 1990a, b). The cation-exchange capacity increases from 64 to 98 meq/100 g. The addition of Ca²⁺ cations in altering solutions increases the proportion of newly formed low-charge smectite layers at the expense of the high-charge ones.

The question that arises is: will the smectite formed during the alteration experiments have the same chemical compositions as the low-charge smectite layers in the original mixed-layer? If this is the case, the dissolution of the mixed-layered mineral is incongruent and affects only the kaolinite and the high-charge smectite layers. Actually, the new smectite is closer to the beidellite pole than the mixed-layer smectite (Table 2, Fig. 5). The increasing Al for Si substitutions in the tetrahedral sites are due to the chemical conditions imposed by the congruent dissolution of the smectite-kaolinite mixed-layer (pH and the activity of Al in solution) which favours the formation of tetra co-ordinated Al (MERINO *et al.*, 1989). The geometric phase relations in Fig. 5 show that the interlayer charge of the new smectite is not

Table 2. Average chemical compositions (wt%) and cation-exchange capacities (CEC, meq/100 g) for the experimentally altered mixture of kaolinite-smectite mixed-layer + quartz. 1 = starting material; 2 = material reacted with deionized water; 3 = material reacted with 0.43M CaCl₂ solution

	1	2	3
SiO ₂	44.22	58.17	44.41
Al ₂ O ₃	24.46	27.20	21.40
Fe ₂ O ₃	2.00	1.91	2.06
MgO	0.92	0.88	0.66
TiO ₂	1.81	0.58	1.18
MnO	0.27	0.10	0.02
CaO	1.57	2.54	2.47
Na ₂ O	0.31	0.34	0.07
K ₂ O	0.30	0.36	0.13
CEC	63.80	98.20	98.30

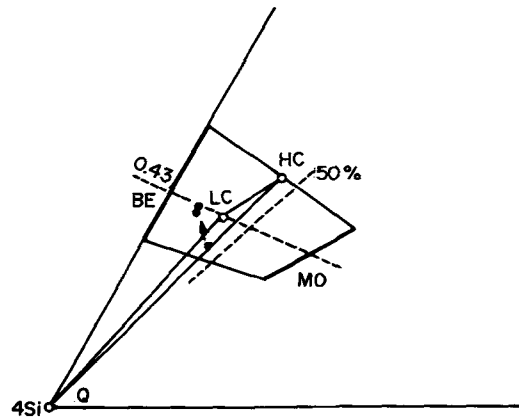
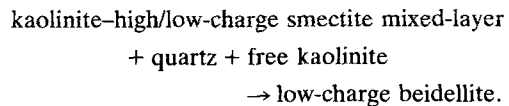


FIG. 5. Representation in the $M^+-4Si-R^{2+}$ system of the alteration reaction of the mixture kaolinite-smectite mixed layer + quartz which produces a low-charge beidellite (PROUST *et al.*, 1990a, b). The direction of the reaction is given by the arrow: the starting point is the composition of the mixture and the end points are the compositions of the low-charge beidellites produced by the deionized water and the CaCl₂ solution experiments. HC and LC represent the possible compositions of the high-charge and the low-charge smectite layers. Q = quartz; MO and BE are theoretical compositions of montmorillonites and beidellites, respectively.

necessarily different from that of the original low-charge layers. Its value must be close to the upper limit of the low-charge domain in order to respect the proportions of the three mixed-layer components. Nevertheless, the new smectite is more beidellitic; thus, it is highly probable that both high-charge and low-charge smectite layers of the kaolinite-smectite mixed-layers are dissolved. On the whole, the reaction should be written:



This reaction is practically identical to that described by SRODON (1980) who synthesized a series of kaolinite-smectite mixed-layers starting with a Wyoming bentonite where the interlayer charge was 0.45. Unfortunately, as the chemical compositions of these minerals is not known, it is not possible to verify if the interlayered smectite is identical to the Wyoming bentonite (layer charge originating in the octahedral position). The crystallization of low-charge smectite is favoured by the presence of Ca²⁺ ions (EBERL, 1978; EBERL *et al.*, 1978; HOWARD and ROY, 1985).

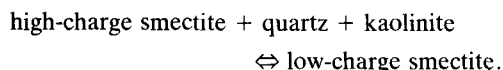
Application to engineered barriers

According to the experimental results, the use of kaolinite-smectite mixed-layers as materials for engineered barriers seems to be justified from the point of view of the expandability and the cation-exchange

capacity properties. Indeed, the mineral reaction produced by hydrothermal alteration increases the low-charge smectite proportion at the expense of the high-charge ones and the mixed-layered kaolinite. The new smectite produced is beidellitic.

CONCLUDING REMARKS

Pure smectites as well as those forming mixed-layers with illite or kaolinite react heterogeneously in hydrothermal processes due to the presence of high-charge and low-charge layers. These processes produce or consume kaolinite and quartz depending on the direction of the reaction:



The direction of the reaction does not depend on the origin of the layer charge because beidellitic as well as montmorillonitic smectites are apparently concerned by the same process. The direction appears to depend on the $t \times T$ variable: low-charge smectites react with kaolinite and quartz to give high-charge ones in deep diagenetic series or geothermal fields (high $t \times T$); high-charge smectites produce low-charge ones with kaolinite and quartz in surface or subsurface conditions (low $t \times T$).

The prediction of the long-term behaviour of a clay-type engineered barrier must, therefore, take the heterogeneity of the dioctahedral smectites into account. The important fact that emerges from all the data available from natural environments or laboratory experiments is that the alteration of such a barrier by hot fluids will first induce a recrystallization of the smectite, before transforming it to less expandable mixed-layers. From this point of view, the kaolinite-smectite mixed-layer seems to be a better material for engineered barriers than Wyoming-type bentonite because the alteration reaction produces an increase in the expandability and cation-exchange capacity properties. Whatever the choice between these two clay materials, it is clear now that the durability predictions based on the reaction kinetics must take into account the heterogeneity of smectites.

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