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Adsorption of caesium ions by some materials used in the manufacture of PVC-based surface coatings

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An attempt was made to establish the nature of and some of the factors influencing the adsorption of caesium ions in solution on to a range of solid materials; polyvinyl chloride (PVC), barytes, china clay, whiting, carbon black, titania, asbestos, chosen since they are all used in the manufacture of a range of products used for surface coatings and storage vessels. Particular attention was paid to the use of products containing these compounds which are recommended for use in radioactive areas, both for the storage of radioactive materials and the protection of surfaces, where contamination can present problems. The adsorption processes were investigated by preparing and analysing the characteristics of the adsorption isotherms of caesium ions on to powder samples using a batch equilibration technique, and as was to be expected the predominant mechanism appeared to be one of ion exchange. It was confirmed that titania, and to a lesser extent china clay, whiting and carbon black, played a major part in the adsorption process. It is clear that the quality of any final product will depend on the process used in its manufacture, which in turn can be related to its potential for contamination in a radioactive facility.

1. Introduction

Radioactive substances, especially when they are handled at high specific activity, can present serious problems of surface contamination with risks to the health of personnel and experimental difficulties due to cross-contamination, or changes in concentration of standard solutions due to adsorption on the walls of storage containers. The contamination properties of surfaces have been extensively studied in the past but the work now reported represents the first stage of an experimental investigation of the principal materials used in the formulation of various products based on a single polymer of polyvinyl chloride. The storage problem has been investigated by Eichholz *et al.* [1] and Mellish [2]. Ikeda and Akaishi [3] have reported on the problems associated with the adsorption of radionuclides on storage containers and analytical apparatus.

Much of the work on assessment of the contamination properties of surfaces has involved the contacting of the liquid phase with a solid, the latter usually being in sheet form, and estimating the degree of contamination from the adsorption on the solid surface using a radioactive labelled ion in solution. The surfaces used have been in many cases those of a manufactured plastics product consisting of several compounds combined physically and/or chemically; such a heterogeneous system is complex and it is understandable that the results obtained are variable and of an empirical nature.

A simple test procedure was reported by Tompkins *et al.* [4] for comparing the adsorption of selected radioelements from carrier-free solutions, (e.g. phosphoric acid ^{32}P in hydrochloric acid, barium chloride ^{140}Ba in hydrochloric acid and sodium iodide ^{131}I in sodium bisulphite), on to materials used for surface coverings in radiochemical laboratories. The technique involved contacting the contaminant solution with plaques of glass, stainless steel and lead, for a 1 h period, and measuring the adsorbed activity before and after a standardized decontamination procedure.

Starik *et al.* [5] have investigated the adsorption of various radioisotopes, (including ^{137}Cs), on polythene and polytetrafluorethylene using a contact method between the solid, in disc form, and the solution for a range of pH values. A time of 1 h was considered sufficient for adsorption equilibrium to be reached; from measurements of the equilibrium activity on the sample and in solution an adsorption coefficient was evaluated and used for comparison purposes.

Methods using flow techniques for the investigation of adsorption at the solid/solution interface have been described by Green and Corey [6] and Grice *et al.* [7].

A test method for the assessment of the decontamination properties of surfaces has been described by Smith [8] and his paper summarizes the experimental work carried out in support of British Standard BS 4247: Part 1: 1967 "Recommendations for the Assessment of Surface Materials for use in Radioactive Areas – method of test for ease of decontamination". The test involves the contamination of the sample surface with a solution of mixed radio-isotopes (cobaltous chloride ^{60}Co and caesium chloride ^{134}Cs) and determination of the residual radioactivity after a two stage decontamination process. The limitations of the procedure are recognized and a revised British Standard is being prepared. Such a method may however provide an estimate of the ease of decontamination of a surface and hence a relative measure of the suitability of the material for use in a particular environment.

2. Experimental

The powder samples used in this work were supplied commercially, together with detailed analyses of their composition, and were typical of those compounds incorporated into the range of PVC products. No attempt was made to grade the powders, representative samples being taken from the bulk for each experiment.

The specific surface areas of the samples were measured using the BET technique with krypton gas (research grade) as adsorbate; the results are shown in Table I.

