

Appendix A

Glossary of Terms

AMSA: The Association of Metropolitan Sewerage Agencies represents the interests of the country's largest wastewater treatment agencies. AMSA maintains a key role in the development of environmental legislation and implementation of environmental rules, guidance and policy.

Anode: The positively charged electrode. When electrolytically desilvering photo processing solutions, the sulfite is oxidized at the anode.

Batch Process: The collection of silver-rich solution into a tank or container which is processed through a silver recovery or management system.

Biocide: A chemical that discourages the growth of bacteria.

Cathode: The negatively charged electrode. When electrolytically desilvering photo processing solutions, metallic silver is deposited on the cathode.

Code of Management Practice (CMP): The site-specific plan implemented by the individual processing facility for the purpose of controlling and reducing discharges of silver to the POTW.

Continuous Process: The processing of silver-rich solution in a continuous flow from the processing machine through a silver recovery or management system.

Cradle-to-Grave: A phrase used to describe the tracking system for hazardous waste. All parties in the waste chain — generator, transporter, storage, and disposal facilities — use a common manifest that identifies them, the waste, and the final disposition of the waste.

CRC: A chemical recovery cartridge which recovers silver through a process known as metallic replacement.

Distillate: The liquid recovered by condensation during the process of distilling or concentrating used processing solutions and wash waters.

DOT: Department of Transportation

Effluent: The solution exiting a process or piece of equipment.

Electrolytic Silver Recovery: A method of recovering silver in which a direct current is applied across two electrodes immersed in a silver-rich solution. Silver plates onto the cathode and the thiosulfate is oxidized at the anode.

Good Housekeeping: Maintenance of a neat, orderly and clean working environment.

Influent: The solution entering a process or piece of equipment.

Ion Exchange: A reversible exchange of ions between a solid (resin) and a liquid (water containing ionized salts). When used with photo processing solutions, ion exchange removes silver and replaces it with ionized salts.

Large Photographic Processing Facility: A facility which produces on average more than 20 gallons per day (GPD) of silver-rich solution and uses more than 10,000 GPD of process wash water.

Low-Silver Solution: A solution containing insufficient silver for cost effective silver recovery. Low-silver solutions include used developers, bleaches, stop baths, prebleaches, stabilizers following washes, and wash waters.

Medium Photographic Processing Facility: A facility which produces on average more than two gallons and less than 20 gallons per day (GPD) of silver-rich solution and uses less than 10,000 GPD of process wash water.

Metallic Replacement: A method of recovering silver from silver-rich solutions by an oxidation-reduction reaction with elemental iron and silver thiosulfate to produce ferrous iron and metallic silver. The device used is commonly called a chemical recovery cartridge (CRC).

Minilab: An establishment having a combined color printer and processor capable of offering on-site photographic film processing and printing services.

Milligrams per Liter (mg/L): Amount of a substance in relationship to the whole. mg/L is the same measurement as parts per million (ppm).

Off-Site Silver Recovery and Management: Removal of silver-rich solutions from a facility by a hauling service to a recovery facility.

On-Site Silver Recovery and Management: The management and treatment of silver-rich solutions on the premises in which the silver-rich solutions are generated.

Parts per million (ppm): Amount of a substance in relationship to the whole. PPM is the same measurement as milligrams per liter (mg/L).

Pollution Prevention: Any practice that reduces or eliminates waste at the source.

POTW: Publically Owned Treatment Works. A wastewater treatment facility (WWTF) owned by the public (municipality or service authority).

Preventive Maintenance: A set of procedures routinely performed on equipment and processes to reduce the risk of a malfunction.

Pretreat: To change the characteristic of a waste by treatment before it is discharged to a POTW.

Significant Industrial User (SIU): Any industrial user that: discharges an average of 25,000 GPD or more of process wastewater to a POTW; contributes a process waste stream which makes up five percent or more of the average dry weather hydraulic or organic capacity of the POTW; or, is designated as such by the Control Authority on the basis that the industrial user has a reasonable potential for adversely affecting the POTW's operation or for violating any pretreatment standard.

Silver Recovery: The process of reclaiming silver from silver-rich solutions such as fixers, bleach-fixes, washless stabilizers, and low flow washes.

Silver-Rich Solution: A solution containing sufficient silver that cost-effective recovery could be done either on-site or off-site. Silver-rich solutions include fix, bleach-fix, stabilizer from washless systems, and low flow wash.

Silver-Estimating Test Paper: A test paper coated with an analytical reagent which reacts by changing color in relationship to the amount of silver in solution. A reference color code allows users to estimate the approximate amounts of silver in solution.

Small Photographic Processing Facility: A facility which produces on average less than 2 gallons per day (GPD) of silver-rich solution and uses less than 1,000 GPD of process wash water.

Source Reduction: A decrease in the production of both the volume and toxicity of liquid waste.

Spill: Unintended release of liquid that is not in the ordinary course of events.

Squeegee: Physical device (e.g. rollers, blades, etc.) used on processors to remove residual surface liquids before the film or paper travels from one processor tank to the next.

Sewer: An underground conduit for carrying wastewater to a POTW.

The Silver Council: A national group of trade associations, technical societies, municipalities, and government agencies whose members represent over 360,000 facilities that process photographic materials.

