Environment
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The Technology of Silver Recovery for Photographic Processing Facilities

Kodak's health, safety, and environmental publications are available to help you manage your photographic processing operations in a safe, environmentally sound and cost-effective manner. This publication is part of a series of publications on silver management designed to help you optimize silver recovery. It will help you understand available silver-recovery technologies and which technology is right for your facility.

A number of techniques are available to remove silver from silver-rich photographic processing solutions. Of these, three are used in virtually all practical methods of silver recovery. They are:

- Electrolysis
- Metallic replacement
- Precipitation

Additionally, ion-exchange technology can be used to treat washwaters to remove silver. This technology is typically used when you must meet stringent discharge requirements, and capital and operating costs are a secondary concern.

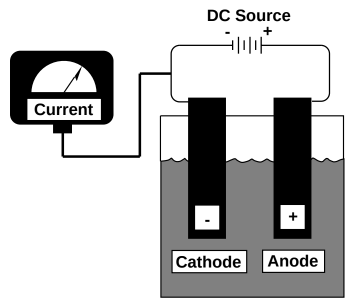
Other technologies, such as reverse osmosis, distillation, and evaporation, can produce a silver sludge; however, they only alter the silver concentration and do not actually remove silver from solution. Methods that are successfully used in other industries to recover silver, such as electrowinning, may not be applicable to photographic processing solutions, as they tend to cause significant solution decomposition.

ELECTROLYSIS

In the process of electrolysis, or electrolytic silver recovery, a direct current is passed through a silver-rich solution between a positive electrode (the anode) and a negative electrode (the cathode).

During this electrolytic process, an electron is transferred from the cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode. In a simultaneous reaction at the anode, an electron is taken from some species in solution. In most silver-rich solutions, this electron usually comes from sulfite.

A Typical Electrolytic Silver Recovery Cell



An overview of the reactions is:

Cathode:

$Ag(S_2O_3)_2^{-3} + e^- \rightarrow$
$Ag^0 + 2(S_2O_3)^{-2}$

or

Silver Thiosulfate Complex + Electron → Metallic Silver + Thiosulfate

Anode:

$SO_3^{-2} + H_2O \rightarrow$
$SO_4^{-2} + 2H^+ + 2e^-$

or

Sulfite + Water → Sulfate + Hydrogen Ions + Electrons

Electrolysis produces a nearly pure metallic silver, contaminated only slightly by some surface reactions that also take place. The plated silver should be greater than 90 percent pure.

Kodak Environmental Services

TERMINAL ELECTROLYSIS

In solutions high in iron, such as bleach-fixes, the silver plating proceeds more efficiently in a slightly alkaline state; in other words, at a higher pH. You may need to add sodium hydroxide, sodium carbonate, or sodium bicarbonate. Do this in a well-ventilated area and do not exceed a pH of 8, as ammonia may be released.

The electrolytic recovery process is efficient and cost effective, utilizing reusable equipment and little or no chemical additions. The efficiency of the system is dependent, among other things, on the availability of silver-rich solution at the cathode surface. In current commercial recovery equipment, this is accomplished in one of two ways—

- The cathode is moved within the solution. The most common application is the rotary cathode cell. The negative current is applied to a rotating drum in the solution and the silver plates onto the drum. Because of the high mass-transfer efficiency of electrolytic cells of this design, they can be used successfully to treat iron-rich bleach-fixes that are traditionally difficult to desilver.
- The liquid is rapidly pumped over the stationary cathode. This design often tends to be somewhat less efficient than rotating cathode cells; however, these units usually require less maintenance.

Electrolytic silver recovery has its disadvantages. Attempts to accelerate the recovery process, or to desilver to silver concentrations below 200 mg / L—by extending the residence time in the cell or increasing the current density (amperage / cathode surface area) on the cathode—will produce an inferior, black, crumbly silver-sulfide-contaminated plate, which reduces the cell efficiency dramatically.

Bleach-fix solutions, in particular, should be adjusted to the alkaline pH range of 7.8 to 8.0 to prevent the iron complex from oxidizing and resolubilizing the plated silver. (You should not leave bleach-fix in a cell when it is turned off, since the solution may resolubilize or dissolve the silver off the cathode.)

