

INTEGRATING NEW SEPARATIONS TECHNOLOGIES INTO THE UNDERGRADUATE CURRICULUM

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Chemical engineering educators strive to prepare their students for a professional career that may well extend forty years into the future. One way to meet this demand is to introduce emerging separations technologies into the undergraduate curriculum. This increases the value of the students' undergraduate education since they acquire knowledge in subjects that practicing engineers may not be familiar with and which may become important during their professional lives.

One method of introducing new separations technologies is to develop problems using processes developed at the U.S. Bureau of Mines. Its Office of Technology Transfer publishes information on processes that have been developed on a laboratory scale and that are available for licensing. This information is in the public domain, and enough data is provided to perform scaleup calculations. Three problems have been developed using this approach. The first, "Pilot Plant to Leach Platinum from Catalytic Converters," was presented in this journal.^[1] In it, Joe Agman, Jr., owns a chemical plant that recovers silver from used photographic material. He is interested in diversifying and hires a student to design and test a pilot plant to learn more about leaching platinum from used catalytic converters. The problem was first assigned in a reactor design course at Stevens Institute of Technology several months before it was announced that the process had been licensed and commercialized.^[2,3] The students in the class were proud to know that they had

tackled a problem practicing engineers were working on.

Two additional problems and their solutions are being presented in this paper. The problems are presented in a personal format. Additional information of industrial significance is included in the problems to create an interesting and believable scenario.

Problem 1

Plutonium Recovery from Wastewater Using Metalloprotein Affinity Metal Chromatography^[4-7]

This problem requires mass balances for scaleup of a process to recover plutonium from wastewater generated at a former nuclear weapons production facility, using a state-of-the-art chromatography technique. It can be assigned in an introductory chemical engineering or separations course.

Imagine you like to live dangerously. You enjoy sky diving and driving race cars. As a student, you always waited until the night before exams to start studying. You have just accepted employment as a site remediation engineer at the 560-square-mile Hanford nuclear site located in south-central Washington. Plutonium for nuclear weapons was produced here from 1943 to 1987, resulting in 1100 waste sites. Highly radioactive waste was stored in tanks, but between 1946 and 1966, low-radiation-level liquid waste was *intentionally* discharged to the soil. As a result, there is a 150-square-mile plume of hazardous chemicals and radionuclides, and billions of cubic meters of contaminated soil. More than 60 million gallons of highly radioactive waste have accumulated in 177 tanks. Sixty-eight of the single-shell tanks have or are suspected of leaking (double-shell tanks were used starting in 1968). Little documentation is available.^[4] While most people would be nervous about working in this environment, you are pleased by the apparent job security—



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there is enough radioactive waste to last your whole career!

Your first assignment is to design a pilot plant to study the feasibility of recovering plutonium from aqueous waste streams. You will be scaling up a process, metalloprotein affinity metal chromatography, developed at the University of Alabama and funded by the U.S. Bureau of Mines.

Background • Affinity chromatography is a separation technique where a solution passes through a packed bed filled with a porous stationary solid. The material to be separated is adsorbed (attached) to the solid, while the remainder of the solution passes through the column. To recover the material, solvent conditions are altered so that the separated material desorbs from the solid. Typical solid supports are characterized by large surface areas and include silica, alumina, polymers, and carbohydrates such as cellulose and Sepharose. The adsorption properties of all these solid supports can be modified by bonding different molecules, or ligands, to their surface. Many researchers in this area use Sepharose because it is commercially available and has a successful history.^[5]

Metalloproteins are biological molecules that selectively and stoichiometrically bind to metal ions under certain conditions. This selectivity is the result of millions of years of biological engineering due to evolution. Changes in pH, salt concentration, etc., can cause the metal ions to be released.

The metalloprotein transferrin is involved in Fe^{3+} transport in living organisms. It is found in blood serum, milk, and eggs. Transferrin preferentially binds to the ferric ion, but will also bind to Cr^{3+} , Cu^{2+} , Mn^{2+} , Co^{3+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , numerous trivalent lanthanides (including holmium), Th^{4+} , and Pu^{4+} (tetravalent plutonium ion, form of plutonium found in contaminated water). Transferrin is available commercially as conalbumin—egg white transferrin.^[6,7]

In this problem, the transferrin is covalently bonded to the porous solid support Sepharose. The solid is loaded into a column, and a solution containing plutonium ions passes through the column. The plutonium ions are preferentially and stoichiometrically adsorbed by the transferrin, which has been immobilized onto the solid. A flow diagram of the adsorption step is presented in Figure 1a. To recover the plutonium from the column, a solution with a low pH is passed through the column, causing the plutonium to desorb. A flow diagram of the desorption step is presented in Figure 1b. The plutonium is thus removed from the initial solution and concentrated using metalloprotein affinity metal chromatography. The column can be repeatedly reused.