Appendix B

Electrolytic Silver Recovery

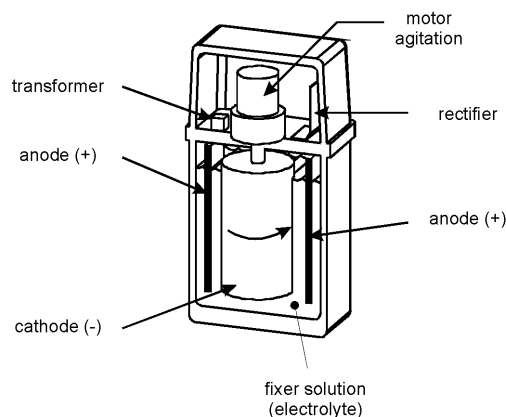
Electrolytic recovery is an efficient and cost-effective silver recovery technology first used in 1931. Since then the equipment has evolved and been refined so that today's electrolytic units are reliable and consistent. The equipment is continuously reused and few additional chemicals are required to perform the recovery operation.

B.1 How it Works

Throughout this discussion, refer to the diagram in the right-hand column. In electrolytic silver recovery two electrodes are immersed in silver-rich solution. Electric current reduces the silver-thiosulfate complex in the solution and plates almost pure silver metal onto the cathode — the negatively charged electrode. The cathode is typically made of stainless steel. The amount and quality of the silver plated out depends upon the operating amperage and the length of time the solution is exposed to the current.

There are two basic types of electrolytic equipment: one in which the cathode rotates in the solution and the other in which the solution flows around a stationary cathode. Either type of equipment is capable of recovering a significant amount of the silver from the silver-rich solutions. Electrolytic units must be used in conjunction with another system.

Electrolytic Unit



In-line electrolytic silver recovery

By using in-line electrolytic silver recovery on fix solutions, the amount of silver in solution is significantly reduced. This results in less silver carried over into the final wash water and subsequently discharged to the sewer. Where the use of in-line silver recovery is possible, mixing and chemical usage can be reduced by up to 50%, further increasing the cost effectiveness of this technology. This approach may not be feasible in all circumstances. Solution overflow from in-line systems must be treated by another system to further reduce the silver concentration.

B.2 Operation/Maintenance

The electrolytic unit must have enough capacity to treat peak volumes of silver-rich chemical effluent produced by the

lab. It must also be designed for the type of effluent to be treated (i.e., combined fix, bleach-fix and stabilizer/rinse). The manufacturer/supplier of the electrolytic unit can help the lab choose the appropriate equipment and provide preventive maintenance information. Generally, electrolytic units are monitored for the following: pH, silver concentration, sulfite concentration, time and amperage, and, mechanical operation. All of these are discussed below.

a. pH

For best results, electrolytic recovery requires that the pH be between 7.5 - 8.5. The pH of the incoming solution can easily be checked with pH estimating papers. The lab owner should contact the electrolytic unit supplier for help in establishing ideal pH levels and procedures for maintaining the range. Newer electrolytic units may not require pH adjustment.

Color processing - The pH of the combined solutions overflow from color processing will be about 7.5. Bleach-fix and fix solutions from color processes that contain iron-complex oxidizing agents are not as easy to desilver electrolytically.

The optimum pH range for silver-rich solutions containing iron is 7.8 - 8.5.* Under acidic pH conditions (pH < 7.0), the iron-EDTA complex used in bleaches and bleach-fixes will oxidize the silver plated on the electrode and move it back into solution. As the pH becomes more basic, (pH > 7.0), the oxidizing power of this iron-EDTA complex is reduced and

* It is highly recommended not to exceed a pH of 8.5. Above this level significant ammonia air emissions are released.

the plating of silver onto the electrode becomes more efficient.

Black & white processing - Fix solutions from black and white processes are easy to desilver electrolytically and require little, if any, pH adjustment.

Attempts to achieve higher efficiencies than those recommended by the manufacturer can actually lead to lower silver recovery. By over extending the plating time or significantly raising the current density, sulfiding will occur. This results in coating the cathode with a black sulfide precipitate rendering it unsuitable for continued silver recovery.

b. Silver concentration

The concentration of silver in the combined overflows from color processing will typically range from approximately 1,800 - 3,000 ppm **prior** to electrolytic recovery.

Recovery efficiency is directly related to silver concentration; the higher the silver concentration, the higher the plating efficiency. Replenishment rates play an important role in determining this concentration level. Over replenishment dilutes the amount of silver. When silver concentration falls below 1,000 ppm, plating efficiency decreases significantly thus reducing the recovery rate of the electrolytic unit.

It's very important to calibrate replenishment rates on the film and paper processors routinely.

c. Sulfite concentration

In the plating process, for each atom of silver plated out of solution the process

consumes one atom of sulfite. It's necessary, therefore, to have sufficient sulfite in the solution. This is particularly important with in-line electrolytic silver recovery where the fix solution is continually recirculated through the processing tank. Any degradation of the fixer can affect the final product. Check with the equipment manufacturer or chemical supplier to find out if you should be using a fix with an increased level of sulfite.

d. Time and amperage

Many of the electrolytic silver recovery units sold today are automatic so the operator doesn't have to set plating current and batch times — two critical factors in electrolytic silver recovery. The correct plating current must be maintained to drive the silver out of solution and onto the cathode. If the plating current is too high or the plating time too long, the silver deposited on the cathode will be black and sludgy, with much of it falling off the cathode and collecting on the bottom of the electrolytic unit. This situation, known as *sulfiding*, results in a low-quality silver and a mess to clean. To avoid sulfiding, follow the manufacturer recommendations for setting both the plating time and amperage.

Bleach-fix and fix solutions from color processes that contain iron-complex oxidizing agents may require higher current densities and longer times.

e. Mechanical operation

General mechanical preventive maintenance should be conducted periodically to ensure the plating current is correct, the cathode is rotating or the

pump is working, and the color of the silver on the cathode is creamy-grey rather than black or white. The silver should be harvested (removed from the cathode) periodically and sent to the refiner.

