

## CHAPTER II

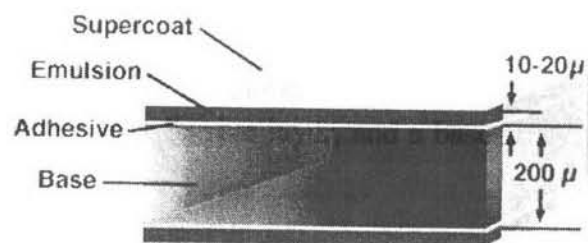
### LITERATURE REVIEWS OF RADIOGRAPHIC WASTES

#### 2.1 Radiographic Film

Radiographic film is used for industrial purposes and medical services. This film is one category of “black and white” film besides micrographic film and graphic art film. It consists of greater amounts of silver than that in any other types of film due to its radiation-sensitive silver halide (AgX), which is scattered on the gelatin of the emulsion layer on both sides of a polyester sheet (i.e., the film base). The silver content of photographic materials, which is called the coating weight, varies from less than 1 to 8 grams per square meter. X-ray (medical, industrial, and dental films) contains coating weight of silver approximately 4-6 grams per square meter (Hilliard, 2000).

##### 2.1.1 Composition of Radiographic Film

Radiographic film consists of four important layers: a protective (super coat) layer, an emulsion layer, an adhesive layer, and a base layer as shown in **Figure 2-1** (Gambhir, 2004).



**Figure 2-1** Cross-section of radiographic film.

1) The protective layer or super coat layer is generally made from non-photosensitive gelatin mixed with ingredient chemicals for making film surface smooth and polished (Silawatchananai, 1985). This layer prevents scratches on the film.

2) The emulsion layer is a photosensitive coating of the film base, usually made of silver halide crystals suspended in a gelatin base. The film contains silver in the form of silver-iodo-bromide of ca. 90-99% of silver bromide and 1-10% of silver iodide. These silver-halide compounds assist the light sensitivity of the film (Peantumdee, 2000 and The Encyclopedia of Medical Imaging Volume I, 2004). Sulfur-containing compounds are often added to react with silver halides to form silver sulfide at the crystal surface, which is called a sensitivity speck, to increase photosensitivity. The emulsion layer is thin enough so developing, fixing, and drying processes of the film can be accomplished in a reasonable time.

Other chemical substances added to the emulsion are hardening agents and sensitizers. Hardening agents are chemical compounds to make the gelatin tough and more resistant to swelling and softening in the subsequent handling and processing operations. Sensitizers are special organic substances to increase the silver halides' sensitivity to certain colors (Eaton, 1986).

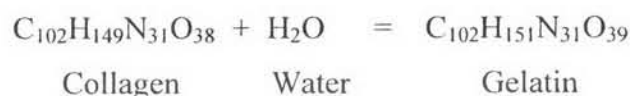
3) The emulsion attaches to the film base by the adhesive layer (subbing layer). Generally, it comprises of major amounts of polyvinylidene chloride and polyacrylonitrile polymerized with relatively small percentages (0.5 to 3%) of polymerizable acids or alkyl ester. Itaconic, acrylic or methacrylic acids are examples of the polymerizable acid (James, 1976).

4) Modern radiographic films utilize a polyester film base which has outstanding mechanical properties compared to cellulose nitrate and cellulose triacetate films (The Encyclopedia of Medical Imaging Volume I, 2004). The latter films are often used in special applications where dimensional stability, film strength, and resistance to extremes of temperature are important (Eaton, 1986.). Both triacetate and polyester are colorless, so blue-tinted base is added into film to be pleasant when looks at (Peantumdee, 2000).

### 2.1.2 Gelatin

Gelatin has proven to be the most satisfactory colloid for photographic emulsions because it has no chemical effect on the silver halides. It keeps the silver halide grains uniformly dispersed which is very important to the finished photographic film. Additionally, dry gelatin is stable for a long period of time which results in reasonably permanent products, either before or after processing. It also allows processing solutions to quickly penetrate through its structure without destroying the toughness or permanence.

Gelatin is a natural product derived from hydrolysis of collagen, a complex organic material obtained from selected hides and ears of calves. Collagen is changed slowly over a considerable period of time and, under suitable conditions, breaks down into gelatin, as shown below (Tientanacom, 1980).



