Sorptive Removal of Cesium-137 and Strontium-90 from Water by Unconventional Sorbents.

II. Usage of Coal Fly Ash

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It has been shown that coal fly ash is a good adsorbent for both radionuclides of ^{137}Cs and ^{90}Sr. Radiocesium adsorption is maximal around the neutral region whereas radiostrontium adsorption increases with pH, especially above pH 8. Cesium retention sharply drops with ionic strength while strontium adsorption increases sharply and steadily at low and moderate concentrations of the inert electrolyte, respectively. The suggested mechanisms of radionuclide retention by fly ash is specific adsorption of Cs^+ and irreversible ion-exchange uptake of Sr^{2+}. The isotherm of adsorption is a Langmuir approximation of the B.E.T. multi-layered sorption. Acid pretreatment of fly ash, though not increasing radionuclide sorption capacity, may be useful in preventing the leach-out of other contaminants from the sorbent into water during the adsorption process.

I. INTRODUCTION

Cesium-137 and ^{90}Sr are two persistent radionuclides in the natural environment which essentially emerge as a result of fallout from nuclear bomb tests and reactor accidents. In Turkey, both radionuclides became a matter of public concern after the Chernobyl accident, and attention was focused on rediocesium and strontium analyses in tea and milk products, respectively.

It is important to study the adsorption behaviour of cheap and easily available sorbents for these radionuclides both for emergency action and for building engineered barriers around a contaminated site to prevent leakage. A number of metallurgical solid wastes may serve as unconventional cost-effective sorbents for these radionuclides. In this respect, bauxite wastes (red muds) and coal fly ashes, which have been extensively used in our department for heavy metal removal and water treatment[1]-[3], proved to have a potential for radionuclide adsorption with noticeably high capacities for Sr^{2+}/red mud combinations[4]. This work aims to quantify the adsorption capability of fly ash for both radionuclides.

II. EXPERIMENTS

1. Radionuclide (Adsorbate) Solutions

A 0.42 cm^3-flacon standard of ^{137}CsCl(185 MBq) and 0.75 cm^3-flacon of ^{90}Sr(NO$_3$)$_2$ in 1 M HNO$_3$(185 MBq) were supplied from Amersham International Ltd.; the contents of the flacons were dissolved and diluted to 100 cm^3 with distilled water (stock solutions). The working solutions were prepared by diluting 0.1 or 0.2 cm^3–aliquots of the stock solutions to 100 cm^3.

2. Methods for Adsorption, Measurements and Calculations

A liquid-solid ratio (V/m in cm^3/g) of 250 was conserved in batch adsorption tests as in previous work[4]. Thus 0.100 g of the adsorbent was contacted with 25 cm^3 of the working solution for 4 h, *i.e.*, a time period found to be sufficient to reach equilibrium in preliminary experiments, at room temperature (25 °C) in a thermostatic shaker/water bath.

The initial activity (A_i) of the working solutions were 2,060 and 2,265 Bq/cm^3 for the radiocesium(I) and strontium(II) solutions, respectively, corresponding to the molar concentrations of 2.526×10^{-8} M of Cs^+ and 9.33×10^{-8} M of Sr^{2+}, well below the solubility limits of the corresponding sparingly soluble salts, *e.g.*, SrCO$_3$. The final activity (A_f) after the batch tests was found by measuring the beta-activity of the centrifugate (3,000 r.p.m.) using an ERD Mullard G-M tube type MX 123 system with halogen extinction.

Since blank tests showed that there was no noticeable radionuclide adsorption on the glass walls of the shaking flasks, the adsorption percentage (Ads.,%) was calculated using the equation,

$$\text{Ads., } \% = (A_i - A_f) \times 100/A_i, \qquad (1)$$

and the distribution coefficient for adsorption (K_D^{ads}, cm^3/g) was derived using the formula

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$$K_D^{ads} = \frac{(A_i - A_f)}{A_f} \cdot \frac{V}{m}$$

$$= \frac{\text{Ads.},\%}{(100 - \text{Ads.},\%)} \cdot \frac{V}{m} \ (cm^3/g). \tag{2}$$

The distribution coefficient for desorption (K_D^{des}, cm^3/g) was found by the aid of desorption percentages (Des.,%) measured after contacting the radionuclide-loaded sorbent with distilled water at a (V/m) ratio of 250. The conditions for desorption experiments were identical with those of adsorption.

