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Use of Egyptian minerals in the treatment of low level radioactive waste

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ABSTRACT

The fixation of ^{144}Ce, ^{137}Cs, ^{90}Sr, ^{60}Co, ^{232}Th, ^{233}U, ^{237}Np, ^{239}Pu and ^{241}Am from aqueous and phosphate solutions on Egyptian red brick, Egyptian pumice stone and Egyptian ceramic was studied as a function of pH, phosphate concentration, age of the radioelement, its hydrolytic behaviour and rates. It was found that most of these variables play a considerable role in the fixation. There was a reduction in the fixation rate which appears to be associated with the expected formation of negatively charged colloids and the simultaneous reduction in the number of positively charged ionic and colloidal species. Egyptian red brick was selected as a local mineral to improve the storage and release of low radioactive liquid wastes to the environment.

INTRODUCTION

The treatment of high or intermediate level wastes of small volume is usually carried out by using synthetic inorganic compounds and chemically treated minerals. The high degree of selectivity of inorganic sorbents and exchangers permits a more economic treatment. The economics, however, are somewhat different for the processing of large volume and low level wastes. In this case the utilization of inexpensive minerals may be justified.

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The use of natural minerals in sorption and exchange reactions in the treatment of radioactive wastes is now possible [1]. Studies are being made in France on different minerals such as sepiolite, activated aluminium oxide and crude vermiculite. At the Hans-Meitner Institut für Kernforschung, a pelagonite tuff which is commercially available under the name of *Filtrolite* has been used for some time for selective removal of cesium and some other radionuclides from radioactive effluents. A natural mineral of the zeolite type has been used on a large scale at the radioactive waste treatment station of the Casaccia nuclear centre. Kaolinite, montmorillonite and vermiculite minerals were extensively studied in Korea. Two natural sorbents, namely dolomite and pyrolusite, were investigated for large scale treatment of radioactive effluents in the U.S.S.R. In general minerals which are useful for the treatment of radioactive wastes are silicates, oxides, halides, carbonates, phosphates and sulphates. Different possibilities in specifying the amount of material, and the different mechanisms and kind of operation are available [2]. For waste disposal applications, the following are relevant: pure ion exchange capacity, sorption capacity, and total exchange capacity [3].

As a part of general investigations on the use of local minerals in the treatment of low-level and large volume of radioactive liquid waste, the present study illustrates the fixation of some fission products and actinides on some Egyptian minerals, namely Egyptian red bricks, Egyptian pumice stone and Egyptian ceramic.

EXPERIMENTAL CONDITIONS

1. Materials :

All chemicals were of analytical grade. ^{144}Ce, ^{60}Co, ^{137}Cs, ^{90}Sr, ^{59}Fe ^{234}Th, ^{232}U, ^{239}Pu and ^{241}Am were used in the valency state of Ce III, Co II, Cs I, Sr II, Fe III, Th IV, U VI, Pu IV and Am III. The Prolabo type 292 pH-meter was used to measure the pH of solutions. β-activity was measured by an end-window G. M. counter, α-sources were counted by a ZnS scintillation counter, and γ-activity was counted by a NaI crystal (detection limit being equal to 0.03 pCi for α-sources).

2. Sample preparation :

Egyptian red brick, ceramic and pumice stone were reduced in size using a porcelain mortar and sieved to ensure that all the samples had a particle size of 80 to 100 mesh. The samples were stirred several times with HCl 4 N, then with distilled water and were left overnight at room temperature. The samples were heated at 80°C and a known quantity of each sample was weighed and transfered to a column. Distilled water was added to the column and was shaked thoroughly till a homogeneous phase was reached. The

column was washed by 100 HCl 2 N, followed by washing with 500 ml distilled water [4].

The column consisted of a pyrex glass tube, 180 mm long and inner diameter 15 mm, with a reservoir of 250 ml capacity at the upper part of the column. The sample particles were loaded into the column to a height of 5 cm (4 g) and supported on glass wool plug. The chemical composition of each sample was determined by chemical analysis [5].

