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DEVELOPMENT AND EVALUATION OF ION-EXCHANGE SILVER RECOVERY PILOT PLANT

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An ion-exchange silver recovery pilot plant was designed, constructed, and operated to determine the feasibility of using ion-exchange resins to recover silver from spent photographic fixer solutions. Results indicate that ion-exchange silver recovery is technically feasible since the silver concentration in the fix tank can be maintained below 0.5 gm Ag^+/ℓ with complete recycle of the fixer solution, the ion-exchange resin can be regenerated, and the silver can be recovered from the regenerant solution by electrolysis. (It takes three

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times as long to regenerate the resin as it does to saturate it with silver from the fixer solution.) Cost evaluation of the ion-exchange silver recovery system indicates that this method is not the most economical for recovering silver from fixer solutions; electrolytic recycling appears to be more economical.

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ABBREVIATIONS AND SYMBOLS

A	plating area of electrolytic unit
BOD_5	five-day biochemical oxygen demand
C	total amount of silver adsorbed by resin, equiv Ag^+
C_e	equilibrium silver concentration in solution, gm/ℓ
C_f	silver concentration in silver nitrate solution, gm/ℓ
C_i	silver concentration in recycled fixer solution, gm/ℓ
C_o	initial silver concentration in fixer solution, gm/ℓ
F	flow rate of fixer solution, ℓ/min
F_f	flow rate of silver nitrate solution, ℓ/min
L	total height of ion-exchange resin bed, cm
LD_{50}	lethal concentration for 50 percent of organisms
M	molar concentration, moles/ℓ of solution
M_{Ag}	equivalent weight of silver, gm/mole
PE	polyethylene
PVC	polyvinyl chloride
S	cross-sectional area of column, cm^2
V_B	volume prior to breakthrough, mℓ
V_E	effluent volume between breakthrough and exhaustion, mℓ
V_R	total volume of resin bed, ℓ
V_S	volume of resin bed not included in exchange zone, ℓ
$[X]$	concentration of species X in solution
Z	height of exchange zone, cm
meq	milliequivalent
q	resin capacity for silver, equiv Ag^+/ℓ of resin
q_e	equilibrium resin capacity for silver, equiv Ag^+/ℓ of resin
ε	resin bed porosity (dimensionless)

<u>Chemical Reagents</u>

Ag^+	silver ion
$AgNO_3$	silver nitrate
$Ag(S_2O_3)_2^{-3}$	-3 silver thiosulfate complex ion
$Ag(S_2O_3)_3^{-5}$	-5 silver thiosulfate complex ion
$HC_2H_3O_2$	acetic acid

ABBREVIATIONS AND SYMBOLS (Concl'd)

$NaBr$	sodium bromide
$NaC_2H_3O_2$	sodium acetate
Na_2SO_3	sodium sulfite
$Na_2S_2O_3 \cdot 5H_2O$	sodium thiosulfate pentahydrate
$R_2S_2O_3$	thiosulfate on resin
$SO_3^=$	sulfite ion
$S_2O_3^=$	thiosulfate ion

SECTION I
INTRODUCTION

1. BACKGROUND

The United States Air Force does a large amount of photographic film processing at installations throughout the United States. The discharge of wastes from these processes can have a significant impact upon local ecosystems if these wastes are not adequately treated. Therefore, it is necessary that the Air Force investigate methods for treating photographic wastes to reduce the amount discharged into the environment.

Photographic wastes include spent photographic fixer solutions containing high concentrations of both silver and organic chemicals, and tailing solutions containing much lower concentrations of these components. Spent photographic fixer solutions generally contain about 64 gm/ℓ of thiosulfate ($S_2O_3^{=}$), 10 gm/ℓ of sulfite ($SO_3^{=}$), up to 7 gm/ℓ of silver (Ag^+), and various amounts of other chemicals.* The five-day biochemical oxygen demand (BOD_5) for such solutions is 30 to 35 gm/ℓ (ref. 1). Tailing wastes, generated by the carryover of fixer solutions into rinse waters, contain much smaller amounts of silver and organic chemicals. In both solutions, however, the silver concentration greatly exceeds the allowable effluent discharge concentrations now established and the solutions are extremely toxic to many biological systems. Characteristic discharge limits include those of Illinois, which has a maximum allowable silver concentration limit of 0.0005 mg/ℓ and Alaska, which has a limit of 0.001 of the lethal dose which kills 50 percent (LD_{50}) of the most sensitive organism (ref. 2). Many other states have not yet established limits; however, their limits will undoubtedly be commensurate with those of Illinois and Alaska.

Considerable savings in treating spent photographic fixer solutions can be realized if a significant amount of silver can be recovered. A single Versamat 1411 processor, used at a number of Air Force installations, may process film containing as much as $11,664 worth of potentially recoverable silver each year (ref. 3). This potential savings is an added incentive to the implementation of treatment systems which can effectively remove and recover silver from fixer solutions.

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*The exact composition of fixer solutions is not known since this is considered proprietary information.

Current technology involving the removal of silver from photographic waste solutions encompasses metallic replacement, chemical precipitation, and electrolytic plating (ref. 4). Another method involves the use of ion-exchange resins to separate the silver from the spent fixer solutions. Unfortunately, this method is considered uneconomical since these resins have a limited capacity; there is also the problem of reclaiming the silver from the resin (refs. 4, 5).

A report (ref. 3) from the Civil Engineering Research Division of the Air Force Weapons Laboratory (AFWL) indicates that strong anion-exchange resins can efficiently remove silver from spent fixer solutions. Furthermore, this report suggests that these resins can be regenerated with a sodium thiosulfate solution and that the silver can be reclaimed by chemical precipitation or by electrolytic methods. The macroreticular resins used in the above study were tougher and had larger pores than the older gel-type resins and it is believed that these resins provide more complete removal of high molecular weight ions (ref. 6). However, the AFWL report also indicates that the resin capacity is significantly decreased in a short period of time because of fouling and that unless a method is found to prevent this fouling, the use of strong anion-exchange resins to treat photographic fixer solutions is not feasible. As a result of these findings, investigations into the exact nature of resin fouling, and methods of preventing it, have been carried out to help determine the feasibility of an ion-exchange silver-recovery system (refs. 7, 8).

Two types of fouling can occur with photographic solutions: organic fouling, and inorganic fouling. Organic fouling results from long-term use of an ion-exchange resin with natural waters which are subject to accumulations of decaying vegetation (ref. 9). This type of fouling is very persistent once it has occurred. It can be minimized, but it is difficult to prevent when ion-exchange resins are used with natural waters. Organic fouling is believed to be the result of a buildup of humic acids on the resin (ref. 9). Inorganic fouling may be caused by the formation of colloidal inorganic precipitates near exchange sites. The colloidal charge is thought to neutralize the charged exchange site. The most common form of inorganic fouling with photographic fixer solutions appears to be the precipitation of colloidal sulfur and silver sulfide. This type of fouling can be prevented by treating the resin with a dilute sodium acetate solution before it is used with a silver-containing photographic solution. A complete discussion of inorganic fouling and its prevention in photographic fixer solutions is given by Buyers (refs. 7, 8).

2. OBJECTIVES

The objectives of this project were (1) to design, develop, and test an ion-exchange silver-recovery system to process Air Force generated photographic fixer solutions (ref. 10), and (2) to evaluate this system against current silver-recovery operations practiced by the Air Force (ref. 11).

3. SCOPE

The project was divided into two phases: a laboratory phase (Phase I), and a pilot-plant phase (Phase II). Phase I included the reconfirmation of fouling mechanisms, the development of defouling or fouling prevention techniques, and a determination of the type and extent of application of the ion-exchange system (ref. 10). The results obtained during Phase I are presented in reference 8. Phase II of the project included the design, construction, and operation of an ion-exchange silver-recovery pilot plant for use with a Versamat 11-cm processor. The information obtained from the operation of this pilot plant was evaluated to determine the extent of application of the ion-exchange silver-recovery system. These results and this evaluation are presented in this report.

SECTION II
PILOT-PLANT DESIGN

At the present time, the most common method of recovering silver from spent photographic fixer solutions at U.S. Air Force installations is the metallic replacement cartridge method (ref. 12). Since metallic replacement contaminates fixer solutions, the effluent from these cartridges cannot be reused and must be discharged as waste, generally into sanitary sewers (ref. 12). Furthermore, since fixer baths are operated at high silver concentrations, generally between 0.5 and 5.0 gm/ℓ (refs. 5, 13, 14), as much as 20 percent of the silver can be carried over by the film into rinse waters which are subsequently discharged (ref. 12). Thus, design of the ion-exchange silver-recovery pilot plant was directed toward providing a system which could accomplish the following:

(1) remove silver from fixer solutions and permit subsequent recovery of the silver,

(2) eliminate the discharge of fixer solutions by recycling them after removing the silver, and

(3) reduce the carryover of silver into rinse waters by maintaining a low silver concentration ($\leq$ 0.5 gm/ℓ) in the fixer solution.

An ion-exchange silver-recovery system which meets the above design objectives is shown in figure 1. The fixer solution is circulated in a closed loop through the fix tank and an ion-exchange column. Silver thiosulfate complex ions are removed from the solution as it passes through the column so that the silver concentration in the fix tank remains low. When the ion-exchange resin becomes saturated with silver, it is regenerated by removing the silver with a thiosulfate regenerant solution circulating through the column. (After the resin is regenerated, the column can be used again to remove silver from the fixer solution.) The regenerant solution is circulated in a closed loop through both the column and an electrolytic processor which plates out the silver. This entire procedure can be continued indefinitely provided the resin does not foul or otherwise lose its capacity for silver.

With the exception of the small amounts carried out with the film, no chemicals are discharged. The only additional chemicals required are those necessary to replenish those lost through evaporation or carryout. In addition, once a steady-state operating condition is reached, virtually all the silver

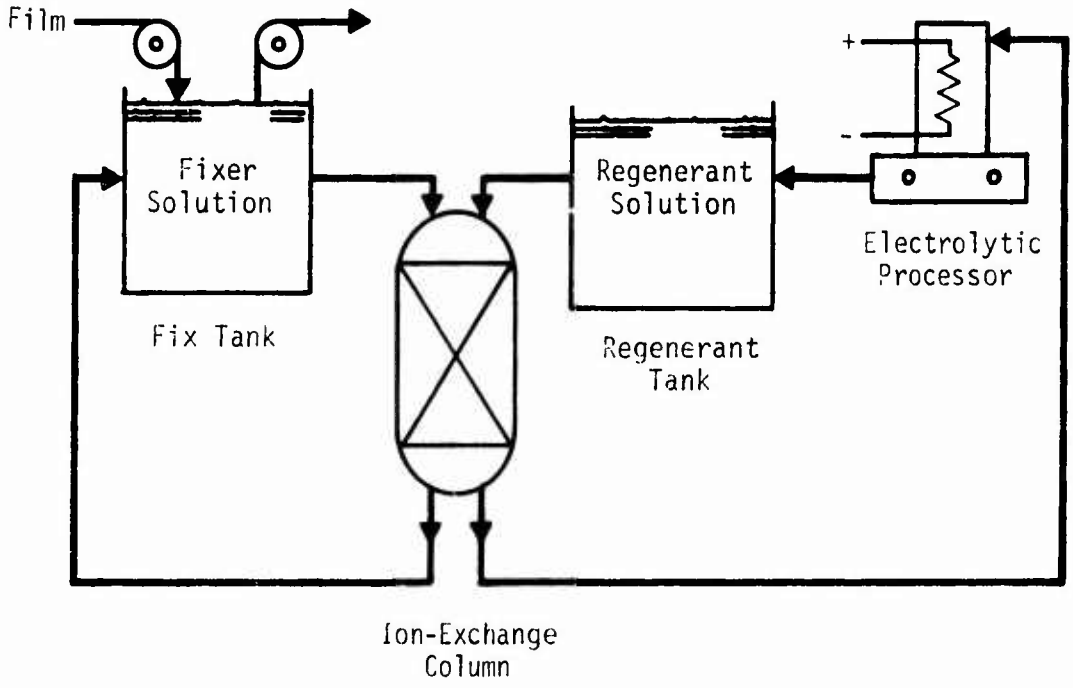


Figure 1. Ion-Exchange Silver-Recovery System

removed from the film by the fixing process (except that carried out with the film) can be recovered.

The design of the ion-exchange column depends on (1) the rate at which silver enters the fixer solution from the film (i.e., the type of film and the rate at which it is fixed), (2) the equilibrium capacity of the resin for silver in the form of thiosulfate complexes, (3) the rate at which silver is removed from the fixer solution by the ion-exchange resin, and (4) the hydraulic characteristics of the resin bed, such as pressure drop and backwash. In addition, the design may be limited or otherwise influenced by the size of the system in relation to the space available at Air Force photographic laboratories.

For the pilot-plant study, the film fixing process was simulated by the addition of silver to the fixer solution in the form of a concentrated silver nitrate solution. The rate at which this solution was added was equivalent to the addition of 1.25 gm/min or 75 gm/hr of silver. This rate is slightly greater than that obtained when a Versamat Model 1411 processor is used to fix 9-1/2-in.-wide aerial film during a typical operation (ref. 3). This rate was

chosen for the pilot-plant study because it represents a typical film processing rate utilizing a Versamat 11-cm processor. (Other silver addition rates can be achieved with this processor depending on the type of film and the rate at which it is fixed.)

The ion-exchange resin used was Amberlite IRA-900, a strongly basic macroreticular anion-exchange resin manufactured by Rohm and Haas Company. This resin is a polystyrene-matrix material containing bound quaternary ammonium groups. Some physical characteristics of this resin are as follows:

Ionic Form: Chloride

Shape: Spherical Particles

Moisture Content: 60 to 64%

Density: 40.0 to 43.0 lb/ft^3

Effective Size: 0.43 to 0.52 mm

Screen Grading (Wet): 16 to 50 mesh (U.S. Standard Screens)

Note: A complete list of physical and hydraulic characteristics of this resin is given in reference 6.

The equilibrium silver capacity of Amberlite IRA-900 in solutions containing 0.5 M thiosulfate is shown in figure 2. These values can be represented by the Langmuir-type relationship

$$q_e = \frac{0.395\ C_e}{1 + 0.783\ C_e}$$

where q_e is the capacity (for silver) of the resin which is in equilibrium with a fixer solution with a silver concentration (ref. 8). From figure 2, the capacity of the resin in equilibrium with a 0.5-gm/ℓ silver solution is approximately 0.14 equiv Ag^+/ℓ of resin. For example, 1 liter of Amberlite IRA-900 in equilibrium with a fixer solution containing 0.5 gm/ℓ of silver can adsorb a maximum of 15 gm of silver. Thus, it takes 5 liters of resin to adsorb the silver added to the fixer solution during 1 hr of pilot-plant operation (i.e., the silver addition rate is 75 gm Ag^+/hr), provided, of course, that equilibrium conditions are reached throughout the resin bed.