Gelatin is a hydrophilic (water-loving) colloidal material. It can absorb water up to ten times its weight. In its solid dry state, gelatin is a vitreous, brittle, tasteless, odorless, hard, transparent, solid material, faintly yellow to honey-like in color (Tientanacom, 1980; Gelatin Manufacturers Association of Asia Pacific, 2005). The properties of gelatin in solution might be different depending on its pH, electrolyte content, thermal history, aging, concentration, source and manufacturing procedure. The percentage composition of gelatin is given as: C 50.5%; H 6.8%; N 17.5%; and O 25.2% (Tientanacom, 1980). Such percentages can be different depending on the type of gelatin source and production process of gelatin. The molecular weight of gelatin is as high as  $5 \times 10^5$  [g/gmole] plus small amounts of different structured compounds due to the diverse origins (Carroll, 1980).

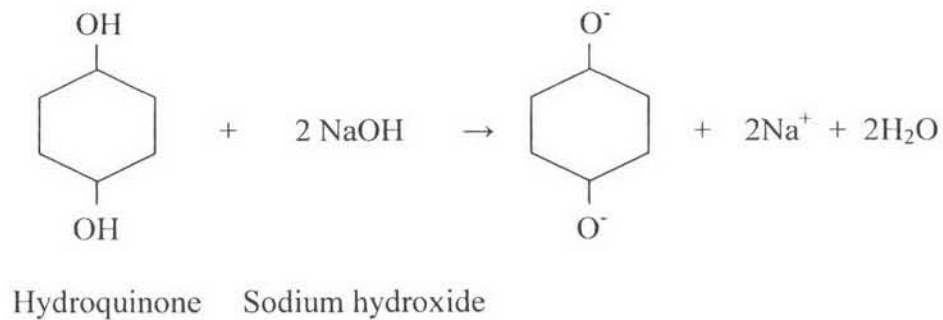
When gelatin is hydrolyzed completely, it will break down into simple amino acids. Eighteen amino acids are, at minimal, present in the gelatin molecule. Basically, amino acid residues in gelatin are joined through peptide bond;  $-\text{CH}_2\text{-NH}-$

CO-. In each molecule, amino acids contain two special groups: amino group (-NH<sub>2</sub>) and carboxylic group (-COOH).

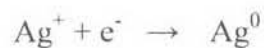
## 2.2 Film Processing

When light hits the grains of the sensitive silver halide (AgX) in the emulsion on radiographic film, a change takes place in the physical structure of the grains. Exposed silver halide (AgX<sup>\*</sup>) becomes sensitized silver ion, which is a better oxidizing agent than unexposed silver ion, and an invisible latent image is then created on the exposed film.

In the first step of developing radiographic film, the film is placed in a developer solution. Exposed silver ions (Ag<sup>+</sup>) in AgX<sup>\*</sup> are reduced to metallic silver (Ag<sup>0</sup>) by developing agent (hydroquinone) and activator (sodium hydroxide) in developer solution. The reaction can be represented as followed.



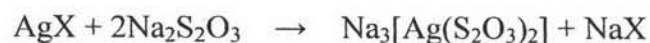
The negative hydroquinone can give up electrons to silver ion and forms metallic silver as followed.



This process intensifies the latent image on the film and makes it visible. However, the film still contains numerous of unexposed silver halides after developing process.

Then the film is placed in a fixer solution to remove the unexposed silver halide to be reduced; this makes the image more permanent. In this step, the unexposed silver halide is dissolved in the form of silver thiosulfate into the fixer