$$K_D^{des} = \frac{(100 - \text{Des.},\%)}{\text{Des.},\%} \cdot \frac{V}{m} \ (cm^3/g). \tag{3}$$

The equilibrium capacities of the sorbents for Cs^+ and Sr^{2+} were determined by passing 10^{-3} M CsCl and 10^{-1} M $SrCl_2$ solutions (each inoculated with $0.1 \ cm^3$ of the correspending radionuclide stock solution as tracer per $100 \ cm^3$ of the non-radioactive solution) through a column, 0.5 cm in diameter and 6 cm long, filled with 1 g of the adsorbent, at an elution rate of 2 cm^3/min. The passage of solutions was terminated when the infiltrate and eluate activities were equalized *i.e.*, ion retention stopped. The eluate activity *vs.* throughput volume curves were integrated accordingly (Sr^{2+} adsorption-elution is exemplified in **Fig. 1**) to derive the equilibrium adsorption capacity as mmole-radionuclide per g-adsorbent.

3. Sorbents

Coal fly ash was recovered from the cyclones and electrostatic precipitators of T.E.K. Afşin-Elbistan Thermal Power Plant and had the following average composition[5][6]:

Constituent	Percentage interval	Constituent	Percentage interval
SiO_2	21.94-22.68%	Na_2O	0.88- 0.98%
Al_2O_3	11.85-12.36%	K_2O	1.08- 1.37%
Fe_2O_3	3.57- 3.89%	SO_3	11.12-12.40%
CaO	40.84-42.47%	Loss on	
MgO	2.33- 5.76%	ignition	1.76- 1.85%

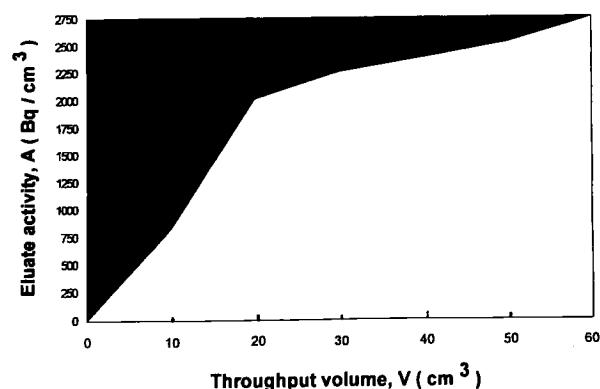**Fig. 1** Adsorption-elution curve for 0.1 M $SrCl_2$ of $A_i=$ 2,750 Bq/cm^3 (The shaded part is integrated for finding the equilibrium capacity of F_w.)

Almost 99% of the fly ash could pass through a 200-mesh sieve. The bulk density of the raw ash is 1.05 g/cm^3 while the specific gravity is 2.70 g/cm^3. The fly ash was washed with ten-fold distilled water for several (5-6) times, filtered and dried (F_w). The pH of the filtrate was *ca.* 9.

A part of the water-washed fly ash (F_w) was further activated with acid. For this purpose, 100 g of F_w was treated with 1 dm^3 of 2% (by wt.) HCl in boiling solution for 2 h, and this treatment was repeated several (5-6) times. Here, Shiao's activation procedure[7] for red mud was modified by using dilute acid due to the high solubility of fly ash in more concentrated acidic solutions. The solid product was thoroughly washed with water (final filtrate pH *ca.* 8), filtered, and oven-dried at 100 ±5 °C to produce the acid-treated (F_a) sorbent.