The silver contained in fixer solutions is present in the form of silver thiosulfate complexes, primarily the -3 complex, $Ag(S_2O_3)_2^{-3}$, and the -5 complex,

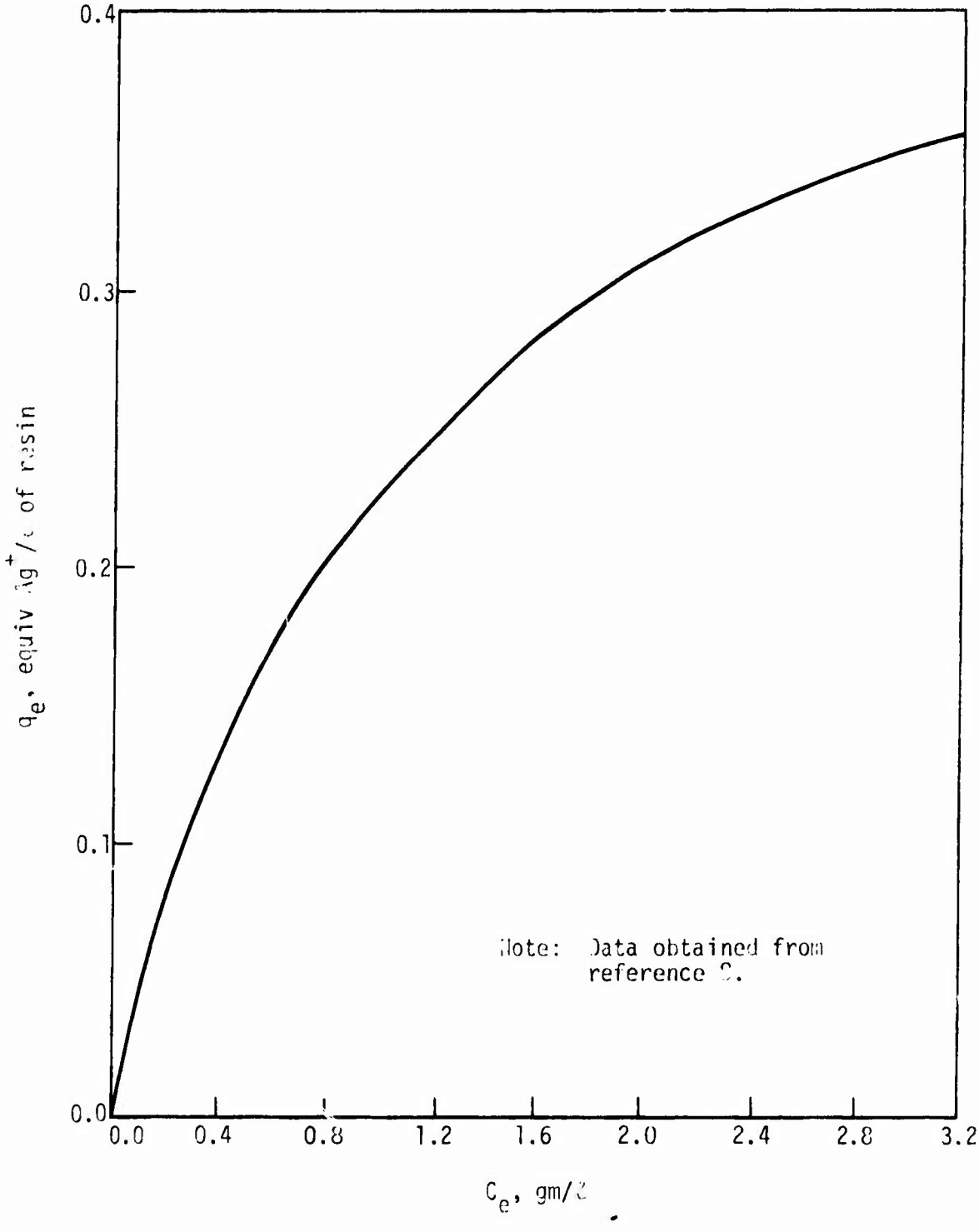


Figure 2. Equilibrium Silver Capacity of Amberlite IRA-900 in 0.5 M Thiosulfate Solutions

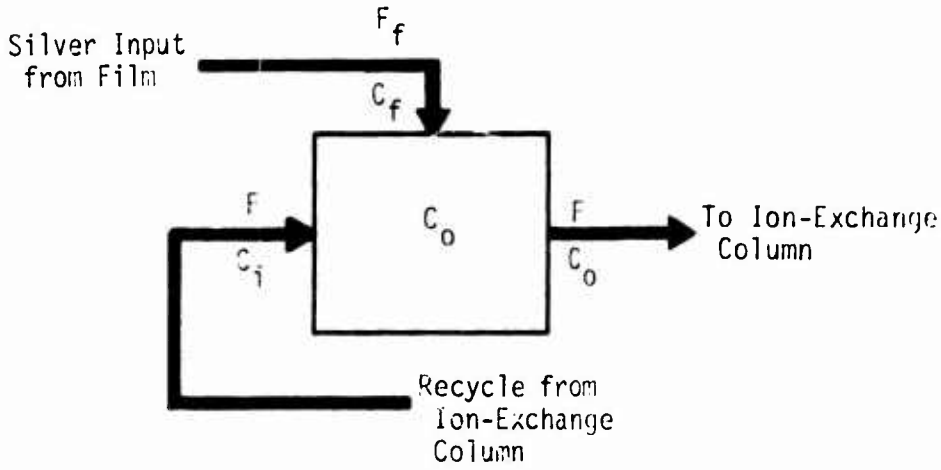


Figure 3. Mass Balance on Silver Around Fix Tank

$Ag(S_2O_3)_3^{-3}$ (ref. 3). The rate at which silver is removed from the fixer solution by the resin depends primarily on the effective rate of mass transfer of these complex ions from the solution onto and into the resin (ref. 15). There are five different steps involved in the ion-exchange process, any of which can be rate controlling. However, for design purposes they are often grouped into a single step termed *effective mass transfer rate*. This rate of mass transfer is influenced by a number of conditions including the type of resin, the height of the resin bed, the complex ion concentration in the solution flowing through the resin bed, and the flow rate of the solution (ref. 16). For a given complex ion concentration (e.g., the complex ion concentration in a 0.5 M thiosulfate solution containing 0.5 gm/ℓ of silver) and type of resin, the main factor affecting the mass transfer rate is the solution flow rate, or, expressed in a more general way, the superficial velocity of the solution (i.e., the velocity of the solution through an empty column). Thus, it is useful to know the fixer solution flow rates anticipated during pilot-plant operations.

The flow rate of the fixer solution can be found from a mass balance on silver around the fix tank as illustrated in figure 3. If the fixer solution

loses silver only in the ion exchange column, a mass balance on silver gives

$$F_f C_f + F C_i = F C_o \tag{1}$$

where F_f and F are the flow rates of the silver nitrate solution and the fixer solution, respectively, and C_f, C_o, and C_i are the silver concentrations in the silver nitrate solution, the fixer solution leaving the fix tank, and the recycled fixer solution, respectively. Silver input from film is modeled by the addition of silver nitrate. F_f, the flow rate of silver nitrate solution, is negligible with respect to F and $F_f + F$ is very nearly equal to F. Solving eq. (1) for the flow rate, one obtains

$$F = \frac{F_f C_f}{C_o - C_i} \tag{2}$$

As previously mentioned, the silver input rate for the pilot plant was set at 1.25 gm Ag^+/min (i.e., $F_f C_f$ = 1.25 gm Ag^+/min) and the silver concentration in the fix tank was limited to a maximum of 0.5 gm Ag^+/ℓ (i.e., C_o = 0.5 gm Ag^+/ℓ). Although the ion-exchange resin can remove essentially all the silver from solution, leakage may occur in some cases, so an upper limit of 0.05 gm Ag^+/ℓ was assumed for the recycled stream (i.e., C_i = 0.05 gm Ag^+/ℓ). Substituting these values into eq. (2), one obtains

$$F = \frac{1.25}{0.5 - 0.05} = 2.78\ \ell/\text{min}$$

Thus, for the given silver input rate, the flow rate of the fixer solution must be at least 2.78 ℓ/min or 0.735 gal./min if the fix tank is to remain at a silver concentration of 0.5 gm Ag^+/ℓ. This flow rate corresponds to the superficial velocities shown in table I for several different column diameters.

One measure of the rate of mass transfer in an ion-exchange column is the height of the exchange zone. This height can be estimated from laboratory data obtained at a superficial velocity corresponding to that anticipated in the pilot plant or large-scale unit. During Phase I of this project, laboratory data were taken for an ion-exchange strip cycle operating at a superficial velocity of 22.7 cm/min (ref. 8). This corresponds to the superficial velocity

Table I

SUPERFICIAL VELOCITY FOR FIXER SOLUTION

Inside Diameter of Column, in.	Superficial Velocity, cm/min
1	549
2	137
3	61.0
4	34.2
6	15.2
12	3.81

Flow Rate: 2.78 ℓ/min

attained in a pilot-plant column having a diameter between 4 and 6 in. (table I). The breakthrough curve for this laboratory run is shown in figure 4.

One way to determine the height of the exchange zone is from an analysis of the breakthrough curve in a manner similar to that used for purely adsorption operations (ref. 16). However, this method can be used only if the total height of the resin bed is large relative to the height of the exchange zone. It is apparent from figure 4 that this is not the case (i.e., $V_B + V_E$ is not large relative to V_E).

An alternate method for determining the height of the exchange zone makes use of the equilibrium exchange capacity of the resin (ref. 17). The height of the exchange zone, Z, is given by

$$Z = \frac{V_E C_o}{S(q_e + \varepsilon C_o)} \tag{3}$$

where V_E is the effluent volume collected between the point of breakthrough and the point of exhaustion, C_o is the initial silver concentration in the fixer solution, S is the cross-sectional area of the column, q_e is the equilibrium exchange capacity of the resin (i.e., the capacity of the resin which is in equilibrium with a solution having a silver concentration of C_o), and ε is the resin bed porosity. For the laboratory run shown in figure 4, these parameters

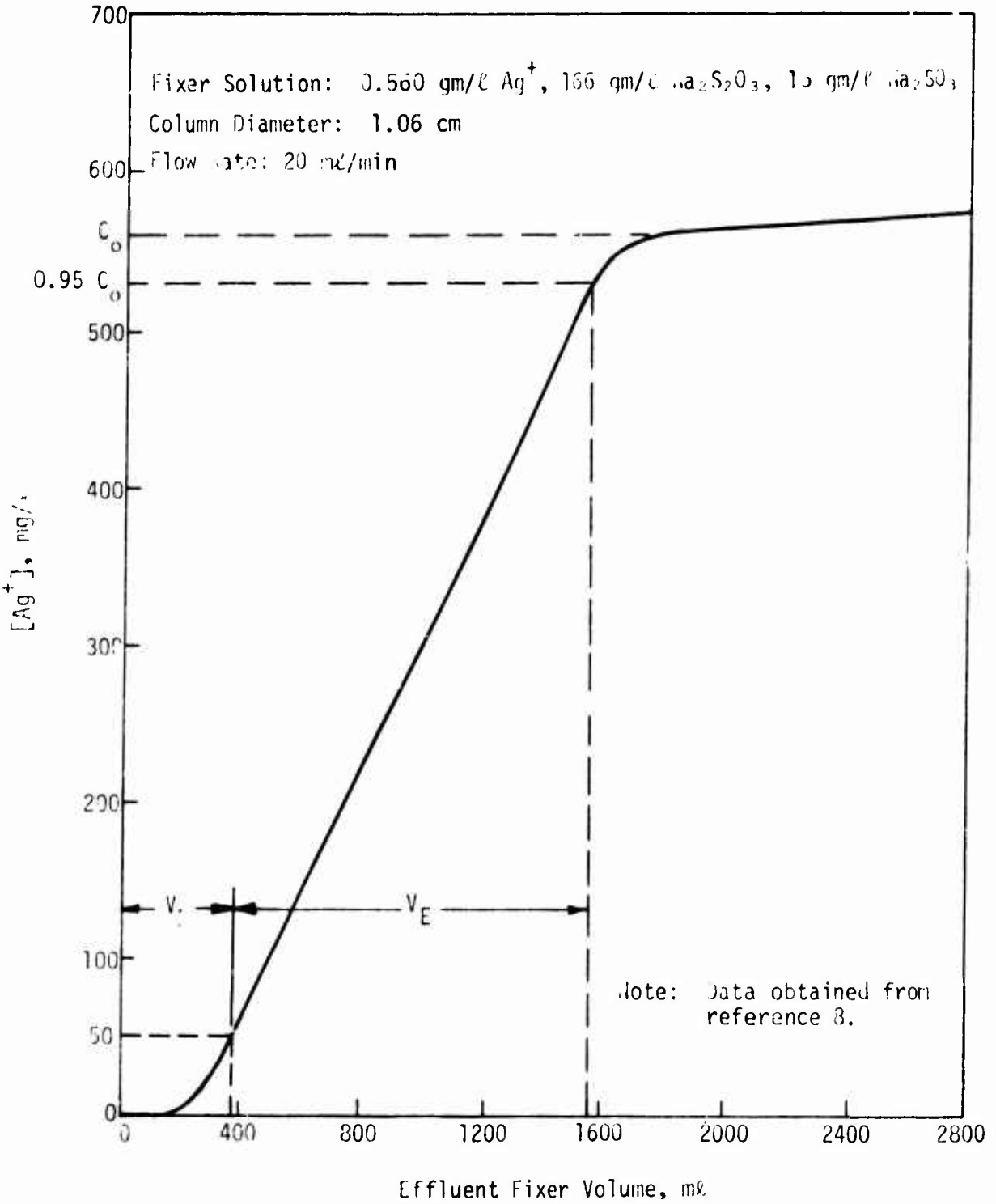


Figure 4. Breakthrough Curve for Laboratory Run

are as follows:

V_E = 1560 - 370 = 1190 cm^3

C_o = 0.560 gm Ag^+/ℓ = 0.00523 meq Ag^+/cm^3

S = 0.833 cm^2

q_e = 0.16 meq/cm^3 (from figure 3)

= 0.40 (assumed)

Substituting these values into eq. (3), one obtains

$$Z = \frac{1190(0.00523)}{0.883\ [0.16+(0.40)(0.00523)]} = 43.5 \text{ cm}$$

This indicates that the height of the exchange zone for the laboratory run operated at a superficial velocity of 22.7 cm/min was 43.5 cm. Thus, on the pilot-plant scale, a 4-in.-diameter column should have an exchange zone height somewhat greater than 43.5 cm. Similarly, a 6-in.-diameter column should have an exchange zone height somewhat less than 43.5 cm.

The foregoing information can be used to estimate the type of column required for the pilot-plant study. Schedule 40 pipe, 4 in. in diameter, was selected for the pilot-plant column. This size pipe has an outside diameter of 4.500 in., an inside diameter of 4.026 in., and a cross-sectional area of 0.0884 ft^2 or 79.1 cm^2 (ref. 18). Since none of the exchange zone can be used to recover silver (i.e., the silver concentration throughout the exchange zone is greater than the maximum allowable value of 0.05 gm Ag^+/ℓ), the total height of the ion-exchange resin bed, L, can be estimated from the relationship

$$L = 1.00Z + \frac{C}{Sq_e} \tag{4}$$

where Z is the height of the exchange zone, S is the cross-sectional area of the column, q_e is the equilibrium capacity of the resin (determined from figure 2), and C is the total amount of silver that is to be removed from the fixer solution, i.e., the total amount of silver which must be adsorbed by the resin (ref. 17). As previously stated, 75 gm of silver is added to the fixer solution during 1 hr of operation. Thus, 75 gm of silver must be removed from the fixer solution by the resin during the same period of time in order to maintain the

silver concentration at or below 0.5 gm/ℓ. Under these conditions, the parameters in eq. (4) are as follows:

$C = 75 \text{ gm } Ag^+ = 700 \text{ meq } Ag^+$

$q_e = 0.14 \text{ meq } Ag^+/cm^3$

$S = 79.1 \text{ cm}^2$

$Z = 43.5 \text{ cm}$

Substituting these values into eq. (4), one obtains

$$L = (1.00)(43.5) + \frac{700}{(79.1)(0.14)} = 106.7 \text{ cm}$$

Thus, a resin bed 106.7 cm high is required to maintain the fixer solution concentration at 0.5 gm Ag^+/ℓ for 1 hr. Table II gives the resin bed heights required to maintain these fixer solution conditions for various periods of operation for a silver addition rate of 1.25 gm Ag^+/min.

Table II

RESIN BED HEIGHT REQUIRED FOR VARIOUS PERIODS OF PILOT-PLANT OPERATION

Operating Period, hr	Total Silver Adsorbed, gm	Resin Bed Height, cm
1	75	106.7 (3.5 ft)
2	150	169.9 (5.6 ft)
3	225	233.1 (7.7 ft)
4	300	296.3 (9.7 ft)
5	375	358.6 (11.8 ft)
6	450	421.8 (13.8 ft)
7	525	485.0 (15.9 ft)
8	600	548.2 (18.0 ft)

SECTION III
PILOT-PLANT CONSTRUCTION

The ion-exchange columns for the pilot plant were constructed of 4-in.-diameter, schedule 40, polyvinyl chloride (PVC) pipe. Each column was 4 ft (122 cm) high and contained 7.71 liters (0.274 ft^3) of Amberlite IRA-900 anion-exchange resin which reached a height of 2 1/2 ft (76.25 cm) in the column. The remaining 1 1/2 ft (46.75 cm; a volume of 0.364 ft^3 or 10.30 liters) was left to allow for a 60-percent expansion of the resin bed during backwash operations as suggested by the manufacturer (ref. 6). Both ends of the column were glued to 4-in., schedule 80, PVC slip flanges. These flanges were bolted to 4-in., schedule 80, PVC blind flanges, the faces of which were drilled to accommodate 1/2-in., schedule 40, PVC couplings. A 1/8-in.-thick neoprene rubber gasket, a 30-mesh polyethylene (PE) screen, and a layer of glass wool (to prevent the resin from being washed from the column) were placed between the flanges to provide a leakproof seal. (See figure 5.) One ion-exchange column was constructed of Plexiglas tubing (4-in. inside diameter, 4 1/2-in. outside diameter) with flanges of 3/4-in.-thick Plexiglas glued to each end. This column was constructed so that visual observations could be made during pilot-plant operations.

