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SOIL COMPONENTS THAT INFLUENCE THE CHEMICAL BEHAVIOR OF ^{239}Pu

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ABSTRACT

Soil components that influence the extractability of ^{239}Pu from an artificially contaminated kaolinitic soil in relation to pH have been examined. This was done by using an equilibrium batch technique with CH_3COOH-NH_4OH and HNO_3-NaOH extracting systems. Soil organic matter and free iron oxides had an appreciable effect depending on the pH and the extracting system. The free silica and alumina and amorphous alumino-silicates had lesser influence. With the untreated soil (control), the CH_3COOH-NH_4OH system generally extracted more ^{239}Pu than did the HNO_3-NaOH system in the acidic pH range, whereas the latter system extracted markedly greater amounts of it in the alkaline pH range. With the soil from which the organic matter was removed, the CH_3COOH-NH_4OH system extracted appreciably greater amounts of ^{239}Pu than the HNO_3-NaOH system in the acidic pH range, but there was only little, if any difference between the two extracting systems in the alkaline pH range. The causes and the implications of these results are discussed.

The increasing use of Pu as an energy source intensifies its potentialities as a biological hazard. This, in turn, intensifies the need to obtain information regarding its form and physical and chemical reactions in various natural environments. As part of this effort, an appreciable amount of work has been done to determine the concentration of Pu in soils and the extent of its movement in soils (Krey and Hardy, 1970; Romney, Mork and Larson, 1970; Bliss and Dunn, 1971; Hardy, Krey, and Volchok, 1973; Essington et al, 1976; Nevissi, Schell, and Nelson, 1976; Krey et al, 1976; Nyhan, Miera, Jr., and Neher, 1976; and others). However, very little is known about the changes that occur in the chemical and physical forms of Pu after it enters the soil.

This paper deals with the influence of several soil components (organic matter, free iron oxides, and free silica, alumina, and amorphous aluminosilicates) on the chemical behavior of ^{239}Pu in an artificially contaminated kaolinitic soil. The influence of the soil components was determined over a pH range from 1.5 to 12.7 using an equilibrium batch extraction technique. Extractability rather than sorption is emphasized in this paper, because it is indicative of the Pu fraction that is transferred in soils and has implications on biological availability.

MATERIAL AND METHODS

The soil studied was Aiken clay loam, which is a slightly acidic (pH 6.6), kaolinitic soil. Its chemical properties together with those of the soil treated as described below have been reported previously (Nishita, Hamilton, and Steen, 1978).

The influences of the various soil components on the extractability of ^{239}Pu were determined by selectively removing certain soil components and interpreting the effect of their removal. The procedure was given in detail previously (Nishita, 1977; Nishita and Hamilton, 1977). Briefly, treatment I was the $CaCl_2$ treatment of the virgin soil. This removed the water soluble organic matter and salts and kept Ca as the dominant cation on the soil exchange complex while the other exchangeable cations were reduced. This treatment was also applied after each of the following treatments, which were done in sequential manner. Treatment II removed the HCl-soluble organic matter and salts including the carbonates. Treatment III was the H_2O_2 treatment to remove organic matter and dissolved Mn oxides and some residual carbonates, if originally present. Treatment IV, which was the digestion of samples in $Na_3C_6H_5O_7$ - $NaHCO_3$ - $Na_2S_2O_4$ mixture, removed the free iron oxides. Treatment V (Na_2CO_3 digestion) partially removed the free silica and alumina, amorphous alumino-silicates, and residual organic matter.

The extraction of the soil was done by the equilibrium batch method. Two g of soil material (oven dry basis) were placed in 50-ml polyethylene centrifuge tubes (Oak Ridge type) in duplicate, moistened by 5 ml of distilled water, contaminated with 50 µl of stock solution of ^{239}Pu in 3 $\underline{M}$ HNO_3, mixed by swirling, and allowed to stand for about 1 hr. Twenty ml of extracting solution were then added. Each suspension was equilibrated for 48 hr with continuous mixing on a mechanical shaker and then centrifuged at 18,800 gravity for 10 min to obtain the equilibrium extract. The concentration of ^{239}Pu in the extract is considered the extractable fraction.