Mineralogical analysis of both adsorbents by X-ray diffractometric (Rikagu), electron microscopic (Jeol 733 Superprobe) and X-ray fluorescence spectroscopic (Philips) instrumental techniques indicated the coexistence of amorphous and crystalline phases, the amorphous slag phase constituting the majority of the material with spherical particles of various size. The X-ray diffractogram of the fly ash, F_w, identified calcite ($CaSO_3$): 50.61%, anhydrite ($CaSO_4$): 32.19%, quartz (SiO_2): 9.02%, $CaSO_4 \cdot 0.62H_2O$: 4.70%, and hematite (Fe_2O_3): 3.49% in the crystalline phase. The fly ash (F_a) sample was embedded in polyester resin, polished with diamond paste, and the electron micrograph (See **Photo. 1**) showed heterogenous amorphous slag particles on which subsequent elemental analysis of selected spots by the XRF technique yielded CaO: 41-52%, SiO_2: 27-38%, Al_2O_3: 13.0-13.3%, FeO: 2.6-4.9%, MgO : 1.0-4.3% and other oxides up to 2%. The related literature concerning XRD data of the raw (untreated) fly ash samples from the same source reports the presence of lime, anhydrite, ferrite spinel, melilite, mullite and brown millerite in the crystalline phase[8].
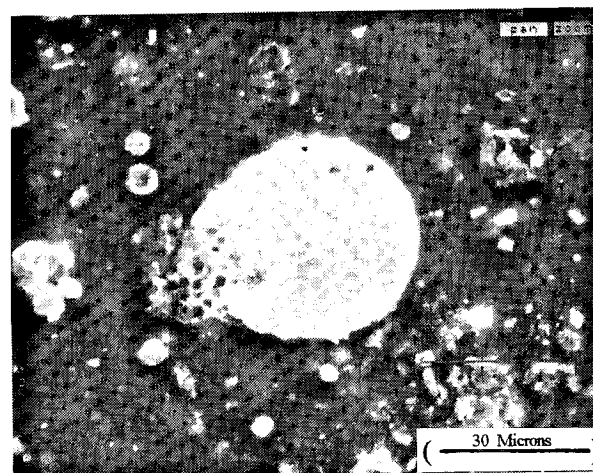
The specific surface areas of the adsorbents, mea-

Photo. 1 Electron-micrograph of mostly amorphous fly ash, F_a

sured by the B.E.T. method[9] (Micromeritics Surface Area Analyzer), were 10.2 and 14.3 m^2/g for F_w and F_a, respectively.

Thermal analysis data (Shimadzu TGA Instrument) for the identification of Brønsted and Lewis acid centers on the surface were collected by temperature-controlled expelling of volatiles from the surface, cooling, ammonia gas adsorption, heating up to 600 °C, cooling, and differentiating the thermogravimetric curve of NH_3 desorption. The derivative peak at 399 °C for the F_w sample corresponded to a single type of acid center on the surface which lied in the transition range of Brønsted and Lewis acidities (*i.e.*, 400 °C), and the actual amount of ammonia gas desorbed from the surface constituted a small percentage of the total mass of sample. When the individual PZC values of the fly ash constituents are considered, this acid center may be assumed to arise from α-SiO_2 (quartz).

PZC measurements by potentiometric titration of the adsorbent suspensions at different ionic strengths (*i.e.*, titration of a suspension containing 0.2 g adsorbent in 50 m*l* NaCl solution of concentrations 0.2, 0.4 and 0.8 M by 0.1 M HCl as titrant, pH recorded *vs.* titrant volume) yielded the PZC values of 6.5 and 6.3 for F_w and F_a, respectively.

4. Study of Adsorption Parameters

The pH adjustments of the radionuclide solutions was made by stepwise addition of 10^{-2} M HCl and 10^{-2} M NaOH solutions. Although the Cs^+ adsorption-pH curve (**Fig. 2**) was obtained in this manner, an ionic strength adjustment (I=0.05, NaCl) was necessary for Sr^{2+} solutions as the radiostrontium adsorption in neutral medium (pH 7) significantly increased in an inert electrolyte-containing solution than in water (See **Fig. 3**).
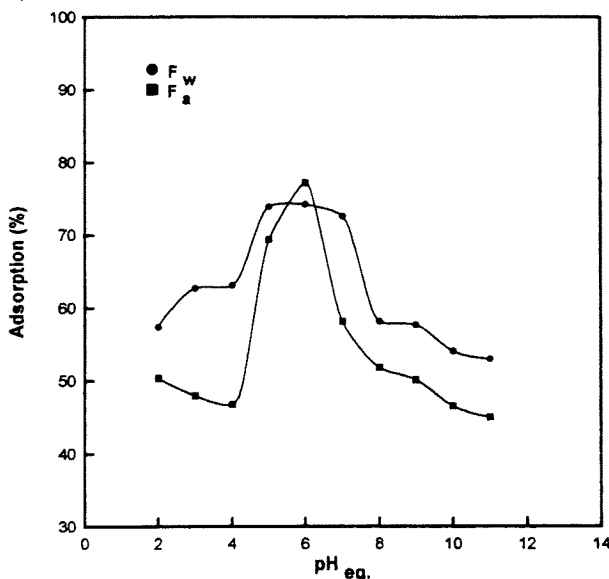
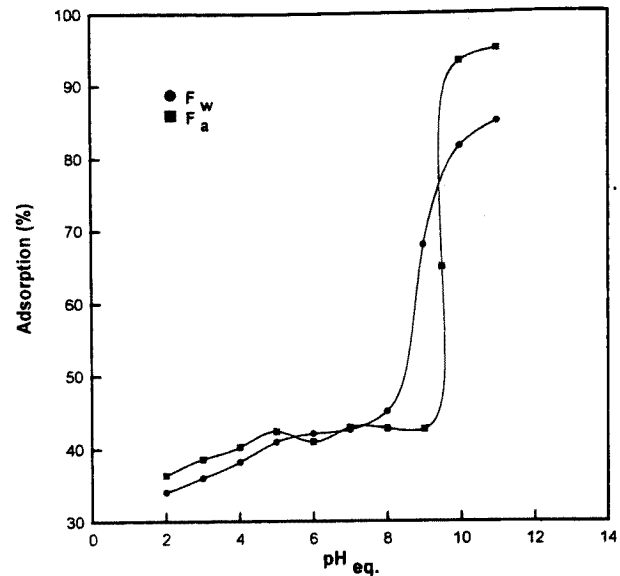**Fig. 2**   Radiocesium adsorption as a function of equilibrium pH

