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Use of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium and Other Elements from Phosphoric Acid Solution

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Abstract

An amidoxime-group-containing fibrous adsorbent which was made by the radiation-induced grafting of acrylonitrile onto a synthetic fiber was applied to the recovery of uranium and other elements (V, Ti, Fe, etc.) from phosphoric acid solution of a fertilizer plant. The adsorption amount of these elements increased in proportion to the concentration of amidoxime groups introduced in the adsorbent. The distribution of the metals adsorbed in 24 h was homogeneous in the adsorbent containing more than 4.9 meq/g amidoxime groups while it was limited to the surface region of the adsorbent containing 1.5 meq/g amidoxime groups. The rise in the pH of the solution brought about by adding sodium hydroxide produced a maximum amount of adsorption at pH = 3. The concentration factors for U, V, Ti, and Fe were 2.8×10^2, 8.6×10^3, 4.2×10^3, and 6.1×10^2, respectively.

INTRODUCTION

With the growth of nuclear power, new uranium resources other than uranium ores have been explored in order to secure a supply of uranium for the future. Many studies have been made on the recovery of uranium from seawater, since the estimated reserve of uranium in seawater is 4.5×10^9 tons, which is about one thousand times the terrestrial resources, in the cost range up to \$50/lb U_3O_8 (*1–15*). Another important

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alternate source of uranium is the phosphoric acid solution from the manufacture of fertilizers (*16–18*). Phosphoric acid from fertilizer plants usually contains 10–300 ppm uranium as compared to 3 ppb contained in seawater (*19*, *20*). In 1978 the annual production of uranium as a by-product from phosphoric acid in the United States was 3300 tons, which is ~10% of total uranium production (*21*, *22*).

The method widely used for the recovery of uranium from phosphoric acid solution is solvent extraction. However, this method is not economical if the phosphoric acid plant capacity is below 1.5×10^5 ton P_2O_5 per year (*16*), or if the phorphoric acid solution contains less than 200 ppm U (*23*). Actually, most countries outside the United States have phosphoric acid plant capacities smaller than this limiting capacity. In order to recover uranium and other useful elements from such small plants, which is also important from the environmental point of view, a method other than solvent extraction must be found.

The application of adsorbents to the recovery of uranium and other useful elements from phosphoric acid solution has scarcely been tried. One of the reasons may be insufficient study of adsorbents suitable for recovery from highly acidic phosphoric acid. An amidoxime-group-containing adsorbent, AOF, synthesized by the radiation-induced graft polymerization of acrylonitrile onto tetrafluoroethylene–ethylene copolymer fiber followed by amidoximation with hydroxylamine, was previously found to have excellent properties for the adsorption of uranium from seawater and a high stability when contacted with acid (*24*, *25*). AOF was used in the present study for the recovery of uranium and other useful elements, such as vanadium and titanium, from phosphoric acid solution in order to investigate the feasibility of the adsorption process in fertilizer plants.

EXPERIMENTAL

Three types of adsorbent, AOF-I, -II, and -III containing amidoxime groups of 1.5, 4.9, and 8.4 meq/g-Ad, respectively, were prepared as described previously (*24*). Before each use, AOF was conditioned by treatment with 2.5% potassium hydroxide solution for 20 min at 80°C.

In order to first study the adsorption properties of AOF, batch experiments were carried out on the adsorption of copper ions. One liter of a copper ion-containing buffer solution of 15 m*M* was placed in contact with 0.5 g of the preconditioned AOF with stirring for prescribed periods at 30°C.

A waste phosphoric acid solution from the washings or scrubbers obtained from a fertilizer manufacturing plant was used for the experiments. Batch experiments were carried out in which 0.1 g of the preconditioned AOF was contacted with 1 L of solution or alternatively 0.05 g AOF with 500 mL solution with continuous agitation at 25°C.

The adsorbed copper content was obtained by elemental analysis. The analysis of adsorbed uranium was done using a spectrophotometric method employing Arsenazo-III reagent and also by the use of a Jarrell-Ash Argon plasma emission spectrophotometer, Model ICAP-575 mark-II. Analysis for elements other than uranium from phosphoric acid solution was done with a Jarrell-Ash atomic absorption and flame emission spectrophotometer, Model AA-8200. The distribution of copper within AOF was observed with a JEOL electron probe x-ray micro-analyzer (EPMA), Model JXA 733.