The pH of the equilibrium extract was measured by the use of a glass electrode. Two extracting systems were used, e.g. HNO_3 - NaOH system and CH_3COOH - NH_4OH system. In the former system, the pH was adjusted to the desired level by adding appropriate amounts of either HNO_3 or NaOH. In the latter system, CH_3COOH was titrated with NH_4OH to obtain the desired pH. Thus, the acetate moiety was constant (0.8 M) for all the pH levels studied. The dose of ^{239}Pu applied is indicated in the figures. The ^{239}Pu was applied in the IV oxidation state. It was prepared by digesting the ^{239}Pu stock solution in 8 M HNO_3 (Rydberg and Sillen, 1955).

For radioassay, 10-ml aliquots of the equilibrium extracts were prepared for counting according to the method devised by Wood, et al (1976) with slight modification. In the method, organic matter and silica were eliminated with HNO_3 and HF, respectively. The ^{239}Pu was separated by coprecipitation with iron hydroxide and purified by using ion exchange techniques. The final eluate was evaporated to dryness on stainless steel planchets and counted using an alpha spectrometer system equipped with silicon surface barrier detector (2.54 cm dia. Ortec Model BR-028-450-100). In determining the alpha activities of the evaporated eluates, sufficient counts were collected to assure that the error of measurement did not exceed 5 percent at the 5 percent significance level.

RESULTS AND DISCUSSION

CH_3COOH-NH_4OH System

Figure 1 shows the effects of CH_3COOH-NH_4OH system on the extractability of ^{239}Pu from treated and untreated Aiken c.l. With the untreated soil (Fig. 1A), the extractability of ^{239}Pu increased from pH 2.3 to a peak between pH 3.6 to 4.7. Above pH 4.7, the ^{239}Pu extractability decreased progressively to a minimum (0.17 percent of dose) at pH ~9, and increased slightly from pH ~9 to pH ~10.2 and sharply above pH ~10.2. The maximum extractability was 6.9 percent of dose in the acidic pH range and 16.1 percent of dose in the alkaline range.

Treatment I, which removed the H_2O-soluble organic matter and salts, caused a small increase of ^{239}Pu extractability relative to that of the control up to pH ~7.8 (Fig. 1B). The increase was significant at the 5 percent level of significance using the Students' t-test (Alder and Roessler, 1977). Above pH ~7.8, treatment I was not significantly different from the control.

Treatment II, which removed the HCl-soluble organic matter and salts, generally increased the ^{239}Pu extractability relative to that of the control over the entire pH range studied. The amount of increase, however, varied with the pH. The removal of the HCl-soluble substances had a greater effect on the extractability of ^{239}Pu than the removal of water-soluble substances.

Although treatments I and II had some effect on the magnitude of the extractable fraction, the general pattern of the ^{239}Pu extractability curves remained similar to that for the control. The initial increase of ^{239}Pu is ascribed to increasing complexation of ^{239}Pu by the CH_3COO^- ions resulting from increasing addition of NH_4OH to increase the pH. The neutralization of CH_3COOH by NH_4OH produces NH_4^+ and CH_3COO^- ions. The NH_4^+ ions can then exchange off a fraction of the adsorbed ^{239}Pu ions from the soil exchange complex, while the CH_3COO^- ions form complexes with them. Plutonium is known to complex with CH_3COO^- ions (Gel'man et al, 1962; Taube, 1964; Cleveland, 1970; Moskvin, 1971). A peak is attained between pH 3.6 to 4.7. At the peak, the sorption of the hydrolysis products of ^{239}Pu is believed to become the dominant factor, and thereafter there is a progressive increase of sorption (decrease of extractability) with increasing hydrolysis, polymerization, and colloid formation with increasing pH. Polyvalent radionuclides may pass from ionic to the colloidal form via their hydrolysis, precipitation, coprecipitation, or adsorption under various conditions (Schubert and Conn, 1949; Kepák, 1971). The hydrolysis, polymerization, and colloid formation have been shown with Pu solutions by a number of investigators (Connick, 1954; Ockenden and Welch, 1956; Brunstad, 1957, 1959; Samartseva, 1962a, 1962b, 1963; Grebenshchikova and Davydov, 1965; Lloyd and Haire, 1973; Costanzo, Biggers, and Bell, 1973; and others). The more ready sorption of hydrolysis products of hydrolyzable ions compared to their nonhydrolyzed ions has also been shown by many investigators (Matijević et al, 1960, 1961; Stumm, Huang, and Jenkins, 1970; James and Healy, 1972; Tewari et al, 1972, 1975; Loganathan, Burau, and Fuerstenau, 1977; and others). The sharp increase of ^{239}Pu extractability above pH 10.3 was due to the extraction of alkali-soluble organic matter with which the ^{239}Pu was associated. This is shown clearly by treatment III.