Fig. 3   Radiostrontium adsorption as a function of equilibrium pH at constant ionic strength (I=0.05, NaCl)

The effect of inert electrolytes (*i.e.*, NaCl) on adsorption was followed at pH 7 for both radionuclides (**Figs. 4**(a) and (b)). The variation of adsorption was within the limits of experimental errors when the inert electrolyte NaCl was substituted with CH_3COONH_4 (*i.e.*, a pH 7 buffer) of the same ionic strength.

The temperature dependence of adsorption was studied at three different temperatures (25, 50 and 75 °C) in stoppered flasks placed in a thermostatic water bath agitator.

The adsorption data at room temperature for equilibrium solution activities up to 6,000 and 12,000 Bq/cm^3 for radiocesium and strontium, respectively, were interpreted by the aid of Freundlich and Langmuir isotherms, the latter yielding higher correlation coefficients (r>0.99). The adsorption isotherms (**Figs. 5**(a) and (b)) and distribution coefficients (**Figs. 6**(a) and (b)) are depicted in the corresponding figures.

A Langmuir equation[10] assumes a hyperbolic relation between adsorption and equilibrium activity in solution;

$$(A_i - A_f)V/m = \frac{BQ^0 A_f}{A_s + (B-1)A_f}, \tag{4}$$

where B is a constant expressing energy of interaction with the surface, A_s the saturation activity of the radionuclide in solution, and Q^0 the activity of the radionuclide adsorbed per unit weight of sorbent (Bq/g) in forming a complete monolayer on the surface. Equation (4) may be linearized to;

$$[(A_i - A_f)V/m]^{-1} = (A_s/BQ^0)A_f^{-1} + (B-1)/BQ^0$$

$$= sA_f^{-1} + i, \tag{5}$$

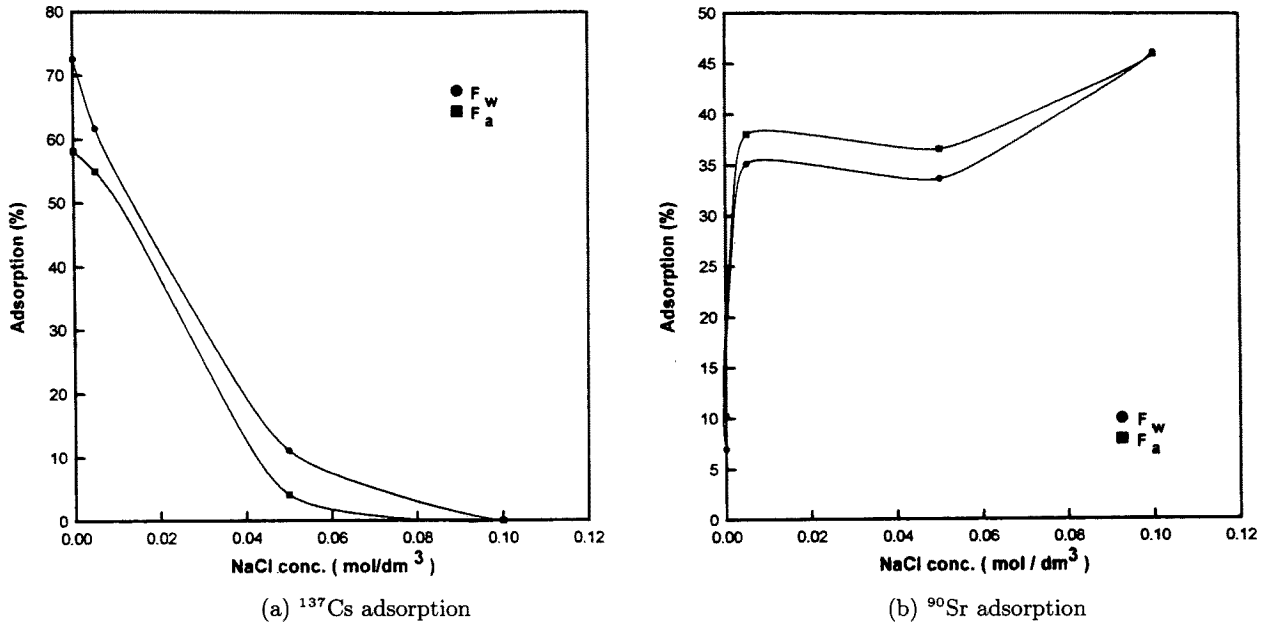according to which the reciprocal of radionuclide activ-

