SEPARATIONS

Composite Fiber Adsorbent for Rapid Uptake of Uranyl from Seawater

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Composite fiber adsorbent was developed as a new material for the recovery of uranium from seawater. Finely powdered adsorbent was entrapped into the fibril of the supporting material such as polyethylene or a copolymer of ethylene and vinyl acetate. Silica was added as the third component. The relative ratio of chemical adsorbent, supporting material, and silica was usually 1:1:1. This composite fiber adsorbent gave a large adsorption rate such as 200 μg of U/g of Ads by 1-day contact in a seawater batch test. This adsorption rate shows a dramatic improvement of the adsorption rate from the particle absorbent, illustrating the advantageous use of fiber adsorbent for the recovery of uranium.

Recovery of uranium directly from seawater is an interesting possibility to get a stable huge energy source. Hydrous titania was first investigated as the adsorbent (Davies et al., 1964; Keen and Takai, 1968; Ogata and Kakihana, 1969; Kanno et al., 1970). Other methods were tried as well (Ishibashi et al., 1969; Kim and Zeitlin, 1971; Heide et al., 1973). Through compiled efforts, the adsorption method is now established as being the most promising proposal (Harrington et al., 1974; Kanno, 1981; Campbell et al., 1979; Driscoll, 1983). Furthermore, organic chelating resins among the proposed adsorbents are recognized as the best to give excellent characteristics of uranyl adsorption directly from seawater (Egawa and Harada, 1979; Egawa et al., 1987; Schwochau et al., 1982). We have reported on several "uranophiles" having extraordinary large formation constants as well as large selectivities with uranyl ion (Tabushi et al., 1979a, 1985; Tabushi and Kobuke, 1985). Polymer adsorbents functionalized toward these uranophiles were demonstrated to recover uranyl successfully from seawater (Tabushi et al., 1979b, 1980). We have also reported that the chelating resin functionalized with dithiocarbamate adsorbed uranyl with ca. 40 μg of U/g of resin/day, simply by immersing the adsorbent in a sea current (Kuroshio near Japan) (Tabushi et al., 1984). This range of adsorption rate, 40 μg of U/g of resin/day, is much higher than that reported for hydrous titania. In spite of these significant improvements obtained for adsorption characteristics in the past, the value is still not satisfactory in view of the economical feasibility (Driscoll, 1983; Koske et al., 1983). The most important factor contributing to the total recovery cost is recognized as the plant construction cost by several independent preliminary cost estimations. The scale of the plant can be reduced only by the development of a new adsorbent having a greater adsorption rate per unit area or unit volume. The required improvement of the adsorption rate may reach around 500 μg of U/g of Ads/day in the above cost estimations. Such an enormous increase of the adsorption rate seems to be difficult through a simple extension, modification, or improvement of the known adsorbent systems. Introduction of some sort of dramatic change of ideas seems to be required at this point. Here, we would like to introduce a new composite fiber adsorbent to improve the adsorption characteristic. This adsorbent successfully demonstrated the adsorption rate as high as 200 μg of U/g of Ads/day.

Experimental Section

Materials. The chemicals were products of Wako Junyaku, Nakarai Kagaku Chemical, or Tokyo Kasei Kogyo Co. Ltd. and were used directly without further purification unless otherwise noted. Tetraethylene glycol dimethacrylate was purchased from Shinnakamura Kagaku Co. Ltd. This was diluted with ether, and the solution was washed with 0.1 N NaOH to remove the polymerization inhibitor, MEHQ, before use. After successive washings with a saturated NaCl solution and distilled water, ether was evaporated and the residual oil was dried in vacuo at room temperature for 5 h. Triethylene glycol dimethacrylate and divinylbenzene were similarly treated as above to remove the polymerization inhibitor. Acrylonitrile was distilled under reduced pressure of nitrogen before use.