Treatment III, which removed the organic matter and Mn oxides, significantly increased the extractability of ^{239}Pu in the pH range below pH ~9 relative to treatment II and drastically reduced the extractability above pH 10.3 (Fig. 10). The effects observed were considered to be due primarily to soil organic matter since its concentration (2.31 percent organic-C) was much greater than that of the HNO_3-extractable Mn (0.15 percent). The marked reduction of ^{239}Pu extractability in the pH range above pH 10.3 after treatment III indicates that the high extractability under treatment II was due to the presence of alkali-soluble organic matter with which part of the ^{239}Pu was associated. This is supported by the fact that the soil extract above pH 10.3 was dark brown in color for treatment II (as well as for the control and treatment I), but was colorless for treatment III. The high extractability of soil organic matter in alkaline solutions is well-known (Mortensen, 1965; Kononova, 1966). The enhanced ^{239}Pu extractability in the pH range below pH ~9 after the removal of soil organic matter shows that a fraction of ^{239}Pu (up to about 11 percent of dose) was strongly fixed on the organic matter before its removal even against the complexing action of the CH_3COO^- ions. The ^{239}Pu extractability in the pH range above pH ~9 was from 0.3 - 0.5 percent of dose, indicating that its extractability from the inorganic fraction of the soil is low under strongly alkaline condition.

Treatment IV, which removed the free iron oxides, significantly reduced the ^{239}Pu extractability relative to that after treatment III in the pH range below pH ~9 (Fig. 1E). Above pH ~9, there was no significant difference between the two treatments. The effect observed perhaps occurred as a result of the exposure of additional ion adsorption sites with the removal of iron oxides. One evidence for this is indicated by the increase of the cation exchange capacity of the soil from 16.53 meq/100 g before the removal of iron oxides to 17.98 meq/100 g after their removal. The blocking action of iron oxides may be surmised from the fact that iron oxides occur as cementing materials and partial coatings on the surface of soil clays (Carroll, 1958; Mehra and Jackson, 1960; Jenne, 1968; Anderson and Jenne, 1970; and others).

Treatment V, which partially removed free silica and alumina, amorphous alumino-silicate, and residual organic matter, did not appreciably affect the extractability of ^{239}Pu relative to treatment IV (Fig. 1F). The ^{239}Pu extractability ranged from 0.53 to 4.26 percent of dose over the whole pH range studied. Assuming that the residual soil material after treatment V is mainly kaolinite, the results indicate that ^{239}Pu is strongly associated with kaolinite even in the presence of CH_3COO^- ions, which form complexes with ^{239}Pu.

HNO_3-NaOH System

Figure 2 shows the extractability of ^{239}Pu with HNO_3-NaOH extraction system. Except for a slight peak at pH ~3.6, the ^{239}Pu extractability from the untreated soil (control) generally decreased with increasing pH to a minimum (0.63 percent of dose) at pH ~6.9 (Fig. 2A). Above pH ~6.9, it increased progressively to a maximum (47.52 percent of dose) at pH ~11.5 and then decreased.

Relative to the control, treatment I had only slight effect on the extractability of ^{239}Pu between pH 1.5 and pH ~6.9 (Fig. 2B). Between pH ~6.9 to pH ~11.8, there was a small reduction of its extractability, indicating perhaps that a small amount of ^{239}Pu was associated with water soluble organic component before its removal. Treatment II had only slight, if any, effect on ^{239}Pu extractability relative to that of the control, except between pH ~9.5 and pH ~11.8 (Fig. 1C). The minimum extractability (0.29 percent of dose) occurred at pH 6.5. The small reduction between the latter pH range probably indicated again that a small amount of ^{239}Pu was associated with soluble organic component before its removal.