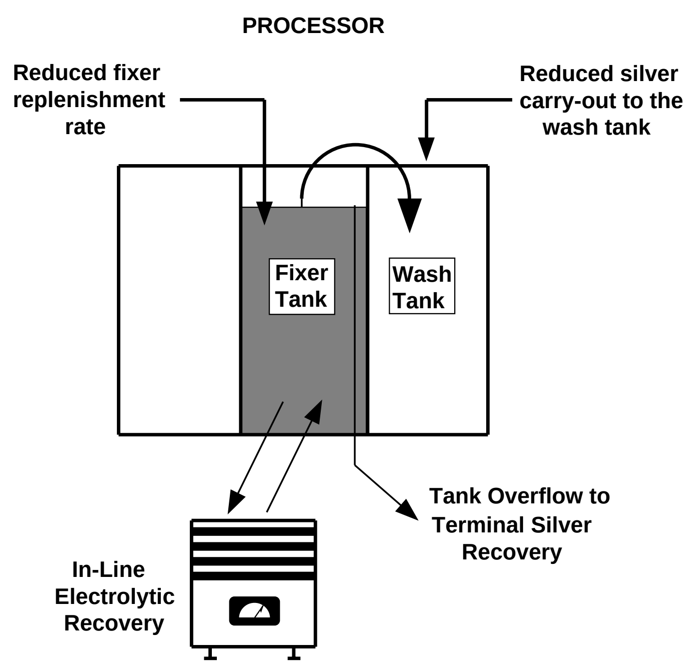
You can use electrolysis only as a primary treatment. Post-electrolysis silver concentrations are generally in the several-hundred-milligram-per-litre (ppm) range. If you must achieve a low regulatory limit, use some other type of secondary silver recovery such as metallic replacement or precipitation using TMT (tri-mercapto-s-triazine).

IN-LINE ELECTROLYSIS

In-line electrolytic fixer recirculation is used in some photographic processing facilities. With this technology, fixer is recirculated between the processing tank and a specially designed electrolytic silver-recovery unit. Some of these units have electronics that automatically control the silver concentration in the recirculating solution, usually in the range of 250 to 1,000 mg / L. Since the silver concentration in the fixer is significantly decreased, silver in the following wash tank is also reduced due to less silver "carry-out" with the film or paper to the wash during processing.

If needed, you can add more sulfite to the fixer or you can use a special high-sulfite fixer formulation that compensates for sulfite depletion during the electrolysis and recirculation. In certain processes, up to a 50% reduction in fixer replenishment rate is possible, since properly adjusted equipment does not significantly degrade most fixer components.

In-Line Electrolytic Fixer Recirculation



You must optimize recirculating systems by monitoring the silver concentration in the flow returning to the processor tank. You can easily do this by using the KODAK Colorimetric Silver Test Kit or KODAK Silver Estimating Test Paper.

When using recirculating electrolytic equipment, you will need to perform additional silver recovery on the fixer-tank overflow to recover silver to a level sufficient to meet local regulatory limits.

METALLIC REPLACEMENT

The basis for metallic replacement is the reduction by metallic iron (usually present as "steel wool") of the silver-thiosulfate complex to elemental silver. The commercial equipment you can use for the recovery are often referred to as Metallic Recovery Cartridges[1] (MRCs) or Chemical Recovery Cartridges (CRCs).

The most common source of iron is fine steel wool, chosen for its surface area. The steel wool is wound on a core or chopped up and packed into a cartridge. Some cartridge manufacturers utilize other forms, such as iron particles glued to fiber glass or iron-impregnated resin beads, or wound iron screening material. For best results, the silver-rich solutions are slowly metered into the cartridge and through the iron medium. The silver is left behind in the cartridge while iron is solubilized and carried out by the solution.

Like the electrolytic process, metallic replacement is a reduction-oxidation process. An overview of the reaction is:

$$2Ag(S_2O_3)_2^{-3} + Fe^0 \rightarrow 2Ag^0 + Fe^{+2} + 4S_2O_3^{-2}$$

or

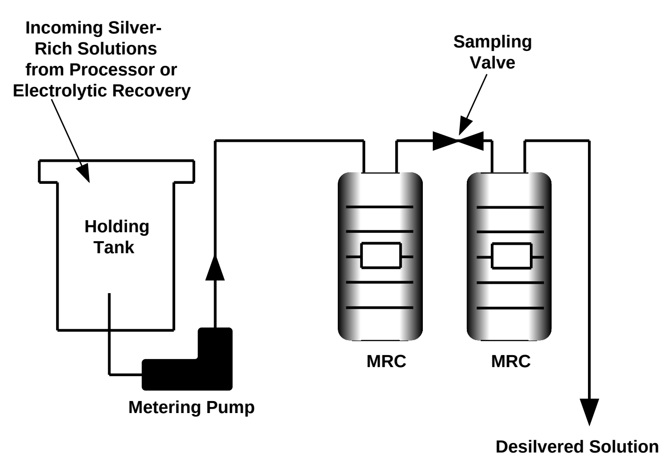
Silver Thiosulfate Complex + Metallic Iron → Metallic Silver + Ionic Iron + Thiosulfate

The final silver concentration is affected by flow rate, iron surface area, contact time, pH, original silver concentration, thiosulfate concentration, and the volume passing through the cartridge. If the MRC is operating properly, the silver concentration may be reduced to less than 5 mg/L.