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RESULTS AND DISCUSSION

Adsorption of Copper

The adsorption ability of AOF was studied with a copper-ion-containing solution at pH 6. The effects of amidoxime group concentration, [F.G.], and adsorption time on adsorption of copper are shown in Fig. 1. The adsorption proceeds quickly in the initial 1–3 h and then levels off. Such a fast leveling off indicates that the diffusion of the metal-ion-containing solution inside the adsorbent is rapid.

Figure 2 shows the relationship between the adsorption amount of copper and [F.G.] in the adsorbent at adsorption times of 0.25, 0.5, 1, and 24 h. In all cases the amount of adsorption is roughly proportional to the amidoxime group concentration. As shown in Table 1, the efficiency of the adsorbent estimated from the slopes of these straight lines increases from 0.33 mol Cu^{2+} per 1 mol amidoxime ligand at 0.25 h to 0.62 Cu^{2+} mol/mol-ligand at 24 h.

The adsorption of copper with AOF is based on chelate formation between copper ions and the amidoxime ligands of the adsorbent. When it is considered that amidoxime is either a bidentate ligand or a monodentate ligand (*26*), and that copper makes a square planar chelate, there may be at least two chelate forms. The first case is where one copper ion and two bidentate amidoxime ligands make a chelate, which requires the ratio $[Cu^{2+}]/[\text{amidoxime}] = 0.5$. The second case is where one copper ion and four monodentate amidoxime ligands make a chelate, which requires $[Cu^{2+}]/[\text{amidoxime}] = 0.25$. The ratio of 0.62 observed after 24 h

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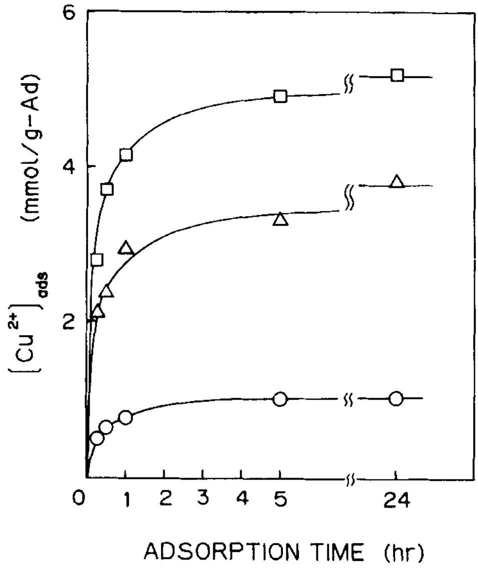

FIG. 1. Amounts of Cu^{2+} adsorbed with (○) AOF-I, (△) AOF-II, and (□) AOF-III: concentration of Cu^{2+} in the solution = 15 m*M*, pH = 6.

adsorption indicates that the adsorption of copper ion with AOF is mainly based on the first case. Based on the possibility that poly(acrylamidoxime) can even be a tridentate ligand (*13*), it is probable that this ratio could become larger than 0.5.

There may be another possibility for increasing this ratio above 0.5. Although the adsorption is based on chelate formation, there does not necessarily need to be complete chelate formation between metal and ligands. Adsorption is also possible if a chelate is made of metal, ligands of the adsorbent, and other ligands like water. That is, aquo-type chelate structures are also possible. In this case the ratio [metal]/[ligand other than water] is large. This assumption seems to be reasonable because the present ligands are fixed to the long graft chains of poly(acrylonitrile). The high molecular weight of the chains, estimated as 10^5–10^6 (*28*), may cause some portion of the ligands not to participate in chelate formation, and this requires aquo-type chelate formation as mentioned above.

Figure 3 shows changes in the distribution of adsorbed copper ions with adsorption time in the cross section of the adsorbent fiber. In the case of AOF-I, the adsorption layer does not change with adsorption time. Clearly, amidoxime groups are located only in the surface region.

