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Recent Advances in the Chemistry and Applications of the Diphonix Resins

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The Diphonix class of ion exchange resins is characterized by the presence of geminally substituted diphosphonic acid groups chemically bonded to a polymer matrix. Regular Diphonix contains gem-diphosphonic groups chemically bonded to a sulfonated styrene-divinylbenzene matrix. Modification of the properties of Regular Diphonix are achieved by the introduction of additional functional groups such as anion exchange groups in Diphonix-A and phenolic groups in Diphonix-CS. Diphosil has a silica matrix in which the gem-diphosphonic groups are chemically bonded to an organic polymer graft that surrounds the silica particles. Applications of the Diphonix resins range from treatment of a variety of radioactive waste to iron control in hydrometallurgy and semiconductor manufacture.

The Diphonix Class of Ion Exchange Resins

Diphonix resin is a new bifunctional chelating ion exchange that contains geminally substituted diphosphonic groups and sulfonic acid groups chemically bonded to a styrene-divinylbenzene polymeric network (*1*). The rationale for the introduction of bifunctionality into the resin has been discussed as a coupling of an access mechanism that allows all ions into the matrix rapidly and a recognition mechanism where a second ligand in the matrix selectively complexes a targeted metal ion (*1*). In the case of Diphonix, the sulfonic acid groups are the access functionality and the gem-diphosphonic acid groups are the recognition functionality. Hereinafter this resin will be referred to as Regular Diphonix resin. The preparation and properties of Regular Diphonix resin have been described in a series of publications (*1-9*). Regular Diphonix resin is now available commercially from Eichrom Industries, Darien, IL.

During the last few years three new Diphonix-type resins have been synthesized and characterized. Each new resin retains the basic gem-diphosphonic acid functional group but in one case a silica-based matrix is used in place of the styrene-divinylbenzene matrix and in the other two cases additional functional groups are introduced to enhance the selectivity of the resin for specific ions or groups of ions. The silica-based Diphonix (called Diphosil) is prepared by grafting silica gel with an organic polymer and then chemically bonding the gem-diphosphonic acid groups to the organic graft (*10*). The other two Diphonix resins consist of modified organic

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polymer networks. In one of the modified Diphonix resins, called Diphonix-A, anion exchange functionalities are introduced by replacing styrene with 4-vinylpyridine and then quaternizing the pyridinium nitrogen (*11*). In the other modified Diphonix resin, called Diphonix-CS, phenolic groups are introduced by polymerizing phenol/formaldehyde within a polymer network slightly modified from Regular Diphonix (*12*). Figure 1 depicts the structures of the four different types of Diphonix resin.

Properties of Diphonix Resins. The unique feature of Regular Diphonix, Diphosil, and Diphonix-A resins is their ability to rapidly sorb a wide number of metal ions from highly acidic media, even in the presence of complexing anions. Figure 2 compares the uptake of selected metal ions, as measured by their distribution ratios, for Regular Diphonix and two of the modified Diphonix resins from 0.1 to 10 M HNO_3. The data in Figure 2 show that the modified Diphonix resins are very similar to Regular Diphonix with regard to their uptake of cations but, as expected, Diphonix-A shows a much higher uptake of Tc as the pertechnetate ion. The kinetic properties of these three resins are depicted in Figure 3 using U(VI). All three show very rapid uptake of U(VI) from 0.1 M HNO_3. Rapid exchange kinetics are one of the major features of the Diphonix resins. Another noteworthy characteristic of Diphonix resins is the insensitivity of the sorption of certain metal ions, such as the tetra- and hexavalent actinides and iron (III), to different matrices. Figure 4 shows the effect of increasing concentrations of selected complexing anions on the uptake of Th(IV) on Regular Diphonix. (With HF, Np(IV) was utilized.) Tetravalent actinides are known to form strong complexes with complexing anions such as fluoride and oxalate. As the data in Figure 4 show, only when the concentration of these acids exceeds 1 M, does the distribution ratio begin to decline significantly. Figure 5 shows the influence of commonly occurring cations on the D_{Th}. Only Fe(III), which is also strongly complexed by the diphosphonic ligand, shows any significant effect, and it must be present in near stoichiometric amounts before D_{Th} is depressed.

Diphonix-CS is a new ion exchange resin specifically designed for the removal of Cs^{+1} and Sr^{+2} from highly alkaline media (*12*). Figure 6 shows the distribution ratios of Cs and Sr as a function of sodium hydroxide concentration. Data points for Regular Diphonix are shown for comparison. As one can see, the uptake of Cs is significantly improved with Diphonix-CS. The improved uptake of Cs is no doubt due to the presence of the phenolic groups. In alkaline media Diphonix-CS rapidly sorbs both Cs and Sr and shows very good radiation stability at least up to an absorbed dose of 200 Mrads (*12*).

Applications of Diphonix Resins

Because of the diversified nature of the four different Diphonix resins, there are a variety of applications of these unique ion exchange materials. Some of these applications are strictly potential and others are already in use in facilities ranging from pilot-scale to full scale operations.

Radioactive Waste Treatment. The first application of Regular Diphonix resin was the removal of actinides from mixed-waste at Argonne National Laboratory-East. These wastes were generated in-house as a result of ongoing programs in the nuclear fuel cycle and research in actinide chemistry. Tables I and II show typical compositions of mixed-waste solutions processed in a special facility designed to handle at one time volumes of wastes up to 55 gallons (*13*). Generally, two one-half liter Diphonix columns were used in tandem to ensure high-levels of decontamination.

