Investigation of the utility of chemically treated indigenous minerals in radioactive waste treatment

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Abstract

Ion exchange studies have been carried out on two indigenous micaceous minerals treated with (i) Sodium cobaltinitrite and (ii) sodium chloride + hydrogen peroxide, and their utility in radioactive liquid waste treatment assessed.

Key words : Mica, vermiculite, ion-exchange, equilibrium uptake, radioactive wastes, breakthrough capacity.

1. Introduction

Vermiculite, a weatheration product of mica, is formed in nature by the hydrothermal action and percolation of ground water on mica. It has a cation exchange capacity, which is much higher than that of parent mica. The association of any mica with vermiculite results in decreased exchange capacity. Therefore, transformation of mica to vermiculite is a desirable proposition.

As part of our continuing research programme of evaluating indigenous minerals regarding their utility in radioactive liquid waste treatment, some micaceous minerals, which were evaluated earlier[1] were subjected to two different chemical treatments [(i) with sodium cobaltinitrite and (ii) with sodium chloride + hydrogen peroxide] so as to bring about the vermiculitization of mica. These vermiculitized products were subjected to physico-chemical investigations. The results are briefly described in this communication.

2. Materials and methods

Materials

Two minerals evaluated in the earlier work[1], *viz.*, A. V. (Amin's vermiculite)—a mineral close to a vermiculite and S. V. (Seshaiya's vermiculite)—a mineral close to a mica,

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were taken up for the transformation studies. Reagents and chemicals used were of A.R. grade.

Methods

The apparatus used and the methods adopted for the physico-chemical studies were the same as those described in the earlier work[1].

Ion exchange studies were made by batch and column methods using the radioactive tracers Cs^{+}-134, Rb^{+}-106, Sr^{++}-85, 89, Ba^{++}-133, Co^{++}-60, Mn^{++}-54 and Zn^{++}-65.

Procedure adopted for vermiculitization:

Method I

Sodium cobaltinitrite treatment: Method adopted by Robert and Pédro[2] was used in the transformation work. The washed products free from the yellow precipitate were kept in contact with 1 $\bar{M}$ $MgCl_2$ solution (200 ml) for four days with occasional shaking to have Mg^{++} as the uniform interlayer cation in the products. The resultant products were washed with distilled water (termed as series I in these studies) and then dried in an oven at 315° K.

Method II

Sodium chloride $(3\bar{M})$ + H_2O_2 *(5 per cent) treatment:* Method adopted by Le Dred[3] has been used in this transformation work. The final exfoliated products were given the $MgCl_2$ treatment as described under Method I. These are termed as series II products in these studies.

3. Results and discussion

3.1. *Chemical analyses*

Pure vermiculite possesses[4, 5] (*a*) high percentage of MgO + CaO (~ 20 to 24 per cent), (*b*) practically negligible K_2O (*c*) high total water content (~ 18–20 per cent) and (*d*) higher percentage of Fe^{+3} compared to Fe^{+2}. In the case of a mica, (*a*) K_2O percentage is quite high (> 8 per cent), (*b*) total water content is small (~ 2–5 per cent) and percentage of Fe^{+2} is more than Fe^{+3}.

On examination of the analytical results (Table I), it can be concluded that minerals A.V. and S.V. are close to a vermiculite and mica respectively[1].

Investigations on A.V. were carried out with a view to find out whether any further vermiculitization was possible in this mineral. The increase in MgO and slight decrease in K_2O observed in A.V. (I) and (II) (Table I) suggests vermiculitization. However, a substantial reduction in the total water content is brought about by both the chemical

Table I

Results of chemical analyses

Minerals	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	Total H_2O 1373° K	Total
A.V. (n)	33·56	16·07	7·00	0·50	18·03	4·73	0·08	0·19	0·82	19·02	100·00
A.V. (I)	34·88	20·94	7·49	0·50	20·00	2·10	0·05	0·11	0·80	13·01	99·88
A.V. (II)	38·12	17·42	5·85	0·39	19·62	4·56	0·06	0·15	0·82	13·60	100·59
S.V. (n)	44·64	19·11	0·30	4·80	7·18	2·01	1·29	13·70	2·07	4·02	99·12
S.V. (I)	46·07	17·20	2·64	4·04	8·57	2·01	1·29	10·30	2·10	5·78	100·00
S.V. (II)	40·24	20·48	4·57	2·05	10·36	2·13	1·30	7·22	2·20	9·20	99·75

(n) = Natural mineral. (I) = Series I product. (II) = Series II product.

treatments. It is, therefore, inferred that processes other than vermiculitization may also be simultaneously taking place.

