Solvent Extraction and Gas Absorption Using Microchannel Contactors

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Abstract

Microchannel devices offer many technical advantages over conventional technologies for chemical separations. The overall objective for microchemical separations is to achieve extremely high throughput per unit hardware volume by engineering devices with high contact area to volume ratios, micro-thin films, and uniform flow distribution. Pacific Northwest National Laboratory's proprietary sheet architecture is being used to construct microchannel devices consisting of channels that are 50 to 500 μm deep and separated by porous contactor plates. Rapid mass transfer occurs between immiscible fluids, both gases and liquids, as they flow through the channels. By immobilizing the interface, both co-current and counter-current flow are achieved. The resulting improvements in heat and mass transfer rates through the devices result in dramatic improvements in productivity and efficiency.

Devices have been fabricated and tested for both solvent extraction and gas absorption. Data are presented for cyclohexanol extraction from water, carbon dioxide absorption into diethanolamine, and carbon monoxide and carbon dioxide absorption into copper ammonia formate solutions. Mass transfer models based on first principles have been developed for co-current and counter-current flow for solvent extraction and gas absorption. Such predictive models are useful for evaluating the relative importance of resistances to mass transfer, predicting full-scale performance, and comparing microchannel separators with conventional technologies. Experimental data are compared with theoretical prediction.

Applications for microchannel separations technology include radiochemical processing; cleanup of fuel-cell feed gases; in situ resource utilization for space exploration; recovery and sequestration of carbon dioxide for carbon management; and other separations of interest to the chemical, environmental, and pharmaceutical industries.

1 Introduction

Concepts are being developed to provide capabilities for engineering and fabricating devices containing channels and wall-thicknesses that are 100 μm deep or less with features as small as 1 to 10 μm. These capabilities allow engineering of chemical processes in devices that are orders of magnitude smaller than conventional chemical process equipment. The advantage arises from highly uniform flow distribution at micron length-scales, giving extremely rapid heat and mass transport rates that result in very short residence times and high throughput per unit hardware volume [1-3]. Progress in developing microtechnology for all traditional chemical processing unit operations, including heat exchangers [4], reactors [5] separators [6,7], and actuators [8,9], will facilitate miniaturization of entire chemical processes. Although traditional economies of scale are not realized with microtechnology, the potential exists for economies of mass production [10,11] analogous to the dramatic reductions in manufacturing costs experienced in the microelectronics industry.

Microchannel contactors are being developed that allow for rapid contacting of two immiscible fluids to facilitate chemical separations. Figure 1 illustrates the concept for solvent extraction in a simple two-channel geometry. The solvent and raffinate streams flow through separate channels separated by a micro-porous

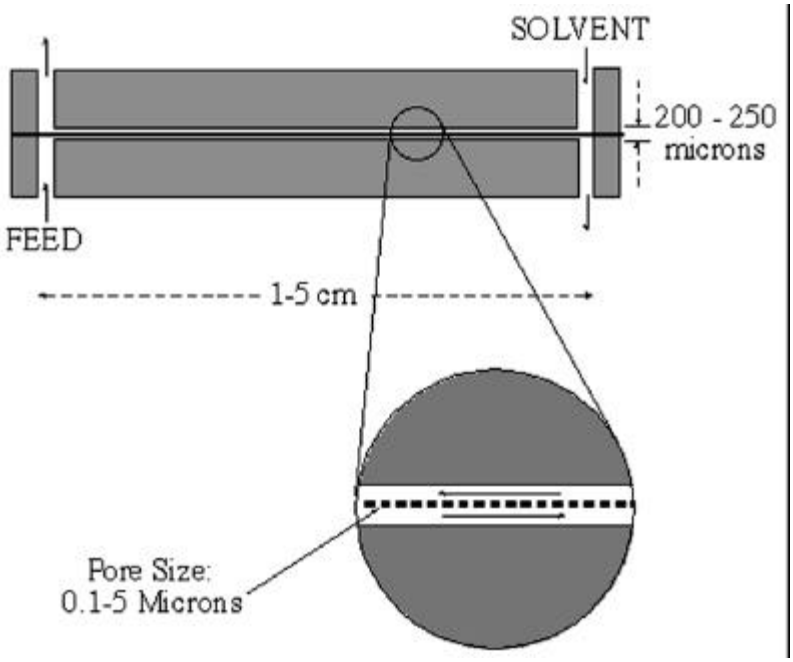

Figure 1. Representation of microchannel architecture for chemical separations

contactor plate, which allows for either co-current or counter-current operation. The channel heights are on the order of 100 μm, the micro-porous plate is 10 to 50 μm thick, and the channel length is typically 1 to 20 cm. The concept is scaled-up to multi-channel devices with high overall volume efficiency using Battelle's proprietary sheet architecture [12,13].