Another application of Regular Diphonix resin for waste treatment took place at a southeastern United States nuclear fuel fabricator that faced the need to significantly lower the concentration of alpha-emitting species in its wastewater to comply with new

Table I. Analytical Chemistry Laboratory Generated Mixed Waste from ICP/AES

Constituents:	
	Al, Ba, Ca, Co, Cr, Cu, Fe, Cd, Mg, Mn, Ni, Pb, Sr, Ti, V, Zn, Zr
Acids:	
	HNO_3, HCl, H_2SO_4
Major Hazardous Constituents:	
	Cu 10^{-2} M, Cd $5x10^{-2}$ M
Actinides	
	U (10^{-4} to 10^{-5} M), ^{237}Np, ^{239}Pu, ^{241}Am (~ one µCi/5 gal)

Decontaminations in the range of 10^4 to 10^5 were obtained using two columns in series each containing 0.5 liters of Regular Diphonix.

Table II. Typical Composition of Actinide Containing Acidic Mixed-Waste Solutions

Constituent	M
HNO_3	0.1 - 0.01
$NaNO_3$	0.80 - 1.0
Na_2SO_4	0.14 - 0.20
NaCl	0.17 - 0.20
Mg	0.07
Al	$5x10^{-4}$
Ca	0.10
Fe	$1x10^{-3}$
Mo	$3x10^{-6}$
Zr	$4x10^{-6}$
Total Actinides in 208 L (55 gal)	
^{238}Pu	$6x10^{-6}$ g
^{239}Pu	$2x10^{-2}$ g
^{241}Pu	$7x10^{-5}$ g
^{241}Am	$1.3x10^{-4}$ g
Total alpha	$4x10^9$ d/m

Decontamination of ~10^4 was achieved using two columns in series each containing 0.5 liters of Regular Diphonix ion exchange resin.

environmental restrictions (*14*). Regular Diphonix was tested on a pilot-scale and found to afford the necessary decontamination for compliance. Table III summarizes

Table III. Results of Testing Uptake of Alpha-Emitting Species from Wastewater System Neutralization Tank Contents using Regular Diphonix Resin

Alpha Concentration in Feed (pCi/mL)	Influent pH	Alpha Concentration in Effluent (pCi/mL)
1.2	6.7	0.043
0.78	7.0	0.022
0.47	8.2	0.043
0.16	11	<0.03
0.49	13	0.054

Source : Adapted from ref. 14.

some of the test results. A full-scale unit will soon be in place to treat much larger volumes of waste.

Regular Diphonix resin has also been successfully tested for the treatment of low-level radwaste (LLRW) generated at the Northeast Utilities, Millstone nuclear power plant (*14*). In this application Regular Diphonix resin removes radioactive Co and Zn from an effluent stream originating from floor and equipment drains. Effluent from a Regular Diphonix column followed by a conventional anion exchange column in series showed no detectable Co. Decontamination factors (DFs) of >1000 for Co were achieved in pilot-test runs. In general, the Diphonix resin showed consistently superior DFs over conventional cation exchange resin for Co and Zn with throughputs at least three times greater than conventional cation exchange resin. No breakthrough of Co and Zn were detected even after passing the equivalent of 45,000 gallons of waste per cubic foot of resin bed. Although Regular Diphonix resin is more expensive than standard strong acid cation exchange resin, the much greater waste minimization achieved with Diphonix more than offsets its higher cost. The utility spends approximately $750 per cubic foot to dispose of spent ion-exchange resin (*14*). Conservative estimates show that the Diphonix resin system will produce roughly one-fifth the volume of spent resin than a standard cation resin-based system.

Applications of Diphosil, the silica-based diphosphonic resin, and scale-up studies for its commercial production are currently in progress at Eichrom Industries. Many of the application of Regular Diphonix in radioactive waste treatment could be performed by Diphosil. Diphosil is, however, 85% inorganic and, therefore, has the possible advantage of being a more desirable waste form. A potential application of Diphonix-A and Diphosil is the purification of water used in steam turbines and as a coolant in nuclear power plants. The absence of sulfonic groups and their ability to sorb a wide range of cations and, in the case of Diphonix-A, anions such as chloride, sulfate, and silicate should give them major advantages in producing ultra-pure water. Conventional sulfonic acid-based cation exchange resins have the undesirable property of producing low concentrations of sulfuric acid due to the hydrolysis of sulfonic acid groups attached directly to phenyl groups. Unlike Regular Diphonix, Diphonix-A and Diphosil do not contain sulfonic acid groups because their hydrophilicity is achieved by other means.

As mentioned above, Diphonix-CS was specifically designed to remove both Sr and Cs from the alkaline supernate present in the high-level waste tanks at Hanford and Savannah River sites. (Regular Diphonix only sorbs Sr. See Figure 6.) But unlike inorganic materials, such as the crystalline silicotitanates currently undergoing testing, both Cs and Sr can be eluted from Diphonix-CS with 1 M HNO_3 (*12*). To date Diphonix-CS has only been tested with alkaline waste simulants (*12*). Column test runs have been favorable for Cs removal but improvements in the stripping of Sr need to be made.

Iron Control. One of the most useful properties of Diphonix resins is their ability to strongly retain trivalent iron even from highly acidic solutions (*2,4*). Iron is a ubiquitous element in hydrometallurgy. In the production of copper by solvent extraction and electrowinning, the presence of Fe is particularly troublesome in the electrowinning operation. High concentrations of iron decrease current efficiency because of the oxidation of Fe(II) at the anode and the reduction of Fe(III) at the cathode. Iron accumulates in the electrowinning cells because the sulfuric acid in the spent electrolyte is continuously recycled to strip copper from the loaded organic extractant.