Silica used was Tokusil GU-N, a product of Tokuyama Soda. Hydrophobic Silica, Aerosil R972, was obtained from Nippon Aerosil Co. Ltd. The mean diameters of these silicas were 20 (15–25) and 10 nm, respectively. Aluminum tris(dodecylaminopropionate), TPP1002, was a product of Sanyo Kasei Kogyo Co. Ltd. and was used as an amphiphilic surfactant. Polyethylene was obtained from Mitsui Petroleum Chemistry. Hi Zex 2100 J was used for most runs, but a high molecular weight polyethylene (HPE), Ult Zex 3021FP, was also used. The melt flow indexes of these samples were 6.5 and 2.1 g/10 min, respectively. A copolymer of ethylene and vinyl acetate, EVA, with a vinyl acetate content of 28%, was a product of Mitsui Petrochemical Co. Ltd.

The poly(acrylamidoxime) particles were donated from Mitsubishi Kasei Co. Ltd. as a sample. Poly(acrylonitrile) was obtained from a suspension copolymerization of acrylonitrile, tetraethylene glycol dimethacrylate, di-

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vinylbenzene, and ethylvinylbenzene in weight ratios of 60, 31, 5 and 4, respectively. This copolymer was treated with hydroxylamine according to the conventional method. The particle size was measured in our laboratory as sieve 40–200 in a dry state.

Apparatus. Infrared spectra were recorded by using an infrared spectrometer, Hitachi 260-50. The colorimetric determination of uranyl ion by the arsenazo method (Ohnishi and Koide, 1965) was conducted by using a high-sensitive spectrophotometer, Union Giken SM-401.

Preparation of Acrylonitrile Copolymer. Acrylonitrile was copolymerized with tri- or tetraethylene glycol dimethacrylate and divinylbenzene under suspension and emulsion polymerization conditions. The ester composition in the copolymer varied from 10% to 40% relative to acrylonitrile, and the divinylbenzene contents were in the range of 0–2%. In order to get polymer particles as small as possible, the reaction mixture was agitated well by using a vibromixer at a high frequency. The copolymer obtained from the suspension polymerization was filtered, washed with methanol, and dried in vacuo without applying heat so as to avoid an undesirable aggregation of individual particles. The dry copolymer was ground by use of a mortar or a freezer mill operating at liquid nitrogen temperature. The fine powder, passed through a sieve 400 (≤ 37 μm), was used for the fibril production process. The distribution of particle sizes was analyzed by a Horiba CAPA-500 analyzer, and the average size was determined to be 14 μm. In the case of emulsion polymerization, the whole suspension was subjected to a centrifuge at 8000 rpm for 20 min. The supernatent was discarded and methanol was added to the residual pasty material and subjected again to a centrifuge. This procedure was repeated 3 times and the polymer obtained was dried without an external heating.

The acrylonitrile copolymer was incorporated into fibrils directly or after conversion of the nitrile to amidoxime functionalities by treatment with 3% NH_2OH in MeOH, according to the procedure by Egawa and Harada (1979). When the nitrile function was incorporated into the composite fiber, the fiber was then treated with 3% NH_2OH in MeOH. The conversion of the nitrile to the amidoxime functionalities was ascertained by the disappearance of the CN absorption at 2235 cm^{-1} in the IR spectra.

Incorporation of Adsorbent into Fibrils. A typical procedure is as follows: finely powdered adsorbents (6 g), in the form of the nitrile or the amidoxime functionality, were mixed well with silica (Tokusil GU-N, 6 g). To this mixture, polyethylene (6 g) and surfactant (TPP 1002, 0.2 g) were added. Then, the mixture was added to 120 mL of n-hexane in an autoclave having a nozzle of 1.5-mm diameter at the bottom. The suspension was stirred vigorously and heated to 150 °C and kept at that temperature for 20 min. Then the content was ejected into the atmosphere through the value. The solvent was flash-evaporated to produce fine fibrils entrapping the adsorbent into its fiber structure. The apparatus is illustrated in Figure 1.

When ethylene–vinyl acetate copolymer (EVA) was used as a matrix polymer, the acetate moiety was hydrolyzed after fiber formation by the treatment with 0.3 N NaOH in methanol under reflux for 3 h.