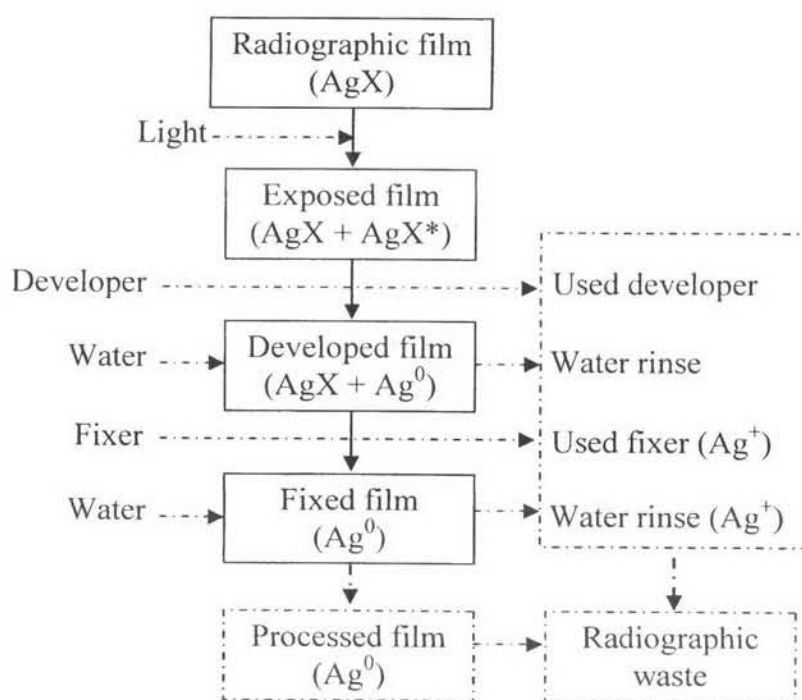
solution (Eaton, 1957; Colorado Industrial Pretreatment Coordinators Association, 2004) as shown in the following reaction.



Silver thiosulfate

After this process, the film can be safely exposed to light. The overall development process of radiographic film is illustrated in **Figure 2-2**.

Wastes such as film scraps, spent fixer, spent developer, rinse-water, and spilled chemicals are mainly generated within hospital radiology departments' premises.



**Figure 2-2** Overall developing process.

### 2.3 Radiographic Solution

Two types of solution, which are used in the radiographic process, are as followed.

### 2.3.1 Developer Solution

Developer solution is a photographic chemical to react with the exposed silver halide to make latent image visible. In general, pH of developer is approximately 10. The main constituents of developer solution are shown in **Table 2-1**.

**Table 2-1** Constituents of photographic developer.

Function	Chemical substance	Reason
1. Solvent	Water	It can penetrate and swells the gelatin, and dissolves a mixture of chemical in the developer.
	Diethylene glycol	In special cases, it is added to keep organic chemicals in solution.
2. Developing agent	- Hydroquinone (C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> )	It is capable of changing the exposed grains of silver halide to metallic silver; having no appreciable effect upon the unexposed grains in the emulsion.
	- Para-aminophenol	
	- Paraphenylene diamine	
3. Preservative	Sodium sulfite (Na <sub>2</sub> SO <sub>3</sub> )	It can prevent oxygen in air reacting with developing agent to form highly colored oxidation products (brown color), keeps the developer clear, and reduces the rate of the oxidation by the air.
4. Activator	- Sodium carbonate - Sodium hydroxide - Borax	It makes the developing agent more active. (Developer highly active in alkali)
	Sodium sulfite	
5. Restrainer	Potassium bromide (KBr)	It can retard the action of developer on the unexposed silver halide in unexposed areas or prevent development fog image.

**Table 2-1** Constituents of photographic developer (cont.).

Function	Chemical substance	Reason
6. Miscellaneous chemical	Sodium sulfate (Na <sub>2</sub> SO <sub>4</sub> )	It is added to a developer when used under higher temperature than normal. The sulfate can prevent gelatin from excessive swelling in developer at high temperature.
	Sodium thiocyanate	It is used when formulates a fine-grain developer that gives a more uniform deposit of silver grains in the image.
	Benzotriazole	It is used for minimizing the formation of fog.
	Calcium/magnesium salt	It is a water softener.

**Source:** Eaton, 1957; Tharapipat, 1998.

### 2.3.2 Fixer Solution

Fixer solution is a photographic chemical to remove the unexposed silver halide and makes image more permanent. Normally, the fixer has pH approximately 4-5. The main constituents of fixer solution are shown in **Table 2-2**.

