

## CHAPTER V



### DISCUSSIONS

#### 5.1 Quantity of Silver from Various Fixing Solution Waste

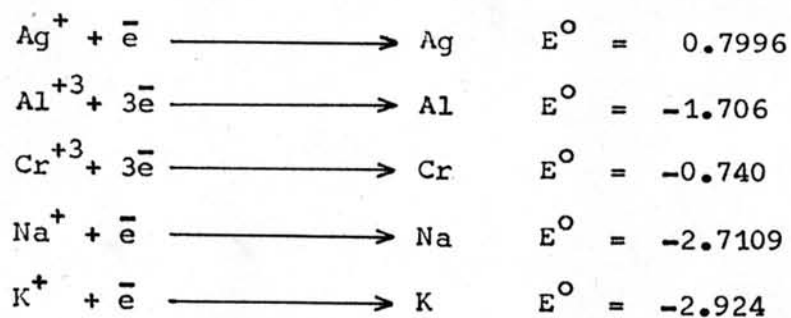
It is apparent from the experimental results in Table 4.2 that, as for various fixing solution waste, silver concentration is approximately in the range 3.2 - 11.2 grams per litre ( $[Ag]$  mean = 5.780 g /l , standard deviation = 0.544 g /l ). The highest silver concentration range belongs to the fixing solution waste from X-ray lab and hospital and is 6.5 - 11.2 g /l . The fixing solution waste from other sources are variable in the range 3.2 - 8.2 g /l. The wide variety of total quantity in grams per day from various source are 19.5 - 378 g /day, corresponding to a volume of fixing solution waste of 3 - 66 l / day. The pH range of the solution waste is 4.72 - 6.65.

The variable silver concentration can be explained by the following factors which significantly influence the amount of silver from the various fixing solution waste, (1) The type of film or paper used ; different types of film or photographic paper do not have the same silver content. Also, equivalent products of various manufacturers may differ in silver content, this results in various amount of silver in fixing solution waste.

(2) The level of exposures : longer exposure will cause more metallic silver on film and longer less amount of silver is dissolved into fixing solution. (3) The processing method and equipment employed : different film or paper are processed differently using different chemicals which have different activity. (4) The degree of exhaustion of fixing solution waste which depends on the user. The quantity of silver discarded per day depends on the extent of photographic production of each company. The available pH in fixing solution waste depends on the pH and quantity of chemical solution used in developing film or paper and also depends on the different in fixing solution formular itself.

#### 5.2 The choice of Voltage, $E_{app}$ , Applied to The Electrolytic Cell.

The constant current electrolytic cell is recommended in this silver recovery process, because of the fact that silver is far removed in the electromotive series from the other metallic ions in the fixing bath as follows :



The working electrode potential may be allowed to deviate in the range in which the other metallic ions in the fixing bath will not co-deposit. Then the constant potential method is not necessary. Equipment in the later process is complicated and relatively expensive.

It is apparent from Figures 4.1, 4.2 and Table 4.5 that, the decomposition potentials of the pure silver complex ( $\text{NaAgS}_2\text{O}_3$ ) and those of the used fixing solution at the same cathode rotating speed are almost the same, exception at the speed of 500 r.p.m., since the main substance in the both solution is the same silver complex salt ( $\text{NaAgS}_2\text{O}_3$ ). But at speed of 500 r.p.m. the other ions which present in used fixing solution may increase conductivity of the used fixing solution.

The decomposition potentials decreased with increase in cathode rotating speed for both solution. This phenomenon may be explained as follow : increasing rotating speed increased agitation of solution, and thus caused decreasing of concentration over potential; then the decomposition potential was smaller.

The current at which the first black particles ( $\text{Ag}_2\text{S}$ ) were formed increased with increasing in cathode rotating speed. Then the higher rotating speed can be used with higher current to deposit silver rapidly using shorter time without unwanted reaction occurred. From Table 4.5, its current is equal to 0.35 amp. at 0 r.p.m. for used fixing solution. Then we should expect to use

current at 0.3 amp. (or current density = 0.3 asd.) at which the black particles of  $\text{Ag}_2\text{S}$  do not occur any more for silver concentration of 7.5 g / l , After that the corresponding voltage used to produce this current should be considered from the curve on Figure 4.2. It is in the range of 0.72 - 1.26 for 0 - 1,000 r.p.m. of cathode rotating speed. The exception for zero cathode rotating speed is that the voltage applied should be 1.30 volts, because  $E_{\text{app}}$  must be equal to or greater than  $E_D + iR$

The decomposition potential obtained by extrapolation has, strictly, no exact meaning, but it does serve to indicate the approximate minimum value of the applied voltage which must be exceeded in order to carry out an electrolysis fast enough to be of value in practice.

