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Pilot-Scale Evaluation of Supported Liquid Membrane Extraction

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ABSTRACT

An evaluation of a solvent extraction system employing supported liquid membranes has recently been completed by Rockwell Hanford Operations. The focus was on a pilot-scale, tube and shell arrangement configured for continuous operation. The tube bundle consisted of 333 polypropylene microporous fibers with a total surface of 3.6 m^2.

Results are reported for the evaluation of operating parameters such as flow rates and corresponding aqueous pressure differences, solvent impregnation techniques, and test system durability. Chemical and physical test results, including permeability data, are also reported for the systems nitrate ion/nitric acid/tertiary amine and (nonradioactive) Group IA-IIA metal/nitric acid/phosphoric acid extractant.

INTRODUCTION

Nuclear fuel reprocessing at the Hanford Site has traditionally relied on solvent extraction and ion exchange techniques to separate dissolved inorganic constituents from aqueous solutions. The use of such methods for separation of trace species can be a costly undertaking, and has prompted continual evaluation of potential separation process refinements. A recent addition to the array of available solvent extraction methods is the supported liquid membrane (SLM). The information presented in this paper focuses on an engineering evaluation of a pilot-scale hollow-fiber SLM module. The work was performed by Rockwell Hanford Operations' process development organization.

The objective of the engineering evaluation was to determine operating characteristics of the SLM module in light of its potential applicability to waste and process solution treatment. Various parameters, including momentum and mass transfer behavior plus durability and reliability of a typical commercially available unit, were studied. Results of preliminary investigations are presented here, along with a brief overview of beneficial SLM characteristics.

BACKGROUND

A SLM may be described as a thin, microporous polymer film containing an (aqueous) immiscible organic solution. The organic solution is composed of a diluent that is impermeable to dissolved species and a carrier (extractant) capable of undergoing reversible reaction with selected inorganic species.(1) The transfer of material from one boundary of a SLM to the other occurs by facilitated transport, which permits both high selectivity plus relatively large mass fluxes and provides the driving force for studying possible SLM applications.

Potential candidate feeds for SLM separations include a wide variety of aqueous fuel reprocessing solutions. The only streams excluded from consideration are those either producing highly radioactive fields or containing concentrated mineral acids, which are capable of decomposing the polymeric membrane materials. The remaining candidates for SLM separation at the Hanford Site are predominantly low-level aqueous wastes. These generally contain trace amounts of radioactive cesium, strontium, miscellaneous fission products, uranium and transuranium elements, and chemical process products such as nitric acid, iron, aluminum, trace nickel, and trace chromium. Radioactive constituents often include fission product iron, technetium as pertechnetate ion (TcO_4^-), and platinum metal compounds.(2) Solutions of these compounds in weak nitric acid may be most applicable to a SLM separation process.

Past development work with SLM separation has focused on membrane preparations, on mechanisms of separation, and on quantitative characterization of separations. Several studies on membrane separations have investigated facilitated transport(3,4) and have screened applicability of SLMs to various separations.(1,5,6) Generally, application screening studies have been with flat sheet membranes or single hollow-fiber modules and have resulted in determination of permeability with respect to feed rate or stirring rate at isothermal conditions. No studies with large-scale hollow-fiber modules have been documented, and several areas of uncertainty currently exist in our understanding of SLM extraction processes. These areas include operating characteristics, long-term durability and reliability, scale-up effects, and verification of diffusion models upon which future design correlation may be based.

The investigations described here study some areas of uncertainty. Specifically addressed are operating characteristics, achievable pressure drops and flow rates, membrane impregnation and solvent removal techniques, observations regarding system design effects, and verification of laboratory bench-scale results for potentially useful separa-

tions. The specific application tests focus on nitric acid removal and separation of strontium from simulated low-level waste solution. These systems were chosen in order to demonstrate the potential usefulness of SLM separations.