As with the CH_3COOH-NH_4OH system, the general pattern of the extractability curve after treatment I or II was similar to that for the control. The general tendency of decrease of extractability with increasing pH to pH ~6.9 may be ascribed, as above, to increasing extent of hydrolysis, polymerization, and colloid formation. The progressive increase of ^{239}Pu extractability *between pH ~6.9 and pH ~11.8 is ascribed again to the ex*traction of alkali-soluble organic matter. The cause of the decrease of extractability above pH ~11.8 is not well-understood, but as explained before (Nishita and Hamilton, 1977), it might be explained in several ways. With increasing concentration of the potential determining OH^- ion, the sorbent and the sorbed ^{239}Pu hydroxide probably became increasingly negative in charge. This then may cause less sorption of ^{239}Pu hydroxide due to mutual repulsion of like charges. The repulsed ^{239}Pu hydroxide being highly insoluble under alkaline condition was then less extracted even though complex-forming, alkali-soluble organic matter was present. The values of solubility product of $Pu(OH)_4$ found by various investigators range between 7×10^{-48} and 7.2×10^{-56} (Perez-Bustamente, 1970). Another mechanism might be the increase of sorption of ^{239}Pu *due to interfacial* hydroxide precipitation as proposed by Loganathan, Burau, and Fuerstenau

(1977) for the sorption of Co and Zn by hydrous manganese oxide.

Relative to treatment II, treatment III enhanced the extractability of ^{239}Pu between pH ~3.3 and pH ~6.6 and drastically reduced it above pH ~6.6 (Fig. 2D). Depending on the pH above ~6.6, the ^{239}Pu extractability ranged from 0.03 to 0.73 percent of dose after treatment III, whereas it ranged up to a maximum of 38 percent of dose before this treatment. Thus, a very marked effect of alkali-soluble organic matter was demonstrated again. The cause of the increased ^{239}Pu extractability between pH ~3.3 and pH ~6.6 is not known. This effect appears to be related to the presence of iron oxides, since their removal (treatment IV) eliminated the effect (Fig. 1E). The effect observed perhaps suggests the involvement of electrical charges on these components. The hydrolysis and polymerization products of tetravalent Pu are positively charged in the pH range below the isoelectric points, which occur at pH 8 - 8.5 (Grebenshchikova and Davydov, 1965). The magnitude of the positive charge of Pu decreases as hydrolysis and polymerization progress with increasing pH. According to Sumner (1963), the precipitated iron oxides have isoelectric points in the region pH 6 - 7 and are positively charged below pH 6. Furthermore, below pH 6, the negative charge on the clay (kaolinite was used) was reduced by the mutual neutralization of the positive charges on the iron oxide and the negative charges on the clay and/or the negative charges on the clay being physically blocked by iron oxide coating. From these facts, it follows that the enhanced extractability of ^{239}Pu (reduced sorption) observed between pH ~3.3 and pH ~6.6 may be a result of both mutual repulsion of like charges and reduced attraction between unlike charges. These effects are masked in the presence of soil organic matter (Fig. 2D).

A comparison of treatment IV and V (Fig. 2F) shows that the partial removal of free silica and alumina, amorphous alumino-silicate, and residual organic matter increased the extractability of ^{239}Pu below pH ~3.5. Above pH ~3.5, there was no appreciable difference between the two treatments. Within the latter pH range, the ^{239}Pu extractability ranged from 0.04 to 1.16 percent of dose. Thus, the residual soil material, presumably predominantly kaolinite, strongly sorbed ^{239}Pu over a wide pH range.

Comparison of Extracting Systems

Comparison of CH_3COOH-NH_4OH (Fig. 1) and HNO_3-$NaOH$ (Fig. 2) extracting systems shows several notable differences. Before the removal of organic matter (treatment III), ^{239}Pu extractability by CH_3COOH-NH_4OH system was greater than by HNO_3-$NaOH$ system roughly between pH 3.6 and pH 6.5. On the alkaline side, the relative extractability was reversed. The HNO_3-$NaOH$ system extracted markedly greater amounts of ^{239}Pu than the CH_3COOH-NH_4OH system. The threshold for the sharp increase of ^{239}Pu extractability with the HNO_3-$NaOH$ system was at pH ~7, whereas that with the CH_3COOH-NH_4OH system was at pH ~10.2. After the removal of organic matter, the ^{239}Pu extractability by CH_3COOH-NH_4OH system was increased relative to that by the HNO_3-$NaOH$ system in the acidic pH range, whereas there was only slight, if any, difference in the alkaline range roughly above pH 8.

