



**Printers'
National
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Fact Sheet

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Reduce Image Processing Costs: Minimize Waste And Recover Silver

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Introduction and Background

This fact sheet describes how printers can take actions that will help them to recover silver while generating less waste during image processing. These wastes typically include film, developer, fixer, and wash water, all of which require proper management and disposal. Film, fixer and to some extent wash water, can contain silver, which is a regulated metal. These can also contain hydroquinone, though hydroquinone is not regulated under RCRA as a hazardous waste. This fact sheet describes how to manage these wastes in an environmentally sound manner, and emphasizes the importance of recovering silver from both a business and environmental perspective.

Silver-Containing Wastes

Typical silver-containing wastes include used fixer, wash water, and film. If liquid wastes contain five (5) ppm or more of silver, or if solid wastes contain this concentration of leachable silver, these wastes are classified as hazardous based on U.S. EPA industrial wastewater effluents. Local waste water treatment authorities (POTWs) typically establish an effluent limit for silver discharges in the range of 0.5 to 2 ppm, but these local authorities may set the discharge limit much lower. If a printer is authorized to discharge fixer solution and washwater to a wastewater treatment plant, it is important to know the discharge limit for silver and what silver recovery options exist for meeting the discharge limit. Never discharge silver-bearing, or any other industrial wastewater to a septic system. Besides being illegal, this could cause serious contamination and create an expensive cleanup responsibility for your company.

Silver Recovery Options

Recovering silver from image processing wastes helps to reduce the costs associated with image processing, as well as helping to achieve compliance with wastewater discharge limits. Silver recovery also conserves silver resources, a precious metal. The primary silver recovery options used by printers include chemical recovery cartridges, electrolytic recovery, and ion-exchange. Chemical precipitation, although less common, is another option to consider.

The amount of silver that is recovered is a function of pH and residence time. To maximize the amount of silver recovered, these two factors should be controlled to the maximum to extend the silver removal process.

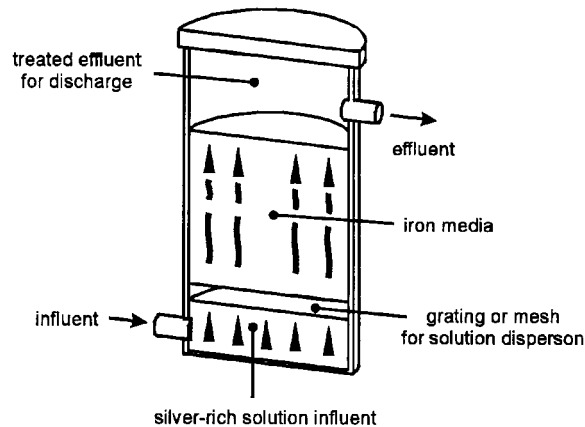
To confirm that a selected silver recovery option is achieving the required discharge limits, it is important to routinely test the effluent being discharged from the print shop. Test papers or test-kits should be used weekly. Recognize that these are limited in their sensitivity and cannot detect low concentrations of silver. At appropriate times, which depend on the technology employed, a sample should be pulled from the shop's effluent and analyzed by an environmental analytical laboratory to confirm that discharge limits are being met. Good business practice would suggest that annual or semiannual testing would provide a good data set of effluent characterization. Maintain a log of all effluent test dates and results.

It is important to properly maintain the silver recovery units. Simple management practices such as dating the chemical recovery canisters and ion exchange units can be employed. Employees need to be trained how to correctly operate and maintain whatever system is installed. Records of equipment maintenance should be maintained.

Chemical Recovery Cartridges (CRC)

This method of silver recovery is also known as metallic replacement and is considered very economical. Cartridges/canisters are filled with steel wool or other iron-containing media. The metallic iron exchanges places with dissolved silver when spent fixer is passed through the unit. A properly designed, maintained and operated single cartridge is capable of recovering more than 95% of the silver. A second cartridge in series produces a system capable of removing over 99% of the silver. Recognize that these types of units have a certain lifetime and need to be changed on a regular basis. The frequency of changing is dictated by silver concentration and flow.

