Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Evaluation of the SREX Solvent Extraction Process for the Removal Of ^{90}Sr and Hazardous Metals from Acidic Nuclear Waste Solutions Containing High Concentrations of Interfering Alkali Metal Ions

Donald J. Wood[a]; Jack D. Law[a]
[a] Idaho National Engineering Laboratory, ID

To cite this Article Wood, Donald J. and Law, Jack D.(1997) 'Evaluation of the SREX Solvent Extraction Process for the Removal Of ^{90}Sr and Hazardous Metals from Acidic Nuclear Waste Solutions Containing High Concentrations of Interfering Alkali Metal Ions', Separation Science and Technology, 32: 1, 241 — 253

To link to this Article: DOI: 10.1080/01496399708003197

URL: http://dx.doi.org/10.1080/01496399708003197

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 241-253, 1997

EVALUATION OF THE SREX SOLVENT EXTRACTION PROCESS FOR THE REMOVAL OF ^{90}SR AND HAZARDOUS METALS FROM ACIDIC NUCLEAR WASTE SOLUTIONS CONTAINING HIGH CONCENTRATIONS OF INTERFERING ALKALI METAL IONS

Donald J. Wood and Jack D. Law
Idaho National Engineering Laboratory
P.O. Box 1625
Idaho Falls, ID 83401-5213

ABSTRACT

The SREX process, which was developed at Argonne National Laboratories, has been evaluated for its effectiveness for the decontamination of radioactive liquid waste at the Idaho Chemical Processing Plant located at the Idaho National Engineering Laboratory. The extraction solvent consists of 0.15 M 4',4',(5')-di-(t-butyl-dicyclohexo)-18-crown-6 in either 1.2 M TBP/Isopar L®. Suppressed extraction due to matrix interferences limits D_{Sr} values to the range of 3-4 in batch extraction experiments. The SREX solvent has been shown to be effective in the removal of non-radioactive Pb from liquid wastes, in addition to the extraction of ^{90}Sr. The information from this study has been used to develop a proposed flowsheet for the treatment of liquid waste in centrifugal contactors.

INTRODUCTION

The removal of hazardous and radioactive components from acidic waste streams resulting from the operations of nuclear fuel reprocessing facilities is critical to minimizing the cost associated with the disposal of such streams. Aqueous separation methods are currently under development at the Idaho Chemical Processing Plant (ICPP) located at the Idaho National Engineering Laboratory (INEL) [1,2]. The SREX process, a solvent extraction process initially developed by Horwitz et al. at Argonne National Laboratories, is being evaluated for the removal of the fission product, ^{90}Sr, from acidic nuclear waste solutions which contain high concentrations of alkali metal ions. The presence of matrix ions such as Na^+, K^+, Ca^+, and Li^+ has been shown to limit the distribution coefficient of Sr in the extraction process [3]. However, the distribution coefficient values remain sufficiently high to provide an effective multistage countercurrent process for quantitative removal of ^{90}Sr. The SREX process was initially developed using a diluent of 1-octanol for 4',4'(5')-di-(t-butyldicyclohexo)-18-crown-6 (DtBuCH18C6). This solvent composition was shown to provide highly efficient extraction of ^{90}Sr from acidic simulated wastes. It has subsequently been determined that 1-octanol may not be suitable for use in a sequential processing scheme in which the SREX process is followed by the TRUEX process for the removal of the transuranic components from the aqueous stream[4,5]. It is believed that trace quantities of the 1-octanol is carried in the aqueous stream from the SREX process to the TRUEX process, which results in the poisoning of the TRUEX solvent. This deleterious effect on the TRUEX process has resulted in the need to identify alternative diluents for use in the SREX process. The development laboratories at Argonne National Laboratories have identified an alternative diluent for use in a solvent referred to as a "modified SREX solvent". This solvent is a ternary mixture containing 0.15 M 4',4',(5')-di-(t-butyl-dicyclohexo)-18- crown-6, 1.2 M tributyl phosphate as a phase modifier, and Isopar L®, which is an proprietary isoparaffinic hydrocarbon diluent. This formulation of the SREX solvent appears to provide satisfactory decontamination results and eliminates the TRUEX compatibility problems encountered with 1-octanol.