The pilot plant flow process is shown in figure 6. All piping was 1/2-in., schedule 40, PVC pipe and fittings. All valves were 1/2-in. PVC ball valves. With the exception of the pressure gages located on the inlet and outlet lines of the columns, all materials in contact with the solutions were PE, PVC, epoxy, or stainless steel (These materials are inert to typical fixer solutions.)

The fixer solution was kept in a 30-gal. PE tank (i.e., the fix tank) and circulated through the columns with a Flotec Model R2PI-1000 variable-flow, positive-displacement pump manufactured of epoxy plastic. The solution flow rate was measured with a Brooks Model 1305 stainless steel rotometer. The regenerant solution, sodium acetate solution, and backwash solution were also kept in 30-gal. PE tanks and circulated by a second variable-flow Flotec pump. The regenerant solution was circulated by a third Flotec pump from a 30-gal. PE holding tank through an Argenta Model 30 electrolytic silver-recovery unit manufactured by Future Systems, Inc. A 5-gal. PE tank contained the silver nitrate solution. This solution was added to the fix tank at a constant rate by a March Model 210-5 piston metering pump.

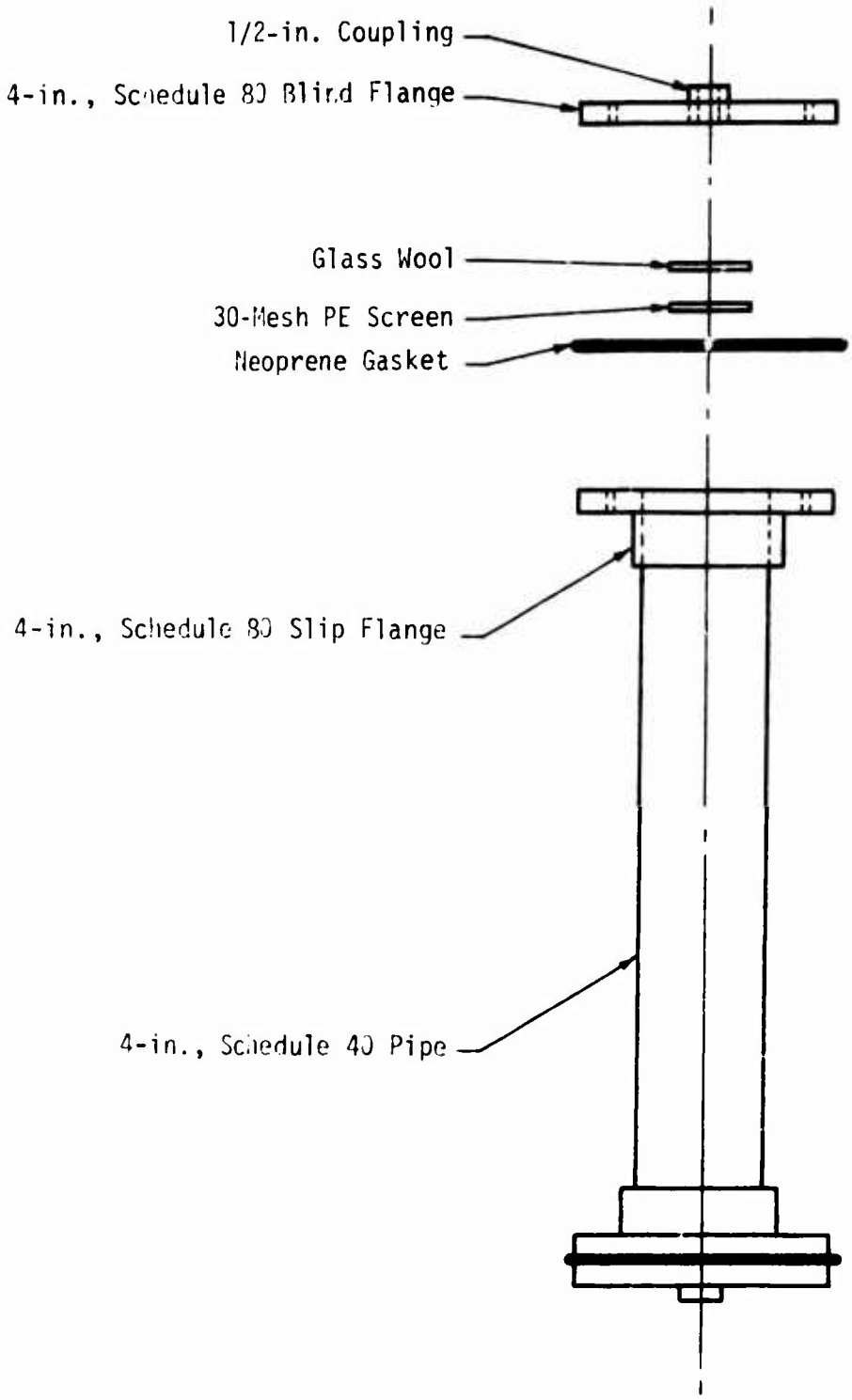


Figure 5. Ion-Exchange Column for Pilot Plant

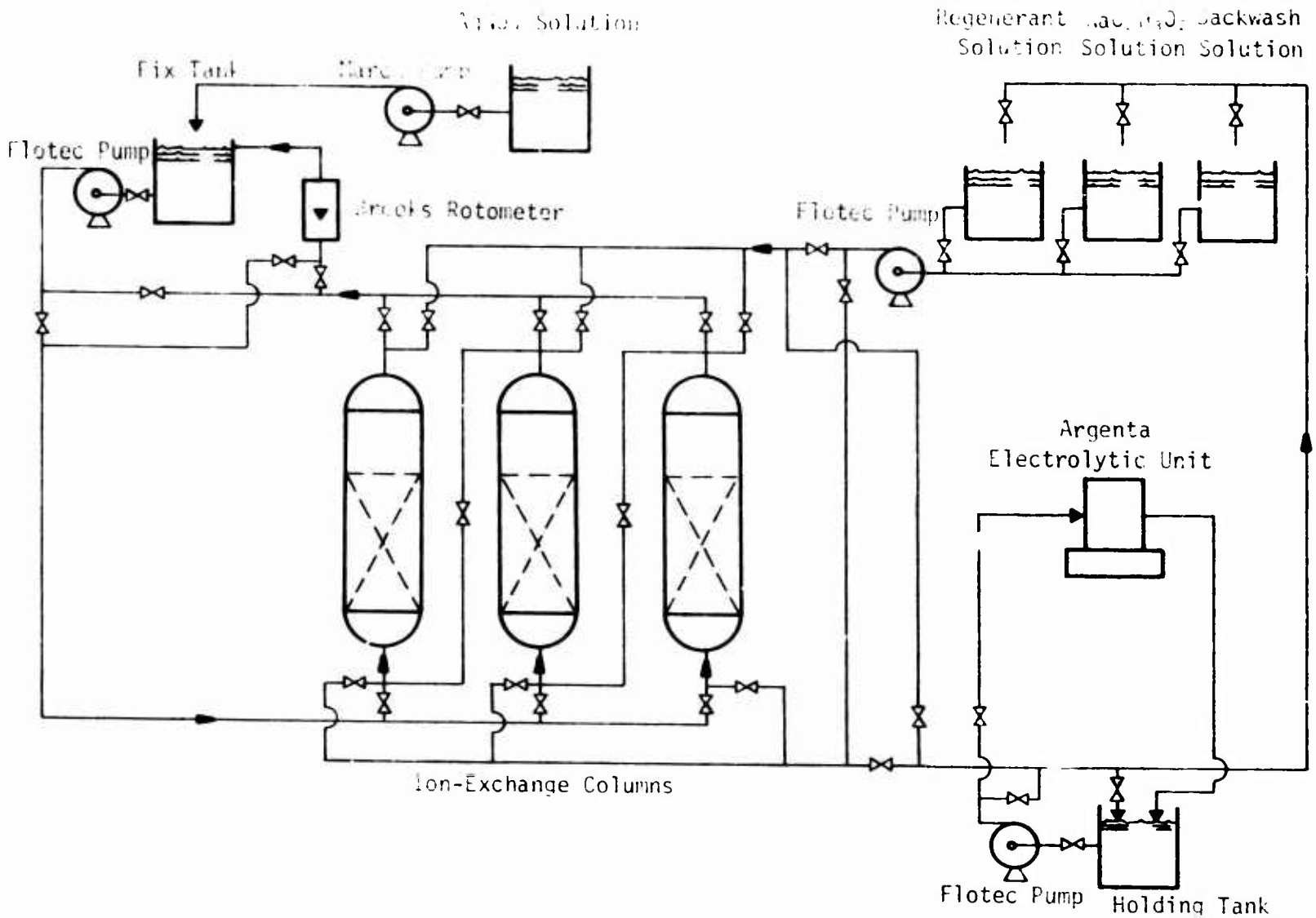


Figure 6. Pilot-Plant Flow Process

Ion-exchange resin in the chloride form was purchased from Rohm and Haas Company. Thus, before it could be used with fixer solutions it had to be converted from the chloride form to the thiosulfate ($S_2O_3^{=}$) form. This was accomplished by soaking the resin for several days in a 3.0 M sodium thiosulfate solution. The resin was then washed with distilled water and loaded into the columns.

SECTION IV
OPERATING PROCEDURES

Operation of the pilot plant involved three steps: a stripping cycle, a regeneration cycle, and a silver-recovery step. Although some of these steps can be performed simultaneously, each step was carried out separately so that detailed information could be obtained from each.

Prior to each stripping cycle an acetate pretreat solution, composed of 41.0 gm/ℓ (0.5 M) of sodium acetate ($NaC_2H_3O_2$) in distilled water, was circulated through the columns at a rate of 0.50 ℓ/min (51.6 liters of solution/min-liters of resin, or 6.31 cm/min) for 2 to 3 hr. The resin was pretreated to prevent local (in resin pore) acidity increases during the stripping cycle (ref. 8).

1. STRIPPING CYCLE

Approximately 40 liters of a synthetic fixer solution was used for the stripping cycle. The composition of this solution is given in table III. This fixer solution was circulated at a rate of 2.78 ℓ/min (298 liters of

Table III
FIXER SOLUTION COMPOSITION

Component	Amount* (per liter of solution)
$AgNO_3$	0.79 gm**
$Na_2S_2O_3 \cdot 5H_2O$	120 gm
NaBr	5 gm
Na_2SO_3	20 gm
$NaC_2H_3O_2$	20 gm
$HC_2H_3O_2$ (glacial)	~50 ml***

* Brought to a volume of 1.0 liter with distilled water.

** Equivalent to 0.5 gm of silver. (This value varied during operation as indicated by the experimental results.)

*** Adjusted to a pH of 4.6 with glacial acetic acid.

solution/min-liter of resin, or 34.2 cm/min) from the fix tank through the ion-exchange columns, where the silver was removed, and back into the fix tank. (This flow rate varied somewhat for each run.) At the same time, 1.25 gm Ag^+/min (i.e., 19.7 mℓ/min of a solution containing 100 gm of $AgNO_3$/ℓ) were added to the fix tank to simulate the input of silver from the photographic film. Since a resin bed height of at least 3.52 ft (107.1 cm) is required for 1 hr of operation (table II), the fixer solution was pumped upward through two columns connected in series (i.e., 2 x 2 1/2 ft = 5 ft of resin). The solution was circulated through columns 1 and 2 for about 1 hr or until the silver concentration in the effluent stream from column 2 exceeded the maximum allowable value of 0.05 gm Ag^+/ℓ. At this time, the circulation was changed to go through columns 2 and 3 until the effluent silver concentration from column 3 reached 0.05 gm Ag^+/ℓ. The fixer solution and the effluents from each of the columns were sampled at 5- or 10-min intervals and analyzed for silver content and pH. All flows were then stopped and the columns were drained of any remaining solution.

This procedure allows the first two columns to become *saturated* with silver (i.e., reach their equilibrium capacities). Only the final column in the chain will not be saturated since it must contain the exchange zone. Approximately eight columns are necessary for a full 8 hr of operation. Since all columns are identical, the results obtained from the three pilot-plant columns are representative of the full-scale system.

2. REGENERATION CYCLE

Following the stripping operation, a regeneration cycle was carried out for each of the columns. The columns were regenerated by circulating the regenerant solution through the column to remove the silver adsorbed by the resin. Approximately 40 liters of a regenerant solution (table IV) was circulated at an average flow rate of 0.50 ℓ/min (51.6 liters of solution/min-liter of resin, or 6.31 cm/min) as suggested by the manufacturer through a single column into a holding tank. The solution leaving the column was sampled at 10-min intervals to determine the rate at which silver was removed from the resin. The silver was then recovered from the regenerant solution by electrolysis.

The regenerant solution was passed through the column a second time, in the same manner, to continue regeneration of the column, and was again electrolyzed to recover the silver. These two operations of regeneration and

Table IV

REGENERANT SOLUTION COMPOSITION

Component	Amount* (per liter of solution)
$AgNO_3$	0.318 gm**
$Na_2S_2O_3 \cdot 5H_2O$	745 gm
Na_2SO_3	20 gm
$NaC_2H_3O_2$	20 gm
$HC_2H_3O_2$ (glacial)	50 ml***

* Brought to a volume of 1.0 liter with distilled water

** Equivalent to 0.2 gm of silver. (This value varied during operation as indicated by the experimental results.)

*** Adjusted to a pH of 4.6 with glacial acetic acid.

electrolysis were continued until at least 90 liters of the regenerant solution were circulated through the column or until the effluent silver concentration reached a constant value (i.e., the effluent silver concentration in the regenerant solution did not change with time). At this point, the column was considered regenerated to the greatest extent possible under the existing conditions.

This entire procedure was repeated for both the second and third columns. After all three columns were regenerated, the columns were backwashed with distilled water as suggested by the resin manufacturer. This operation was carried out to remove extraneous material and to reclassify the resin. After this operation, the resin was again used for silver stripping of the fixer solution.

3. SILVER RECOVERY

The electrolytic recovery of silver from the regenerant solution was accomplished with an Argenta Model 30 silver-recovery unit. The regenerant solution was circulated at a flow rate of 3.8 ℓ/min from a holding tank through the electrolytic unit, where metallic silver was plated out, and back into the tank. Electrolysis was discontinued when the silver concentration was reduced to 0.20

to 0.25 gm Ag^+/ℓ. Silver concentration was determined from periodic sampling of the solution. The time required to remove the silver from the 40 liters of regenerant solution depended on the current density used during the recovery operation. Since low silver concentrations were desired (i.e., $<$ 0.5 gm Ag^+/ℓ), a low current density was necessary to prevent the formation of silver sulfide. These low current densities require much more time to plate out the silver than the more commonly used high current densities.

Samples were analyzed for silver content with a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer. The samples were diluted (when necessary) with a Labindustries Automatic Dilutor and the absorbance was measured and compared with an absorbance curve determined from standard silver solutions containing approximately the same concentrations of other components (e.g., sodium thiosulfate, sodium sulfite, sodium acetate, etc.) as in the samples; i.e., either the fixer solution or the regenerant solution (tables III and IV). In addition, the pH of the samples was determined with a Corning Digital 112 Research pH Meter calibrated with standard buffer solutions.

SECTION V
TEST RESULTS

1. PRESSURE DROP AND FLUIDIZATION

Pressure drop through the ion-exchange resin bed was determined for three solutions: distilled water, fixer solution containing no silver, and regenerant solution. The results of these pressure drop measurements are shown in figure 7. Although only one measurement was made with the regenerant solution, the pressure drop line for this solution was assumed to be parallel to the other two lines.

Results with the distilled water agreed with those reported by Rohm and Haas (ref. 6). The other two solutions gave much higher pressure drops than the distilled water at the same flow rate. This was due to the different physical properties of the solutions, primarily the viscosities which are much different for the fixer solution (contains 0.5 M thiosulfate) and the regenerant solution (contains 3.0 M thiosulfate) than for distilled water (contains no thiosulfate).

The ion-exchange resin bed was completely fluidized at a water flow rate of 0.254 gpm (2.91 gpm/ft^2) which gives a pressure drop of 0.38 psi/ft of resin. From figure 7, a similar pressure drop occurs for a fixer solution flow rate of 0.097 gpm (1.10 gpm/ft^2), and a regenerant solution flow rate of 0.0425 gpm (0.48 gpm/ft^2). Thus, for the fixer solution flow rate of 2.78 ℓ/min (0.735 gpm or 8.32 gpm/ft^2) required in the pilot-plant experiment, it was impossible to run the resin bed in a fluidized state. A larger diameter column would be necessary to operate under fluidized conditions.