TABLE I Specific surface areas by BET (Kr adsorption)

Material	Function in PVC formulation	Specific surface area $m^2 g^{-1}$
Titania	pigment	10.8 ± 1.0
China Clay	filler	7.3 ± 1.0
Asbestos	filler	30.5 ± 3.0
Barytes	filler	0.83 ± 0.1
Carbon Black	filler/pigment	98.1 ± 10.0
Whiting	filler	2.85 ± 0.3
Polyvinyl chloride	base	1.06 ± 0.1

Caesium solutions labelled with ^{137}Cs were chosen as the contaminant because ^{137}Cs satisfied the following requirements: (i) it has a simple solution chemistry, (ii) it is a γ-emitter and could be measured using a scintillation counting assembly, (iii) it has a long half life (30 years) obviating any need for decay corrections.

In order to ensure that the radiation emitted separately in the transition from ^{137m}Ba to ^{137}Ba (stable) did not interfere in the counting of samples containing ^{137}Cs, all these samples were allowed to stand for at least 10 min (equivalent to 4 half-lives of ^{137m}Ba) prior to counting, to allow the activity of any ^{137m}Ba, separately adsorbed, to decay to an insignificant level.

2.1. Preparation of test solutions

All test solutions were made up in 100 ml lots containing 2 μCi of active caesium, (supplied by R.C.C. Amersham as chloride in 1 M hydrochloric acid) the latter being measured in 2 ml aliquots from the stock using an automatic micropipette. The volume to 100 ml was made up using "Elgastat" water or a solution of inactive caesium chloride. These latter solutions were prepared by direct weighing on a microbalance and dissolving in "Elgastat" water, (for higher concentrations), or by weighing and dilution from a large volume (for lower concentrations). They were then stored for 1 week below 10° C prior to use, in polypropylene containers.

2.2. Measurement of adsorption isotherm

Construction of the adsorption isotherm was based on a batch method, each point being measured separately. All apparatus used for the dispensing and storage of solutions was made from polypropylene. Decontamination of apparatus after use was achieved by soaking for 24 h in 5% Decon 90 solution after which it was washed 6 times in tap water followed by one wash each with distilled and "Elgastat" water respectively. Storage was in a dust-free environment. The procedure was as follows:

(i) The pH value of a sample of the test solution was recorded, using a Pye-Ingold EO7 combined glass and reference electrode, after which the sample was discarded; in all cases the initial pH value was 5.4.

(ii) Test solutions of 100 ml volume were prepared as described previously, covering a range of at least 10 different solution concentrations; these were then stored for 1 week before use.

(iii) A 2 ml sample, containing $x\,\mu$g of Cs, was extracted from the test solution and stored in a glass microbeaker for the determination of the ***initial*** count rate C_0. Standard deviation, σ, in $[C_0] = 2\%$.

(iv) 10 g of the powder sample were added to the test solution and the mixture shaken continuously for 1 h, after which it was allowed to stand for a further 2 h.

(v) After this time a further 2 ml sample of test solution was carefully removed from the clear liquid above the settled powder sample, placed in a microbeaker and counted to determine the ***equilibrium*** count rate, C_e. Standard deviation, σ, in $[C_e] = 2\%$.

(vi) The above procedure was repeated for the range of concentrations of the prepared test solutions.

(vii) The final pH value of the solution was measured.

From the initial and equilibrium count rates the amount of caesium adsorbed on to a sample, expressed as $\mu g\,g^{-1}$, and the concentration of caesium in solution at equilibrium, expressed in $\mu g\,ml^{-1}$, were determined.

$$\text{Cs adsorbed on sample} = x(C_0 - C_e)/C_0\ \mu g\,g^{-1}$$

$$\text{Cs in solution at equilibrium} = xC_e/C_0\ \mu g\,ml^{-1}$$

Adsorption isotherms as in Fig. 1 were then prepared from the whole series of experiments, each point being measured in duplicate.