Adsorption Characteristics. The fiber composite material, dried at 50 °C for 5 h in vacuum (50 or 150 mg each for one batch), was immersed in 10 mL of 1 N NaOH for 12 h. After the alkaline treatment, the sample was neutralized by 0.1 N HCl. A slow and gradual elution of alkali from the material needed a successive portionwise
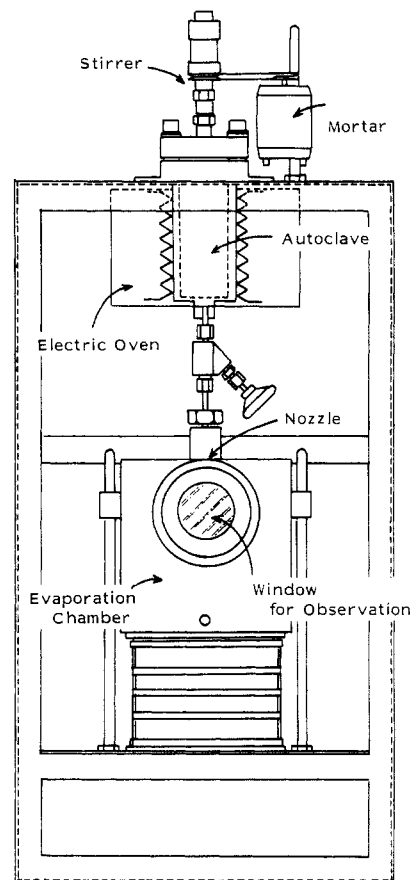

Figure 1. Apparatus for preparing composite fiber adsorbent.
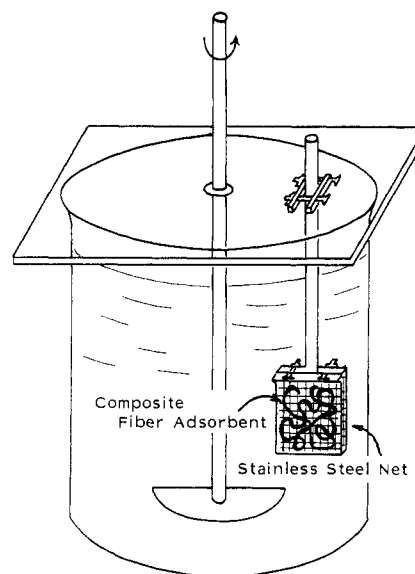

Figure 2. Experimental setup for the evaluation of adsorption rate.

addition of HCl. The complete neutralization was confirmed by no further pH change on standing for 30 min after the previous addition of HCl. The fiber material was washed with distilled water.

The fiber composite adsorbent treated above was held between a folded stainless steel net (3 × 4 cm^2, no. 14). The fiber material was developed to distribute evenly in the whole area of the net. (See Figure 2.) This net was hung down from the plastic cover of the beaker through a plastic rod made of poly(methyl methacrylate) into 5 L of natural seawater. The seawater was thermostated at 25.0 ± 0.05 °C and swirled with at a constant speed

(450–480 rpm) by a poly(tetrafluoroethylene) blade driven by a mechanical stirrer to make a flow of around 50 cm·s⁻¹ (1 knot) relative to the adsorbent. The rate was adjusted so that the typical velocity of sea current could pass through the adsorbent. The pH of seawater was checked did not change before or after the adsorption and showed values in the range of 8.20–8.25 in the whole experiments. After 24 h of immersion, the fiber was picked out and treated 3 times for 1 h each with 10 mL each of 1 N hydrochloric acid. The combined solutions were concentrated almost to a dryness and analyzed by recording absorptions at 665 nm of UO_2–Arsenazo III complex. The uranyl concentration in the remaining seawater was also determined according to the procedure by Ohnishi et al. (1977). The total decrease of the quantity in seawater was ascertained to correspond to that liberated from the adsorbent by the above liberation procedure.

Results and Discussion

Fundamentals of Adsorption Processes. The barriers against the achievement of large adsorption rates of uranyl from seawater can be divided into three factors: 1. slow mass-transfer rate at the phase boundary between bulk seawater and the adsorbent, 2. slow intraparticle diffusion rate of the uranyl species, and 3. slow rate of the ligand-exchange reaction.

