

CHAPTER III

PROPOSED SILVER RECOVERY TECHNOLOGY FOR RADIOGRAPHIC FILM

3.1 Introduction

Silver is a precious metal, which can be feasibly recycled from silver-contaminated wastes. With an increasing demand for silver in the world, the secondary production of silver from scraps and other forms of wastes has become a new supply in the market (Handerson, 2003). Owing to its considerable silver content, radiographic waste such as used films and spent fixer is a secondary silver source that has been receiving more focus.

In Thailand, almost all of the silver recovered from radiographic waste is processed by small “house” factories, which utilize various recovery methods and have no treatment of their second-generation wastes. The fate of silver from domestic origins would demonstrate in silver contaminated work. Unrecoverable processed silver eventually goes down the drain and becomes a hazardous contaminant to the environment as shown in **Figure 3-1**.

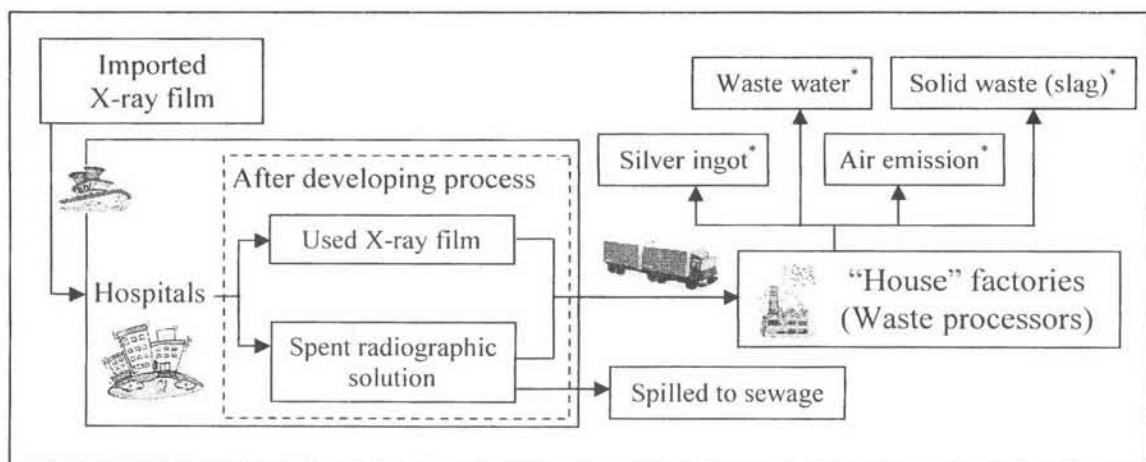


Figure 3-1 Distribution of silver contaminant assigned as (*) from “house” factories.

Recently, it has been realized that radiographic waste management in Thailand should be established in order to monitor and control the silver contaminant and the related stakeholders, especially the waste processors, before the pollutant is discarded into the environment. According to waste management policy, waste minimization has been increasingly campaigned for all over the world. The “cleaner production or clean technology” concept has been widely implemented by many types of firms. These agreements encourage recovery silver from radiographic waste.

From the literature review, it was found that the majority of previous studies on silver recovery technology focused on waste silver-bearing solutions. In fact, the recovery of silver from film waste is more complicated than it is from waste solutions. Thus, this work has focused on the technology used for the recovery of silver from used radiographic film, with an emphasis on clean technology.

This chapter reports on silver recovery from radiographic film. Instead of using high temperature conditions and highly toxic solutions, we investigated the use of a weak acid, as a leaching agent to remove silver. Acetic acid, oxalic acid, and malonic acid were used in this work. The investigation of the chemical leaching process was carried out by determining the effects of acid type, temperature, aging time, acid concentration and film size. The composition and morphology of silver sludge from the chemical leaching process was also included in the study to verify a presence of metallic silver product and an absence of a formation of an explosive silver complex i.e., silver oxalate. In addition, the proposed technology was compared with present technology in order to select an appropriate method that offers a feasible and environmental-friendly way to recover silver from the film waste.

3.2 Objectives

3.2.1 To study and to investigate 5 major operating parameters that effect on efficiency of acid leaching technique of silver from radiographic medical film i.e., film size, temperature, retention (leaching) time, acid type, and acid concentration.

3.2.2 To explain reaction/mechanism of silver leaching from silver sludge at optimal condition by analyzing of sludge morphology using XRD and SEM-EDX techniques.

3.2.3 To conduct a comparative evaluation of CO₂ emission between the proposed leaching technique and the existing technology used in Thailand.

3.3 Literature Reviews

The extraction of metallic silver from used photographic film can be divided into two steps. The first one is the leaching of silver metal from processed photographic film and the second is the recovery of silver from the developed solution. The common methods being used for leaching silver metal from used radiographic film involve thermal, mechanical or physical, and chemical treatments.

3.3.1 The Thermal Method

The most common method for silver recovery from processed radiographic film is a burning process. The used film is incinerated at high temperatures (> 980°C) and the silver is recovered from the ash by smelting and refining processes (Ishikawa et al., 1993; Smarntarn, 2001). Generally, the yield from the burning process is less than 95% depending on the further treatment system (Moreno, 1986). This method can extract silver from large amounts of spent films. Nevertheless, it is very expensive and the temperature is difficult to control. When the temperature is too high, some of silver would be lost through the flue gas (Hochberg, 1988) and a large quantity of air pollution would be created.

3.3.2 The Biological Method

The biological method is an interesting process for recovering silver; it employs “alkaline protease” enzymes to decompose the gelatin layer of processed film. This enzymatic reaction can be used for recovering the silver. Although no toxic chemicals are used in this process, a long retention time (approximately 60 min to 180 min, (Fujiwara et al., 1991)) is required. For this reason, the biological process is not preferable for industrial purposes. **Table 3-1** demonstrates the optimal conditions for using the biological process to recover silver from used film.

Table 3-1 Literature data on the biological method.

Chemical/Microorganism	pH	Temperature (°C)	References
Alkaline protease (Protease B18) from <i>alkalophilic thermophile</i>	13	85	Fujiwara et al. (1991)
Alkaline protease B21-2 from <i>alkalophilic Bacillus sp</i>	10.5	40	Ishikawa et al. (1993)
Alkaline protease from <i>Aspergillus oryzae U1521</i>	9	45	Smarnantarn (2001)

3.3.3 The Physical Method

The physical method leaches silver through a mechanical process. At the beginning, only a mechanical method of high shear force was used. Buser and Rettig (1988) recovered silver from photographic film that had a polyester base by using high shear force. The films were cut into small pieces about 2 to 20 millimeters at their longest dimension and mixed with hot water at a temperature of 60°C to 93°C at a solid level of at least 25 percents by volume. The mixture was stirred until the silver halide emulsion was completely removed.

Afterwards, the researchers started to apply chemical substances to the mixture. A caustic alkali solution (sodium hydroxide and potassium hydroxide) was tested as a film digesting agent. However, sodium hydroxide became preferred as disclosed by Hochberg (1989). From this study, it was found that, solely, a mechanical treatment was not good enough to separate silver halide from spent film and consumed a great amount of energy.

3.3.4 The Chemical Method

The chemical method recovers silver by leaching and precipitation. The recovery yield is close to 99% (Moreno, 1989). It is a simple technique with low

capital; however, hazardous substances are involved in the process. This technique has been extensively investigated for many years as indicated in **Table 3-2**.

As the results stated in **Table 3-2**, it can be summarized that the significant factors for chemical leaching are chemical type, film size, chemical concentration, temperature, leaching time, and pH. The limitations of each factor can be described as followed.

3.3.4.1 Type of Chemicals

Single and mixed chemicals have been applied in the chemical process to leach silver. Several chemicals have been used such as cyanide solution, ferric chloride, sodium hydroxide, nitric acid, etc.; however, some of them are toxic, corrosive, and flammable as summarized in **Table 3-3**.

3.3.4.2 Film Size

Radiographic film should be chipped into small sizes before being fed in a chemical process to increase the leaching efficiency. The film size is various from 1-50 mm at its longest dimension.

3.3.4.3 Chemical Concentration and pH

The chemical concentration of the leaching agent varies from low (1-10% of oxalic acid) to high (65% of nitric acid). The pH of a solution is a measure of the molar concentration of hydrogen ions (H^+) in the solution. The relationship between the concentration and pH can be described by a simple logarithmic equation below:

$$pH = -\log[H^+]$$

Table 3-2 Chemical leaching method for silver recovery.

Chemical	Concentration by weight	pH range	Temperature (°C)	Retention time (min)	Film size	References
Strong alkaline solution		At least 9.0	25			Kunihira and Kyoichi (1982)
Sodium cyanide and hydrogen peroxide	30% H ₂ O ₂		Room temperature		Not more than 10 mm in size	Moreno (1986)
Caustic alkali solution, or water			60-93		2-20 mm at its longest dimension (Preferable at 5-7 mm)	Buser et al. (1988)
Ferric chloride (FeCl ₃)	10-26% (Optimal at 16%)	Up to about 2 (Preferable up to 1)	35-50 (Preferable at 35-40)			Messerschmidt (1988)
Nitric acid	50%					Laungchonlatan (1988)
Caustic alkali solution (NaOH, KOH)	At least 7%	Not more than 4	60-93	15-45	2-30 mm at its longest dimension	Hochberg (1989)
Photographic development waste solution			15-35 (Preferable at 15-20)	30-300	2-5 cm at its longest dimension (Preferable at 2.5x2.5, 3.5x3.5 cm ²)	Tyngbin et al. (1993)
Oxalic acid	1-10%		97	5	Film pieces	Syed et al. (2002)
Nitric acid	Concentrated (65%)				Film pieces	Ajiwe and Anyadiegwu (2000)

Table 3-3 Summary of chemical substances and their nature.

Toxic substance	Nature of chemical substance	References
Sodium cyanide +Hydrogen peroxide	<ul style="list-style-type: none"> • Cyanide compound retained in environment for a long period of time • Highly reactive • Highly explosive 	Moreno (1986)
Ferric chloride	<ul style="list-style-type: none"> • Corrosive 	Messerschmidt (1988)
Sodium hydroxide	<ul style="list-style-type: none"> • Corrosive 	Hochberg (1988)
Nitric acid	<ul style="list-style-type: none"> • Highly toxic • Highly corrosive • Flammable 	Laungchonlatan (1988) Ajiwe and Anyadiegwu (2000)
Photographic development waste solution	<ul style="list-style-type: none"> • Difficult operational and treatment procedures 	Tyngbin et al. (1993)

3.3.4.4 Temperature and Retention Time

The temperature and the retention time of the leaching process are in the range of room temperature to 100°C and 15-300 minutes, respectively. It was found that there is a relationship between temperature and retention time. For example, leaching at a high temperature could reduce the retention time of the process. However, suitable conditions should be selected not only to provide good efficiency but also to protect the environment.