The most common mechanical problem with electrolytic units is a poor electrical connection to either the anode or the cathode. It is important that terminals and wires do not come in contact with solutions. Corroded terminals or cables will result in poor plating.

The person who is responsible for silver recovery should follow all manufacturer recommendations for preventive maintenance and keep accurate records of any maintenance performed.

- **Make sure you receive the operations and maintenance manuals for your silver recovery equipment. These manuals are part of the purchase price of your equipment and you are entitled to them.**
- **Obtain data from the silver recovery equipment manufacturer/supplier demonstrating the performance capability of the equipment. For example, if you are required to recover silver to 99 percent efficiency, ask the manufacturer to provide you with data showing the equipment can achieve this level.**

Appendix C

Chemical Recovery Cartridges

Chemical recovery cartridges are a relatively low cost method of achieving a fairly high level of silver recovery.

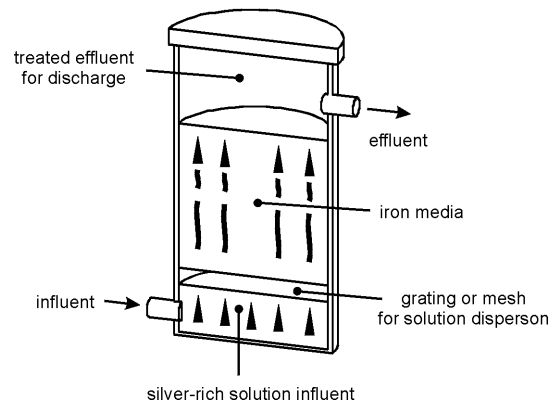
C.1 How it Works

A typical chemical recovery cartridge (CRC), also known as a metallic replacement cartridge, is shown in the diagram on the right.

Metallic replacement is a process that occurs when a solution containing dissolved ions of an active metal such as silver, contact a more active solid metal such as iron. The more active metal, iron, which is contained in a cartridge, reacts with the silver and dissolves in solution. The less active metal, silver, becomes solid and collects in the cartridge.

In essence, the dissolved silver in solution changes places with the solid iron in the cartridge. The exchange reaction is dependent upon the contact of the silver-thiosulfate in solution with the iron surface. To ensure good and controlled contact, metallic replacement is accomplished by metering the silver-rich solutions through a cartridge of iron. As silver is removed from the solution, the iron metal filler in the cartridge becomes depleted. The cartridge is then replaced with a new cartridge and the accumulated silver sludge is sent to be refined.

Chemical Recovery Cartridge



There are a variety of CRCs on the market today. They contain iron in the form of chopped steel wool, spiral wound steel wool, a heavy iron mesh similar to door screening material, or iron chips imbedded in a fiberglass support.

A properly designed and maintained single-cartridge CRC system is capable of recovering more than 95 percent of the silver from silver-rich solutions when used in accordance with manufacturer-specified flow rates. A system utilizing two cartridges in series is capable of recovering 99 percent of the silver.

C.2 Operation/Maintenance

The manufacturer/supplier of the CRC can help the photo processor choose the appropriate equipment. This is also the

best source of preventive maintenance information. Generally, chemical recovery cartridges are monitored for the following: flow rate, channeling, obstruction, pH, and, cartridge capacity.

a. Flow rate

The length of time the silver-rich solution is in contact with the iron is critical for effective silver recovery. If the solution flows through the CRC too quickly, it will not contact the steel wool long enough for the iron/silver reaction to occur. The lower the flow rate, the better the recovery.

A pump is used to meter the solution at a prescribed rate from the holding tank to the first CRC in the series. To ensure proper flow rate, calibrate the metering pump each time the CRCs are replaced. Consult the manufacturer for the optimum flow rate.

b. Channeling

As the recovery cartridge is used, the active surface area is used up and small channels will begin to develop in the iron material. This is known as *channeling*. It also occurs when a CRC is used only intermittently due to low volume. When a small volume of solution enters the CRC and sits on the surface, it slowly eats through the steel wool, forming a vertical shaft or channel as it goes. As more solution enters the CRC, it takes the path of least resistance and flows through the channel, thus contacting very little of the steel wool in the cartridge. This causes only a small amount of the iron to be used (that along the channel). When channeling occurs, only low levels of silver are recovered and high levels are discharged from the CRC.

To avoid channeling: (1) select the proper size CRC for the average volume of film and paper processed in your lab, and (2) fill the CRC with water just prior to introducing chemical solutions into it.

c. Obstruction

When the iron in solution contacts air, iron hydroxide or rust forms. If the rust is allowed to build up in the lines leading into and out of the CRCs, it can eventually restrict the flow of solution causing the solution to back up. The CRC may also leak around the fittings and cover.

Obstruction also occurs when the center core of the CRC is crushed or damaged and the solution cannot pass through it. If this happens, replace the CRC with a new one. Consult the CRC supplier for information.

Finally, rust that passes through the CRC can eventually build up in the floor drain, requiring expensive drain cleaning.