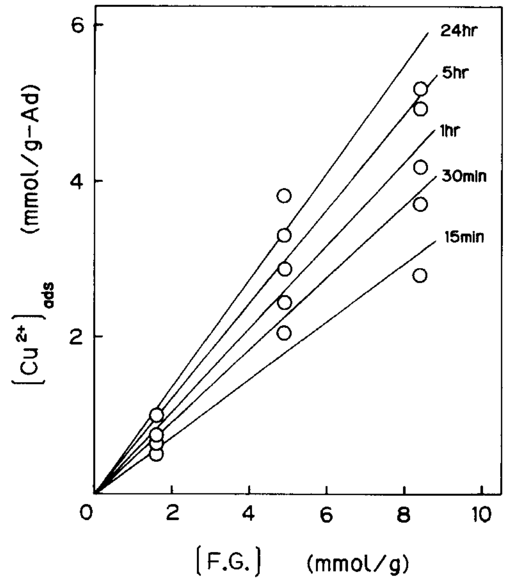

FIG. 2. Effect of [F.G.] on copper adsorption with AOF-II at various adsorption time.

On the other hand, amidoxime groups are homogeneously distributed in AOF-III. The adsorption layer change is remarkable in the case of AOF-II. The result that it takes 24 h for the adsorption layer to reach the core layer of the adsorbent indicates that the concentration of amidoxime groups decreases gradually from the surface to the core.

In order to clarify the stability of the present adsorbent under acidic conditions, the adsorption of copper was carried out with solutions of different pH's. Figure 4 shows that adsorption is significantly affected by

TABLE 1
Change in Efficiency of Adsorption with Time

Time (h)	Efficiency[a] (mol/mol)
0.25	0.33
0.5	0.44
1	0.5
5	0.61
24	0.62

[a] Calculated from the slopes of the lines in Fig. 2.

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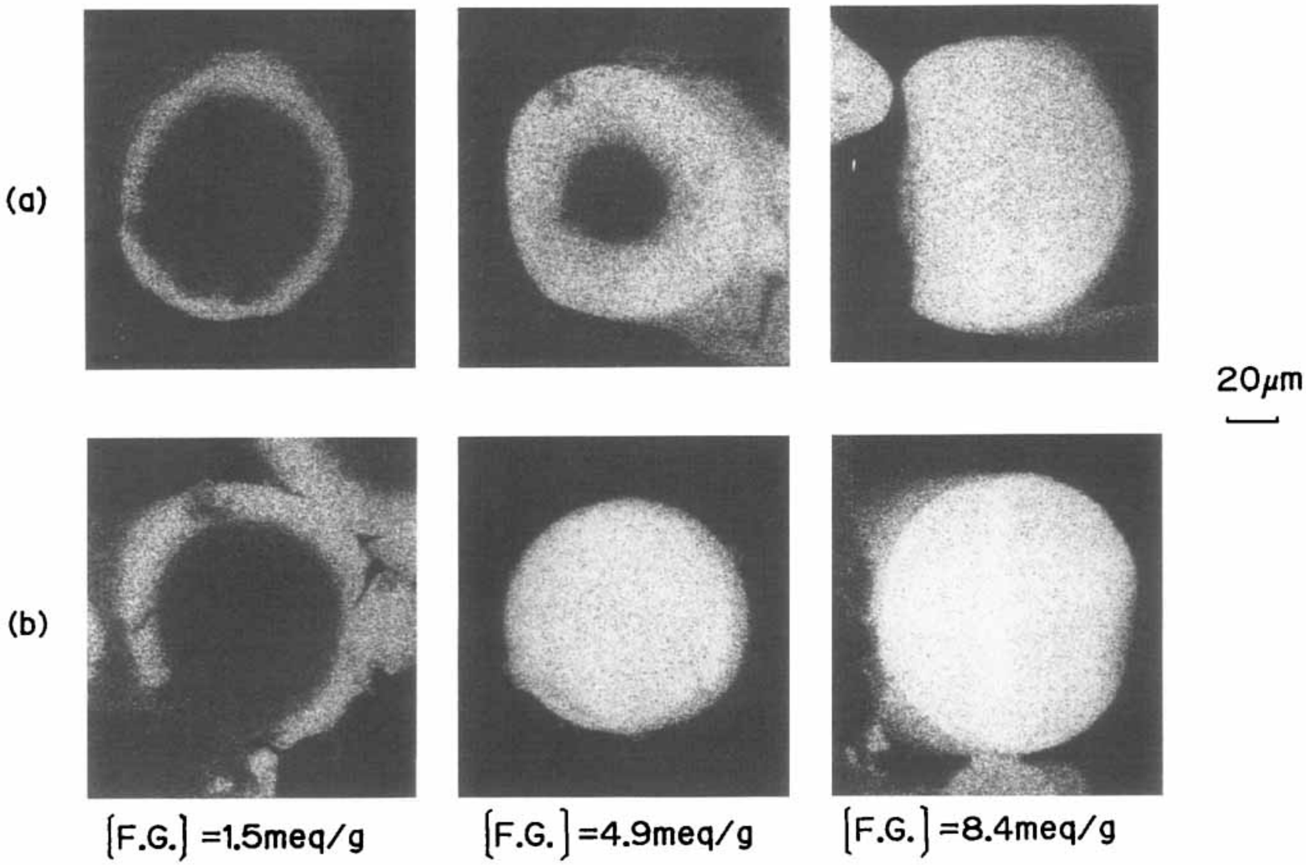