(a) ^{137}Cs adsorption

(b) ^{90}Sr adsorption

Fig. 4 ^{137}Cs and ^{90}Sr adsorption at pH 7 as a function of inert electrolyte (NaCl) concentration

(a) ^{137}Cs

(b) ^{90}Sr
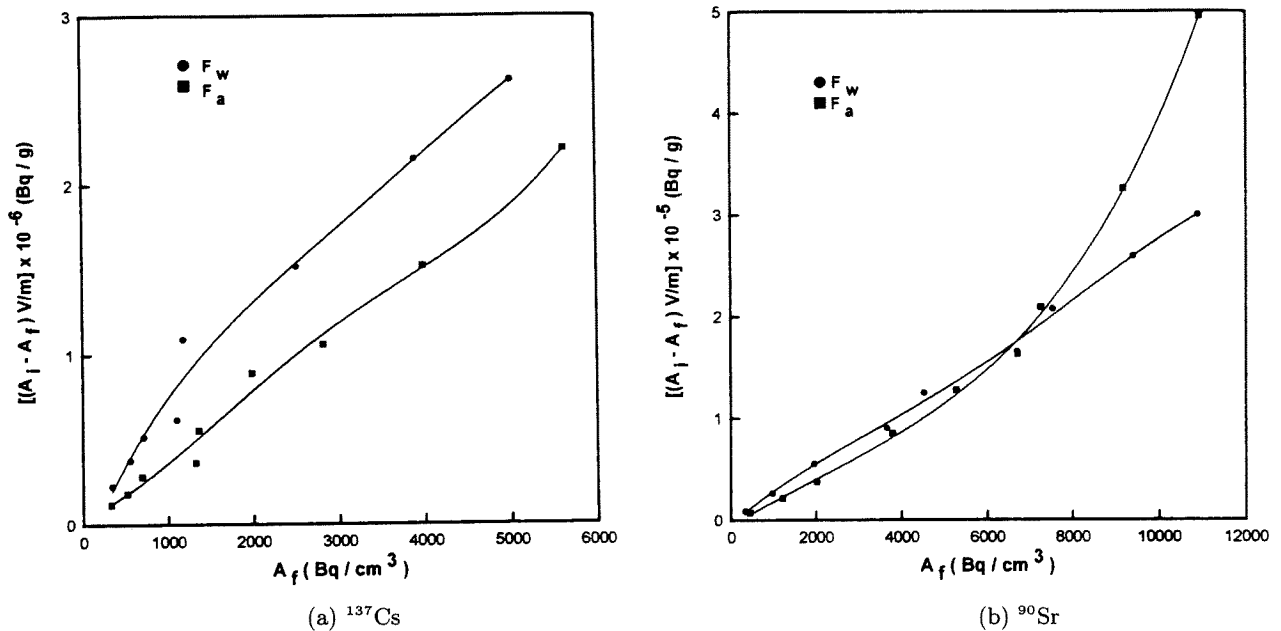
Fig. 5 Adsorption isotherms of ^{137}Cs and ^{90}Sr uptake by fly ash