Monitor the system regularly for obstruction. Remove the lines and rinse them with hot water each time the CRCs are replaced. Do this more often if there are several hours each day when no solution is flowing through the CRCs. Be sure to run the overflow system downhill so there's no chance of back-up.

d. pH

For best results with CRCs, the pH should be between 6.8 - 8.0. If the pH is too low, the steel wool is etched too quickly reducing the life of the CRC. If the pH of the solution is too high, etching does not occur so the silver/iron exchange reaction can't take place. Also, at higher pH levels,

iron hydroxide (rust) is formed which can cause obstructions in the lines and drains. Try to maintain a consistent pH in the influent going to the CRCs. This is best accomplished by plumbing the silver-rich overflow directly from the processors to the silver recovery system. Manually emptying waste tanks tends to introduce a lot of pH variation into the system. Normally, a solution containing bleach-fix, fix and stabilizer/rinse will not require pH adjustment. Work with your equipment supplier to determine the best pH for your CRCs.

e. Cartridge capacity

Each type of CRC has a limited capacity to recover silver depending on the type and amount of iron used and conditions in the photo lab. Manufacturers generally rate the capacity of their CRCs in both gallons of solution and time. For example, depending on the silver concentration of the solution going in, a CRC might have the capacity to desilver 100 gallons of solution or last 12 weeks, whichever comes first. Ask the manufacturer to help you in selecting CRCs appropriate for your lab.

Keeping a log

Keep a silver recovery log to record all of the checks and testing you do on your silver recovery equipment. As soon as the weekly check (done with silver-estimating test papers) shows color, you know the chemical recovery cartridge has failed and it's time to change it. When you install a new CRC, mark the installation date on the cartridge.

Check with your local POTW authorities to find out how long to keep these records on file.

The person who is responsible for silver recovery should follow all manufacturer recommendations for preventive maintenance and keep accurate records of any maintenance performed.

- **Make sure you receive the operations and maintenance manuals for your silver recovery equipment. These manuals are part of the purchase price of your equipment and you are entitled to them.**
- **Obtain data from the silver recovery equipment manufacturer/supplier demonstrating the performance capability of the equipment. For example, if you are required to recover silver to 99 percent efficiency, ask the manufacturer to provide you with data showing the equipment can achieve this level.**

Appendix D

Precipitation

Precipitation was the first practical silver recovery method used in our industry more than 50 years ago. Silver can be precipitated using a wide variety of compounds (precipitants) that form insoluble complexes when added to silver-rich waste streams. Because precipitating agents such as sulfide are potentially hazardous they should only be used by staff who have been fully trained. Newer precipitants are now available that are more reliable and nonhazardous.

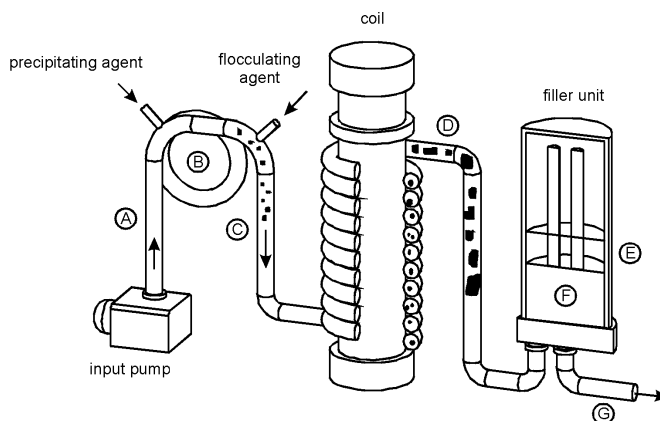
D.1 How it Works

While they work on the same principles, precipitation units for small/medium photo processors are designed differently from those for large photo processors. Both are discussed below.

Precipitation for Small/Medium Photo Processors - A typical precipitation unit for a small or medium photo processor is shown in the diagram on the right. Refer to it as we discuss the precipitation process.

The silver precipitation process is accomplished by metering silver-rich solutions (A) into a reaction vessel. A prescribed amount of precipitant is added according to the manufacturer's direction. The silver-rich solids begin to form immediately (B). A flocculating agent is added next to increase the size of the precipitate particle (C). A reactor coil

Precipitation Unit for a Medium Photo Processor

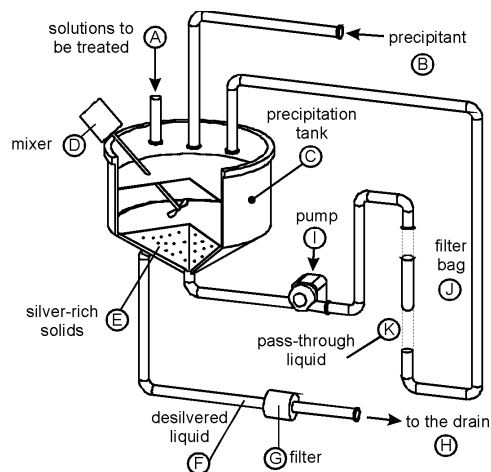


provides the mixing and residence time necessary to promote the growth of the precipitate particles. When the solution exits the reactor coil (D) it is allowed to settle so that the silver-rich solids can be filtered out. The desilvered liquid can be discharged to the drain (G), while the sludge containing silver is collected (F) and sent to a silver refiner. A properly designed and maintained system is capable of recovering at least 99.9 percent of the silver from silver-rich solutions.

Precipitation for Large Photo Processors - In a large photo processor environment, precipitation is generally used as a secondary system following electrolytic silver recovery. This results in a high grade silver yield from electrolytic recovery plus a final effluent low in silver.

A typical precipitation unit for a large photo processor is shown in the diagram below. Refer to it as we discuss the precipitation process.

Precipitation Unit for a Large Photo Processor



Following electrolytic silver recovery, the silver-rich solutions (A) are pumped into a cone bottom precipitation tank (C). A propeller mixer (D) is started and the precipitant is added (B). The batch is mixed for several minutes to make sure the precipitant is completely dissolved in the solution. Silver-rich solids begin to form almost immediately (E).