EXPERIMENTAL

Objectives

Specific objectives of the experimental investigation include the following:

- Evaluation of pressure drop across both tube (fiber lumens) and shell sides of the tube-in-shell, hollow-fiber SLM module
- Demonstration of a functional SLM system design to include provision for membrane impregnation with solvent, subsequent solvent removal, and continuous feed and strip solution circulation in tube and shell sides of the module
- Evaluation of concentration changes as a function of previously identified independent variables (flowrate, initial permeate concentration) for HNO_3 extraction
- Demonstration of SLM extraction of a typical low activity waste solution constituent, strontium, using stable strontium nitrate dissolved in weak HNO_3.

Test results should help guide future SLM designers. Pressure drop (ΔP) data, for instance, are important in two ways. First, data on flowrate versus ΔP can be used to establish friction factors and subsequent pumping power relationships for both tube and shell sides. Next, the maximum throughput rate for the SLM will be bounded by a practical operating pressure difference across the membrane (internal fiber lumen pressure versus external shell pressure). If a module operates in counterflow mode, the membrane ΔP at the feed inlet end of a long fiber may be great enough to force organic liquid from the membrane pores into the shell side.

Validity of permeability correlations used in evaluating small-scale, hollow-fiber SLM modules may also be checked with the data from these tests. Diffusion models have been developed by a number of investigators, but have only been verified in limited, bench-scale tests.(1,3,5) These currently used models generally assume very low permeate concentrations and a large excess of carrier molecules within the membrane. Large-scale tests with simulated plant solutions differ greatly from this ideal because permeate feed concentrations and volumes are higher. Variances are noted and discussed further as an aid to possible future improvements in SLM modeling.

A final specific objective in this preliminary study is a demonstration of strontium removal from simulated acidic waste. The

strontium, prepared by dissolution of strontium nitrate in nitric acid, is pumped through the SLM module containing di(2-ethylhexyl)phosphoric acid (D2EHPA) in n-dodecane. This system is operated in a once-through configuration. Results are reported for continuous operation, and the efficacy of the separation is evaluated as an indication of potential utility.

Equipment

The SLM module used in pilot tests is an Enka hollow-fiber module TMD 805 with a 3.6-m^2 (total internal) membrane surface area containing 319 (functional) hollow fibers. Module length is 2 m. Each fiber has an inner diameter of 1.8 mm and a membrane thickness of 0.45 mm with 75% void volume. Average pore diameter is 0.2 μm. The module is configured as a tube-in-shell, and the hollow fibers are potted with epoxy resin within the glass fiber-reinforced epoxy shell. A typical SLM module of this type is shown in Figure 1, and is very similar in design to a tube-in-shell heat exchanger.

The SLM module configuration is illustrated in Figure 2. The module is mounted vertically onto an engineering laboratory test support frame, together with pumps, valves, pressure sensors and flow meters. The vertical SLM arrangement ensures simultaneous flow through the fibers and permits complete drainage when desired. Product and strip solution receiver tanks are located above the SLM module and gravity drain to the feed tanks when desired. Organic solution (diluent plus carrier) is fed into the top of the SLM tubes to impregnate fiber membranes. All tanks are fiberglass or polypropylene, and all components are connected by 9-mm polypropylene tubing and compression fittings. Differential pressures across the fiber bundle and the shell ports are measured by Magnehelic differential pressure gauges, and actual operating pressures are indicated on Matheson 0- to 100-kPa gauges. Flows are simultaneously actuated in both fibers and shell (to avoid application of potentially damaging ΔP across the membranes) using Electromni electrically actuated motor valves. Flowrates are measured with Ametek stainless steel rotameters.

Aqueous tube-side acid concentrations are measured by a Cole-Palmer Model 5982 pH meter and by NaOH titration with phenol red endpoint indicator. Shell-side hydroxide concentrations are determined by HNO_3 titration. Strontium concentrations are measured by inductively coupled plasma (ICP) spectrometry with auxiliary indications via pH measurement.

