The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and which elucidate difficult concepts. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu) or Mark A. Burns (e-mail: maburns@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

DESIGN OF A PILOT PLANT TO LEACH PLATINUM FROM CATALYTIC CONVERTERS

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The transition from academia to industry can cause much anxiety for students. The following problem can be assigned in kinetics and reactor-design courses after the completion of material on ideal isothermal batch reactors, plug-flow reactors, and continuous-flow stirred-tank reactors, or as a take-home problem in a senior design course.

This problem should demonstrate to the students that they have acquired the ability to solve real-life problems on a scale that they can visualize. It also points out the value of reference books and the complexity of design.

PROBLEM

Joe Agman, Jr., is the owner of a small chemical plant in Pennsylvania that recovers silver from used photographic material such as negatives and X-ray plates. After the coatings have been removed, the plastic strips are shredded and sold to a recycler.

Joe is worried that his business may become obsolete because the Environmental Protection Agency has declared silver to be a hazardous substance, and also because Polaroid and Kodak are researching selenium-based photography and pictures stored on CDs.

Joe would like to diversify, so he read with interest an article about a new process that the U.S. Bureau of Mines developed for recovering platinum-group metals (PGMs) from used catalytic converters. Platinum-group metals include platinum, palladium, and rhodium. Joe is seriously considering the purchase of license rights for the process, but first needs to perform pilot-plant studies to determine if he can make a reasonable profit on his investment.

Unfortunately for Joe, he never received his chemical engineering degree. His father owned the plant before he died, and Joe, knowing he had a guaranteed job, never worked very hard in college. He preferred to skip classes, ignore homework assignments, and watch reruns of the first *Star Trek.*

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Joe has hired you to design a pilot plant, then to supervise its operation. Pictorial information on the process is given in Figure 1.[1] For design purposes, you may assume that 100% of the PGMs are platinum and that one mole of NaCN complexes with one mole of Pt. The catalyst is 0.2 wt.% Pt, the remainder being mainly alumina (Al_2O_3), with trace contaminants such as Pb found in gasoline. The density of alumina is 3.9 gm/cm^3. The weight of catalyst in one catalytic converter is about 10 pounds.

You decide to recover the PGMs from a single catalytic converter in six hours so that work can be completed in one shift. First, you produce a flow diagram and equipment list, and then you contact vendors found in the *Thomas Register* to determine equipment costs. A technician will be hired to help you assemble and operate the pilot plant. You make a list of proposed experiments, develop a timetable, and submit a proposal and budget to Joe. He approves the project, and you begin to order equipment.

A screw feeder will supply the crushed catalyst and other solids to a leaching vessel, which is a batch reactor. The operations of crushing and feeding take about fifteen minutes. Ten pounds of water, adjusted to a pH of 10 with sodium hydroxide is next added to the leaching vessel. Twice the stoichiometric amount of sodium cyanide is then added

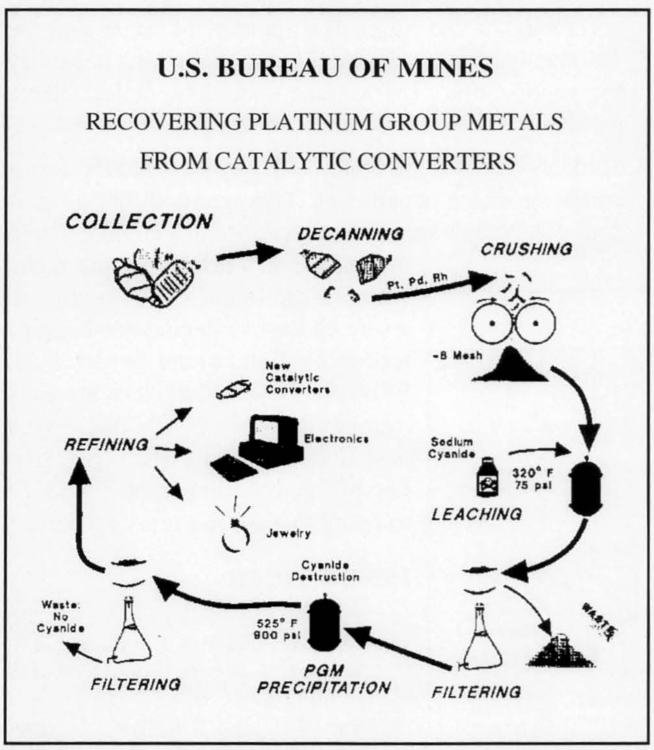

Figure 1. *Pictorial depiction of platinum recovery.*

(2 moles NaCN added per mole of Pt in the feed), taking an additional fifteen minutes. The catalyst is leached for one hour at 320°F, and virtually 100% of the platinum is complexed with the cyanide in solution.

