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Final Report**Radionuclide Separations Using Pillared Layered Materials****Contract No. 725AJ0015-3C****Los Alamos National Laboratory**

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Executive Summary

A series of clays and layered titanates were pillared and calcined to convert their essentially two dimensional structure to three dimensional porous structures with high surface areas. The pillaring agents were alumina, zirconia, chromia and silica based. The pillared clays, particularly those containing Zr pillars, achieved moderate (K_d as high as 13,700 ml/g with V:m = 28) selectivities for Sr^{2+} . In contrast, the silica pillared titanates showed exceptional affinities for Sr^{2+} with K_d values in excess of 100,000 ml/g in 5M $NaNO_3$ + 1M $NaOH$. These latter results suggest a more detailed study of the pillared titanates in the presence of simulants closely resembling real waste solutions.

Objective

The objective of this project is to prepare an all inorganic strontium specific sorbent or ion exchanger for the removal of highly alkaline nuclear waste solutions.

The Approach

Our strategy was to prepare pillared layered materials so as to make their inner surfaces accessible to ion exchange reactions. Two types of layered compounds were chosen for pillaring, clays and sodium titanates. Both classes of compounds have shown a marked affinity for Sr^{2+} but have not been tested under the severe conditions present in nuclear waste solutions.

I. Pillared Clays and Micas

A. Introduction to Pillared Clays

Pillared clays represent a new class of microporous materials that have potential for use as catalysts. A great deal of progress has been made in recent years in our understanding of these materials, particularly as relates to their catalytic behavior. We will concern ourselves in this article to recent work relating to their preparation.

A brief introduction will be given for those new to the field. The impetus behind the original work was to create porous three dimensional structures from two-dimensional clay minerals. It was felt that, since smectite clays have a low layer charge and if an inorganic polymeric cation was chosen that had a high positive charge, pores greater than those available in zeolites would be obtained. The initial choice of polymer was the aluminum Keggin ion $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. A straightforward calculation based upon the range of layer charges in smectite or swelling clays and a +7 charge on the pillaring cations indicates that the distance between pillars should be 17-29Å. Subtracting the width of the pillar, assumed to be about 7Å after dehydration leaves a free distance of 10-22Å. From the amount of aluminum incorporated the average charge lies between 4 and 5. Thus, the pores are smaller than the calculation indicates. However, many different pillaring agents have been used and the pore size depends

upon the choice of pillaring agent and several other factors. Therefore, a section will be devoted to this subject. First we will begin with some information on the nature of the clay minerals used for pillaring.

B. Description of Smectites

The smectites or swelling clays have structures that consist of aluminum or magnesium-oxygen octahedra sandwiched between layers of silica tetrahedra (Figure 1). In a unit cell formed from twenty oxygens and four hydroxyl groups there are eight tetrahedral sites and six octahedral sites. When all the octahedral sites are filled with Mg^{2+} , a magnesium talc of ideal formula $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$ is the result. Such a talc has no imbalance of charge and no ion exchange properties. The smectites are distinguished by the type and location of their cation substitutions. For example, Li^+ may substitute for Mg^{2+} in the octahedral layer to produce a positive charge deficiency. This deficiency is compensated by cations, usually Na^+ or Ca^{2+} residing between the layers. Substitutions may also take place in the tetrahedral sites (Al^{3+} for Si^{4+}). The principal smectite clay minerals and their ideal compositions are listed in Table 1. Typically the positive charge deficiency ranges from 0.4 to 1.2 e per Si_8O_{20} unit. These values translate to an ion exchange capacity range of 0.5-1.5 meq/g. More usual values are 0.7-1.0 meq/g. If the charge deficiency arises from octahedral substitution, then this excess negative charge is distributed over all the oxygens in the framework. These clays tend to be turbostratic, that is, the layers are randomly rotated about an axis perpendicular to the layers. However, should the smectite have been formed by substitution at tetrahedral sites, then the extra charge is more localized and the resultant clay tends to exhibit greater three dimensional order.

Clay mineral compositions are often given in terms of 10 oxygens rather than 20. The formula in which the octahedral layers is a divalent ion such as Mg would have three Mg sites and is termed a trioctahedral clay. Similarly if a trivalent ion such as Al^{3+} dominates in the octahedral layer, two of the three available sites are occupied and the clay is termed dioctahedral. Smectities and mica layers are also termed 2:1 to indicate that there are two tetrahedral sheets to one octahedral

sheet comprising the layer.