FIG. 3. Distribution of Cu^{2+} in AOF as a function of [F.G.]: (a) adsorption time = 15 min. (b) 24 h.

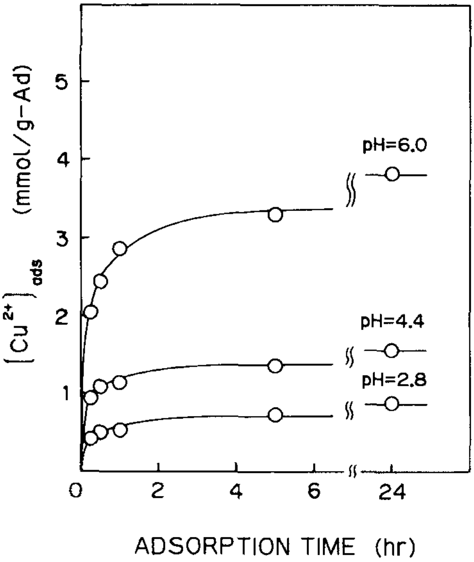

FIG. 4. Amount of Cu^{2+} adsorbed with AOF-II at different pH's.

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the acidity of the solution. The decrease in the amount of adsorption is especially remarkable when the pH is lowered from 6.0 to 4.4. One of the reasons for this decrease may be based on the relation between the pH value of the solution and the pK_a of the ligand. Adsorption with the ligand of high pK_a is unfavorable when the pH of the solution is low. Although the pK_a of amidoxime has not yet been reported (probably higher than 8.0), lowering the pH suppresses the chelating ability of the amidoxime ligand, which, on the other hand, enables the extraction of adsorbed metals with acid (*24*).

Adsorption from Phosphoric Acid

Table 2 summarizes the concentration of the elements found in a waste phosphoric acid solution. The concentration of calcium is much larger than those of other elements because this waste phosphoric acid solution was obtained by the reaction of $Ca_{10}(PO_4)_6F_2$ with sulfuric acid. Aluminum, iron, and magnesium belong to the next most abundant group, the concentration of which is ~50 ppm. The concentrations of such elements as titanium, vanadium, and uranium are relatively small (less than 1

TABLE 2
Analysis of Waste Phosphoric Acid Solution

Element	Amount (ppm)
Aluminum	42
Calcium	1216
Chromium	0.5
Copper	1
Iron	40
Magnesium	59
Manganese	2
Platinum	0.7
Titanium	0.8
Uranium	0.8
Vanadium	0.8
Zinc	1
Zirconium	0.2

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ppm). In the following experiments, the efficiency of recovering these rare elements in waste phosphoric acid was studied.

Figure 5 shows the adsorption amounts of Ti, V, and U obtained by AOF-II. Although the concentrations of these metals in the solution are comparable, as mentioned above, the adsorption of V proceeds most effectively. On the other hand, the amount of U adsorbed scarcely increases even if the adsorption time is extended.