**Table 2-2** Constituents of photographic fixer.

Function	Chemical substance	Reason
1. Fixing agent (known as HYPO)	- Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )	It dissolves unexposed silver halide without attacking gelatin and affecting developing image. The thiosulfates form very stable complex compounds with silver ions, and effectively reduce concentration of free silver ions in solution. Thus, sodium- and ammonium thiosulfates can act as silver halide solvents.
	- Ammonium thiosulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_3$ )	
2. Solvent	Water	It can penetrate and swells the gelatin, and dissolve a mixture of chemical in the fixer.
	Diethylene glycol	In special cases, it is added to keep organic chemicals in solution.
4. Preservative	Sodium sulfite ( $\text{Na}_2\text{SO}_3$ )	It reacts with colloidal sulfur to form sodium thiosulfate.
5. Hardener	Potassium alum	It prevents excessive swelling and softening of emulsion during washing.
6. Buffer	- Acetic acid - Sodium sulfite - Boric acid	The buffer prevents the change of pH. The solution must be buffered and have a large reserve acidity at the same time. Boric acid is added to improve the buffer action and anti-sludging characteristics.
	Sodium bisulfite	

Source: Eaton, 1957; Tharapipat, 1998



## 2.4 Silver

### 2.4.1 Silver Properties

Silver is a precious metal, which is lustrous, ductile, soft, white solid. It has the highest electrical and thermal conductivity of all metals. It is a rare element, occurring in the earth's crust. The main sources of silver ore are native silver, argetide (silver sulfide), and carargyrite (silver chloride). It can exist in numerous oxidation states; metallic silver ( $\text{Ag}^0$ ) and monovalent silver ion ( $\text{Ag}^+$ ) are the most common. It resists oxidation due to excellent light reflection; however, it tarnishes through reaction with atmospheric sulfur compounds. The properties of silver are shown in **Table 2-3**.

Silver is insoluble in water and alkalis, and it is resistant to most common acids except nitric acid, hot sulfuric acid, and alkali cyanide solutions. All silver compounds are insoluble owing to the solubility of less than 0.01 mg/l. The solubility product constants of some of silver compound are shown in **Table 2-4**.

### 2.4.2 Source and Use

**Table 2-5** shows that the photographic industry consumes about 45% of total silver consumption by industry.

Some of the anthropogenic sources of silver in the environment are emissions from smelting operations, manufacture and disposal of certain photographic and electrical appliance, coal combustion, and cloud seeding. The estimated loss of silver to the environment in the United States was 2,470 metric tons in 1978, mostly to terrestrial and aquatic ecosystems. The photography industry alone accounted for about 47% of all silver discharge into the environment from anthropogenic source as shown in **Table 2-6** (Eisler, 1996).

**Table 2-3** Properties of silver.

Property	Silver (Ag)
Atomic number	46
Atomic weight	107.8682
Electron configuration	[Kr] 4d <sup>10</sup> 5s <sup>1</sup>
Isotope, %	
106.9015	51.84
108.9048	48.16
Atomic diameter, pm	2883
Ionic radius, pm	126
Crystal structure	fcc, Fm3m
Boiling point (°C)	2,187
Melting point (°C)	961.93
Water solubility	Insoluble
Ionization energy (eV)	
Ag → Ag <sup>+</sup> + e <sup>-</sup>	7.574
Ag <sup>+</sup> → Ag <sup>+2</sup> + e <sup>-</sup>	21.960
Ag <sup>+2</sup> → Ag <sup>+3</sup> + e <sup>-</sup>	36.10

Source: Kirk, 1997

**Table 2-4** Silver compound solubility at 25°C (Ksp).

Property	Silver (Ag)
Silver (I) acetate (AgCH <sub>3</sub> COO)	1.94 x 10 <sup>-3</sup>
Silver (I) oxalate (AgC <sub>2</sub> O <sub>4</sub> )	5.40 x 10 <sup>-12</sup>
Silver (I) bromide (AgBr)	5.35 x 10 <sup>-13</sup>
Silver (I) iodide (AgI)	8.52 x 10 <sup>-17</sup>

Remarks: Silver oxalate (or Ethanedioic acid) is rather insoluble and explosive (violently decomposed at 140°C).