Figure 2 is a idealized view of the top (or bottom) of a single-clay layer. The tetrahedra form hexagonal arrays of oxygen atoms with open half-cavities somewhat similar to a crown ether arrangement. The interlayer cations can nest in the cavities allowing the layers to approach each other closely when the clay is dry. However, because there is a mismatch between the central octahedral layer and the tetrahedral layers distortions of the hexagonal array occur as shown in Figure 3.

Smectite clays swell spontaneously when immersed in water and in the swollen condition it is possible to insert inorganic polymers to keep the layers from approaching each other closely. This process is called pillaring and is shown schematically in Figure 4. The most favored pillaring agent is the aluminum Keggin ion, but many other inorganic polymers, as shown in Figure 5, have been used.

Micas have the same structure as smectite clays, but ion exchange capacities of 2-2.5 meq/g. Because of the high layer charge micas do not swell. The interlayer cation is most invariably K^+ . This is because K^+ fits snugly into the hexagonal cavities in the clay layers. The layers approach each other to a very close distance surrounding the potassium ion with twelve oxygens. There is just one such pocket for each K^+ . Because of the tightness with which the K^+ is held in micas they do not swell or exchange with other ions. In order to pillar micas it is first necessary to convert them to the sodium form in which the basal spacing increases to $\sim 12\text{\AA}$. In this condition the mica can be pillared. However, the normal technique of removing K^+ involves the use of sodium tetraphenylborate in a very tedious process. We have developed a much simpler procedure as described in the Experimental Section.

C. Experimental Section

1. Smectite Clays. The as received clays were ground to a fine powder and washed clean of impurities by sedimentation. The general procedure for pillaring was to prepare a slurry containing 2-5% of clay and add the slurry to the solution of pillaring agent. The pillaring solutions consisted of

a. A 0.2M solution of AlCl_3 to which had been added 0.2M NaOH until $\text{pH}=4-4.2$. This treatment converts the Al^{3+} solution to the polymeric $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}$ Keggin ion. An NMR spectrum reveals a sharp peak at 63 ppm showing that the Keggin ion is the major species present.

b. A 0.01-0.04M solution of chromium acetate was used for pillaring.

c. A 0.1M solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was used for the pillaring with $[\text{Zr}(\text{OH})_x]_n^{4n-nx}$ polymeric species. The general procedure was to add the clay slurry to the pillaring solution in the desired ratio and hold at 60°C for 3-10 h. The solid was then recovered by filtration, washed and calcined at 350°C . The samples prepared are listed below.

1. Al_{13} (Keggin ion) - Pillared saponite-TYT-I-013-41
Calcined at 350°C , basal spacing 18.5 Å
2. Cr-pillared Saponite TYT-I-075-43C
($\text{Cr}(\text{NO}_3)_3 + \text{NaOH}$ solution)
Calcined at 350°C , basal spacing 18.06 Å
3. TYT-I-061-31H Cr-pillared saponite
Calcined at 350°C , basal spacing 24.25 Å
4. Zr-Pillared Saponite
 - (a) TYT-I-050-13N - high level of Zr
Calcined at 350°C , basal spacing 25.4 Å.
 - (b) TYT-I-053-13P - low Zr uptake
Calcined at 350°C , basal spacing 21.46 Å
5. Al_{13} - Pillared Montmorillonite
 - (a) TYT-I-03-0M
Calcined at 350°C , then treated with 0.1M HCl to remove excess Al and dried at 200°C , basal spacing 19.13 Å.
 - (b) TYT-I-03-0F
Calcined at 350°C , basal spacing 14.9 Å.
6. Zr-pillared mica - TYT-I-084-52c (mica 3)
Calcined at 350°C , basal spacing 14.9 Å.

The mica of sample 6 was a synthetic phlogopite of ideal formula $\text{NaMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$.

2. Treatment of Micas

In order to convert the potassium micas to sodium micas, they were treated with a 1M NaCl solution at 170-210°C for 20 h. Several such treatments were necessary to achieve 90-95% conversion. The micas so treated were the phlogopite whose formula was given above and biotite of ideal formula $K(Mg,Fe)_3Si_3AlO_{10}(OH)_2$.