The advantages and disadvantages of typical methods used for silver recovery are summarized in **Table 3-4**. Among these methods, chemical leaching seems to be the simplest method and most appropriate for the small “house” factories in Thailand. This method applied with a clean technology approach would involve selecting a new

leaching chemical(s) that provides chemical safety, high efficiency and less environmental impacts. In addition, the relationships between the leaching factors i.e., chemical type, film size, chemical concentration, temperature, and leaching time, were studied.

Table 3-4 Advantages and disadvantages of available silver recovery techniques.

Method	Advantages	Disadvantages
Thermal method	<ul style="list-style-type: none"> Recovery of silver Energy yielded High processing capacity 	<ul style="list-style-type: none"> • High capital and maintenance cost of the furnace • Hazardous flue gas emissions (soot and smoke) • Difficult to control the temperature
Biological method	<ul style="list-style-type: none"> • Recovery of silver • Recovery of film base • Environmental-friendly • Inexpensive 	<ul style="list-style-type: none"> • Long residence time • Difficult to control the system
Physical method	<ul style="list-style-type: none"> • Recovery of silver • Recovery of film base 	<ul style="list-style-type: none"> • Low efficiency • High consumption of energy
Chemical method	<ul style="list-style-type: none"> • Recovery of silver • Recovery of film base • Low capital cost • Simple process 	<ul style="list-style-type: none"> • Use of toxic substances such as hydrogen peroxide, cyanide solution, nitric acid, etc.

3.4 Experimental Design

The experiment on chemical leaching of silver from radiographic medical film was realized. From the reviews, the following notions were formulated.



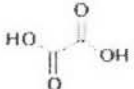
1) Organic acids with carboxylic group i.e., acetic acid, malonic acid, and oxalic acid, are used instead of toxic or corrosive substances e.g. strong inorganic acids, strong alkali, cyanides etc. The properties of selected weak organic acids were presented in **Table 3-5**.

2) Important operating parameters of a typical chemical reactor i.e. time, concentration, and temperature, are considered.

3) It is worthwhile to confirm the effect of film size on leaching efficiency.

4) A batch mode experiment is preferable due to its simplicity of operation and control at various conditions.

Table 3-5 Properties of test acids.

Weak acid	Structure	Boiling point (°C)	Solubility
Acetic acid		117.9	Soluble in all proportion
Malonic acid		140	10g/100ml
Oxalic acid		190	10g/100ml

3.4.1 Materials and Chemicals

3.4.1.1 Radiographic Film

Processed radiographic film used in this study was contributed by public hospitals, which are Ramathibodi Hospital (Bangkok Metropolitan), Bang-Bo Hospital (Samutprakan Province), and Thanyaburi Hospital (Pathumthani Province).

3.4.1.2 Reagents

All chemicals used in this study were of analytical grade and were used without additional purification. The chemicals are the followings.

- 1) Acetic acid, (100%, BDH)
- 2) Malonic acid, (98%, Fluka)
- 3) Oxalic acid (99.5-102.5%, Ajax)
- 4) Nitric acid (65% HNO₃, Lab-Scan)
- 5) Silver standard solution (1000 mg/l Ag, Merck)

3.4.2 Analytical Instruments

The analytical instruments used in this study, as in Appendix A, are followed.

- 1) Atomic Absorption Spectroscopy (Perkin Elmer instruments Model AA analyst 800)
- 2) X-Ray Diffractometer (Bruker Model D8 Advance)
- 3) Scanning Electron Microscope (JEOL Model JSM 6400) equipped with Energy Dispersive Spectroscopy.
- 4) Microwave for digestion (Milestone Model ETHOS SEI)
- 5) Ashing Furnace (Cabolite Model AAF 1100)
- 6) Digital pH meter (SensionTM Model 51935-00)

3.4.3 Experimental Set-up

The experimental equipment is shown in **Figure 3-2**. A round bottom glass of 250 mL was served as a batch reactor. 5 grams of processed film and 50 mL of acid solution were added in the reactor vessel. The vessel was placed on an electrical heater with a magnetic stirrer to keep completely-mixed condition. An automatic temperature control was connected to maintain a set temperature. When leaching occurred at 100°C, a condensing tube and an electrical cooler were installed to condense a vapor with 20°C circulating water.

After a set period of leaching i.e., retention time, the leached film was rinsed and incinerated in an electrical furnace at 500°C for 3.5 hours. The residue (ash) was then digested with 10 mL of concentrated HNO₃ solution. The liquid mixture was heated to 175°C in a microwave digester and maintained for 10 minutes to ensure a complete digestion (a clear liquid could be observed).

The remaining leaching solution together with the rinsed water (when film was separated) was filtered with No. 42 ashless filter paper (Whatman). The filter paper with sludge was dried at 105°C for 2 hours and cooled down in a desiccator. The dried filter was incinerated and digested in the same way as previously described.

The silver concentrations in the digested solutions of leached film and sludge were measured in triplicate by atomic absorption spectroscopy (AAS). The determination of silver content was conducted by the multiplication product of its concentration and volume. The entire procedure is summarized and demonstrated in **Figure 3-3**.

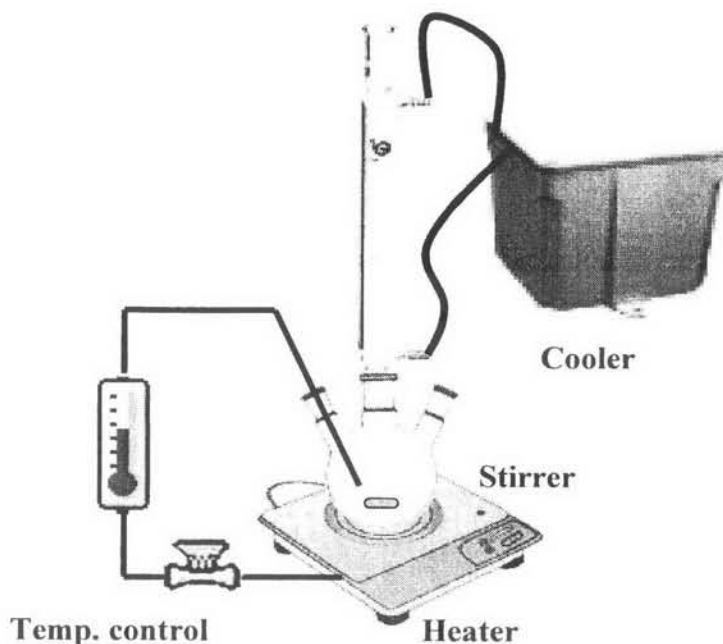


Figure 3-2 Experimental set-up.

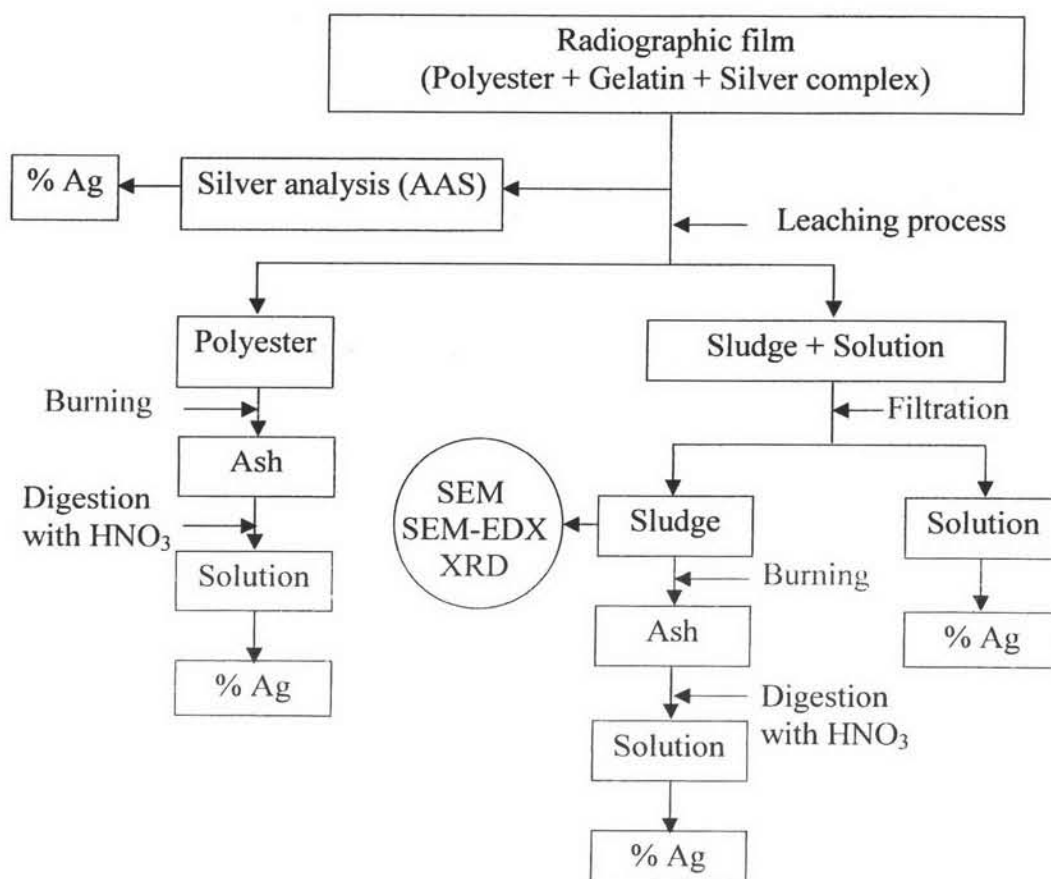


Figure 3-3 Schematic of experimental set-up

3.4.4 Methodology

3.4.4.1 Preparation of Experimental Film

Processed radiographic film was cut to uniform sizes i.e., 1x1, 1x2, and 1x4.5 cm \times cm (so-called film chips). 5 grams of the uniform film chips were weighed on a four-digit balance.

3.4.4.2 Preparation of Acid Leaching Solution

50 mL of 1, 3, and 5% (w/v) of acetic acid, malonic acid, and oxalic acid diluted with deionized water, was used as a leaching solution for each batch test.

3.4.4.3 Variations of Temperature and Retention Time

The experiment was carried out at specified temperatures and retention times at 60, 80, 90, and 100°C and 10, 15, 20, 35, 40, 60, 90, and 120 minutes, respectively.

The whole experimental procedures are shown in **Table 3-6**.

Table 3-6 Experimental conditions of the leaching process.