**Table 2-5** Breakdown of industrial consumption of silver by major categories.

Category	Percent of total
Photography	45
Electrical and electronic products	25
Sterlingware, electroplated ware, and jewellery	11
Brazing alloys and solder	5
Others	14
<b>Total</b>	<b>100</b>

Source: Spectrum; 2005

**Table 2-6** Estimated release of silver to environment in the United States in 1978.

Ecosystem	Source category	Metric tons
1. Atmosphere (3.7%)	Metal production	30
	Urban refuse combustion	10
	Coal and petroleum combustion	9
	Iron and steel production	7
	Cloud seeding	3
	Cement manufacture	2
	Others	30
2. Aquatic (28.5%)	Soil erosion (natural source)	438
	Urban run off	72
	Sewage treatment plants	70
	Photographic developing	65
	Photographic manufacture	54
	Others	6

**Table 2-6** Estimated release of silver to environment in the United States in 1978 (cont).

Ecosystem	Source category	Metric tons
3. Terrestrial (67.8%)	Photographic industry	630
	Urban refuse	445
	Sewage treatment	220
	Metal production	165
	Electrical contacts and conductors	150
	Alloys and solders	60
	Others	5

Source: Eister, 1996

The major source of silver contamination of water is silver thiosulphate complexes in photographic developing solution that photofinishers discharge directly into sewers (Guevara, 2005). The silver-contaminated wastes pose potential hazards towards public health and environment for the reason that it typically contains significant concentrations of silver.

### 2.4.3 Silver Toxicity

Silver soluble salt is more toxic than insoluble salts; soluble silver ion is the most toxic form of the chemical species. Silver, as silver ion  $[Ag^+]$  is known to intoxicate aquatic organism laboratory testing, although large industrial losses to aquatic environment are probably infrequent because of its economic value as a recoverable resource (Eisler, 1996).

The acute toxicity of silver to aquatic species varies drastically by the chemical form and correlates with the availability of free ionic silver. Ionic silver in aquatic system is rapidly complexed and sorbed by dissolved and suspended materials. In natural water, complexed and sorbed silver species are at least one order of magnitude less toxic to aquatic organisms than the free silver ion (Eisler, 1996).

Silver, silver ions and its compounds have been reported to have higher bioconcentration factors in marine flora and fauna than in the fresh water organisms. **Table 2-7** shows the toxic effect of silver on aquatic insects. Though it seems that the accumulation of silver by terrestrial plants from soils is low; silver (as silver nitrate) showed an adverse effect on sensitive laboratory mammals at total concentrations as low as 250 µg/l in drinking-water (brain histopathology), 6 mg/kg in diet (high accumulation in kidneys and liver), or 13.9 mg/kg body weight (lethality) (World Health Organization, 2002).

Silver may enter mammal bodies through inhalation, ingestion, and movement across mucous membranes or broken skin. Ordinarily, the highest concentration of silver in mammals is found in the liver, spleen and, to a certain degree, in muscles, skin, and brain. In the human body, the primary sites of deposited silver are the liver, skin, adrenals, lungs, muscle, pancreas, kidney, heart, and spleen; silver also accumulates in blood vessel walls, the trachea, and bronchi (Eisler, 1996).

Silver was not mutagenic, carcinogenic, or teratogenic to tested animals by normal routes of exposure. However, it was found that silver compounds can cause “argyria”, makes some area of skin and other body tissues turn gray or blue-gray when exposed to silver for a long period of time (several months to many years). The discoloration condition is thought to be only a cosmetic problem (U.S. Public Health Service, 1990).

Subsequently, the United State Environmental Protection Agency (U.S.EPA.) has set up the standard of silver for public drinking water supplies not exceeding 1 mg/l or 1 ppm, while OSHA and NIOSH have recommend that the concentration of silver in workplace air shall not exceed 0.01 ppmv for TLV-TWA (Center for environmental Health Sciences at Dartmouth, 2005). A solid waste that contains silver in excess of 5 mg/l by using the Toxicity Characteristic Leaching Procedure (TCLP), this concentration falls into hazardous material category – D011 (U.S.EPA., 2006).