As the cartridge is used, particularly with steel wool, channels or bypasses may start to form. These grow with time, and eventually the steel wool may begin to collapse internally and silver breakthrough can occur well before the iron is consumed. Iron consumption in a MRC is related to the volume of solution passing through the cartridge, and the solution's silver content and pH.

To prevent undesirable silver losses and discharges from an exhausted cartridge, a system usually consists of two cartridges in series. You should test the output from the first cartridge on a regular basis for silver breakthrough using the KODAK Colorimetric Silver Test Kit or KODAK Silver Estimating Test Paper. When the first MRC is exhausted, remove it from the sequence, move the second cartridge into the lead position, and place a fresh cartridge in the second position.

Two Metallic Replacement Cartridges with Holding Tank & Metering Pump



1. Cartridges used in the metallic replacement process for recovering silver have been described as chemical recovery cartridges (CRCs), metallic recovery cartridges (MRCs), and silver recovery cartridges (SRCs).
The photographic industry has avoided the term SRC to prevent theft of the cartridges during shipment. The term CRC is closely associated with the original Kodak product which was protected by a U.S. Patent. Therefore, we will use MRC as a generic term to refer to metallic replacement.

You can use metallic replacement as either a primary or secondary (tailing) treatment for solutions treated primarily by electrolysis. You cannot reuse solutions passed through metallic replacement cartridges for further photographic processing, since the dissolved iron and other reaction by-products will contaminate solutions in the processor tank.

Like electrolysis, metallic replacement has its drawbacks. It may not consistently reduce silver concentrations to very low compliance levels. Without good flow-rate control and proper system maintenance, random variations in effluent silver concentrations may occur. Silver sludge from cartridges is relatively expensive to refine, and frequently the recovered silver barely pays for the materials and equipment used to collect it. How you decide to use MRCs depends on your desired silver-recovery efficiency and the discharge codes you must meet. Some codes limit iron discharge which may restrict your use of MRCs.

PRECIPITATION

Precipitation can remove silver from silver-rich solutions, reducing it to very low levels. Properly applied, levels can be reduced to the low ppm (part-per-million) range. Until recently, precipitation has not been as widely used as a silver-recovery technique. Common precipitating agents classically have been alkali metal salts of sulfide (sodium sulfide, potassium sulfide, etc) which will form silver sulfide in solution; the silver sulfide is removed by filtration.

The lack of acceptance of the silver sulfide precipitation-filtration process can be attributed primarily to two factors:

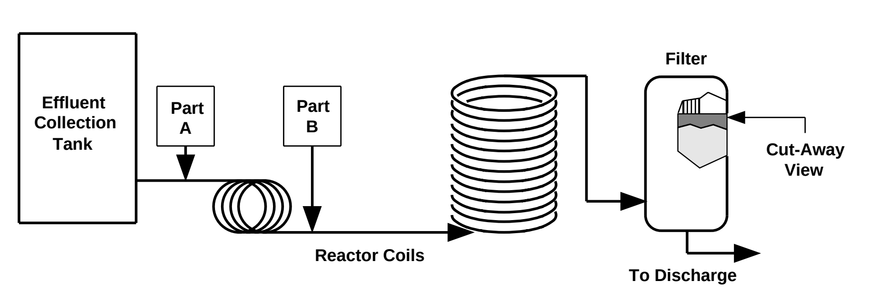
- You must measure the solution silver concentration accurately prior to sulfide addition to prevent overdosing and toxic hydrogen sulfide gas from being discharged. Until recently, no easy, readily available, analytical technique existed to measure the silver concentration before treatment.
- The silver sulfide precipitate is difficult to filter, plugging filter media.

Sulfide desilvering is most effective in centralized facilities when used by trained personnel.

Other precipitating procedures generally involve converting the silver in solution to the metallic state by adding strong reducing compounds such as borohydrides. These techniques are best used by solution service companies or centralized treatment facilities staffed with technical professionals. There are serious safety considerations when handling chemicals like borohydrides.