The use of the modified SREX diluent for the treatment of wastes containing high concentrations of alkali metal ions has not been demonstrated previously. This paper summarizes the investigation of the modified SREX solvent using TBP and Isopar L® for the removal of ^{90}Sr from acidic alkali wastes at the ICPP. Also included in this report are initial results of the investigation of the extraction of Pb by the SREX process.

EXPERIMENTAL METHODS

Reagents

4,4'(5')-di-(tert-butyldicyclohexo)-18-crown-6 (DtBuCH18C6) was obtained from Eichrom Industries, Inc. (Darien, IL) and used as received without further purification. The isotopes, ^{85}Sr ($t_{1/2}$ = 64.8 days, γ = 514 KeV) and ^{90}Sr ($t_{1/2}$ = 29 years, β = 0.546 KeV), and ^{210}Pb ($t_{1/2}$ = 22.3 years, β = 17 KeV) were obtained as nitric acid solutions from Isotope Product Laboratories (Burbank, CA). Reagent grade 1-octanol was received from Fisher Scientific. Isopar L® is a proprietary isoparaffinic hydrocarbon solvent which was obtained from Exxon Chemicals in a sample quantity and used as received. All other reagents were obtained as reagent grade chemicals from various manufacturers.

Simulated Sodium-Bearing Waste

The simulated waste solutions used in this study were prepared from non-radioactive chemicals according to procedures reported previously [1]. The composition of the simulant was prepared to represent an average of chemical compositions found in sodium-bearing waste tanks at the Idaho Chemical Processing Plant. The composition of the simulant is presented in the Results and Discussion section of this report.

Batch Extraction Experiments

Each of the experiments in this study were performed at room temperature (27 ± 2 °C) with equal volumes of the appropriate aqueous solution and organic extractant. The organic and aqueous solutions were placed in glass centrifuge tubes and placed on a vortex-motion mixer for 1 minute unless otherwise stated. Following mixing, the samples were immediately placed in a centrifuge for one minute at 5000 rpm. After centrifugation, the phases in each sample were separated for analysis with small volume Pasteur pipets. In experiments which required acid concentration measurements, aliquots of the solutions were titrated with sodium hydroxide using a phenolphthalein indicator.

Radioactive Tracer Experiments.

The radioactive tracers which were employed in batch extraction experiments were dispensed with a small volume motorized pipet (Rainin Instrument Co., Inc.) directly into individual aqueous solutions in test tubes. The tracer solutions were of sufficient activity to allow a small volume of tracer to be added which did not significantly increase the total volume of the aqueous samples. The analysis of both the organic and aqueous phases was performed by gamma spectrometry when ^{85}Sr was employed as the tracer. When ^{90}Sr or ^{210}Pb was employed, each phase was analyzed by liquid scintillation. Corrections for the grow-in of the daughter isotopes were performed for each phase in the liquid scintillation measurements. The measured activities in each phase were utilized to determine distribution coefficients for the measured species. The distribution coefficient for a solution component x is defined as follows:

$$D_x = \frac{[X]_{org}}{[X]_{aq}}$$

where $[X]_{org}$ and $[X]_{aq}$ are the equilibrium concentrations of species x in the organic phase and aqueous phase, respectively.

Batch Contact Flowsheet Experiments

Each of the batch-contact flowsheet experiments included solvent pre-equilibration prior to contact with the aqueous feed solutions. Pre-equilibration was performed by contacting the solvent three times with equal volumes of sodium-bearing waste simulant in the case of the tracer experiments. Each experiment consisted of nine batch contacts performed successively. Three extraction steps were performed by contacting equal volumes of the SREX solvent with the desired aqueous feed in each step. The organic phases from the extractions were then contacted with equal volumes of a nitric acid solution three times. The organic phase was then contacted with a dilute nitric acid solution three times to strip the extracted species. The aqueous phase was sampled for direct measurement in each of these experiments. In the case of experiments which utilized radioactive tracers, each organic phase was sampled for direct analysis as well. In certain experiments where radioactive tracers could not be used, selected organic phases were back-extracted with an appropriate stripping reagent using an organic to aqueous phase volume ratio of 0.25. The resulting solutions were sampled for analytical measurement. The data obtained from these measurements were used to determine distribution coefficients and mass recoveries.

RESULTS AND DISCUSSION

Comparison of Octanol and Isopar L® Solvents.