The biotite was pillared by the aminosilane technique. The pillaring agent was (3-aminopropyl)-trimethylsilane, $NH_2(CH_2)_3Si(OCH_3)_3$. Since it is an amine, the silane intercalates between the mica layers and upon refluxing, the $Si(OCH_3)_3$ groups hydrolyse to $Si(OH)_3$ and polymerize by condensation of water.

D. Results

Evidence of pillaring was obtained from X-ray data. The original sodium clays have basal spacing of $\sim 12 \text{ \AA}$. On heating to 350°C the spacings are reduced to $\sim 10 \text{ \AA}$. Pillaring expands the basal spacings to 16 $\text{\AA}$ and above and on heating to 350°C form oxide pillars that keep the layers apart. In Figure 6 we show the X-ray powder pattern of the sodium form of saponite. It has a basal spacing of 12.6 $\text{\AA}$ which indicates that a layer of water molecules as well as sodium ions is present in the interlayer space. Figures 7-10 provide examples of the Al₁₃, Zr, and chromium pillared saponite, respectively. The basal spacing of the pillared saponite is given by the first reflection indexed as (001). In Figures 7, 8 and 9 a (002) reflection is also present at half the (001) d-spacing. It is interesting to note that for the zirconium pillared clay the (002) reflection is more intense than the (001) reflection. This is quite unusual and bears further investigation. The product whose X-ray pattern is shown in Figure 10 was prepared by addition of Na_2CO_3 to $Cr(NO_3)_3$ followed by refluxing. We note that this product has a much lower basal spacing (15.4 $\text{\AA}$) than the product prepared from chromium acetate (Fig. 9).

These pillared clays were submitted to Los Alamos National Laboratory (LANL) for evaluation of their selectivities towards Cs^+ and Sr^{2+} . The simulant solutions used were DSSF-7 and CC. The samples (250 mg) were contacted with 7 ml of the simulant for 2 hrs (28 ml/g). The results are presented in Table 1 along with pertinent data on the pillared clays.

The uptake of Cs^+ from both solutions was negligible. However, some rather high K_d values were obtained for Sr^{2+} in the DSSF-7 solution. These results are encouraging and indicate the need for more study of the pillared clays. The mica sample was a sodium phlogopite prepared by a hydrothermal procedure. Since micas have about twice the exchange capacity of smectites, this pillared mica may have a reasonable capacity in addition to a high K_d .

Pillared Biotite

Natural biotite has the ideal formula $\text{K}(\text{Mg,Fe})_3\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ and the K^+ was displaced by sodium hydrothermally. It was pillared with silica by the aminosilane process (see later) and calcined to 450°C . X-ray patterns, first of the sample dried at 60°C and then calcined to 450°C , are shown as Figures 11 and 12, respectively. Since the layer thickness is $9.6 \text{ \AA}$, there is a gallery height of $6.9\text{-}5.9 \text{ \AA}$ present in the calcined pillared biotite. Sr^{2+} has an ionic radius of somewhat smaller than K^+ (1.13 for Sr^{2+} to 1.33 for K^+) and needs half as many sites as K^+ because of its double charge. Thus, it was thought that the expanded mica would have a high affinity for Sr^{2+} . The K_d for Sr^{2+} for this pillared biotite in $5\text{M NaNO}_3 + 1 \text{ M NaOH}$ was 350 ml/g . The volume to mass ratio was 200 and the conc. of Sr^{2+} was 64.5 ppm . While this value may be small relative to what is needed it still represents removal of 63% of the Sr^{2+} in the presence of about 8000 times as much sodium ion. The amount of Sr^{2+} taken up was 0.092 meq/g as opposed to 2.5 meq/g for the exchange capacity of the original mica. If the $V:m$ was reduced to 28 as was done for the results shown in Table 2, the K_d would be many times the observed value. However, it should be remembered that the pillars cover about half the layer surface.

II. Pillared Titanates

A. Introduction

The following report will describe the synthesis of silica pillared titanates and their resulting selectivity's for the uptake of Sr^{2+} in simulated Hanford waste. Two types of pillaring reagents were used to develop materials with variable interlayer distances.