(a) ^{137}Cs
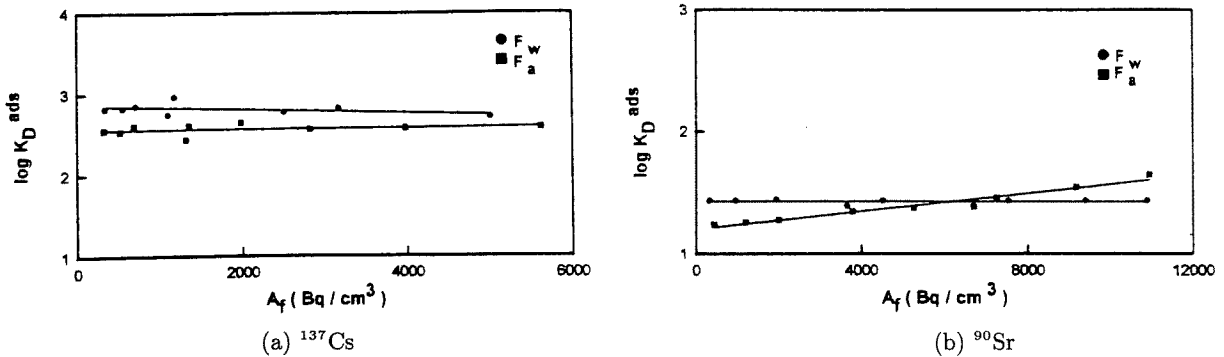
(b) ^{90}Sr

Fig. 6 Distribution coefficients of ^{137}Cs and ^{90}Sr uptake by fly ash

ity retained in the sorbent varies linearly with the reciprocal of the final radionuclide activity in solution (Slope=$s=A_s/(BQ^0)$ and intercept=$i=(B-1)/(BQ^0)$).

It is known that B.E.T. isotherm of multilayered adsorption[9] expressed as

$$(A_i - A_f)V/m = \frac{BQ^0 A_f}{(A_s - A_f)[1 + (B-1)(A_f/A_s)]}, \quad (6)$$

may be transformed in the linearized form[4] into a Langmuir expression on the condition that $A_f \ll A_s$, *i.e.*, the radionuclide activity in solution is far beyond saturation[11].

III. RESULTS AND DISCUSSION

The water-washed (F_w) and acid-treated (F_a) adsorbents did not leach out any new contaminants to aqueous solution during the batch tests, *e.g.*, blank tests for the dissolution kinetics of fly ash as traced by Ca^{2+} ion dissolution in neutral solution *vs.* time confirmed this fact.

The slight increase of adsorption observed for both radionuclides with temperature pointed out to the chemical nature of adsorption rather than ion uptake merely by electrostatic interactions with the adsorbent surface. The radionuclide adsorption capacities of sorbents (as found using the integration method demonstrated in Fig. 1) were 0.91×10^{-2} mmol $Cs^+/g \cdot F_a$, 1.08×10^{-2} mmol $Cs^+/g \cdot F_w$, 1.64 mmol $Sr^{2+}/g \cdot F_a$, and 1.89 mmol $Sr^{2+}/g \cdot F_w$. The slight capacity drop by acid treatment may be attributed to the loss of acid-soluble constituents of fly ash responsible for adsorption (*e.g.*, $CaSO_4$ constituent which may aid Sr^{2+} sorption in the form of sparingly soluble $SrSO_4$).

However, acid treatment may be necessary for preventing the leach-out of new contaminants into water during the adsorption process in accord with EPA regulations[12] expected from environmentally safe sorbents.

The retained radionuclides were not considerably desorbed, *i.e.*, the percentage desorption was about zero for ^{90}Sr, and up to 1.6 and 2.4% for ^{137}Cs with F_w and F_a, respectively, at low initial solution activities. Thus the distribution coefficients for desorption (K_D^{des}) were much higher than those for adsorption (K_D^{ads}) which may be attributed to irreversible fixation as a mechanism involved in the uptake of these radionuclides[13][14]. Similar findings have been reported in the literature regarding irreversible fixation as the primary mode of Cs sorption[15]-[18] on other geological materials and soil types.