The replacement of the 1-octanol diluent in the SREX process by 1.2 M TBP in Isopar L® has the potential of eliminating some difficulties in the practical implementation of the SREX process. The selection of Isopar L® as the diluent for the modified process will provide compatibility with the TRUEX process which is being considered as the method for actinide removal at the INEL. Isopar L® has chemical and physical properties which are suitable for use in a radioactive waste processing environment and will likely encounter few safety concerns upon implementation.

Experiments have been performed to verify previous reports regarding the performance of the modified diluent and to compare its extraction characteristics to that of the 1-octanol diluent. The extraction of nitric acid by these diluents from the aqueous phase has been studied for the purpose of comparison. Figure 1 shows the equilibrium concentration of acid in the organic phase as a function of the equilibrium concentration of acid in the aqueous phase for each diluent. The extraction of acid by the octanol solvent is less than that of the Isopar L solvent over the range of acid concentrations expected to be encountered in the processing of INEL wastes.

A comparison of the dependence of the distribution coefficient for Sr^{2+} on nitric acid concentration is shown in Figure 2. These data indicate that the constants which govern the extraction of Sr into the two solvents are dissimilar. The extraction of Sr by the modified SREX solvent is significantly lower across the entire range of acid concentrations studied.

Batch Contact Flowsheet Development

Batch contact flowsheets were evaluated to determine the fundamental extraction characteristics of the SREX solvent. This information may be useful in the design of

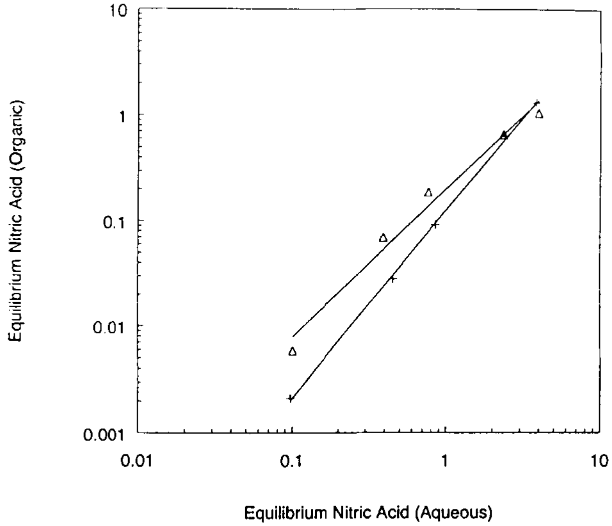

FIGURE 1. Equilibrium concentrations of nitric acid for 0.15 M DtBuCH18C6 in 1-octanol (+) and 1.2 M tributyl phosphate in Isopar L (Δ).

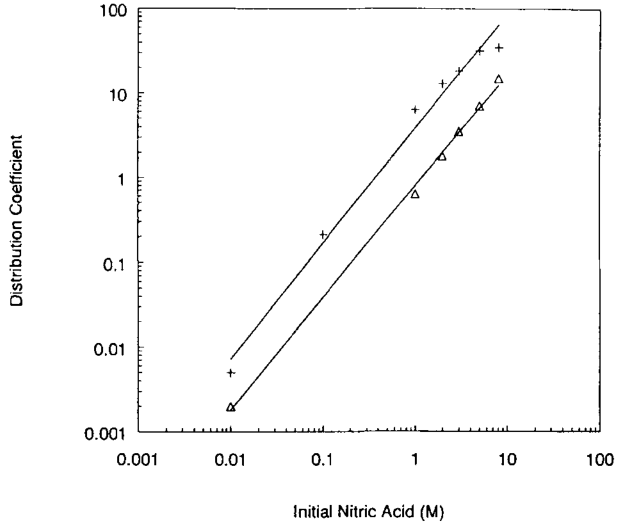

FIGURE 2. Dependence of Sr extraction upon nitric acid for 0.15 M DtBuCH18C6 in 1-octanol (+) and 1.2 M tributyl phosphate in Isopar L (Δ).

effective counter-current processing flowsheets for demonstration with simulated and actual waste. The composition of actual and simulated SBW is presented in Table 1.