The charge from the leaching vessel is then filtered and washed with another 10 pounds of water. The mother liquor and wash water are pumped into the precipitation vessel, taking another fifteen minutes. The contents of the precipitation vessel—which contains platinum-cyanide complexes and unreacted NaCN—are heated to destroy 99.99% of the NaCN and Pt-CN, causing the Pt to precipitate out of the solution. The destruction of the CN^- occurs according to the reaction

$$CN^- + 2H_2O \rightarrow NH_3 + HCOO^- \quad (1)$$

The rate of destruction of NaCN is known to be

$$-\frac{\partial[\text{NaCN}]}{dt} = k_1[\text{NaCN}] \quad (2a)$$

$$k_1 = 3.78 \times 10^8 \exp(-11{,}320/T(°K))\ \text{sec}^{-1} \quad (2b)$$

Tan and Teo[2] indicate that it takes longer to destroy the Pt-CN complex. The corresponding rate can be taken as

$$-\frac{\partial[\text{Pt}-\text{CN}]}{dt} = k_2[\text{Pt}-\text{CN}] \quad (3a)$$

$$k_2 = 5.0 \times 10^7 \exp(-13{,}720/T(°K))\ \text{sec}^{-1} \quad (3b)$$

The charge from the precipitation vessel is then filtered and washed, consuming yet another fifteen minutes. The precipitate is cyanide-free and contains 70 wt.% Pt, the remainder being inerts. The waste water is treated to remove lead and other impurities before being discharged.

You must

1. *Draw a flow diagram of the process. Where can you find the names of companies that sell equipment such as pumps?*
2. *Determine the size of the leaching vessel.*
3. *Decide whether the precipitation vessel should be a plug-flow reactor, a batch reactor, or a CSTR. Calculate the size of the vessel and the temperature that is needed to complete one batch in the specified time period. Estimate the vapor pressure, assuming that it is the same as saturated water at this temperature.*
4. *Determine what safety precautions you should take. Obtain a copy of the Material Safety and Data Sheets from the department.*

SOLUTION

1. The flow diagram is shown in Figure 2. The process is semi-automated—the operator must introduce solids and control the volume of distilled water added to the system. Temperature is controlled automatically, but the operator must initiate leaching, filtering, and precipitation, and must remove the solids from the filter. As already mentioned, students can locate companies that manufacture equipment such as pumps from the *Thomas Register.*

2. The leaching vessel should be large enough to accommodate the 10 pounds of crushed catalyst, the 10 pounds of water, and the added NaCN and NaOH. Since the volume of NaOH and NaCN are negligible, the corresponding volume is

$$V = 10\,\text{lb}\ H_2O\left(454\frac{\text{gm}}{\text{lb}}\right)\left(1\frac{\text{cm}^3}{\text{gm}}\right) + 10\,\text{lb}\ Al_2O_3(454)\left(\frac{1}{3.9}\right)$$

$$= 5,700\ \text{cm}^3 = 1.5\ \text{gal} \qquad (4)$$

a. To estimate the amount of NaOH required, note that at a pH of 10, $[OH^-] = 1 \times 10^{-4}$ M (gm moles/liter). Thus the moles or mass of NaOh to be added are

$$\left(1\times10^{-4}\ \text{M}\right)(10\ \text{gal})\left(3.785\frac{\text{liter}}{\text{gal}}\right) = 0.003785\ \text{gm moles} = 0.15\ \text{gm} \qquad (5)$$

b. The required amount of NaCN is

$$\left(0.002\frac{\text{gm Pt}}{\text{gm catalyst}}\right)\left(454\frac{\text{gm}}{\text{lb}}\right)(10\,\text{lb catalyst})\left(\frac{1}{195.08}\frac{\text{gm mole Pt}}{\text{gm Pt}}\right)$$

$$\times\left(49.007\frac{\text{gm NaCN}}{\text{gm mole NaCN}}\right) = 2.2\ \text{gm NaCN} \qquad (6)$$

Thus, the actual amount of NaCN added is twice this, or 4.4 gm.