Next, the tank of solution is allowed to sit for several hours to provide sufficient time for the silver-rich solids to settle to the bottom (E). A flocculating agent (not shown on the diagram) is also added along with the precipitating agent to increase the size of the silver-rich solids. If the solids are too small they will clog the filter in the later steps of the process (J).

After settling, the desilvered liquid (F) is pumped out through a filter (G) and

discharged to the drain (H). The remaining slurry containing the silver-rich solids is pumped (I) from the bottom of the cone and through a series of filter bags (J) that capture the silver. Only one filter bag is shown in this diagram. This silver is sent to a refiner.

Any liquid that passes through the filter bags (K) is directed back to the precipitation tank (C) and combined with the next batch.

D.2 Operation/Maintenance

The manufacturer/supplier of the precipitation unit can help the photo processor choose the appropriate equipment. This is also the best source of preventive maintenance information. Generally precipitation units are monitored for the following: silver concentration and the amount of the precipitate.

a. Silver concentration

Extremely low concentrations of silver in the incoming solution will affect the efficiency of the precipitation unit. For optimum performance, keep the concentration fairly stable by combining the overflows of silver-rich solutions. For example, avoid dumping large proportions of stabilizer into the precipitation unit. Try to blend it gradually with the other overflows.

b. Amount of precipitate

When the silver concentration of the incoming solution is low or where the discharge limits are less restrictive, the amount of precipitate may need to be reduced. Consult with the manufacturer.

Appendix E

Evaporation/Distillation

Evaporation and distillation are generally used in conjunction with off-site management. These processes reduce the volume of effluent to be taken off-site for treatment and disposal. When the off-site management costs are based on the volume of solution, evaporation and distillation may help to reduce costs.

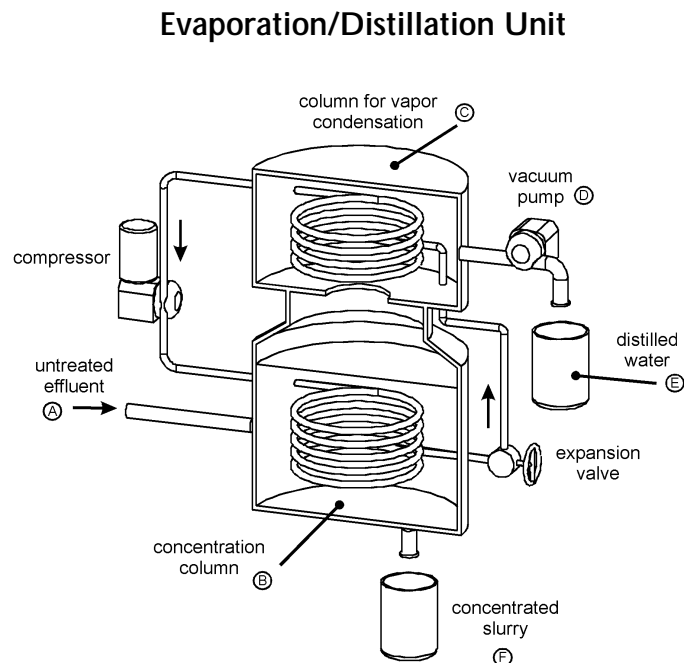
E.1 How it Works

Because evaporation releases fumes to the air, permits are often required to operate an evaporator. Most equipment used today consists of both evaporation and distillation where the water vapor is boiled-off, captured and condensed, and the fumes are contained.

A typical distillation unit is shown in the diagram on the right.

In distillation, the untreated effluent (A) is directed into the concentration column (B) where the solution is heated to its boiling point. The vapors are captured in a column for condensation (C) and cooled, resulting in a distillate of essentially water.

The distilled water is pumped out (D) and can be discharged to the drain or captured (E) and used to mix secondary chemicals. Since the distillate contains ammonia and sulfite, using it to mix developers is not generally recommended. Depending upon the unit, 80 to 100 percent of the water is



removed leaving a silver-rich slurry or solid (F) to be managed off-site.

E.2 Operation/Maintenance

Routine cleaning is the most important preventive maintenance operation. Dried chemistry and dust can easily accumulate within the unit reducing the performance of the equipment. Intake and overflow screens along with air filters must be checked and cleaned periodically. The distillation chamber should be inspected and cleaned.

Appendix F

Off-Site Management

The following information applies only to photo processors who are shipping waste off-site.

In some situations, off-site silver recovery is the best option. For example:

- Photo processors required to meet excessively restrictive silver concentration limits may be forced to ship the solutions off-site for treatment.
- For photo processors discharging to a septic tank and leach field, there is no option; they must haul. ***Photo processing chemicals must not be discharged to septic systems.*** This could cause an upset that would destroy the microorganisms responsible for breaking down the waste water.

F.1 Off-Site Requirements

Solutions containing 5 ppm or greater of silver are currently classified as hazardous waste. In order to transport these solutions off-site, the photo processor must fulfill the requirements for transporting hazardous waste. In this section, we're going to discuss the Federal requirements for off-site silver recovery. Since individual states may enact stricter regulations, make sure you check with your state hazardous waste agency for its specific requirements.

a. Generator category

If you're shipping waste photo processing solutions containing 5 ppm or more of silver, it's important that you know how to determine your hazardous waste category. The specific requirements for accumulation, storage and manifesting vary depending on the category.

The chart on the next page shows the three categories established in the federal Resource Conservation and Recovery Act (RCRA). These categories, as shown across the top of the chart, are:

- Conditionally exempt small quantity generator
- Small quantity generator
- Large quantity generator

To determine your category, track the monthly volume of waste photo processing solutions containing 5 ppm or more of silver produced in your lab to be sent off-site.