Figure 3 displays the experimental flowsheet used for the purpose of comparison of 1-octanol and the modified SREX solvent for the removal of Sr from simulated SBW. This experiment consisted of three extraction contacts, three scrub contacts, and three strip contacts performed in succession as shown. This flowsheet experiment was performed with both of the diluent compositions using a ^{85}Sr tracer for radioactive determinations of distribution coefficients in each contact. Table 2 displays the measured D_{Sr} values for contacts 1-9 for each diluent composition.

The data in Table 2 indicates that the D_{sr} values for the 1-octanol and the Isopar L® solvents are similar for the extraction contacts 1-3, with the modified solvent being slightly higher than that of 1-octanol. The data shown in Figure 2 indicates that the octanol solvent should yield higher values of D_{sr} than the Isopar L® solvent. The reverse trend shown in the data in Table 2 is likely a result of a difference in selectivity for the interfering ions which are present in the simulated SBW. The measured distribution coefficients in this experiment indicate that either solvent should provide acceptable extraction efficiencies for use in the removal of ^{90}Sr from SBW.

Co-extraction of Group I and Group II Ions.

It has been shown previously that the presence of group I and group II metal ions in acidic solutions present interferences in the removal of ^{90}Sr by the SREX process [3]. The measured distribution coefficients for Sr in SBW are limited to the range 3-4 when the SREX solvent is employed in batch contacts. These values are very low compared to the expected values in the absence of interfering ions. The primary interferences present in SBW are the Na^+ and K^+ ions. These components are present in SBW in concentrations of 1.4 M and 0.14 M, respectively. The co-extraction of these ions with ^{90}Sr will result in the presence of non-radioactive components in the high-activity waste stream under processing conditions. The resultant increase in high-activity waste volume presents a possible increase in disposal costs and, therefore, is an important consideration in the development of the SREX process.

Batch contact flowsheets have been performed to measure the concentrations of coextracted Na^+ and K^+ from simulated SBW. The original SREX solvent, using 1-

TABLE 1. MOLAR COMPOSITION OF ACTUAL AND SIMULATED SBW

Component	Actual SBW	Simulated SBW	Component	Actual SBW	Simulated SBW
H^+	1.63	1.35	Mo	--	0.0015
Al	0.75	0.65	Na	1.44	1.26
B	--	0.17	Ni	--	0.002
Cd	<0.004	0.002	Pb	--	0.001
Ca	0.065	0.039	Sr	--	1.7E-4
Ce	--	3.88E-4	Zr	0.001	0.001
Cs	--	7.4E-4	Cl	--	0.035
Cr	0.005	0.006	F	--	0.097
Fe	0.021	0.031	NO_3^-	5.01	4.46
Hg	0.004	0.003	PO_4^-	--	<0.01
K	0.143	0.19	SO_4^-	--	0.039
Mn	--	0.014			

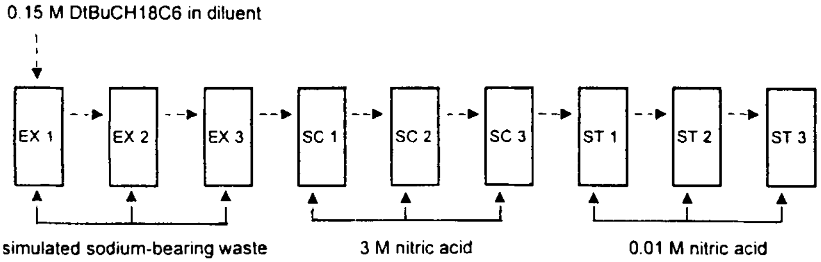

FIGURE 3. Experimental flowsheet for extraction of Sr from simulated SBW.

TABLE 2. STRONTIUM-85 DISTRIBUTION COEFFICIENTS FOR CONTACTS 1-9.

Contact Number	SREX Solvent	Modified SREX Solvent
1	3.61	4.66
2	3.99	4.11
3	3.32	3.76
4	13.0	3.76
5	16.7	3.94
6	18.1	3.97
7	3.03	0.35
8	0.14	0.16
9	0.02	0.41

octanol, was employed in this experiment for the purpose of comparision to previous ion interference studies. The flowsheet arrangement was identical to that described above for Sr extraction. The aqueous solution employed in the extraction contacts was a diluted solution of simulated SBW. This solution was obtained from aqueous raffinate solution which was the result of a counter-current demonstration of the TRUEX process at the INEL. This solution was used to simulate the feed to the SREX process during actual waste processing in a sequential flowsheet which utilizes the TRUEX process followed by the SREX process. The initial concentrations of Na, K, and Sr in this diluted SBW were measured to be 0.96 M, 0.12 M, and 4.5E-4 M, respectively. The measured equilibrium concentrations of Na, K, and Sr in the aqueous phase from each contact are provided in Table 3.