During the operation of the pilot plant, however, the resin became graded; i.e., the heavier, larger-diameter resin particles gradually moved to the bottom of the bed and the lighter, smaller-diameter particles moved to the top. As a result, the lower part of the resin bed (i.e., the part containing the larger particles) achieved a fluidized state even at the high flow rate of the fixer solution. Figure 8 illustrates how the resin was distributed in the column under these conditions. A completely fluidized bed could have been achieved if all the resin were composed of the larger particles.

2. SILVER STRIPPING

Four independent silver stripping runs were made with the synthetic fixer solution. (Data from these stripping runs are given in appendix I.) However, run

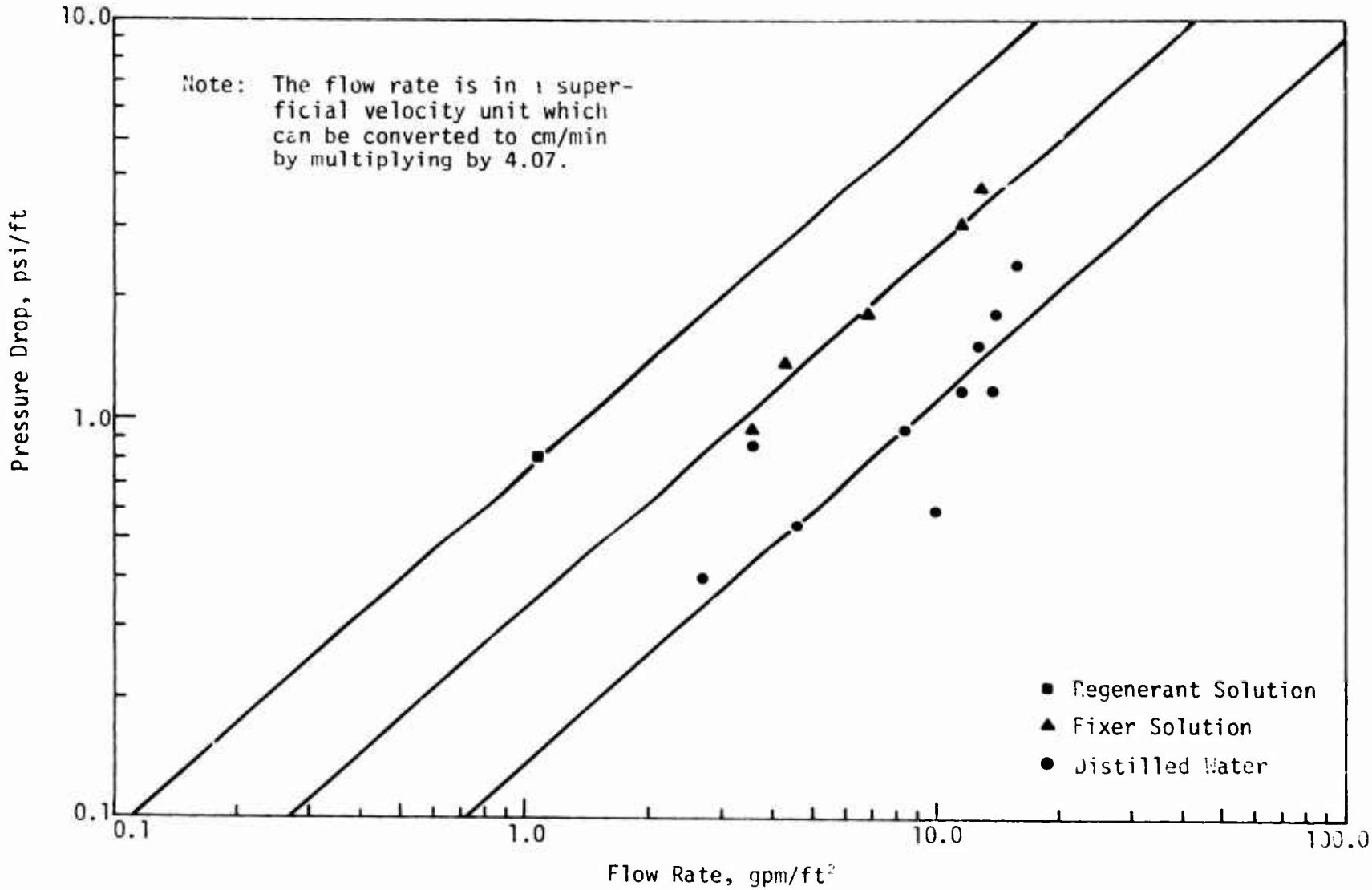


Figure 7. Pressure Drop Through Ion-Exchange Resin Bed

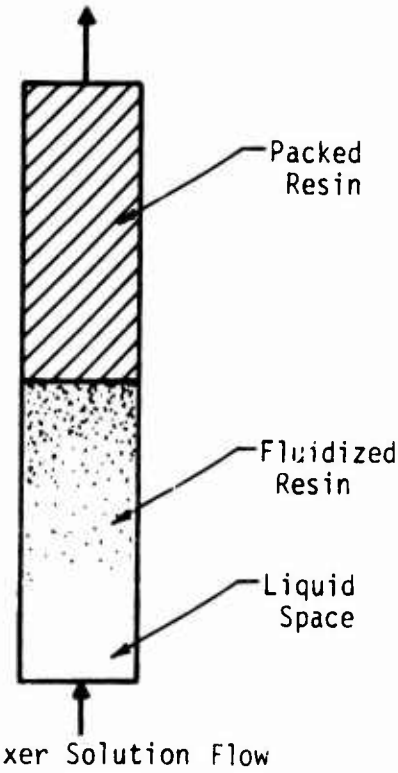


Figure 8. Resin Distribution in Ion-Exchange Column

1 failed, probably because the pH of the fixer solution was not adequately controlled during the stripping operation; it reached an unexcepted low of 4.0 by the end of the run. A metallic grey solid, possibly silver sulfide, appeared both in the fixer solution and on the resin. As a result, both the resin and the solution were discarded and the remaining stripping runs were made with new resin and fixer solution. Run 1, however, did point out the importance of adequate pH control. Thus, prior to each stripping operation, the fixer solution was adjusted to a pH of 4.6 and an additional buffer ($NaC_2H_3O_2$) was added to help maintain the pH during the operation.

The results of strip runs 2, 3, and 4 are shown in figures 9, 10, and 11, respectively. (pH data are given in appendix I.) The effluent silver concentrations from column 3 in strip run 2 are not shown in figure 9 since these values were negligibly small. The effluent silver concentrations from column 3 in strip run 3 are not shown in figure 10 since only two columns were operated during this run.

The silver concentration in the fix tank solution in both runs 2 and 3 steadily increased during the operating period and, after a short time, it

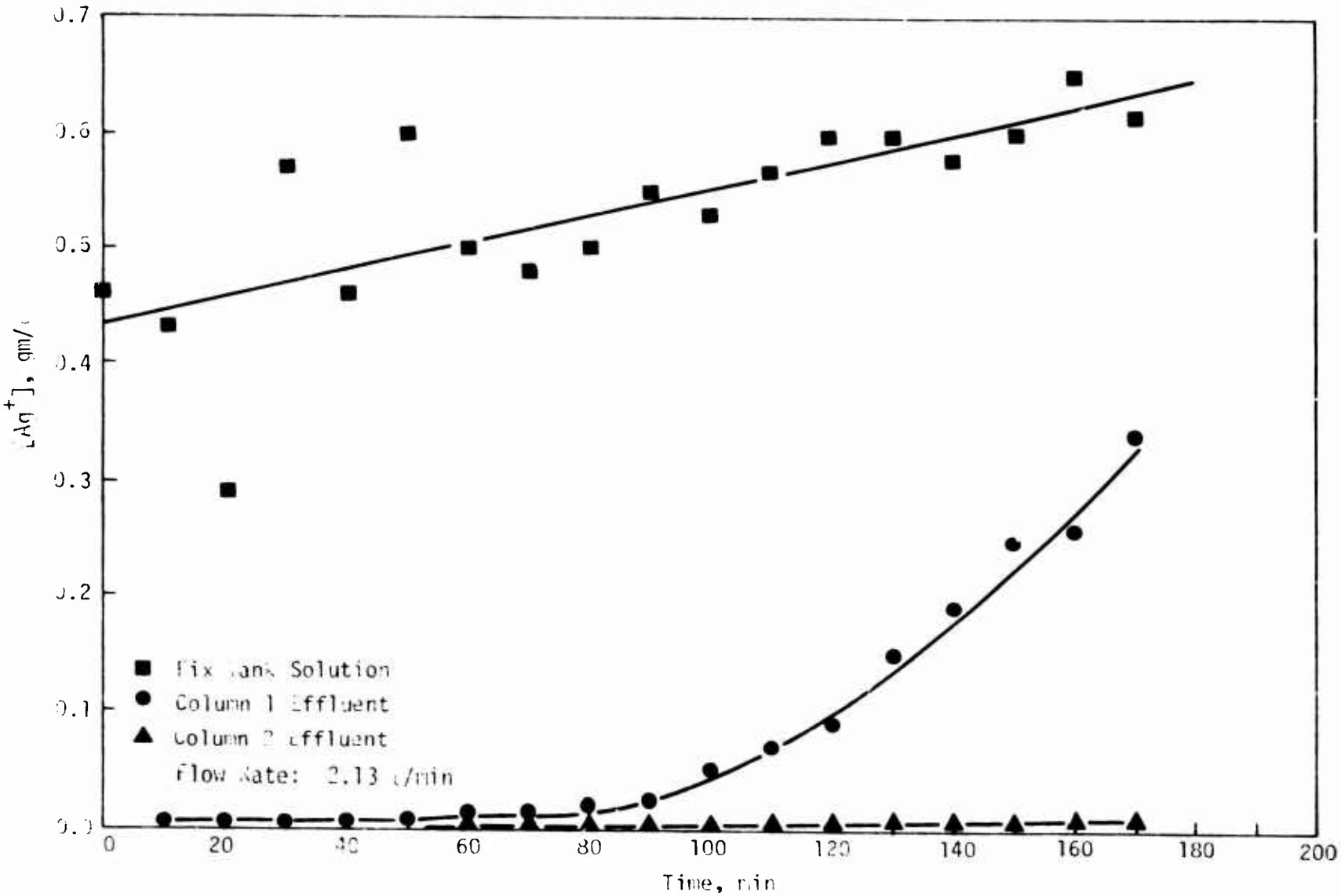


Figure 9. Strip Run 2 Data

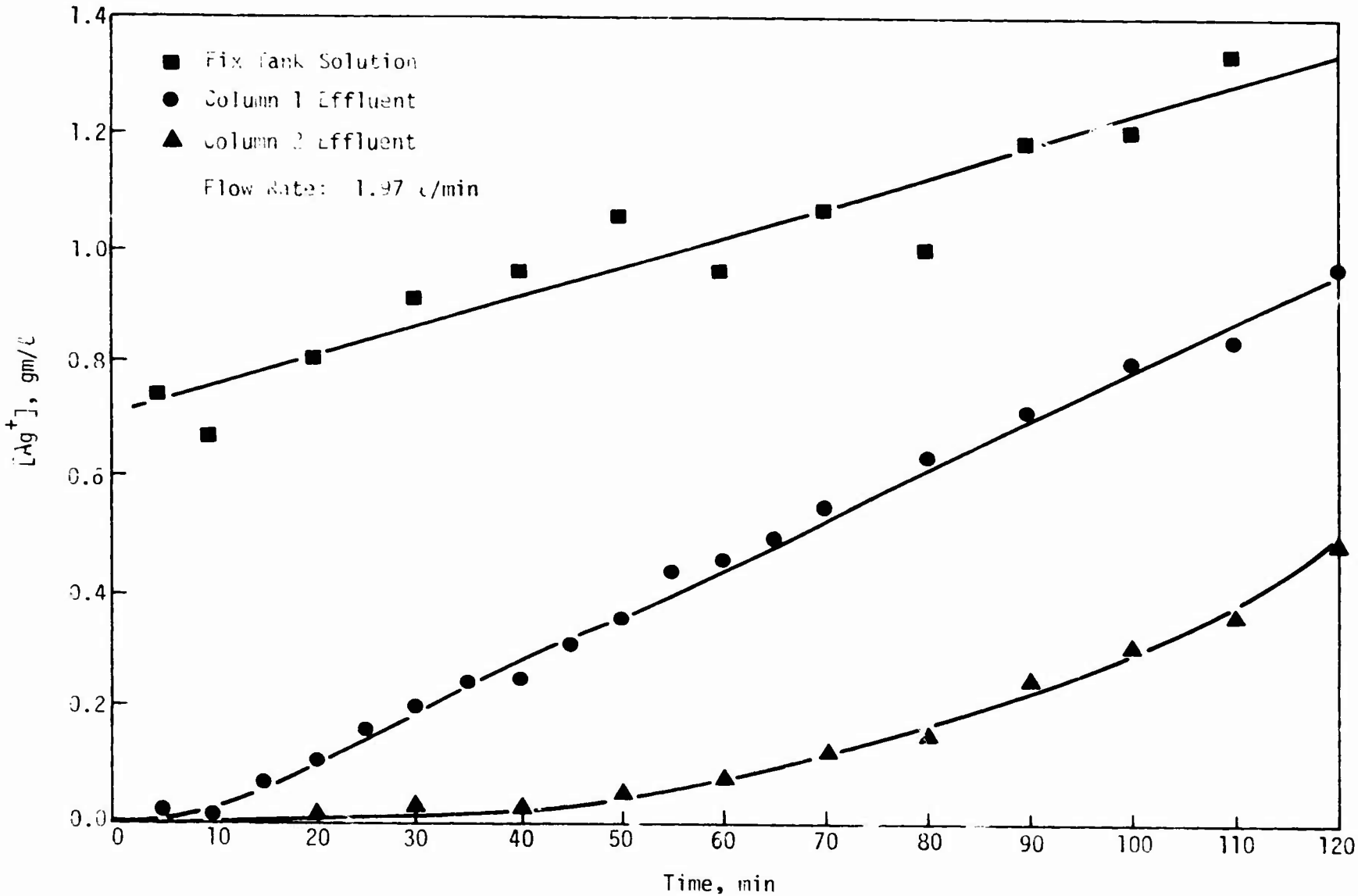


Figure 10. Strip Run 3 Data

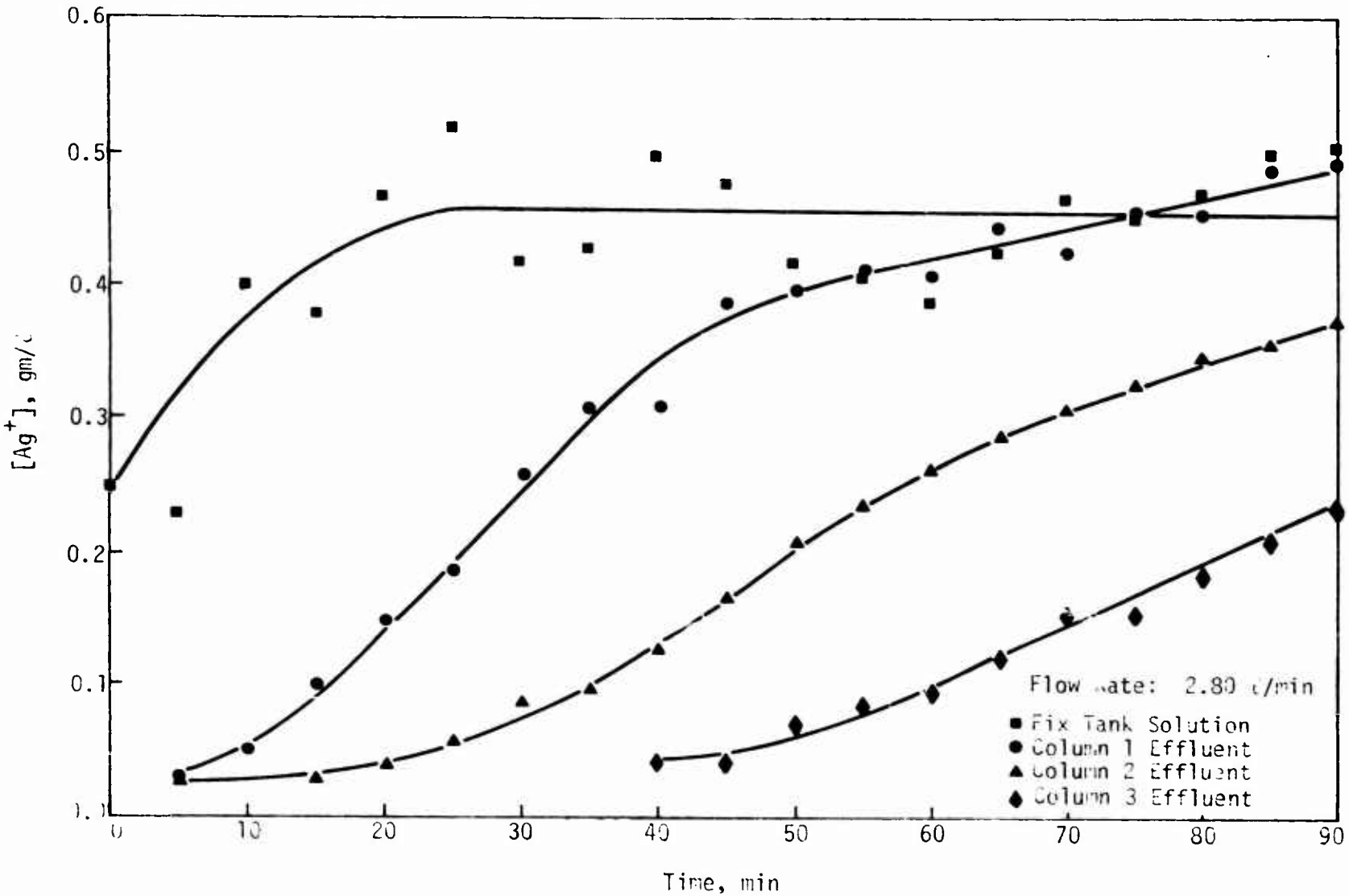


Figure 11. Strip Run 4 Data

exceeded the maximum acceptable value of 0.5 gm Ag^+/ℓ. In run 2, this was caused primarily by an incorrect fixer solution flow rate of 2.13 ℓ/min which was too low to maintain the silver concentration below 0.5 gm Ag^+/ℓ. In run 3, the increase in the silver concentration was due both to a low fixer solution flow rate (1.97 ℓ/min) and to an unacceptable high silver concentration in the effluent from column 2 being returned to the fix tank (fig. 10).