The mass-transfer rate, F (mequiv/(cm²·s)), at the phase boundary is expressed by (Helfferich, 1962)

$$F = D\Delta C/\delta \qquad (1)$$

where D, ΔC, and δ denote the diffusion constant (cm²/s), a concentration gradient across the phase boundary (equiv/dm³), and a thickness of the phase boundary (cm), respectively. The thickness of the phase boundary is expressed by

$$\delta = 2r_0/Sh \qquad (2)$$

where r_0 and Sh are the particle radius and the Sherwood number. The latter is a function of the Reynolds (Re) and Schmidt (Sc) numbers as follows:

$$20 < Re < 150\,000 \qquad Sh \simeq 0.37Re^{0.6}Sc^{1/3}$$

$$Re < 20 \qquad Sh \simeq 2 + 0.37Re^{0.6}Sc^{1/3}$$

where $Re = 2v_0/\nu$ and $Sc = \nu/D$, ν = kinematic viscosity, and v = flow rate.

If we use some typical values for the uranium recovery process by a particle adsorbent, Re and Sh numbers are obtained in the ranges 2–100 and 10–80, respectively. Here, the r_0 and v values employed were 1×10^{-4}–1×10^{-3} m and 1×10^{-2}–5×10^{-2} m²·s⁻¹, respectively. The other constants, ν and D, were $\simeq 1 \times 10^{-6}$ and 3.4×10^{-10} m²·s⁻¹, respectively. This calculation gives 10–60 µm for the thickness of the phase boundary. It follows that a greater mass-transfer rate at the phase boundary is obtainable by a smaller δ, which is provided by a smaller particle radius, r_0, and a larger flow rate, v. These requirements are apparently contradictory in the actual adsorption process. If one simply pays attention to the loss of the adsorbent, the small particles cannot be subjected to a rapid flow of seawater unless some sort of special technique to avoid the loss is developed. A unique method to overcome these contradictory requirements will be proposed in the following sections.

Factors 2 and 3 are concerned primarily with the nature of the adsorbent and ligand themselves. Particularly in these matters, we have been trying to make appropriate adsorbents, and recently we reported a successful molecular design of kinetically favorable uranophiles (Tabushi

et al., 1985). Therefore, these factors will not be treated in this article.

Composite Fiber Material. Adsorbents of smaller diameters are obviously desirable for the larger adsorption rate as described above. In fact, such a relationship has already been observed for the hydrous titania adsorbent (Kanno, 1981). In order to substantiate the use of such small adsorbents, particularly in a rapid sea current, we will introduce here a fiber composite adsorbent. The principle is as follows. The real chemical adsorbent with diameters of the order of 10^1–10^2 µm was supported in a network of fibers composed of a matrix polymer. The matrix polymer should serve as a supporting material and can be inert to the adsorption process. Polyethylene was found to be satisfactory for the matrix, but other tough materials can be used as well. In this way, the tiny adsorbent particles could be subjected directly to a rapid current of seawater.

The idea of the fiber composite material was originally developed for the preparation of "synthetic paper" from polyethylene or other petroleum products. Here inorganic salts, silica or kaoline, were added in order to raise the opacity of synthetic paper (Sakai et al., 1979). As heterogeneous catalysts, small particles of Raney Ni or Pd were also treated with fibrous polyethylene or related polymeric materials to give composite hydrogenation catalysts. The technique to support particles smaller than the submicrometer range has been successfully developed and is now applied to the preparation of uranyl adsorbent.

The advantages of the use of this fiber composite adsorbent are as follows:

1. Small particles can be directly used as an adsorbent. This is thought to be the basic requirement for obtaining the higher adsorption rate as discussed above.

2. These tiny particles are included in a network of fibers in a suitable form to be subjected to a rapid flow of seawater.

3. The mechanical properties of the composite materials are determined primarily by those of the matrix polymer and are almost independent of the nature of the adsorbent itself. Thus, the factors affording superior mechanical properties and excellent adsorption behaviors can be investigated independently and combined into an appropriately designed composite adsorbent.