Various contact times have been used by other workers in this field but in the majority of cases the adsorption had been shown to be substantially complete in 2 h (e.g. Tompkins *et al.* [4] used 1 h; Eichholz *et al.* [1], 2 h for ^{137}Cs on polypropylene and glass; Benes and Kucera [9], 1 to 2 h). A separate continuous flow experiment [10] confirmed this in the case of PVC and titania, and indicated a rapid initial adsorption stage, probably ion exchange, during the first 60 sec of contact

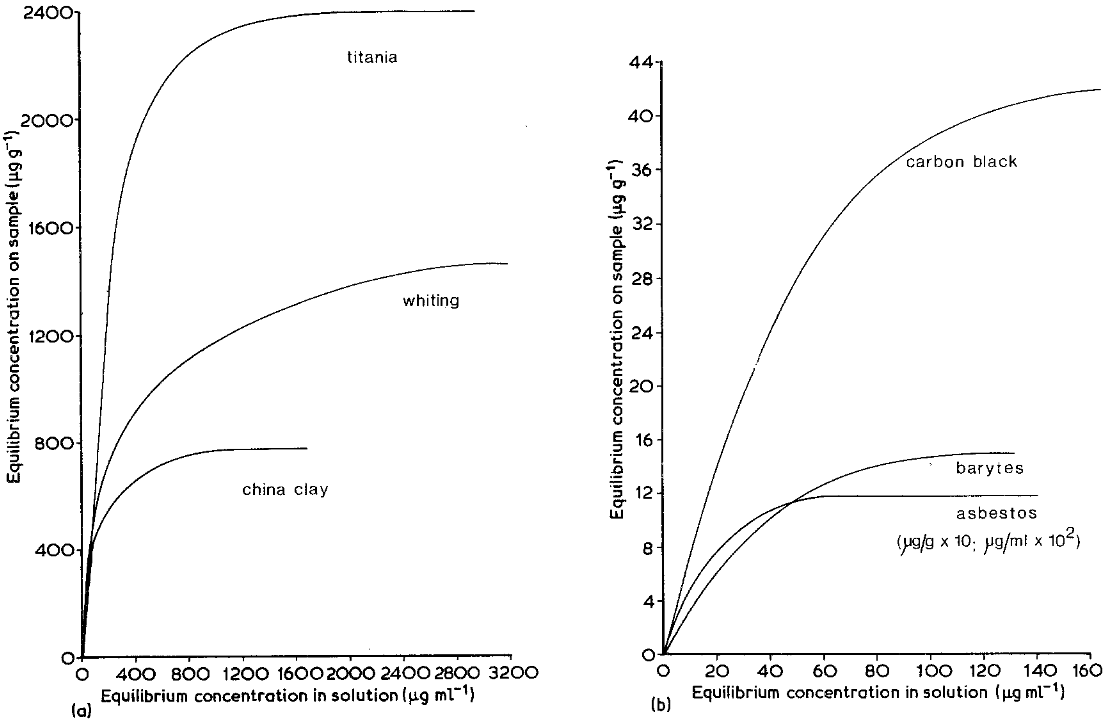

Figure 1 Adsorption isotherms.

TABLE II Experimental pH variations

Material	Initial pH	Final pH range
Titania	5.4	6.5–5.5
China Clay	5.4	6.2–6.1
Asbestos	5.4	10.2–9.3
Barytes	5.4	8.6–8.1
Carbon Black	5.4	8.7–8.0
Whiting	5.4	8.3–7.7
Polyvinyl Chloride	5.4	8.0–5.9

followed by a less rapid, possibly diffusion stage, taking place in up to 60 min. Further experiments over periods of 6 and 24 h showed a continuing but not significant increase in adsorption.

Whenever ion exchange is the predominant adsorption mechanism it is to be expected that the extent of any adsorption will be dependent on the initial pH of the exchange solution. An increase of pH encourages OH^- to enter the inner part of the polarized double layer, increasing the cation exchange capability and the adsorption of cations. These effects have been amply demonstrated by Amphlett [11] and Starik [5], but will have only a marginal effect on the adsorption over the pH changes found in this work; these changes are summarized in Table II. In fact it is probable that the initial value of pH is the critical value influencing the adsorption process.

3. Results

The results of all the experiments, carried out in duplicate, are presented in Fig. 1; with the exception of results in the plateau regions the experimental standard deviation was of the order of 3%.

The adsorption on to titania, whiting and barytes, Fig. 1a, was high and these materials can be expected to influence the quality of the manufactured product. The adsorption on to PVC, asbestos and carbon black, Fig. 1b, was very low, and in the case of asbestos accompanied by a large increase in pH of the exchange medium.