Chemical Recovery Cartridge



Three problems can occur with CRCs:

Channeling: Occurs when the flow rates are too low. The chemical reaction takes place unevenly, removing the media and creating a less-restricted path. Once this occurs, then the silver laden solution will pass through the unit and very little silver will be recovered.

Oxidation (rust): Occurs when air enters the system. This obstructs the flow, as does a crushed media or plugged pipe, and limits the reaction and effectiveness of the system.

Pass-through: Occurs when the flow rate through the system exceeds the reaction rate.

To most effectively operate a CRC system, do the following:

Install a direct connection from the fixer overflow or electrolytic recovery unit to a holding tank so that an adjustable valve can control the flow of solution to the CRC. An air lock should be added in the line prior to the first CRC by creating a loop with the tubing connecting the holding tank to the CRC. This operates similar to a J-trap used in plumbing.

Ensure that the flow of fixer through the canisters is metered slowly enough to avoid pass-through and quickly enough to prevent oxidation. The equipment manufacturer or the operating manual will specify the optimum flow rate specific to the size of the CRC.

Maintain the inflow pH of the bleach fixer solution as close to 6.5 as possible in order to extend the life of the iron mesh cartridge in ion exchange units. If using an electrolytic unit with color film, then it is best to maintain the inflow pH of the bleach fixer between 7.0 and 8.0. If using an ion exchange unit with an iron mesh cartridge, the pH of the bleach-fixer solution may be 6.5 or above.

Depending on facility size, use one or more canisters in series. If you generate less than 0.5 gallons of fixer per day, only one canister is needed. A second canister with such low flows could oxidize and/or channel by the time the first canister is exhausted. Consult with your vendor to determine the proper number of units and configuration.

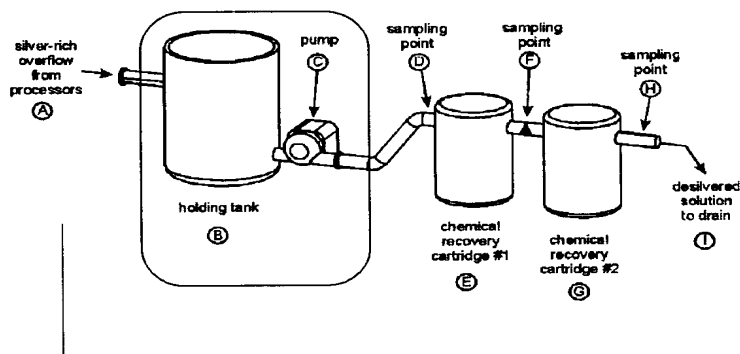
Install clear tubing and sample ports between and after canisters. Visually monitor the effluent at least weekly and use silver-estimating test papers or a chemical test kit. Brown solution indicates that either oxidation is occurring or that the first canister is spent and should be replaced. An indication that oxidation may be taking place is to look for air bubbles in the lines between the holding tank. To determine whether the first canister is spent, compare the CRC actual use time versus its expected lifetime.

When changing out canisters, remove the upstream canister and put the downstream canister in the upstream position. Fill a new canister with water before installing it in the downstream position to prevent the steel wool from oxidation. Calibrate the metering pump. Flush silver bearing solutions (e.g., fix or wash water) from canisters with clean water three times before sending them off-site. Treat the rinse water by discharging it through the CRC unit.

Ship the used and properly back flushed CRC as nonhazardous waste to a metal refiner who will extract silver for reuse.

In order to determine when canisters should be replaced and assure that the system is operating properly, log the date and condition of the canister each time they are replaced in the CRC.