The data shown in the table shows that all three of the listed ions are extracted by the SREX solvent. The extraction of K^+ and Na^+ compete with Sr^{+2} for available extractant in this system. This has the effect of limiting the Sr distribution coefficient, which is measured in the extraction contacts, to approximately 4. It is significant that the equilibrium concentration of K in the organic phase from contact 3 was calculated to be approximately 0.12 M by mass balance determinations. The concentration of

TABLE 3. MOLAR CONCENTRATION OF IONS IN AQUEOUS PHASES.

CONTACT	K^+	Na^+	Sr^{2+}
1	0.04	0.87	9.2E-5
2	0.09	0.91	1.7E-4
3	0.11	0.91	2.3E-4
4	0.04	0.05	2.1E-4
5	0.03	0.001	1.4E-4
6	0.01	0.001	1.2E-4
7	0.01	<0.001	2.6E-4
8	0.02	<0.001	1.5E-4
9	0.01	<0.001	8.2E-6

DtBuCH18C6 in the organic phase is 0.15 M. The assumptions that K^+ forms a 1:1 complex with the macrocycle and that the extraction of K^+ is entirely due to complexation with DtBuCH18C6 leads to the approximation that 80 percent of the extractant is complexed with K. The competition presented by the K^+ ion in SBW presents the greatest interference for the extraction of ^{90}Sr. Contacts 4-6 which consist of 3M nitric acid scrubs are effective, however, in the removal of K^+ from the loaded organic solvent. This suggests that the co-extracted K^+ ions will likely be removed from the loaded organic by a few stages of nitric acid scrubs in a counter-current processing flowsheet. The mass recoveries for Na^+ in this experiment were poor. The low concentrations detected in the aqueous phases of stages 7-9 indicate, however, that co-extraction of the Na^+ ion presents little interference in comparison to the K^+ ion.

Extraction of Pb by the SREX Solvent.

Recent development efforts at the INEL to develop the SREX process for application to INEL radioactive wastes has included counter-current flowsheet testing in a

5.5 cm centrifugal contactors using simulated SBW. This work is summarized elsewhere [6]. During one of the experimental runs, a finely divided white precipitate was encountered in the aqueous phase while attempting to strip the loaded organic stream with 0.01 M nitric acid. Analysis of this precipitate indicated that it consisted primarily of a mixture of Pb complexes. A study of the extraction behavior of Pb^{+2} from SBW by the SREX solvent has been performed to explain this observation.

The dependence of Pb^{+2} extraction on the initial nitric acid concentration in the aqueous phase in batch contact experiments is shown in Figure 4. The modified SREX solvent was used in this experiment. The extraction of Pb^{+2} is approximately linear across the range of acid concentrations studied. It is important to note that the values obtained for D_{Pb} are considerably higher that the values determined for D_{Sr} with the same solvent. This indicates that the modified SREX solvent is a stronger extractant for Pb^{+2} than for Sr^{+2}. The molar concentrations of Sr and Pb in actual SBW are in the range 1E-4 to 1E-3. The result for extraction will be that Sr and Pb will both be quantitatively removed in a SREX processing flowsheet.

Batch contact flowsheet experiments have been performed to evaluate and compare the behavior of Pb using the SREX solvent and the modified SREX solvent. These experiments utilized the same flowsheet arrangement which is shown in Figure 3. The aqueous phases from each contact 1-9 were sampled at equilibrium for determination of Pb. Values for the distribution coefficients were determined indirectly by mass balance calculations. These values are plotted for each contact in Figure 5. It can be seen from the graphical data that the 1-octanol solvent provides generally higher distributions for Pb than the Isopar L® solvent. Additionally, the D_{Pb} values are considerably higher that the measured D_{Sr} values listed in Table 2 for each solvent. The values obtained for D_{Pb} in contacts 4-6 indicate that a 3 M nitric acid solution will not be effective for removing extracted Pb from either organic solvent. However, 0.01 M nitric acid may successfully strip both Sr and Pb from each solvent.

