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Short Communication

Interaction of cesium with Trombay basalt

Z. A. Khan, Satya Brat and V. B. Godse
Repository Project Section, Waste Management Division, Bhabha Atomic Research Centre, Bombay 400 085, India.

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Abstract

This paper deals with the interaction modes of cesium with Trombay basalt. Column and batch experiments have been summarised, contribution of adsorption and chemisorption towards total uptake has been calculated, the effect of temperature on these parameters and the feasibility of the particular formation in cesium immobilisation have been discussed.

Key words: Interaction, uptake, adsorption, chemisorption, distribution coefficients, immobilisation.

1. Introduction

Solidified high level waste in the repositories will pose a serious problem if leached out due to environmental factors. ^{137}Cs, because of its long half-life and energy , is the prime cause of concern from radioactive waste management point of view, It is imperative to understand its interaction with sub-surface formations of candidate repository/storage site. The studies include two sets of experiments *viz.* column and batch. Efforts have been made to evaluate the contribution of chemisorption and adsorption in the total uptake of cesium by Trombay basalt.

2. Materials and Methods

2.1. *Materials*

An undisturbed basalt core (5.3 cm dia) containing minute cavities filled with zeolite and other secondary minerals was procured from Trombay area. The core was cut into three portions along length. One of 14.2 cm length was used for column studies. From the cavities of the second, zeolite fill was extracted and subjected to TGA, DTA and X-ray analyses. The third was crushed to < 2 mm size. Physico-chemical characteristics like chemical analyses and identification of mineralogical constituents indicated the presence of illite, feldspar and quartz (Table I). 10^{-2} M conc. solution of Cs^+ was prepared by dissolving A.R. grade CsCl in distilled water. Its pH was adjusted to $\simeq 7.0$ and was tagged with ^{137}Cs.

Table I
Physico-chemical characteristics of basalt

		Chemical Analyses (%)	
Core			
Effective porosity	: [illegible]	SiO_2	48.10
Void ratio	: 7.87×10^{-2}	Al_2O_3	14.75
Surface area	: 0.34×10^{-3} m^2/g	Fe_2O_3	4.05
Crushed basalt			
Total soluble salts	: 0.11%	FeO	5.08
CEC	: 0.812 meq/g	CaO	10.62
Surface area (< 2 mm size)	: 1.91 m^2/g	MgO	8.60
Surface charge density	: 0.268 meq/m^2	TiO_2	1.40
pH	: 7.60	MnO	0.14
		Na_2O	2.33
		K_2O	0.40
		P_2O_5	0.20
		Loss on ignition	8.71
		H_2O	1.30

2.2. *Methods*

Column studies: In a specially designed glass column, the basalt core was mounted over glass wool and glass beads. Inlet and outlet of the column were connected to a glass reservoir through a sigma pump with the help of teflon tubing. Cesium solution was filled in the reservoir and leak proof-closed system was made. The solution was passed through the column at constant rate (≈ one ml/minute) continuously for about 20 days. Upward flow was followed to have proper interaction of the solution with the core. One ml of the sample of the circulating solutions was periodically drawn from near the top of the core. It may be mentioned here that the pH of the effluent solution was nearly constant (±0.2) during the column studies. The activity of ^{137}Cs in each sample was determined by counting with well type NaI(Tl) gamma scintillation detector attached to a single channel analyzer. The percentage uptake of the feed, rate of uptake μg/g/h for the intervals of sampling and Kd (Cs^+ per g of basalt/Cs^+ per volume of solution) were calculated. After complete saturation, the core was taken out, dried at room temperature and mounted on a similar second column system. Desorption studies were carried out by circulating rain water (pH = 4.65, Na^+ ≈ 4 to 5 and Ca^{++} ≈ 2 to 3 ppm) till complete desorption. As there was no ground water at the site, rain water, which is a source of ground water recharge, was used. Desorption percentages with respect to total feed, sorbed Cs^+ and distribution coefficient were calculated by sampling, counting and calculating as in the previous case.

Batch studies: These studies were carried out in 14 numbers of marked 250 ml PVC bottles. Ten grams of crushed basalt (−200+240 B.S. mesh size) and 100 ml of cesium solution were added to each. The bottles were tightly closed with the help of inner lids and screwed caps. Two sets of seven bottles each were kept at a constant temperature (333 K) in water bath and at room temperature (303 K). The bottles were intermittently shaken. After two hours from the start of the interaction, one bottle from each of the sets was taken out, and centrifuged at 3000 r.p.m. for 15 minutes and solid and liquid phases were separated. Cs^+ concentration in the liquid was determined by counting one ml of the samples as in column studies. Similarly the uptake was studied for 4, 6, 10, 16, 24, 26 and 28 hours of contact times by drawing one bottle from each of the sets. For the desorption studies, 100 ml of distilled water was added to each bottle containing the contaminated basalt samples. The treatment was repeated as in the uptake case. Care was taken to have equal time of uptake and desorption for the respective samples. Cs^+ content of liquid samples was determined. Uptake, desorption, retention with respect to the total feed and Kd values* were calculated.