Procedure • The metalloprotein transferrin was first immobilized to the solid support, CNBr-activated Sepharose B, purchased from Pharmacia Biotech Inc. The manufacturer's recommended procedure was followed.^[6,7] Specifically, 2.0 gm of transferrin was immobilized on 15 gm of CNBr-activated Sepharose B.

In laboratory-scale feasibility experiments, holmium was recovered from solutions rather than plutonium, for safety considerations. For scaleup, assume 1 mole of plutonium is adsorbed for every 1 mole of holmium salt adsorbed. It was found that this column could adsorb the holmium found in 50 mL of a solution into which 45.3 gm $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved.

A buffered solution at a lower pH (pH=4) was used to

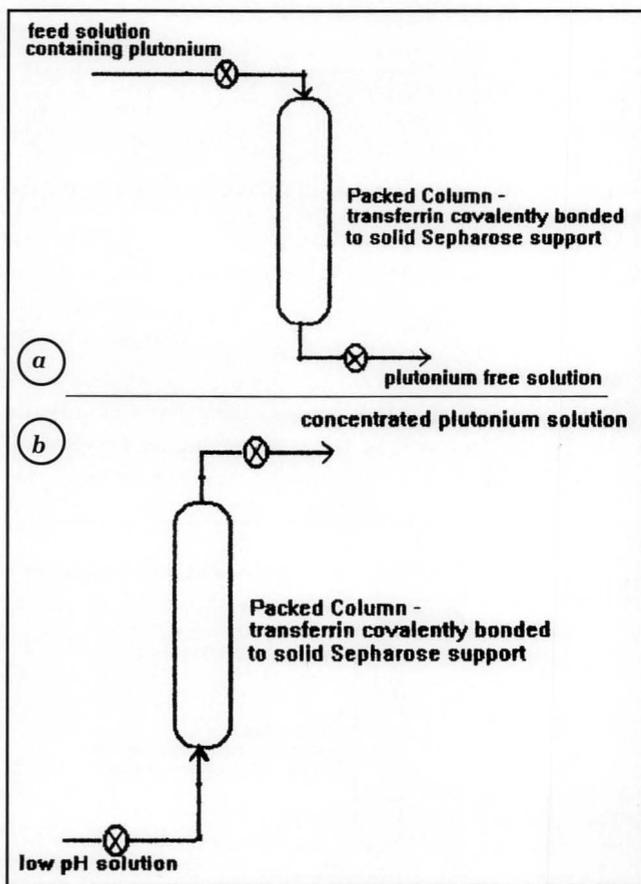


Figure 1

- (a) Flow diagram for adsorption of plutonium
(b) Flow diagram for desorption of plutonium using low pH solution.

desorb and recover the holmium. All the holmium was desorbed into 0.8 mL of this solvent.

Assignment • You will be designing a pilot plant to concentrate the plutonium solutions found in the single-shell tanks. The volume of solution in these tanks is 530,000 to 1,000,000 gallons. You wish to process 40-gallon batches of the solution. Assume the feed concentration is $16.3 \text{ gm}^{239}\text{Pu}^{4+}/\text{L}$. A schematic diagram of the system is presented in Figure 2.

- How many grams of transferrin should be immobilized onto the solid support?
- How many grams of solid support CNBr-activated Sepharose B will you need?
- Suppose 1 gm of ^{239}Pu desorbs into 0.5 mL of low-pH solvent. For a tank initially containing 1,000,000 gallons, estimate the final volume. The density of plutonium is 17.14 gm/cm^3 .