Factors	Conditions
1. Acid type	<ul style="list-style-type: none"> • Acetic acid (CH₃-COOH) • Oxalic acid (HOOC-COOH) • Malonic acid (HOOC-CH₂-COOH)
2. Film size (cm×cm)	<ul style="list-style-type: none"> • 1x1, 1x2, and 1x4.5
3. Acid concentration (% w/v)	<ul style="list-style-type: none"> • 1, 3, and 5
4. Temperature (°C)	<ul style="list-style-type: none"> • 60, 80, 90, and 100
5. Retention time (minutes)	<ul style="list-style-type: none"> • 10, 15, 20, 35, 40, 60, 90 and 120

3.4.4.4 Silver Recovery Efficiency (SRE)

The efficiency of silver recovery (SRE) was defined as the amount of silver found in sludge from leaching process divided by the sum of the amount of silver remained on the leached film and the amount of silver in sludge as followed.

$$\text{SRE (\%)} = \frac{\text{Ag in sludge}}{(\text{Ag on film} + \text{Ag in sludge})} \times 100$$

3.4.4.5 Reuse of Acid Leaching Solution

When the batch test of 1x1 cm×cm film chips digested in 5% (w/v) oxalic acid solution at 100°C for 20 minutes was finished, and the leached films and sludge were separated from the solution; a trial was made to determine a repeatability of the spent leaching solution.

The spent solution was then reused as an acid leaching solution in the same manner as the newly prepared solution. The trials were made at 1, 5, 10, 15, 20, and 25 times.

3.4.4.6 Morphology of Silver in Processed Film and Sludge

The morphology of silver in processed film and sludge from the batch test of 1x1 cm² film chips digested in 5% (w/v) oxalic acid solution at 100°C for 20 minutes was examined by the following techniques.

1) SEM-EDX

The microstructures of silver on the processed film and sludge were observed by a JEOL JSM 6400 Scanning Electron Microscope (SEM) equipped with Linkis Energy Dispersive Spectroscopy (EDS). A thin layer of the specimen was sprinkled on adhesive tape on a brass bar. The excess was blown away with an air spray. The specimen was then coated with gold palladium alloy in the JEOL JFC-1100E Ion sputtering device and transferred into the JEOL JSM-6400 sample chamber at the accelerating voltage of 15-40 kV. This method examined a limited spot of each specimen at 1000, 3000, and 7000 magnifications on different positions in order to obtain the representative image.

2) XRD

Silver compounds of the sludge were identified by a powder X-ray Diffraction (XRD) spectrometer (Bruker Model D8 Advance). XRD patterns were obtained with a computer controlled diffractometer equipped with a copper X-ray tube and a scintillation detector. A graphite monochromator was used for producing diffracted lines according to a single X-ray wavelength with low background. The X-ray was generated with a current of 40 mA and a potential of 40 kV. The specimens were scanned from 10 to 70 degrees (2 θ) in 0.015 step increments.

3.4.4.7 Estimation of CO₂ Emission

In order to clarify that the chemical leaching process using organic acids as silver leachants is a “Green Technology”, it was arbitrarily decided to compare major energy consumption in the chemical process with that in the thermal treatment (combustion) process employed in the existing recycling factory.

The energy consumption in 2 experiments where 1x1 cm \times cm film chips digested in 5% (w/v) oxalic acid solution at 90°C for 60 minutes and at 100°C for 20 minutes was recorded and CO₂ emissions were estimated using US.EPA Unit Conversion, Emissions Factors, and Other Reference Data (November, 2004). The detailed calculations can be found in Appendix B.

3.5 Results and Discussions

3.5.1 Effect of Test Parameters

The results of the chemical leaching of silver from processed film based on the specified experimental parameters are, respectively, presented as the followings.

3.5.1.1 Effect of Film Size

Table 3-7 shows a series of leaching tests under various conditions. The silver recovery efficiencies (SREs) from the film chips of 1x1, 1x2, and 1x4.5 cm \times cm dimensions are explicitly shown that the small the dimensions, the better the SREs were obtained at all specified acid types and concentrations, set temperatures, and set retention times.

The smallest chips of 1x1 cm \times cm dimension showed the best SRE in all test conditions when compared with the 1x2 and 1x4.5 cm \times cm sizes. The 1x4.5 cm \times cm pieces tended to stick together; this resulted in a considerable part of film chips which were inaccessible for leaching. The smaller-sized pieces rarely stuck to each other; when the leaching process finished, the leached chips (merely, film base) had a transparent appearance.

Table 3-7 Silver Recovery Efficiency (SRE) of different film sizes.

Film size (cmxcm)	Temp (°C)	Time (min)	% Silver Recovery Efficiency (SRE)								
			Acetic acid			Malonic acid			Oxalic acid		
			1%	3%	5%	1%	3%	5%	1%	3%	5%
1x1	60	10	0.16	0.25	0.63	0.63	3.27	2.56	0.22	0.61	1.23
1x1	60	35	0.63	0.43	1.88	1.97	2.77	5.12	3.77	4.45	6.31
1x1	60	60	0.52	0.47	8.78	5.31	5.85	13.28	5.71	10.65	14.74
1x1	80	10	0.14	1.08	2.46	2.40	2.77	4.31	1.23	3.23	4.28
1x1	80	35	1.07	1.06	3.11	5.49	10.24	12.74	5.63	12.20	17.92
1x1	80	60	1.57	1.74	6.35	6.96	7.87	18.08	33.88	35.41	42.92
1x1	100	10	0.21	5.67	11.33	3.08	13.81	27.98	7.56	28.42	64.68
1x1	100	35	0.36	6.32	12.65	3.47	18.94	37.83	48.80	69.55	98.73
1x1	100	60	2.99	8.32	17.41	5.76	22.39	48.92	96.99	97.20	97.91
1x2	60	10	0.15	0.21	0.67	0.32	2.25	2.31	0.38	0.55	1.13
1x2	60	35	0.34	0.39	1.45	1.55	2.67	4.59	2.83	1.74	5.05
1x2	60	60	0.47	0.57	7.03	5.41	4.33	12.02	5.24	6.57	15.42
1x2	80	10	0.11	0.41	1.84	1.89	1.79	3.94	0.89	1.51	2.33
1x2	80	35	0.39	0.97	2.76	4.67	5.42	10.48	4.74	12.25	16.04
1x2	80	60	0.98	1.22	5.10	4.88	7.21	19.11	29.72	39.04	40.82
1x2	100	10	0.19	4.31	10.05	2.65	4.32	22.34	0.25	22.61	30.94
1x2	100	35	0.33	5.72	11.42	3.11	13.20	31.72	29.04	60.07	74.40
1x2	100	60	1.87	7.91	17.88	5.45	20.41	45.07	75.29	88.42	95.32
1x4.5	60	10	0.12	0.36	0.56	0.18	1.47	3.26	0.41	0.49	0.61
1x4.5	60	35	0.20	0.40	1.16	1.46	1.35	5.02	1.01	2.68	4.20
1x4.5	60	60	0.13	0.48	5.13	3.56	5.27	11.42	2.07	5.73	12.29
1x4.5	80	10	0.12	0.34	1.31	0.29	1.13	3.68	0.74	1.38	1.36
1x4.5	80	35	0.14	0.11	1.98	4.19	8.32	9.27	3.82	9.77	12.68
1x4.5	80	60	0.13	0.74	5.26	5.82	5.62	15.20	31.05	33.15	39.31
1x4.5	100	10	0.13	3.98	8.66	0.70	3.29	7.22	0.36	19.91	28.13
1x4.5	100	35	0.46	4.85	8.69	2.53	10.55	23.91	24.40	57.12	71.55
1x4.5	100	60	1.78	7.32	15.41	5.39	19.65	44.32	88.36	80.42	92.87

Additional test runs were conducted under 100°C at 20-minute retention time with 5% (w/v) solutions of acetic acid, malonic acid, and oxalic acid. **Table 3-8** and **Figure 3.4** distinguish again the significant effects of film sizes on SREs.

Table 3-8 Silver Recovery Efficiency (SRE) of different film sizes at specified 100°C, 20-minute retention time, and 5% (w/v) acid concentrations.

Film size (cm×cm)	% SRE at 20 min. Retention time		
	Oxalic acid	Malonic acid	Acetic acid
1x1	98	37	12
2x1	87	31	10
4.5x1	65	25	9

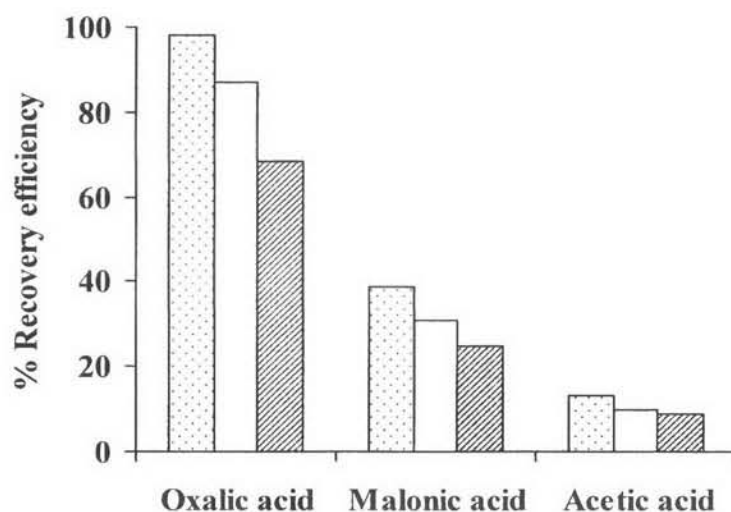


Figure 3-4 Silver Recovery efficiency (% SRE) of the leaching experiments at 100°C, 20 minute retention time, with 5% (w/v) solutions of test acids at different film sizes.

(▣) 1x1 cm×cm, (□) 1x2 cm×cm and (▨) 1x4.5 cm×cm

3.5.1.2 Effect of Acid Type

The effect of acid types on SRE is demonstrated in **Table 3-7** and **Table 3-8**. At the same film sizes, set temperatures, set retention times, and acid concentration, it

was found that oxalic acid appeared to be the best leaching chemical among the test acids as its SREs was higher than those of malonic acid and acetic acid, respectively.

The superiority in SREs of oxalic acid over malonic acid and acetic acid can be explained that oxalic acid, simply, consists of two carboxylic groups (-COOH); while malonic acid consists of 2 carboxylic groups and 1 alkyl group (-CH₂-) (i.e., same active groups; but longer chain) and acetic acid consists of only 1 carboxylic group and 1 alkyl group (-CH₃) (i.e., fewer active group). The carboxylic group represents an ionization of hydrogen ion in the leaching solution.

3.5.1.3 Effect of Acid Concentration

The effect of acid concentrations on SRE is also indicated in **Table 3-7**. At the same film sizes, set temperatures, and set retention times, when 1, 3, 5% (w/v) oxalic acid was used as a leaching chemical; it was discovered that 5% (w/v) oxalic acid showed higher SREs in all comparable cases.