Figures 6 and 7 show the relation between the adsorption amounts of Ti and V and adsorption time at various [F.G.], respectively. The adsorption amount increases with time. The adsorption rate of Ti and V is much slower than that of copper from the copper ion-containing solution, as shown in Figure 2. In the latter case, 1 day was enough to obtain equilibrium adsorption. On the other hand, equilibrium was not reached in the former case even after 7 days. The slow adsorption of Ti and V from phosphoric acid may be partly due to the low concentration of these elements in the solution. The concentration of both Ti and V was less than 1 ppm while that of copper was ~1000 ppm under the present conditions. Another possible reason for the slow adsorption is related to the fact that the phosphoric acid contains many kinds of metals, anions, organic and inorganic unknown substances, etc. Therefore, the adsorption is competitive among these substances, which decreases each adsorption amount when compared with the adsorption from a solution containing only one metal ion.

Figure 8 shows the relation between [F.G.] and adsorbed amounts of

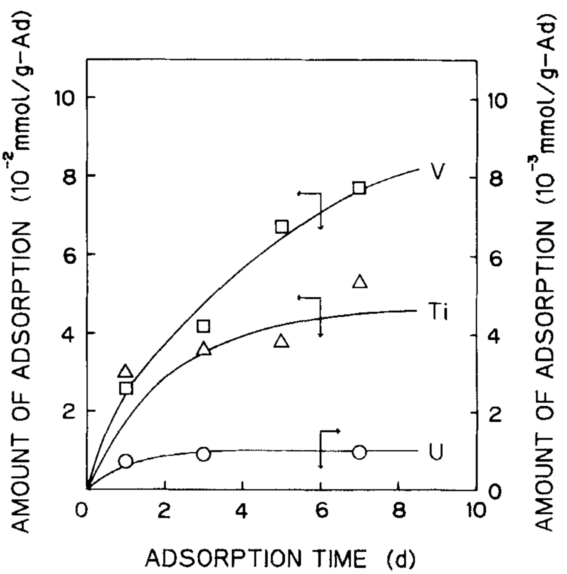

FIG. 5. Amount of V, Ti, and U adsorbed with AOF-II from the waste phosphoric acid solution: pH = 2.3.

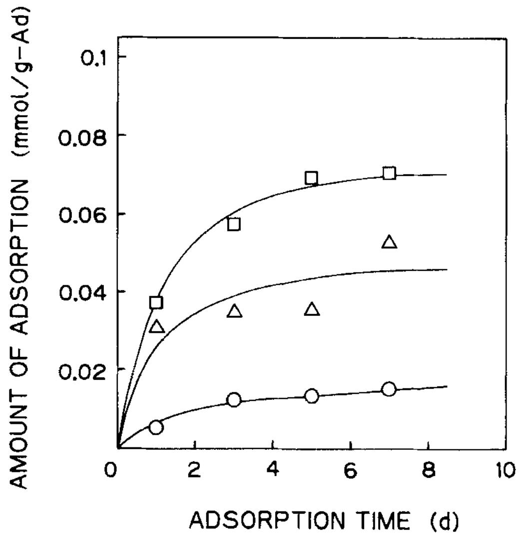

FIG. 6. Adsorption of Ti from the waste phosphoric acid solution with (○) AOF-I, (△) AOF-II, and (□) AOF-III.

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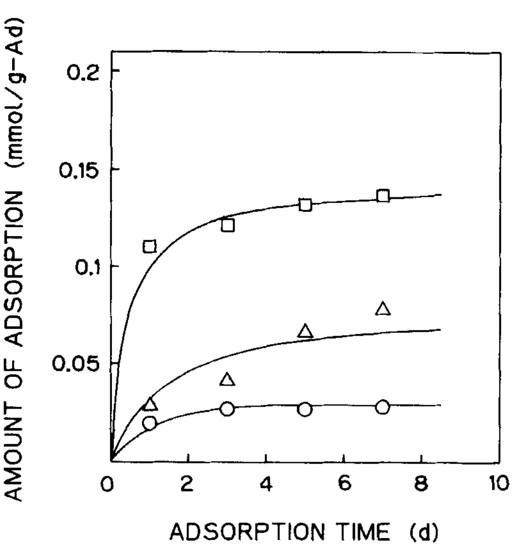

FIG. 7. Adsorption of V from the waste phosphoric acid solution with (○) AOF-I, (△) AOF-II, and (□) AOF-III.