Solution

a Since plutonium and holmium both bond stoichiometrically to the transferrin, the grams of transferrin need is

$$\frac{(2 \text{ gm transferrin})(440)}{(45.3 \text{ gm Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O})(239)} \left(\frac{16.3 \text{ gm Pu}}{\text{L}} \right) \left(\frac{3.783 \text{ L}}{\text{gal}} \right) (40 \text{ gal}) = 201 \text{ gm transferrin} \quad (1)$$

Note the molecular weight of the holmium salt is 440 and the atomic mass of the plutonium ion is 239.

b The mass of CNBr-activated Sepharose needed is

$$\left(\frac{15 \text{ gm Sepharose}}{2 \text{ gm transferrin}} \right) (201 \text{ gm transferrin}) = 1504 \text{ gm} \quad (2)$$

c The concentrated volume of a tank that was initially 1,000,000 gallons will be the volume due to the solution and the volume of the plutonium, assuming perfect solu-

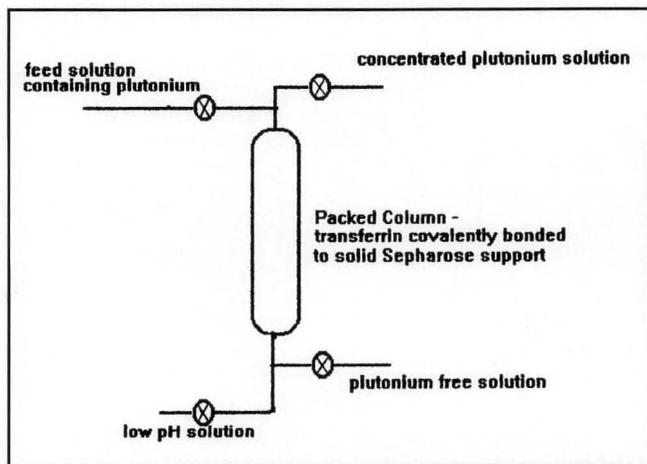


Figure 2. Schematic of adsorption column.

tion behavior:

$$\left(\frac{0.5 \text{ mL}}{\text{gm Pu}} \right) + \left(\frac{1 \text{ mL}}{17.14 \text{ gm Pu}} \right) \left(\frac{\text{L}}{1000 \text{ mL}} \right) \left(\frac{16.3 \text{ gm Pu}}{\text{L}} \right) \left(\frac{3.785 \text{ L}}{\text{gal}} \right) (1 \times 10^6 \text{ gal}) = 39,850 \text{ gallons} \quad (3)$$

A substantial reduction in volume is achieved.

Problem 2

Design of a Novel Froth Flotation System for Coal Purification^[8-17]

The second problem requires some of the calculations necessary to scale up a process to recover coal fines from an aqueous slurry. It can be assigned in an introductory chemical engineering, senior design, or separations course. Industrial applications of froth flotation include the initial concentration of copper, lead, zinc, molybdenum, phosphate, potash, nickel, fine coal, and other mineral commodities from ores, de-inking of paper for recycling, and wastewater treatment.^[8-12] Froth flotation is a separation technique that is mentioned in commonly used undergraduate chemical engineering texts,^[13,14] but is not usually studied in detail.

You are employed at a mid-sized company involved in coal cleaning. In your area of the plant, coal is recovered from an aqueous slurry containing finely sized solids. These solids are 82 wt.% coal, 18 wt.% ash. The coal is purified and

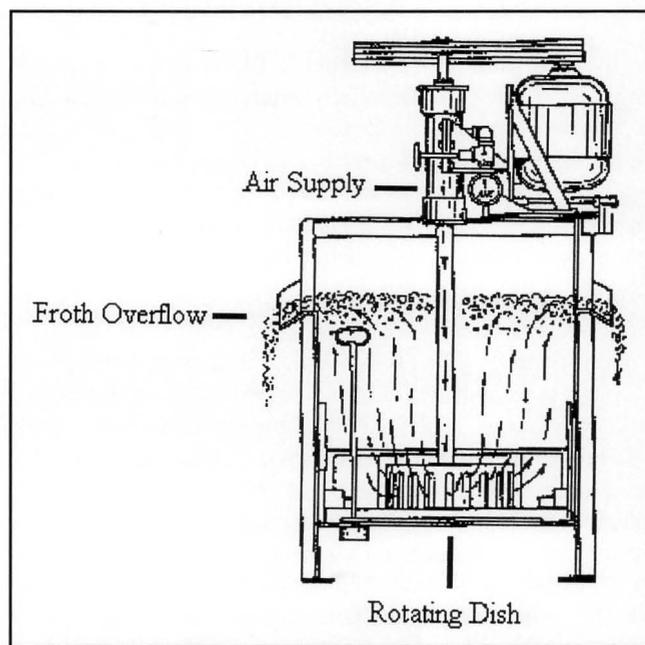


Figure 3. Agitair flotation system^[8]