Since the influent silver concentration to the ion-exchange columns (i.e., the fixer solution) was not constant, it was difficult to construct a breakthrough curve and, hence, to determine the height of the exchange zone and the resin capacity for runs 2 and 3. However, it is apparent from figures 9 and 10 that the capacity of the resin was much greater in run 2 than in run 3. This behavior was not unexpected since the resin used in run 2 was new resin; i.e., the resin was not previously exposed to fixer solution or *conditioned* by long-term use. To what extent the resin capacity decreases after being used for a time is not known. However, previous studies have indicated that a noticeable decrease in resin capacity generally occurs between the first and second silver stripping operations when the same resin is used (ref. 8).

The results of strip run 4 (fig. 11) are much more realistic of pilot-plant stripping operations. During this run, the silver concentration in the fix tank was successfully maintained below 0.5 gm Ag^+/ℓ with total recycle of the fixer solution. In addition, the effluent silver concentration data for column 2 provided a breakthrough curve (fig. 12) from which the height of the exchange zone and the resin capacity were estimated. The effluent volumes (i.e., the absissa values in figure 12) for the breakthrough curve were determined by first multiplying the fixer solution flow rate by the total time elapsed at the moment a particular effluent sample was taken, and then subtracting the volume of solution required to fill the first two columns.

The capacity of the resin for silver can be estimated from the breakthrough curve together with the relationship

$$q = \frac{C_o V_B}{M_{Ag} V_S (1-\varepsilon)} \quad \text{(ref. 8)} \qquad (5)$$

where q is the resin capacity for silver, C_o is the influent silver concentration of the fixer solution, V_B is the volume of the fixer solution circulated through the column prior to the breakthrough point (fig. 12), M_{Ag} is the

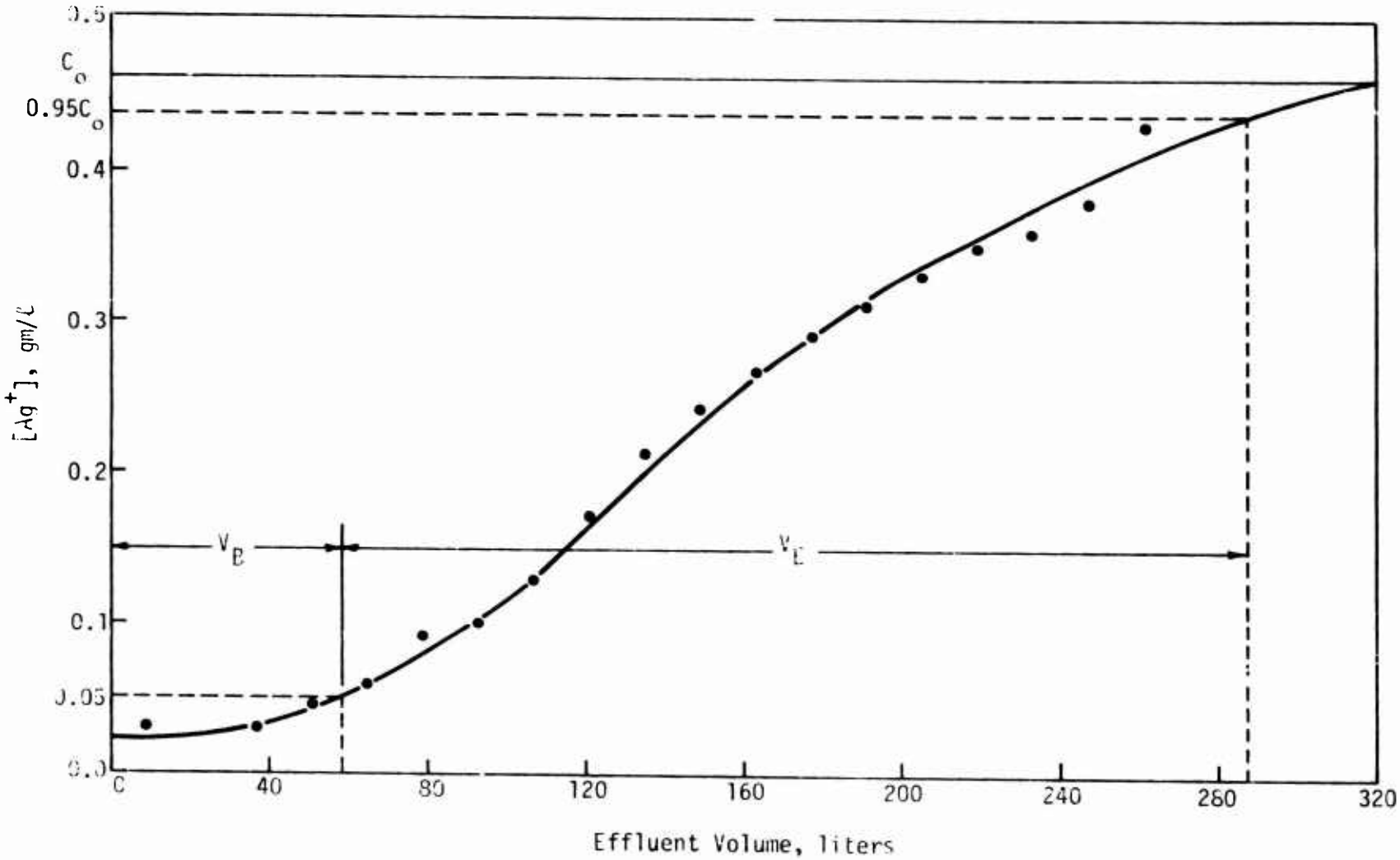


Figure 12. Breakthrough Curve for Column 2 Strip Run 4

equivalent weight of silver, V_S is the volume of the resin bed not included in the exchange zone and ε is the resin bed porosity (assumed to be 0.40). The volume of resin not included in the exchange zone, V_S, is given by

$$V_S = V_R - ZS \tag{6}$$

where V_R is the total volume of the resin bed, Z is the height of the exchange zone, and S is the cross-sectional area of the column. The height of the exchange zone, Z, is determined by

$$Z = \frac{V_E C_o}{S(q + \varepsilon C_o)} \tag{7}$$

This relationship is similar to eq. (3), except that q is the actual capacity of the resin rather than the equilibrium capacity, q_e. Equations (5), (6), and (7) can be solved for Z, q, and V_S using the values from the breakthrough curve in figure 12. These values are as follows:

C_o = 0.46 gm Ag^+/ℓ = 0.0043 meq Ag^+/cm^3
V_E = 287-58 = 229 liters
V_R = 2(7.71) = 15.42 liters
M_{Ag} = 107 gm Ag^+/equiv
V_B = 58 liters
S = 79.1 cm^2
ε = 0.40

From these values, the actual resin capacity, q, and the height of the exchange zone, Z, were estimated.

$$q = 0.09 \text{ equiv } Ag^+/\ell \text{ of resin}$$

and

$$Z = 136 \text{ cm}$$

The actual resin capacity is somewhat less than the equilibrium capacity of $q_e \approx 0.14$ equiv Ag^+/ℓ of resin determined from figure 2. This result is not unexpected since the equilibrium values in figure 4 were determined using new resin while the actual capacity from the pilot-plant run was determined using regenerated resin. The resin was not and cannot be regenerated to 100 percent of its initial capacity by the methods followed in this study. Thus, an actual resin capacity of 64 percent of the equilibrium capacity for new resin appears to be a realistic value. In addition, the height of the exchange zone (136 cm or approximately 3 ft 8 in. of resin) is also a realistic value in view of the flow rates achieved in the pilot plant. These values indicate that each pilot-plant column was capable of adsorbing 74.3 gm of silver (i.e., approximately the amount of silver added to the fix tank during 1 hr of operation) and that the height of the exchange zone extended into two columns. Thus, three pilot-plant columns connected in series could operate for approximately 1 hr and 25 min (fig. 11) before reaching exhaustion.

These stripping results indicate that an ion-exchange system could successfully remove silver from fixer solutions and maintain the silver concentration in the fix tank below 0.5 gm Ag^+/ℓ. However, for design purposes, the resin capacity for silver is only 64 percent of the equilibrium capacity of new resin. Furthermore, the height of the exchange zone is somewhat larger than desired. This can be avoided by using a larger diameter column. A larger diameter column would also provide room for additional resin and, perhaps, reduce the superficial velocity of the fixer solution through the column to permit fluidization of the resin particles. However, fluidization of the resin would probably not be an advantage because of the significant backmixing which occurs under these conditions.

3. REGENERATION OF ION-EXCHANGE RESIN

Following the stripping operation, the resin was regenerated by circulating a regenerant solution through each column. The regenerant solution was basically a 3.0 M thiosulfate solution with 0.20 to 0.25 gm/ℓ of silver (table IV). The high ratio of $S_2O_3^=$ to Ag^+ (i.e., high relative to that found in spent fixer solutions) was used to alter the equilibrium conditions existing between the silver thiosulfate complexes adsorbed on the resin and the silver thiosulfate complexes present in the solution. This equilibrium relationship can be

illustrated by

$$(2n-1)\ R_2S_2O_3 + 2[Ag(S_2O_3)_n]^{-(2n-1)} \rightleftarrows$$

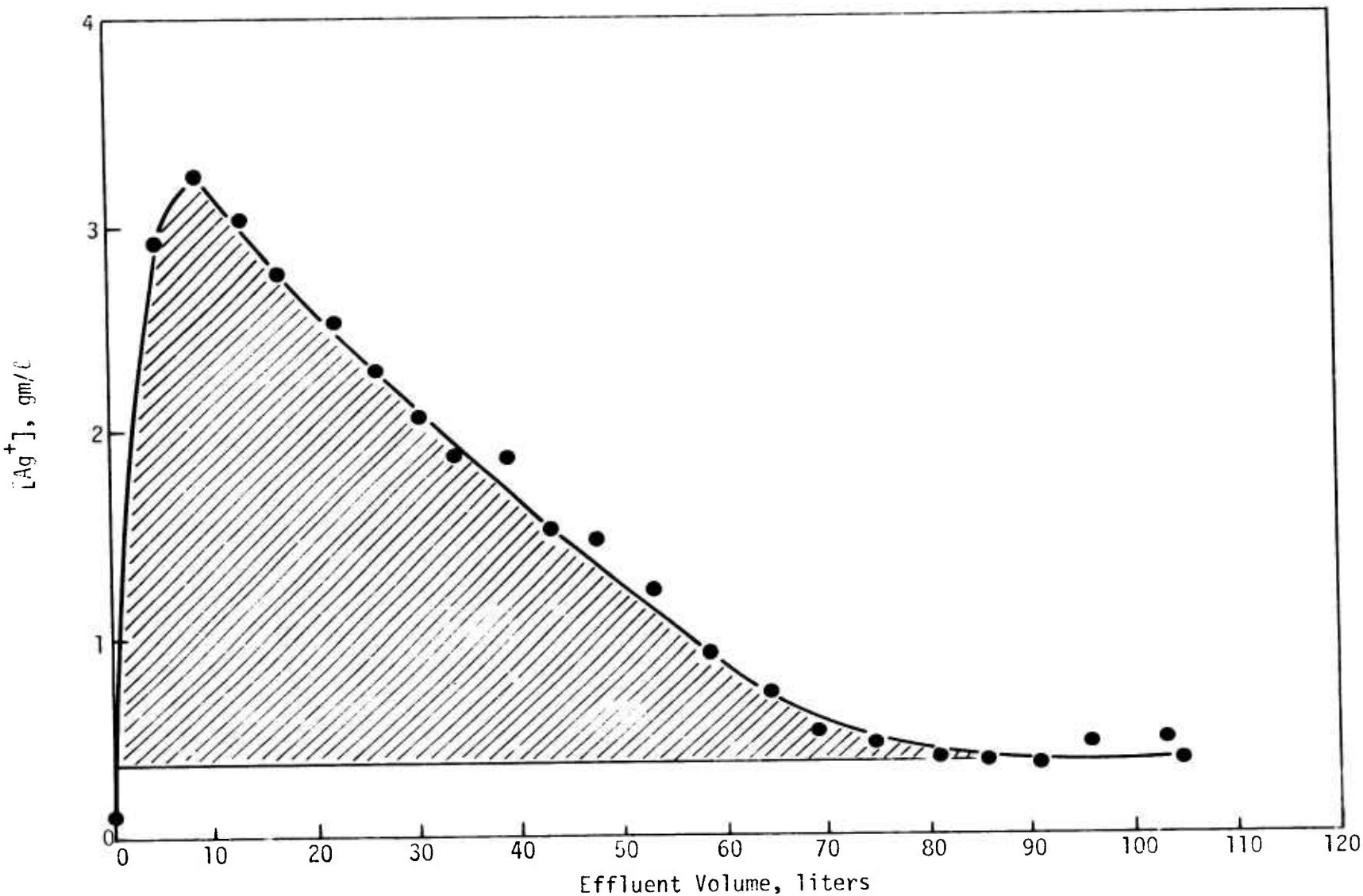
$$R_{4n-2}[Ag(S_2O_3)_n]_2 + (2n-1)S_2O_3^{=} \qquad (8)$$

for n = 1, 2, 3. A low $S_2O_3^{=}$-to-Ag^+ ratio (e.g., the fixer solution) favors the formation of silver thiosulfate complexes which forces eq. (8) to the right as required during the stripping cycle. A high $S_2O_3^{=}$-to-Ag^+ ratio (e.g., the regenerant solution) provides a high concentration of free thiosulfate ions which forces eq. (8) to the left as required during the regeneration cycle.

Obviously, the most ideal regenerant solution is one which has the highest possible thiosulfate concentration and no silver. Such a solution could potentially remove all the silver adsorbed by the resin. However, since the silver is recovered from the regenerant solution by electrolysis, it is impossible to obtain a solution containing no silver. Under these conditions, it is also impossible to completely restore the resin to its original capacity. The extent to which the resin can be restored to its original capacity depends on the $S_2O_3^{=}$-to-Ag^+ ratio in the regenerant solution.