Chemicals used in this study included the following:

- Reagent grade HNO_3, $NaNO_3$, and NaOH from Baker Chemical Company
- Trilauryl amine (TLA) from Eastman Kodak Company
- N-dodecane (diluent) from the Humphrey Chemical Company.

All aqueous chemical solutions were prepared using deionized water. Solid NaOH was weighed before blending with water to make deacidification strip solution.

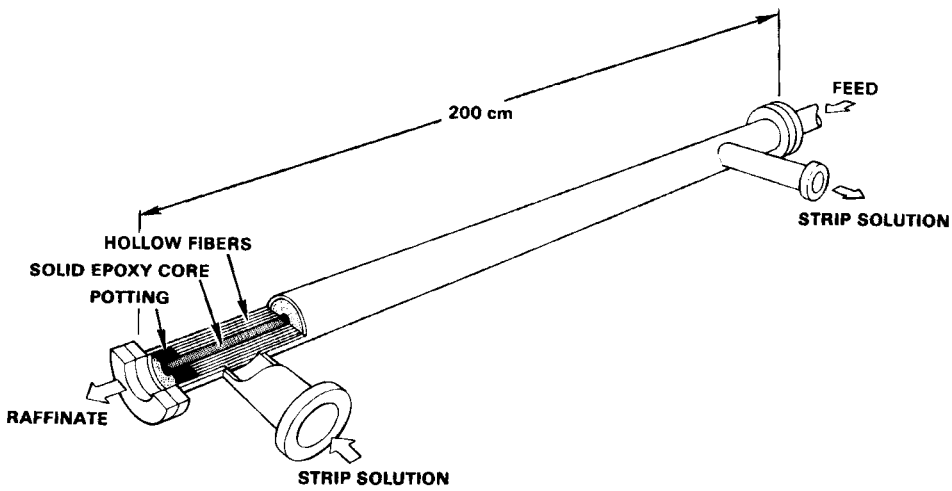

FIG. 1. Supported liquid membrane module.

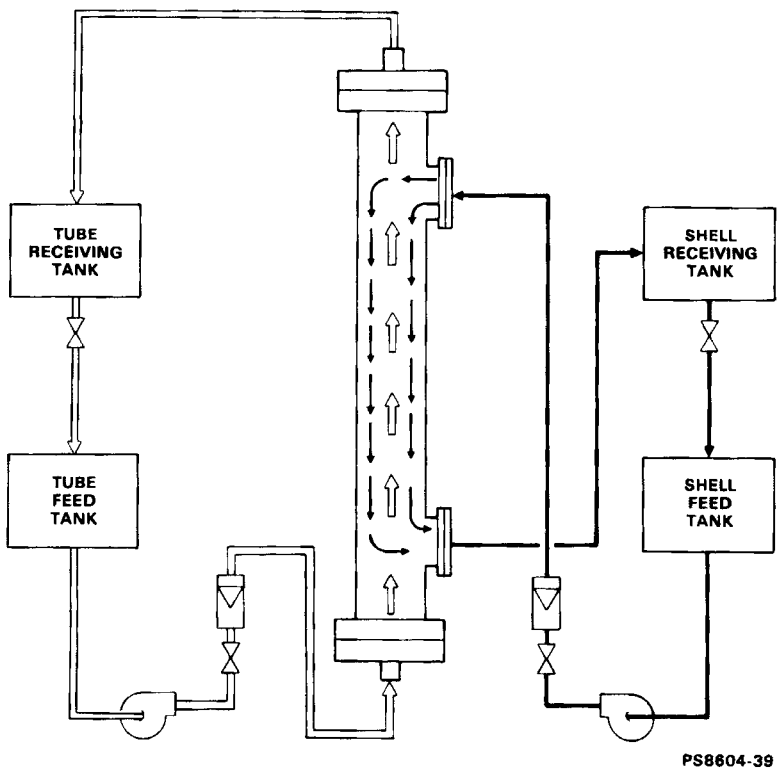

FIG. 2. Module configuration.