The traditional solution to iron-buildup involves bleeding out some electrolyte, which results in the loss of an expensive additive used to prevent corrosion of the lead anode; namely cobalt. Regular Diphonix resin has been shown to effectively remove Fe(III) from the spent electrolyte solution thus improving the operating efficiency of the electrowinning plant (*15*). Copper(II) and cobalt(II) are not bound by the resin because of the high (1.5 $\underline{M}$) concentration of sulfuric acid. Regeneration of the Diphonix column is achieved by a novel stripping procedure using a 0.3 to 0.8 $\underline{M}$ sulfurous acid solution in 2 $\underline{M}$ H_2SO_4 containing 1 to 2 g/L of Cu(II). Stripping is generally carried out at a temperature of 65 to 75 °C. Under these conditions Fe(III) is reduced to Fe(II). The mechanism of the iron reduction is believed to be due to the formation of a small concentration of Cu^{+1} formed by reduction of Cu^{+2} by sulfurous acid, and a small displacement of Fe(III) from the diphosphonic groups by hydrogen ion. Copper(I) then rapidly reduces Fe(III) to Fe(II) by a one electron transfer. The overall stripping reaction is described by the following equation:

$$2\ \overline{Fe(III)R} + 4H^+ + H_2SO_3 + H_2O \rightarrow 2Fe^{+2} + H_2SO_4 + 2\ \overline{H_3R}$$

where $\overline{Fe(III)R}$ and $\overline{H_3R}$ denote Fe^{+3} and H^+ bound to Diphonix. Note that copper, the key reducing agent, does not appear in the equation. Figure 7 depicts the entire iron removal cycle. The effluent from the strip cycle is added to the heap leaching solution.

Eichrom Industries successfully completed pilot studies at several SX-EW sites and a full-scale unit is now in operation at the Mexicana de Cananea mine in Sonora, Mexico. Figure 8 shows a photo of the iron control system at Mexicana de Cananea. This unit has a design capacity to remove approximately one metric ton of iron per day from the Cananea copper electrowinning circuit. Eichrom is also pursuing the application of its iron control process at other copper producing sites and is developing flowsheets utilizing Regular Diphonix resin for the control of iron in the production of other metals, specifically Zn, Ni, and Co.

Acknowledgments

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Figure 1. Structures of the four different types of Diphonix ion exchange resins. Adapted from refs. 1, 10, 11, 12.

Figure 2. Distribution ratios of selected metal ions as a function of nitric acid concentration in the aqueous phase. A. Regular Diphonix, B. Diphosil, C. Diphonix-A. Adapted from refs. 1, 2, 10, 12.

Figure 3. Fractional attainment of equilibrium for uranium(VI) uptake from 0.1 M nitric acid. A. Regular Diphonix, B. Diphosil, C. Diphonix-A. Adapted from ref. 4.

Figure 4. Distribution ratio of thorium(IV) on Regular Diphonix as a function of the aqueous concentration of selected complexing acids. Nitric acid concentration was 1 M throughout. Adapted from ref. 5.

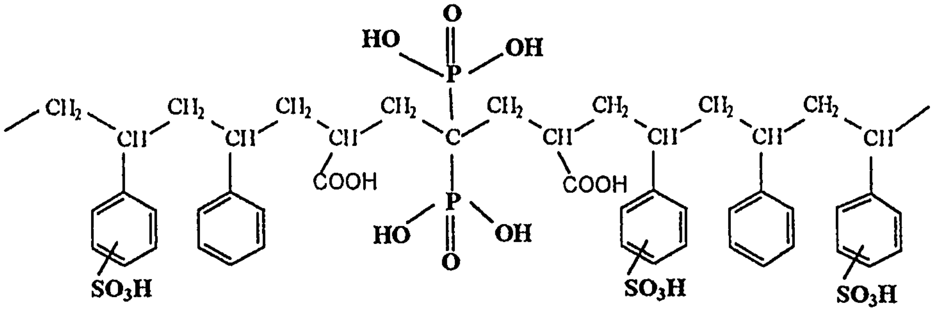
Figure 5. Distribution ratio of thorium(IV) as a function of the aqueous concentration of selected nitrate salts. Nitric acid concentration was 1 M throughout. A. Regular Diphonix, B. Diphosil. Adapted from ref. 5.

Figure 6. Distribution ratios of Sr^{+2} and Cs^{+1} on Diphonix-CS and Regular Diphonix as a function of the aqueous concentration of sodium hydroxide. Adapted from ref. 12.

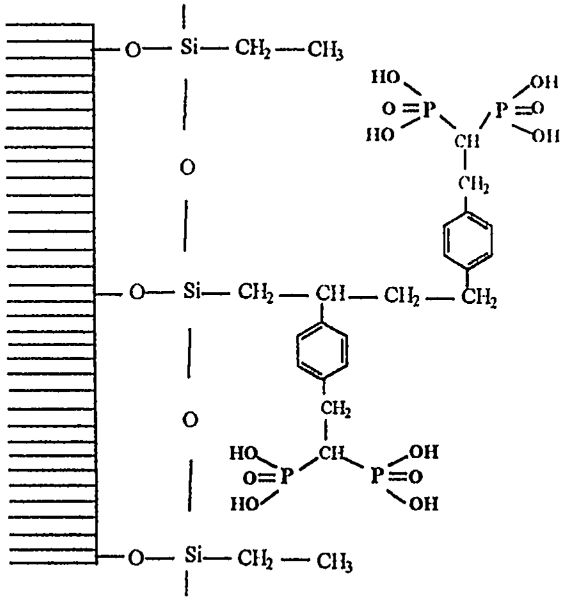
Figure 7. Schematic drawing depicting Eichrom's Iron Control System applied to the electrowinning of copper.