Although the contactor plate facilitates counter-current operation, it also adds mass transfer resistance, which can be minimized by reducing thickness, increasing porosity, or reducing tortuosity. Tortuosity is eliminated by microfabricating cylindrical or conical holes in thin substrate materials. Interfacial forces immobilize the fluid-fluid interface within the pores of the contactor plate, and the maximum pressure difference that the contactor plate can support without breakthrough is a function of pore size, contact angle, and interfacial tension. Pressure differentials ranging from several inches to tens of inches of water column are typical. Breakthrough pressure constrains the operating range of the microchannel contactors.

The most promising near-term applications for microchannel based separations are for cases where size and/or weight are extremely significant. NASA's In Situ Resource Utilization (ISRU) program is planning near-term missions to Mars that will include chemical processes for converting the carbon dioxide and possibly water in the Martian environment to propellants, oxygen, and other useful chemicals [14]. The launch mass of future missions will be dramatically reduced by not having to bring all of the resources necessary for the visit and the return flight from earth. Obviously, extraterrestrial chemical plants will need to be compact, lightweight, efficient and able to operate reliably for prolonged periods in reduced gravity environments. A second example is the development of fuel-cell powered vehicles by the Office of Transportation Technology of the U.S. Department of Energy. One approach for supplying hydrogen to the fuel cell is to reform gasoline or methanol on board. Two important challenges for microchemical separations are scrubbing of sulfur and carbon monoxide, which are catalyst poisons. A final example where size is important due to the impact on costs is in the treatment of high-level radioactive wastes, such as the waste stored in tanks at the Hanford site in Eastern Washington State. Reducing the size of the equipment required to process the waste has enormous cost savings potential due to infrastructure and other scaled costs.

2 Theoretical

Three parameters are useful for characterizing the performance of microchannel contactors for a given application. Mass transfer performance is characterized by the inverse of the mass transfer Peclet number defined as

$$\frac{1}{\mathrm{Pe}_m} = \frac{w\, L\, D_s}{Q\, h} \tag{1}$$

that is used for both the solvent and raffinate channels. Here, w is channel width, L is channel length, D_s is the solute diffusion coefficient in the solvent or raffinate

phase, *Q* is flowrate of the solvent or raffinate phase, and *h* is channel height. The inverse of the Peclet number is used because a larger value corresponds to greater mass transfer.

The second performance parameter is residence time, which is a metric for the size of the device;

$$T_R = \frac{w\ h\ L}{Q} \tag{2}$$

The final performance parameter reflects the constraint on the maximum pressure drop across the contactor plate, referred to as the breakthrough pressure. For counter-current flow, the minimum breakthrough pressure required is equal to the sum of the pressure drops along the lengths of the raffinate and solvent channels. Using the pressure drop equation for 2-dimensional Pouiseille flow in a closed channel, the pressure drop scales by the relationship

$$\Delta P \propto \frac{L\ Q}{w\ h^3} \tag{3}$$

These three scaling parameters are used to size and scale the microcontactor architecture for a given application, as described below.

Performance of microcontactor devices can also be predicted more precisely using numerical solutions of the transport equations with the appropriate geometry and boundary conditions [7]. These equations are solved as an initial value problem for co-current flow using the Crank-Nicholson [15] implicit method of finite differences, and as a boundary value problem for counter-current flow. Solutions are used for comparison to experimental results, predicting full-scale performance, and comparing microchannel separators to conventional technologies.

The design objectives for applying the microchannel technology to solvent extraction are to achieve the desired separation requiring a given number of theoretical stages and minimize equipment size while not exceeding the breakthrough pressure constraint for the contactor plate. To allow size comparison between microchannel hardware and conventional technologies, a size metric defined as the residence time divided by the theoretical number of stages is adopted that is analogous to the height equivalent of a theoretical plate (HETP) [16].