Techniques

Investigations performed during this evaluation study are described below.

- Impregnate SLM module fibers with 0.1M TLA in n-dodecane diluent by closing all outlet valves, adding organic solution into the tubes, and allowing the solution to reside in the tubes for at least one hour. Then drain all excess organic solution from both tube and shell sides. Evaluate the degree of impregnation by comparing solution holdup to theoretically calculated holdup.

- Evaluate flow characteristics of the module system. This involves pumping fluid (initially demineralized water) through both tube and shell sides and recording inlet and outlet pressures and differential pressures for each side. Flow rates range in both tube and shell sides to about 6 L/min.

- Evaluate mass transfer characteristics by extracting nitric acid across fiber walls. The feed HNO_3 composition varies from 0.01 to 0.20 mol/L with 1.0 mol/L $NaNO_3$ added for maintenance of high ionic strength, while the strip solution is composed of 1.0 mol/L NaOH. Determine acid concentration changes as functions of residence time by processing measured volumes of feed in multiple passes. Each pass of a test run will have a starting concentration equal to the previous passes' ending acid concentration and each test run will use a different feed rate and residence time. Use strip solution flows equal to feed flows.

- Demonstrate strontium extraction from feed composed of 0.01 mol/L $Sr(NO_3)_2$ dissolved in HNO_3. First remove TLA from fiber walls by filling the fibers and shell with acetone. Drain the acetone and air dry the module, then add 0.10 mol/L D2EHPA in n-dodecane to the fiber walls. Perform strontium extraction using 0.01 mol/L HNO_3 strip solution. Use equal feed and strip solution flow velocities.

RESULTS AND DISCUSSION

Membrane Impregnation

Membranes were originally filled with a 0.10 mol/L TLA in n-dodecane solution for nitric acid extraction tests and eventually with a 0.10 mol/L D2EHPA in n-dodecane solution for strontium extraction tests. As the tubes filled with the organic solution, the resulting hydrostatic pressure on the lower ends of the fibers created a pressure difference between tube and shell sides of the module. This caused organic solution to flow through the fiber walls and into the shell. As a result, both tubes and shell had to be filled with organic solution to ensure complete impregnation of membranes.

Organic solution was removed from the membranes using acetone. However, this procedure required special care and rapid execution because several components of the system (including the epoxy shell) were not chemically resistant to acetone.

Hydrodynamics

The flow characteristics of the SLM module were very straightforward. The pressure drop attributed to the SLM module was minimal as compared to the total head (including liquid column) required. This was true for both the tube and shell sides of the module. The measured head losses were essentially the same as calculated values, thus making hydrodynamic design uncomplicated. Typical values for ΔP between inlet and outlet sides of the tubes and shell are shown in Figure 3.

Nitric Acid Extraction

Nitric acid extraction studies via facilitated transport across supported liquid membranes have previously been performed on laboratory-scale modules. Correlations and models have been established for such systems assuming dilute ($<1 \times 10^{-2}$ M) HNO_3 solutions.