Figure 8. Commercial installation of Eichrom's Iron Control System at Mexicana de Cananea plant site.

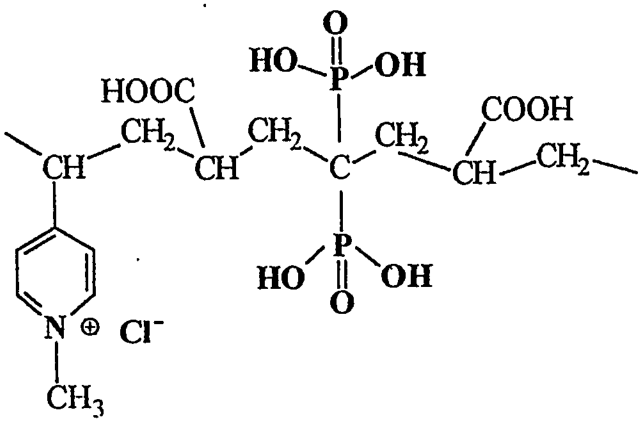
REGULAR DIPHONIX



DIPHOSIL



DIPHONIX-A



DIPHONIX-CS

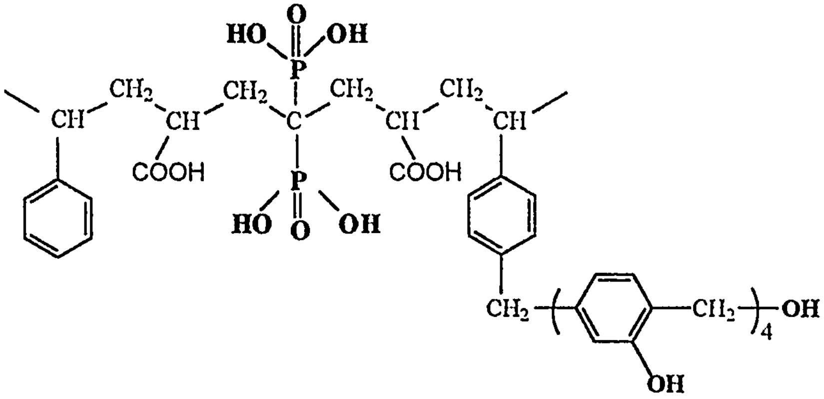
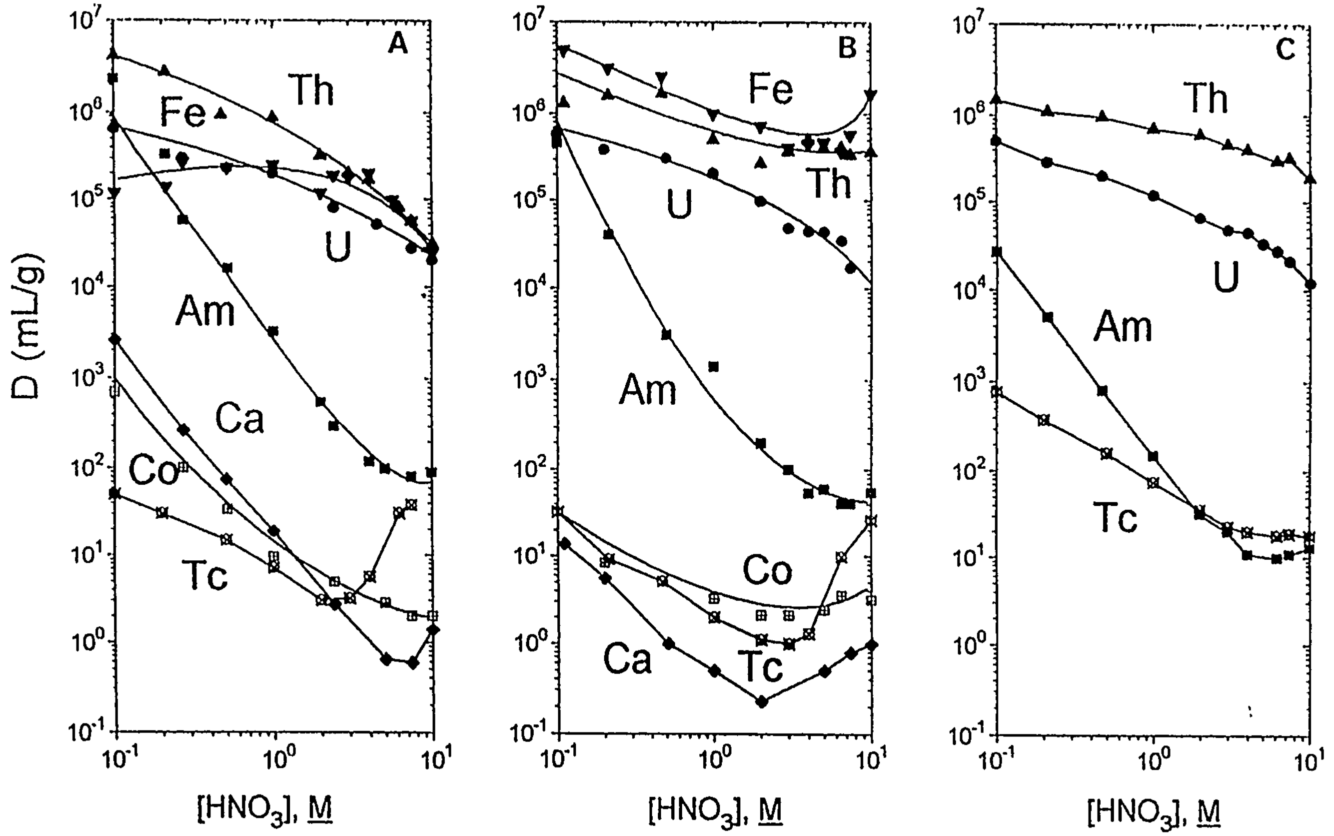