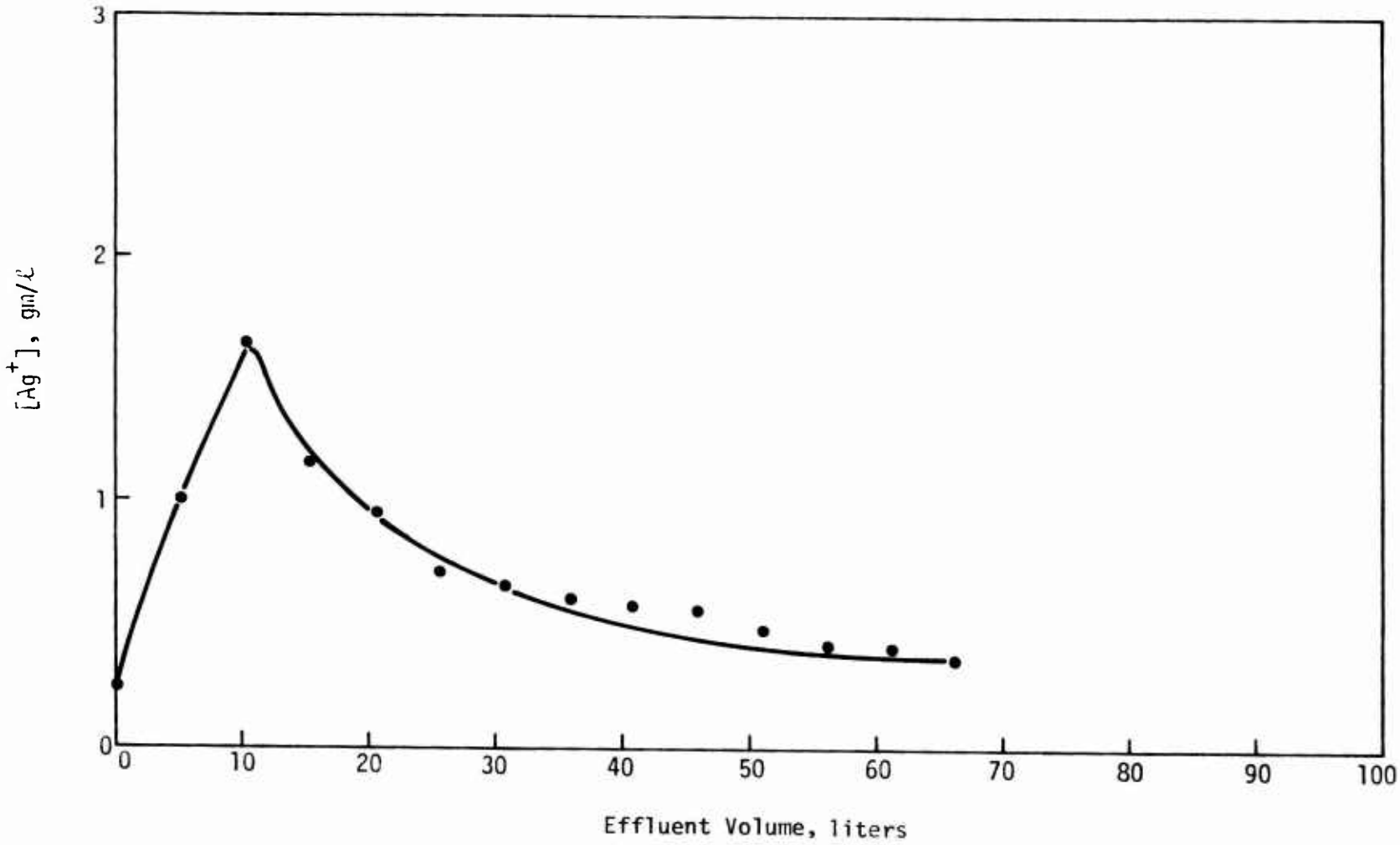
As the regenerant solution circulates through the column, the silver is removed from the resin until the solution and the resin reach equilibrium conditions. At this point, no further silver is removed from the resin and regeneration is terminated. In most cases, equilibrium conditions are achieved only after an extended regeneration period so that regeneration is usually terminated at some predetermined point as the system approaches equilibrium. For the pilot-plant study, regeneration was terminated when the silver concentration in the regenerant solution leaving the column showed no significant change. In general, the silver concentration in this effluent solution approaches that of the influent regenerant solution (i.e., 0.20 to 0.25 gm Ag^+/ℓ). The silver remaining on the resin is then in equilibrium with the silver in the regenerant solution.

The results of the pilot-plant regeneration runs, using a regenerant solution with the composition given in table IV, are shown in figures 13 and 14. Figure 13 shows the regeneration data for columns 1 and 2 for strip run 2.



(a) Column 1

Figure 13. Regeneration Data for Strip Run 2



(b) Column 2

Figure 13---Concluded

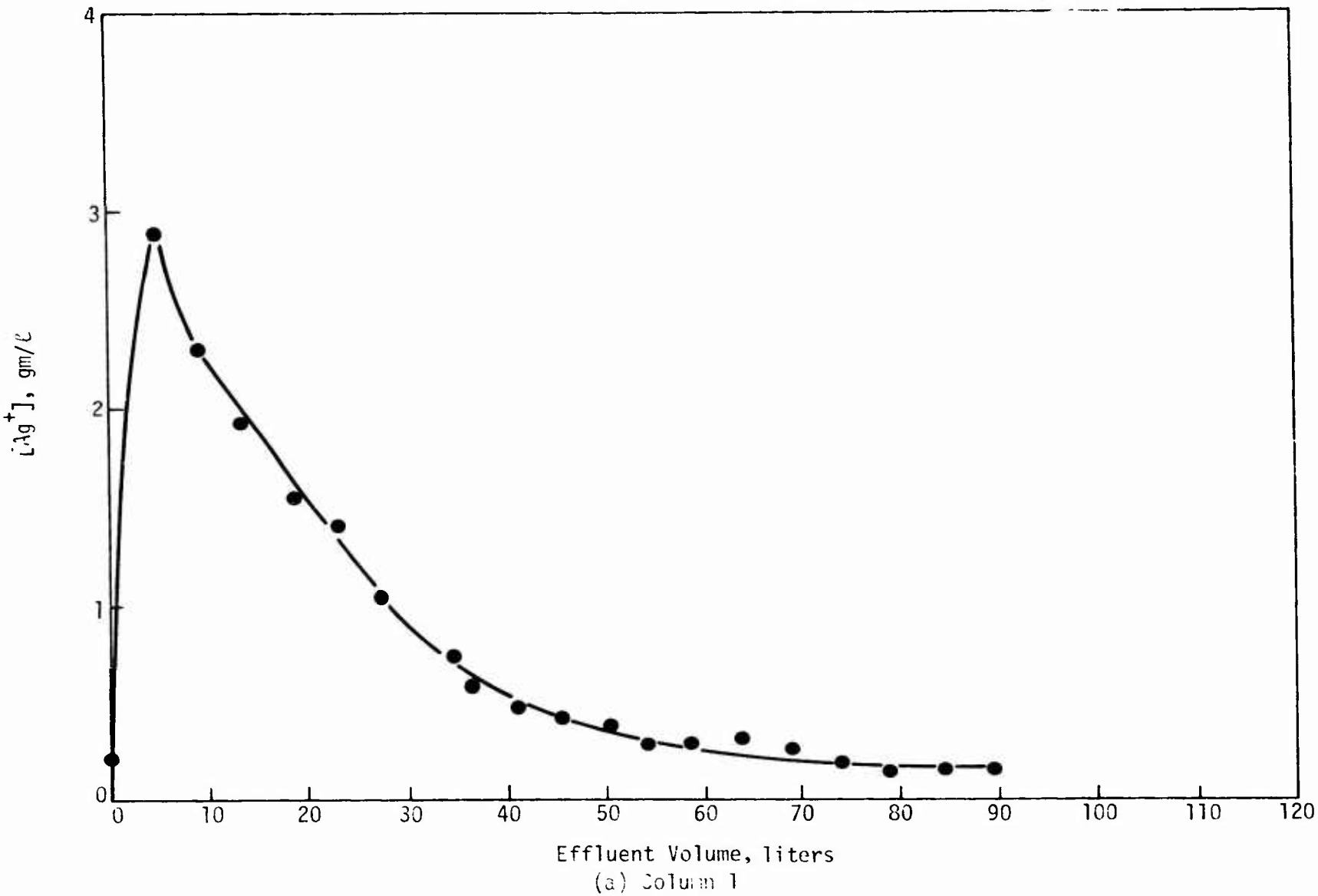
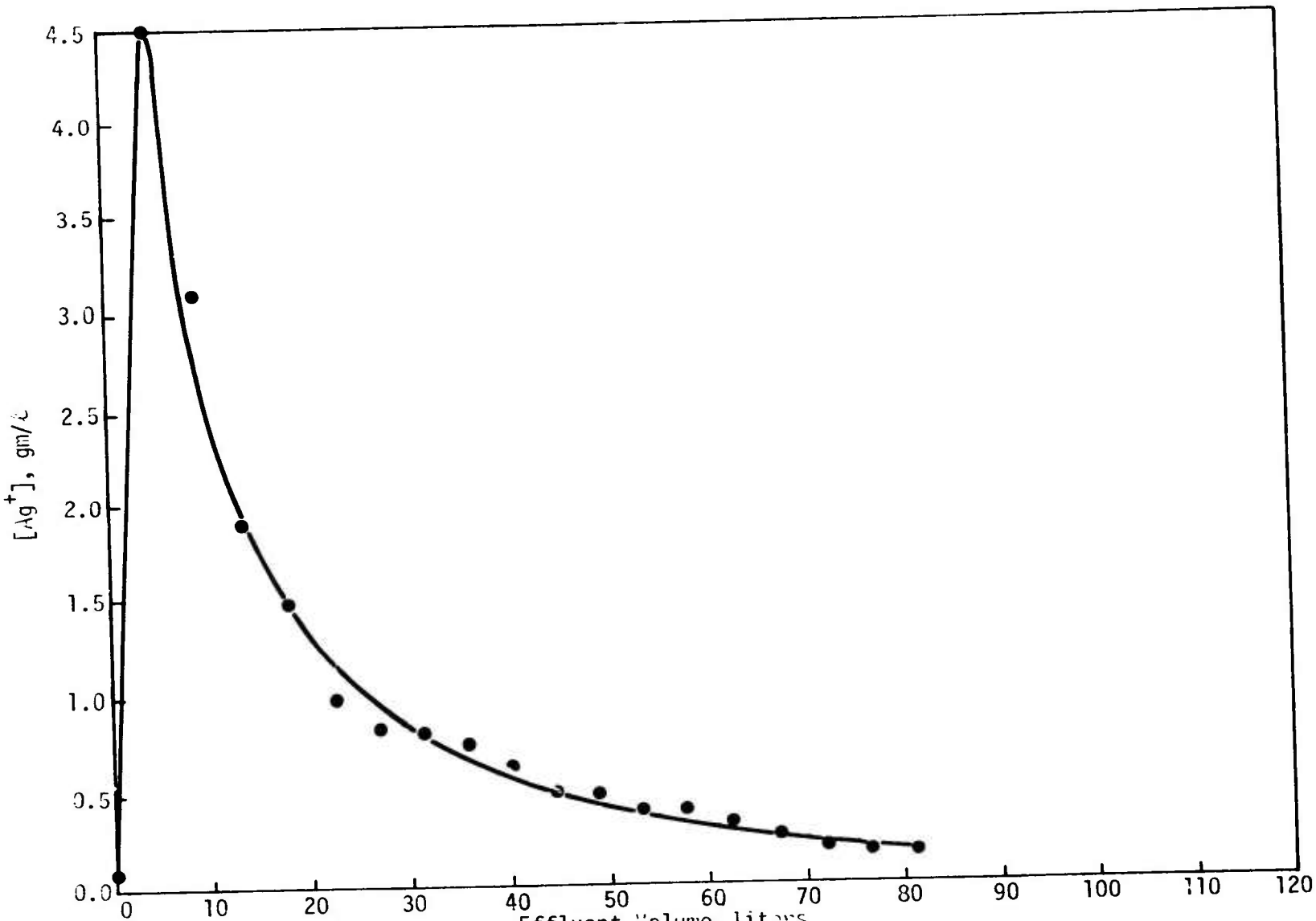
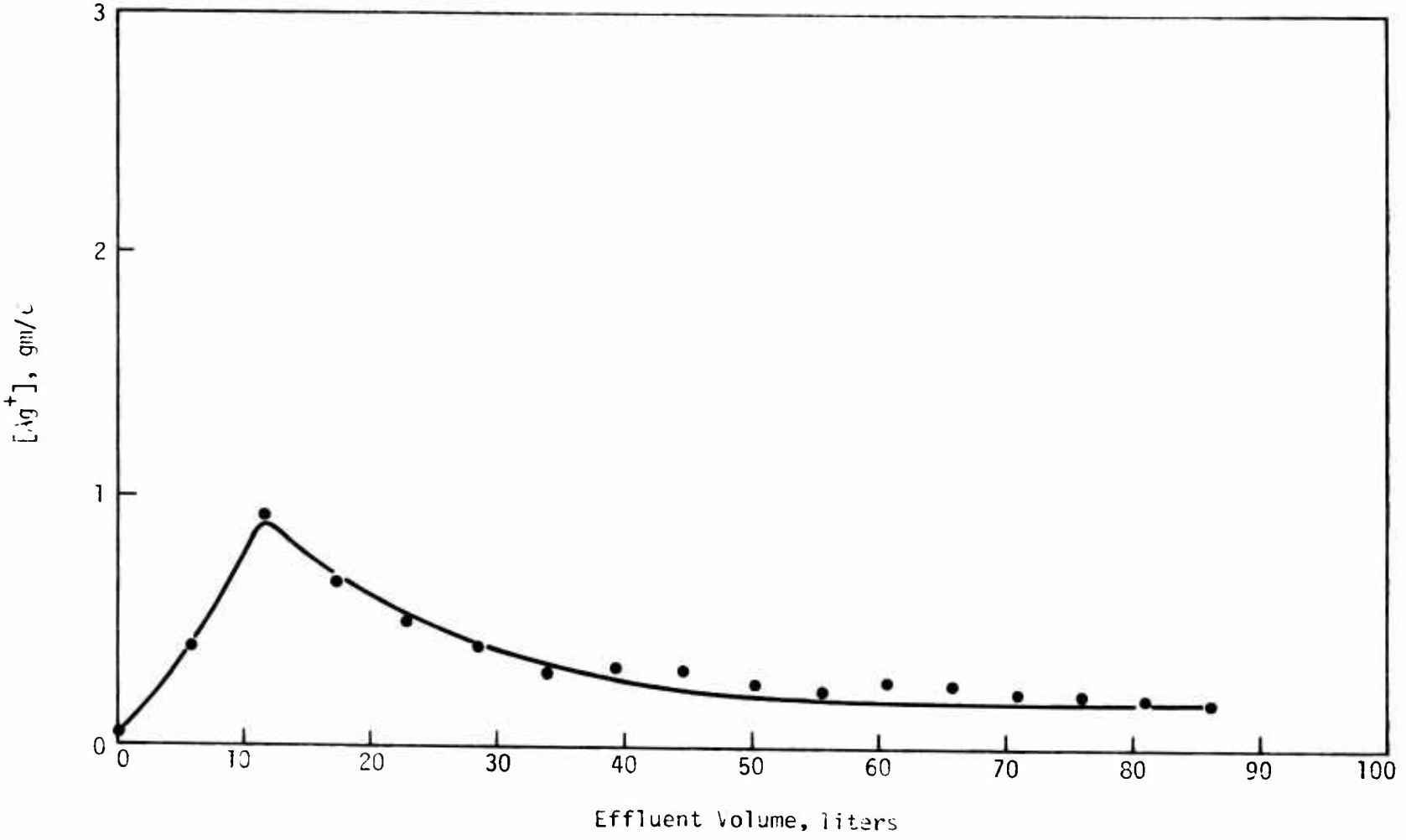


Figure 14. Regeneration Data for Strip Run 3



(b) Column 2

Figure 14---Continued



(c) Column 3

Figure 14---Concluded

Similarly, figure 14 shows the regeneration data for columns 1, 2, and 3 for strip run 3. (No regeneration data were obtained for strip runs 1 and 4.) Silver concentration data and pH data for these regeneration runs are given in appendix II.

The area under these curves (illustrated in figure 13a by the shaded portion) gives the amount of silver removed from the resin for the corresponding regeneration run. The amount of silver removed in each of the five regeneration runs is given in table V. These values vary considerably, making it difficult to estimate the average amount of silver removed from each liter of resin regenerated. It should be noted, however, that column 2 in strip run 2 and column 3 in strip run 3 were not fully saturated with silver so that the amount of silver removed from the resin was smaller for the corresponding regeneration runs. Regeneration runs 2-1 and 3-2 indicate that relatively large amounts of silver were removed from the resin. These values lie between the estimated resin capacity of 0.09 equiv Ag^+/ℓ of resin and the equilibrium resin capacity of approximately 0.14 equiv Ag^+/ℓ of resin. Unfortunately, regeneration run 3-1 indicates that a smaller amount of silver was removed (0.072 equiv Ag^+/ℓ of resin) than that removed from the previous regeneration run (regeneration run 2-1: 12.0 equiv Ag^+/ℓ of resin). This might indicate that the resin capacity decreases with continued use. Of course, the resin will not last indefinitely, but capacity decreases of the magnitude indicated above are unacceptable. More regeneration runs with the same resin must be made before any conclusions concerning this decrease in resin capacity can be made. On the other hand, it seems reasonable to assume that the resin capacity will show a

Table V

SILVER REMOVAL BY REGENERATION

Regeneration Run	Strip Run	Column	Amount of Silver Removed		
			gm Ag^+	gm Ag^+/ℓ of resin	equiv Ag^+/ℓ of resin
2-1	2	1	92.3	12.0	0.112
2-2	2	2	22.4	2.9	0.027
3-1	3	1	59.2	7.7	0.072
3-2	3	2	102.0	13.2	0.123
3-3	3	3	14.0	1.8	0.017

large decrease initially (because of the silver contained in the regenerant solution), and then remain relatively constant for some time. This time is determined to a large extent by the success of the resin fouling prevention techniques used (refs. 7, 8).