3. Procedures

Effect of pH *on fixation and elution*

Each group of solutions of 1 000 ml of 1 N HNO_3 was spiked with one of the radioactive element (each solution contained approximately 5×10^2 μCi). The solutions were adjusted to a pH range from 0.5 to 10 using 1 M NH_4OH solution. Each solution was then passed through the column. The fixed quantity of the radionuclide, at a certain pH, was removed from the column by 30 ml of 6 N HCl followed by 20 ml of distilled water [4]. The effluent and the eluent acid solutions were evaporated to a small volume and quantitatively transfered to a clean watch glass of 3 cm diameter. The percentage of the fixed and the non-fixed radionuclide on the mineral samples, at each pH, was calculated by comparison with the same radionuclide initially spiked.

To study the effect of the age of the radionuclide, at different pHs, six groups of ten solutions of 300 ml 1 N HNO_3 were spiked with the radioactive element. The solutions were adjusted to a pH range from 0.5 to 10 using ammonia. The solutions were stored for 5, 60, 180, 300 and 360 min, etc. after the preparation and before passage through the column. Elution was done by 30 ml of 5 N HCl. The percentage of the fixed and the non-fixed radionuclide, at each pH and at a certain age, was then calculated as above.

In order to study the effect of phosphate ions on adsorption, series of experiments were prepared using solutions contaminated with the radionuclide and 300 mg of calcium phosphate [6]. The pH was adjusted to a range from 0.5 to 6.2 (at pH > 6.5 phosphate ion precipitates). Elution was done using 30 ml of HCl 5 N. The percentage of fixed and non fixed radionuclide on each mineral, at each pH, was then calculated as above.

Optimum flow rates of fixation and elution

Different solutions of 300 ml 1 N HNO_3 spiked with ^{144}Ce were prepared at pH = 5 (pH at which maximum fixation occurred). Each solution was passed through the column with different flow rates of 1, 3, 5, 7 and 10 ml/min. The fixed cerium was eluted by 30 ml HCl 6 N at the same flow rates. The percentage of fixation was calculated by comparison with the same radionuclide spiked initially.

Minimum acid concentration and volume needed for complete elution

Groups of experiments were prepared at pH = 5 using ^{144}Ce as spiked radionuclide; 30 ml of HCl at concentrations of 6, 4, 3, 2, 1, 0.5 and 0.2 N were used for elution. The percentage of fixation was then calculated for each eluent concentration.

Optimum amount of mineral needed for fixation

Solutions of 300 ml of 1 N HNO_3, were spiked either with ^{144}Ce, ^{90}Sr, or ^{59}Fe and 1 ml of 4×10^{-4} M of $CeCl_3$, $SrCl_2$, and $FeCl_3$ respectively were adjusted at pH = 5, then passed through different columns containing different amounts of the mineral namely 0.5, 1, 1.5, 3, 7, 10, 15, 30 and 25 g. Cerium was eluted using 30 ml HCl 6 N. The percentage of cerium fixed in each case was then calculated. These experiments were repeated using the same weight of the minerals (4 g) and different concentrations of carrier ranging between 10^{-5} M and 10^{-3} M were added to the radioactive solutions.

3 RESULTS AND DISCUSSION

The chemical composition of Egyptian red brick, ceramic, and pumice stone is given in Table I.

TABLE I

CHEMICAL ANALYSIS OF THE MINERALS

Compound	In red brick (%)	In ceramic (%)	In pumice stone (%)
SiO_2	50.10		40.30
Al_2O_3	25.95	igneous rocks	27.95
Fe_2O_3	7.20	particulary	25.1
TiO_2	0.20	basalt	0.20
CaO	3.10		2.8
MgO	1.90		2.2
Na_2O	1.00		1.00
KO_2	0.24		0.24
Price of ton (US dollars)	50	600	1 000

Preliminary experiments indicated that fixation of radionuclides element on each mineral and elution from it were completely independent of the flow rate. The optimum acid concentration and volume needed for complete removal of the radionuclide from the mineral was found to be reached with 30 ml of HCl 1 N for each 4 g of the contaminated material. The

capacity of cerium retention, at pH = 5, was found to be equal to 0.52 m.eq/g, 0.38 m.eq/g, and 0.45 m.eq/g for Egyptian red brick, Egyptian ceramic, and Egyptian pumice stone respectively. Figure 1 shows the effects of concentrations on fixation of the radionuclides.

