

UPTAKE OF ACTINIDES AND OTHER IONS BY DIPHOSIL, A NEW SILICA-BASED CHELATING ION EXCHANGE RESIN

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1 INTRODUCTION

A new chelating ion exchange resin, Diphonix, containing geminally substituted diphosphonic acid ligands bonded to a styrene-based polymeric matrix, was recently developed and characterized.¹⁻⁸ Its high affinity for actinides even in very acidic solutions has been attributed to the capacity of the resin to chelate actinides through either ionized or neutral diphosphonic acid ligands, leading to metal complexes of high stability.¹ Based on this property, the Diphonix resin has found application in mixed waste treatment and in analytical procedures for separation and determination of actinides in soil and bioassay samples.^{9,10}

The only effective way of stripping actinides from the resin is to use as stripping agents compounds belonging to the family of aqueous soluble diphosphonic acids, which contain the same ligand group as the resin.¹ After stripping, the aqueous diphosphonic acid has to be thermally degraded for further processing of the actinides, leading to solutions containing high concentrations of phosphoric acid. An alternative procedure is to destroy, through wet oxidation, the whole resin bed used to sorb the actinides. This procedure is time and reagent consuming. Therefore, it may be desirable in most cases to leave the actinides on the resin which becomes a solid waste. In this case it would be preferable that some or all of the polymeric resin matrix be replaced by an inorganic material, to avoid possible generation of gases due to slow radiolytical degradation of the organic polymer. Therefore, a new version of the Diphonix resin has been prepared, where the chelating diphosphonic acid groups are grafted to a silica support. The new material is called Diphosil, for Diphonix on silica.

In this paper, some results on the equilibrium and the kinetics of uptake of a number of actinide species and of other metal ions of nuclear, environmental or hydrometallurgical interest by the new Diphosil material are reported. A more complete account of the investigation on the metal uptake properties of the Diphosil resin will be published elsewhere.¹¹

2 EXPERIMENTAL

2.1 Resins

The Diphosil resin was prepared as follows; 10 g of porous silica (Davisil™, 60-100 mesh size, Aldrich) were reacted at reflux for 12 hours with a mixture of trichloroethylsilane (TCES) and trichlorovinylsilane (TCVS) in 30 mL toluene. After toluene and acetone washes, the material was dried and grafted with vinylbenzyl chloride (VBC). The grafting procedure was performed by immersing the silica-TCVS/TCES

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material in a mixture of VBC and azobis(isobutyro)nitrile (AIBN) initiator in toluene, heating at 80 °C for 8 hours under continuous stirring. The grafted material was then washed with toluene and extracted with this solvent for 10 hours. In a separate flask, the tetraisopropyl ester of methylenediphosphonic acid was dissolved in toluene and reacted with sodium metal. After the reaction was completed, the VBC grafted silica-TCVS/TCES material was added and the mixture heated for 24 hours at reflux. The material was then washed with acetone, acetone/water and water, hydrolysed with 3 M HCl for 3 hours and finally extensively washed with water.

The Diphonix resin in the H⁺ form and 50-100 mesh size was obtained from Eichrom Industries, Inc., Darien, Illinois. Figure 1 reports representative structures of the two resins. Table 1 reports their capacity and density determined following literature procedures.¹² Phosphorus elemental analysis was carried out by digesting a resin sample with perchloric/nitric acid (2:1 v/v) followed by reaction with amidol and ammonium molybdate.¹³ The capacity values reported in Table 1 are consistent with the resin formulae given in Figure 1.

2.2 Uptake Measurements

The sorption of ²⁴¹Am, ²³⁹Pu, ⁵⁹Fe, ⁴⁵Ca, and freshly purified ²³⁰Th and ²³³U at tracer level concentration from aqueous solutions of different compositions was measured at room temperature (24 ± 1 °C) following the same procedure reported previously.^{1,8} Dry weight distribution ratios, *D*, were calculated as

$$D = \left(\frac{A_o - A_f}{A_f} \right) \left(\frac{V}{w} \right) \quad (1)$$

where *A*_o and *A*_f are the aqueous phase activity (proportional to concentration) before and after equilibration, respectively, *w* is the weight of dry resin (g) and *V* is the volume of the aqueous phase (mL). In the experiments on the uptake of Al(III), analyses of the metal were performed by spectrometry. In each experiment, the amounts of metal and of resin were chosen in such a way that the resin capacity was always in large excess over the metal. Duplicate experiments showed that the reproducibility of the *D* measurements was generally within 10 %, although the uncertainty interval was substantially higher for the highest *D* values (*D* ≥ 10³).