An average volume of 90 liters of regenerant solution was required to regenerate a single column (i.e., 11.7 liters of regenerant solution per liter of resin). Since the regenerant solution was circulated through a column at a rate of 0.50 ℓ/min (equivalent to 51.6 liters of solution/min-liter of resin) as suggested by the manufacturer, it took an average time of 3 hr to complete the regeneration cycle. In comparison, less than 1 hr was required to saturate the column with silver during the stripping operation. Thus, it took approximately three times as long to regenerate the resin as it did to saturate it. Of course, it may be possible to increase the regenerant solution flow rate to speed up the regeneration process. However, it is very likely that additional regenerant solution will then be required, resulting in approximately the same amount of time for regeneration. The effect of solution flow rate on the rate of regeneration may be a useful objective for future studies involving ion-exchange resins.

4. ELECTROLYTIC RECOVERY OF SILVER

After the regenerant solution was circulated through a column to remove the silver from the resin, it was electrolyzed to recover the silver and to return the silver concentration in the regenerant solution to its initial value. An Argenta Model 30 silver-recovery unit, manufactured by Future Systems, Inc., was used to recover the silver. This unit has a maximum plating current of 25 amp, a plating surface of 384 in.^{2} (2300 cm^2), and is capable of recovering up to 2.5 troy oz/hr (77.6 gm/hr) of silver. The silver concentration in most fixer solutions (including the regenerant solution) can be reduced to 0.02 troy oz/gal. (0.165 gm/ℓ) without sulfiding, using this unit in a continuous recycle mode of operation (ref. 19).

Data from a typical electrolytic silver-recovery run using 30 liters of solution are shown in figure 15. Silver concentration and pH data for this run (run A) is tabulated in appendix III. To achieve a low silver concentration in the regenerant solution without causing decomposition of the thiosulfate (i.e., sulfiding), a low current density of 1.13 amp/ft^2 (i.e., a plating current of 3 amp) was used. This is the maximum current density permissible

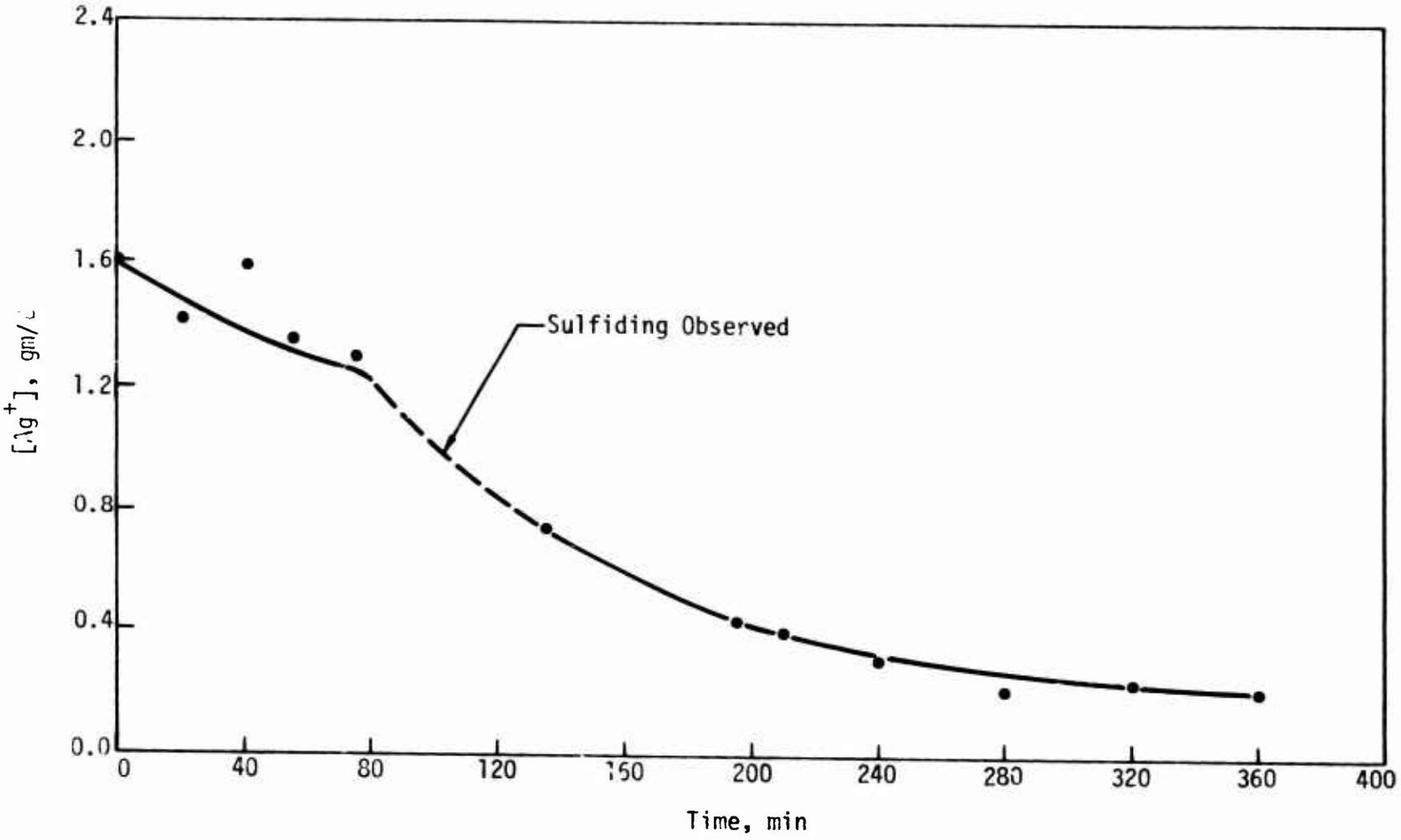


Figure 15. Typical Electrolytic Silver-Recovery Data

for plating silver from photographic fixer solutions containing less than 1.0 gm/ℓ of silver (ref. 5). As a result of this low current density, considerable time was required to electrolyze the regenerant solution and bring the silver concentration down to 0.20 to 0.25 gm Ag^+/ℓ. As indicated in figure 15, it required 4 to 5 hr to electrolyze the 30 liters of regenerant solution. Since approximately 90 liters of regenerant solution were required to regenerate each column, it took 900 min, or 15 hr, to bring the regenerant solution silver concentration to its initial value so that it could be reused. Thus, for each liter of resin, the 11.7 liters of solution required for regeneration took 117 min or almost 2 hr to electrolyze.

Higher current densities were used to electrolyze some regenerant solutions. (See electrolytic run 2-1-a in appendix III.) As expected, significant sulfiding occurred on these runs. Some sulfiding also occurred at the lower current densities as indicated in figure 15. However, it was a relatively small amount and, with careful current density and pH control, it could probably be eliminated. It is quite important to maintain adequate pH control (the pH should be between 4.5 and 5.0, preferably 4.5) to prevent sulfiding (ref. 5). Sulfiding can be inhibited by keeping the sulfite concentration in the regenerant solution high (table IV). Since it is used up during electrolysis, additional sulfite must be added periodically (ref. 5).

In addition, any solid particles formed by sulfiding or other chemical reactions, may be removed by circulating the solution through a 75-micron filter as suggested by Future Systems, Inc. (ref. 19).

Silver concentrations as low as 0.05 gm Ag^+/ℓ can be achieved if a batch-type electrolytic system is used with very low current densities (ref. 4). These current densities are usually about 0.2 amp/ft^2 (less than 20 percent of the current densities used in this study). Obviously, with such low current densities, the electrolytic operation will require more time than that encountered in this study.

The time required to electrolyze the regenerant solution can be decreased by increasing the surface area available for plating. This, of course, means that additional electrolytic units are needed.

SECTION VI
COST EVALUATION

There are two approaches for reducing the discharge of pollutants into the environment from photographic film processing. One is to treat the waste stream from the process to remove any pollutants which it may contain; the other is to eliminate the waste stream from the process so that no waste treatment is necessary and, of course, no pollutants are discharged. The first approach is the one commonly used at Air Force installations today. Spent photographic fixer solutions are circulated through metallic replacement cartridges which recover much of the silver. Up to 99 percent of the silver can be recovered if the cartridge is used properly (ref. 4). The silver-free solution is then discharged into a sanitary sewer system which carries it to a general waste treatment system where it is treated prior to discharge into natural waters. In most cases, however, conventional treatment methods (e.g., trickling filters, activated sludge system, etc.) are not adequate to meet current or proposed discharge standards, particularly for silver. Thus, the second approach, that of zero discharge from the process, is highly desirable.

There appears to be two methods of operating a photographic process with zero discharge. Both methods, electrolysis (ref. 8) and ion-exchange resin processing, require recycling of the fixer solution following removal of the silver deposited by the film. The electrolytic method appears to be limited to fixer solutions with silver concentrations greater than 0.5 gm Ag^+/ℓ (refs. 4 and 5). On the other hand, ion-exchange resins can be used with any fixer solution silver concentration including those below 0.5 gm Ag^+/ℓ (ref. 8). Note, however, that although the fixer solution is not itself discharged, neither method gives a completely zero discharge. In both cases there is some carryover of fixer solution into the rinse waters which are eventually discharged into the sanitary sewer system.

Since silver discharges from photographic film processes utilizing metallic replacement cartridges do not meet proposed silver discharge standards, a recycle system such as that used with the ion-exchange and electrolytic methods may be necessary. However, unless carryover of fixer solutions into rinse waters is eliminated or at least significantly reduced, silver discharges may still exceed the proposed standards. This is particularly true at installations where a large amount of photographic film is processed.

To fairly evaluate an ion-exchange silver-recovery system, it should be compared with a realistic alternative. Since processes utilizing metallic replacement cartridges cannot meet silver discharge standards, a more realistic alternative would be an electrolytic recycle system. Such a system can potentially accomplish the same results as an ion-exchange system.

The following evaluation was based on a silver addition rate of 1.25 gm Ag^+/min, 8 hr a day, 5 days a week, for 1 yr. This is equivalent to a film processing rate of 4.7 ft/min of 9 1/2-in.-wide aerial film containing an average of 0.266 gm Ag^+/ft^2 of film (ref. 4)--a total of 600 gm Ag^+/day, or 156,000 gm Ag^+/yr. The silver concentration of the fixer solution was maintained at 0.5 gm Ag^+/ℓ for both methods so that carryover into rinse waters was identical. It was also assumed that the photographic film processing system was installed and operating so that the only costs involved were those of the particular silver-recovery and recycle system used. In addition, costs of capital items were depreciated over a 10-yr period.

1. ELECTROLYTIC SYSTEM

In the electrolytic system, the fixer solution is circulated from the fix tank through an electrolytic unit (where the silver is plated out) and back to the fix tank. The fixer solution is recycled so that there is no discharge of the solution. The silver is plated out at the same rate at which it enters the solution with the film (i.e., 1.25 gm Ag^+/min or 600 gm Ag^+/day). If the current density in the electrolytic unit is maintained at 1.1 amp/ft^2, which is the maximum current density permissible for fixer solutions with a silver concentration of 0.5 gm Ag^+/ℓ (ref. 5), the size of the unit required for plating out 1.25 gm Ag^+/min is

$$A = \frac{(1.25 \text{ gm } Ag^+/\text{min})(96{,}400 \text{ coulomb/equiv})}{(60 \text{ sec/min})(107 \text{ gm } Ag^+/\text{equiv})(1.0 \text{ coulomb/amp-sec})(1.1 \text{ amp/ft}^2)}$$

$$= 17.1 \text{ ft}^2$$

Since the Argenta Model 30 electrolytic unit has a plating surface of 2.66 ft^2, 6.4 (i.e., 7) of these units are needed. At a cost of $815.45 each, this amounts to a capital expenditure of $5,700 or $570/yr based on a 10-yr depreciation schedule.

The maximum power requirement for each electrolytic unit is 330 w. The amount of electrical energy required to operate seven of these units 8 hr a day, 5 days a week, for 1 yr is 4,810 kwhr. At a base price of $0.015/kwhr, the cost of operating the electrolytic units is approximately $72.10/yr.

If 50 gal. of fixer solution are required to fill the fix tank and electrolytic units, and if 10 percent of this amount must be replaced each week because of evaporation and carryover, a total of 310 gal. or 1,174 liters of fixer solution would be needed each year. At a cost of $6.00/25 gal. (ref. 3), this amounts to $74.30/yr.

The manpower requirement to maintain the electrolytic units is estimated to be 2 manhours/day, 5 days a week. If labor costs $4.00/hr, this amount is $2,080/yr.

The total savings per year using an electrolytic recycle system is as follows:

Item	Cost, $/yr
Electrolytic Units	570.00
Chemicals	74.30
Power	72.10
Labor	2,080.00
	2,796.40
Revenue*	10,040.00
	7,243.60

*Income from the sale of 156,000 gm Ag^+/yr (5020 troy oz/yr) at $2.00/troy oz.

Based on the amount of film processed each year, the amount of money saved is $15.65/1000 ft² of film.

2. ION-EXCHANGE SYSTEM

An ion-exchange silver-recovery system, such as the one presented in this study, requires a number of capital items including tanks, ion-exchange columns, electrolytic units, and pumps. The ion-exchange columns are designed to handle the silver deposited in the fixer solution from one, 8-hr day of film processing. With a resin capacity for silver of 0.09 equiv Ag^+/ℓ of resin (determined from the pilot-plant study), 62.4 liters (2.20 ft^3) of resin are required to remove

the 600 gm of silver processed each day. Two ion-exchange columns, each with a capacity of 2.20 ft^3, are required. (One column is regenerated while the other is used.) The installed cost of each of these units is estimated to be $1,275. The total capital cost for the ion-exchange columns is $2550 or $255/yr based on a 10-yr depreciation schedule. The cost of replacing all the resin (i.e., 4.40 ft^3) once each year is $294.80. This is based on the current price of Amberlite IRA-900, which is $67/$ft^3$.

Since the silver is eventually recovered by electrolysis, one or more electrolytic units are required. With an ion-exchange system, however, the regenerant solution can be electrolyzed over a 24-hr period instead of an 8-hr period as with the electrolytic recycle system. Thus, the size of the electrolytic unit is based on a plating rate of (1.25)(8/24) = 0.417 gm Ag^+/min. The size of the unit required for this rate is 5.7 ft^2 based on a current density of 1.1 amp/ft^2. Thus, 2.14 (i.e., 3) electrolytic units of the type used in the pilot-plant study are needed. At a cost of $815.45 each, this amounts to $2,450 or $245/yr. The power required to run these units for a year is the same as that for the electrolytic recycle system (4,810 kwhr). The cost for this power is $72.10/yr.

Three solutions are required for this system: a fixer solution, a regenerant solution, and an acetate pretreat solution. The amount and the cost of the fixer solution are 20 percent more than those for the electrolytic recycle system--372 gal. (1,410 liters) and $89.16 a year. (The additional solution is needed to fill the ion-exchange column.) Approximately 100 gal. of regenerant solution are also needed and about 10 percent of this is replaced each week to account for chemical changes in the solution because of electrolysis. At a cost of $9.00/25 gal., a 1-yr supply costs $223.00. In addition, a centrifugal pump, costing approximately $100 ($10/yr based on a 10-yr depreciation schedule), is needed to circulate the regenerant solution and a 125-gal. tank, costing about $175 ($17.50/yr), is needed to hold it. The pump uses approximately 2,060 kwhr of electricity each year; this is a cost of $30.90/yr. An acetate pretreat solution (60 gal.), tank (75 gal.), and pump are also required. The cost of 372 gal./yr of this solution is estimated to be $44.50/yr (a rate of $3.00/25 gal.). The tank, pump, and power costs are as follows: the tank is $100 or $10/yr; the pump is $100 or $10/yr; the power for the pump is $30.90/yr.

The manpower requirement for an ion-exchange system is estimated to be 6 manhours/day, 5 days a week. (Since it takes three times as long to regenerate

a column as it does to saturate it, it takes 24 hr to generate a column after an 8-hr day of film processing.) If labor costs $4.00/hr, this amounts to $6,240/yr.

