Photographic Processing Waste Management

Overview

Photoprocessing wastes may contain silver, which is considered a toxic heavy metal by the United States Environmental Protection Agency (EPA). The silver is primarily present as a soluble silver thiosulfate complex. Silver sulfide is present in smaller amounts. Depending on the stage from which the waste originates and the type of film processed, the silver concentration can range between 5 mg/L and 12,000 mg/L. Therefore, **photoprocessing solutions and spent rinse waters are classified as hazardous wastes**. In addition to photoprocessing solutions and spent rinse waters, films and negatives may contain high silver concentrations and require management as hazardous wastes.

It is illegal to dispose of hazardous wastes via drains, normal trash, or any other means which would result in a release to the environment or discharge to the city sewer system. Photoprocessing solutions and spent rinse waters at Weill Cornell Medicine (WCM) must either be collected and sent to Environmental Health and Safety (EHS) for disposal or processed to remove the silver before drain disposal. All films and negatives must be collected and sent to EHS.

Applicability

The Photographic Silver Waste Management procedure applies to WCM faculty, staff, students, and visitors using photoprocessing chemicals, photographic film and other silver-containing film (e.g. x-rays).

Responsibilities

Environmental Health and Safety (EHS) provides proper guidance for the management of hazardous silver-bearing photographic wastes that complies with local, state, and federal laws and regulations. EHS also assists Generators and Departments in the selection of proper silver recovery equipment and ensures the proper disposal of Generator's containerized hazardous wastes.

Departments are responsible for identifying those areas where film processing is conducted and ensuring that all hazardous silver-bearing photographic waste is managed appropriately.

Generator(s) are responsible for managing all wastes as detailed in WCM's Waste Disposal Procedures. If silver recovery equipment is utilized, then the Generator(s) must ensure equipment is properly maintained per any equipment design specifications, or other responsibilities as defined within a service agreement established between the Generator and vendor.

Procedure

Departments identify those areas and persons within their facilities which generate hazardous silver-bearing photographic wastes. Identified generators must ensure that these hazardous wastes are managed via one of the two procedures described below:

DISPOSAL VIA WCM'S WASTE DISPOSAL PROCEDURES

If the Generator chooses not to pursue the use of silver recovery equipment for the management of photoprocessing solutions and spent rinse waters, the Generator must ensure that this waste is containerized, handled, stored, and otherwise managed as specified in WCM's Waste Disposal Procedures. Once the waste containers are full, the generator must submit a chemical waste via Salute to Environmental Health and Safety (EHS). EHS will collect the waste for off-site treatment and disposal.

All films and x-rays must be containerized, handled, stored, and otherwise managed as mandated by WCM's Waste Disposal Procedures.

SILVER RECOVERY PROCESSING

Depending on the quantity of waste generated, silver recovery processing may prove financially beneficial to a generator. Generators choosing to recover silver must procure the silver recovery equipment and associated services, though EHS should be contacted to assist in the selection of the silver recovery equipment that matches the needs for the location being served. Use the following discussion as well as Tables 1 and 2 to help choose the best silver recovery method for your circumstances. Greymart Environmental Services (http://www.greymartrecovery.com/) is a New York City-based company which is capable of providing a variety of silver recovery systems, installation, and services to match specific needs. However, other companies which provide similar equipment and services are available.

Electrolysis, or electrolytic recovery, and metallic replacement are the most common methods used for silver recovery from photo processing wastewaters. During electrolysis, an electric current reduces the silver-thiosulfate complex and plates almost pure silver metal onto an electrode. If the unit is placed in-line and closed-loop fixers are used, chemical use can be reduced by up to 50%. Efficiencies above 90% are easily obtainable when recovering silver from black and white processing fixers. However, while efficiencies approaching 90% are possible when recovering bleach-fix and fixer solutions from color processing, higher current densities, longer times, and pH adjustments are necessary due to iron complexes present. In addition, over-extending the electrolysis time or raising the current density can result in lower efficiencies due to sulfide precipitation on the cathode. To reduce concentrations below 5 mg/L, electrolysis must be followed by another recovery method, such as metallic replacement or ion exchange.

Metallic replacement makes use of the fact that iron is more active than silver. Silver in solution will exchange with solid iron through an oxidation-reduction reaction. 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 more than 95% of the silver from silver-rich solutions (such as fixer and bleach-fix) while a series of two cartridges can recover more than 99%. A series arrangement will also prevent breakthrough, which occurs as small channels develop in the iron. However, for flows less than 0.5 gallons of fixer per day, one canister is adequate. Although low silver concentrations are removed with metallic replacement, the iron catalyst will be consumed more quickly due to the reduced protection from corrosion.