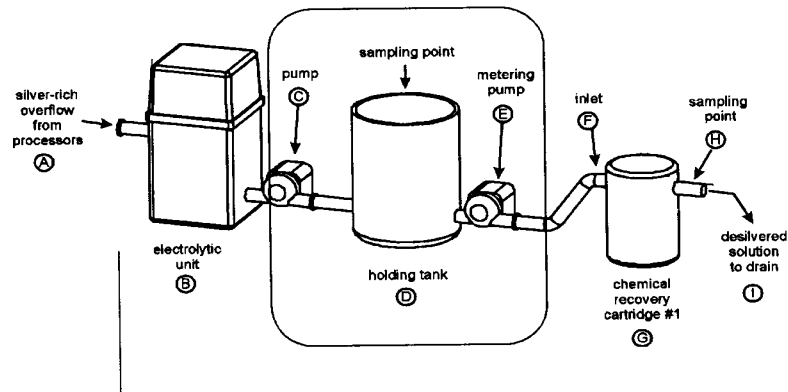
Keep a log of any measurements taken as evidence that discharge limits are being met.



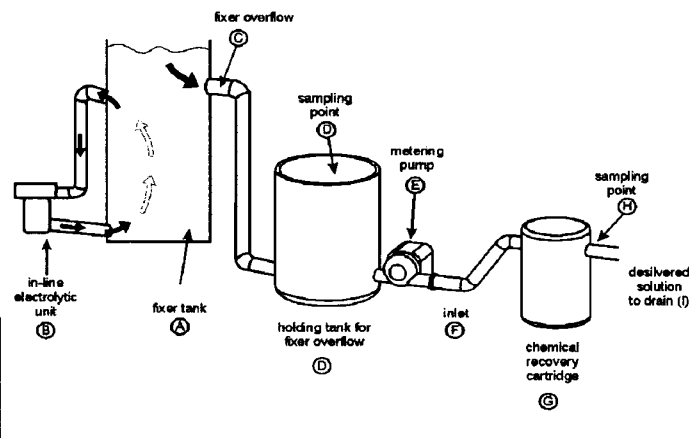
Electrolytic Recovery Units

In electrolytic recovery units, a direct current is applied across two electrodes, which causes positively charged silver to become "plated" onto the negatively charged electrode (i.e., cathode) in the form of high-grade silver. Electrolytic recovery is most effective on silver-rich solutions, such as fixer solution. However, electrolytic recovery can only reduce the silver concentration to about 200 ppm. There are two approaches where these types of units can be utilized:

Terminal Units: It is recommended that at least one CRC be used following an electrolytic recovery unit, which is placed at the end of the fixer overflow.



In-Line Units: Electrolytic recovery can also be used in conjunction with a fixer recycler system to filter and recirculate fixer, thus minimizing the amount of waste fixer generated. In-line electrolytic recovery should be complemented with one or more CRCs connected to the fixer overflow prior to the spent fixer being discharged.



The nature of the chemical reaction involved requires that the electrolysis process be monitored for pH, silver and sulfite concentrations, residence time, and amperage. Terminal units processing color bleach fixer should keep incoming fixer pH above 7.5 to prevent iron from oxidizing and dissolving plated silver. Terminal and in-line units should keep fixer pH below 8.5 in order to avoid significant ammonia generation. Black and white processing rarely requires pH adjustment. A silver recovery efficiency of 90% can be maintained if the silver concentration of the incoming fixer is sufficiently high, typically 2,000 - 4,000 ppm. Using in-line electrolysis, fixer replenishment rates can be reduced by over 50% in some applications. The replenishment rate should be calibrated routinely to assure optimal silver concentration. Sulfite is consumed during the electrolytic silver recovery process. In-line systems may require adjustments to the pH levels (increase) and sulfite levels in the fixer to operate properly. Sulfite test strips and pH meters or test strips are available.

To avoid this problem all together, “electrolytic” fixer solution is available. These solutions are formulated for closed loop recirculation systems. Electrolytic fixer solution not only maintains proper sulfite concentration, but pH does not have to be adjusted up either.

If the amperage supplied to the electrolysis unit is too high or the residence time too long, the plated silver contains excess sulfide that softens and contaminates the silver, causing cleanup problems and emissions of smelly hydrogen sulfide gas. Many units have automated time and amperage control. Good management practice would suggest that an effluent sample should be analyzed every six months when using terminal electrolytic recovery or every three months for in-line units.