A design procedure is followed where first an operating point is selected at a given channel height, channel length, and flow rate that will accomplish the required separation while meeting the ΔP constraint. From this operating point, the flow rate (Q) and the inverse of the channel length (1/L) are varied proportionally while keeping the channel height constant to maintain a constant pressure drop. A flow rate and channel height combination is selected that will accomplish the required separation. The second step of the design procedure is to vary the parameters such that the pressure drop and Peclet number are kept constant. This is achieved by decreasing the flow rate (Q), the square root of the

channel length ($L^{1/2}$) and channel height (h) proportionally in order to further miniaturize final device. The mass transfer resistance of the contactor plate will become more significant as the other dimensions are reduced, causing a decrease in the number of theoretical number of stages, which can be corrected by returning to step one of the procedure.

The procedure has been applied to the extraction of acetone from water using 1,1,2-trichloroethane. Theoretical predictions result in a design point for 8 theoretical stages of separation that corresponds to a channel height of 50 μm, a channel length of 4.5 cm, and a flow rate of 0.07 ml/min per cm of channel width. This design point gives a 2.4 second residence time per theoretical stage for the raffinate stream, and an HETP of only 0.6 cm.

Table 1 compares the predicted performance of microchannel devices to conventional solvent extraction technologies for acetone extraction into 1,1,2-TCA. The flow capacity decrease is more than offset by the reduction in the HETP, resulting in a potential order of magnitude reduction in hardware volume when compared to high-efficiency structured packing. As much as two orders of magnitude size reduction is possible over conventional sieve tray columns.

3 Experimental Data

Both solvent and gas absorption experiments have been performed using microchannel contactor test devices. Experimental data have been collect for the extraction of cyclohexanol from water using cyclohexane as the solvent, and for extracting acetone from water using 1,1,2-trichloroethane. Gas absorption experiments experiments have included the removal of carbon dioxide from a mixture of CO_2 and N_2 using diethanolamine (DEA) solutions as the absorbent, and for scrubbing CO from a H_2 rich stream using copper ammonia formate solutions.

Table 1. Comparison of microchannel contactor performance to conventional technologies

	Capacity [$cm^3/cm^2/s$]	HETP [cm]	T_{res}/Stage [sec]
Sieve Trays	1	100-250	100-250
Structured Packings	0.8-5	20-180	10-80
Microchannels	0.2	0.25-5	1-20

Data are presented in Figure 2 for the extraction of acetone from water using 1,1,2-TCA. The same device and contactor plate are used in both co-current and counter-current flow configuration. As the flow rates are decreased, equilibrium effluent concentrations are approached in co-current operation, while counter-current flow is able to achieve greater than one theoretical stage. The data are also compared to predicted performance in Figure 2. In both flow configurations, actual performance does not meet expected performance, possibly due to non-