recovered by froth flotation. Froth flotation is a separation technique for separating solids or oils in an aqueous solution based on differences in hydrophobicity. In this process, the feed stream is agitated and air is bubbled through the solution. A froth forms that rises to the surface. The hydrophobic coal particles tend to collect in the froth (bubble-to-particle attachment), while the more hydrophilic ash tends to stay in solution. The froth is then separated from the solution. A typical flotation unit is the Agitair flotation machine shown in Figure 3. Air is supplied through the pipe in the center of the vessel and is dispersed through the rotating disk at the bottom. The froth overflows at the top of the vessel.

One disadvantage of froth flotation is that it tends to be a slow process, with the bubble-to-particle attachment the rate limiting step. One way to increase the rate of bubble-to-

particle attachment is to increase the agitation, but this can dislodge the coal from the bubbles, reducing the yield. Because the bubble-to-particle attachment and the bubbles rising to the surface through the solution (called pulp) occur in a single unit, optimizing one step tends to hurt the other.

The plant owner would like to increase capacity, but space limitations present a problem. It is for this reason that you have been assigned the task of designing a froth flotation pilot plant capable of processing 50 gpm of liquid feed (not including air) to study a potentially more efficient system for froth flotation. Background information is given below.

Novel Froth Flotation System • The U.S. Bureau of Mines has recently developed a rapid froth flotation system that separates the flotation into two discrete units.^[12,15-17] This system allows optimization of both the bubble-to-particle attachment and the bubble-solution separation. It has been shown to be eighteen times faster than conventional froth flotation on a laboratory scale.

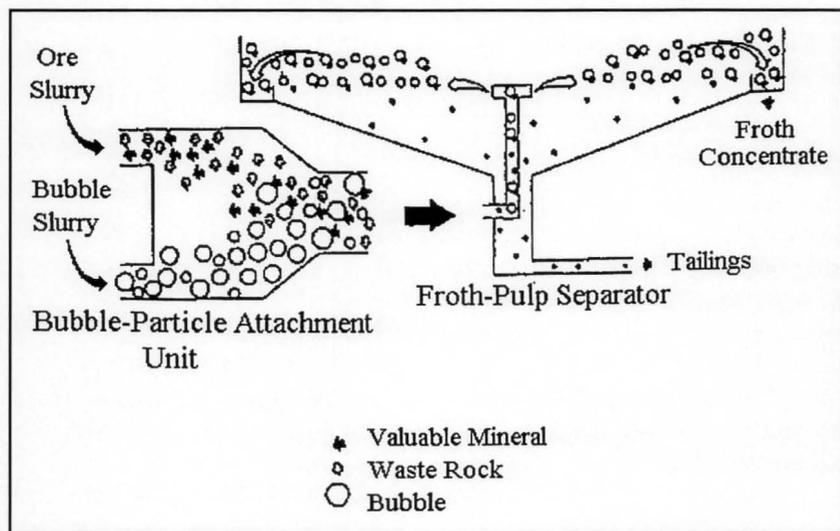


Figure 4. Schematic diagram of the rapid flotation system.^[12]

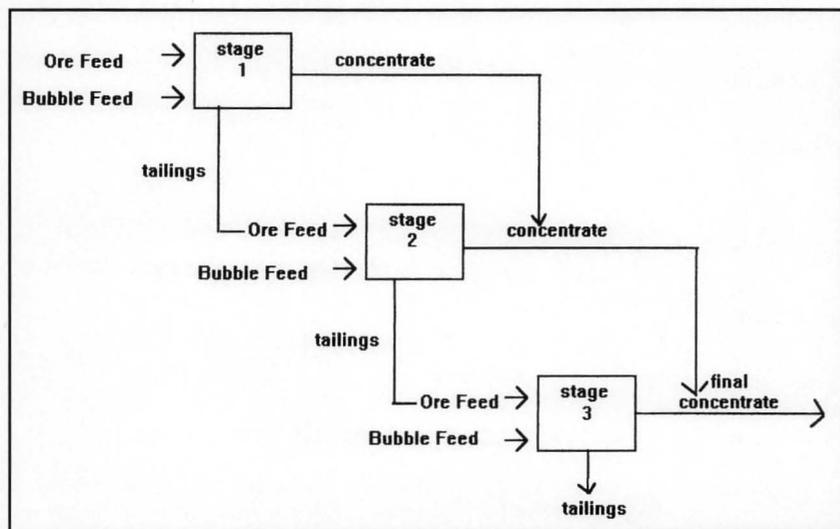


Figure 5. Schematic diagram of a three-stage continuous rapid flotation system.^[12]

