

The Silver Fix: How Much Is Your Waste Worth?

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Did you know that recovered silver can be sold for as much as 80% of its current market value? So how much is your waste fixer worth? Typical waste fixer may have between 2000 and 4000 ppm silver content before recovery. Based on an average concentration of 3000 ppm per gallon and today's silver prices of \$4.25 per troy ounce, waste fixer may be worth \$1.50 per gallon. But the true savings is in disposal cost—if the fixer is disposed as a hazardous waste, it may cost \$3.00 per gallon. Companies that recover silver from their photo developing processes stand to save \$4.50 per gallon! For companies generating three gallons of waste fixer per day, savings from disposal costs alone are almost \$2340 and return from recycled silver would be \$1170—generating a positive cash flow of \$3510 per year! Even with the cost of the equipment, this represents a significant savings and eliminates the long-term liabilities associated with hazardous waste disposal.

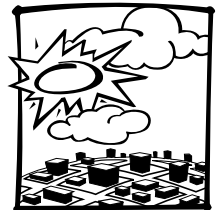
As much as 80% of the total silver processed for black and white positives and almost 100% of the silver processed in color work ends up in the fixer solution. Therefore, used fixer should never be discharged to the sanitary sewer without proper silver recovery, and should never be put into storm drains, septic systems or dry wells, or poured onto the ground. Silver is also present in rinse water following the fix bath because of carryover. If the local POTW has very stringent limits for silver discharges, facilities may need a primary silver recovery unit, which removes the bulk of silver, in combination with a "tailing" unit to further treat the relatively low silver concentration in the outlet of the primary treatment. Wastes and process waters should only be discharged with approval, preferably in writing, from their local POTW.

Many silver recovery technologies are available to recapture silver in aqueous solutions: precipitation, ion exchange, metallic replacement, reductive exchange,

electrolytic recovery, reverse osmosis, and electro dialysis. Of these technologies, metallic replacement and electrolytic units are most commonly used in recovery of silver from photographic solutions. The amount of waste fixer and the level of silver removal needed will influence the choice of technology. Wichita and Kansas City, Kansas (as of 2001), use the Code of Management Practices (CMP) approach in lieu of traditional concentration-based discharged limits for silver discharges. The CMP requires different percentages of silver recovery for four categories of dischargers, based on gallons of silver-rich solutions generated and gallons of process wastewater discharged each day. For more information on CMPs, see the Web site listed at the end of this Fact Sheet.

Metallic replacement uses a canister filled with iron steel wool, which reacts with silver thiosulfate in the wastewaters, whereby the iron replaces the silver in solution and the silver settles out as a sludge of silver salt compounds. The canister is then sent to a facility that will further process the sludge to recover the silver. Metallic replacement cartridges (MRCs), sometimes called chemical recovery cartridges (CRCs), cannot be reused, and the effluent contains high iron concentrations, which must be controlled to reduce plugging of the MRC and buildup in the drain lines. Canisters usually cost less than \$100, depending on amount of recovery media (iron steel wool) in the canister, and are available for gravity-flow and metered-flow applications. MRC systems are well-suited for small generators of waste fixer.

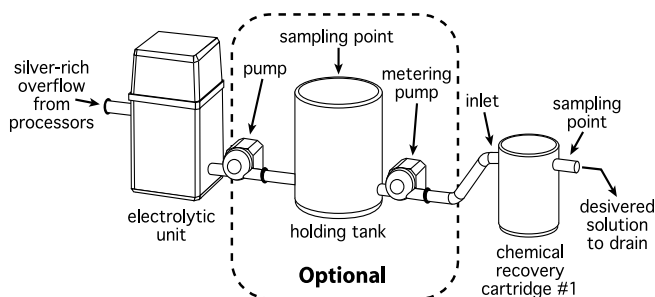
Electrolytic silver recovery applies controlled current to the solution in a metal plating-type system to remove the silver by plating it out of the solution. Silver is deposited on the cathode in nearly pure form; however, the treated fixer effluent may still contain up to 500 ppm silver. For this



reason, MRCs are usually used in series after an electrolytic system to further reduce the silver concentration in the effluent. Systems using an electrolytic unit followed by two metallic replacement canisters are capable of reducing silver content to 5 ppm in the final effluent. Small electrolytic units with a four-gallon tank capable of recovering .375 troy ounces of silver per hour can be purchased for \$800.

Hard piping from the photo processor, to the recovery unit, to the POTW is preferred because the recovery unit is then considered "part of the wastewater treatment process," so the fixer would not count as a hazardous waste. However, if the waste fixer is removed from the photo processor and is stored before it is recovered or disposed, either on-site or off-site, the waste fixer must be included in the facility's monthly hazardous waste generation rate.

The following equipment configuration for an electrolytic unit and two MRCs arranged in series are recommended to improve sampling and monitoring of the system to maintain maximum silver removal and compliance:



- A series of canisters is recommended for maximum recovery of silver. When canisters are used in a series, the first canister removes the bulk of the silver, and the second polishes the effluent of the first and also serves as a "safety" if the first unit becomes overloaded. When the first canister is exhausted, the second becomes the first, and a fresh unit replaces the second. Changeout is recommended when the silver in the effluent of the first cartridge reaches 25% of the incoming concentration.

- Use silver-estimating test strips to evaluate silver content and pH paper to monitor pH of the solution passing through the canisters. Metallic replacement units are most efficient between pH 5 and 5.5.
- Weekly testing is recommended to assure proper unit operation.

Silver recovery can also be done on the fixer bath solution by using an in-line configuration with an electrolytic unit. This type of arrangement is the most efficient method of silver recovery and reduces the greatest waste, because it also reduces the use of fixer. Where the use of in-line silver recovery is possible, chemical usage can be reduced by 50%, further increasing the savings. A slip stream of fixer is continuously recirculated through the electrolytic unit, desilvered, and sent back into the fixer tank for reuse. Because the silver concentration is kept at a low, fixed amount, the concentration of silver carried over into the wash is very low. Besides reduced fixer use, the silver flake recovered is a very high grade silver with more value; however, a specially formulated fixer may be needed if it is to be recycled.

Case Study

A well-known, high-volume printer installed fixer and developer recycling equipment. During a trial period of three months, a reduction of over 60% on fixer consumption and 55% on developer consumption was realized for a savings of \$14,000 in raw materials. In addition, the equipment recovered over 45 kgs of silver from the waste chemicals for a return of \$7,000 for silver.

Resources

www.kodak.com/US/en/corp/environment/kes/silver/discharges.jhtml#code (Code of Management Practices (CMP) guidance for equipment selection, proper operation & maintenance, and monitoring of silver recovery and management systems)

www.p2pays.org/ref/01/00048.htm (explanations, diagrams, and operation of MRC and electrolytic systems)