Ion-Exchange

This method relies on a column of positively charged resins in various shapes (e.g. beads) attracting and holding negatively charged silver thiosulfates. Ion exchange is best used to recover silver from dilute solutions, less than 1%, such as washwater. In these applications, a single ion exchange column typically removes 90% of the incoming silver, and two columns in series can achieve 99% removal efficiency. Properly managed ion exchange systems can remove silver to 0.1 to 0.5 ppm, but are costly to purchase and operate. High silver thiosulfate concentrations will actually remove silver from the resin, so ion exchange cannot be used for silver-rich fixer solution.

In order to precipitate the silver as insoluble silver sulfide, which remains in the column, the column is taken off-line and the beads are occasionally rinsed with a dilute sulfuric acid. The column is then placed back in service. After several rinsings, the column is removed and sent to a silver refiner or reclaimer where the resin is smelted to recover the silver.

If a low silver discharge limit requires more removal than can be accomplished by electrolytic recovery followed by CRCs, an ion exchange unit can be employed. In this case, the de-silvered outflow still needs to be diluted with the wash water overflow prior to entrance into the ion exchange column at a silver concentration near 20 ppm.

For proper operation of an ion exchange column, biological growth and solution flow rate must be managed. Algae, bacteria and fungi commonly grow among the resin beads, feeding on the processing chemicals. These must be routinely treated with a biocide or they can coat the beads or impede solution travel. The solution must flow past the resin beads slowly enough for the ion exchange to occur. Typically the maximum flow rate is stated as less solution than one bed volume of resin per minute.

Wash water can be reused after it is passed through an ion exchange system and filtered. Wash water recycling systems can reduce fresh water consumption by about 50%. Control of biological growth becomes more important in this configuration.

Chemical Precipitation

Silver-rich solutions, such as fixer can be discharged to a holding tank or similar container to which a prescribed amount of chemical precipitant is added. Alkali metal salts of sulfide (sodium sulfide, potassium sulfide, etc.) have been commonly used as precipitating agents. The silver will settle out. After the clear liquid is removed, the silver sludge is filtered and sent to a silver refiner.

Chemical precipitation and filtration is not as widely accepted as the other methods previously described in this factsheet. Precipitation requires special training and should only be undertaken by trained personnel in adequately equipped facilities. Filtering can be difficult and plugged filter media is a common problem.

Silver precipitators for in-house recovery have been developed. Information about specific experiences with such units may be available through the PrinTech listserv, which can be accessed by following the instructions on the PNEAC website (www.pneac.org).

Recommendations

The Silver Council provides guidance for handling silver from photographic processing, categorizing its recommendations by the size of the photoprocessor in its Code of Management Practice. The CMP is an alternative compliance approach for silver discharges that relies upon a performance-based standard and not a numerical or technology-based one. Many municipalities throughout the United States are now permitting facilities that discharge silver-laden waste water to follow these guides in lieu of other practices and activities.

Table 1. Silver Council Code of Management Practice for Commercial Imaging

Facility Category	Fixer Overflow gal/day	Wastewater Volume gal/day	Recommended Silver Recovery %*
Small	< 2	< 1,000	90
Medium	> 2 but < 20	< 10,000	95
Large	> 20	< 25,000	99

*Discharge still must meet ppm limits of silver content

Facility Category	Silver Recovery Technology 1	Silver Recovery Technology 2	Silver Recovery Technology 3
Small	1 or 2 CRCs with manufacturer specified flow control*	Electrolytic recovery followed by 1 CRC with flow controls.	Off-site management
Medium	Terminal or in-line electrolytic recovery followed by 1 CRC with flow controls.	Two or more CRCs with flow controls.	Off-site management
Large	Terminal electrolytic recovery followed by 2 CRCs with flow controls.	In-line electrolytic recovery followed by 2 CRCs with flow controls.	Off-site management

* Facilities generating less than 0.5 gallons of fixer per day should not use a second CRC since it would probably oxidize before recovering silver.