4. Components other than the chemical adsorbent may also be added to improve overall physical and chemical properties of the composite adsorbent. This includes the use of hydrophilic components as the additive.

Thus, the particles of the adsorbent (≤ 37 µm) were suspended well in n-hexane with polyethylene, silica, and surfactant in an autoclave. The temperature was raised to 150 °C to dissolve polyethylene. The content was then ejected through a nozzle having a diameter of 1.5 mm and a length of 1.0 mm into the atmosphere to give a flash evaporation of the solvent. This procedure gave microfibril of polyethylene which contained the adsorbent and silica in the fiber structure. Silica was added to give "hydrophilic channels" in the polyethylene fibril for the access of hydrophilic uranyl species. In order to incorporate hydrophilic silica well into a hydrophobic framework of the matrix polymer, a small amount (usually 5% of the matrix) of surfactant was also added.

The alternative idea combining 3 and 4 may involve the use of the hydrophilic matrix polymer. It should be noted here that the hydrophilic matrix polymer does not necessarily mean a weak mechanical property. Poly(acrylamidoxime), by treatment with an alkaline solution, is simply dissolved in aqueous solution, but hydrophilic and

Table I. Adsorption of Uranyl from Seawater by Use of Composite Fiber Adsorbent

no.	U, μg^b	μg of U/g of Ads^c	source of methacylate^a	AN:TEGMA:DVB	polymn method	chemical adsorbent:PE:silica: surfactant	concn of PE, g/L in hexane
1	(7.6)		Te	1:0.4	S	1:1:1:0.05	50
2	(3.9)		Te	1:0.4	S	1:1:1^d:0.05	50
3	(7.6)		Te	1:0.15	S	1:1:1:0.1	50
4	(8.6)		Te	1:0.15	S	2:1:1:0.15	50
5	6.54	131	Te	1:0.1	E	1:1:1:0.1	50 ,
6	9.54	191	Te	1:0.1:0.003	S	2:1:1:0.15	35
	10^e	200					
7	6.82	136	Tr	1:0.1:0.003	S	1:1:0.5:0.05	50
8	4.77	95	Tr	1:0.1:0.003	S	1:1:0:0.05	50
9	7.86	157	Tr	1:0.1:0.003	S	1:1:1:0.05	35
10	6.17	123	Tr	1:0.1:0.02	E	1:1:1:0.05	50
11	8.55	171	Tr	1:0.1:0.02	E	2:1:1:0.05	35
12	6.17	123	Te	1:0.1:0.02	E	1:1:1:0.05	50
13	6.39	128	Te	1:0.1:0.02	E	1:1:1:0.05	50 HPE
14	5.35	107	Te	1:0.1:0.02	E	1:1:1:0.1	50 HPE
15	6.43	129	Te	1:0.1:0.02	E	1:1:1:0.05	50 HPE/EVA
	1.8	36	Te	1:0.08:0.03	S	particle	

^{a} Abbreviations: Tr, dimethacrylate ester of triethylene glycol; Te, dimethacrylate ester of tetraethylene glycol; S, suspention polymerization; E, emulsion polymerization; HPE, polyethylene of higher molecular weight (see Experimental Section); EVA, copolymer of ethylene and vinyl acetate. ^{b} Values in parentheses are based on 150 mg of adsorbent. See details in the text. ^{c} Weight of the adsorbent (g of Ads) includes the weight of the matrix polymer and silica as well as the chemical adsorbent. ^{d} Hydrophobic silica was used. ^{e} Test under identical conditions except the change of the seawater source.
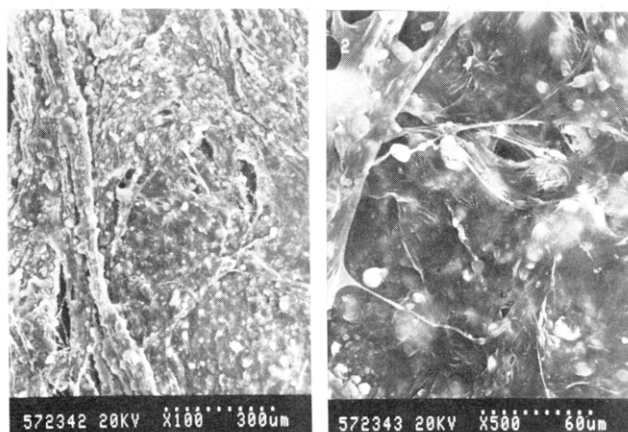

Figure 3. Electron micrograph of composite fiber adsorbent. Bridge parts show the chemical adsorbent which is wrapped by the matrix polymer.

