Investigation of the utility of some minerals of Indian origin in radioactive waste treatment

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Abstract

Ion exchange studies have been carried out on vermiculite and mica samples of Indian origin with a view to utilise them in the treatment of low and intermediate levels of radioactive liquid wastes. Details of their practicability in radioactive waste management in India are indicated.

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

1. Introduction

The elimination of radioactive ions like $Cs^+ - 137$ and $Sr^{++} - 90$ from the solutions of spent nuclear fuels is quite difficult and depends upon the stability of the exchanger in high radiation field. It is known that clay-minerals in general, and among them vermiculite[1-3] in particular, occupy a favourable place.

As part of our continuing research programme of evaluating minerals of Indian origin regarding their utility in radioactive waste treatment, two indigenous micaceous minerals have been systematically examined. A gist of the results obtained is given in this communication.

2. Materials and methods

Materials : The two mineral samples named after the suppliers were designated as (i) Amin's vermiculite (A.V.) and (ii) Seshaiya vermiculite (S.V.). Reagents and chemicals used were of A.R. grade.

Methods : Chemical analyses were carried out, following the standard methods adopted earlier by Riley[4] for such analyses. Evaluation of the ferrous content was carried out, following the method of Ingamells.[5] Differential thermal analyses (D.T.A.) were carried out with a heating rate of $6°$ K/min. using an apparatus fabricated by Chemistry Division of Bhabha Atomic Research Centre.[6] An automatic recording 'Stanton' thermobalance, with a heating rate of $6°$ K/min. was used for T.G.A. X-ray analyses were carried out using Philips X-ray machine PW 1010 using $CuK\alpha$ radiations (34 K.V., 18 m.a.) and Ni filter.

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 $Zn^{++}-65$.

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3. Results and discussion

3.1. *Chemical analyses* : Pure vermiculite possesses, (*a*) high percentage of MgO + CaO (20 to 24 per cent), (*b*) practically no K_2O, (*c*) high total water contents (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 (*c*) percentage of Fe^{+2} is more than that of Fe^{+3} (Table I).

Table I

Chemical analyses of the minerals

Constituents	A.V.	S.V.
SiO_2	33·56	44·64
Al_2O_3	16·07	19·11
Fe_2O_3	7·00	0·30
FeO	0·50	4·80
MgO	18·03	7·18
CaO	4·73	2·01
Na_2O	0·08	1·29
K_2O	0·19	13·70
TiO_2	0·82	2·07
H_2O (1373° K)	19·02	4·02
F'	...	...
Total	100·00	99·12

On examination of the analytical results (Table I) of the two mineral samples chosen for investigation, in the light of the above-mentioned guidelines, the following qualitative conclusions can be arrived at :

(i) Mineral A.V. shows good similarity to vermiculite.

(ii) Mineral S.V. shows good similarity to mica.