For example, if your lab processes only color negative film and prints, add the volume of fix, bleach-fix and stabilizer/rinse used in one month. If it's 100 kilograms or less (approximately 220 pounds or 25 gallons), your lab falls into the category of conditionally exempt small quantity generator.

Hazardous Waste Category*		
<i>Conditionally Exempt Small Quantity Generator (CESQG)</i>	<i>Small Quantity Generator (SQG)</i>	<i>Large Quantity Generator (LQG)</i>
Facility that generates no more than 100 kilograms of hazardous waste per month	Facility that generates greater than 100 but less than 1,000 kilograms of hazardous waste per month	Facility that generates greater than 1000 kilograms of hazardous waste per month
* Any photo processing waste containing 5 ppm or more of silver is considered hazardous under the Resource Conservation and Recovery Act (RCRA). Most states and municipalities have additional regulations for discharge and transport of silver and silver-bearing wastes. For more information contact your local state hazardous waste agency.		

b. Generator identification number

SQGs and LQGs must obtain an EPA identification number before shipping waste off-site. This 12-character number identifies both your site where the waste is produced and the type of waste. It's a key element of tracking the waste from *cradle-to-grave*. Your state hazardous waste agency can provide you with the proper paperwork.

Federal law does not require that CESQGs obtain an EPA ID number. Some states, however, may require an ID number for *all* waste generators.

c. Accumulation and storage

CESQGs must never accumulate more than 1,000 kilograms (kg) of waste at any time. (1,000 kg is approximately 300 gallons.)

SQGs must never accumulate more than 6,000 kg of hazardous waste for more than 180 days. (6,000 kg is approximately 1,600 gallons.)

LQGs must not accumulate hazardous waste on-site longer than 90 days. In all cases, wastes must be stored in tanks and containers suitable for photographic waste. In addition:

- Clearly mark each container with the words *Hazardous Waste* and with the date you began to collect waste in that container.
- Use only containers in good condition.
- Keep containers closed except when you fill or empty them.
- Inspect areas where containers are stored, at least weekly, looking for leaks and deterioration.
- Provide secondary containment where it's required.

d. Labels and marks

Containers of silver-rich chemicals must be properly labeled and marked. The label shown on the next page contains the six required elements:

HAZARDOUS WASTE	
Federal Law Prohibits Improper Disposal	
If found, contact the nearest police or public safety authority, or the U.S. Environmental Protection Agency	
Accumulation Start Date: June 6, 1996	EPA Waste #: D011
Generator Name: Best One-Hour Photo	
Address: 1500 Main Street	
City: Your Town	State: NY Zip Code: 02143
EPA ID #: XX9876543210	Manifest #: 554332
DOT Proper Shipping Name, Class, UN#, and packing group:	
RQ Hazardous waste liquid, n.o.s. (silver), Class 9,	
NA 3082, Packing group III	

1. accumulation start date,
2. EPA waste identification number,
3. site name and address where the waste was produced (generator name),
4. EPA generator identification number,
5. manifest number, and
6. Department of Transportation (DOT) shipping name for the waste.

e. Manifests

The manifest is a multi-copy document used to track the waste from the time it leaves the generator (the photo processor), to the time the receiver treats, recycles or disposes of it. Each party in the link — generator, transporter, receiver — have EPA identification numbers and each must complete its portion of the manifest.

The producer is responsible for obtaining numbered manifest forms from the state hazardous waste agency. All links in the chain keep a copy of the manifest and receive copies from the other links to

acknowledge receipt of the waste. Manifests must be kept on file by the producer for at least three years.

Manifests are not required for CESQGs. Some transporters, however, may still ask that they be used to help the transporter and receiver fulfill their requirements.

f. Spill response and training

SQGs and LQGs are required to develop emergency plans and train employees on emergency response so that if a spill or accident occurs, the photo processor is ready. Generally, the plans must include procedures and identify the necessary spill control/response equipment.

F.2 Precautions

One important element of the *cradle-to-grave* waste management system is liability. Once you've generated the waste, you retain some responsibility even after turning it over (consigning it) to a licensed transporter and a licensed receiver. This means you must choose your waste management partners carefully.

Talk with your colleagues, trade associations and state hazardous waste agency to get the names of licensed companies that could handle silver-bearing photo processing wastes. Choose a firm with a good reputation. Verify their EPA identification numbers and any required permits. Visit their site to look at their equipment and the general condition of their operation. Choose carefully and with confidence.

Appendix G

Ion Exchange

Ion exchange technology can be used to recover silver from dilute processing solutions and wash waters. Keep silver levels as low as possible in wash water by installing and maintaining squeegees and monitoring replenishment rates.

Ion exchange is recommended for use only to remove silver from wash water. It is *not generally recommended* for use with bleach-fix and fix solutions.

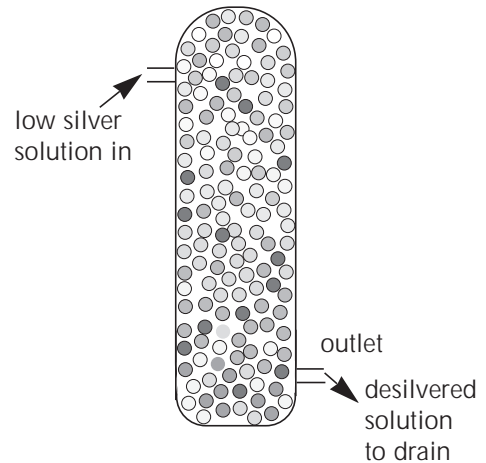
G.1 How it Works

Ion exchange is a reversible exchange of ions between a solid (resin) and a liquid (water containing ionized salts). When ion exchange is used with low-silver solutions, the silver thiosulfate in solution is adsorbed to the resin in the column. Periodically, the resin is rinsed with a dilute sulfuric acid solution to decompose the silver thiosulfate to silver sulfide, which remains in the ion exchange column. The resin is reused for many cycles and is then incinerated to recover the silver accumulated in it.