The greater effectiveness of CH_3COOH-NH_4OH system in extracting ^{239}Pu in the lower pH ranges is due to the fact that CH_3COO^- ion is a stronger complexing agent than NO_3^- ion (Taube, 1964) and that the CH_3COO^- ion concentration was relatively high. The CH_3COO^- ion concentration of the $CH_3COOH-NH_4OH$ system was constant at 0.8 M for all pH levels, whereas the NO_3^- ion concentration of the HNO_3-NaOH system was 0.128 M or lower depending on the adjusted pH. The much higher extractability of ^{239}Pu by the HNO_3-NaOH system in the alkaline pH range is due to the greater efficiency of NaOH in extracting alkali-soluble soil organic matter than NH_4OH.

Extractability of ^{239}Pu in Relation to Several Other Transuranics

Figure 3 shows the extractability of ^{239}Pu in relation to those of ^{237}Np, ^{241}Am, and ^{242}Cm from the untreated Aiken c.l. The extractability of the latter transuranics was determined previously in the same manner as the present experiments. The data for ^{241}Am and ^{242}Cm were reported previously (Nishita, 1977; Nishita and Hamilton, 1977; Nishita, Hamilton, and Steen, 1978). The ^{237}Np results are from unpublished data. The predominant oxidation state of ^{239}Pu after the 48 hr equilibration period in the present experiment is considered to be the tetravalent state. This is inferred from the fact that not only was Pu (IV) the form applied, the Pu (III) may be oxidized to Pu (IV) by O_2 in the air (Newton and Baker, 1956; Anonymous, 1974). The Pu (V) and (VI) are reduced to Pu (IV) by soil organic matter and clays (Bondietti, Reynolds, and Shanks, 1976). Neptunium 237 was applied in the V oxidation state, whereas ^{241}Am and ^{242}Cm were applied in the III state.

With the $CH_3COOH-NH_4OH$ system, the differences, if any, among ^{239}Pu, ^{241}Am, and ^{242}Cm were small in the pH range below 10. The extractability of ^{237}Np, however, was drastically greater than these transuranics in this pH range. Above pH 10, the relative extractability was ^{242}Cm > ^{239}Pu, ^{237}Np > ^{241}Am.

With the HNO_3-NaOH system, the differences between ^{241}Am and ^{242}Cm extractabilities were generally small, if at all, in the pH range roughly below pH 7. Below pH 2.5, the ^{239}Pu extractability was appreciably less than ^{241}Am or ^{242}Cm, but between pH 2.5 and pH 7, ^{239}Pu tended to be greater than ^{241}Am or ^{242}Cm. The ^{237}Np extractability was drastically greater than ^{239}Pu, ^{241}Am, or ^{242}Cm below pH 7. Above pH 7, the relative extractability of these transuranics varied somewhat with pH. Perhaps, notable is the fact that between pH 7 and pH 11.5, the extractability of ^{239}Pu was the greatest, indicating relatively strong association of this radionuclide with alkali-soluble organic matter. *The extractability of* ^{241}*Am was the* least over the entire alkaline pH range, indicating that this radionuclide was least strongly associated with alkali-soluble organic matter.

GENERAL DISCUSSION

The results show that several soil components may influence the extractability of ^{239}Pu. Soil organic matter and free iron oxides had an appreciable effect depending on the pH and the extracting system. The free silica and alumina and amorphous alumino-silicate had lesser influence. The minimum *extractability of* ^{239}*Pu in the untreated soil with the* CH_3COOH-NH_4OH *system* was 0.17 percent of dose at pH ~9, while that with HNO_3-NaOH system was 0.63 percent at pH ~7. In the organic matter-deficient soil, the minimum extraction was 0.27 percent of dose at pH ~10 and 0.03 - 0.05 percent of dose between pH 7.0 and pH 8.2 for the CH_3COOH-NH_4OH and HNO_3-NaOH systems, respectively.

Some practical implications may be drawn from the present results in the event of real contamination of soils of the type studied. Under soil pH condition below the pH of the minimum extractability, the ^{239}Pu movement in the soil under the leaching action of water is likely to be greater the lower the soil pH. In the soil pH condition above that of minimum extractability, the ^{239}Pu movement is likely to be relatively high in the untreated soil containing organic matter, but very low in the soil containing practically no organic matter. The ^{239}Pu extractability after the removal of soil organic matter was 0.03 to 0.73 percent of dose in the pH range above 7.0 using the HNO_3-NaOH system, which as pointed out above, contained no added complexing agent on the alkaline side except the OH^- ion. It is evident that the extractability was in general very low, but not zero. Thus, however small, some movement of ^{239}Pu is likely to occur under alkaline conditions even in the soil containing no organic matter. The significance of this probable small movement from the standpoint of radiological hazard remains to be determined.