In order to check if the SRE could be enhanced by increasing the acid concentrations, the extra experiment was carried out with 1x1-cm_xcm film chips by using oxalic acid as a leaching chemical at 100°C, 20-minute retention time. It was observed that the SREs did not differ significantly when the acid concentrations were raised to 6 and 7% (w/v) as shown in **Figure 3-5**.

3.5.1.4 Effect of Temperature

The effect of temperature on SRE is clearly shown in **Figure 3-6**. When the experiments were done at 60, 80, 90, and 100°C, using 5% (w/v) acetic acid, malonic acid, and oxalic acid solutions with 1x1 cm_xcm film chips at 10-minute retention time. The SRE increased when the temperature was elevated.

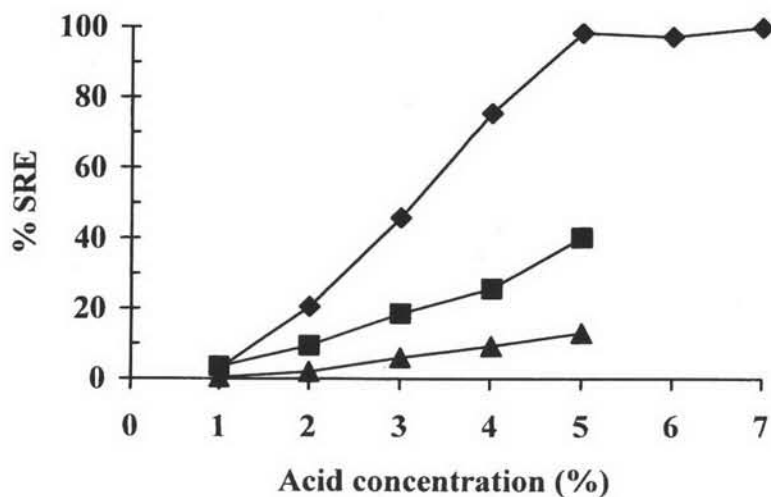


Figure 3-5 Silver Recovery efficiency (% SRE) of the extra experiment using 6% and 7% (w/v) of oxalic acid leaching of 1x1 cm \times cm processed film chips at 100°C, 20 minutes.

(◆) oxalic acid, (■) malonic acid, and (▲) acetic acid

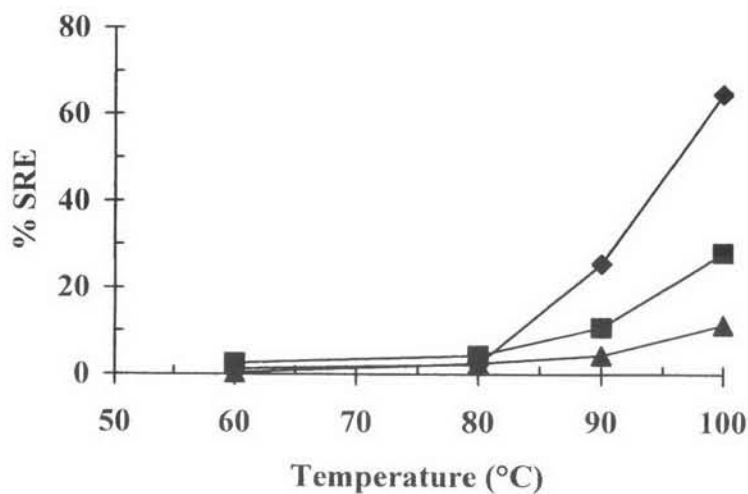


Figure 3-6 Silver Recovery efficiency (% SRE) of 1x1 cm \times cm processed film chips at 10-minute retention time with 5% (w/v) solutions of test acids at 60, 80, 90, 100°C.

(◆) oxalic acid, (■) malonic acid, and (▲) acetic acid

As the concept of material recycling is of value to this study, the characteristics of the leached film base and the spent solution are addressed. Except for the protective and emulsion gelatin layers, the film base should not be deteriorated in order to maintain the film base integrity and the chemical property of the spent solution for recycling or reuse purpose. Therefore, 100°C was decided to be an upper limit of the leaching temperature. As seen in the experimental data, inadequate reactions took place at temperatures less than 80°C. It was then deemed that temperatures higher than 80°C promoted the dissolution of the gelatin and the reaction worked quite well in a range of 90-100°C.

Table 3-9 summarizes the SRE data of all the test runs when oxalic acid was used as a leaching chemical. The relationship between acid concentrations and temperatures at retention times of 10 and 20 minutes are illustrated **Figure 3-7** and **Figure 3-8**. At low temperatures, an increase in acid concentration has a slight effect to enhance the SRE of the chemical leaching process. On the other hand, at high temperature, an increase in acid concentration greatly elevates the SRE.

Table 3-9 Silver recovery efficiency (% SRE) of oxalic acid leaching process.

Film size (cm×cm)	Temp (°C)	Retention time (minutes)	Silver recovery efficiency (% SRE) of oxalic acid		
			1% (w/v)	3% (w/v)	5% (w/v)
1	60	10	0.22	0.61	1.23
1	60	20	2.16	2.22	3.56
1	80	10	1.23	3.23	4.28
1	80	20	3.05	7.72	9.43
1	90	10	4.31	15.61	19.83
1	90	20	5.03	19.99	32.67
1	100	10	7.56	28.42	64.68
1	100	20	16.01	45.74	98.28

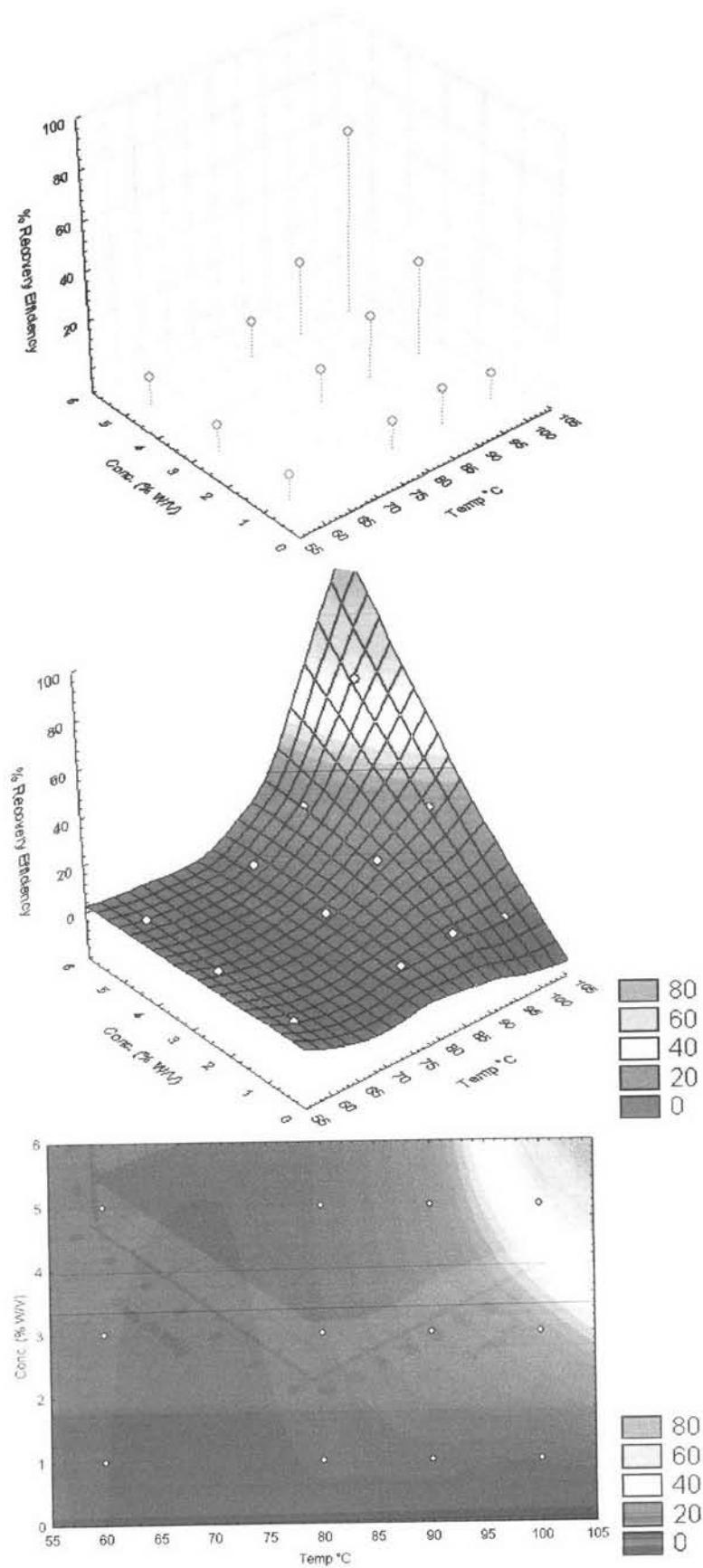


Figure 3-7 % SRE at 10-minute retention time using 1x1 cm² processed film chips and 1, 3, and 5% (w/v) concentrations of oxalic acid.