In the case of mineral S.V., there is an increase in MgO and H_2O contents and decrease in K_2O, which suggest the vermiculitization process. Using these as criteria of vermiculitization it is concluded that better vermiculitization is achieved by Method II compared to Method I.

3.2. *Differential thermal analyses (D.T.A.) and thermogravimetric analyses (T.G.A.)*

D.T.A. and T.G.A. of the natural, series I and series II minerals are included in Fig. 1. D.T.A. of A.V. [series I, curve *a* (I)] clearly shows a dual low temperature endothermic peak, which may be attributed to the presence of Mg^{++} and Ca^{++} ions in the interlayer position of the mineral at slightly high relative humidity[6]. The resolution of these two peaks is, however, unsatisfactory in the other two cases [Curves *a* and *a* (II)]. Series I, S.V. [curve *b* (I)] shows two ill-separated initial endothermic reactions, which are more prominent than those shown by the natural mineral, (curve *b*) indicating that some vermiculitization has taken place in this product. D.T.A. curve of series II, S.V. [curve *b* (II)] shows well defined peaks in this region. The exothermic peak at 923° K is attributed to structural alteration of this product.

T.G.A. curves [*a*′, *a*′ (I), *a*′ (II) for A.V. and *b*′, *b*′ (I), *b*′ (II) for S.V.] included in the same figure confirm the conclusions arrived at by D.T.A.

3.3. *X-ray analyses*

X-ray analyses data (Table II) of series I and series II products of A.V. show a slight decrease in spacings from 1·414 nm to 1·36 nm and 1·381 nm respectively, which may be due to the exchange reaction taking place between Mg^{++} and Ca^{++} ions. In the case of series I and series II products of S.V., the appearance of the '*d*' values at 1·413 nm and 1·414 nm respectively confirm that vermiculitization has taken place in both the cases. In the case of series II stronger intensity corresponding to 1·414 nm spacing indicate better vermiculitization. Further it may be mentioned here that the presence of 1·028 nm and 1·072 nm spacings indicate that the conversion of mica to vermiculite is incomplete.

3.4. *Ion exchange studies*

3.4.1. *Batch method (equilibrium uptake studies)*

Equilibrium uptake values (Table III) observed with 1 $\bar{M}$ NaCl solution (100 hr contact time) show a very little (relative) increase in the case of series I and series II products of AV, whereas there is an appreciable (relative) increase in the Na^+ uptake in the case of