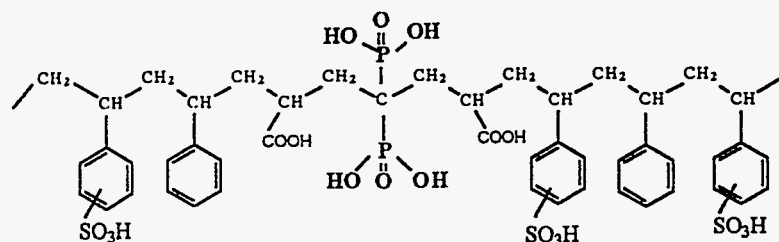
The experiments on uptake kinetics were performed following the same discontinuous technique described previously.⁴ The primary kinetic data, *D* vs. time, were normalized by converting them into fractional attainment of equilibrium vs. time data, using eq. 1. The kinetic data were then plotted according to the previously derived equation 2:⁴

$$\ln(1 - F) = -kt \quad (2)$$

where *k* is the experimentally observed overall rate constant and the fractional attainment of equilibrium, *F*, is defined as the amount of metal in the resin phase at time *t* divided by the amount of metal in the resin phase at equilibrium.

Equation 2 has been reported to hold for film-diffusion control with infinite solution volume for the limiting case of isotopic exchange on ion exchange resins.^{14,15} Based on the considerations discussed in our previous study of the kinetics of metal uptake by the Diphonix resin,⁴ eq. 2 should apply to the kinetic data obtained in this work.

DIPHONIX RESIN



DIPHOSIL RESIN

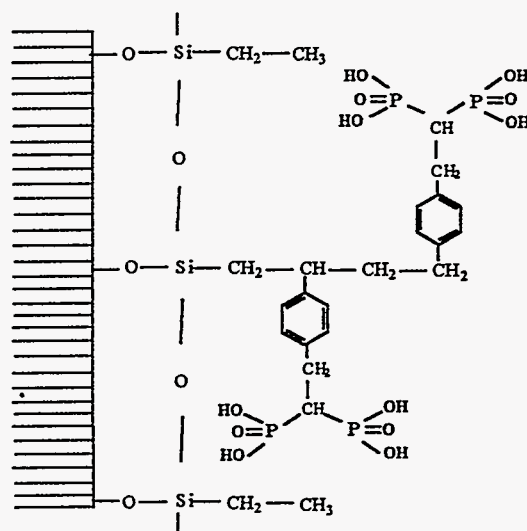


Figure 1 Chemical structures of the Diphonix and Diphosil resins.

Table 1 Capacity and Density of the Diphonix and Diphosil Resins

	Diphonix	Diphosil
P capacity (mmol/dry g)	1.64	0.68
Total H capacity (mmol/dry g)	7.31	1.36
Sulfonic H capacity	2.42	/
Wet density (g/mL)	1.16	1.50
Bed density (g dry resin / mL bed)	0.30	0.39

3 RESULTS AND DISCUSSION

3.1 Uptake of metal ions

In comparing the tracer concentration level metal uptake data obtained with the Diphonix and the Diphosil resins, a number of factors must be considered.

The first factor is the different nature of the two resins. Although the Diphonix resin has a higher P capacity (see Table 1) than the Diphosil resin, in the former material the diphosphonic acid groups are homogeneously dispersed through the whole volume of the bead, while in the Diphosil resin they are concentrated in a surface layer where the ligand groups are closely packed. The higher concentration of ligand groups on the surface of

the Diphosil resin may facilitate the interaction of incoming metal ions with more than one ligand at the same time, thus favoring complexation of metal ions with a higher charge and more complex coordination geometry, such as the tetravalent actinides.

Another factor to be considered is that the benzene ring separated by a CH_2 group from the diphosphonic acid group of the Diphosil material will somewhat reduce the basicity of the $\text{P}=\text{O}$ group, reducing the tendency of the ligand for metal complexation.

Finally, the presence of other functional groups on the Diphonix resin, such as the sulfonic acid group, may play a role in the binding of metals. The sulfonic acid groups may take part in metal uptake by providing negatively charged sites which can contribute to the metal charge neutralization.

All these factors, that is, concentration and packing of the ligand, $\text{P}=\text{O}$ basicity, coordination number and geometry of the metal species, charge neutralization requirements, surface reaction (Diphosil) vs. involvement of bulk material (Diphonix), make a complete description of the interaction between the two resins and metal ions quite difficult and the relative behavior of each single metal species difficult to predict.