All isotherms were basically of the L-type, (Giles classification [12]) with minor variations, (notably in the case of asbestos), suggesting adsorption on independently localized sites, probably ion exchange sites. These characteristics can also be examined by a modified form of the Langmuir equation for adsorption at the gas–solid interface.

The modified Langmuir equation takes the form:

$$\frac{C}{x/m} = \frac{1}{k_1 k_2} + \frac{C}{k_2},$$

TABLE III Values of constants derived from isotherms

Material	Modified Langmuir plot	
	k_1	k_2
Titania	0.014	2469
China Clay	0.011	825
Asbestos A	3.7	1.8
B	very small	1.18
Barytes A	0.015	26.8
B	0.125	15.95
Carbon Black A	0.01	82.9
B	0.034	49.7
Whiting	0.0024	1666

where C denotes equilibrium concentration in solution in $\mu g\,ml^{-1}$ and x/m is the equilibrium concentration on the sample in $\mu g\,g^{-1}$. Thus a plot of $C/(x/m)$ as ordinate against C should be a straight line (assuming Langmuir type adsorption), having a gradient of $1/k_2$ and intercept on the ordinate of $1/k_1 k_2$; these plots are shown in Fig. 2.

It can be shown that k_1 is inversely related to the activation energy and serves as a measure of the affinity for adsorption of ions on to the surface; if k_1 is small the affinity is high and vice versa. k_2 is directly proportional to the adsorption capacity of the adsorbent. For each material the values of the two constants derived from the respective isotherms were determined and listed in Table III. For titania, china clay and whiting the modified Langmuir plots were approximately linear, whereas those for asbestos and carbon black consisted of two distinct linear portions, designated by A and B in Table III; in the case of barytes some curvature was evident which was resolved into two linear portions A and B.

The adsorption isotherms were examined closely in two distinct regions of interest, i.e. the initial part of the curve, the gradient of which is related to the affinity of the caesium ion for the adsorbing surface, and the final saturation or plateau value corresponding to completion of monolayer adsorption.

In all cases a form of plateau was evident although with one exception all the experimental plateau values were below the value calculated for complete monolayer cover, based on BET specific surfaces, indicating adsorption at a limited number of available sites, (Table IV). The estimation of maximum monolayer coverage, (assuming this to be the case from the plateau), was based on a radius for the hydrated Cs^+ ion of 0.329 nm giving a conversion factor of 5.1×10^2 $\mu g\,g^{-1}$ per $m^2\,g^{-1}$.