3.2. *Differential thermal analyses (D.T.A.) and thermogravimetric analyses (T.G.A.):* D.T.A. and T.G.A. of samples A.V. and S.V. are included in Fig. 1 along with those reported in literature for vermiculite and mica. A comparison indicates a good similarity between the appropriate pairs, confirming thereby the conclusions of chemical analyses. It may be mentioned here that mineral A.V. shows an extra endothermic peak at 830° K, which is not exhibited by pure vermiculite. It may be due to the presence of illite[7] mineral (hydrous mica) or montmorillonite[8] in vermiculite. T.G.A. results confirm the conclusions arrived at by D.T.A.
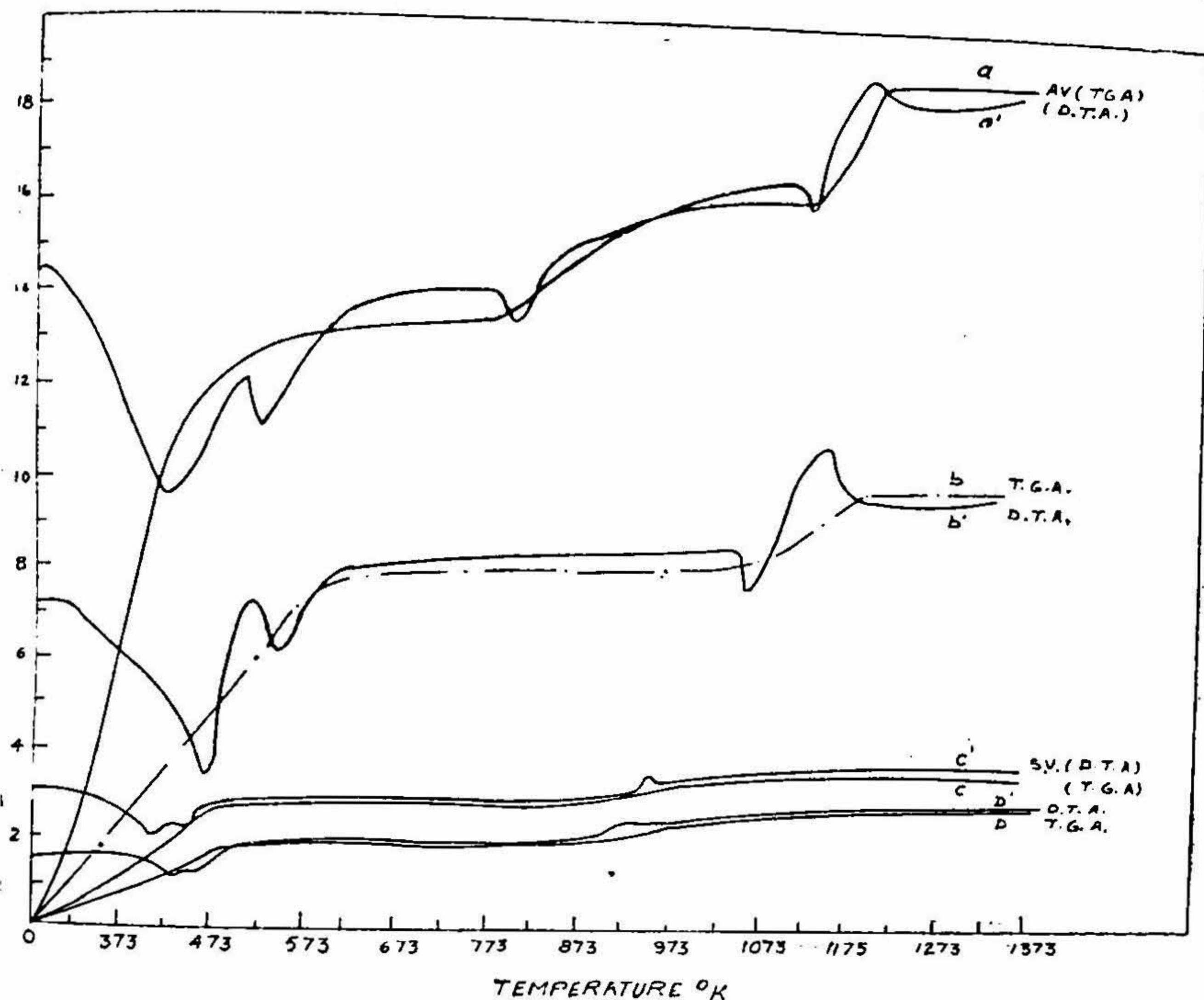
FIG. 1. D.T.A. and T.G.A. curves.

Cuc		Y-axis
a, c	:	Water loss per cent
b, d	:	Water loss per cent × 2
u'	:	m.v. × 1 + 14
b'	:	m.v. × 2 + 7
c'	:	m.v. × 1 + 3
d'	:	m.v. × 2 + 1·5

where m. v. is millivolt, 14, 7, 3 and 1·5 are the digits added to draw the figure.

3.3: *X-ray analyses* : A.V. and S.V. show most of the predominant lines corresponding to a vermiculite[9] and biotite mica[10] respectively (Data not given).