This is clearly illustrated in Figures 2 and 3. Figure 2 shows a comparison of the uptake of actinide species by the two resins measured as function of the aqueous acidity. With both resins, the almost complete lack of acid dependency for hexavalent and tetravalent actinides indicates coordination of neutral metal salts by the $\text{P}=\text{O}$ groups of the ligand without displacement of hydrogen ions. These results have been discussed at length in some of our previous studies.^{1,6} Comparing the behavior of the two resins, for $\text{Am}(\text{III})$ and $\text{U}(\text{VI})$ the data show little change in going from the Diphonix to the Diphosil resin, with the former exhibiting slightly higher D values. However, the previously anticipated higher uptake of tetravalent actinides is clearly shown by the $\text{Pu}(\text{IV})$ data. The $\text{Th}(\text{IV})$ data show that the uptake by the Diphosil material is much less sensitive to the acidity than with the Diphonix resin. The slow decline of the D values of tetravalent actinides in the range of high aqueous nitric acid concentrations has been explained as mostly due to the competition of nitric acid with the metal for the phosphoryl groups of the resin.¹ This competition should be less effective if the basicity of the phosphoryl groups is reduced, in agreement with the trend indicated by the $\text{Th}(\text{IV})$ -Diphosil data.

Figure 3 reports similar data for $\text{Al}(\text{III})$, $\text{Fe}(\text{III})$ and $\text{Ca}(\text{II})$. The comparison of the uptake data of $\text{Al}(\text{III})$ and $\text{Fe}(\text{III})$ shows that the Diphosil resin exhibits a much higher affinity for trivalent iron and a much lower affinity for aluminum relative to the Diphonix resin. It is known that aqueous soluble diphosphonic acids form stronger complexes with iron (III) than with aluminum. For example, with methylenediphosphonic acid (MDPA), 1:1 and 1:2 complexes are reported with log values equal to 19.9 and 26.6 for $\text{Fe}(\text{III})$ and to 14.1 and 23.0 for $\text{Al}(\text{III})$.¹⁶ Thus, a better complexation of $\text{Fe}(\text{III})$ over $\text{Al}(\text{III})$ by the two resins is expected and indeed verified. However, the Diphosil resin seems to magnify the difference in complexation of the two metal species by the diphosphonic acid group. This, in turn, may be an indication that in the Diphonix resin the sulfonic acid groups also play a role in the binding of $\text{Al}(\text{III})$, role which would obviously be absent in the case of the Diphosil resin.

As already discussed in the case of $\text{Th}(\text{IV})$, the $\text{Fe}(\text{III})$ -Diphosil D values in the high acidity range do not drop with increasing acidity. Again, this can be explained by the reduced competition of the acid with the metal for the less basic $\text{P}=\text{O}$ groups of the Diphosil resin.

$\text{Ca}(\text{II})$ exhibits substantially lower D values with the Diphosil resin. It is difficult to attribute this behavior to a single reason. The most obvious explanation would be the involvement of the sulfonic groups of the Diphonix resin in the uptake of these metals. Yet, at least in the case of the alkali earth cations, it has been demonstrated previously, based on the identical relative affinity measured with the two resins for the cations of the series Ca , Sr , Ba , and Ra , that in the Diphonix resin the cations are bound mainly to the diphosphonic acid groups.⁷