Eastman Kodak Company has developed a technology for on-site silver recovery by precipitation. This silver precipitation technique utilizes a chemical called TMT (tri-mercapto-s-triazine). TMT produces an insoluble silver compound that is more easily filtered than silver sulfide. For many processes, silver levels may be reliably and consistently reduced to an average of less than 1.5 ppm. Advantages of TMT include consistent low silver discharges and reduced cost. Commercial units are available for several applications. These include units designed for large photographic processing facilities and minilabs. The semi-automatic TMT silver precipator was designed to desilver up to 75 gallons per day of silver-rich photographic processing solutions from small facilities such as minilabs.

Semi-Automatic TMT Silver Precipitator



ION EXCHANGE

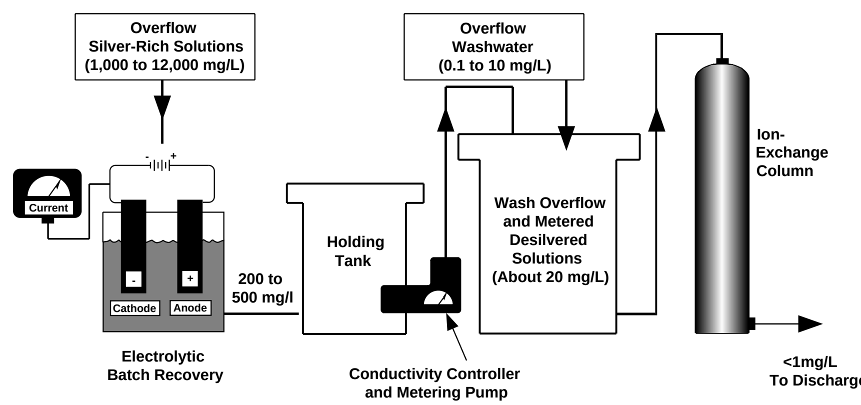
Ion exchange refers to the substitution of an ion in solution for one that is bound on a large polymer molecule. The most familiar use of ion exchange is as a water softening technique. A water softening system typically consists of a resin column and a tank containing a salt solution used for resin regeneration. The polymer, or resin, supplied as small beads and packed in columns, is chosen for its affinity for certain dissolved chemicals to be removed from solution.

The resin is treated, or "activated," by filling all its exchange sites with an exchange ion such as chloride or sodium during the regeneration cycle. As the solution to be treated is passed through the packed resin column, the resin releases its exchange ion for an ion of higher preference. In the water softener, that ion might be a water-hardening ion such as calcium. In photographic processing washwaters, it can be the silver thiosulfate complex.

Ion exchange works best on dilute solutions like washwater. Typically, you would use it when you must treat washwaters to meet very low silver regulatory limits. A well-controlled ion-exchange system can remove silver to about 0.1 to 0.5 ppm. Unfortunately, smaller photographic processing facilities may not be able to operate an effective ion-exchange system because of the required space, cost, and technical expertise.

To treat more concentrated solutions, you can combine washwater and electrolytically desilvered solutions and treat them by ion exchange. The concentrated solutions, after primary silver recovery, are metered into the washwater tank to maintain a conductivity in the wash of about 2000 to 2500 uS / cm (microsiemens per centimetres). If the thiosulfate level is allowed to get too high, it will compete for exchange sites on the resin, resulting in low capacity and silver passing through the column.

A Typical Washwater Treatment System Using Ion Exchange



There are two ion-exchange scenarios which differ only in the regeneration step, where the silver is removed from the active sites on the resin.

- **Elution Regeneration—**When the ion-exchange column is exhausted (i.e., unable to absorb additional silver), a concentrated solution of thiosulfate (hypo) is passed through the column and collected separately. This hypo solution elutes the silver off the resin beads and carries it from the column. The thiosulfate solution is then desilvered electrolytically. The excess thiosulfate is rinsed from the column and it is ready to remove more silver. You can save the thiosulfate regeneration solution and reuse it again.
- **In-Situ Regeneration—**When the ion-exchange column is exhausted, a diluted solution of a sulfuric acid is sent through the resin bed (do not use nitric acid). The acid breaks down the silver-thiosulfate complex being held by the resin. One of the by-products of this decomposition is silver sulfide, an extremely insoluble form of silver, that is precipitated within the resin bead itself. The resin exchange sites are freed for further silver recovery, while the silver sulfide remains in the beads. Each regeneration cycle uses a fresh batch of dilute sulfuric acid (2% by volume) as regenerant. Used regenerant should be neutralized before disposal. Eventually, the capacity of the resin starts to drop off, necessitating more frequent regeneration. When the resin needs replacing, remove the used resin and send it for refining. Load a fresh bed of resin in the column and activate it by regeneration.