3.4. *Ion-exchange studies* :

3.4.1. Batch method (equilibrium uptake studies) : Curves A.V. (C) and S.V. (C) in Fig. 2 represent the variation of equilibrium uptake of Na^+ ion as a function of the initial concentration of NaCl employed (in the range 0·0625-1·0 M, pH ~6·8) while curves A.V. (T) and S.V. (T) in Fig. 2 depict the variation in uptake as a function of time (when 1 M NaCl solution is equilibrated with the minerals). The uptake of
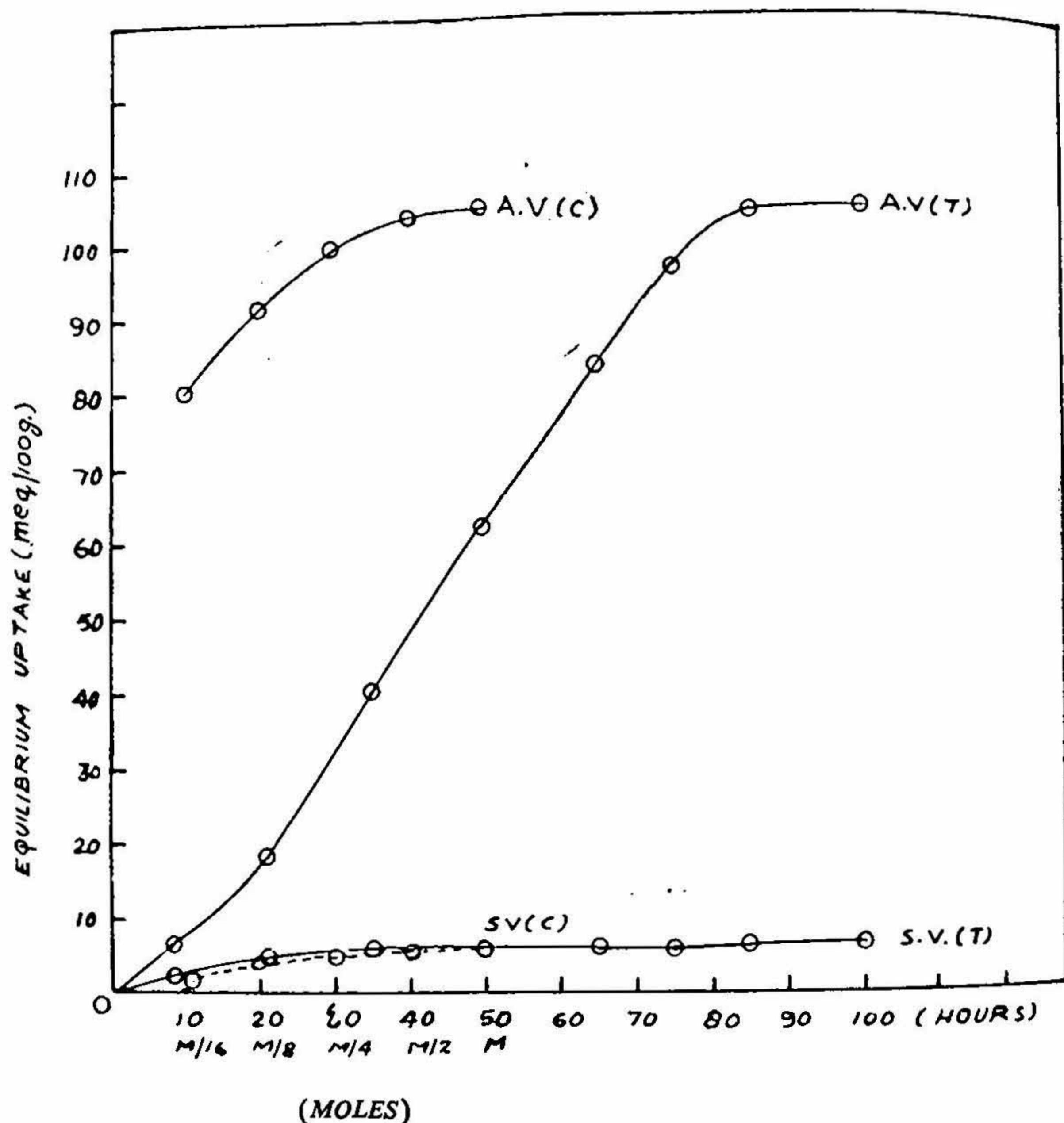
FIG. 2. Variation of equilibrium uptake with time and concentration.