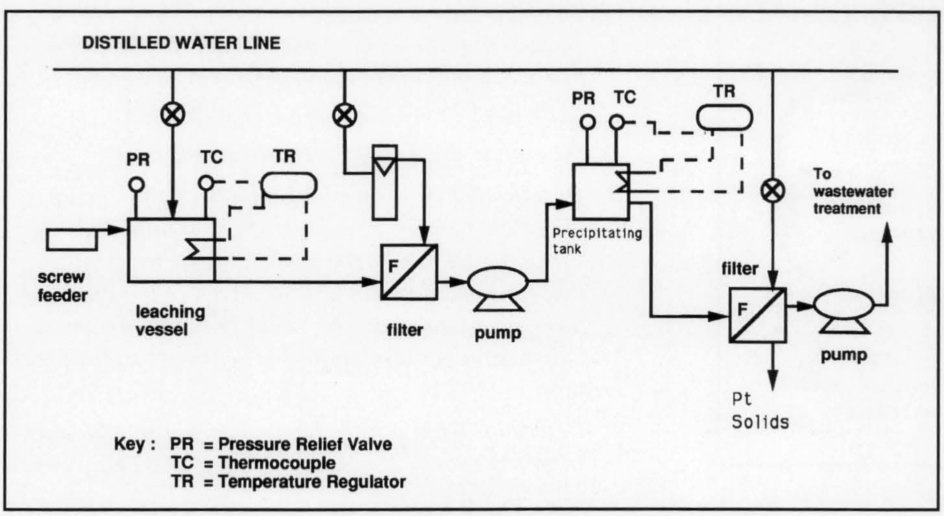

Figure 2. *Flow Diagram*

3. The two reactions must be considered independently. Since destruction of the Pt-CN complex is slower than destruction of the NaCN, and they are initially at the same concentration, destruction of the Pt-CN complex is the rate-limiting step. The residence time can be up to four hours when all steps are taken into account. For a batch reactor

$$t = -C_{A0}\int_0^x \frac{dx}{r_A} = C_{A0}\int_0^x \frac{dx}{k_2 C_A} = C_{A0}\int_0^x \frac{dx}{k_2 C_{A0}(1-x)} \qquad (7)$$

where

- t time (sec)
- C_{A0} initial concentration of Pt-CN (gm moles/liter)
- C_A concentration of Pt-CN (gm moles/liter) at time t
- x conversion (0.9999)
- $k_2(\text{sec}^{-1})$ given in Equation (3)

Integration, rearrangement, and solution yields a temperature inside the batch reactor of 547K or 525°F. From steam tables, the pressure in the precipitation vessel will be approximately 850 psia. The batch reactor is the best choice—too long a plug-flow reactor would be required for a residence time of four hours and the temperature in a CSTR would be above the critical temperature of water due to the high conversion required.

The precipitation vessel must be large enough to accommodate the original 10 pounds of water and the 10 pounds of wash water. Head space is also necessary for vaporization. The volume should be at least three gallons.

4. Students obtained the Material Safety Data Sheets from a computer in the department. They verified that no gaseous compounds were being produced that could increase the pressures. Vessels were designed with pressure-relief valves venting to a safe container. Recommended protective clothing would be obtained. From the safety data, the students learned that when NaCN reacts with acid it forms deadly HCN gas. On-line pH analysis should be employed to verify that the solutions are basic.

REFERENCES

1. Private communication from G.B. Atkinson and R.J. Kuczynski, U.S. Bureau of Mines, Reno Research Center, Reno. NV
2. Tan, T.C., and W.K. Teo, "Destruction of Cyanides by Thermal Hydrolysis," *Plating and Finishing,* p. 70, April (1987) ❐