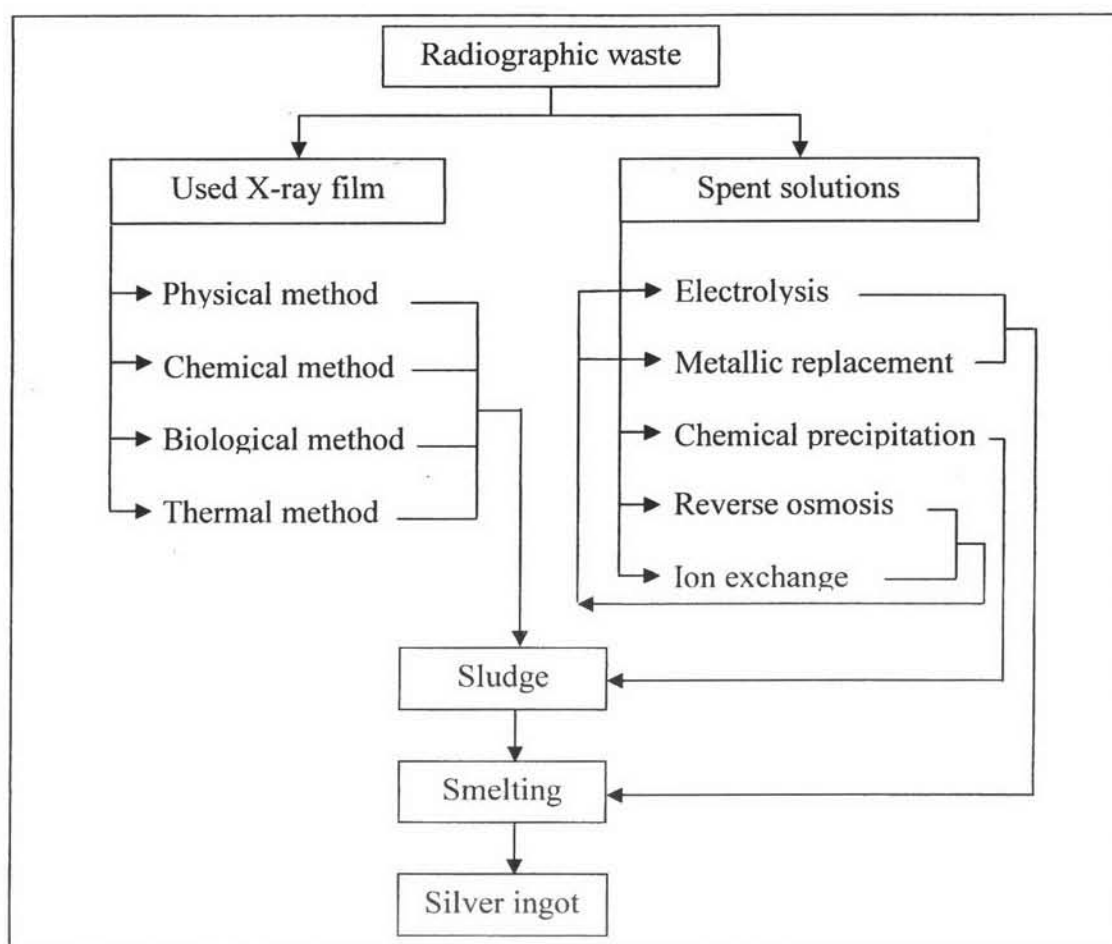
**Table 2-7** Toxic effect (threshold toxicity) of metals on a test aquatic insect.

Element	Concentration (mg/l)	Organism
Barium	29	Daphnia Magna
Cadmium	0.1	Daphnia Magna
Chromium	0.7	Daphnia Magna
Cobalt	5.0	Daphnia Magna
Copper	0.027	Daphnia Magna
Lead	5	Daphnia Magna
Mercury	0.03	Daphnia Magna
Nickel	6	Daphnia Magna
Silver	0.03	Daphnia Magna
Zinc	1.8	Daphnia Magna

Source: Nopakaew, 1996

### 2.5 Silver Recovery Technology

With respect to recovery technologies, there are several techniques for recycling of silver from certain photographic wastes which can be divided into developed film and spent solutions (i.e., developer or fixer). A simple depiction of these recovery methods is shown in **Figure 2-3**.