There exists a series of layered titanates with the general formula of $M_2Ti_nO_{2n+1}$ where M is either Na, K, or Cs and $3 \leq n \leq 5$.¹⁻³ The value of n is directly proportional to the size of the alkali metal used in the synthesis procedure and the ratio of M to Ti in the reaction mix. All of these compounds are made by solid state reactions. The idealized structures are shown in Figure 13. A fourth layered titanate which is not represented in the series above, was reported by Grey et. al.³ at the same time as the $Cs_2Ti_5O_{11}$. At this time, the material was reported as a hexatitanate where n took on a value of 6. Grey and coworkers⁴ continued to investigate the structural properties of the "hexatitanate" and discovered that a more accurate formula description would be $Cs_x[Ti_{2-x/4}\square_{x/4}]O_4$ where $\square$ = vacancies and x varies between 0.61 and 0.65. Unlike the kinked titanates which form needle shaped crystallites, this material forms platelet or micaceous crystals. This material will therefore be referred to as the platelet titanate or PT in the following text. The fifth and final titanate examined was first reported by Clearfield and Lehto.⁵ The structure of this compound is not known. However it is indeed a layered material with an analytical formula of $Na_4Ti_9O_{20}$. These five titanates were pillared with silica and then tested in a Hanford simulated waste to determine their affinities for Sr^{2+} .

The distribution coefficients K_d , in units of g/g, were used to determine the affinities for Sr^{2+} . These values can be converted to the typical mL/g by using the density of the solution which was found to be 1.37 g/mL.

B. Experimental Section

Reagents used were of analytical grade or better and were used without further purification.

Similar procedures to those found in the literature were used to synthesize the original titanate materials.¹⁻⁵ They were then converted to the hydrogen form by reaction with HCl solutions whose concentrations varied between 0.1 and 1.0 M. 0.1 M HCl solutions were used for the PT and nonatitanates. The solids were collected by either filtration or centrifugation and then contacted a second time with fresh HCl solutions to assure complete exchange of the H^+ for the alkali metal. Intercalation of amines was achieved by reaction of the protonated solid with a 40 to 60 % by

volume amine solution, which was also 0.1 M in HCl, in a round bottom flask with condensing column attached. The amines used were either propylamine, PA (Aldrich 98 %), or hexylamine, HA (Aldrich 99 %). The reaction times were 3-4 days and the reaction temperatures were between 50 and 60 °C.

Impregnation or intercalation of the siloxanes was achieved by using two different methods. The first follows a similar method reported by Landis et. al.⁶ The hexylamine intercalated solids were reacted with tetraethylorthosilicate, TEOS, in a ratio of solid : TEOS by weight of 1:15.9. The mixture was capped using parafilm and allowed to react for 3 days. The reaction was done at room temperature for the first and third day but was heated to 50 °C on the second day for 5 h. The product was collected by filtration with the final bit of solid being rinsed from the reaction flask using ~3 mL of TEOS. The pillared product was obtained by calcination of the impregnated material at 500 °C in a muffle furnace for 2 h. The second method uses 3-aminopropyltrimethoxysilane, ATS. The procedure is similar to that reported by Sylvester et. al.⁷ 1-2 g of the propylamine intercalated titanate was mixed with 100-200 mL of distilled, deionized water (DDI) and sonicated for 0.5 h. After sonication, the mixture was then heated to ~80 °C with vigorous stirring. In a separate container, 9 g of ATS was mixed with 100 mL of DDI. This solution was then heated for 2 h at 75-85 °C. After this time period, the solution was then mixed with the stirring solid/water mixture and refluxed overnight. The products were collected by centrifugation and washed 4 times using DDI and then dried overnight in a 55 °C oven. The pillared products were obtained by calcination at 500 °C for 2 h in a muffle furnace.

Ion exchange reactions were conducted using a solution containing 5 M NaNO₃, 1 M NaOH, and 91.7 ppm Sr²⁺. The solution weight (g) to solid weight (g) ratio was 200:1 for all samples examined. An example reaction would be mixing 10 g of the ion exchange solution with 0.0500 g of inorganic exchanger in a plastic 70 mL bottle, shaking for 22-24 h, and then filtering through a Gelman membrane 0.2 µm filter. The filtrates are then analyzed for Sr using either an ARL Spectrascan VI DCP-AES or a Varian 250 plus Atomic Absorption unit. Due to the fact that Sr²⁺ is absorbed on glass, plastic equipment was used throughout the ion exchange experiments.