The adsorption maximum for radiocesium is around the neutral region (Fig. 2). The Cs^+ cation, having a large ionic radius and a small hydration number[19], shows the ability to compress the electric double layer around the adsorbent particles and reduce the electrokinetic potential favouring adsorption. Thus, Cs^+ adsorp-

tion may be attributed to the great polarizibility of this cation resulting in its attraction by the induced dipoles of the adsorbent surface[19]. However, the pH of the dispersion medium strongly affects the electrokinetic potential of the adsorbent particles as both H^+ and OH^- ions have great adsorbability, causing spontaneous unipolar orientation of the dipoles of the dispersion medium establishing a permanent dipole structure, *e.g.*, on particles of fly ash suspensions. Since Cs^+ ion is essentially retained by specific adsorption *via* compression of electric double layer, these permanent dipoles caused by H^+ and OH^- ions decrease Cs^+ uptake in both acidic and alkaline regions (See Fig. 2) down to a level where ion-exchange sorption of Cs^+ prevails. Cesium adsorption shows a striking maximum at a pH interval around the PZC of both adsorbents (*i.e.*, pH: 6.3-6.5). The strong Cs^+ cation adsorption expected at pH>pH_{pzc} is not realized probably due to the increased permanent dipolar character of the adsorbent by OH^- ions in solutions of pH>8. This situation is quite similar to radiocesium adsorption in red mud[4] except for the fact that Cs^+ did not adsorb at all on red mud in strongly acidic and alkaline suspensions, indicating the more significant role of ion-exchange mechanism in the sorption of radiocesium on fly ash.

On the other hand, radiostrontium adsorption increases with pH especially above pH 8 (Fig. 3), in accord with ion-exchange uptake of Sr^{2+} on the surface hydroxyl (-$\overline{SOH}$) sites of the sorbent accompanied by the release of hydrogen ions. The reaction equation for this postulated ion-exchange[20] is

$$-\overline{SOH} + Sr^{2+} \rightleftharpoons -\overline{SOSr^+} + H^+, \quad (7)$$
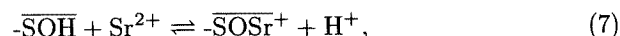
which should be pH-dependent. Moreover, coordinative bidentate binding in the form of $\overline{(-SO)_2Sr}$ as well as the -$\overline{SO\text{-}SrOH}$ surface complexation may be possible at high pH[20]. It may be inferred from reaction equation (7) that Sr^{2+} sorption by ion-exchange would be favoured by the neutralization of H^+ ions released from the -$\overline{SOH}$ sites. The magnitude of the equilibrium capacity of fly ash for Sr^{2+} also provides evidence for ion-exchange retention.

In the pH region where the rate of adsorption was highest, *i.e.*, 8<pH<10 in Fig. 3, a linear relationship was observed between log K_D^{ads} and equilibrium pH in accord with ion-exchange retention, and the number of protons released per bound Sr^{2+} ion could be found from the slope of this line. The fact that this proton number turned to be less than unity has been reported in the literature for other hydrated oxides which showed metal adsorption without giving off an equivalent amount of protons[11].

One point worthy of notice in Sr^{2+} adsorption was the fact that the 42.6% and 42.9% adsorption percentages observed at pH 7 in 0.05 M NaCl solution for F_w and F_a, respectively, dramatically dropped to 10.2% and 7.0% when ionic strength was negligible as that of almost

pure water. Thus, radiostrontium adsorption in pure water at neutral pH sharply increases with ionic strength, this effect being observable even at low concentrations of NaCl and CH_3COONH_4 as inert electrolytes. There may be two reasons for this behaviour:

(1) The dissociation of the acidic surface hydroxyl groups ($-\overline{SOH}$) is promoted with increasing ionic strength[19] so that Sr^{2+} uptake is enhanced by $-\overline{SO}^{(-)}$.

(2) Silica is a major constituent of the fly ash sorbent, both in the crystalline (as quartz) and in the amorphous phases. Quartz (α-SiO_2) has a PZC of $2.5^{[22][23]}$ which means that at least a part of fly ash is capable of cation adsorption throughout the weakly acidic-neutral region.

Now, the equilibrium constant, K_H^{Sr}, for the ion-exchange reaction symbolized by Eq. (7) should be less than that of the reaction

$$-\overline{SONa} + Sr^{2+} \rightleftharpoons -\overline{SOSr}^+ + Na^+, \qquad (8)$$
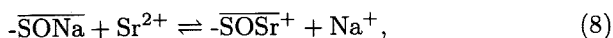
the equilibrium constant of which is K_{Na}^{Sr}, in other words, $K_H^{Sr} < K_{Na}^{Sr}$ due to the weak acidity of $-\overline{SOH}$. Thus, it should be easier for the Sr^{2+} cation to desplace a surface Na^+ ion (by the ion-exchange mechanism) and be retained at neutral pH than to displace a surface proton; K_d^{ads} should increase in the presence of an inert electrolyte like NaCl.