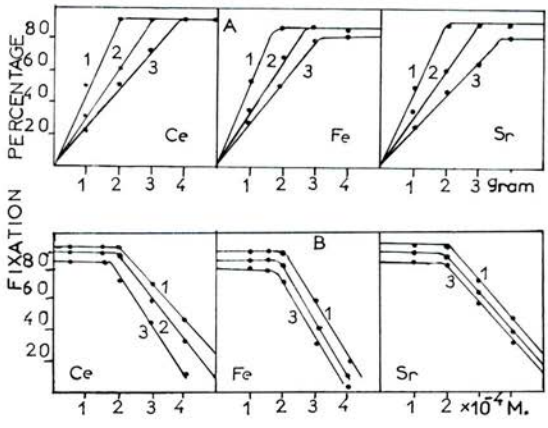

FIG. 1. — Fixation percentage for some radionuclides as a function of concentration. A. Fixation percentage of solutions spiked with the radionuclides in presence of 1 ml of 4×10^{-4}M of the carrier, with different amounts of the minerals. B. Fixation percentage of solutions spiked with the radionuclides in presence of different carrier concentrations, on 4 g of minerals.

Figure 2 represents the variations of the fixation of radionuclides from aqueous solutions as a function of pH. The maximum fixation of radionuclides on minerals occurred at $3.5 < pH < 7.5$. GRABENSCHIKOVA [7] and KRAUS [8] showed that from $2 < pH < 7.5$ colloidal Ce III, U VI,

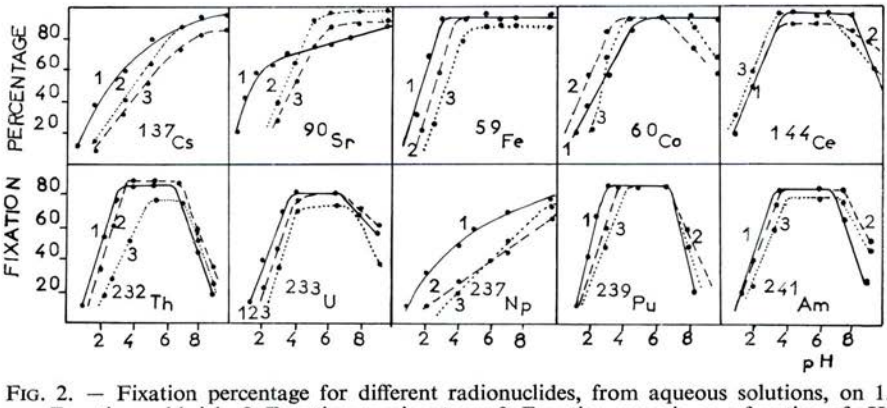

FIG. 2. — Fixation percentage for different radionuclides, from aqueous solutions, on 1. Egyptian red brick; 2. Egyptian pumice stone; 3. Egyptian ceramic, as a function of pH.

Th IV, Pu IV and Am III had a positive charge. Since fixation of the radionuclides studied on the different minerals depends on the pH and consequently on the charge of the radionuclide, it can be concluded that the charge on the studied minerals must be negative above pH 2 (pH at which fixation begins). It is therefore possible to postulate that fixation of the studied radionuclides on the different minerals is due to the formation of positively soluble hydrolysed species of the radionuclides, at such pH which could be attracted on the negatively charged minerals. According to VOLD [9], the major forces, in this case, are long range Van Der Waal's forces of attraction. At pH < 3 and > 7.5, fixation of the radionuclides studied decreased with pH. A number of effects may be responsible such as a

TABLE II

VARIATION OF THE FIXATION PERCENTAGE OF THREE MINERALS WITH THE RADIONUCLIDE AGE (AT pH 5 0.2)