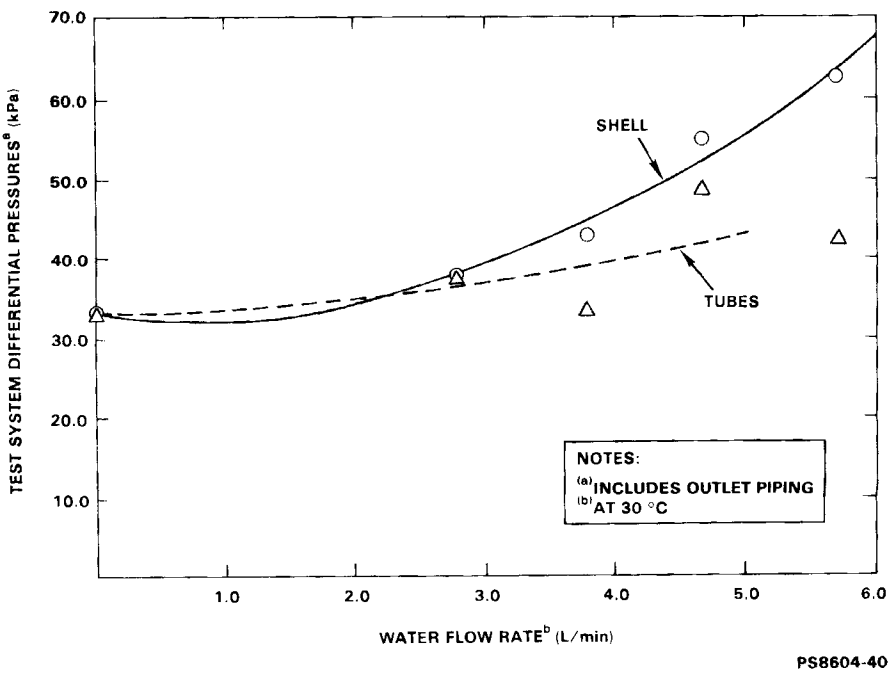

FIG. 3. Supported liquid membrane system flow characteristics.

The continuous-flow, pilot-scale SLM tests discussed in this report relied on relatively concentrated (~0.2M) HNO_3 solutions (dilute solution composition could not be accurately measured on such a large scale). This new situation dictated investigation of a different modeling technique.

Previous descriptions of nitric acid extraction across an SLM with TLA as the carrier have been based on the following:

$$H^+ + NO_3^- + \overline{TLA} \xleftrightarrow{K} \overline{TLAHNO_3} \quad (1)$$

$$[\overline{TLA}]_o = [\overline{TLA}]_e + K[H^+][\overline{TLA}]_e \quad (2)$$

where:

$[\overline{TLA}]_o$ = analytical TLA concentration

$[\overline{TLA}]_e$ = concentration of TLA not complexed with HNO_3

K = equilibrium constant ($[NO_3^-] = 1M$)

Equations 1 and 2 summarize the chemical equilibria associated with trilaurylamine extraction of HNO_3.(7) The bar indicates organic phase species. Assuming that HNO_3 transport occurs at steady state and that concentration gradients are linear, the following expressions apply to aqueous diffusion film flux, J_a, and the equivalent membrane flux, J_o:

$$J_a = (D_a/d_a)\,([H^+] - [H^+]_i) \quad (3)$$

$$J_o = (D_o/d_o)\,[\overline{TLAHNO_3}] \quad (4)$$

where:

D_a = diffusivity of HNO_3 in the aqueous solution

d_a = thickness of the aqueous boundary layer

D_o = diffusivity of $TLAHNO_3$ in the organic solution

d_o = membrane thickness

$[H^+]_i$ = the HNO_3 concentration at the aqueous feed-membrane interface.

If the reaction kinetics are instantaneous and diffusion resistance through the strip solution boundary layer is negligible, the following equation is obtained:(1)

$$J = \frac{K[\overline{TLA}]_e\,[H^+]}{K[\overline{TLA}]_e\,(d_a/D_a) + (d_o/D_o)} \quad (5)$$

For a continuous system the flux is defined as:

$$J = \frac{-d[H^+]V}{d\tau A} \tag{6}$$

where:

τ = residence time

V = volume holdup in the tubes

A = liquid membrane area (membrane area x porosity)

At relatively high HNO_3 concentrations, uncomplexed TLA, $[TLA]_e$, approaches zero, and Equations 2 and 5 may be simplified and integrated to yield:

$$[H^+]_{in} - [H^+]_{out} = \frac{-[\overline{TLAHNO_3}]D_O A\tau}{d_O V} \tag{7}$$

Permeability for this system is given by:

$$P = \frac{J}{[H+]} = \frac{-[\overline{TLAHNO_3}]\ D_O}{[H^+]\ d_O} \tag{8}$$

Equation 7 demonstrates that at constant temperature (constant D_O) and at relatively high nitric acid concentrations, the acid flux is constant once steady flow conditions are established.