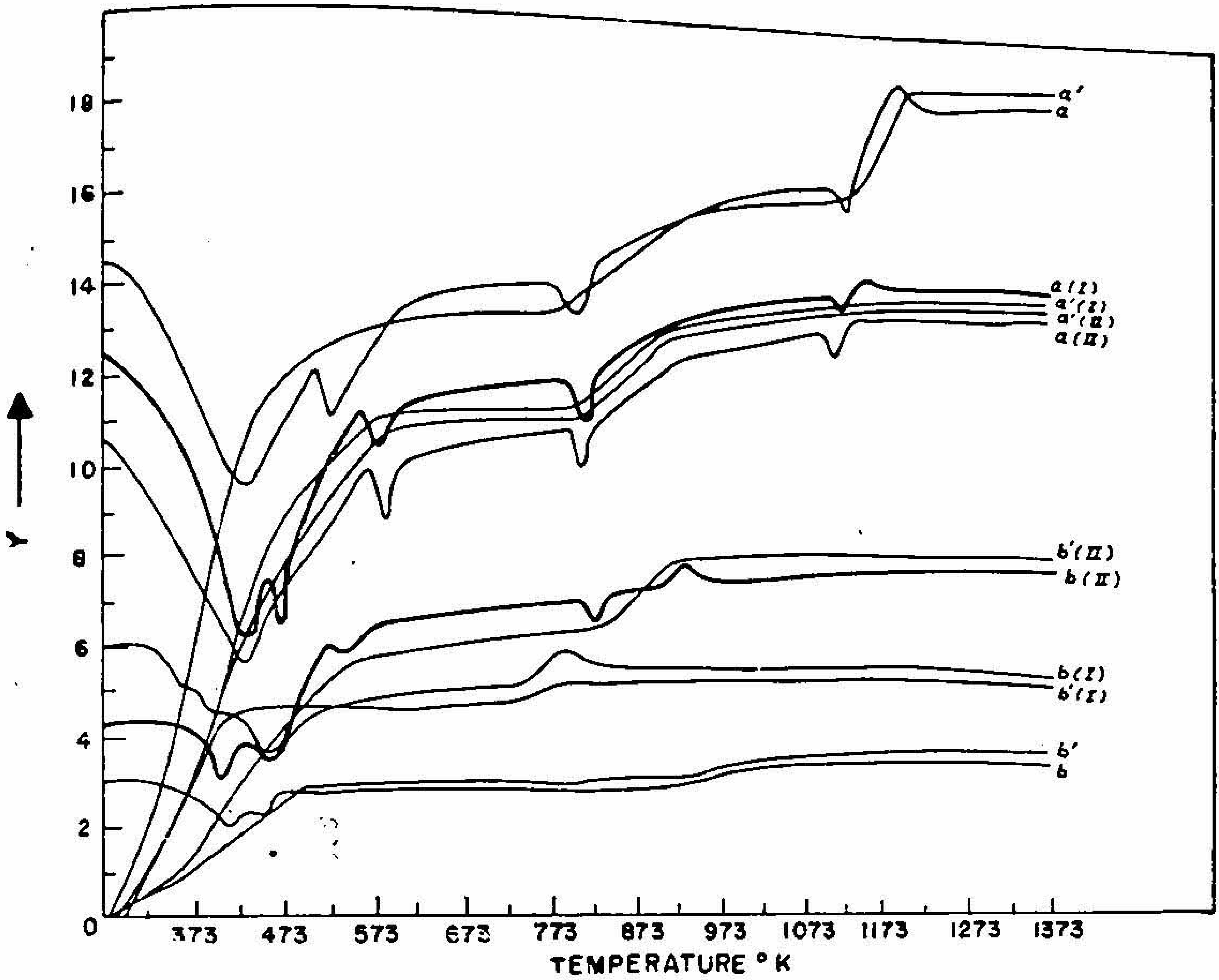

FIG. 1. D.T.A. and T.G.A. curves.

Curves

a', *a'* (I), *a'* (II)—T.G.A. natural, Series I, Series II (A.V.)

b' b' (I), *b'* (II)—T.G.A. natural, Series I, Series II (S.V.)

Y-axis : water loss percentage.

a, *a* (I), *a* (II)—D.T.A. natural, Series I, Series II (A.V.)

b, *b* (I), *b* (II)—D.T.A. natural, series I, series II (S.V.)

Curve	*Y-axis*
a	m.v. × 1 + 14·5
a (I)	m.v. × 1 + 12·5
a (II)	m.v. × 1 + 10·7
b	m.v. × 1 + 3
b (I)	m.v. × 1 + 4·4
b (II)	m.v. × 1 + 6·0

Where m.v. is millivolt multiplied by a factor of 1 and the last digits are arbitrarily added to draw the figure.

Table II

X-ray data

Minerals

A.V. (n)		A.V. (I)		A.V. (II)		S.V. (n)		S.V. (I)		S.V. (II)	
dnm	I/Io	dnm	I/Io	dnm	I/Io	dnm	I/Io	dnm	I/Io	dnm	I/Io
1·414	10							1·413	3	1·414	6
		1·36	10	1·381	10						
						0·983	10	1·028	10	1·072	10
				0·738	1						
0·711	1	0·708	1	0·694	1						
		0·500	1	0·500	1						
		0·455	1	0·473	2					0·450	3
				0·444	1			0·433	2		
								0·418	2		
								0·371	2		
0·363	2	0·363	2	0·367	2			0·363	2		
		0·356	6	0·356	4						
						0·330	8	0·330	6	0·336	5
0·319	1	0·319	3	0·319	3					0·319	1
								0·316	2		
						0·313	2			0·311	1
0·293	3	0·293	2	0·293	3						
						0·289	1			0·289	1
				0·281	6						
				0·264	2						
										0·262	4
								0·260	5		
		0·258	5	0·258	1	0·258	4				
0·256	1					0·256	2				

		0·251	1	0·255	1						
0·238	1	0·237	5	0·238	5	0·241	3	0·241	3	0·241	3
						0·225	1	0·225	2	0·228	2
										0·219	2
						0·215	4	0·215	3		
								0·210	2		
										0·207	1
		0·2014	1			0·199	5	0·198	2		
						0·181	2	0·180	4	0·182	1
		0·1735	1	0·1735	1						
				0·1670	4					0·167	4
		0·1663	3			0·166	6	0·166	7		
0·1536	4			0·1536	6						
		0·1530	5			0·153	8	0·153	8	0·154	7
				0·1435	1						
		0·1425	2								
								0·137	3		
						0·135	4				
		0·1328	2	0·1328	4						

(n) = Natural mineral. (I) = Series I product. (II) = Series II product.