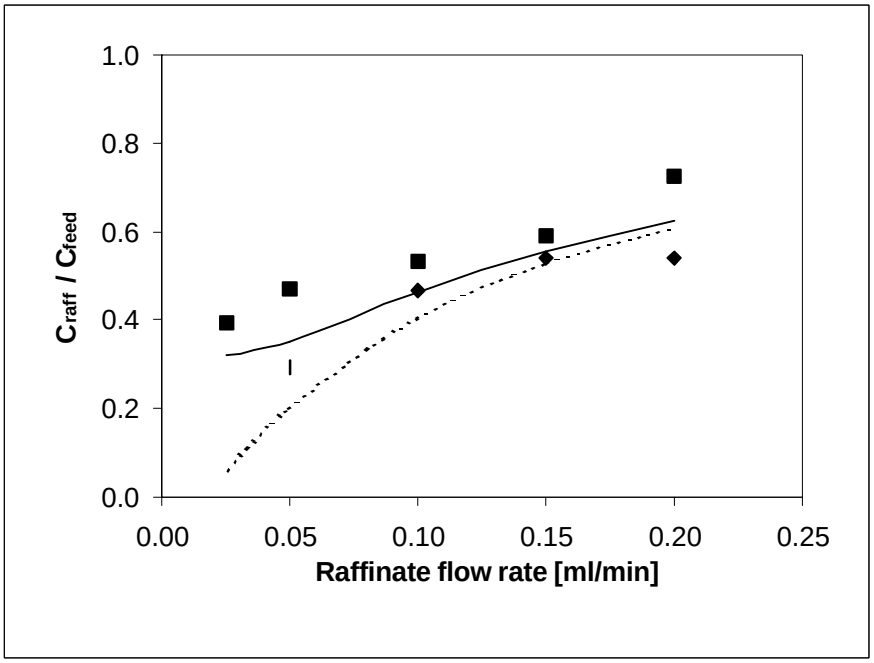

Figure 2. Raffinate to feed concentration ratio as a function of flow rate in the extraction of acetone from a 1 g/L aqueous solution using 1,1,2-trichloroethane as the solvent; equal flow rates; 240 μm deep, 8 cm long flow channels; and a 180 μm thick contactor plate in co-current flow (■) and counter-current flow (◆). Finite difference solutions of the transport equations are shown for co-current (—) and counter-current (- - -) flow.

idealities, such as poor flow distribution, or errors in physical parameters, such as diffusivities, channel dimensions, or in the equilibrium distribution coefficient.

Figure 3 illustrates the performance of microchannel devices in gas absorption. Over 90% of the carbon dioxide is removed in less than 10 seconds from a stream containing 25% CO_2. Increasing the concentration of absorbent molecule, in this case DEA, is shown to have diminishing returns. Similar results have been obtained using copper ammonia formate solutions to scrub CO from a H_2 rich stream, where CO is reduced from 1% to less than 10 ppm in 1.3 seconds gas residence time from a stream also containing 25% CO_2 and 4% H_2. Over 99% of the CO_2 was also removed with only 10% loss of H_2 hydrogen.

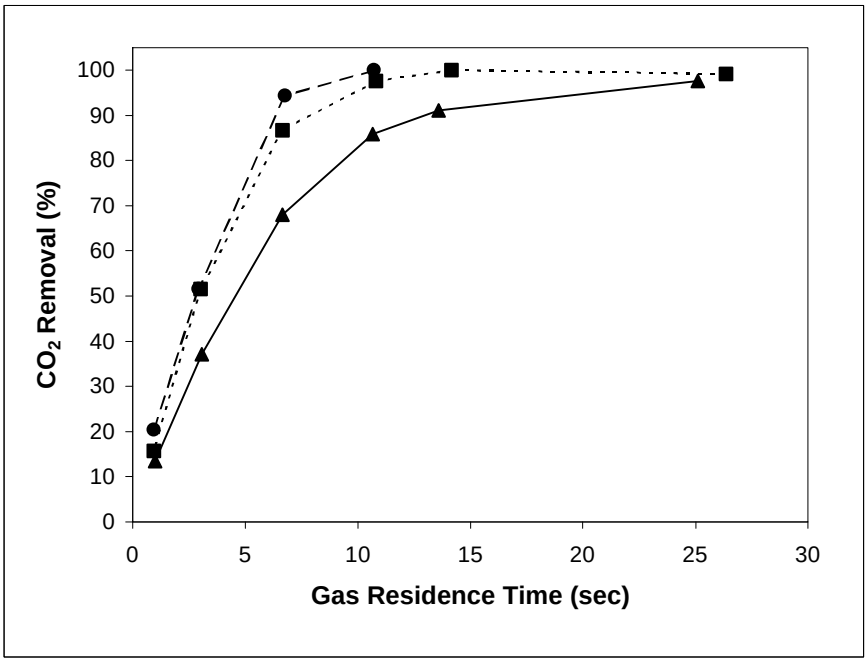

Figure 3. Absorption effectiveness as a function of gas residence for removal of CO_2 from a 25% CO_2 and 75% N_2 gas stream into a 10% diethanolamine solution (▲), 20% diethanolamine solution (●), and 40% diethanolamine solution (■) at a liquid residence time of 26 seconds.

4 Summary

Miniaturizing chemical separations equipment by an order of magnitude or more is likely through the development of microchannel contactor technology. Progress is being made to reduce the residence time per theoretical stage for solvent extraction and other applications to 1 second, with values for the height equivalent of a theoretical plate (HETP) approaching a fraction of a centimeter. Data have been presented illustrating performance of microchannel test devices for solvent extraction and gas absorption. The most likely applications for near-term market penetration are cases where reduced size and weight can have an enormous impact.

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