Age time (min.)	^{144}Ce (%)			^{59}Fe (%)			^{235}U (%)			^{239}Pu (%)		
	1	2	3	1	2	3	1	2	3	1	2	3
5.....	95	90	95	90	90	85	80	80	75	80	80	80
60.....	91	84	88	81	80	78	76	73	71	75	75	72
180.....	80	72	73	72	68	67	64	61	58	68	66	60
300.....	71	63	61	65	61	60	59	57	54	60	59	56
600.....	62	55	56	58	52	50	56	52	50	55	50	51
1440.....	43	39	40	38	36	34	32	26	24	30	24	20

1. Egypian red brick; 2. Egyptian pumice stone; 3. Egyptian ceramic.

change in the structure of the minerals, or in the physico-chemical state of the ion in solution, or in the binding properties of the active group [10]. At pH > 7.5 the charge on the radioactive elements, at such activity, becomes negative [7, 8]. Since the charge on the mineral is always negative, there should be a net repulsion between the surface and the radionuclide particles. At pH < 2.5 fixation decreased. The higher the acidity, the lower the fixation. This is due to competition between H^+ and the positively charged radionuclide [11].

Aging of the radionuclide decreased fixation on the minerals (Table II), aged particles being larger and less charged. Also variation of the charge would cause a variation in the force of repulsion or attraction [12] between the radionuclide particle and the mineral surface. It is possible to assume that the decrease in adsorption, as the age of the particle increases, is due to the disappearance, from the solution, of small positively charged particles as these combine to form negatively charged colloids which due to their negative charge are repelled by the mineral surface.

Figure 3 illustrates the variation of the radionuclide fixation in a phosphate medium, as a function of pH. At pH < 3, fixation decreased more than in the aqueous phase, because of the formation of negative phosphate complexes [13] which should reduce fixation on negatively charged surface. At 4 < pH < 6.2, formation of phosphate complex is not expected to take place, thus resulting in an increase in the adsorption of the radionuclide on the minerals.

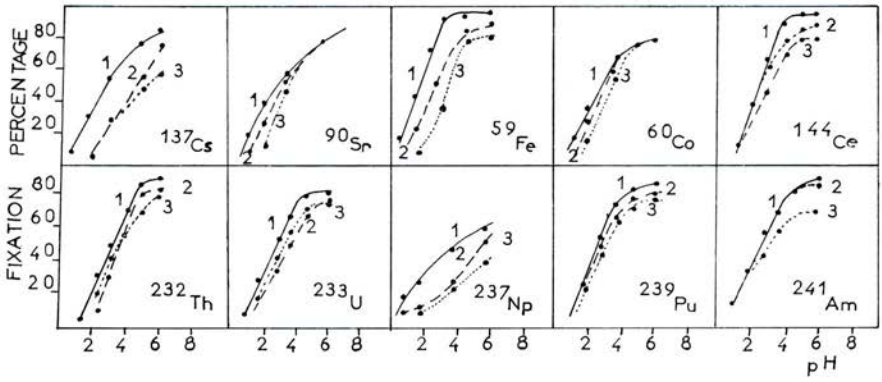

FIG. 3. — Fixation percentage for different radionuclides, from phosphate solutions, on 1. Egyptian red brick; 2. Egyptian pumice stone; 3. Egyptian ceramic, as a function of pH.

From these results, since fixation is related to the radionuclide pH, hydrolytic behaviour, age, concentration and valency, it can be concluded that an adsorption phenomenon has occurred between the radionuclide studied and the different minerals, which gives high probability of using such materials as local materials to treat low-level radioactive wastes at pH ranging between 3.5 and 7.5.

Technical comparisons between the three minerals showed that, although percentage of fixation of fresh radionuclides on the surfaces is nearly identical, yet Egyptian red brick is the most suitable adsorbant for the following reasons:

1. Egyptian red brick is not affected by acids. It was observed that Egyptian ceramic was rapidly reduced in size and changed to powder after a short time of use, which affected the flow rate largely;

2. Egyptian red brick can be used several times after treatment with HCl 0.5 N, while Egyptian pumice stone surface is poisoned after two or three utilisations. Moreover economic comparisons between efficiency and selectivity of the three minerals for radioisotope removal, and required decontamination level, showed that Egyptian red brick (the cheapest in Egypt) is the most suitable adsorbant which can be used as an Egyptian local material to treat low-level radioactive waste.

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