

Silver Recovery from Photographic and Imaging Wastes

April 1998 - TI#17316 Introduction About Silver Environmental Effects of Silver Types of Silver-Containing Photographic Wastes Regulation of Imaging Waste Streams and Discharges Recovering Silver from Fixer Solutions and Rinse Waters DRMS Precious Metals Recovery Program

Silver Recovery from Photographic and Imaging Wastes

The processing of photographic and radiographic (x-ray) image films and papers is a major source of silver-containing waste discharges in the Air Force. The Air Force has been recovering silver from these waste streams for many years. Recovering silver from image processing wastes helps offset the costs associated with image processing and aids in achieving compliance with regulatory limits on silver concentrations in discharges. Silver recovery also conserves a non-renewable precious metal resource.

This Fact Sheet addresses the environmental effects of silver, principal types of silver-containing photographic wastes, applicable environmental regulations, and commonly available silver recovery technologies, including support services provided by the Defense Reutilization and Marketing Service (DRMS). Potential generators of photographic and imaging wastes are hospitals, dental clinics, photographic laboratories, printing plants, microfilm and microfiche producing facilities, and hobby craft shops.

About Silver

Silver is a naturally occurring element and a precious metal. Forty percent of all silver used in the United States is used in photographic and imaging materials (approximately 70 million troy ounces/year). Silver is unique in its ability to react to light and produce images in applications such as photography and radiography (x-rays). No other metallic element possesses these properties. Silver is released from photographic films, papers, and plates during development and printing processes and can be successfully recovered from waste streams (i.e., used processing chemicals) for reuse.

Environmental Effects of Silver

Silver is released from image processing operations as silver thiosulfate, which degrades in the presence of oxygen to primarily silver sulfide, and to a much lesser extent, silver halide complexes. These compounds are non-toxic to plants and organisms, very stable, insoluble, and immobile in the environment. Silver is not significantly taken up by plants and does not bioaccumulate.

In January 1991, the Environmental Protection Agency (EPA) deleted the interim primary maximum contaminant level (MCL) for silver, established under the Safe Drinking Water Act (SDWA), based on the finding that silver posed no adverse human health effects. However, silver continues to be designated a "priority pollutant" under the Clean Water Act. In addition, under the Resource Conservation and Recovery Act (RCRA), silver is listed as an indicator that a solid waste is hazardous (toxicity characteristic) when present in leachate at a concentration of 5.0 milligrams per liter or greater.

Unlike silver sulfides and halides, the hydrated or "free" silver ion is potentially toxic to aquatic organisms. However, this form of silver is rarely found in the environment because it combines so readily to form non-toxic complexes with common organic materials found in natural waters. The "free" form of silver is not a normal component of photographic and imaging waste streams.

Although silver in its most common forms has no adverse human health effects and no apparent adverse environmental effects, because it is a precious metal capable of being reclaimed and reused, it is economically (and environmentally) sound to do so.

Types of Silver-Containing Photographic Wastes

When light-sensitive silver halide compounds in photographic films or print papers are exposed to light, they undergo a chemical change and form a "latent" image (not visible to the naked eye). The latent image is amplified in a chemical bath during the "development" process and is stabilized during the "fixing" process. The exposed silver halides are chemically reduced to elemental silver (blackened) during the development process, thereby making the image visible on the film or paper. The unexposed, and therefore undeveloped, silver halides are converted during the fixing process to water-soluble compounds. The unexposed silver compounds are then dissolved from the film/paper and are found in greatest concentration in used fixer solutions, and in lesser quantities in rinse waters. (Typically, fresh photo processing solutions contain no silver, and insignificant amounts of silver are found in used developer solutions.) Nearly all the silver in imaging wastes is in the form of silver thiosulfate complexes, which are non-toxic and highly stable in the environment.

Discarded imaging films and papers are also silver-containing wastes. Since they are dry solid wastes, they are easily managed and are generally sold directly to a contractor for silver recovery. This fact sheet does not address technologies for recovering silver directly from imaging films or papers.

Fixer Solutions

In a typical film processing operation, the fixer bath is continuously augmented with fresh fixer solution to maintain its quality and strength. Consequently, there is a continuous overflow discharge of used fixer solution from the fixer bath. The concentration of silver compounds suspended in the used fixer bath discharge can vary greatly depending on the type and amount of film being processed, but frequently exceeds 5,000 parts per million (ppm). Because of this high silver concentration, silver recovery from fixer solutions is very cost effective.

Rinse Waters

When developed images (films or papers) are moved from the fixer bath to the rinse, they still carry a small amount of silver, which is removed by the rinse water. Rinse waters contain low concentrations of silver ranging from less than 1 ppm to as high as 200 ppm. Although there is little economic benefit to recovering silver from rinse water, environmental regulations may prohibit discharge of untreated rinse water to treatment works or the environment if the silver concentration exceeds specified concentrations.

Regulation of Imaging Waste Streams and Discharges

Silver-containing effluents discharged from image development processes or from silver recovery equipment are subject to regulation depending on how and where they are discharged, and how much pre-treatment (silver recovery) it has undergone.