A plot of $[H^+]_{out}$ versus τ yields a straight line of slope

$$\frac{-[\overline{TLAHNO_3}]\ D_O A}{d_O V},$$

which is directly proportional to permeability and flux. Figure 4 presents test data that demonstrate this concept for three different experimental runs. As expected, the slope of the characteristic curve is unaffected by flow rates once flow is well established. The diffusivity of the acid-loaded carrier is estimated at 3.6×10^{-5} cm²/s for curves b and c, and is proportional to the slope. The characteristic curve for extraction of HNO_3 from concentrated solution (>1 x 10^{-3} mol/L HNO_3) using TLA, reported by Danesi and Cianetti was also linear.(7) However, for weak acid solutions, Danesi and Cianetti showed a logarithmic relationship between acid concentration and time:(7)

$$\ln = \frac{[H^+]}{[H^+]_O} = -(Q/V)P\tau \tag{9}$$

$$P = \frac{J}{[H^+]} = \frac{K[\overline{TLA}]_O}{K[\overline{TLA}]_O\ (d_a/D_a) + (d_O/D_O)}$$

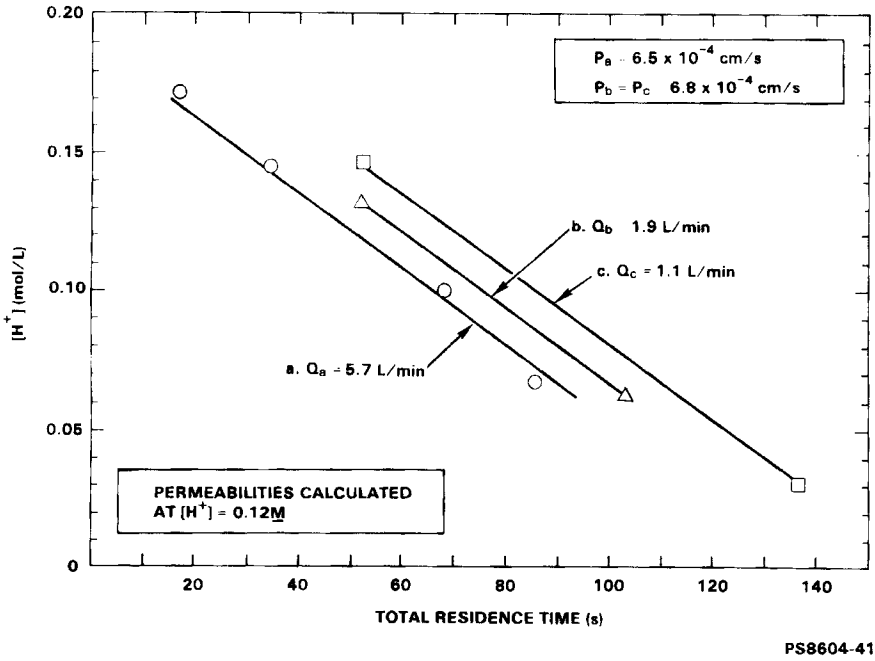

FIG. 4. Supported liquid membrane extraction of nitric acid with trilauryl amine.

Diffusion for weak acid solutions is, therefore, controlled by both film and membrane resistances as compared to diffusion resistance in only the membrane for strong acid solutions.

As a result of using relatively high HNO_3 concentrations, water is extracted from the shell side to the tube side of the SLM module. This was demonstrated during pilot-scale SLM tests. The feed solution used was initially 1M $NaOH_3$ and ~0.2M HNO_3, and the strip solution was 1M NaOH. As the extracted HNO_3 partially neutralized the NaOH, water was extracted to maintain the NaOH concentration in the strip solution and decrease the $NaNO_3$ and HNO_3 concentrations in the feed solution. Table 1 illustrates this water transfer behavior for three different test runs.