The pH values of most soils range from about 3.0 to 10.5 (Cole, 1949). The range for good plant growth is generally narrower, since certain plant nutritional and/or soil structural problems usually occur at both extremities of the range. The pH range within which the lowest ^{239}Pu extractability in the present soil appeared to be from pH 7 to pH 10. This suggests that raising the soil pH to the alkaline side, perhaps by liming, might reduce the availability of ^{239}Pu to plants.

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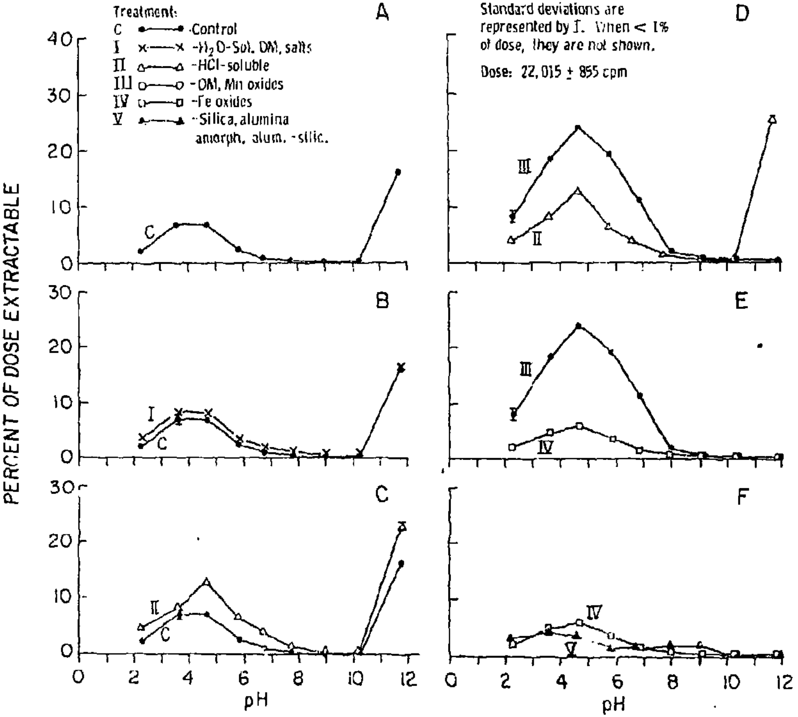

FIG. 1. Effect of pH on the extractability of ^{239}Pu from Aiken clay loam chemically treated to remove various components. $CH_3COOH-NH_4OH$ system.