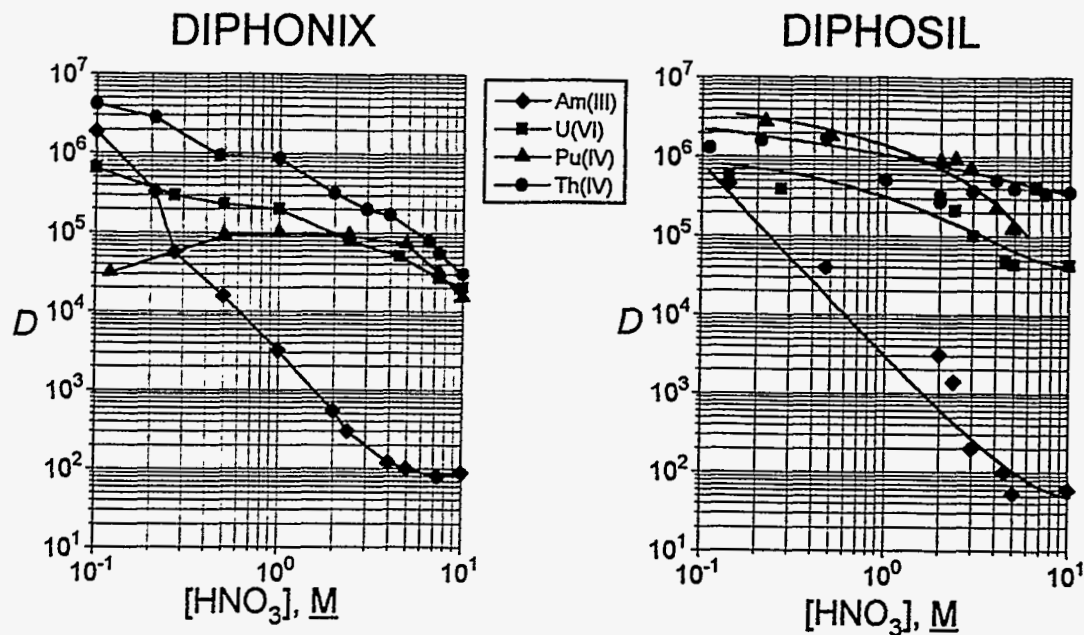


Figure 2 Comparison of the uptake of Am(III), U(VI), Pu(IV) and Th(IV) by the Diphonix and the Diphosil resins from nitric acid solutions.

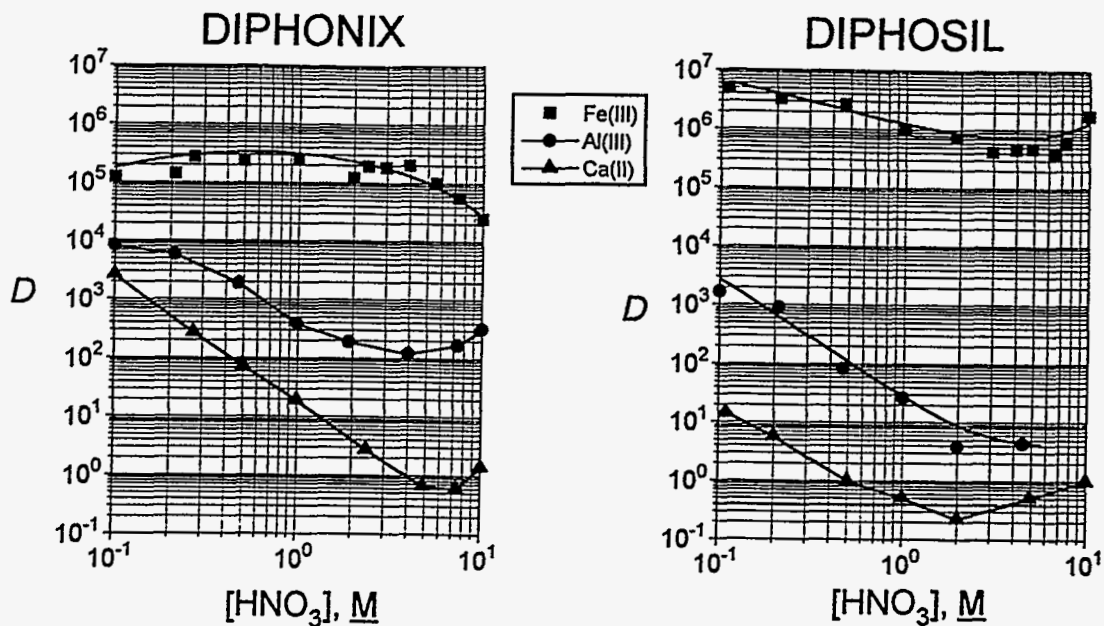


Figure 3 Comparison of the uptake of Al(III), Fe(III) and Ca(II) by the Diphonix and the Diphosil resins from nitric acid solutions.

3.2 Kinetics of metal uptake

Figure 4 reports the rate of uptake of Am(III) by the Diphonix and the Diphosil resins. The data are plotted according to eq. 2, that is, in the form of fractional attainment of equilibrium vs time plots. The data show that in most cases about 99% of the equilibrium distribution is reached within 5 - 10 minutes of contact, that is, with both resins, and especially with the Diphosil one, the uptake of metal species at tracer concentration level is very rapid. From a more general point of view, the data show, as

expected based on the very low metal concentration, that the metal uptake is film-diffusion controlled for at least 90 % of the process.