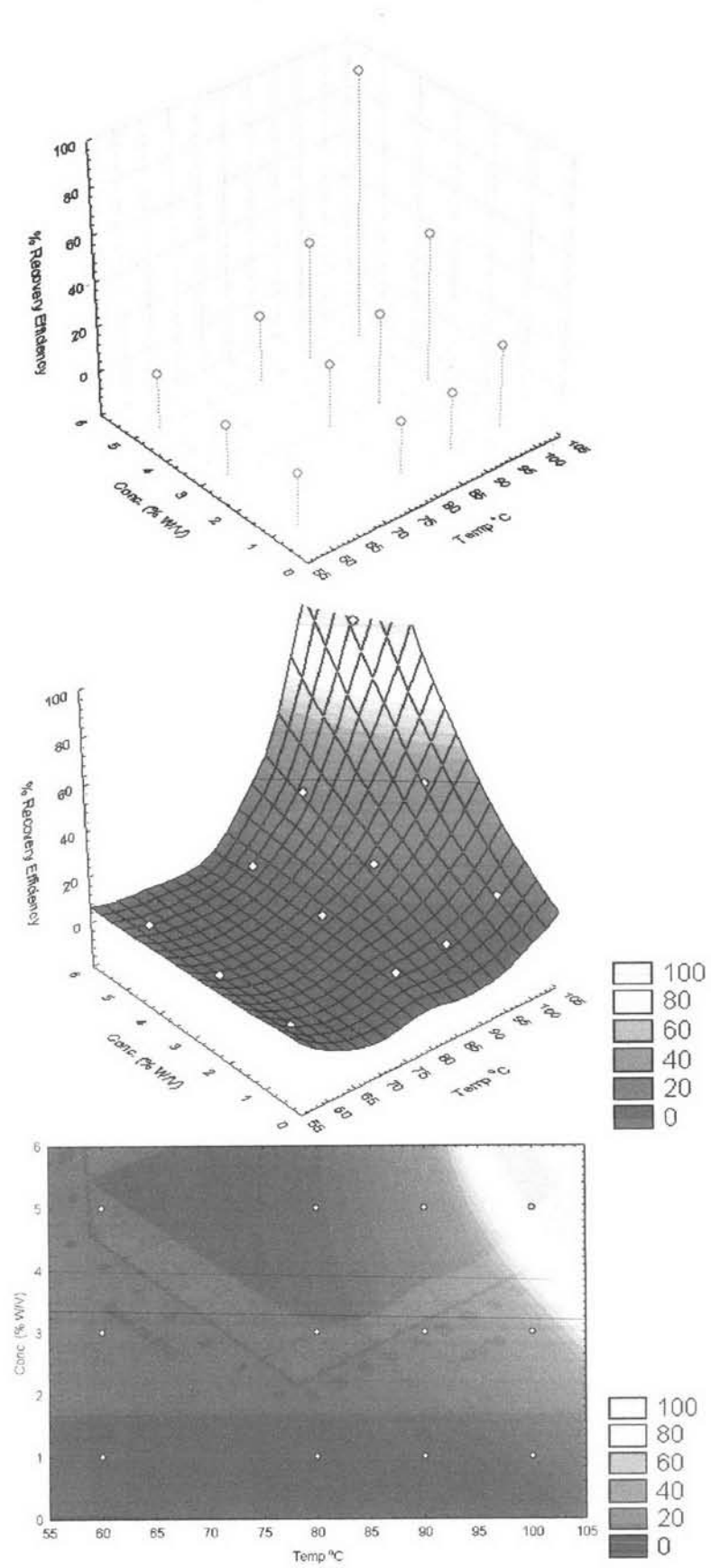


Figure 3-8 % SRE at 20-minute retention time using 1x1 cm_xcm processed film chips and 1, 3, and 5% (w/v) concentrations of oxalic acid.

3.5.1.5 Effect of Retention Time

From the experimental data in **Table 3-7**, the conditions in which silver was leached out from the 1x1 cmxcm film chips by 1% and 5% (w/v) oxalic acid are shown in **Figure 3-9** and **Figure 3-10**, at temperatures of 90 and 100°C, respectively.

The effect of the retention time on the SRE of chemical leaching process was investigated by varying the retention times from 10 to 100 minutes (in **Figure 3-9**) and from 10 to 120 minutes (in **Figure 3-10**). The higher the temperature offered the higher SRE. At the acid concentration was 1% and 5% (w/v), SRE increases from 4 to 98% and 20 to 98%, respectively.

In addition, when focusing on the conditions where SRE was more than 95%, the retention time at 90°C decreased from 90 to 60 minutes when the acid concentration increased from 1% to 5% (w/v). Similarly, the retention time at 100°C decreased from 60 to 20 minutes. These results also confirm the effect of acid concentration on SRE.

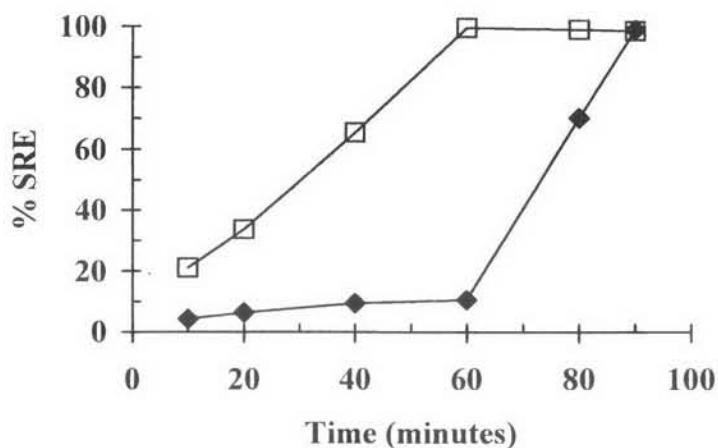


Figure 3-9 Silver Recovery efficiency (% SRE) of 1x1 cmxcm processed film chips at 90°C, and the retention times of 10, 20, 40, 60, 80, and 90 minutes. (◆) 1%(w/v) oxalic acid and (□) 5% (w/v) oxalic acid

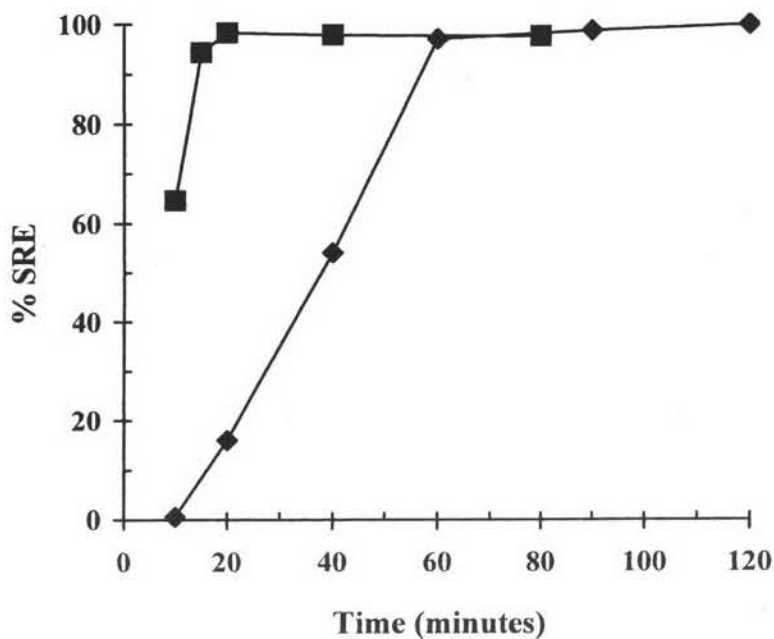


Figure 3-10 Silver Recovery efficiency (% SRE) of 1x1 cm \times cm processed film chips at 100°C by refluxing at 10, 20, 40, 60, 80, 90, and 120 retention times. (◆) 1%(w/v) oxalic acid and (□) 5% (w/v) oxalic acid

Figure 3-11 and **Figure 3-12** present a relationship between the acid concentration and the retention time at temperature 90 and 100°C. At short retention times i.e., from 10 to 35 minutes, the acid concentration enhanced SRE. On the contrary, acid concentration considerably increases the removal efficiency at long retention times i.e., 35 to 90 minutes.

Several triplicate tests were carried out, to leach silver from 1x1 cm \times cm film chips by using a 5% (w/v) oxalic acid, and SRE of 98-99% was achieved. It was found that the optimal conditions were at 90°C, 60-minute retention time, and at 100°C, 20-minute retention time.

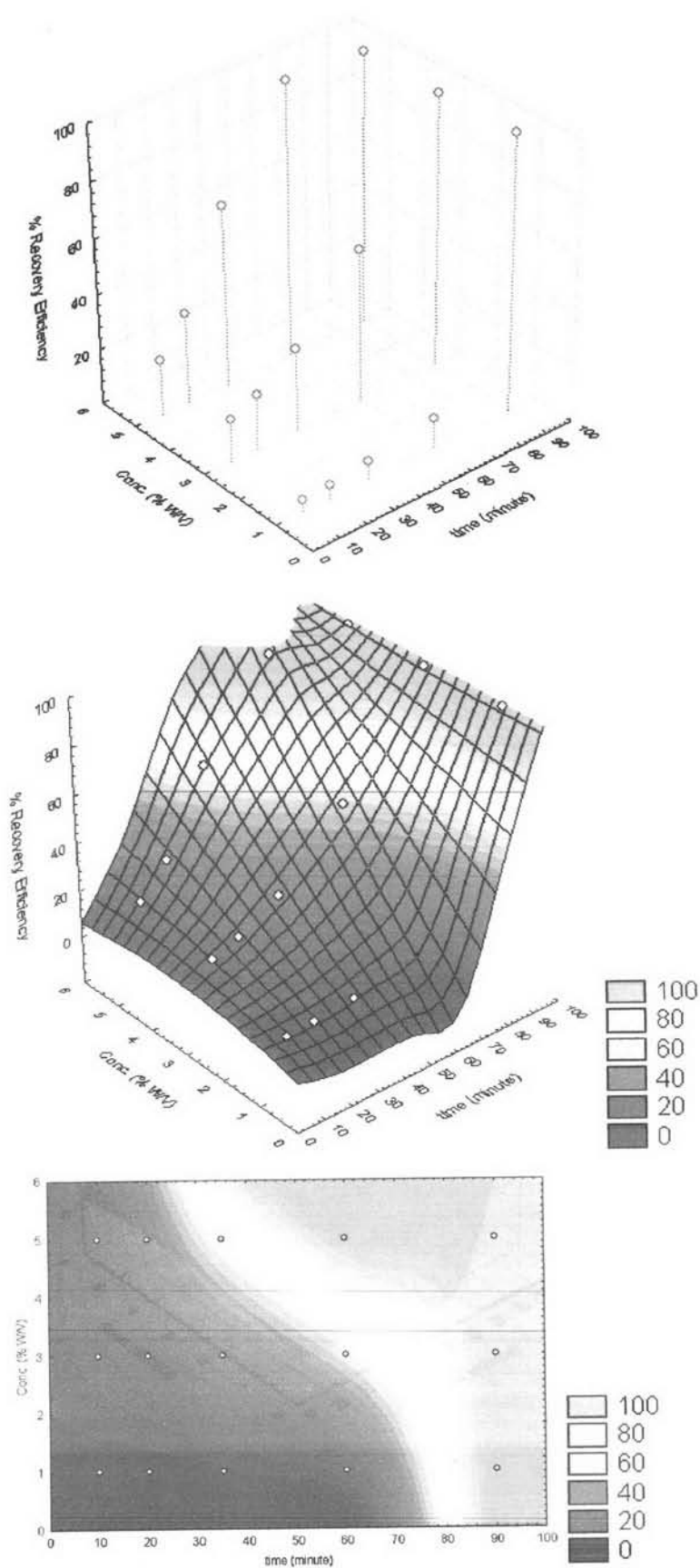


Figure 3-11 % SRE at 90°C using 1x1 cm \times cm processed film chips and 1, 3, and 5% (w/v) concentrations of oxalic acid.

