

A New Method for the Removal of Radioiodine by Treated Natural Clay

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ABSTRACT. An improved method of decontaminating radioiodine wastes with natural phosphate clay treated with silver nitrate is described. An uptake efficiency of 8 meq/100 g clay within 10 min reaction time is attained. The study revealed that 10 g of natural phosphate clay treated with 1% silver nitrate solution gives an optimum uptake. The uptake of iodide by silver treated phosphate clay is a rapid irreversible process.

There are many ways in which a water source may become contaminated with radioactive compounds. Undoubtedly, the most serious hazard is that of radioactive fallout from nuclear explosion. Particularly hazardous for ground water contamination are the radioisotopes of ^{90}Sr , ^{131}I , ^{106}Ru and ^{137}Cs .

In the fallout on Nagasaki and Hiroshima (Solomon Silver 1968), 21 thyroid cancers were found 15 years after the atomic bomb explosion (air dose 80 rads). Children and pregnant women are mostly affected by iodine-131 release. In view of the high price of synthetic ion exchangers and their limited availability when an emergency situation might occur, it seemed worthwhile to investigate the practical applicability of some natural occurring materials such as clay or charcoal.

In a series of investigations (Al-Suhybani *et al.* 1982 & 1983) we studied the decontamination of uranium, thorium and fission product ^{90}Sr (simulated by ^{85}Sr) on natural clay, treated natural clay and natural phosphate clay. We could reach a high decontamination factor for actinide elements, almost equal to that attained by cationic synthetic resins; nearly 200-240 meq/100 g treated clay. With ^{85}Sr we reached a capacity of 12 meq/100 g with argillaceous clay (Hallaba *et al.* 1983), as carbonaceous clay are saturated with Ca and Mg ions competing with Sr ions.

Nevertheless, this can be considered a high decontamination ratio as ^{90}Sr is found in nature as a carrier free radioisotope.

The decontamination of solutions containing radioiodine represents a complex problem because different chemical forms can simultaneously occur in the solution, *e.g.* (I^- , IO_3^- , I_2). With respect to active carbon or other common sorbents, little information is available about the sorption of iodine compounds. Iodide solutions are liable to oxidation by air depending on pH of the solution. In natural and alkaline media, the reaction proceeds slowly in presence of light. No sorption of iodide ions on peat (a natural bituminous compound found in Europe) was observed (Lettinga 1972).

In this study, we succeeded, by a new technique, in the removal of radioiodine up to 8 meq/100 g treated clay.

This is considered a great achievement since one curie of iodine-131 contains 0.8×10^{-5} g, thus 8 meq contains nearly 1 g iodine/100 g treated clay. This means that 100 g of treated clay can adsorb $\frac{1}{0.8 \times 10^{-5}} = 10^5 \text{Ci}$.

Supposing that the commercial supplied carrier free solution may contain a quantity of 100 to 1000 times of carrier of that calculated we arrive at a figure of 100 curies iodine-131 per 100 g treated clay which is a large quantity of decontaminated radiation. Similar calculations could be applied to radioiodine-125.

Experimental

Three local natural clays of different composition (Table 1) were chosen to decontaminate effluents containing radioiodine by means of static slurry experi-

Table 1. Chemical composition of the clay minerals.

Sample	Colour	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	Na ₂ O %	K ₂ O %	H ₂ O %	LOI %	Cl ⁻ %	P ₂ O ₅ %	Total
C-4*	Light Yellow	7.38	3.68	5.66	23.4	16.63	1.21	1.07	1.05	39.07	0.15	—	99.6
C-5*	Grey Black	52.47	17.72	4.94	0.68	2.97	1.7	4.17	6.73	7.75	0.52	—	99.65
C-7**	White Phos- phate powder	1.6	0.35	0.1	55.48	0.07	0.07	0.07	0.29	27.08	—	13.85	99.4

* Chemical analysis kindly performed by the National Research Centre, Dokki, Cairo, Egypt.

** Chemical analysis kindly done by Mr. M. IB. ABDULAZIZ.

ments. Radioiodine-125 carrier free in NaOH of pH 7-11, free from reducing agents, for protein iodination, (The Radiochemical Center, Amersham product), was used instead of iodine-131 as it is a less hazardous radioisotope and of longer half life.

In a glass beaker, one microcurie c.f. I-125 was added to 200 ml of distilled water adjusted to known pH, after mixing well 2 g of clay were added with continuous stirring. The uptake by clay was followed by measuring the gamma activity of 2 ml of clear solution obtained by centrifugation of the mixture at different time intervals using a Beckman 5500 gamma scintillation counter. The percent uptake was calculated according to the following:

$$\frac{A_0 - A_t}{A_0} \times 100$$

where A_0 is the original activity, A_t is the activity at time t . Experiments were carried out with the above natural clays and with activated carbon (Koch Light Laboratories) of fine mesh size at different pHs, different concentrations of carrier NaI and with different iodide species, in order to determine the optimum conditions for maximum uptake. Average results of three experiments for each variable are plotted.

The experimental work was carried in a well ventilated fume hood shielded by 5 cm thick lead bricks and the waste solutions were stored in a 1 cm lead shielded waste container, while the radioactive source was stored in a lead cylinder of 5 cm thickness.