3. Results and discussion

3.1. *Column studies*

The uptake and desorption data are graphically presented in figs 1 and 2. The high initial uptake rate per hour is due to effective porosity of the core and is mainly a reflection of the physical state. Once the core is somewhat saturated with the solution, the uptake is due to ion exchange and absorption. The rate of uptake goes on decreasing with the passage of time, with few exceptions as between 182.0 and 200.5, 290.5 and 352.0 and 383.0 and 408.5 hours. This is due to cavitation in the core resulting in delayed diffusion[1]. Uptake by total mass of rock as well as Kd increases until 408.5 hours, but desorption starts thereafter and negative values of uptake rate and decrease in percentage uptake and Kd values are obtained.

High desorption rate in the first 19 hours is also due to effective porosity. Rain water, more or less, expels the Cs^+ solutions from the pore space. From 19 to 122 hours desorption rates gradually decrease. Between 122 and 170 hours there is an increase in desorption rate which may be attributed due to delayed diffusion of Cs^+ through the zeolite cavities imbedded in the mass of the core. The same effect is reflected on Kd values. All through up to 170 hours there is a steady increase in percentage desorption. Thereafter redesorption starts, although the rate is very low and tends to be around zero. To sum up, we may say that $\sim 40\%$ of the initial Cs^+ feed is taken up by the rock, $\sim 17\%$ of which is leached out on desorption. Thus contribution of the adsorption towards total uptake may be 17% and the rest is effect of chemisorption.

3.2. *Batch studies*

Kd values are presented in Table II, and the rest of the data are graphically plotted in figs 3 and 4. Initial low value of Kd in all the four cases is due to slow diffusion. Time, temperature and concentration dependence of Kd are evident from this table. From

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*Kd (distribution coefficient) = (Amount of activity/g of the solid)/(Amount of activity/ml of the solution at equilibrium).

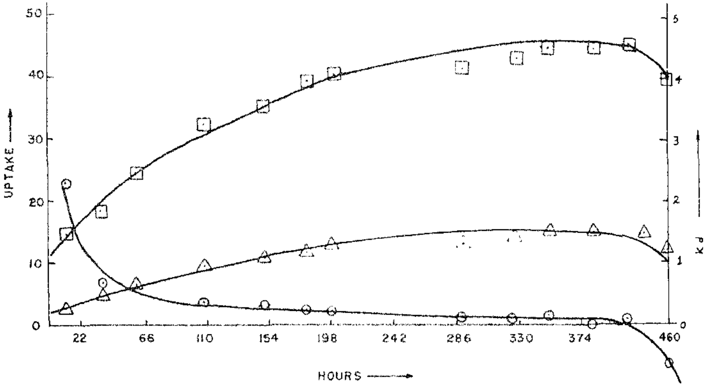

FIG. 1. Interaction of cesium with basalt core. △——△ Kd (ml/g); ⊡——⊡ uptake % of the feed; ⊙——⊙ uptake μg/g/h.

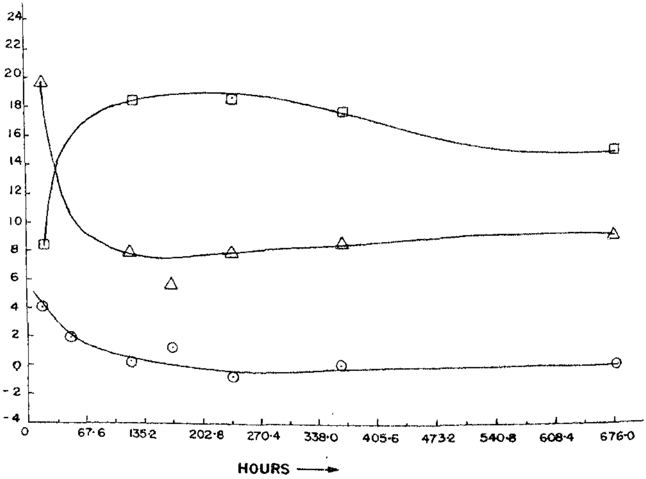

FIG. 2. Desorption of cesium from contaminated basalt core. ⊙——⊙ Desorption μg/g/h; ⊡——⊡ Desorption % g; △——△ Kd.