If the treated or untreated waste stream is discharged directly to a storm sewer or surface water body as a process wastewater, it is regulated as a point source under the Clean Water Act (CWA) and is subject to permitting under the National Pollutant Discharge Elimination System (NPDES). A NPDES permit allows the discharge of treated or untreated wastewater to surface water bodies provided the effluent meets permit-specific quality standards. Silver containing waste streams may require pre-treatment in order to meet NPDES target concentrations for silver (typically 5 ppm or less) and other regulated contaminants that may be present.

If the treated or untreated waste stream is discharged to a Publicly or Federally Owned Treatment Works (POTW/FOTW), it will have to meet pretreatment requirements as determined by the accepting Treatment Works. Discharges from Treatment Works to surface water bodies are subject to NPDES permit requirements. An Air Force installation, whether it operates its own Treatment Works or discharges to a nearby POTW, must ensure its

silver containing discharges are acceptable to the management of the Treatment Works. The Treatment Works operator will determine the concentration of silver that can be accepted from a facility or installation based on the ability of the POTW/FOTW to treat the waste.

An untreated waste stream or post treatment silver sludge that is collected and periodically transported to a silver recovery company, or a waste treatment, storage, and disposal (TSD) facility, may be regarded as a regulated hazardous waste under RCRA if it contains (leaches) silver in excess of 5 ppm or exhibits any other properties which may render it hazardous. Transporters of hazardous photo processing wastes must comply with applicable hazardous waste and Department of Transportation (DOT) regulations when the wastes are shipped off site.

Recovering Silver from Fixer Solutions and Rinse Waters

The most commonly used technology for recovering silver from fixer solutions and rinse waters is chemical recovery, also known as metallic replacement or metal displacement. This technology uses equipment commonly referred to as Chemical Recovery Cartridges (CRC), Metal Replacement Cartridges (MRC), or Passive Silver Cells (PSC). This technology is simple in principle and operation. In most chemical recovery systems, a cartridge or canister filled with steel wool or iron particles is connected to the fixer or rinse bath overflow and the excess solution flows through the unit under gravity. The silver thiosulfate complexes from the solution react with the iron in the steel wool. The iron goes into solution and the silver precipitates with the iron and settles to the bottom of the unit as a sludge. Treated solutions should not be recirculated through these cartridges, but rather should pass through at a slow rate for optimum silver recovery. When used properly, these units can reduce silver concentrations to below 1 ppm in the effluent at a low cost.

To confirm that a selected silver recovery option is achieving the required discharge limits, it is important to periodically test the effluent being discharged. Test papers or test kits are available for this purpose, in addition to confirmatory laboratory analysis.

Silver recovery units require no electricity or special plumbing connections. The units take up little space and are readily available at minimal cost. The units must be replaced regularly as the iron is consumed. Two units are commonly used in series, with the second unit being placed in the lead position when a new unit is installed in the second position. The size of the unit must be matched with the volume and silver concentration of the fixer and/or rinse solution to optimize the amount of time the solution is in contact with the steel wool. These units are designed to be packaged and shipped directly to a silver reclaimer when spent.

Other frequently used technologies for silver recovery include chemical precipitation and electrolytic methods, also available from the DRMS.

DRMS Precious Metals Recovery Program

The easiest and most cost effective way for Air Force installations to recover silver and manage their imaging wastes in accordance with applicable Federal regulations, is to obtain silver recovery units through the Defense Reutilization and Marketing Service (DRMS).

The Defense Reutilization and Marketing Manual (DoD 4160.21-M, August 1997) implements the requirements of the Federal Property Management Regulation, in addition to other appropriate laws and regulations, as they apply to the disposition of excess, surplus, and foreign excess property within the DoD. Chapter 11, "Precious Metals Recovery Program," provides general guidance for acquisition of silver recovery equipment/supplies, as well as turn-in of all excess fine precious metals to DRMO offices. Specific turn-in guidance for imaging films and papers, as well as silver recovery equipment filters, can be obtained by contacting your local DRMO representative. Additional information can be obtained from PRO-ACT or by contacting Ms. Laura Green, Precious Metals Recovery Program, HQ DRMS, DSN 932-7071.

The DRMS's Precious Metals Recovery Program significantly reduces the need for DoD to purchase metals such as gold and silver. Today, DoD commands, installations, and activities turn in most precious metal bearing scrap to DRMS field offices. Once gathered and accounted for, the material is then sent to a refiner. The finished product, 99.9% pure refined metal, is sent to the Defense Industrial Supply Center (DISC), the inventory manager for the Precious Metals Recovery Program. DISC then maintains accountability for the refined metals with storage provided by private firms. A DoD contractor or activity can then requisition precious metals for use on a government contract, thus saving the government money on that contract. On behalf of the Department of Defense (DoD), the DRMS has saved the government \$223 million over the last 20 years though its Precious Metals Recovery Program. More information about the DRMS is available at http://www.drms.dla.mil/.

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