### 5.3 Effect of Cathode Rotating Speed on Current Efficiency

The followings are quoted from the electrolytic analysis of silver procedure.<sup>(10)</sup>

The silver (ca. 0.2 g.) should be present in solution as the nitrate, pure (eg, A.R. grade) potassium cyanide is added to the nitrate solution until the precipitate of silver cyanide is dissolved, and then add an excess such that about 2 g. of potassium cyanide is present in the solution. Dilute to 100 - 120 ml. Electrolyse with 0.2 - 0.5 amp at 3.7 - 4.8 volts at 20 - 30°C about 0.1 g. of Ag is deposited in 3 hours. Alternatively,

electrolyse with a rotating electrode with 0.5 - 1.0 amp. at 2.5 - 3.2 volts 0.2 g. of Ag is deposited in 20 - 25 minutes.

This is the reason used to explain why the rotating electrode is of interest. The favourable point is that the system can operate at the higher current density for rapid processing. It is apparent from the experimental result in Figure 4.4 that, the current efficiency increases with increasing in cathode rotating speed in the range of 0 - 800 r.p.m. (Equivalent to cathode surface velocity of 0 - 1.676 metre per second). After that the current efficiency will decrease with the higher cathode rotating speed, because in the region the air bubbles build up causing increase in resistivity of the solution. Ohmic loss from this effect will reduce the current efficiency of the system. Then the rotating speed of 800 r.p.m. is the recommended speed for this purpose.

The experimental result in Figure 4.3 shows that the decreasing of silver concentration with time at various speed of cathode rotating speed are straight lines with slopes in the range 2.1 - 2.4 in agreement with the theory according to Equation 2.10

$$C = C_0 - \frac{Wm \cdot I}{V \cdot 96,493n} \times t$$

Calculation

$$\frac{dc}{dt} = - \frac{Wm \cdot I \times 3,600}{V \cdot 96,493 n} \quad \text{g / l - hr.}$$



Substituting  $I = 0.3$  amp.,  $W_m = 107.88$  g.,  $V = 0.5$  l.,  $n = 1$

$$\text{Then, } \frac{dc}{dt} = \quad - 2.4148 \quad \text{g / l - hr.}$$

#### 5.4 Effect of pH and Current Density on Current Efficiency

It is apparent from the experimental result in Figure 4.5 that the optimum condition for the electrolytic recovery of silver is, when current efficiency is maximum at 98.82, the pH is 6.5 and current efficiency is 0.5 asd. Increasing the pH tends to increase the current efficiency only in acidity pH region 3.8 - 6.5, after that increasing the pH tends to decrease in the current efficiency. At each pH condition, the current efficiency increases with increasing in current density in the range of 0 - 0.5 asd., after that the current efficiency will decrease; exception at pH 3.8 - 5.5 in which the current efficiency continues to increase until the current density rises to 0.7 asd. From the experimental result in Tables 4.8 - 4.14, the impurity in used fixing solution may deposit to interfere and reduce the current efficiency at high current density and high pH

#### 5.5 Effect of Silver Concentration on Current Density

It is already known that if the silver thiosulfate ions at the cathode fall below a certain minimum concentration, the thiosulfate ions will react at the cathode to become sulfide ions as explained in Chapter II. The experimental result in Figure 4.6 shows that the minimum silver concentration at which silver sulfide

appeared will increase nonlinearly as the cathode current density increases. Since increasing current density tend to increase the rate of deposition of silver at the cathode, the bulk concentration of silver should be high enough to give large concentration gradient which tent to pull up the silver in the vicinity of the cathode, then the thiosulfate ions will not react at the cathode, and silver sulfide will not occur. That means the total silver concentration of the fixing solution must exceed a certain minimum for any specified current density.