While precipitation, evaporation/distillation, ion exchange, and reverse osmosis are potential recovery methods that would meet many low discharge requirements, capital and operating costs preclude them from use by most small generators. Precipitation can be very efficient, generating a sludge with 99.9% or more of the silver from silver-rich solutions, but it is not a common method utilized to recover silver due to the chemicals and skilled personnel required. Evaporation/distillation can concentrate silver-rich solutions to between 8 and 30% of the original volume. However, the residue is unusable for mixing fresh developer solution, although it may be usable for making secondary replenishers (such as bleach, fixer, and stabilizers). 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. However, ion exchange only works on dilute solutions, such as wash waters (although wash baths can have concentrations as high as 200 mg/L), since high concentrations quickly saturate the resin. Reverse osmosis uses pressure and a membrane to filter solutions, removing up to 95% of salts from fixers. It results in a concentrated silver stream that could be sent to a refiner. This technology also works best on dilute solutions, achieving up to 90% efficiency. Electrowinning (used in the plating industry) is also not used for silver recovery from photographic solutions because it can decompose processing chemicals, resulting in fouled equipment and hazardous odors.

Table 1. Silver Recovery Methods

Category	RECOVERY METHOD			
	Electrolysis	Ion Exchange	Metallic Replacement	Precipitation
Typical waste source	Fixer	Rinse water	Fixer	Fixer
Influent (mg/L)	2,000 – 12,000	<30	Low - high	>250
Effluent (mg/L)	20 - 500	0.1 - 1.0	<0.5 - 15	0.3 - 1.5
Efficiency (%)	£90 - 98	>90 - 99.99	>95 - >99	^{3}99.9
Capital cost ($) [A]	2,000 - 30,000	10,000 - 100,000	50 - 3,000	3,300 - 75,000

[A]Based on data from 1998.

Table 2. Comparison of Silver Recovery Methods

Recovery Method	Advantages	Disadvantages
Electrolysis (In-line)	▪ Obtain >90% pure silver ▪ Re-circulate fixer ▪ Reduce chemical use£50% - 70% and mixing labor	▪ Minimum of 5 gal/wk ▪ Used for fixers and high-silver solutions only ▪ Can damage fixer if not properly maintained
Electrolysis (Terminal)	▪ Low refining costs ▪ Moderate capital costs ▪ Able to determine silver recovered	▪ Cannot achieve 5 mg/L alone ▪ Used for high-silver solutions only ▪ Sulfide precipitation possible
Evaporation Distillation	▪ Up to 90% waste reduction	▪ Moderate to high capital costs ▪ Messy sludges
Ion Exchange	▪ 98 – 99.99% removal efficiency from dilute solutions	▪ High capital costs ▪ Fouling problems ▪ May require use of hazardous chemicals ▪ Works best on dilute solutions ▪ Monitoring required for replacement or regeneration
Metallic Replacement	▪ Available for all silver-rich solutions ▪ Low capital costs ▪ Low maintenance ▪ 99% removal possible with 2 units	▪ Channeling at flows £0.5 gpd ▪ Low concentration reduces lifespan ▪ Cannot re-circulate fixer ▪ Cannot determine amount of silver until refined ▪ High smelting and refining costs ▪ Monitoring required for replacement
Precipitation	▪ >99% consistent removal possible ▪ Moderate capital costs ▪ Little maintenance	▪ Higher smelting cost than electrolytic ▪ Ongoing chemical usage ▪ Moderate to high operation costs
Reverse Osmosis	▪ Up to 90% efficiency on dilute streams ▪ No treatment chemicals required	▪ High capital costs ▪ Frequent maintenance required ▪ Works best on dilute solutions ▪ Large installations noisy

Definitions

Generator(s) – A person or group at WCM which produces hazardous chemical waste, including photoprocessing equipment operators their supervisors and those disposing of photoprocessing film.

References

- 6 NYCRR Parts 370 through 374 and 376 – hazardous waste disposal
- 6 NYCRR 371.1(c)(7) – prior notification for scrap metal exemption
- NYC Department of Environmental Protection Sewer Discharge Regulations
- Susan M. Morgan, Erik A. Talley, Mohammed Z. Rahman and Keith E. Morgan; "Need For & Efficiency of Silver Recovery, or Silver Sampling Faux Pas & Fundamental Conclusions" presented at the 16th College and University Hazardous Waste Conference on July 20, 1998 in New Orleans, LA.
- U.S. EPA. "RCRA in Focus: Photo Processing." Copies are available by either contacting EHS or electronically at: http://www.epa.gov/osw/inforesources/pubs/infocus/photofin.pdf.
- Salute Safety, https://ehs.salutesafety.com/users/sign_in