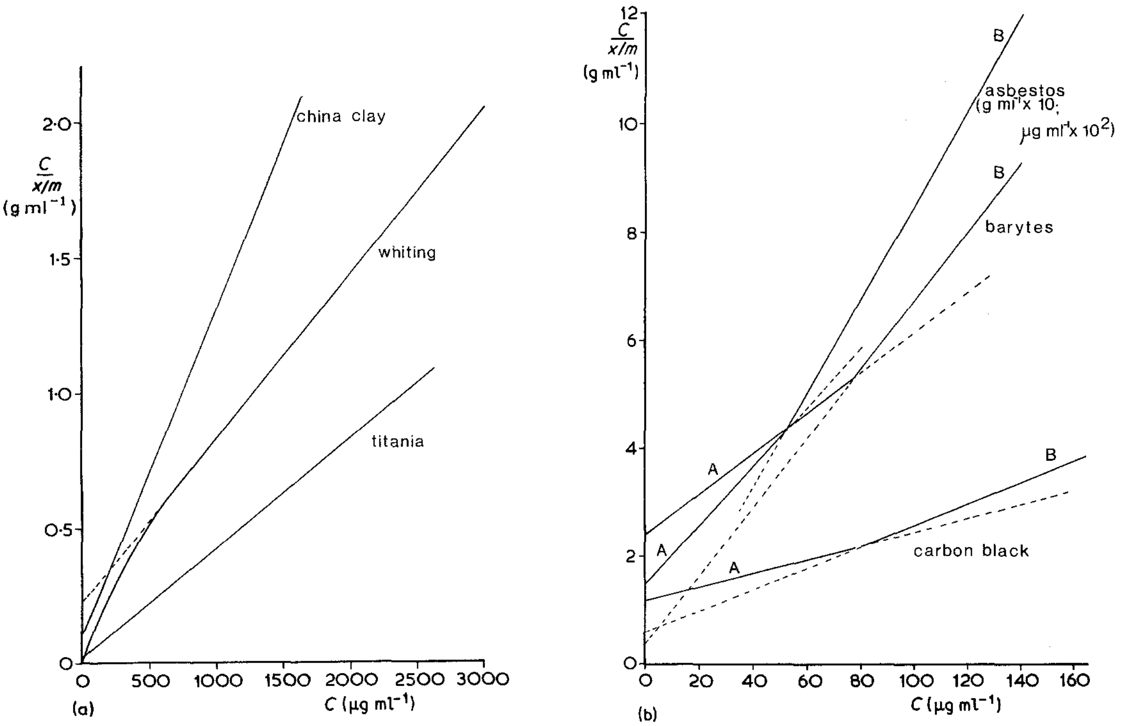

Figure 2 Modified Langmuir plots.

4. Discussion

4.1. Titania

The shape of the isotherm in this case was in close conformity to the common type of solution isotherm, (L-type), and resembled the Langmuir gas adsorption isotherm. The value of the gradient of the initial part when compared with the other materials investigated was by far the greatest indicating a comparatively high solute/adsorbent affinity. The modified Langmuir plot from the isotherm was a straight line indicative of monolayer adsorption and the existence of a plateau suggested saturation of the monolayer by Cs^+. In fact the experimental value of this plateau was only about one half the value estimated from BET, (Table IV) and this could be associated with the presence of certain impurity cations at the surface, i.e. potassium and calcium, which could account for as much as 50% of the adsorption, based on an ion exchange process.

The potassium content of the titania sample was 1700 ppm expressed as oxide (K_2O). It can be shown that the potassium content is therefore 140 mg per 100 g or 3.6 meq per 100 g, (using an equivalent weight of 39 g). The calcium content of 138 ppm as oxide (CaO), can be shown to represent

TABLE IV Estimated and observed plateau values

Material	Concentration for completed monolayer adsorption ($\mu g\, g^{-1}$)		Observed estimated (%)	Observed adsorption ($\mu g\, m^{-2}$)
	Estimated (from BET data)	Observed (from isotherms)		
Titania	5510	2390	43.4	221.3
Barytes	423	15.0	3.5	18.1
China Clay	3720	775	20.8	10.6
Asbestos	15560	1.18	0.008	0.04
Carbon Black	50050	42	0.08	0.43
Whiting	1450	1500	103.0	526.3
Polyvinyl Chloride	540	<1	<0.2	<0.9

a Ca concentration of 9.9 mg per 100 g or 0.5 meq per 100 g (using an equivalent weight of 20 g).

The maximum experimental coverage of caesium ions was 2400 μg Cs per g titania, equivalent to 240 mg per 100 g or 1.8 meq per 100 g (using an equivalent weight of 133 g). The maximum theoretical coverage by caesium ions based on the measured specific surface is almost double this value (Table IV) and nearly equivalent to the potassium content of the sample.

The potassium and calcium (4.1 meq per 100 g), represented the major impurities in the titania, and there is a high probability that a majority of these ions are located at the outer surface as part of an electrical double layer. Divalent calcium ions, despite the double charge, appear to be much more readily exchanged than potassium ions by the caesium [13]. It may be reasonable to presume that all the calcium ions, and about one third of the potassium ions, are exchanged by the caesium. The modified Langmuir plot was however linear throughout and gives a very low value for k_1, indicating a low activation energy for the exchange process.

The titania had a fairly high cation exchange capacity (about 4 meq per 100 g), coupled with a low exchange activation energy; depending on its concentration and location in PVC in a formulated product, it could be a potentially serious source for cation contamination.

4.2. China clay

This material also produced a characteristic L-type isotherm, the gradient of the initial part and the low value of k_1, showing a reasonably high affinity of the caesium ion for the surface comparable with barytes, asbestos and carbon black, although it was less than for titania. The modified Langmuir plot, being linear, indicated monolayer adsorption. The observed plateau value was only about one fifth of the calculated value and this again can be partly attributed to the presence of impurity ions.