Results and Discussion

No uptake was noticed with clay 4 or clay 5 with a carrier free radioiodine solution of pH 5-6. With natural phosphate clay only 12% uptake was recorded. Changing the pH from acidic to alkaline did not improve the uptake. With activated carbon and at low acidity (pH 2) an uptake of 30% was noticed with c.f. radioiodine within 30 min contact time. The uptake is sharply reduced in alkaline medium to 5%. The presence of Cl_2 in water did not improve the uptake. Since active carbon removed ^{125}I only effectively from acidic solutions it cannot be considered an attractive sorbent in the removal of radioiodine from drinking water. Several experiments with phosphatised clay-4 at pH 1 and 2 and natural phosphate clay did not increase the uptake above 10%.

In view of this difficulty of low decontamination, we tried an indirect method of treating phosphate clay. It is known that AgNO_3 reacts with PO_4 ions to form an insoluble Ag_3PO_4 and if this PO_4 is linked to a clay matrix the precipitated silver phosphate will be firmly fixed to this matrix. Silver phosphate is a photosensitive

material (Bailor 1973) and can be reduced to the Ag metal in contrast to AgNO_3 solution, *i.e.* why our white freshly prepared clay turned grey after drying.

Infrared study of the Ag treated phosphate clay showed only the O-P-O bending or stretching vibration (Champan and Thirlwell 1964). On the basis of this assumption 10 g of natural phosphate clay-7 were stirred in a 1% AgNO_3 solution for 60 min, decanted, washed several times, dried at 105°C and used as such in our decontamination studies. Results are shown in Fig. 1, about 40% uptake was achieved with treated clay-4 while 100% uptake with treated phosphate clay; a conclusion that agrees with our assumption. The best pH of uptake for Ag treated phosphate clay was found lying above pH 6.

A study was carried out to find the optimum concentration of Ag taken by 10 g of clay and it was found that a 1% AgNO_3 solution gives the maximum uptake. The uptake of Ag by the clay followed an ideal ion exchange mechanism proved by the linearity of the Freundlich isotherm, Fig. 2.

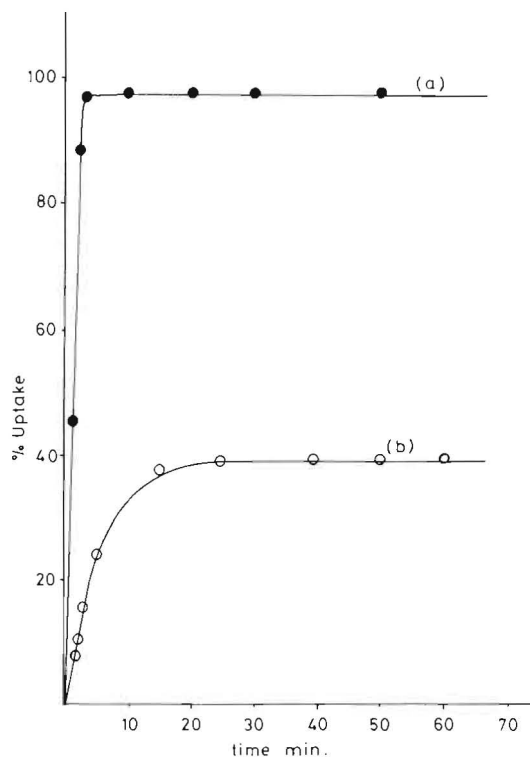


Fig. 1. Effect of time on uptake of radioiodine by C-4 and natural phosphate clay coated with silver nitrate.

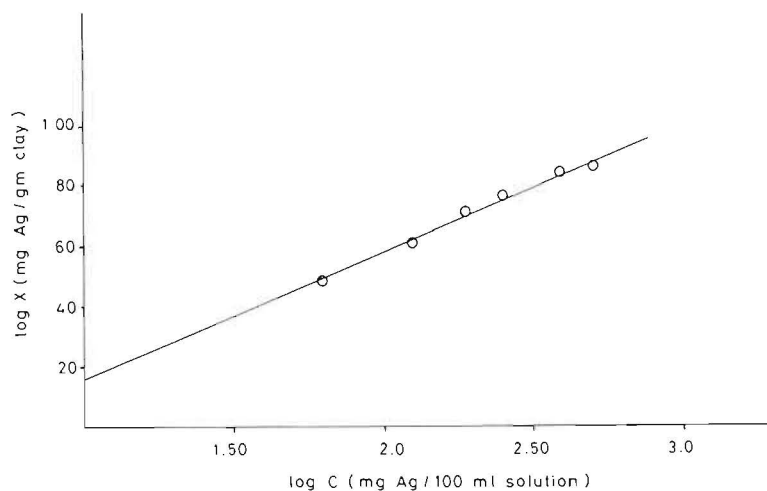


Fig. 2. Application of Freundlich Equation.

Furthermore, a study on the effect of addition of inactive carrier NaI proved that the treated clay can adsorb as much as (0.3 mg NaI/ml) with a 22% uptake, Fig. 3, represented by an average value of 8 meq/100 g treated clay, Fig. 4.