**Figure 2-3** Techniques for recovery of silver from radiographic waste.

### 2.5.1 Silver Recovery from Radiographic Film

There are four common methods being used to leach silver metal from used X-ray films; they are thermal, biological, mechanical or physical, and chemical treatments. The first method relies on combustion for the recovery of silver and energy; while the rest not only recover silver, but also recycle the film base. The silver sludge, obtained from the latter three methods, is smelted and further refined to form silver ingot. Details of this part are described in Chapter 3.

### 2.5.2 Silver Recovery from Radiographic Solution

Silver can be recovered from the spent fixer solution by electrolysis, metallic replacement, chemical precipitation, reverse osmosis, or ion exchange. The last two methods provide a way of increasing silver concentrations in a waste solution, so they

are suitable for solutions with low silver content i.e., rinse water and spent developer solution. Electrolysis and metallic replacements are effective methods that lead in a straightforward way to the retrieval of silver ingot.

### 2.5.2.1 Electrolysis

Electrolysis is an efficient and cost-effective technique. In electrolysis process, electric current is passed through a silver-rich solution between two electrodes (the anode and the cathode). During the process, an electron is transferred from the cathode to silver ion, converting the silver ion to metallic form, which adheres to the cathode as shown.



Metallic silver getting from this process is nearly pure. Recovery efficiency of this technique is more than 90%. To reduce concentrations below 5 mg/L, electrolysis must be followed by another recovery method, such as metallic replacement or ion exchange.

### 2.5.2.2 Metallic Replacement

The concept of metallic replacement is “iron is more active than silver”. Silver in solution undergoes an oxidation-reduction reaction with element iron to produce ferrous ions and metallic silver. Steel wool, iron particles, or iron-impregnated resin are used as the iron source. The iron is placed in a container referred to as a metallic replacement cartridge (MRC), chemical recovery cartridge (CRC), or silver recovery cartridge (SRC). One cartridge can recover silver more than 95% while a series of two cartridges can recover above 99%. Although low silver concentrations are removed with metallic replacement, the iron catalyst will be consumed more quickly due to the reduced protection from corrosion.





### 2.5.2.3 Precipitation

Precipitation is very efficient technique. It can recover silver sludge more than 99% from silver-rich solutions. Silver can be precipitated by using chemicals that form insoluble complexes with silver ion. Certain chemicals such as sulfide, borohydride, and amideboranes, are difficult and potentially toxic to use. Consequently, it is not commonly utilized to recover silver because of the requirements of chemicals and skilled personnel.

### 2.5.2.4 Ion Exchange and Reverse Osmosis

Ion exchange works by attracting the negatively-charged silver thiosulfate complex to positively-charged sites on the resin. The resin can be regenerated with a concentrated solution or replaced. This technology works best on dilute solutions which have concentrations as high as 200 mg/l, achieving up to 90% efficiency.

Reverse osmosis uses pressure and a membrane to filter solutions. It is a concentration process that is efficient to recover silver from dilute photoprocessing solutions and rinse water. An ion is held on one site of a semi-permeable membrane while the water is allowed to pass through the membrane. Typically, more than 90% of silver can be removed by this technique.

The treatment technologies for silver recovery are compared as shown in **Table 2-8**.

**Table 2-8** Comparison of silver-recovery and treatment technologies.

	Electrolysis	Metallic Replacement	Precipitation	Ion Exchange
Recovery efficiency	>90%	>95%	>99%	>90%
Initial silver concentration	2,000 to 12,000 mg/l	Variable	> 250 mg/l	< 30 mg/l
Final silver concentrations	50 to 250 mg/l	0.5 to 15 mg/l	0.3 to 1.5 mg/l	0.1 to 1.0 mg/l
Treatable solutions	Silver-rich solutions	Silver-rich solutions	Silver-rich Solutions	Rinse waters
Capital cost	Medium	Low	Medium	High
Operating cost	Low	High	Medium	High
Advantages	Can produce > 90% pure silver	Can be relatively inexpensive	Consistently low silver concentration	Provides low silver concentration for rinse waters
Disadvantages	Relatively high final silver concentration; usually requires secondary recovery	Difficult to know when to replace iron; discharge of iron contaminated wastewater is limited by some sewer codes	Not currently available for all processes	Expensive; requires expert maintenance