It is possible that some of the potassium ions present as impurity in the china clay sample may have been located in the outer part of the electrical double layer of the particles, (2.2% potassium oxide $\equiv$ 45 meq per 100 g), whereas the majority of the multivalent ions may have been present within the lattice structure, replacing aluminium and silicon atoms and hence not available for exchange. The cation exchange capacity of kaolinite is generally low (i.e. $<$ 5 meq per 100 g) cf. 3 meq per 100 g based on BET results, Table IV, so that the maximum experimental coverage by caesium ions (about 800 μg g^{-1} $\equiv$ 1.8 meq per 100 g), represented rather less than half of the exchange capacity present, probably involving partial surface exchange of potassium.

There is evidence that, for ion exchange on to clay mineral surfaces such as kaolin, dipositive Ca ions are equally, if not more readily, exchangeable with unipositive Cs ions, than with unipositive K ions. From the results it was seen that china clay presented a further potential source of cation contamination.

4.3. Asbestos

The adsorption of Cs^+ on to this material was surprisingly low despite its high wettability, (estimated using a method described by Gomm *et al.* [15]). Interpretation of the results in this case was complicated by large experimental errors associated with this very low adsorption capacity. The gradient of the initial curve was much less steep than that for titania and comparable with china clay and whiting. The structure of asbestos and its high surface area would appear to support this type of adsorption.

The low adsorption capacity is interesting and may be attributable to the structure of the chrysotile asbestos used in this work. The surface of this type of asbestos consists of a layer of brucite (magnesium hydroxide) which causes the fibres to become highly polar and electropositive in character in solution. This state of affairs would therefore be expected to decrease the probability of cation exchange at the asbestos surface, but contamination by anions needs to be reconsidered.

The modified Langmuir plot consisted of two linear portions indicating a deviation from the standard form.

The value of k_1 calculated from the modified Langmuir isotherm was 3.7 suggesting a high activation energy and low probability of caesium exchange. The properties of asbestos appeared to be anomalous with a very high specific surface and wettability, but low affinity for caesium ions.

4.4. Barytes

The isotherm was basically of the L-type, but the plateau was not so clearly defined; using the modified Langmuir isotherm, the estimated value of the concentration for completed monolayer adsorption was 15 $\mu g\,g^{-1}$, representing only 3.5% of the value calculated from BET (Table IV).

The modified Langmuir isotherm clearly established that there were two competing adsorption processes, the initial stage having a value for k_1 of 0.015, only slightly below that for china clay. This represented a low activation energy and hence ease of caesium adsorption but of limited capacity. The second stage had $k_1 = 0.125$ and represented only a moderate affinity for caesium ions. The nature of the exchange adsorption reaction in this case could not be established although a fraction of the calcium impurity may have been involved.

k_2, representing the caesium adsorption maximum, appears to be slightly greater for the first stage compared with that for the second stage, possibly indicating some slowing down of the first stage as the second stage predominated. Due to the relative size of the barium and caesium ions (unsolvated ionic radii 0.129 and 0.169 nm respectively), it is possible that migration of Cs^+ to the inner part of the lattice could have taken place, tending to slow down the adsorption process particularly at the higher concentrations used. It is possible that any ion exchange taking place was limited to barium ions at the surface.

4.5. Carbon black

The results appeared to indicate an L-type isotherm although as in the case of barytes the plateau was not clearly defined. Again the gradient of the initial part of the isotherm was of the same order as for barytes, with a low affinity of caesium ions for the surface; the modified Langmuir-type isotherm indicated a two-stage adsorption process.

The values for k_1 indicated a fairly high affinity of a part of the surface for caesium ions and as in the case of barytes the saturation capacity for this stage was far from being reached, possibly because the sites were within the particles.

4.6. Whiting

This material produced a characteristic L-type isotherm similar in many respects to that for titania, but there were again problems in defining the plateau. The modified Langmuir plot was linear, except for a slight deviation at lower concentrations. The gradient of the initial part of the isotherm was comparatively high, and the value of k_1 very low indicating a high affinity of the surface for caesium ions. Most significant was the agreement between the observed caesium saturation and estimated plateau value, based on the specific surface, indicating good cation exchange properties.

The saturation value of about 1500 μg Cs per g of sample represented a cation exchange capacity of 1.1 meq per 100 g which may be compared with an estimate of 1.6 meq per 100 g if all the sodium impurity (0.05%) is assumed to be present at the surface. Caesium ions are known to exchange very readily with sodium ions. The potassium content was only one fifth of that due to sodium, and probably contributed very little to the cation exchange capacity. It is therefore possible that the caesium was adsorbing up to the maximum cation exchange capacity represented by sodium ions at the surface.