Desorption experiments were performed, no leaching of any radioiodide is traced, if the used treated clay was soaked in distilled water for several days. This proved that radioiodine adsorption is an irreversible process and that iodine is firmly retained on the clay. The contact time of adsorption was infinitely small, it ranges from 5-10 min, while with activated carbon it needed several hours of contact time to remove 70-80% of the c.f. radioiodine from solution at acidic pH. This treated clay would have the potential to considerably reduce iodine migration around the waste canister in the disposal site.

To simulate iodate uptake a c.f. radioiodine solution was treated with an oxidizing agent in presence of HNO_3 at pH 1, boiled for one hour, cooled and an uptake study revealed that iodate ions were absorbed up to 40%, a concentration of iodate ions that can rarely be found in drinking water.

It seems that the capacity of the silver treated phosphate clay can be greatly increased only in case that PO_4 moieties are present in excess on the clay matrix, *i.e.* a clay having a high content of phosphate can interact more rapidly with AgNO_3 and consequently more Ag^+ ions are available to react with radioiodine.

Our results are in good agreement with the work of (Rancon and Rochon 1979) that the best I-sorption is obtained for minerals containing cations capable of forming sparingly soluble iodides.

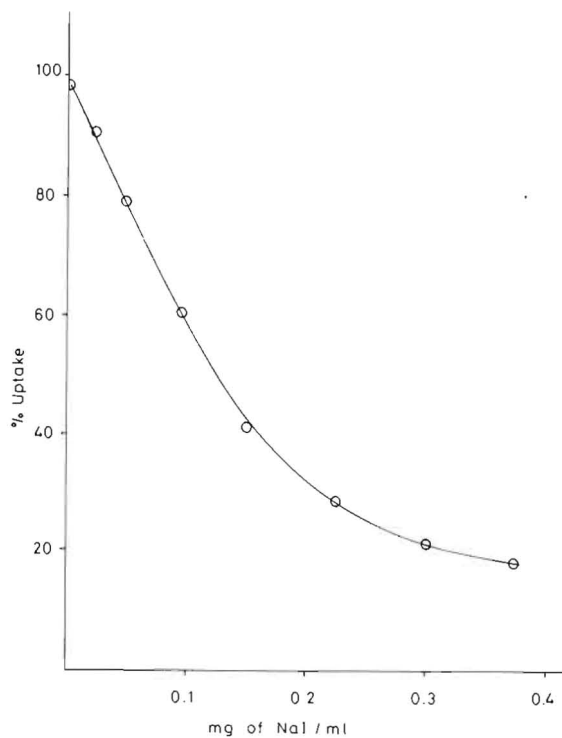


Fig. 3. Effect of carrier iodide on uptake.

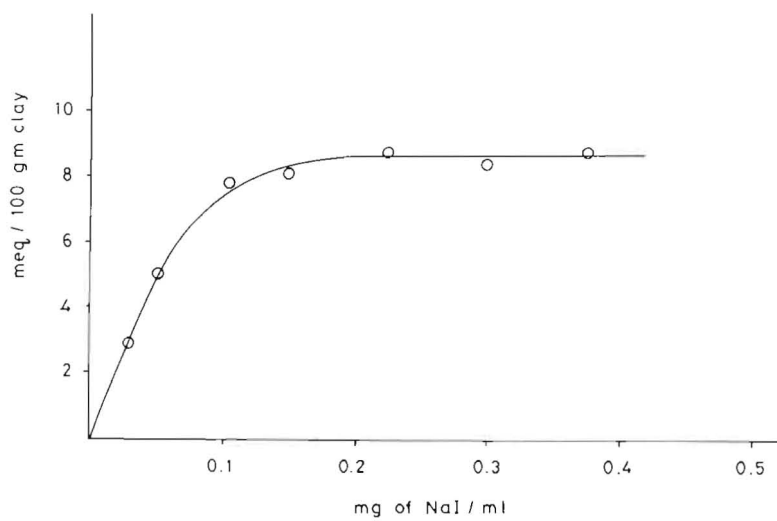


Fig. 4. Capacity of the treated clay with respect to carrier iodide.

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(Received 06/03/1983;
in revised form 23/10/1983)

طريقة حديثة للتخلص من نفايات اليود المشع باستخدام الطفل الطبيعي

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يشرح البحث طريقة جديدة للتخلص من نفايات اليود
المشع بواسطة الطفل الطبيعي المنقى الذي يتوى على مادة
المفوسفات والمعالجة بمحلول نترات الفضة.

لقد قدر ادمصاص اليود على هذا الطفل بحوالي ٨
ملليمكافىء لكل مائة جرام من الطفل وذلك خلال عشر دقائق
من التفاعل.

وجد، بعد الدراسة، أن العينة المحتوية على عشرة
جرامات من الطُّفل الفوسفاتى المعالج بمحلول ١٪ من
نترات الفضة يعطي أحسن النتائج.

يعتبر ادمصاص اليود بواسطة الطفل الفوسفاتى
المعالج بنترات الفضة تفاعلاً سريعاً وفي اتجاه واحد.