A schematic of the process is shown in Figure 4. An in-line mixer is used for bubble-to-particle attachment. An in-line (or motionless) mixer is a generic term for a mixer with no moving parts. It consists of a pipe containing baffles that cause turbulence and hence mixing when liquids or gases pass through them. Downstream of the in-line mixer is a shallow-depth separator. In this unit the bubbles with the coal fines attached rise to the surface and froth forms. After the froth overflows, it is collected and the purified coal is recovered. This shallow-depth separator allows the bubbles to rise and the froth to overflow.

Process Description^[12] • A slurry from a coal cleaning operation and a bubble slurry (bubbles plus water) each enter the in-line mixer through opposite ends of a T-shaped fitting. Before mixing, the coal slurry is conditioned with 1 gm fuel oil per kg ore, for three minutes. The bubble slurry is generated by mixing air and water in a conventional flotation cell. The water is pretreated with 0.1 gm frothing agent, methyl isobutyl carbinol (MIBC), per kg ore. As mentioned previously, the resulting slurry is 5 wt.% solids, of which 82 wt.% is coal. The pH is adjusted to 8.2. The solution then enters three flotation units in series. The froth containing the coal concentrate is collected, and the tailings are sent to waste.

Scale-Up Data^[15] • Experiments per-

formed on a laboratory scale (5-29 L/min) using a three-stage flotation unit (see Figure 5) recovered 93 wt.% of the coal. At optimum conditions, the recovered product was 91.9 wt.% coal, 8.1 wt.% ash.^[9] Scaleup was found to be dependent on three parameters. These parameters and their optimal values are

1. Mixing intensity of the in-line mixture (4.9 watts per 1 L liquid feed/min)
2. Air to solids ratio (1.5 mL air (STP)/gm ore)
3. Bubble residence time; assume the surface area in all three flotation units is equal and the depth is 5.4 cm. The rate of flotation follows first-order kinetics. The percentage of recovery is given by

$$\% \text{ Recovery} = [1 - \exp(-kt_r)] (100\%) \quad (4)$$

where $k = 4.13 \text{ min}^{-1}$ is the first order flotation rate constant, and t_r is the total residence time of a particle in the flotation system (sum of all three stages). The residence time is determined by dividing the total volume of the flotation system by the flowrate.

Assignment • You are to design a pilot plant to study froth flotation using the process developed at the U.S. Bureau of Mines. The flowrate of feed is to be 50 gpm, and you are to recover 93 wt.% of the coal in the feed. The purity of the recovered solids is expected to be 91.9 wt.%. In order to accomplish this, please complete the following tasks:

Mass Balances

- 1 Calculate the optimum flowrate of air (STP) and the overall total flowrate (air plus solution). Assume the specific gravity of the ore is 1.6.
- 2 Calculate the expected yield of coal per 100 gal. of feed and the expected yield of solids.

In-Line Mixer Design

- 3 Estimate the pressure drop and the power requirements in the in-line mixers when the intensity of mixing is 4.9 watts per 1 L liquid feed/min of feed and the flowrate is 50 gpm of liquid feed.

Shallow-Depth Separator Design

- 4 Calculate the bubble residence time, t_r .
- 5 Calculate the total volume required for the shallow-depth separators.
- 6 Calculate the total surface area required for the shallow-depth separators.

Solution

- 1 The optimum flowrate of air is 1.5 mL(STP)/gm. ore. The flowrate of liquid feed is 50 gpm and it is 5 wt.% ore.

First, the mass of ore per volume of feed must be found.

Basis: 100 gm feed, containing 5 gm of ore.