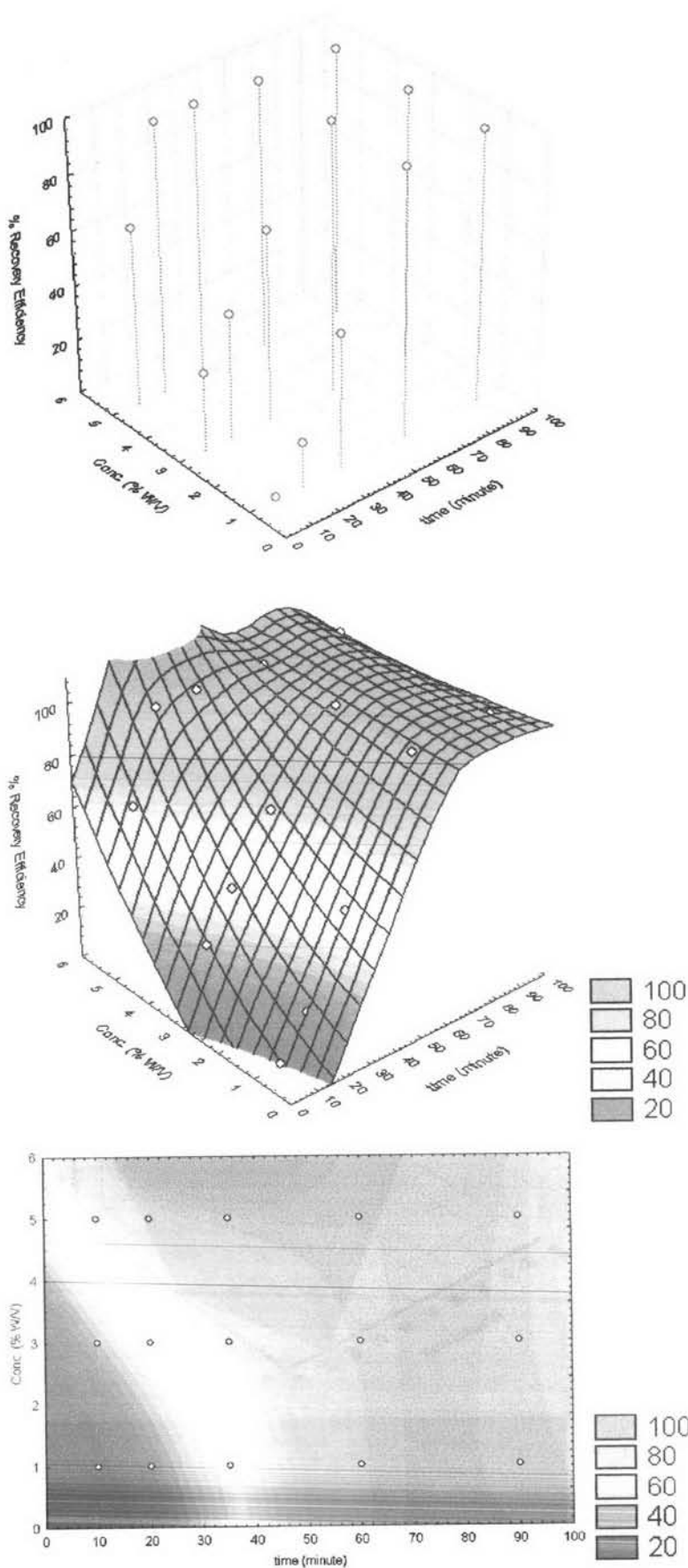


Figure 3-12 % SRE at 100°C using 1x1 cm² processed film chips and 1, 3, and 5% (w/v) concentrations of oxalic acid.

3.5.2 Efficiency of Reused Acid Solution

The optimal condition i.e., 1x1 cm \times cm film chips, 5% (w/v) oxalic acid, 100°C temperature, and 20-minute retention time, were selected in this experiment. The results showed that the spent 5% (w/v) oxalic acid could be reused in a leaching process more than 20 times, as illustrated in **Figure 3-13**. However, SRE decreased as the number of reuse times increased. It was observed that when the spent acid solution was used up to 10 times (first use plus reuse 9 times), the color of the solution changed from a clear solution to a yellow solution which represents high concentrations of gelatin.

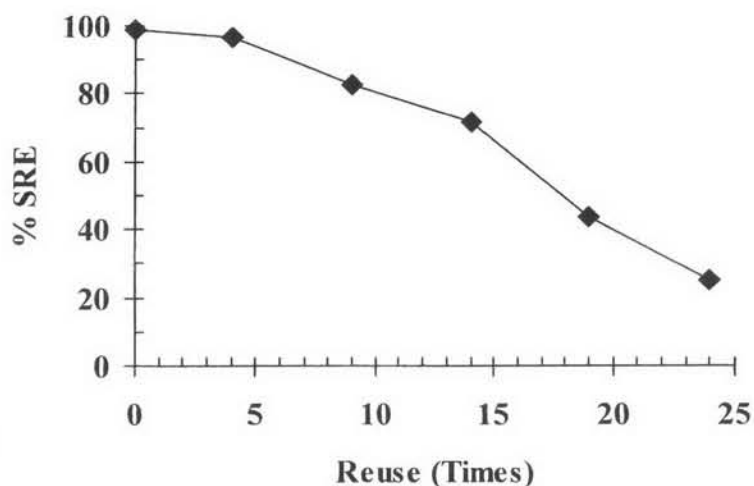


Figure 3-13 Silver Recovery Efficiency (% SRE) of 5% (w/v) oxalic acid versus the reuse times.

3.5.3 Morphology Silver Sludge and Film

Characterizations of silver (i.e., shape and mass content) present in the (unleached) processed film and the sludge (from the batch leaching test of 1x1 cm \times cm film chips using 5% (w/v) oxalic acid at 100°C, 20-minute and 40-minute retention times) were performed by SEM-EDX technique. The XRD technique was used for analysis in order to confirm that an explosive form of silver compounds i.e., silver oxalate was not present in the silver sludge. The results are as followed.

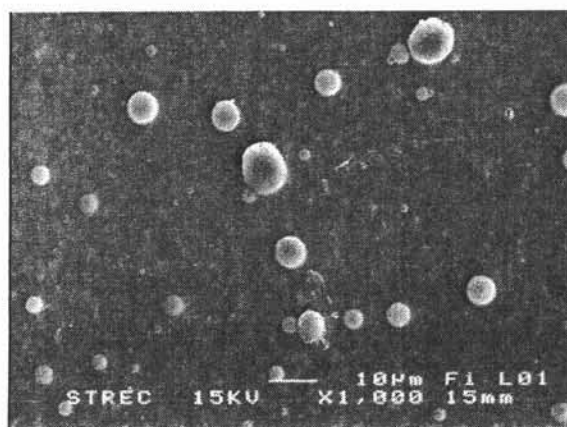
3.5.3.1 SEM-EDX

Figure 3-14 demonstrates the microscopic pictures of the processed film and silver sludge after leaching process, which were scanned using Scanning Electron Microscope (SEM) at three magnifications (1000, 3000 and 7000 times). It was found that particles with spherical form were scatteringly present in the processed (unleached) film and the sludge. These round-shape particles were luminescent under SEM; this is a typical phenomenon of metallic elements when exposed to electron light. In order to identify the metallic elements present in the sludge, the Energy Dispersive X-ray (EDX) was equipped with SEM. The EDX spectra are shown in **Figure 3-15**. The spectra revealed that silver was the major element in the sludge.

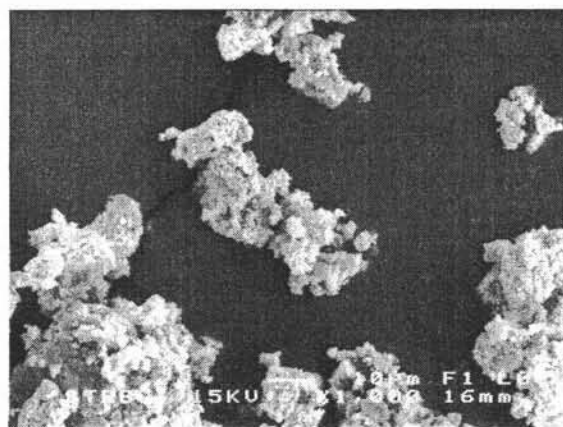
The silver particles (as confirmed by EDX analysis) were surrounded with flaky compounds (presumably gelatin), which is normally present in the emulsion layer of the film. During the chemical treatment, the acid dissolved the gelatin by breaking down the cross-link networks of the compound. As a result, the gelatin became flaky and the silver remained in the same shape. The SEM-EDX analyses of the sludge indicate that oxalic acid only leached the silver from the film sheet without reacting with the silver.

3.5.3.2 XRD

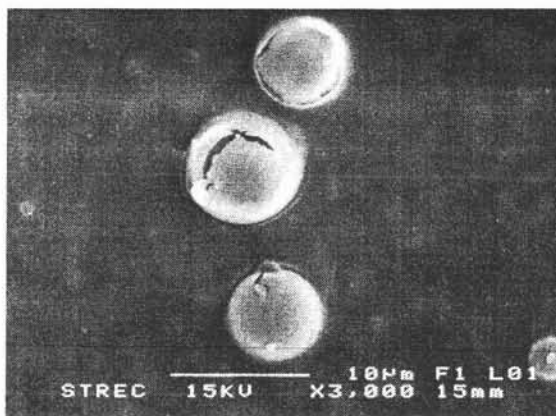
The sludge examined by XRD technique was from 2 different chemical treatments: the first was of the optimal condition where 5% (w/v) oxalic acid was used to leach 1x1 cm \times cm film chips at 100°C and the retention time of 20 minutes, and the second is as the first treatment except for the retention time, which was extended from 20 minutes to 40 minutes. It was expected that the 40-minute retention time would stimulate a formation of silver oxalate (if occurred) to a detectable amount.



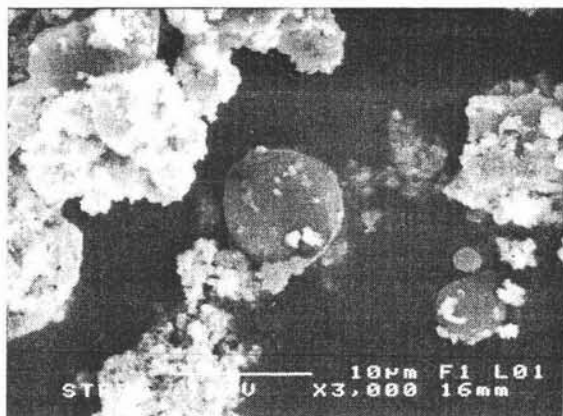
(a) Processed film (X 1,000)



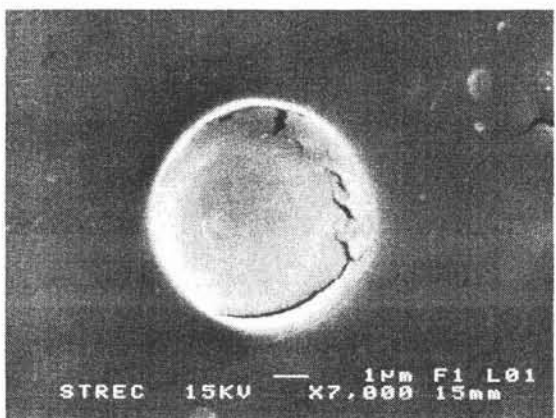
(d) Sludge (X 1,000)



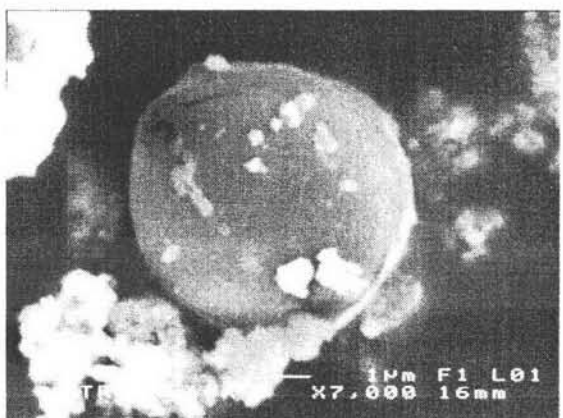
(b) Processed film (X 3,000)



(e) Sludge (X 3,000)



(c) Processed film (X 7,000)



(f) Sludge (X 7,000)

Figure 3-14 Metallic particles in the (unleached) processed film and the sludge from the chemical leaching process.