Figure 4. Electron micrograph of the cross section of composite fiber adsorbent. Chemical adsorbent is included in the folded sheet of fibriles of the matrix polymer.

tough materials can be chosen from a variety of synthetic as well as natural polymers. Such an example is a copolymer of ethylene with vinyl acetate, which was also employed for the matrix polymer.

Fiber Structure. SEM pictures of the surface as well as the cross section of the composite fiber are shown in Figures 3 and 4. The adsorbent is shown by the small particles in Figure 3, distributed well over the whole area of the fibril structure of the polyethylene matrix. Silica powder is too small to be discernible at these magnifications. The adsorbent seems to be wrapped well by the fibril structure. Figure 4 shows a folding of multilayered fibrils, into which the adsorbent is again distributed and wrapped well by the matrix fibrils. In this way, each particle can constitute an active adsorption site, giving rise to a large surface area of the adsorbent. The fibril structure surrounding the adsorbents is most desirable for resistance against a falling off of the adsorbent upon mechanical as well as chemical shocks such as the change of pH or ionic strength in the adsorption and desorption processes.

Adsorption Characteristics of the Composite Fiber Adsorbent. Table I summarizes the experimental conditions for the preparation of composite fiber adsorbents and the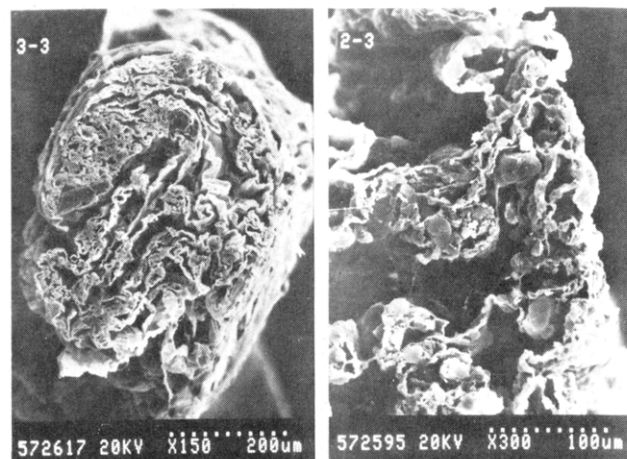ir adsorption data, which were obtained by the 1-day adsorption from 5 L of natural seawater by using 50 mg of the composite adsorbent by use of a batch system at 25 °C under a flow rate of around 50 cm·s^{-1}. In earlier runs (runs 1–4), 150 mg of the adsorbent was used. However, excellent adsorbents recovered most of the uranium in the batch. In order to get information on the relative order of adsorption rates under a more critical condition, the amount of the adsorbent was decreased to 50 mg in later runs. For the sake of comparison, the adsorption datum by using conventional amidoxime particles was also obtained here under a similar experimental condition and is listed in the last row.

The apparent overall adsorption characteristics may be governed by the following factors: 1. compositions of acrylonitrile, tri- or tetraethylene glycol dimethacrylate, and divinylbenzene in the copolymer; 2. the use of tri- or tetraethylene glycol dimethacrylate as a cross-linking agent as well as a reagent to give a large internal hole to bind uranyl ion; 3. polymerization conditions, emulsion, or suspension; 4. the relative ratios of chemical adsorbent, matrix polymer, silica gel, and surfactant; and 5. concentrations of the matrix polymer in n-hexane.