4.7. Polyvinyl chloride

In the case of PVC it was not possible to obtain satisfactory results using the batch technique due to the very low adsorption which resulted in very small differences in count-rate between initial and equilibrium values. Clearly the adsorption capacity for unipositive Cs ions was very low and possibly limited to a few sites with inner layer negative charges due to chloride ions.

From evidence obtained using a continuous flow technique [10] the adsorption of caesium on to PVC and polypropylene appeared to take place in stages with an initial rapid stage being complete in a few seconds and characteristic of ion exchange at the outer part of an electrical double layer, at the solid/solution interface. Over longer periods two further phases of adsorption could possibly be identified each being substantially complete in 1 h and 20 min respectively. These latter stages could be due to diffusion of the radio-element through the electrical double layer and this is in accord with previous work by Tompkins and Bizzell [4].

It is possible however that the low cation exchange may have resulted from the physicochemical formation of peroxides in the PVC during manufacture, which according to Scott *et al.* [14] causes the initiation of hydrogen chloride elimination, but establishes a small number of permanent negatively charged oxygen atoms at the surface.

The low adsorption on PVC is in agreement with results obtained by Kuninori and Hazue [16], who obtained values varying between 0.02 and 0.3%, (using solutions labelled with ^{32}P, ^{35}S, ^{131}I,

^{140}Ba). The experimental data obtained from the isotherms indicates that adsorption affinity (using the gradient of the initial part of the curve as the criterion), decreases in the series: titania > whiting > china clay > asbestos > carbon black > barytes. The adsorption capacity (using adsorption per unit area as the criterion), is shown to decrease in the series: whiting > titania > china clay > barytes > carbon black > asbestos.

By examination of the values of k_1 (Table III) obtained from the modified Langmuir plot, it can be seen that the adsorption affinity appears to decrease in the series: whiting > china clay > titania > barytes > carbon black > asbestos. Again using the k_2 values, the adsorption capacity appears to decrease in the series: titania > whiting > china clay > carbon black > barytes > asbestos.

5. General conclusions

Overall the results indicate that for caesium the adsorption process is predominantly an ion-exchange phenomenon characterized by rapid uptake at selected sites, and in agreement with the conclusions of Mellish *et al.* [2] and Herczynska [17]. In the context of surface coatings for use in active areas where contamination is likely to arise it would appear that the degree of adsorption is not so much dependent on the PVC content, but much more so on the compounds incorporated in the finished material, in particular titania and to a lesser degree china clay, carbon black and whiting. Barytes and asbestos appear to play a very small part in the contamination process. However one important factor which was not considered and which is obviously relevant in this context, is ease of decontamination.

In the formulation of a typical PVC flooring tile as recommended for use in radioactive areas, the incorporation of titania and calcium carbonate (whiting), clearly could present a potential for adsorption and contamination by radioactive cations. The presence of asbestos, (and in some cases carbon black), could provide a potential for wetting and hence for bringing contaminants into closer contact with the surface.

The results for two different samples 1 and 2 of commercial PVC coatings examined by the British Standard test, (BS 4247) are presented in Table V and show a considerable variation in their contamination/decontamination properties. The result for polypropylene sheet is included for comparison purposes. The results (cpm cm^{-2}) represent residual activity after contacting the surface with the isotope solution followed by the two stages, A and B, of decontamination. The difference between the two samples cannot be accounted for by differences in composition, although these are not known with certainty. Examination of the surfaces under a microscope did however reveal that the surface of sample 1 was well protected by a continuous and smooth film of the polymer, whereas the surface of sample 2 was pitted with small protrusions of asbestos fibre. The fibre could clearly provide a channel to conduct the contaminant solutions below the surface. In this case the contaminating cations are adsorbed and trapped beneath the surface in a situation which is inaccessible to the decontaminant.

TABLE V BS test on two samples of PVC commercial products

Sample	Stage A (cpm cm^{-2})	Stage B (cpm cm^{-2})
1	2 300	1 760
2	394 500	394 500
Polypropylene	–	150

These results indicate that in addition to the choice of ingredients, the processes involved in their blending and formulation into sheet are of paramount importance. The PVC polymer has excellent qualities if the manufacturing process of the coating material produces a coherent surface film.

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