Table II
Interaction of Cs^+ with Trombay basalt
Cs^+ concentration = 10^{-2} M
Solid/liquid = 1/10

Time of contact (hours)	Kd (ml/g) at			
	303 K		333 K	
	Uptake	Desorption	Uptake	Desorption
2	5.5	38.5	7.4	33.7
4	9.5	60.7	7.4	25.5
10	10.0	61.4	8.5	30.0
16	10.1	63.7	8.2	33.9
24	11.1	61.5	9.3	34.9
26	10.3	53.2	8.0	28.8
28	10.3	50.9	9.8	34.1

figs 3 and 4, it is noted that, with the passage of time, there is an increase in total uptake but the retention is effectively controlled by desorption. With the rise in temperature, total uptake decreases and there is an increase in desorption resulting in low retention. This indicates the effect of adsorption, which is possibly due to hydrated ionic size and potential[2-4] of Cs^+ and surface charge density[5] of the crushed basalt. Thus, less and less of Cs^+ will be retained with the rise in temperature. Therefore, Cs^+ will not be fully immobilised. The circulating incoming groundwater in basaltic formation will considerably leach it, more so with the rise in temperature. This may lead to apparent possibility of Cs^+ release into the biosphere. The column studies are the simulation of actual field conditions. Kd values determined here can be utilised for calculating the rate of Cs^+ movement by using the following equation[6]:

$$V_i = V_w/1 + \mathrm{Kd}\rho b/\eta$$

where V_i = Velocity of the ionic species (Cs^+); V_w = Velocity of the circulating groundwater; ρ_b = Bulk density of the media (basalt); η = Porosity of the media (basalt).

The rate of groundwater movement in the formation under discussion as reported by Ramachandran *et al*[7] is not only very low but changes seasonally. This gives very low value to V_i. Because of the availability of larger surface area through cracks and crevices, the Kd values are likely to increase. Moreover, Kd is concentration dependent, and hence increases with the decrease in concentration[8]. The relationship is not linear because of nonlinearity between concentration and ionic activity[9]. All these factors give a very low value of V_i thus giving considerable time for Cs^+ retardation before releasing it into the environment.

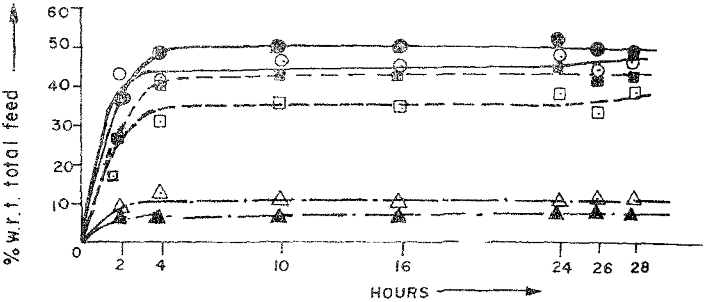

FIG. 3. Interaction of cesium with crushed basalt. ●———● Uptake at 303 K; ▲— — —▲ Desorption at 303 K; ■-----■ Retention at 303 K; ⊙———⊙ Uptake at 333 K; △— — —△ Desorption at 333 K; ⊡— — —⊡ Retention at 333 K.

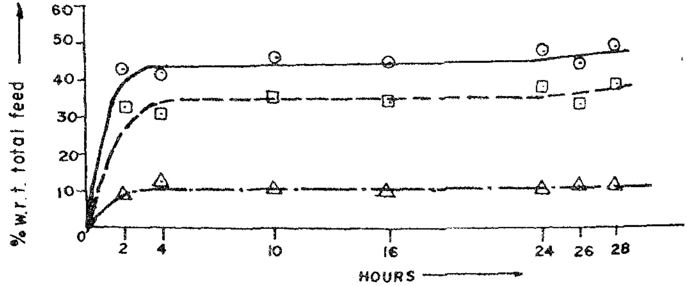

FIG. 4. Interaction of cesium with crushed basalt. ⊙———⊙ uptake; △— — —△ desorption; ⊡—. —. —.⊡ retention at 333 K.

4. Conclusion

The results suggest that the uptake of Cs^+ is considerably governed by adsorption. The values of desorption were found to be more at 333 K compared to at 303 K. A good part of Cs^+ is not firmly immobilised in basalt but due to hydrological conditions there is least possibility of any spread of contamination.

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