Fig. 1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10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
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A
Th
Fe
U
Am
Ca
Co
Tc
$[HNO_3]$, M
B
Fe
Th
U
Am
Co
Ca
Tc
$[HNO_3]$, M
C
Th
U
Am
Tc
$[HNO_3]$, M

Fig. 2

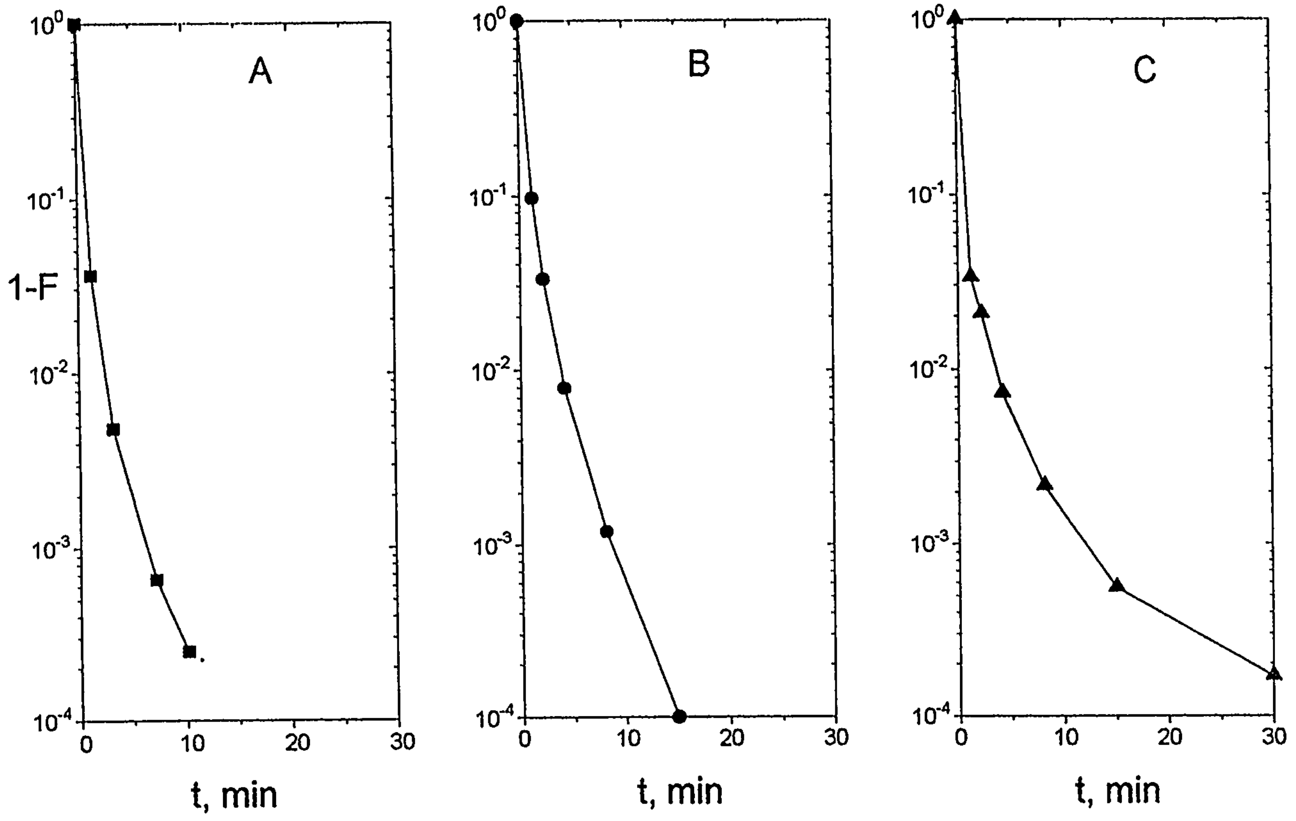
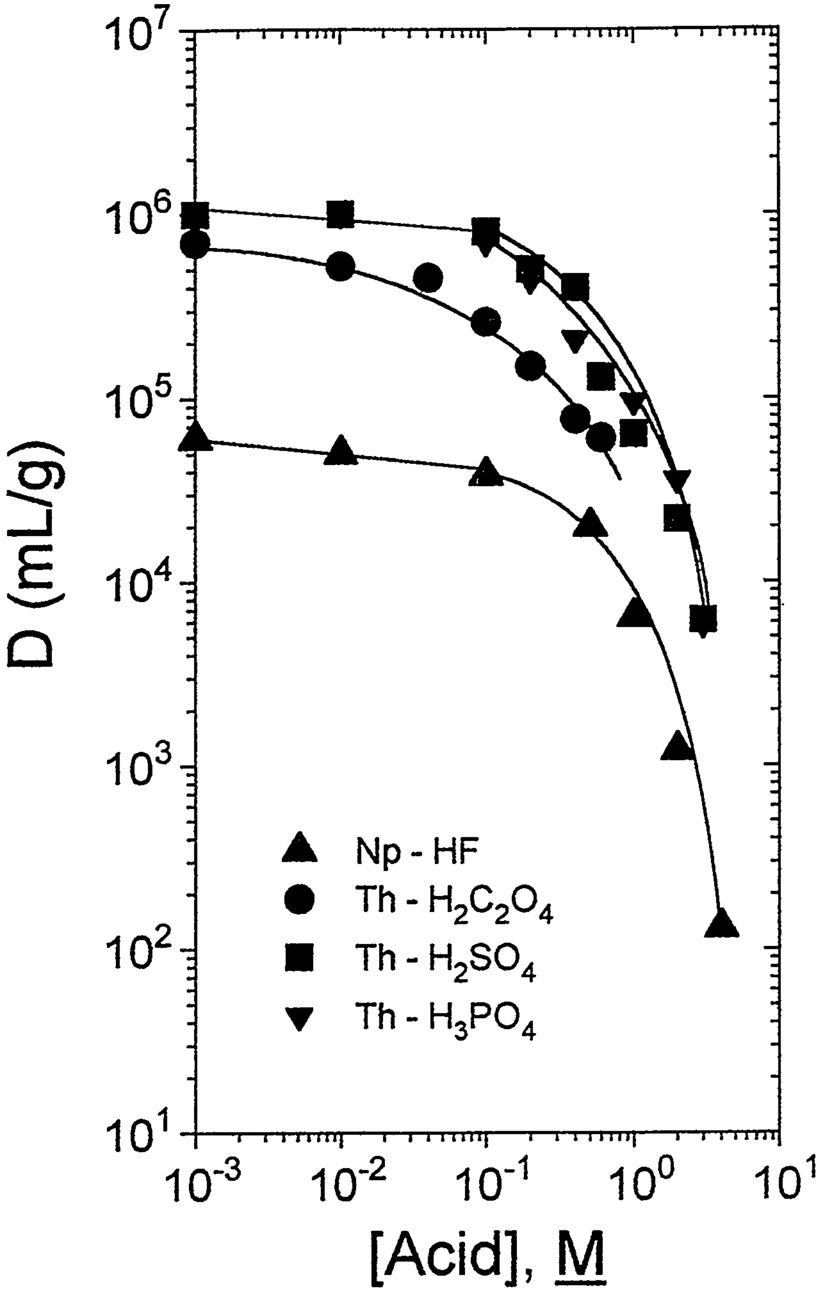
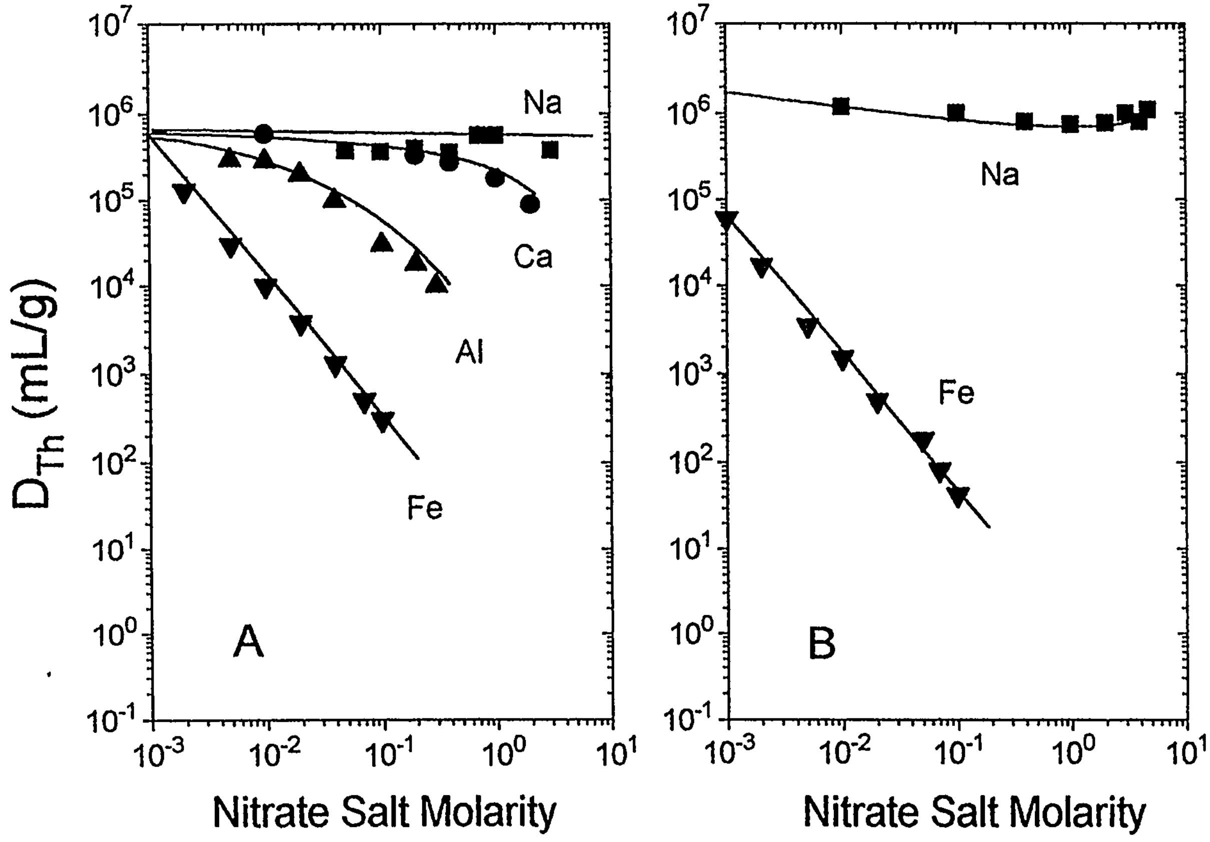