The densities of water and ore are 1.0 and 1.6 gm/mL, respectively. The volume of water, V_{H_2O} , and ore, V_{ore} , may thus be taken as

$$V_{H_2O} = (95 \text{ gm}) \left(\frac{1 \text{ mL}}{\text{gm}} \right) = 95 \text{ mL} \quad (5)$$

$$V_{ore} = (5 \text{ gm}) \left(\frac{1 \text{ mL}}{1.6 \text{ gm}} \right) = 3.124 \text{ mL}$$

The mass of ore per volume liquid feed is thus

$$\frac{5 \text{ gm}}{95 + 3.125 \text{ mL}} = \frac{0.051 \text{ gm ore}}{\text{mL}} = 51 \text{ gm/L} \quad (6)$$

The optimum volumetric flowrate of air is thus

$$(50 \text{ gpm}) \left(\frac{3.785 \text{ L}}{\text{gal}} \right) \left(\frac{51 \text{ gm ore}}{\text{L}} \right) \left(\frac{1.5 \text{ mL air (SPT)}}{\text{gm ore}} \right) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 14.5 \text{ Lpm (STP) air} \quad (7)$$

The overall total volumetric flowrate, Q_{total} , is the sum of the flowrates of the coal slurry and bubble slurry:

$$Q_{total} = (50 \text{ gpm}) \left(\frac{3.785 \text{ L}}{\text{gal}} \right) + 14.5 \text{ Lpm} = 203 \text{ Lpm} \quad (8)$$

This calculation neglects any changes in the volume of the gas due to pressure.

- 2 The expected yield of coal is 93 wt.% of the coal in the feed. The feed ore is 82 wt.% coal. The expected yield of coal is thus

$$(50 \text{ gpm}) \left(\frac{3.785 \text{ L}}{\text{gal}} \right) \left(\frac{51 \text{ gm ore}}{\text{L}} \right) (0.82) (0.93) \left(\frac{1 \text{ lb}}{454 \text{ gm}} \right) = \frac{16.2 \text{ lb coal}}{\text{min}} \quad (9)$$

The solid product is 91.9 wt.% coal. The total weight of recovered solids is thus

$$\left(\frac{16.2}{0.919} \right) = 17.6 \text{ lb/min} \quad (10)$$

- 3 Since the pressure drop in the in-line mixer is the power supplied divided by the flowrate, determination of the in-line mixer simply involves manipulating the units of the

given mixing intensity:

$$\frac{(4.9 \text{ W})}{(1 \text{ L feed/min})} \left(\frac{\text{Nm}}{\text{sec-W}} \right) \left(\frac{14.7 \text{ psi}}{1.01325 \times 10^5 \text{ N/m}^2} \right) \left(\frac{60 \text{ sec}}{\text{min}} \right) \left(\frac{1000 \text{ L}}{\text{m}^3} \right) = 42.7 \text{ psi} \quad (11)$$

The power supplied by the mixer is the product of the power per volume times the volumetric flowrate. The power supplied is thus

$$\frac{(4.9 \text{ W})}{(1 \text{ L feed/min})} (50 \text{ gpm liquid feed}) \left(\frac{3.785 \text{ L}}{\text{gal}} \right) = 927 \text{ W} \quad (12)$$

4 To calculate the bubble residence time, use the flotation rate constant and the required recovery of 93%. Rearranging Eq. (4) to solve for t_r gives

$$t_r = \frac{[\ln(100)/(100 - \% \text{ recovery})]}{k} = \frac{[\ln(100)/(100 - 93)]}{4.13} = 0.644 \text{ min} \quad (13)$$

5 The total volume required in the shallow-depth separators is equal to the product of the overall total volumetric flowrate and the bubble residence time:

$$V_{\text{system}} = Q_{\text{total}} t_r = (203 \text{ Lpm})(0.644 \text{ min}) = 131 \text{ L} \quad (14)$$

6 Since the depth of the separators, h , is 5.4 cm, the required surface area, A , is

$$A = \frac{V_{\text{system}}}{h} = \frac{(131 \text{ L}) \left(\frac{1000 \text{ cm}^3}{\text{L}} \right) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^2}{5.4 \text{ cm}} = 2.4 \text{ m}^2 \quad (15)$$

CONCLUSION

Two problems for the undergraduate curriculum, using new separations techniques, have been presented using processes developed at the U.S. Bureau of Mines. Although the U.S. Bureau of Mines was closed last February due to budget cutbacks, other U.S. government agencies are actively involved in developing new technologies for commercial development, and data is in the public domain. This is a rich source of information for developing state-of-the-art problems. The other agencies include the U.S. Department of Agriculture and the Environmental Protection Agency.

To obtain copies of government-owned patents and patent applications, call (202) 260-7510.

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