C. Results and Discussion

XRD powder patterns of the pillared materials are shown in Figures 14 and 16. From these results it can be seen that the materials pillared with ATS have much lower d-spacings than those pillared using TEOS. Examination of the titanates pillared with TEOS show much higher d-spacings with the highest value being 19.1 Å for the hexylamine nonatitanate (Fig. 1b). It should be pointed out that all the hexylamine intercalated titanates exhibit similar basal spacings of ~21 Å. Interestingly, the d-spacings appear to decrease upon calcination with decrease in layer charge. That is the PT phase which has the lowest layer charge of the titanates made via solid state reactions has the lowest d-spacing, whereas the trititanate whose layer charge is the highest of these materials has the largest d-spacing. The apparent exception to this rule is the nonatitanate whose basal spacing is 19.1 Å. However, since the structure is not known, it is not included in the above series. The surface area for these materials are shown in Table 1. From this data, it is evident that sample 2-33A2, which was pillared using ATS and contains a gallery height of ~6 Å (d-spacing minus the thickness of the titanium layers) has a lower surface area than those compounds pillared using TEOS. The low surface area is attributed to the low d-spacing which may produce difficulties in the migration of N₂ into the interior. The fact that this compound has a kink in the titanium octahedral layer may also prove to obstruct access into the interlayer region. One would therefore expect that the TEOS pillared materials, which have higher d-spacings, to have increased surface areas over that of the ATS pillared.

Table 1. Silica pillared titanates with corresponding d-spacings after calcination at 500 °C and BET surface areas and % micropore surface areas as calculated by the t-plot method.⁸

Sample ID	Titanate type	d-spacing (Å)	% Micropore Surface Area	BET Surface Area (m ² /g)
RC-4-51B	ATS + PAH ₄ Ti ₉ O ₂₀	11.6	---	---
RC-2-33A2	ATS + PAH ₂ Ti ₄ O ₉	12.7	12.7	43.1
RC-4-55D	TEOS + HAH ₂ Ti ₃ O ₇	17.3	90.0	195.1
RC-4-56D	TEOS + HAH ₄ Ti ₉ O ₂₀	19.1	70.9	443.1
RC-4-61B	TEOS + HAH _x Ti _{2-x/4} O ₄	15	86.8	256.7
RC-4-61D	TEOS + HAH ₂ Ti ₅ O ₁₁	15.7	73.5	214.7

materials. Closer inspection of the surface areas of the TEOS pillared M₂Ti_nO_{2n+1} titanates show an increase in the surface areas with decreasing layer charge. This is true even though the d-spacings are decreasing.

Examination of the distribution coefficients, K_d's, were conducted on these materials to determine if pillaring influenced the selectivity's for Sr²⁺ in the presence of 6 M Na⁺. The results are shown in Table 2. For all the materials examined with the exception of 2-33A2, the amount of Sr²⁺ found in the solution was less than the detection limit of 0.14 ppm. A value of 0.14 ppm Sr²⁺ was therefore used in the calculation of K_d.

Table 2. K_d 's for the silica pillared titanates in solutions containing 5 M NaNO_3 , 1 M NaOH , and 91.7 ppm Sr^{2+} .

Sample ID	Titanate type	K_d (g soln/g solid)
RC-4-51B	ATS + $\text{PAH}_4\text{Ti}_9\text{O}_{20}$	$\geq 131,000$
RC-2-33A2	ATS + $\text{PAH}_2\text{Ti}_4\text{O}_9$	2140
RC-4-55D	TEOS + $\text{HAH}_2\text{Ti}_3\text{O}_7$	$\geq 131,000$
RC-4-56D	TEOS + $\text{HAH}_4\text{Ti}_9\text{O}_{20}$	$\geq 131,000$
RC-4-61B	TEOS + $\text{HAH}_x\text{Ti}_{2-x/4}\text{O}_4$	$\geq 131,000$
RC-4-61D	TEOS + $\text{HAH}_2\text{Ti}_5\text{O}_{11}$	$\geq 131,000$

Pillaring of the $\text{M}_2\text{Ti}_n\text{O}_{2n+1}$ titanates produced large increases in the Sr^{2+} K_d 's over that of the unpillared titanates.⁹ The affinity for Sr^{2+} as a function of gallery height for the ATS and TEOS pillared nonatitanate could not be determined due to the high K_d 's exhibited by both types of samples. It is concluded that these materials may have a use for removal of Sr^{2+} from Hanford nuclear waste. However further work is needed to determine the stability of these pillared products as a function of exposure time to concentrated NaOH solutions which are present in the Hanford nuclear waste storage tanks. Studies of the behavior of these compounds in the presence of complexing agents and other 2+ cations are also needed.