The total savings per year using an ion-exchange silver-recovery system is as follows:

Item	Cost, $/yr
Ion-Exchange Columns	255.00
Electrolytic Units	245.00
Pumps	20.00
Tanks	27.50
Chemicals	356.66
Ion-Exchange Resin	294.60
Power	133.90
Labor	6,240.00
	7,572.86
Revenue*	10,040.00
	2,467.14

*Income from sale of 156,000 gm Ag^+/yr (5020 troy oz/yr) at $2.00/troy oz.

On the basis of the amount of film processed each year, the savings is $5.31/1000 ft^2 of processed film.

3. COMPARISON

It should be noted that this evaluation did not include the cost of the equipment and supplies, the labor, or the operating expenses for the actual film processing. Only treatment and recovery costs were considered. One cost, however, that was not included was that of treating the rinse waters which contain the silver lost from the fix tank by carryover. This carryover is approximately the same for each method and is assumed to be from 3 to 5 percent of the total silver removed from the film. At installations where a large amount of film is processed, the amount of silver lost by carryover may exceed the allowable discharge standards. In this case, significant and perhaps expensive treatment of rinse waters will be necessary.

Costwise, this evaluation indicates that an ion-exchange silver-recovery

system is a poor system when compared to an electrolytic recycle system. Although capital costs for the ion-exchange system are about the same as those for the electrolytic system, it is about three times more costly to construct and operate an ion-exchange system. Also, since three solutions are needed for the ion-exchange system, the chemical costs are higher. The resin is also very expensive and, if it must be replaced periodically, it would add significantly to the cost of the system. However, the resin may not have to be replaced as often as indicated. If so, a significant decrease in the cost of the ion-exchange system will be realized. Finally, and most important, the manpower requirements for the ion-exchange system are three times that for the electrolytic recycle system because of the *round-the-clock* effort required to regenerate the resin.

SECTION VII
CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS

The following conclusions are based on the results of the pilot-plant study and the cost evaluation of the ion-exchange silver-recovery system presented in this report:

(1) An ion-exchange silver-recovery system is technically feasible for recovering silver (as a mixture of thiosulfate complexes) from photographic fixer solutions. The fixer solution silver concentration can be maintained below 0.5 gm Ag^+/ℓ with complete recycle of the fixer solution. The resin can be regenerated with a thiosulfate solution from which the silver can be recovered by electrolysis.

(2) A working capacity of 0.09 equiv Ag^+/ℓ of resin for Amberlite IRA-900 anion-exchange resin is approximately 64 percent of the predicted equilibrium capacity of 0.14 equiv Ag^+/ℓ of resin (determined from a Langmuir-type equation). The working capacity, however, appeared to decrease with repeated use

(3) The equilibrium capacity of the resin for silver can never be fully realized since the resin is not regenerated with a pure thiosulfate solution.

(4) An exchange zone height of 136 cm was achieved with the pilot-plant units operating at a superficial velocity of 34.2 cm/min. A larger diameter column will decrease the height of the exchange zone and decrease the pressure drop across the resin bed.

(5) Regeneration of the resin requires 11.7 liters of solution for each liter of resin and a regeneration period three times longer than that required for saturating the column with silver.

(6) Electrolysis of regenerant solutions containing low concentrations of silver (i.e., less than 1.0 gm Ag^+/ℓ) must be carried out at current densities less than 1.1 amp/ft^2 of plating surface.

(7) A comparison of an ion-exchange system and an electrolytic recycle system indicates that the latter is the more economical. This is due primarily to the much longer period of time required to operate the ion-exchange system.

2. RECOMMENDATIONS

The following recommendations are made on the basis of the foregoing conclusions:

(1) Research efforts directed toward the development of an ion-exchange silver-recovery system for fixer solutions should be terminated. Research utilizing ion-exchange resins for removing silver from rinse waters may prove more rewarding since much of the silver carried over into rinse waters must be removed if discharge standards are to be met.

(2) A quantitative evaluation of the effect of silver concentration in the fix tank on the amount of silver carried over by the film into rinse waters should be made. It is the opinion of the authors that with efficient squeegee operation, lowering the silver concentration in the fix tank (i.e., below 1.0 gm Ag^+/ℓ) may not significantly reduce carryover. If this is true, higher fix tank silver concentrations may be used, allowing better silver-recovery efficiency with the recycled fixer solution.

(3) Research efforts should be directed toward developing an efficient electrolytic recycle system for use with photographic fixer solutions. This method has already been successfully established (ref. 8).

APPENDIX I
STRIPPING DATA

Stripping data from runs 1, 2, 3, and 4 are presented in this appendix. Run 1 was carried out under improper conditions and the March pump failed so that no silver was added to the fix tank during the run. Thus, run 1 was not included in the calculations.

Time, min	Fix Tank		Column 1		Column 2		Column 3	
	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH
Strip Run 1								
0	0.912	3.7	---	---	---	---	---	---
5	2.20	3.6	0.162	3.5	---	---	---	---
10	2.19	3.1	0.444	3.6	---	---	---	---
15	2.16	3.2	0.572	3.3	0.128	4.0	---	---
20	2.12	3.9	0.672	3.9	0.145	4.5	---	---
25	2.17	3.8	0.684	3.8	0.157	4.5	---	---
30	2.09	3.7	0.784	3.8	0.159	4.5	---	---
35	2.08	3.7	1.04	3.7	0.552	3.9	0.107	4.5
40	1.58	3.8	1.40	3.8	0.664	3.9	0.229	4.1
45	1.33	3.9	1.23	3.9	0.720	3.7	---	3.9
50	0.880	3.8	1.24	4.0	0.728	3.8	0.416	3.7
55	0.912	3.8	1.18	3.8	0.836	3.8	0.440	3.8
60	0.920	3.8	1.11	3.8	0.892	3.8	0.524	4.0
65	0.836	3.9	1.05	3.9	0.928	3.8	0.584	3.9
70	1.04	3.8	0.996	4.0	0.884	3.8	0.620	3.8
75	0.984	3.8	1.02	3.8	0.880	3.8	0.716	3.9
80	0.972	3.8	0.888	3.8	0.912	3.9	0.744	3.9
85	1.12	3.9	1.02	3.8	0.880	3.9	0.752	3.8
90	1.01	4.0	1.02	3.9	0.944	3.9	0.760	3.8
95	1.14	3.8	1.13	3.9	0.980	3.8	0.792	3.8
100	1.10	3.8	0.988	3.8	0.940	3.8	0.836	3.8

Time, min	Fix Tank		Column 1		Column 2		Column 3	
	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH
Strip Run 2								
0	0.500	4.6	---	---	---	---	---	---
10	0.460	4.6	0.006	4.9	---	---	---	---
20	0.430	4.6	0.008	4.6	0.006	4.9	---	---
30	0.290	4.7	0.006	4.6	0.006	4.9	0.007	4.9
40	0.570	4.9	0.006	4.8	0.006	4.7	0.006	4.8
50	0.460	4.8	0.008	4.8	0.006	4.7	0.005	4.7
60	0.600	4.8	0.009	4.7	0.005	4.8	0.004	5.0
70	0.500	4.8	0.016	4.8	0.005	4.8	0.005	4.7
80	0.480	4.8	0.017	4.7	0.006	4.8	0.004	4.7
90	0.500	4.7	0.020	4.7	0.005	4.7	0.003	4.7
100	0.550	4.7	0.023	4.7	0.003	4.9	0.002	4.8
110	0.530	4.7	0.050	4.7	0.005	4.7	0.004	4.7
120	0.570	4.7	0.070	4.7	0.005	4.7	0.005	4.7
130	0.600	4.7	0.090	4.7	0.005	4.7	0.004	4.7
140	0.600	4.7	0.150	4.7	0.007	4.8	0.004	4.8
150	0.570	4.7	0.193	4.7	0.007	4.9	0.006	4.8
160	0.600	4.7	0.250	4.7	0.007	4.8	0.005	4.7
170	0.650	4.7	0.260	4.7	0.008	4.7	0.004	4.7
180	0.620	4.7	0.340	4.7	0.010	4.7	0.004	4.7
Strip Run 3								
0	0.340	4.7	---	---	---	---	---	---
5	0.740	4.8	0.017	4.7	---	---	---	---
10	0.670	4.8	0.009	4.8	0.015	4.8	---	---
15	---	---	0.061	4.8	---	---	---	---
20	0.800	4.7	0.100	4.8	0.016	4.8	---	---
25	---	---	0.159	4.8	---	---	---	---
30	0.910	4.7	0.193	4.7	0.018	4.8	---	---
35	---	---	0.230	4.7	---	---	---	---
40	0.960	4.8	0.250	4.7	0.028	4.7	---	---
45	---	---	0.310	4.8	---	---	---	---
50	1.06	4.8	0.360	4.8	0.049	4.8	---	---

Time, min	Fix Tank		Column 1		Column 2		Column 3	
	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH	$[Ag^+]$, gm/ℓ	pH
Strip Run 3 (Concl'd)								
55	---	---	0.440	4.7	---	---	---	---
60	0.970	4.7	0.460	4.8	0.074	4.8	---	---
65	---	--	0.500	4.7	---	---	---	---
70	1.08	4.7	0.550	4.8	0.121	4.8	---	---
80	1.00	4.8	0.630	4.7	0.162	4.8	---	---
90	1.18	4.8	0.710	4.8	0.250	4.8	---	---
100	1.20	4.7	0.800	4.7	0.310	4.7	--	---
110	1.33	4.8	0.840	4.7	0.370	4.8	---	---
120	1.27	4.7	0.970	4.7	0.490	4.7	---	---
Strip Run 4								
0	0.250	4.6	---	---	---	---	---	---
5	0.230	4.6	0.030	4.6	0.030	---	---	---
10	0.400	---	0.050	---	---	---	---	---
15	0.380	---	0.100	---	0.030	---	---	---
20	0.470	---	0.150	---	0.040	---	---	---
25	0.510	---	0.190	---	0.060	---	---	---
30	0.420	4.6	0.260	4.6	0.090	4.6	---	---
35	0.430	---	0.310	---	0.100	---	---	---
40	0.500	---	0.310	---	0.130	---	0.045	---
45	0.480	---	0.390	---	0.170	---	0.045	---
50	0.420	---	0.400	---	0.210	---	0.075	---
55	0.410	4.6	0.410	4.6	0.240	4.6	0.090	4.6
60	0.390	---	0.410	---	0.265	---	0.100	---
65	0.430	---	0.450	---	0.290	---	0.125	---
70	0.470	---	0.430	---	0.310	---	0.160	---
75	0.455	---	0.460	---	0.330	---	0.160	---
80	0.475	4.6	0.460	---	0.350	4.6	0.190	4.6
90	0.510	---	0.500	---	0.380	---	0.240	---
95	0.540	4.6	0.545	4.6	0.430	4.6	0.250	4.6

APPENDIX II
REGENERATION DATA

Regeneration data from runs 2 (columns 1 and 2), and 3 (columns 1, 2, and 3) are presented in this appendix. No regeneration data were obtained from runs 1 and 4.

Column 1			Column 2			Column 3		
Volume, ℓ	$[Ag^+]$, gm/ℓ	pH	Volume, ℓ	$[Ag^+]$, gm/ℓ	pH	Volume, ℓ	$[Ag^+]$, gm/ℓ	pH
Regeneration Run 2								
0.00	0.105	5.1	0.00	0.250	4.6			
4.35	2.96	5.2	5.10	1.00	4.9			
8.70	3.23	5.4	10.20	1.64	4.7			
13.05	3.01	5.4	15.30	1.16	4.7			
17.40	2.78	5.3	20.40	0.940	4.6			
21.75	2.56	5.2	25.50	0.700	4.6			
26.10	2.30	5.4	30.60	0.650	4.6			
30.45	2.05	5.2	35.70	0.590	4.6			
34.80	1.87	5.1	40.80	0.570	4.7			
39.15	1.85	5.1	45.90	0.550	4.7			
43.50	1.52	5.1	51.00	0.470	4.7			
47.85	1.45	5.1	56.10	0.420	4.7			
53.25	1.23	4.9	61.20	0.400	4.7			
58.65	0.93	4.7	66.30	0.360	4.7			
64.08	0.73	4.6						
69.45	0.54	4.5						
74.85	0.46	4.5						
80.25	0.38	4.5						
85.65	0.37	4.5						
91.05	0.35	4.5						
95.70	0.46	4.9						
100.35	0.48	4.8						
105.00	0.36	4.8						

Column 1			Column 2			Column 3		
Volume, ℓ	$[Ag^+]$, gm/ℓ	pH	Volume, ℓ	$[Ag^+]$, gm/ℓ	pH	Volume, ℓ	$[Ag^+]$, gm/ℓ	pH
Regeneration Run 3								
0.00	0.220	4.7	0.00	0.060	4.7	0.00	0.050	4.7
4.68	2.90	4.7	4.50	4.50	4.8	5.70	0.380	4.8
9.36	2.47	4.8	9.00	3.10	4.7	11.40	0.920	4.8
14.04	1.93	4.8	13.50	1.90	4.7	17.10	0.640	4.8
18.72	1.52	4.8	18.00	1.48	4.7	22.80	0.490	4.7
23.40	1.40	4.7	22.50	0.980	4.7	28.50	0.390	4.7
28.08	1.00	4.7	27.00	0.840	4.7	33.90	0.286	---
32.76	0.900	4.7	31.38	0.820	4.7	39.30	0.310	---
37.74	0.580	4.7	35.76	0.760	4.6	44.70	0.306	---
42.72	0.500	4.6	40.14	0.660	4.6	50.10	0.254	---
47.70	0.450	4.6	44.52	0.500	4.6	55.50	0.228	4.7
52.68	0.390	4.6	48.90	0.490	4.6	60.60	0.262	---
57.66	0.290	4.6	53.28	0.400	4.6	65.70	0.252	---
62.64	0.270	4.6	57.96	0.410	4.7	70.80	0.212	---
67.74	0.340	4.7	62.64	0.330	4.8	75.90	0.210	---
72.84	0.260	4.7	67.32	0.260	4.7	81.00	0.186	---
77.94	0.170	4.8	72.00	0.200	4.7	86.10	0.174	4.7
83.04	0.130	4.7	76.68	0.190	4.7			
88.14	0.156	4.7	81.36	0.190	4.7			
93.24	0.134	4.7						

APPENDIX III
ELECTROLYSIS DATA

The regenerant solution was electrolyzed following each pass through the column (approximately 35 liters of solution for each pass). Since two or three passes (70 to 105 liters of solution) were required to regenerate each column, electrolysis was carried out two or three times for each column following each run. However, data were obtained from only three electrolysis operations and are presented in this appendix.

Time, min	$[Ag^+]$, gm/ℓ	pH
Electrolysis Run A		
This electrolysis run was not carried out on a regenerant solution from column operations, but on a regenerant solution containing 1.60 gm Ag^+/ℓ and specially prepared for obtaining electrolytic data. The meter setting was 3.0 (equivalent to a current density of 1.13 amp/ft^2"), and the flow rate was set at 4.5 ℓ/min.		
0	1.60	5.0
5	1.45	5.0
10	1.50	4.9
15	1.48	5.0
20	1.41	5.0
25	1.25	5.0
30	1.45	5.0
35	1.35	5.0
40	1.58	5.0
55	1.35	5.0
75	1.29	5.0
135*	0.74	5.0
195	0.43	5.0
210	0.40	5.0
225	0.35	5.0
240	0.30	5.0
265	0.27	5.0
280	0.21	5.0

*Sulfiding was observed at this time.

Time, min	$[Ag^+]$, gm/ℓ	pH
Electrolysis Run A (Concl'd)		
305	0.20	5.0
320	0.23	5.0
345	0.20	5.0
360	0.20	5.0
Electrolysis Run B This electrolysis run was carried out on a regenerant solution specially prepared for obtaining electrolytic data. The meter setting was 3.0 (equivalent to a current density of 1.13 amp/ft^2), and the flow rate averaged 4.5 ℓ/min.		
0	1.50	4.9
30	1.36	4.9
60	1.22	4.9
95	0.98	4.9
120	0.84	4.9
150*	0.70	4.9
180	0.65	4.9
210	0.55	5.0
240	0.38	5.0
270	0.32	5.0
300	0.25	5.0
330	0.23	5.0
Electrolysis Run 2-I-a This electrolysis run was for the first pass of the regenerant solution circulated through column 1 following strip run 2. The meter setting was 10.0 or 3.76 amp/ft^2 for the first 120 min. The setting was then changed to 3.0 or 1.13 amp/ft^2 for the remainder of the run. The flow rate averaged 4.2 ℓ/min.		
0*	0.70	4.6
120	0.31	4.7
165	0.23	4.7
180	0.19	4.7

*Sulfiding was observed at this time.

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