Ion exchange should not be used for recovering silver directly from silver-rich fix and bleach-fix solutions.

These concentrated thiosulfate solutions will strip silver from the resin, and can actually result in *more* silver being discharged from the resin column than is

Ion Exchange Column



present in the feed solution. Ion exchange, therefore, lends itself only to the recovery of silver from wash waters and dilute processing solutions. Typically, more than 90 percent of the silver from wash waters can be removed in a single-column system. Two-columns used in series can provide 99 percent silver removal efficiency.

G.2 Operation/Maintenance

Converting equipment to incorporate a low-flow wash will concentrate the silver and greatly reduce the silver content of the final wash water. Ion exchange technology is most effective when used in conjunction with an in-line silver recovery unit for the preceding fixer solution.

Factors affecting the efficiency of ion exchange include: thiosulfate concentration, flow rate, and biological growth control.

a. Thiosulfate concentration

The capacity of the resin to retain silver is very dependent on the concentration of thiosulfate in the influent. The higher the thiosulfate, the lower the capacity. That's why ion exchange is not recommended for recovering silver from fix and bleach-fix. These solutions are high in thiosulfate.

If you operate under such severe discharge restrictions that you must use ion exchange to recover silver from silver-rich solutions, two steps are required:

1. desilver the silver-rich solutions through an electrolytic unit, and
2. meter the desilvered solutions into the collected wash water overflow at a rate not exceeding their replenishment rate.

These procedures will reduce the silver concentration prior to ion exchange and ensure the thiosulfate levels are controlled.

b. Flow rate

The low-silver solutions must be metered through the ion exchange columns at a prescribed rate in order to allow for the exchange between the silver and the resin to occur. Generally, this should never exceed 1 bed volume of resin/minute.

c. Biological growth control

Algae, bacteria and fungi grow quite readily in ion exchange columns and feed on the dilute photo chemicals. This growth causes two problems: 1) it forms a film on the resin beads, thereby blocking the silver exchange reaction, and 2) it obstructs the flow of solution through the column.

To eliminate the problem of biological growth, the ion exchange column(s) must be flushed routinely with biocide.

Appendix H

Testing for Silver

You must routinely monitor your silver recovery system to make sure it's operating correctly. There are two different testing methods required: approximations utilizing test papers are performed frequently, and exact analytical testing is performed every three months, six months or annually, depending on the size of the photo lab.

H.1 Silver-Estimating Test Papers

Silver-estimating test papers provide only an *approximation* of how much silver is in a solution. The test strips are coated with yellow cadmium sulfide that forms brownish-black silver sulfide when it comes into contact with silver ions. The higher the concentration of silver in solution, the greater amount of brownish-black silver sulfide will be formed. The color formed on the test strip after it has been in solution, therefore, reflects the amount of silver contained in that solution.

Generally, the procedure for using the test strips is as follows:

1. Dip the test strip in the sample solution for two (2) seconds so that the strip is properly wetted.
2. Remove the test strip from solution, shake off any excess liquid, and place the strip on a white card.
3. After about 15 seconds, compare the color on the moist test strip with the color key provided with the test strips. Find the color that most closely matches. That is approximately the concentration of silver in solution.
4. When evaluating a solution that has color, such as bleach-fix, rinse the test strip briefly under running water toward the end of the 15-second waiting period. Take the color of the solution into consideration when you're making the comparison with the color key.

A typical color key scale is shown below. As you can see from the scale of numbers ranging from 0 to 10 g/L* (0 - 10,000 mg/L), the silver readings are only approximations of the actual silver in solution. Note that the lowest detection point is 1 g/L or 1,000 mg/L.

<i>Silver Content of Photo Processing Solution</i>								
<i>Grams per Liter</i>	0	1	1.75	2.5	3.5	5	7	10
<i>Comparison Color Patches</i>								

* Silver-estimating papers are generally scaled in grams per liter (g/L) rather than parts per million (ppm). Remember: mg/L and ppm are the same measurement.

The test strips are helpful in *estimating* the amount of silver in the solution exiting the silver recovery system. Once the solution has gone through primary silver recovery, the concentration of silver should be well below the 500 mg/L mark. Since the lowest range on the silver-estimating test papers is 1,000 mg/L, you should see no or very little color change on the paper. These papers are only useful, therefore, for finding major problems with the silver recovery system.

For example, if you are using chemical recovery cartridges, you are required to test the cartridge effluent using test strips to determine the presence of silver. The effluent should be below 500 mg/L and therefore, not change the color of the test strip. The only thing you've learned from testing the effluent with a test strip is that there are no major problems with the chemical recovery cartridges. A more exacting measurement must be taken periodically to verify the system is actually recovering the percentage of silver required.

H.2 Analytical Testing

An exact analytical measurement is required to verify whether the silver recovery system is achieving a specific percentage recovery. An outside analytical laboratory must be used to analyze the solution samples.

To have a sample of solution analyzed, you should obtain a bottle from the analytical laboratory, fill the bottle with a sample of the solution to be analyzed and bring the bottle to the laboratory. When they have finished the procedure, the analytical laboratory will provide the results of the analysis.