Strontium Extraction

Strontium extraction was demonstrated to give an indication of the possible usefulness of the SLM extraction system. Extraction conditions were not optimized, and the test was not intended to investigate parametric effects. Prior to testing, the TLA/n-dodecane was removed

TABLE 1
Water Transfer from Shell to Tube Sides

Flow rate (L/min)	Acid extracted (mol)	Water removed (L)
1.1	11.27	10.0
1.9	14.91	10.0
5.7	11.79	11.0

from fiber walls, and a 0.10-mol/L solution of D2EHPA in n-dodecane was added as previously described. A single test was then performed with (nominal) 0.01 mol/L Sr^{2+} in weak nitric acid (pH 6.4) feed using dilute nitric acid (pH ~1.5) strip solution. Results using a feed rate of 1.9 L/min and an equal counterflow strip rate showed that 0.01 mol Sr^{2+} extracted in one pass with a residence time of 51.5 seconds. Permeability of the membrane module was not estimated because not enough data points were available to define the characteristic curve. An estimated 0.02 mol H^+ back-extracted from the shell to the tube side of the SLM module, which was to be expected for the ion exchange reaction characteristic of this system. Further tests are warranted to optimize conditions and develop firm strontium diffusion data.

CONCLUSIONS AND RECOMMENDATIONS

The use of SLMs as potential solvent extraction equipment for deacidification has been demonstrated. Advantages of using SLMs as compared to other solvent extraction equipment include the following:

- Extraction and stripping operations in a single stage
- No moving parts
- Reduced solvent inventory
- Ease of operation

Disadvantages of using SLMs include:

- Limited resistance to strong acids
- Limited resistance to high radiation fields
- Absence of continuous solvent cleanup.

The SLM extraction of nitric acid may be accurately predicted by mathematical models. Module hydrodynamic performance can be sufficiently well determined using classical fluid flow calculations and mass transfer performance can be mathematically modeled by applying diffusion theory and chemical reaction kinetics. The correlations established for continuous nitric acid extraction across a pilot-scale

SLM were similar to those established for laboratory-scale batch systems.(7) Thus, scale-up effects appear to be minimal and a significant part of development efforts for deacidification occur on the laboratory scale.

As a result of the pilot-scale evaluation of a SLM module, the following recommendations can be made.

- Impregnate the membranes with organic solution prior to installation in the system in order to minimize the organic volume required and simplify the operation.
- Minimize the shell volume with respect to ΔP to reduce the amount of organic solution required for impregnation.
- Increase the surface area of a module by increasing the number of tubes rather than by increasing the length of each tube. This minimizes the possibility of developing a pressure gradient between the tubes and shell (or vice versa) sufficient to force the organic solution out of the membrane pores.
- When in production, provide interlocks to prevent the differential pressure between the tubes and shell from freeing organic solution out of membrane pores.
- Install the module vertically to ensure simultaneous flow through all the tubes for full utilization of the surface area.
- Optimize the rate of mass transfer by minimizing membrane wall thickness while maintaining a practical maximum allowable differential pressure between the tubes and shell.
- The rate of mass transfer may be optimized by a viable mathematical model. For example, Equation 7 shows that the rate of mass transfer can be improved by the following:
  - Maximizing the concentration of the (complexed) carrier relative to the diluent
  - Increasing the diffusivity of the complexed carrier in the diluent by elevating the temperature within practical limits
  - Increasing the surface area to tube holdup volume ratio by minimizing the tube diameter
  - Maximizing the residence time by decreasing feed rates, increasing the holdup volume(s), adding recycle, etc., as practical.

Work performed thus far indicates that batch applications screening may be successfully performed on the laboratory bench scale, and

that accurate modeling and verification testing on continuous pilot scale can result in optimization of important variables.

Future plans may include the use of SLM extraction of inorganic acid from aqueous process effluents, the presence of which is a potential problem in many chemical operations. Work completed thus far has demonstrated that SLM extraction is feasible for such applications.

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