No.		X-axis
C	:	Effect of concentration (moles)
T	:	Effect of time (hours)

Na^+ observed was $104\cdot3$ meq/100 g and $6\cdot5$ meq./100 g (Table II), in the case of minerals A.V. and S.V. respectively at 100 hours contact time (1 M NaCl solution). These values are in the range expected for a vermiculite and mica respectively.

The equilibrium uptake values observed for K^+, NH_4^+ and Cs^+ (pH $\sim$ 6·8) were much smaller than that of Na^+ (Table II) (1 M solution equilibrated for 100 hours). This can be due to the fact that ions like K^+, NH_4^+ and Cs^+ tend to become fixed and relatively non-replaceable,[11] which prevent any further ion exchange,
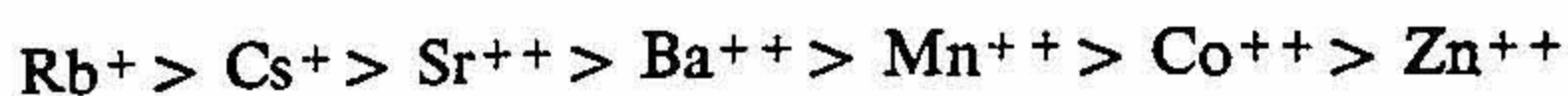
Table II

Equilibrium uptake values (batch method) and breakthrough capacities (column) method with different cations (meq/100 g.)

pH~6.8

Mineral	$NaCl^{(1)}$	$KCl^{(1)}$	$NH_4Cl^{(1)}$	$CaCl^{(1)}$	$CsCl^{(2)}$	$RbCl^{(2)}$	$BaCl_2^{(2)}$	$SrCl_2^{(2)}$	$CoCl_2^{(2)}$	$MnCl_2^{(2)}$	$ZnCl_2^{(2)}$	$CsCl^{(3)}$	$RbCl^{(3)}$	$BaCl_2^{(3)}$	$SrCl_2^{(3)}$	$CoCl_2^{(3)}$	$MnCl_2^{(3)}$	$ZnCl_2^{(3)}$
A.V.	104·3	50·0	50·5	39·5	36·8	39·5	30·0	35·8	23·9	24·6	21·0	59·46	60·30	32·51	37·70	27·25	27·60	22·16
S.V.	6·5	5·0	4·5	5·0	7·5	8·0	5·1	7·8	5·3	6·4	5·1	13·22	13·57	8·51	10·83	7·37	8·20	6·93

[1] Batch method (without radiotracers).
[2] Batch method (with corresponding radiotracers).
[3] Column method (with corresponding radiotracers).

3.4.1.1. Equilibrium uptake studies using the corresponding radioactive tracers (Batch method): Experiments with 10^{-2} M solutions of Cs^+, Rb^+, Ba^{++}, Sr^{++}, Co^{++}, Mn^{++} and Zn^{++} at pH ~ 6.8 showed that the uptake of different monovalent and divalent cations is much more in A.V. compared to S.V. (Table II). 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 were carried out to study the breakthrough capacity of the minerals A.V. and S.V. (Table II) using same solutions as in batch method.