The relation between current density and silver concentration serves as a guide for operation of Eastman model II silver recovery cell in which fixed electrode is used is shown in Table 5.1. From the experimental result in Table 4.16, it is

Table 5.1 The operation guide for Eastman model II silver recovery cell

Current Density asd.	Ag g /l
0.10	1.0 - 1.5
0.17	1.5 - 2.0
0.24	2.0 - 2.5

shown that the electrolytic silver recovery cell with rotating electrode type can deposite silver from fixing solution of lower silver concentration than the fixed electrode type at the same

current density. This is the advantage of the rotating electrode system.

#### 5.6 Effect of Sodium Sulfite Concentration on Current Efficiency

It is apparent from the experimental result in Table 4.18 and Figure 4.7 that, in the pure silver complex solution without sodium sulfite, the current efficiency decreases with time. A study on pure silver complex solution to which regulated concentrations of sodium sulfite had been added, showed that decrease of current efficiency with time could be reduced. The proper quantity of sodium sulfite for prolongation the high current efficiency with time is at least 15 g /l. This observation can be illustrated by the reaction :



If this unwanted reaction takes place at the cathode, it will cause reduction in current efficiency. Addition of sulfite will prevent the occurring of this reaction. Then the high current efficiency with time can be maintained.

#### 5.7 Effect of Chemical Interference

From the experimental results of current efficiency determination on different types of fixing solution in comparism with pure silver complex plus 15 g.  $\text{Na}_2\text{SO}_3$  per litre in Table 4.19, it is found that the current efficiency from each type of



fixing is closed to the current efficiency of pure silver complex + 15 g.  $\text{Na}_2\text{SO}_3$  per litre within the range  $\pm 0.8$ . It can be concluded that there is no measurable influence on current efficiency by different chemicals in the fixing solution

#### 5.8 Economic Analysis of the Electrolytic Silver Recovering Cell.

There are a large number of photographic users throughout Thailand. A small electrolytic silver recovery cell is considered in this work, since a large centralised plant involves large investment and requires waste collection and transportation rendering high operating cost. In determining if an electrolytic silver recovery cell should be introduced into his operation, a photographic shop owner would consider both economic and pollution abatement factors. Factors included in economic evaluation are the price of silver, the potential value of silver bearing waste, the investment, the operating cost and the rate of return on investment.

From the experimental result in table 4.2, the quantity of silver from the various sources are in the range of 19.5-378 grams per day which is equivalent to 2.4-47.3 g /hr. ( Based on 8 hr / day ). Then the maximum capacity of electrolytic cell should be considered within the range of 5-70 g /hr. The ideal design for building the electrolytic recovery cell may be based on optimum operating condition which is already known ( Sections 5.2-5.7 ) and is summarised as follows.

Cathode current density	0.5 Amp/ dm <sup>2</sup> (asd.)
Voltage.	1.2 to 1.5 volt
Temperature.	30°c
Agitation	Cathode surface velocity 1.676 metre per second
Controlled pH of solution.	6.5
Sodium Sulphite concentration	15 g /l
Anode: cathode surface area	3:1

Using all the above information, some basic specifications for each silver recovery capacity were determined and the investment and operating cost were estimated. The results are shown in Tables 5.1 and 5.2 respectively. The rate of investment return was then calculated and shown in Table 5.3. The result shows that investment is very favorable.

Table 5.1 Some basic specifications for each silver recovery capacity.

Specifications Item* \ Silver Recovery Capacity (g/hr)	5	15	30	50	70
Feed Tank Capacity, P.V.C. (litre)	-	40	80	120	180
Electrolytic Tank Capacity, P.V.C. (litre)	15	10	20	30	40
Cathode Area, Stainless steel (dm <sup>2</sup> )	2.5	7.5	15	25	35
Anode Area, Graphite (dm <sup>2</sup> )	7.5	22.5	45	75	105
Output D.C. Power Supply					
Volts	0 - 7	0 - 6	0 - 6	0 - 6	0 - 6
Amps	0 - 2	0 - 5	0 - 10	0 - 15	0 - 22
A.C. Motor, used for (Watts)					
- Rotating Electrode	90	90	125	125	180
- Mixing in Feed Tank	-	125	125	125	125
- Chemical pump	-	125	125	180	180
Electrical Power Consumption(Watts)	110	370	430	520	620

\* Ideal Design based on silver concentration 3.2 g/l, current density = 0.5 Asd.,  
 anode : cathode surface area = 3 : 1 and working hour = 8 hours per day.