Fig. 3



10^7
10^6
10^5
10^4
10^3
10^2
10^1
D (mL/g)
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
[Acid], M
▲ Np - HF
● Th - $H_2C_2O_4$
■ Th - H_2SO_4
▼ Th - H_3PO_4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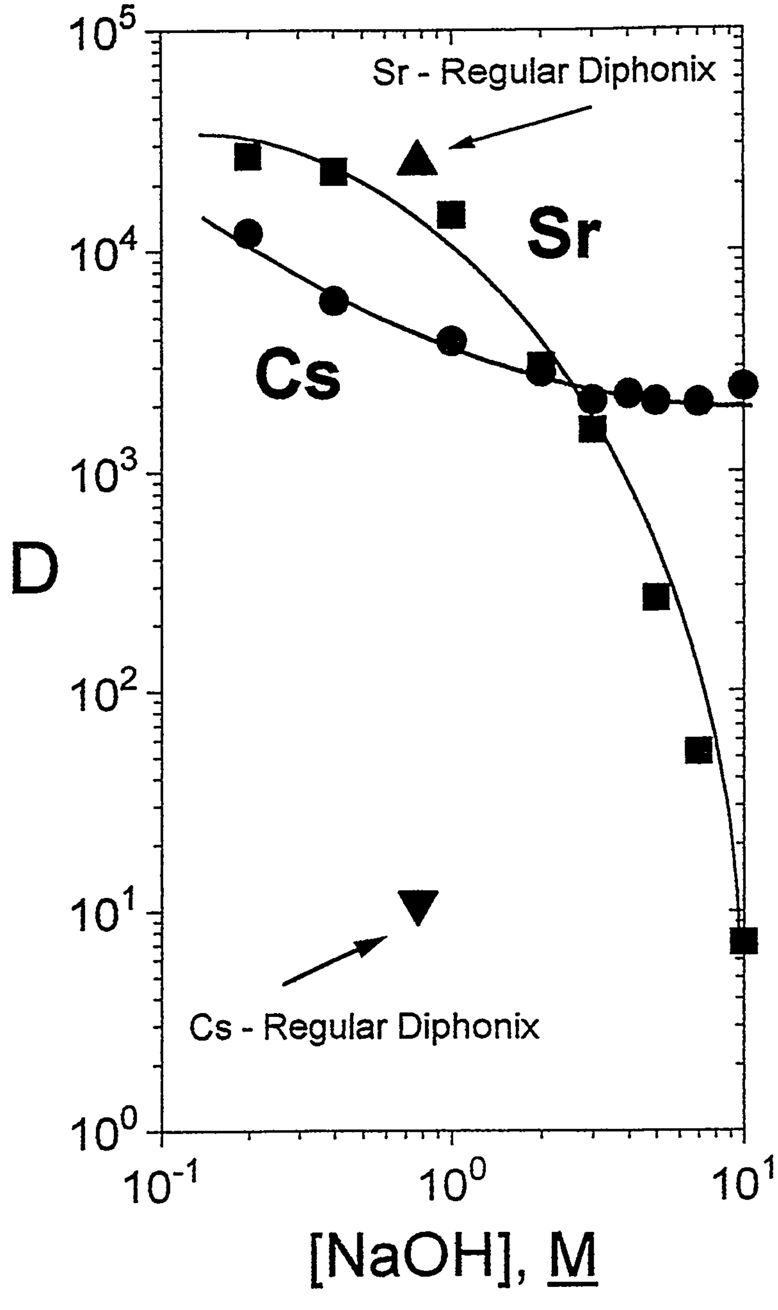
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
Nitrate Salt Molarity
A
Na
Ca
Al
Fe
B
Na
Fe