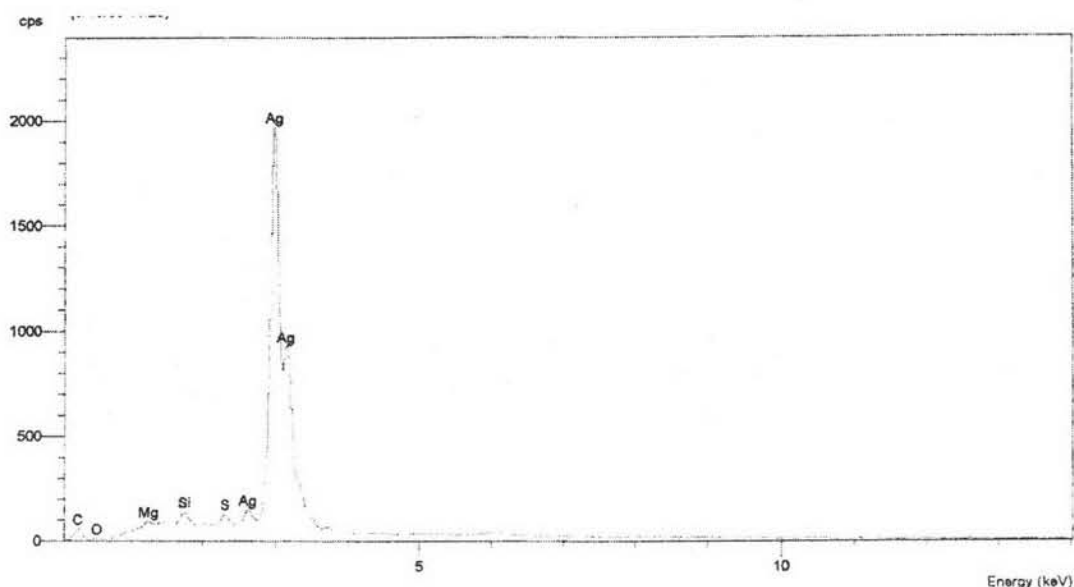
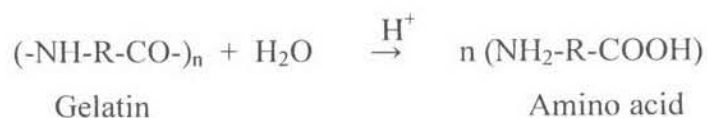


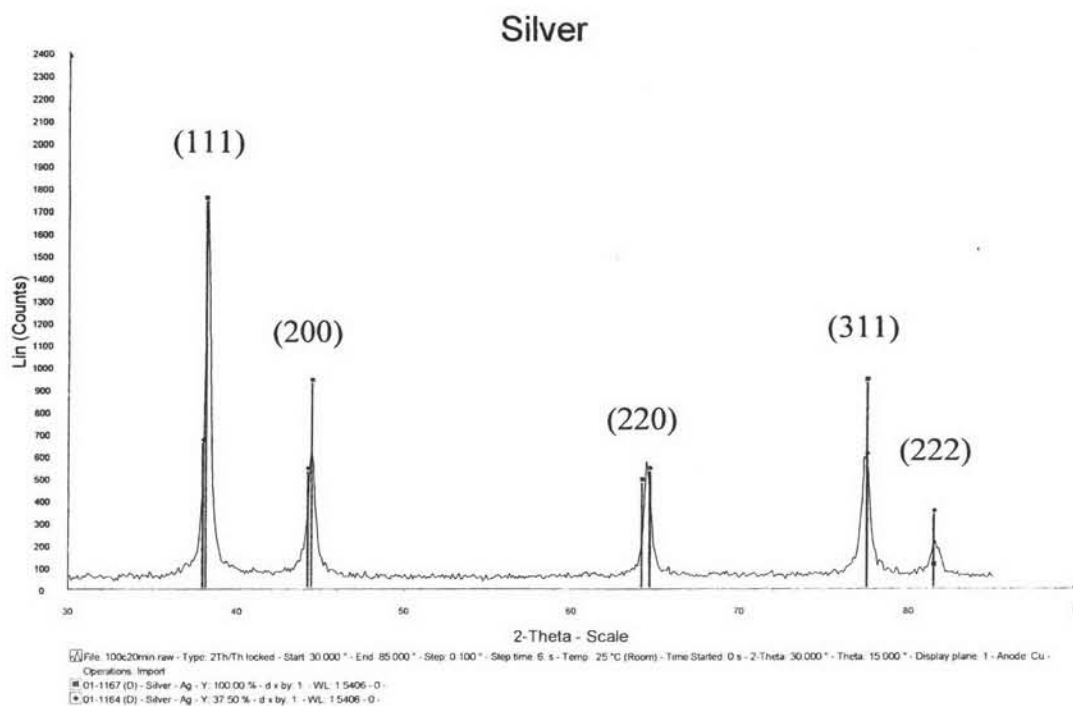
Figure 3-15 Mass content of silver element in the sludge from a chemical leaching process.

The XRD patterns of the sludge are shown in **Figure 3-16**. The patterns showed the diffraction peaks corresponding to the *fcc* silver phase. The major diffraction line of the sludge was presented at 38 (111), 44 (200), 64 (220), 77 (311), and 81 (222) degree 2θ , corresponding to the silver element fingerprint. Other kinds of silver complexes such as silver oxalate (an explosive compound), could not be detected.

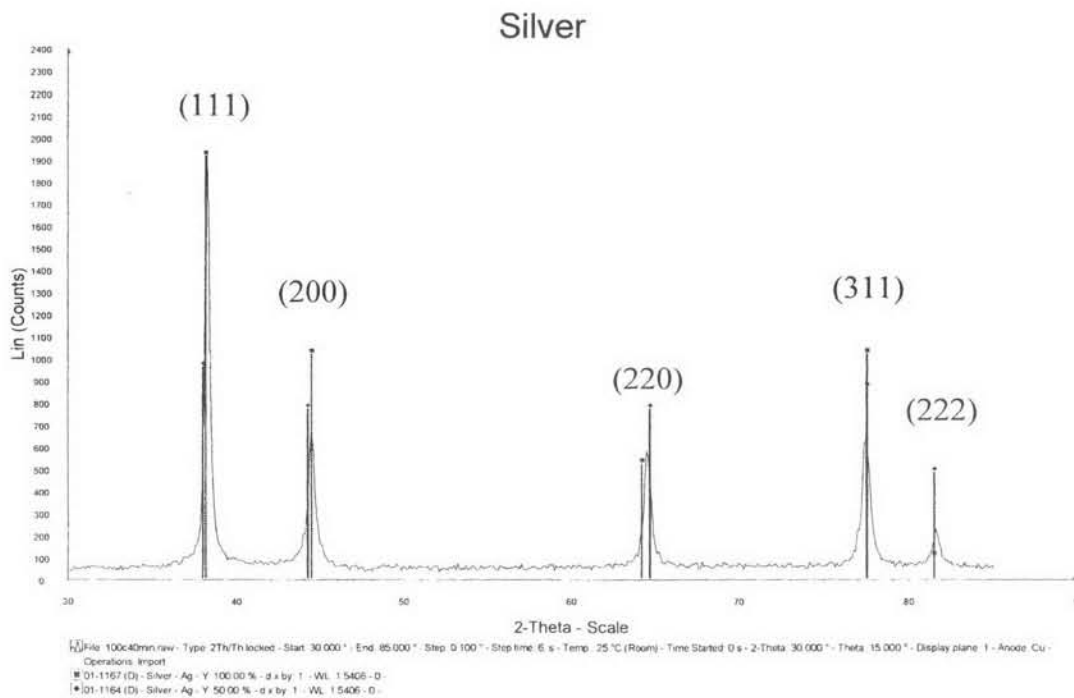
The proposed mechanisms of the leaching process described the reactions are presented in **Figure 3-17**. Metallic silver in spherical form is suspended in a gelatin base that forms an emulsion layer of radiographic film. The chemical leaching process removes the silver from the layer by the use of organic acid to break down the peptide bonds of the gelatin base. The hydrolysis (breakdown) equation is as followed.



At high temperatures and long retention times, the gelatin was digested completely by the organic acid solution and the silver particles were released from the emulsion layer.



(a) 20-min retention time



(b) 40-minute retention time

Figure 3-16 The XRD patterns of the silver sludge from chemical leaching process.

Silver obtained from a leaching treatment with strong inorganic acids generally forms silver complexes with acidic anions; while silver from a treatment of weak organic acids (in this case is oxalic acid) is in a metal form, which is easier to be processed in a refining step i.e., fewer unit operations. In other words, no additional unit to modify silver complexes to metallic prior to the ingot formation is required. The fewer the unit operations, the less operating energy and cost would be spent. Therefore, the treatment by oxalic acid, rather than strong acid treatment, should be preferable.