The significance of each factor will be elucidated in the following. At first, the largeness of the adsorption data

of *all* the composite fiber adsorbents was clearly demonstrated. Composite fiber adsorbents gave values of higher than 100 μg of U on the basis of grams of adsorbent, while the conventional particles gave only 36 μg of U/g of Ads. The highest value of the former attained 200 μg of U/g of Ads for run 6. Note that the weight of the adsorbent refers to the total weight of the composite fiber adsorbent, including not only the chemical adsorbent but also the matrix polymer and silica. The adsorption rates per weight of only the chemical adsorbent, including neither the matrix fiber nor silica, become extremely high, 400 and 480 μg of U/g of chemical Ads for runs 6 and 9, respectively. These values should be directly compared with those obtained by using the conventional particles in the last row. Such a dramatic improvement of the adsorption rate certainly originates from the use of very tiny particles, which should afford a larger surface area per weight adsorbent.

The best adsorption rate in view of micrograms of U/gram of adsorbent was observable at run 6. Here, a lower concentration was employed on preparing a hexane solution of polyethylene in the autoclave, i.e., 35 g/L. This lower concentration means that a larger amount of solvent per matrix polymer should evaporate on ejection into the atmosphere to produce a finer structure of the fibril. All of the composite adsorbents prepared at this concentration (runs 6, 9, and 11) gave excellent adsorption data, as shown by the best three data in all of the runs in the table where the rest of the adsorbents were obtained at 50 g/L. The other important factor contributing to the best adsorption of run 6 is certainly the use of a larger ratio of the chemical adsorbent. Although no antipode sample was prepared for run 6, justification can be obtained by the comparison of the set of runs, i.e., 3 vs 4, where the effect of the surfactant is small (vide infra). Relatively high compositions of the surfactant used in run 6 cannot be an important contributing factor, because the uranyl extraction was worse for run 14, in which a higher surfactant composition than that for run 13 was employed, the other conditions being identical. Use of tetra- rather than triethylene glycol dimethacrylate as a cross-linking agent in run 6 again does not seem to be an important factor contributing to the best data, as shown by the identical adsorption data for runs 10 and 12.

The role of silica may be shown by a smaller uranyl adsorption of run 8 where no silica was used. This result may support the idea that silica provides hydrophilic channels for the approach of hydrophilic uranyl species through the hydrophobic matrix. The idea may also be supported by a smaller adsorption of run 2 in which hydrophobic silica was employed instead of the conventional one. However, the silica content could be reduced to half without decreasing the adsorption rate, judging from the maintenance of the good adsorption rate observed for run 7.

For runs 13, 14, and 15, polyethylene of a higher molecular weight (HPE) and a 2:1 mixture of HPE and ethylene–vinyl acetate copolymer were used as the matrix polymer. The acetate moiety was hydrolyzed by the treatment with alkaline solution, before subjecting the nitrile functionality to the reaction with hydroxylamine. These matrix polymers were used to get an enhanced affinity toward the chemical adsorbent by the effects of a higher molecular weight and of the increased hydrophilicity. This may be expected to lead to a better stability with regard to repeated adsorption–desorption cycles. Detailed analyses of the stability test will be reported in a forthcoming paper which will deal with the adsorption

directly from sea current. It should be noted that the adsorption data for these HPE or HPE/EVA based adsorbents were practically the same as for the PE-based adsorbents described above (cf. run 12).

It is worthwhile commenting here that the adsorption rate of the chemical adsorbent was dramatically improved simply by incorporating the fine powder into the matrix polymer. An alternate approach to get a larger surface area might be the use of fiber adsorbent of its own composition. This method has been pursued as a possibility to get a high adsorption rate, as reported in some previous papers (Katoh et al., 1982). However, the complete conversion of the nitrile to the amidoxime functionalities followed by alkali treatment simply led to the dissolution of the material into the alkaline solution. In order to keep the fiber form, it was therefore required to suppress considerably the conversion of the nitrile to amidoxime functionalities. This requirement comes from the fact that the fiber material should in principle melt with heat or be soluble in the solvent for the fiber processing. Therefore, the formation of the three-dimensional network to maintain the material form as in particles cannot be used. Although an adsorption rate as high as 2000 μg of U/g of Ads after 7 days was reported, the adsorption rate of the material having reasonable physical properties decreased significantly.