Your best source of information concerning sampling procedures and technique is the analytical lab that's doing your work. Work with them closely to get your best results. Here are some general considerations for sampling:

a. *Sample containers*

- Obtain containers from the analytical laboratory.
- Make sure the laboratory knows that you are specifically testing for silver so they provide you with the correct size and type of container.
- Use plastic containers because silver precipitates more easily on the wall of a glass container.

b. *Sample preservation*

- Tell the analytical laboratory NOT to use a nitric acid preservative with the sample. Nitric acid precipitates the silver out of solution, thereby providing an artificially-low silver reading.
- Return the sample to the analytical laboratory as quickly as possible to avoid any change in the make-up of the sample.

c. *Sampling methodology*

- Rinse the sample bottle with the sample once or twice before filling it for analysis.
- Make sure that none of the equipment you are using to collect the sample has been contaminated with another solution or material.

d. Analytical test methods

There are two methods the analytical laboratory can use to detect silver in the sample:

1. Inductively coupled plasma spectroscopy (ICP)
2. Atomic absorption (AA)

Either test will provide the same result.

Appendix I

Forms

Small Photo Processor Worksheet

Answer as many of the questions as you can. Use your best approximations.

1. How many rolls of film do you process each day?
 [Hint! Count all films disregarding the size. Use roll counts from the busiest time of year. If you are doing reprints and enlargements or second sets of prints, add an additional 20 percent.] _____ rolls

2. How much silver -rich effluent does your lab produce each day?
 [Hint! To obtain this number, use one of these methods: _____ gallons
 a) track the daily number of batches put through the silver recovery unit;
 b) track the daily volume of bleach-fix, fix, and washless stabilizer mixed;
 c) add the number of waste tanks emptied each day into the silver recovery unit; OR
 d) use replenishment rates for bleach-fix, fix and washless stabilizer multiplied the by average rolls/day.]

3. How much total process effluent does your lab produce each day? _____ gallons
 [Hint! To obtain this number, use one of these methods:
 a) track the daily volume of chemicals mixed and wash water used;
 b) add the daily number of waste tanks emptied each day; OR
 c) use replenishment rates multiplied by average rolls/day.]

You are a small photo processor *if*
 your answer to question #1. is less than 20 rolls/day. AND
 your answer to question #2. is less than 2 gallons. AND
 your answer to question #3. is less than 1,000 gallons.

.... Small photo processors should go directly to page 8

If your numbers are greater than these values for any one question, you are **not** a small photo processor. Use the worksheet on page 7 to determine if you are a medium, large or SIU photo processor.

Medium and Large Photo Processor Worksheet

The volume of silver-rich and low-silver solutions discharged to the POTW can be estimated by measuring the amount of replenisher and water used during a specific time period. Use this chart along with the instructions on page 6 to calculate waste. An example worksheet is shown on page 7. Use a separate sheet for low-silver solutions.

	Chemical Names			
a) Start date (day/month)				
b) End date (day/month)				
c) Working days (a - b - the number of days closed)				
d) Replenisher tank volume on start date (in gallons)				
e) 1st mix volume (in gallons)				
f) 2nd mix volume				
g) 3rd mix volume				
h) 4th mix volume				
i) 5th mix volume				
j) 6th mix volume				
k) 7th mix volume				
l) 8th mix volume				
m) 9th mix volume				
n) 10th mix volume				
o) Total volume mixed [e + f + g ... + n] (in gallons)				
p) Replenisher tank volume on end date (in gallons)				
q) Chemical volume used (d + o) - p				
r) Average chemical volume discharged (q ÷ c)				
s) Water meter reading on start date (in gallons)				
t) Water meter reading on end date				
u) Water usage (t - s - allowance for domestic flow)				
v) Average water usage (u ÷ c)				
w) Total all the numbers recorded across in line r for silver-rich solutions only				_____ gallons
x) Total all the numbers recorded across in line q for low-silver solutions plus line v (average water usage)				_____ gallons

AAA Photo Lab

SPILL CONTINGENCY PLAN***Spill Response Personnel**

 Name pager/phone

 Name pager/phone

 Name pager/phone
**Environmental
Emergency
Phone**
(999) 999-9999 24 hours a day
7 days a week
EQUIPMENT REQUIRED

- **Gloves**
- **Apron**
- **Goggles**
- **Bucket**
- **Mop**
- **Sponge**
- **Absorbent
Materials**

SPILL RESPONSE PROCEDURES

1. Put on gloves, goggles and an apron.
2. Contain the spill with a mop or absorbent materials available.
3. Check the appropriate material safety data sheet (MSDS) for special handling, ventilation, personal protection, or other pertinent data.
4. Clean up the spill, as directed, using generous amounts of water.
5. Use the mop and sponge to clean the area thoroughly.
6. Package and label all contaminated absorbent materials for off-site disposal.
7. Notify the supervisor or manager that a spill has occurred.

 * This plan will not meet the requirements in all states including California.

Worksheet for Screening Options

Date _____

Option: _____

1. What is the potential for reducing waste and providing other environmental benefits?

2. What is it going to cost in time and materials?

3. How much money will it save in time and materials?

4. How difficult is it to implement?

Pollution Prevention Plan Worksheet

Date _____

Option or activity: _____

Implementation date: _____

Responsibility: _____

Record: _____

Pollution Prevention Plan Worksheet

Date _____

Option or activity: _____

Implementation date: _____

Responsibility: _____

Record: _____

Worksheet for Evaluating P2

Date _____

Option: _____

1. Waste reduction results _____

2. Costs _____

3. Savings _____

Worksheet for Evaluating P2

Date _____

Option: _____

1. Waste reduction results _____

2. Costs _____

3. Savings _____