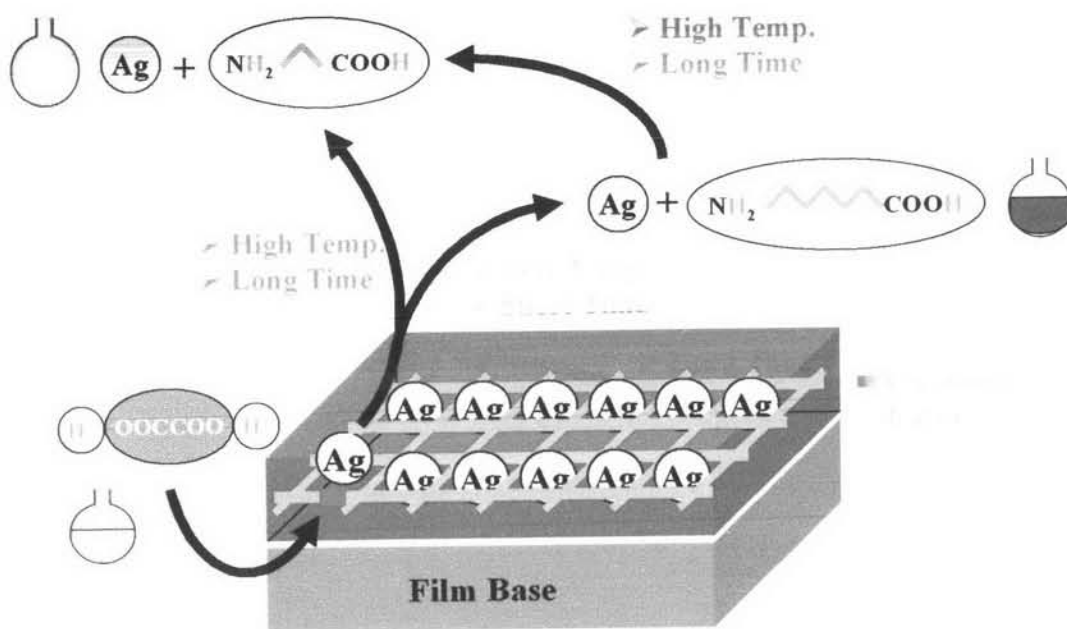


Figure 3-17 Proposed mechanisms of the chemical leaching process by oxalic acid.

3.5.4 Comparison of CO₂ Emissions

3.5.4.1 Comparison of Technology

1) Existing Technology in Thailand

In Thailand, a waste processor who recycles or recovers precious metals from wastes is categorized as a “106-Type Factory” in the attached list of the Ministerial Rule No.15 2002 (B.E. 2544) issued pursuant to the Factory Act 1992 (B.E. 2535). At present, there is only one registered 106-type factory which recovers silver from used X-ray film. The recycling process of this factory is depicted in **Figure 3-18**.

First, the film is brought into a gasification and combustion unit in order to burn the polyester out at a temperature of approximately 830°C using fuel oil grade A. The residues (ash) are further transferred to a smelting unit to get rid of impurities. This unit operates at 1200°C using electricity. In this unit, the silver is transformed into a liquid. Then, the liquid silver is cooled down as far as a crude silver ingot is formed. The crude silver ingot is packed and exported for refining in Japan. The flue gas cleaning system consists of an air cooler, a bag filter, and a wet scrubber to remove airborne pollutants from the combustion and melting units. The operating costs included the expense of flue gas treatment are very high. Due to a lack of raw material i.e., domestic used X-ray film and its extremely high price, this licensed firm has to import used film to supply its recycling facility.

2) Proposed Technology

Considering the proposed process i.e., the chemical leaching process on the commercial scale, used films are immersed into a leaching oxalic-acid solution. Under the design retention time and temperature, a leaching solution is circulated with a pump and heated to 90-100°C by a heat exchanger. The leached film and sludge are separated from the mixed liquor through a series of screening, rinsing, and filtration processes. Filtrate sludge, which contains silver and gelatin, is then transferred to a smelting process, similar to the previously described existing process.

The process schematics of the existing combustion process and the organic acid leaching process are illustrated in **Figure 3-19**.

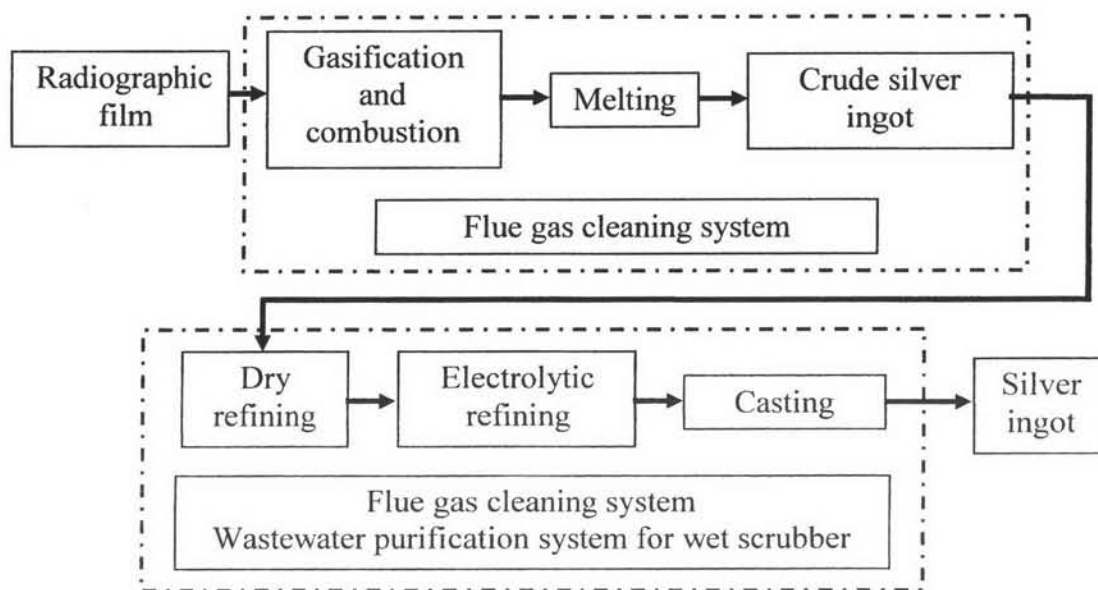


Figure 3-18 The silver recovery process of the licensed 106-type factory.

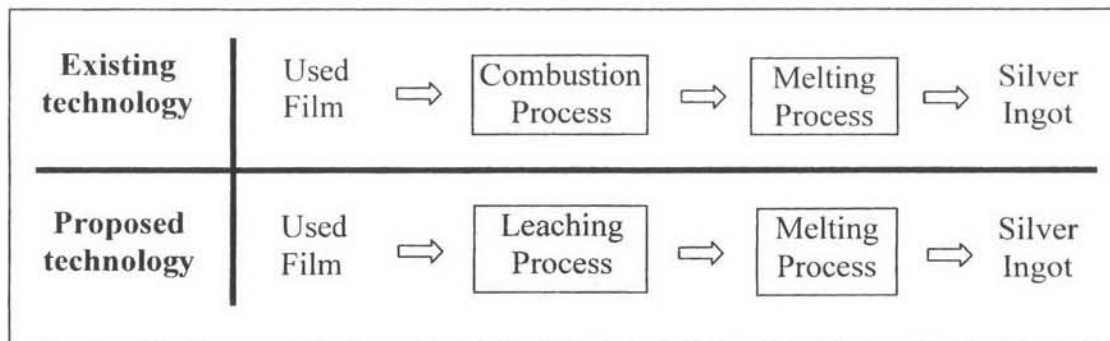


Figure 3-19 Comparison of the existing technology and the proposed process.

3.5.4.2 Estimation of CO₂ Emission

The existing technology described above contributes considerable air pollution to the environment and consumes a large amount of energy i.e., fossil fuel and electricity. Even this factory takes good care of environmental issue; it should have an environmental benefit to be aware of the amount of unintended pollutants released. With respect to a life cycle assessment and/or a material flow analysis, CO₂ is one of

the best candidates for appraisal of a Cleaner Technology. In this study, it is chosen to compare how “green” the existing technology and the proposed process are.

In general, several sources of energy can be used. CO₂ emission factors can be used for comparison of the amount of CO₂ released from various energy sources. **Table 3-10** presents the US.EPA (2004) CO₂ emission factors of coal, natural gas and fuel oil.

Table 3-10 Carbon Dioxide Emission Factors

Fuel	Emission factor	
	Carbon dioxide (lbs/mmBtu)	Carbon dioxide (kg/kw-hr)
Coal (Lignite)	210.47	0.96
Natural gas	116.39	0.53
Fuel oil	159.66	0.73

Source: US.EPA, 2004

The results of estimated CO₂ emissions from a combustion process (the existing technology) and a chemical leaching process (the proposed technology) are shown in **Table 3-11**.

The combustion process involves a furnace, a cooling unit, a bag filter and a wet scrubber. Fuel oil and electricity were used as the energy sources for this process. For each unit, the released amount of CO₂ was estimated to be 5,130, 21, 163, and 58 kg per ton of used film, respectively. The total amount of CO₂ emission was 5,372 kg per ton of used film. The energy used in the purification of wastewater resulted from an air pollution scrubbing unit was not taken into account (information not available).

According to the operation criteria (where SRE > 95%), the uses of 5% (w/v) oxalic acid at 90°C and 60-minute retention time, and at 100°C for 20-minute retention time were taken into considerations in the proposed technology. This process mainly involved heating, stirring, temperature controlling, cooling. The calculations resulted in the total amount of CO₂ emission when processed the film at

90°C, 60-minute retention time and at 100°C, 20-minute retention time were 3,780 and 4,267 kg per ton of used film, respectively. Leaching the film at 90°C, 60-minute retention time polluted the environment in terms of CO₂ emissions 12% less than processing at 100°C, 20-minute retention time. Detailed calculations are shown in appendix B.

The amounts of CO₂ emissions from the chemical process under 2 different operating conditions at 90°C, 60-minute retention time and at 100°C, 20-minute retention time were 70 and 79% of the amount released from the existing process, respectively. The proposed process, therefore, appears to be “greener” and becomes cleaner technology in this context.

Table 3-11 Amounts of CO₂ emissions.

Unit Operations	CO ₂ emissions in kilograms		
	Combustion at 830°C, 6.67 hours	Leaching at 90°C, 60 minutes	Leaching at 100°C, 20 minutes
Combustion/Heater	5,130	3,710	4,205
Stirring unit	-	2	1
Cooling unit	21	-	3
Bag filter	163	-	-
Scrubber/Wastewater treatment unit	58	68	68
Total	5,372	3,780	4,276

3.6 Summary

Oxalic acid was found to be suitable for leaching the silver coated on processed radiographic film. It was obvious that oxalic acid had greater leaching potential, in other words, higher % SRE (Silver Recovery Efficiency), than the other two organic acids i.e., acetic acid and malonic acid. Smaller film size apparently gave positive effect on SRE. The longer retention time and the higher temperature offered better considerable SRE. The optimal conditions that provided a high potential of

removal (> 97% SRE), were found when leaching 1x1 cm \times cm processed film chips by 5% (w/v) oxalic acid at 100°C with 20-minute retention time and at 90°C with 60-minute retention time. A characterization of the silver sludge indicated that the sludge contained metallic silver and no silver oxalate, an explosive compound, was found.

With respect to CO₂ emissions, to our best estimation, it was found that the proposed technology would emit CO₂ ca. 20-30% less than the amount released by the existing technology. Considering that the proposed process used oxalic acid (weak organic acid) instead of strong inorganic acid, which is much less toxic and safe in operations, our proposed technology would be justified to be a green or a cleaner technology.