The data of Figures 4 show that the metal uptake is faster at the lower concentrations of aqueous acid, that is when the equilibrium distribution ratio is higher. Similar data, not reported here, have been obtained for U(VI), Th(IV) and Fe(III). A complete discussion of the effect of selectivity on the ion exchange rate can be found in the literature.¹⁵ Similar results obtained with the Diphonix resin have been previously reported and discussed in detail.⁴ Here it is worth mentioning that the effect is larger with the Diphonix than with the Diphosil resin. The reason for this difference can be understood by considering that with the Diphosil resin the metal ions react only with the ligands contained in a surface layer, and the resin bead is not penetrated by the external solution. The different kinetic behavior at the different acidities is then the true selectivity effect on the rate of uptake. With the Diphonix resin, on the other hand, the metal uptake is accompanied by the resin swelling, which is larger for more diluted external solutions.

4 CONCLUSIONS

The Diphosil resin is a new material containing chelating diphosphonic acid groups grafted to a silica support. The equilibrium and kinetics of the uptake of actinide ions by the new resin have been measured in a variety of conditions and compared with those of the previously investigated Diphonix resin, where the same ligand groups are bonded to a styrene-based polymeric matrix.

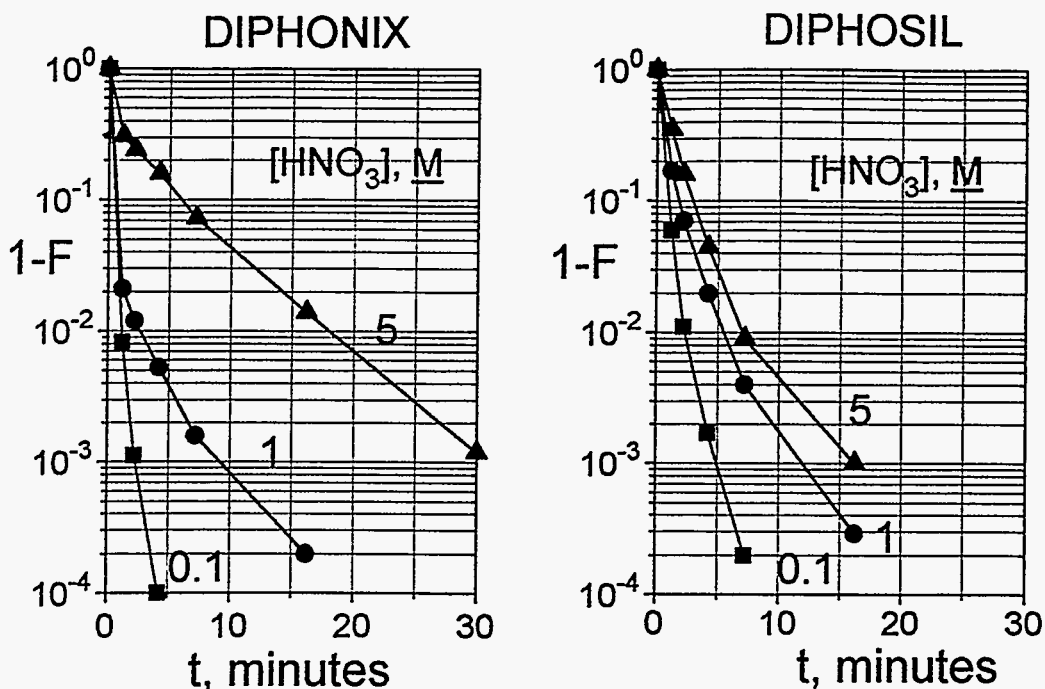


Figure 4 Kinetics of Am(III) uptake by the Diphonix and the Diphosil resins at 0.1, 1 and 5 M HNO₃.

The measurements reported in this paper have allowed us to conclude that :

1. In the uptake of actinide and other ions at trace concentration level the two resins behave quite similarly although with some minor differences.
2. The Diphosil resin exhibits even higher affinity for tetravalent actinides than the Diphonix resin. The uptake of tri- and hexa-valent actinides is essentially the same for the two resins.

3. Ca(II) is substantially less sorbed by the Diphosil resin. Among the trivalent cations, Al(III) is less sorbed and Fe(III) is more sorbed by the Diphosil as compared to the Diphonix resin.
4. The Diphosil resin sorbs the actinide ions at trace concentration level very rapidly even at high acidities, in spite of the lack of swelling.
5. Based on the above results, the Diphosil resin appears particularly well suited for those cases where the recovery and further processing of the sorbed actinides is not required and the loaded resin can be considered as a solid waste. Because about 90 % of the Diphosil weight is silica, the problem of possible generation of gaseous compounds due to the slow radiolytical degradation of the organic components of the resin is minimized.

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