Ion-exchange systems produce relatively clean water that may, in some cases, be recycled through the system. With some additional features to help reduce biogrowth, and possibly destroy hypo (thiosulfate), ion exchange is the basis of most wash-water reuse technologies.

You must take exceptional care to maintain the long-term keeping properties of film or paper when they are processed with recirculated washwater.

REVERSE OSMOSIS

Reverse osmosis is a concentration process by which ions are held on one side of a semi-permeable membrane while the water is allowed to pass through the membrane. You may then treat the concentrate to recover silver. Even more than with ion exchange, cost, maintenance, and space requirements tend to make this technology impractical for most photographic processing facilities.

DISTILLATION AND EVAPORATION

These are additional examples of concentration techniques. The two basic techniques are:

- **Distillation—**The photographic processing effluent is captured in a vessel and heated to evaporate the water. In some apparatus, the solution is actually boiled, the steam being condensed. In others, the solution is merely heated and released into the air (by a fan) to discharge evaporating moisture. Although some pieces of equipment may be capable of producing a solid block from the effluents, the energy requirements can be prohibitive, and heated photoprocessing effluents tend to give off pungent, unpleasant odors. You may need an air emission discharge permit for this type of equipment.
- **Evaporation—**Vacuum distillation, or cool temperature evaporation, is a process by which a vacuum is drawn on a vessel containing the photographic processing effluents. At a sufficiently low pressure, the solution will boil and the water vapor is drawn from the vessel, condensed, and collected. These evaporators can generally reduce the effluent volume by up to 90%, but the initial equipment expense is relatively high.

Evaporation technology may be useful where access to public sewers is not available or the regulatory limits for silver are so stringent that they require transporting silver-rich effluents off-site. You must still treat the concentrate for silver removal. The collected water vapor will contain some organic materials, some ammonia, and possibly some sulfite. It may be used in some cases as make-up water for fresh fixer or bleach-fix.

COMPARATIVE SILVER-RECOVERY AND TREATMENT TECHNOLOGIES

	Terminal Electrolysis	In-Line Recirculation Electrolysis	Metallic Replacement	Sulfide Precipitation	Precipitation	Ion Exchange (only for washwaters)
Typical Initial Silver Concentration	2,000 to 12,000 mg/L	500 to 7,000 mg/L	Variable	Variable	> 250 mg/L	< 30 mg/L
Typical Final Silver Concentration	50 to 250 mg/L	Adjustable—usually 250 to 1,000 mg/L	0.5 to 15 mg/L	0.1 to 1.0 mg/L	0.3 to 1.5 mg/L	0.1 to 1.0 mg/L
Treatable Solutions	Most silver-rich solutions	Fixers in certain processes	Most silver-rich solutions	Most silver-rich solutions	Most silver-rich solutions	Washwaters and very dilute hypo-containing solutions
Capital Cost	$2,000 to $30,000 depending on size and sophistication of equipment	$1,500 to $8,000 depending on size and sophistication of equipment	$50 to $3,000 requires a tank and pumping system for best results	$2,000 to $10,000 "off-the-shelf" equipment not available	$3,000 to $75,000 depending on degree of automation	$10,000 to $100,000
Operating Cost	Low	Low	High	Medium	Medium	High
Advantages	Can produce > 90% pure silver	Minimizes silver carry-out to following wash; reduces replenishment rates	Can be relatively inexpensive	Consistently low silver concentration	Consistently low silver concentration	Provides low silver concentration for washwaters
Disadvantages	Relatively high final silver concentration; usually requires "tailing" (secondary recovery)	May require electronics adjustment; requires terminal treatment system	Difficult to know when to replace; discharges iron, limited by some sewer codes	Requires professional care to avoid releasing potentially hazardous gases; difficult to filter	Not currently available for all processes	Expensive: requires expert maintenance
Application	All photographic processing facilities except very small labs	All photographic processing facilities except small labs	All photographic processing facilities	Solution service companies	Large photographic processing facilities and minilabs	Large photographic processing facilities

MORE INFORMATION

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Kodak also maintains a 24-hour health hotline to answer questions about the safe handling of photographic chemicals. If you need health-related information about Kodak products, call 1-585-722-5151.

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J-210	*Sources of Silver in Photographic Processing Facilities*
J-211	*Measuring Silver in Photographic Processing Facilities*
J-213	*Refining Silver Recovered from Photographic Processing Facilities*
J-214	*The Regulation of Silver in Photographic Processing Facilities*
J-215	*Recovering Silver from Photographic Processing Facilities*
J-216	*The Fate and Effects of Silver in the Environment*

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