- (1) Anderson, S.; Wadsley, A. D. *Acta Cryst.*, **1961**, *14*, 1245.
- (2) Verbaere, A.; Tournoux, M. *Bull. Societe Chim. France*, **1973**, *4*, 1237.
- (3) Grey, I. E.; Madsen, I. C.; Watts, J. A.; Bursill, L. A.; Kwiatdowska, J. *J. Solid State Chem.*, **1985**, *58*, 350.
- (4) Grey, I. E.; Li, C.; Madsen, I. C.; Watts, J. A. *J. Solid State Chem.*, **1987**, *66*, 7.
- (5) Clearfield, A.; Lehto, J. *J. Solid State Chem.*, **1988**, *73*, 98.
- (6) A) Landis, M. E.; Aufdembrink, B. A.; Chu, P.; Johnson, I. D.; Kirker, G. W.; Rubin, M. *J. Am. Chem. Soc.*, **1991**, *113*, 3189. B) Landis, M. E.; Chu, P.; Johnson, I. D.; Kirker, G. W.; Rubin, M. K. *U. St. Pat.*, Aug. 22, **1989**, 4,859,649.
- (7) Sylvester, P.; Cahill, R.; Clearfield, A. *Chem. Mater.* **1994**, *6*, 1890.
- (8) Lippens, B. C.; Linsen, B. G.; de Boer, J. H. *J. Catal.*, **1964**, *3*, 32.
- (9) Cahill, R. C. unpublished results.

Table I. Idealized structural formulae for principal smectite clays.

1. Octahedrally substituted smectites 2. Tetrahedrally substituted smectites

^a Some F⁻ may substitute for (OH)⁻

Table 2. K_d values in ml/g for adsorption of ^{85}Sr and ^{137}Cs for Pillared Clays in DSSF-7 and cc Simulants.

Exp. No.	Clay Type	Pillaring Agent	d-spacing ($\text{\AA}$)*	Surface Area (M^2/g)	K_d		K_d	
					Sr DSSF-7	cc	Cs DSSF-7	cc
TYT-1-03-OF	Montmorillonite	Al_{13}	19.15		182	0.033	6.64	5.44
TYT-1-03-0M	Montmorillonite	Al_{13} + treat with 0.1M HCl	19.13	273	971	0.43	15.8	13.5
TYT-1-013-41	Saponite	Al_{13}	18.5	330	834	0.52	13.3	1.5
TYT-1-053-13P	Saponite	Zr, $\frac{0.4 \text{ meq.}}{\text{g}}$	21.5	252	6767	1.0	3.9	1.04
TYT-1-050-13N	Saponite	Zr, $\frac{20 \text{ meq.}}{\text{g}}$	25.4	278	13,564	1.5	4.2	1.6
TYT-1-075-43C	Saponite	Chromium	21.3	123	2231	2.8	15.4	2.0
TYT-1-61-31H	Saponite	Chromium	24.2	78	4290	2.1	10.3	2.7
TYT-1-084-52C	Synthetic phlogopite	Zr	14.9	115	4534	0.3	28	4.7

*All samples were clacined at 350°C.

Figure 1. Schematic drawing of smectite clay: , octahedrally coordinated Mg^{2+} or Al^{3+} ; , tetrahedrally coordinated ion (Si); , hydroxyl ion; and , oxygen.

Fig. 2. Hexagonal cavities formed by the sharing of corners of clay tetrahedra. The exchange ion fits into the cavity formed by six oxygen atoms from the layer above and an equal number from the layer below.

Fig. 3. Octahedral sheet and part of attached upper tetrahedral sheet of muscovite-2M₁. Adjacent tetrahedra rotate in opposite directions (arrows) so that basal oxygens move towards nearest octahedral site.

Figure 4. Schematic depiction of the clay pillaring process.

Possible $(\text{Cr})_2$ and $(\text{Cr})_4$ hydroxy complexes

Figure 5. Representation of several inorganic polymers used for pillaring of layered materials.

Fig. 6 . X-ray Pattern of Na-Saponite with
expanded 12.6 Å d-spacing

Cu K- α bar

TYT-I-005-1B PAD5/30mA/45kV Pure Saponite

Date: 26-SEP-95 14:34:04 Start: 2.00 step: 50.00 step: 0.040 time: 2.40 7 pt. / deriv. -20

Plot of 2-theta versus X-ray intensity

GRAPH (4.1.1)

Fig.7. XRD of Al_{13} pillared Saponite

Cu K-alpha

TYT-I-019-3E,

AL-PILLARED SAPONIT

GRAPH (4.1.1)

Date: 26-SEP-95 14:37:25

Start: 2.00 stop: 50.00 step: 0.040 time: 2.40

7 pt. / deriv. -20

Plot of 2-theta versus X-ray intensity

Fig. 8. XRD of $[\text{Zr}(\text{OH})_n]_m^{m(4-n)+}$ pillared Saponite.