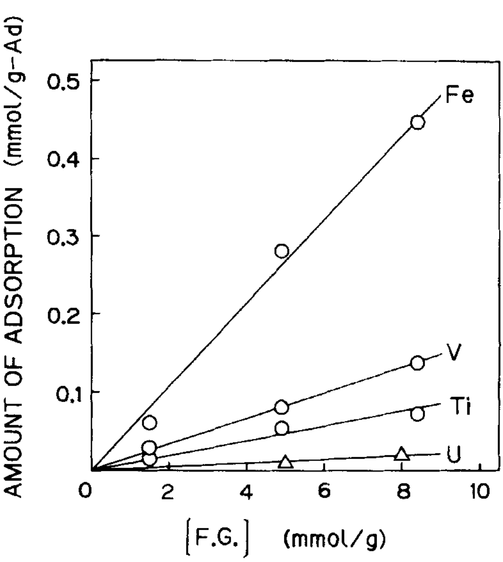

FIG. 8. Effect of [F.G.] on adsorption of Fe, V, Ti, and U from the waste phosphoric acid solution: adsorption time = 7 days, pH = 2.3.

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Fe, V, Ti, and U from the waste phosphoric acid solution. The adsorption amount is in proportion to [F.G.] in all cases. The slope of the straight lines reflects the efficiency of adsorption of each metal with a unit amidoxime ligand if the concentration of metal ion is comparable. The adsorption amounts of both V and Ti correspond to ~1% of [F.G.], while that of U is only 0.02% of [F.G.]. The large slope for Fe does not necessarily mean that the efficiency of the adsorption of Fe is high. In this case, the high concentration of Fe in the phosphoric acid solution (~50 times those of V and Ti) is partly responsible for the high value. Direct comparison in adsorption efficiency among V, Ti, and Fe is, therefore, not possible only from the results in Fig. 8.

The efficiency of adsorption or the concentration factor was obtained as the ratio of amount of adsorbed metal to the initial concentration of the metal in the phosphoric acid solution. Table 3 shows the adsorption amounts in 7 days and concentration factors for Fe, V, Ti, and U. The concentration factor obtained by AOF-III decreases in the order; V > Ti ≫ Fe > U. Such high efficiencies for V and Ti when compared with U and Fe indicate the possibility of the selective adsorption of these metals from the phosphoric acid solution. The adsorption of U, on the other hand, does not seem to be preferable with AOF-III under the present adsorption condition.

It is often observed that the acidity of the solution affects the adsorption of metals. The increase in the amount of copper adsorption with a decrease in acidity as observed in Fig. 4 indicates that a similar effect is expected in the case of U adsorption from the phosphoric acid solution. The acidity of the waste phorphoric acid solution was changed from the original pH (2.3) by adding sodium hydroxide. The amounts of adsorption and the concentration factors of U at various pH's are shown

TABLE 3
Elements Adsorbed from Waste Phosphoric Acid Solution

Metal	Adsorption in 7 days[a] (mg/g-Ad)	Concentration factor[b]
Fe	24.6	6.1×10^2
V	6.8	8.6×10^3
Ti	3.4	4.2×10^3
U	0.2	2.8×10^2

[a] [F.G.] = 8.4 meq/g, pH 2.3.

[b] Ratio of the amount of adsorbed metal to its concentration (mg/g)/(mg/cm^3).

TABLE 4
Effect of pH on the Amount of U Adsorption from the Waste Phosphoric Acid Solution and the Concentration Factor

pH	Adsorption in 7 days[a] (mg/g-Ad)	Concentration factor
2.3	0.23	4.6×10^2
3.2	0.51	10.2×10^2
4.9	0.11	15.5×10^2

[a] [F.G.] = 4.9 meq/g.

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in Table 4. The adsorption increases until the pH value of the solution reaches 3. However, any further increase in pH abruptly decreases the amount of adsorption. This is based on the decrease in the concentration of U in the solution brought about by the coprecipitation of U with calcium when sodium hydroxide is added to the solution. The concentration factor, on the other hand, continuously increases with a rise in pH. Therefore, the efficiency of adsorption itself increases with a rise in the pH of the solution.

From an economic point of view, however, adjusting the pH of the phosphoric acid solution is not desirable. The present results indicate, therefore, that AOF can be applicable to the recovery of V and Ti from the waste phosphoric acid solution while the recovery of U with AOF necessitates an improvement of the adsorption efficiency at the original pH.

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