CONCLUSIONS

This study has shown 1.2 M tributyl phosphate in Isopar L® to be an effective replacement for 1-octanol in the SREX process for the removal of ^{90}Sr from radioactive wastes which

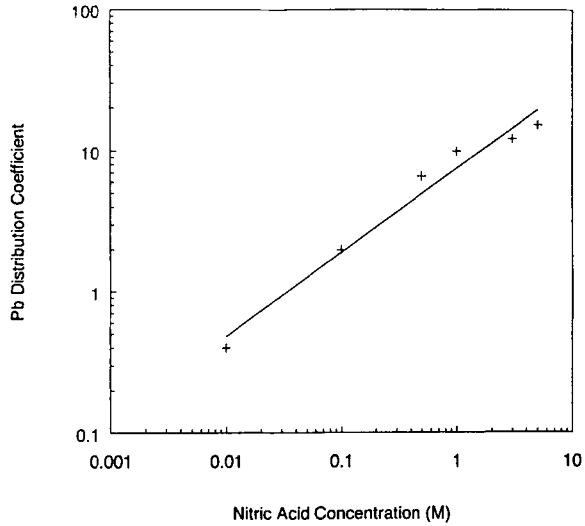

FIGURE 4. Dependence of Pb extraction upon nitric acid for the SREX solvent with a diluent of 1.2 M tributyl phosphate in Isopar L.

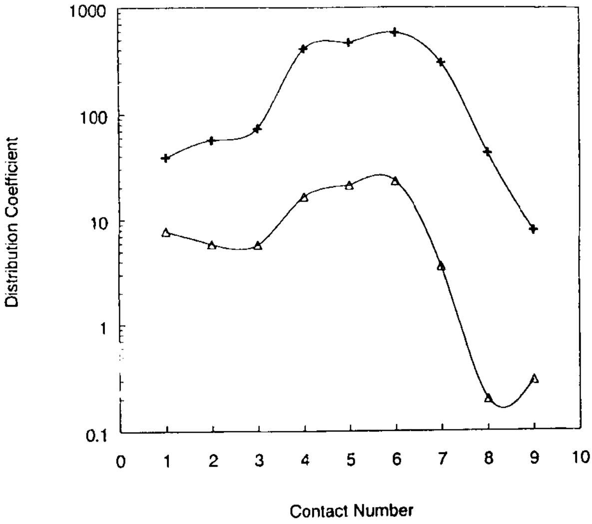

FIGURE 5. Distribution coefficients for Pb in experimental flowsheets with 0.15 M DtBuCH18C6 in 1-octanol (+) and 1.2 M tributyl phosphate in Isopar L (Δ).

contain high concentrations of interfering alkali metal ions. The distribution coefficients for Sr in the modified diluent are believed to be suitable to achieve efficient decontamination ^{90}Sr in waste treatment processes. The coextraction of Pb by the SREX process is highly efficient and concurrent with the removal of ^{90}Sr. The application of this process in counter-current processing is likely to be effective for the simultaneous removal of these components from acidic high-activity wastes.

REFERENCES

1. R.S. Herbst, K.N. Brewer, J.D. Law, T.J. Tranter, and T.A. Todd, TRUEX Partitioning Studies Applied to ICPP Sodium-Bearing Waste, Report WINCO-1206, U.S. Department of Energy, Idaho Falls, Idaho, 1994.

2. A.L. Olson, W.W. Schulz, L.A. Burchfield, C.D. Carlson, J.L. Swanson, and M.C. Thompson, Evaluation and Selection of Aqueous Based Technology for Partitioning Radionuclides from ICPP Calcine, Report WINCO-1071, U.S. Department of Energy, 1993.

3. Donald J. Wood, Terry A. Todd, and Troy J. Tranter, Solvent Extr. Ion Exch. *13*, 829 (1995).

4. Personal communication with E.P. Horwitz, Chemistry Division, Argonne National Laboratory, Argonne, IL, June 1995.

5. Mark L. Dietz, E. Philip Horwitz and Robin D. Rogers, Solvent Extr. Ion Exch. *13*(1), 1 (1995).

6. J.D. Law, D.J. Wood, and R.S. Herbst, Sep. Sci. and Tech., Proceedings on the Ninth Symposium on Separation Science and Technology for Energy Applications, 1995, *in press*.