Table III

Equilibrium uptake values (batch method) and breakthrough capacities (column method) with different cations (meq./100 g. pH ~ 6·8)

Mineral	(1) NaCl	(1) KCl	(1) NH_4 Cl	(2) Cs Cl	(2) Rb Cl	(2) Ba Cl_2	(2) Sr Cl_2	(2) Co Cl_2	(2) Mn Cl_2	(2) Zn Cl_2	(3) Cs Cl	(3) Rb Cl	(3) Ba Cl_2	(3) Sr Cl_2	(3) Co Cl_2	(3) Mn Cl_2	(3) Zn Cl_2
A.V. (n)	104·3	50·0	50·5	36·8	39·5	30·0	35·8	23·9	24·6	21·0	59·46	60·30	32·51	37·70	26·25	27·60	22·16
A.V. (I)	106·8	48·5	41·0	38·1	41·5	31·3	38·4	25·7	28·7	24·3	69·04	72·90	33·34	40·34	32·91	33·53	30·74
A.V. (II)	113·2	44·0	38·5	48·1	50·5	36·8	44·4	36·1	38·5	35·7	96·58	105·7	48·97	50·5	47·82	47·95	45·50
S.V. (n)	6·5	5·0	4·5	7·5	8·0	5·1	7·8	5·3	6·4	5·1	13·22	13·77	8·51	10·83	7·37	8·20	6·93
S.V. (I)	17·7	16·0	10·5	13·8	18·5	12·8	18·2	12·1	15·5	11·0	20·96	22·32	17·99	24·98	13·10	16·78	12·62
S.V. (II)	53·5	23·0	23·5	20·0	22·8	22·0	29·0	22·9	28·8	20·5	41·09	43·66	32·28	36·88	30·66	31·23	30·17

(1) Batch method (without radiotracers)

(2) Batch method (with corresponding radiotracers)

(3) Column method (with corresponding radiotracers)

(n) Natural mineral. (I) Series I product. (II) Series II product.

series I and series II of S.V. The equilibrium uptake values obtained with K^+ and NH_4^+ ions were much smaller than those of Na^+ (Table III) (1 $\tilde{M}$ solutions of NaCl, KCl and NH_4Cl at pH ~ 6·8 were equilibrated). This may be due to the fact that ions like K^+ and NH_4^+ tend to exclude most of the interlayer water of the mineral[6] and thus prevent complete ion exchange.

3.4.1.1. *Equilibrium uptake studies using the corresponding radioactive tracers (Batch method)*

Experiments with 10^{-2} $\tilde{M}$ solutions of Cs^+, Rb^+, Ba^{++}, Sr^{++}, Co^{++}, Mn^{++} and Zn^{++} (Table III, pH ~ 6·8) show less increase in uptake of these different ions in the case of series I products compared to series II products. Order of equilibrium uptake of these different cations is found to be: $Rb^+ > Cs^+ > Sr^{++} > Ba^{++} > Mn^{++} > Co^{++} > Zn^{++}$.

3.4.1.2. *Column method (using corresponding radioactive tracers)*

Column experiments (Table III) were carried out to study the breakthrough capacity of the different treated minerals using same solutions as in batch method. The results of column experiments confirm in general the conclusions of the batch method.

4. Potential application in radioactive waste treatment

The increased exchange capacity of the mineral by chemical treatments like NaCl + H_2O_2 will facilitate removal of practically all active ions such as Cs^{137} and Sr^{90}. The total throughput in a column using vermiculite in its transformed form would be a few times more in terms of column volumes than the one using mica in natural form. Thus this transformation process can be used for the selection of most suitable minerals before application in treatment of radioactive wastes.

5. Conclusion

It can be concluded from these studies that by both these chemical treatments, the mineral A.V. (which is close to vermiculite) undergoes a small noticeable improvement in ion-exchange behaviour as it is already close to vermiculite while the mineral S.V. (a biotite mica) undergoes the vermiculitization process to certain extent. Further the transformation is better with the second method of chemical treatment compared to the first one.

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