The ionic strength dependency (in the presence of inert electrolyte NaCl) of Cs and Sr adsorption at pH 7 is shown in Figs. 4(a) and (b). The decrease of cesium adsorption with an increase in inert electrolyte concentration may be attributed to the coverage of adsorption sites of fly ash by Na^+ ions with the subsequent removal of adsorbed Cs^+ ions. Since it has been reported in related literature[14][24] that extraction with KCl solution is capable of removing species by ion-exchange, especially Cs^+, from the lattice of minerals, it is probable that Na^+ ions is preferentially uptaken by Cs^+-retained sites of the fly ash surface as the NaCl concentration was increased up to 0.10 M (See Fig. 4(a)). Another possibility is the change of electrokinetic potential of the adsorbent particles at moderate concentrations of NaCl establishing permanent dipoles and thereby obstructing the specific adsorption[11] of Cs^+. Contrary to the case of cesium, radiostrontium adsorption sharply increases with ionic strength at low NaCl concentrations, then steadily

increases up to 0.10 M NaCl (See Fig. 4(b)). This behaviour has been explained in detail by the relative difficulty of replacing the protons in weakly acidic $-\overline{SiOH}$ surface groups by Sr^{2+} ions compared to replacing Na^+ ions in the already ion-exchanged $-\overline{SiONa}$ surface species. The relative stability of retained Sr^{2+} at moderate concentrations of NaCl may be attributed to irreversible fixation of radiostrontium at specific surface sites of the sorbent.

The adsorption isotherms at 25 °C in the form of $[(A_i - A_f)V/m]$ vs. A_f curves for radiocesium and strontium are given in Figs. 5(a) and (b), respectively. The Langmuir parameters of the linearized isotherms according to Eq. (5) are presented in **Table 1**.

The fact that some intercept values of the linearized isotherms (Table 1) are negative may be possibly explained by multilayered adsorption on a heterogeneous surface of a composite adsorbent like fly ash. In this case, the linearized isotherm is only an approximation of the B.E.T. isotherm given by Eq. (6) under the condition $A_f \ll A_s$. The distribution coefficients for the adsorption of both radionuclides did not show significant variations (in the logarithmic K_d^{ads} scale) within the concentration range studied (See Figs. 6(a) and (b)).

IV. CONCLUSION

Coal fly ashes of thermal power plants are composite adsorbents capable of removing radiocesium and radiostrontium as well as other heavy metals[1]-[3] from water. The adsorption of these radionuclides may be represented by Langmuir isotherms as an approximation of multilayered adsorption expressed by the B.E.T. equation. Although acid treatment of fly ash has shown no improvement in adsorption capacity, it is recommended so as to prevent trace pollutant leach-out from the adsorbent into water.

Cesium ion essentially sorbs by specific adsorption due to great polarizibility of this cation resulting in its attraction by the induced dipoles of the adsorbent surface. Since the sorbent dispersion exhibits a permanent dipole structure of particles due to surface acidity and alkalinity, Cs^+ uptake is maximal around the neutral region. Cesium adsorption is strongly decreased by the coverage of specific surface sites of the sorbent, e.g., by an inert electrolyte. Strontium sorbs mainly by ion exchange, and a rise in pH definitely favours Sr uptake. A

Table 1 Langmuir parameters[†] of cesium and strontium adsorption on fly ash sorbents

Langmuir parameters		Fly ash adsorbents			
		Cs^+		Sr^{2+}	
		F_w	F_a	F_w	F_a
Slope	: s	1.55×10^{-3}	2.79×10^{-3}	3.6×10^{-2}	5.9×10^{-2}
Intercept	: i	-1.26×10^{-7}	-4.27×10^{-8}	2.27×10^{-8}	-3.37×10^{-6}
Correlation coefficient : r		0.993	0.993	0.999	0.999

[†] With respect to Eq.(5) as $[(A_i - A_f)V/m]^{-1} = sA_f^{-1} + i$

significant initial rise of Sr adsorption is apparent upon an increase in ionic strength by NaCl, then Sr^{2+} continues to replace the surface-adsorbed Na^+ ions and be retained irreversibly upon further increase in NaCl concentration.

Fly ashes, along with other metallurgical solid wastes and clay minerals, may be utilized for constructing 'engineered barriers' around shallow-land burial sites of low-level radioactive wastes.

·ACKNOWLEDGEMENT

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