Cu K-alpha

2-THETA (deg)

GRAPH (4.1.1)

TYT-I-040-12J PAD5/30mA/45kV Zr-Pillared Saponite

Date: 26-SEP-95 14:42:45 Start: 2.00 stop: 50.00 step: 0.040 time: 2.40 7 pt. / deriv. -38

Plot of 2-theta versus X-ray intensity

Fig.9. XRD of Saponite pillared by polymerized Chromium Acetate.

25

I30J.X1

Cu K-alpha

2-THETA (deg)

GRAPH (4.1.1)

TYT-I-062-30J PAD5/30mA/45kV Cr-Pillared Saponite / $\text{Cr}_3(\text{OH})_2(\text{OAc})_7$

Date: 26-SEP-95 14:54:21 Start: 2.00 stop: 50.00 step: 0.040 time: 2.40 7 pt. / deriv. -40

Plot of 2-theta versus X-ray intensity

Fig. 10. XRD pillared with polymerized Chromium nitrate solution.

Cu K-alpha

2-THETA (deg)

GRAPH (4.1.1)

TYT-I-075-43C.2 PAD5/30mA/45kV Cr-Pillared Saponite / $\text{Cr}(\text{NO}_3)_3 \cdot \text{Na}_2\text{CO}_3$

Date: 26-SEP-95 14:48:31 Start: 2.00 stop: 40.00 step: 0.040 time: 2.40 7 pt. / deriv. -40

Plot of 2-theta versus X-ray intensity

Fig. 11. Aminosilane Intercalated Biotite
Uncalcined

27

Cu K-a1

2-THETA (deg)

GRAPH (4.1.1)

SBW-2-35 BIO PILL 60C 40MA/45KV

17:44:23

Start:

2.00

stop:

50.00

step: 0.040

time: 2.40

5 pt. / deriv. -40

Plot of 2-theta versus X-ray intensity

Fig.12. Aminosilane Biotite Intercalate
Heated to 450°C.

Cu K-a1

2-THETA (deg)

GRAPH (4.1.1)

SBW-2-35 BIO PILL 450C AL HOL 50KV/180MA

15:06:09

Start:

2.00

stop:

50.00

step:

0.040

time:

1.00

5 pt. /

deriv.

-40

Plot of 2-theta versus X-ray intensity

Figure 13. Idealized structures of A) $\text{Na}_2\text{Ti}_3\text{O}_7$, B) $\text{K}_2\text{Ti}_4\text{O}_9$, C) $\text{Cs}_2\text{Ti}_5\text{O}_{13}$, and D) Cs_xTi_2 -

B233.X1

Figure 15. XRD powder patterns for ATS pillared PAH₂Ti₄O₉ calcined to 500 °C for 2h.

Cu K- α

2-THETA (deg)

GRAPH (4.1.1)

RC-4-51B SILANE TI9 CAL500C R, ALB, SS=1

Date: 14-JUL-95 16:41:02 Start: 3.00 stop: 55.00 step: 0.020 time: 1.00

Plot of 2-theta versus X-ray intensity

Figure 16. XRD powder patterns for TEOS pillared A) $\text{HAH}_2\text{Ti}_3\text{O}_7$, B) $\text{HAH}_4\text{Ti}_9\text{O}_{20}$, C) $\text{HAH}_2\text{Ti}_5\text{O}_{11}$, and D) $\text{HAH}_x\text{Ti}_2\text{-x/4O}_4$ calcined at 500°C for 2h.

Cu K- α bar Expand=0.6 2-THETA (deg) GRAPH (4.1.1)
 RC-4-55D TEOS PIL HAH₂Ti₃O₇ 500C P.SP
 Date: 6-SEP-95 11:52:03 Start: 2.00 stop: 55.00 step: 0.040 time: 2.40
 Plot of 2-theta versus X-ray intensity

4810.X1
 4818.X1
 4850.X1
 4850.X1

preprints removed,
 ds