The present composite fiber adsorbent gave an adsorption rate as high as 200 μg of U/g of Ads/day. This value is still lower than an economically feasible value such as 500 μg of U/g of Ads/day but seems to open an interesting possibility of developing a new type of adsorbent of remarkably high adsorption rates.

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Registry No. U, 7440-61-1; SiO_2, 7631-86-9; polyethylene, 9002-88-4; (ethylene)(vinyl acetate)(copolymer), 24937-78-8.

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Simulation of Continuous-Contact Separation Processes: Multicomponent Batch Distillation

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The present work describes the use of a numerical procedure for simulation of batch multicomponent distillation in a continuous-contact (packed-column) operation. The method uses a relaxation procedure to simulate both start-up and product withdrawal periods of column operation. Example calculations on a three-component mixture are used to show the effects of varying packing height, boilup rate, reflux ratio, and condenser holdup and to demonstrate that the computational procedure is rapid and stable. Additionally, use of the method in determining optimum operating strategy is illustrated.

Although a substantial amount of work has been done recently on numerical methods for packed-column design and simulation, both the quantity and quality of available packed-column algorithms still rate far below the levels achieved in staged-column simulation. Deficiencies remain evident in several key areas. For example, one major problem that has yet to be addressed adequately is the inability of current numerical schemes to solve, without the threat of encountering convergence difficulties, the complicated systems of nonlinear model equations required for a rigorous treatment of simultaneous mass- and heat-transfer phenomena. Another significant deficiency is the lack of flexibility of most current packed-column algorithms; i.e., they are typically capable of performing calculations on only one type of separation process under a relatively narrow range of operating conditions. Some other aspects of packed-column simulation that have not been considered in a rigorous way include (1) unsteady-state operations of continuous processes and (2) batch processes such as batch distillation.

Considering the problem of nonconvergence to be of paramount importance, it was decided that the primary goal of the work presented here would be to develop a highly stable yet rigorous numerical procedure for packed-column simulation. On the basis of the experience gained from the development of staged column algorithms, a relaxation approach was chosen because of its demonstrated stability of convergence for any physically realizable process. This stability is obtained because a relaxation algorithm closely models the transient behavior of the process from startup to steady-state, i.e., if a steady-state condition is ever achieved. A procedure of this type has been used by von Stockar and Wilke (1977a,b) to converge on the steady-state operations of a simple, three-compo-

nent, packed-column absorption process. Their algorithm was claimed to have "superior convergence properties".

Along with the assurance of convergence stability, an added bonus derived from the use of a relaxation procedure is the capability of simulating unsteady-state as well as steady-state operations. Therefore, a numerical algorithm derived from a relaxation approach may be structured with built-in flexibility so that it could be applied to a variety of continuous-contact separation processes. Following these guidelines, an implicit numerical integration procedure, known as DYNCAL, was developed. This analysis-format program was described in a previous article (Hitch et al., 1987). DYNCAL was used to solve the unsteady-state differential-contactor model equations for packed-column absorption and stripping operations involving nonideal, wide-boiling mixtures. Excellent agreement was obtained between DYNCAL predictions and experimental data obtained from a pilot-scale acid gas removal system that utilized refrigerated methanol to absorb carbon dioxide from a coal gasifier off-gas stream.

A similar algorithm, named DISTCAL, has now been developed to handle the inherently unsteady-state problem of batch distillation involving narrow-boiling mixtures. So far as we can determine, prior to this work, no rigorous numerical procedure for the simulation of batch distillation in a packed column has ever been presented in the scientific literature. The details of the formulation of the model equations and the mathematical structure of the numerical algorithm, DISTCAL, are discussed below. Simulation predictions are evaluated qualitatively through the use of a parametric study to test the validity of the mathematical model and the numerical solution procedure. In addition, a rudimentary product yield optimization is performed to demonstrate a potential application for the simulation.

Development of Algorithm

Before going into the details of the development of the mathematical model and numerical integration scheme

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