Fig. 5



10^5
10^4
10^3
10^2
10^1
10^0
D
10^-1
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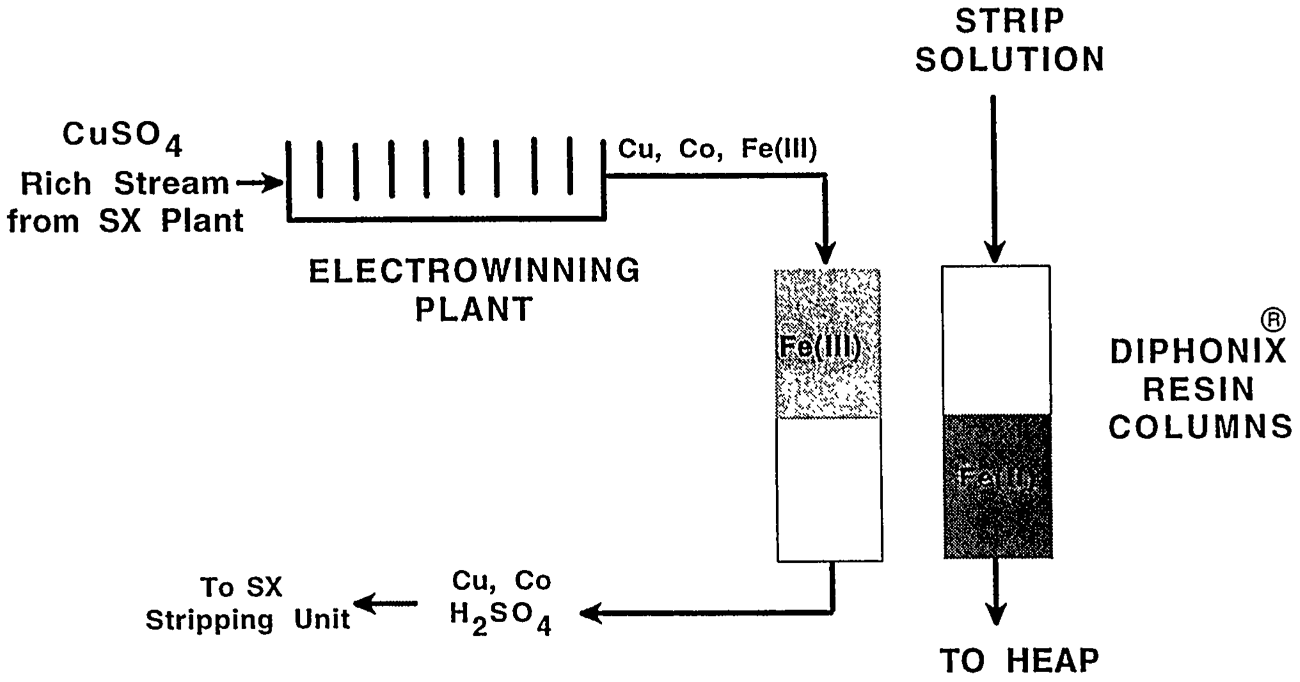
10^1
[NaOH], M
Sr - Regular Diphonix
Sr
Cs
Cs - Regular Diphonix


STRIP
SOLUTION
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Rich Stream
from SX Plant
Cu, Co, Fe(III)
ELECTROWINNING
PLANT
Fe(III)
Fe(II)
DIPHONIX®
RESIN
COLUMNS
To SX
Stripping Unit
Cu, Co
H_2SO_4
TO HEAP

Fig. 7

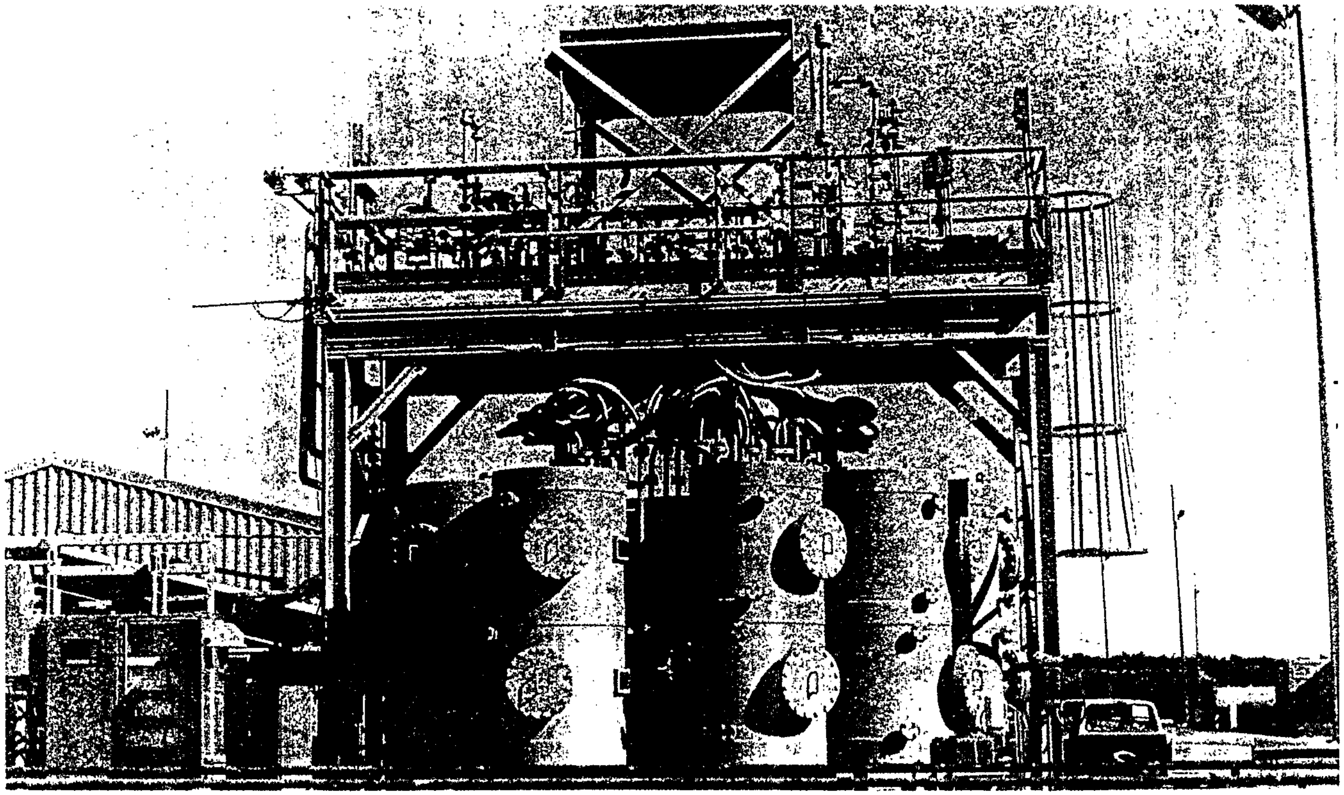

Fig. 8