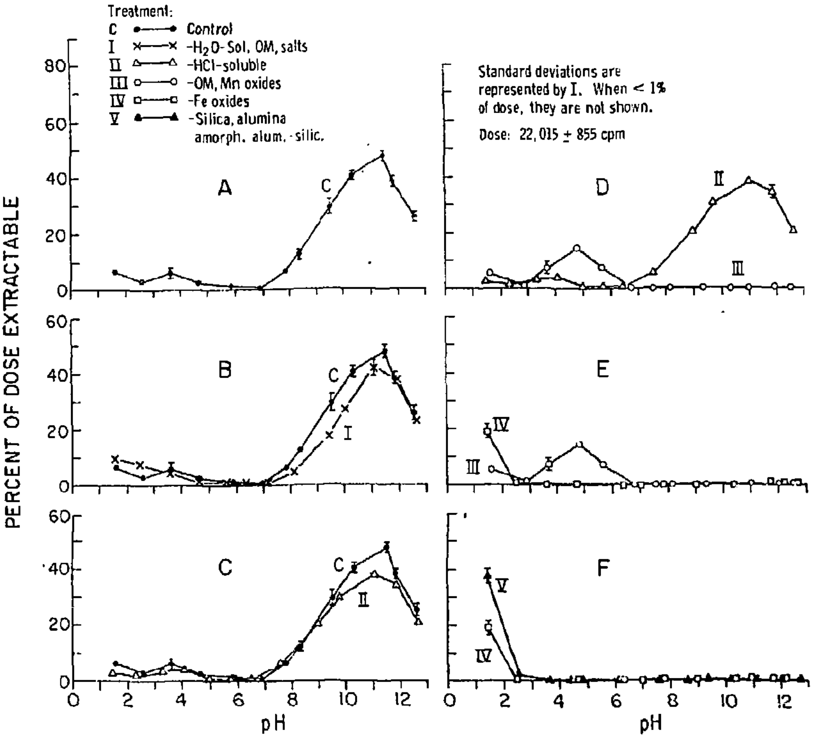

FIG. 2. Effect of pH on the extractability of ^{239}Pu from Aiken clay loam chemically treated to remove various components. HNO_3-NaOH system.

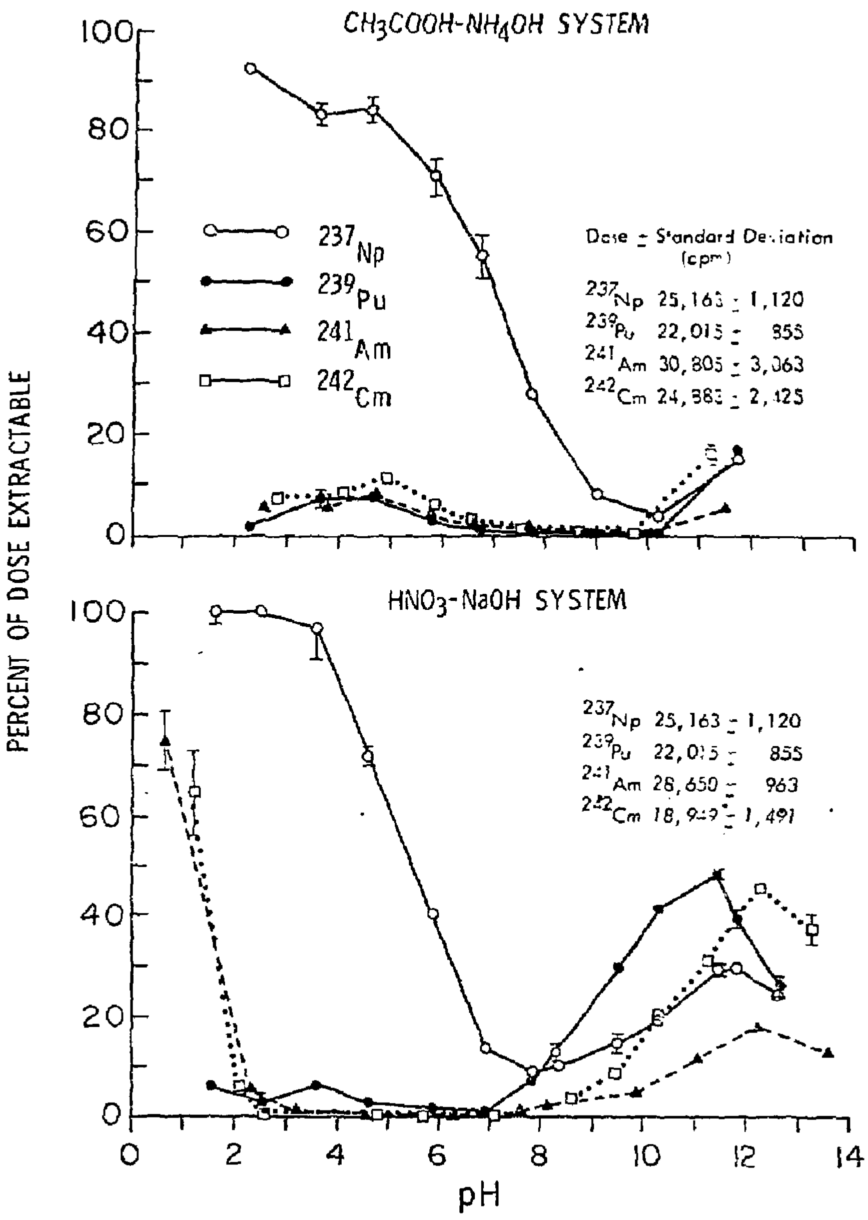

FIG. 3. Relative extractability of ^{237}Np, ^{239}Pu, ^{241}Am and ^{242}Cm from untreated Aiken clay loam. (Vertical lines represent standard deviations of duplicate samples. When < 1% of dose, they are not shown).