Table 5.2 Estimating cost of each silver recovery capacity

(Baht)

Type	Batch	Semi Continuous			
Silver Recovery Capacity g/hr. Item.	5	15	30	50	70
<b>Cell Feed Preparation Equipment</b>					
1. Feed tank	-	2,900	3,700	4,500	6,000
2. Feed tank assembly					
- Chemical pump	-	3,700	3,700	4,200	4,200
- Piping & valves	200	1,200	1,200	1,200	1,200
- Filter	-	800	800	1,500	1,500
- Motor	300	1,300	1,500	1,700	1,900
3. Buffer tank	-	600	600	600	600
<b>Electrolytic Cell</b>					
1. Cell body	1,150	900	1,150	1,350	1,550
2. Electrodes					
- Cathodes	300	600	1,600	2,500	3,500
- Anodes	100	250	500	750	1,100
3. Miscellaneous					
- Cell assembly	500	750	900	1,100	1,600
- Body support	-	400	400	600	600
<b>Electrical Power Supply</b>					
D.C. power supply	6,560	19,160	22,520	24,600	26,360
<b>Total assembly Cost</b>	<b>9,110</b>	<b>32,760</b>	<b>38,770</b>	<b>44,600</b>	<b>50,110</b>

Table 5.2 Estimating cost of each silver recovery capacity(continue)

		(Baht)				
Type	Batch	Semi Continuous				
Item \ Silver Recovery Capacity g/hr	5	15	30	50	70	
Installation Cost	-	3,200	3,800	4,460	4,900	
Total Cost	9,110	35,760	42,370	49,060	55,010	

-The cost of each item is listed in Appendix VII.

-The installation cost is approximated by 10 percent of all assembly cost.



Table 5.3 Rate of return of investment.

Item	Silver Recovery Capacity g/hr				
	5	15	30	50	70
Investment Cost (Baht)	9,110	35,760	42,370	50,960	55,010
Sale per month <sup>+</sup> (Baht)	4,704	14,112	28,224	47,040	65,856
Operating Cost per month (Baht)	282	851	1648	2709	3780
- Electrical Consumption *	(19)	(63)	(73)	(84)	(105)
- Chemical Consumption **	(263)	(788)	(1,575)	(2,625)	(3,675)
Profite per month (Baht)	4,124	13,261	26,576	44,331	62,076
Rate of return of investment <sup>#</sup> (month)	2.20	2.70	1.60	1.15	0.89

<sup>+</sup> Saling price is based on 50 % of the price of 99.99 % purity silver, in March, 1980 (see Appendix II) which is equivalent to 5.60 baht per gram of silver.

\* Electrical Cost is based on 1 baht per kilowatt - hr.

\*\* Chemical consumption for pH adjustment, its cost is approximated 1 baht per litre of fixing solution.

# Based on 70 % Capacity.

## 5.9 Conclusions

5.9.1 The silver content for various fixing solution waste is approximately in the range of 3.2-11.2 g /l. Total quantity is in the range of 19.5-378 g. per day for various sources.

5.9.2 Because of the chemical complexity of a used fixing solution, the current efficiency. The maximum current efficiency obtained from the designed electrolytic cell with rotating cathode is equal to 98.80% at the following operating condition.

Cathode current density	0.5 Amp/ dm <sup>2</sup> (asd.)
Voltage	1.2 to 1.5 Volt
Temperature	30°c
Agitation	Cathode surface velocity 1.676 metre per second
pH	6.5
Sodium sulfite	not less than 15g /l
Anode: cathode surface area	3:1

5.9.3 The operating guide for controlling current density to prevent occurrence of silver sulfide, at various concentration of silver in fixing bath is

Silver Concentration (g /l)	Current density ( asd. )
0.50-1.00	0.10
1.00-1.50	0.30
1.50 and over	0.50

5.9.4 Economic analysis shows that setting up an electrolytic silver recovery cell in a photographic shop is feasible. The operating cost is very low as compared to the price of silver, and the rate of investment return is very rapid, i.e., less than three months.