4. Application in radioactive waste treatment at BARC

The results of the above-mentioned investigations prove the superiority of A.V. compared to S.V. Indigenous natural minerals of the type (A.V.) are, therefore, being employed in ion exchange unit at Trombay, which was set up in 1966 and is in operation since then.[12,13] The unit consists of eight cylindrical mild steel columns of 1.8 meter diameter, four of which operate in parallel, while the other four constitute a stand-by. Each column holds about 2.5 tonnes of natural vermiculite of particle size − 20 + 40 mesh. The flow diagram of the ion exchange unit is shown in Fig. 3.
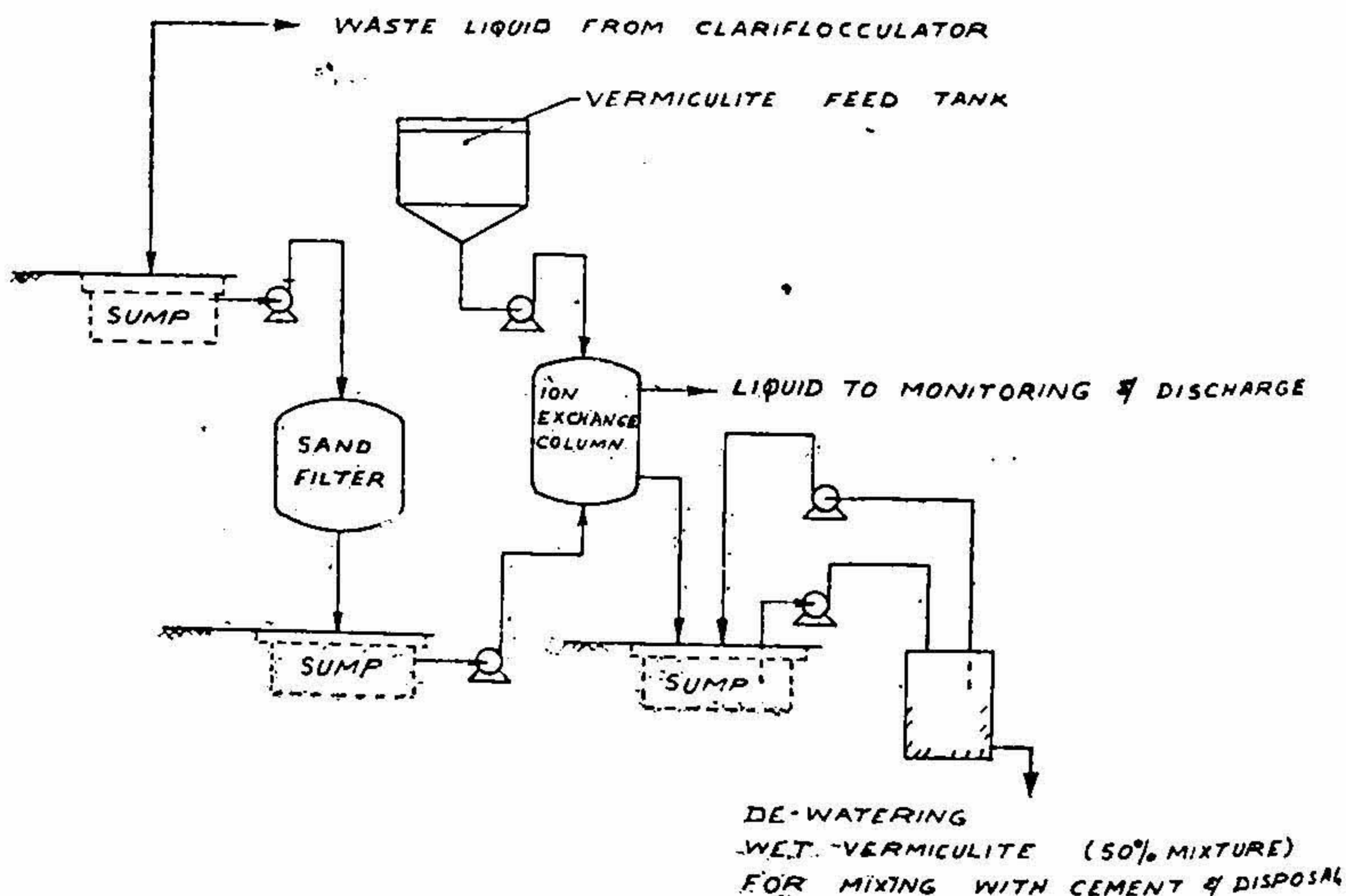

FIG. 3. Flow diagram of ion exchange plant.

It is found that, although vermiculite is very effective for the preferential uptake of radiocesium, the overall performance of the ion exchange unit is dependent upon the type of chemical treatment followed in the first stage. A decontamination factor of 10–15 for the ion exchange unit is obtained and each column can conveniently handle about 850–1,000 bed volumes of radioactive waste before exhaustion.

It is known that vermiculitization of mica by chemical treatment yields products with better ion exchange capacity. (These will, therefore, be of interest in radioactive waste management.) In view of this it was felt that a systematic investigation of vermiculitized products of micaceous minerals of Indian origin will be worth undertaking. Results of these investigations will be reported in the next communication.

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