Table 2: Image Processing Wastes - Management Alternatives and Pollution Prevention

Photo Processing Waste	Waste Management Alternatives	Pollution Prevention Opportunities
<p>FILM scraps have silver remaining in the un-removed emulsion. You may be required to perform a TCLP (toxicity) test prior to disposal.</p>	<p>Recycle film. If film cannot be recycled it often can be disposed as non-hazardous waste, because commercial and professional films/papers usually pass a TCLP test. Contact the vendor to obtain the results of TCLP tests, otherwise, test before discarding</p>	<p>Consider using an imagesetter to reduce the amount of film required to produce a plate.</p> <p>Consider using a "direct-to-plate" or computer-to-plate system that does not contain silver halide.</p>
<p>FIXER stops the chemical reaction initiated by the developer. A small print shop generates approximately 1 or 2 gallons of waste fixer each day. Undeveloped silver is removed from the film and goes into suspension in the fixer. Used fixer can contain as much as 3000-4000 ppm of silver.</p>	<p>Recover silver via electrolytic recovery unit, chemical recovery cartridges (CRCs), or chemical precipitation. Silver needs to be removed before the fixer is discharged to a wastewater treatment plant.</p>	<p>To reduce the amount of fixer waste generated:</p> <p>Use an acid stop bath prior to the fixing bath to help keep the pH of the fixer low by preventing developer carryover.</p> <p>Keep fixer covered when not being used to prevent oxidation and minimize emissions.</p>
<p>WASH BATHS remove developer and fixer residues from the film. Silver can be carried from the fixer solution into a wash bath; concentrations can reach as high as 3-5 ppm. A small print shop generates approximately 100 to 400 gallons of image processing wash water each day.</p>	<p>Use ion-exchange to recover silver from wash waters.</p> <p>Wash water should not be discharged to a wastewater treatment plant unless it meets the discharge limits for silver</p>	<p>To reduce the amount of wash water generated:</p> <p>Replace parallel wash systems with counter current wash systems (but be aware that an increase in the concentration of silver in the wash water will result, making effective recovery even more important).</p> <p>In counter current wash systems, rinse water is used in the initial film wash step and fresh water is introduced only at the final rinse stage. If an ion-exchange system is used, recirculate the effluent from the unit.</p>

WASTE MANAGEMENT ALTERNATIVES & POLLUTION PREVENTION OPPORTUNITIES

Silver-containing wastes with more than 5 ppm silver, principally untreated fix, are classified as hazardous waste and need to be managed as such. Reducing and preventing the generation of these wastes can decrease the cost of disposal, and can offset the cost of treatment through the sale of recovered silver. Table 2 includes descriptions of the silver-containing wastes generated by image processing and descriptions of possible waste management alternatives and pollution prevention opportunities associated with each.

On-Site And Off-Site Recovery

One alternative to recovering silver with an on-site process is to ship your silver containing solutions off-site to a silver recovery company. Generally, if you ship wastes off-site you need to contract with a hauler that has a hazardous waste transportation license and follows all DOT hazardous materials transport regulations. For a directory of regulatory agencies that can assist in providing this and other related information go to the PNEAC web site (www.pneac.org) and click on Compliance Info and State-specific Compliance Information. These agencies should be able to assist in locating companies that provide both on-site and off-site recovery services in your state. Your telephone directory yellow pages are also a good source of information about silver recyclers in your immediate area.

Other Resources For Silver Recovery Or Other Relevant Environmental Or Technical Issues

The following are also available through links at the PNEAC web site:

The Silver Council: www.silvercouncil.org

This website provides full-text downloads of these documents:

Code of Management Practice for Silver Dischargers

Code of Management Practice Guide for Commercial Imaging

Graphic Arts Technical Foundation (GATF): www.gain.net

The Photo Marketing Association (PMA): www.pmai.org

Specific questions about technology, equipment, vendors can be posted on the PrinTech listserv. To subscribe, simply follow the instructions on the PNEAC web site at www.pneac.org.

For more information or to contact someone from PNEAC please visit www.pneac.org and post your request using "Ask PNEAC".

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