



Environment

I N F O R M A T I O N F R O M K O D A K

J-213 \$9.00

Refining Silver Recovered from Photographic Processing Facilities



Regardless of the technique your photographic processing facility uses to remove silver from photographic processing solutions, you must send the silver-bearing materials to a refiner to complete the recovery process. In addition, photographic films and papers may also be a source of silver from photographic processing facilities; they also require refining. Each silver-bearing material from recovery, or washwater treatment, has unique characteristics such as physical appearance and typical silver content.

The process of refining each silver-bearing material is different, and the costs associated with each process can vary greatly. Once you understand the types of silver-bearing materials that your photographic processing facility generates and how they are refined, you can easily determine if you are receiving the maximum value for your silver.

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.

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SILVER-BEARING MATERIALS FROM SILVER RECOVERY

The three common techniques used to recover silver from silver-rich photographic processing solutions each produce a silver-bearing material that is unique. The resulting materials differ in both appearance as well as typical silver content.

FLAKE SILVER

Electrolytic silver-recovery units produce a metallic silver flake. The flake should be a grayish-brown solid. Improper operation of an electrolytic silver-recovery unit can cause a black silver sulfide to form on the plate which reduces the efficiency of the unit. The silver flake from a properly operated silver-recovery unit should be high purity metallic silver. The plated silver is typically greater than 90% silver by weight. Electrolytic silver recovery usually produces the highest purity material compared to other silver-recovery techniques commonly used in a photographic processing facility.

METALLIC REPLACEMENT CARTRIDGE (MRC) SLUDGE

Exhausted MRCs¹ contain a silver-rich sludge. The consistency of the sludge can vary, but typically the MRC will contain a dark liquid sludge that is a combination of degraded metallic iron and collected silver. The amount of silver recovered by a MRC can also vary greatly. This is affected by conditions such as the flow rate and pH or by the length of time the MRC is used. If fully exhausted, a MRC should contain 20–40% silver by dry weight. When making this

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.

calculation, be sure to account for the weight of the liquid contained in the MRC (approximately 8 pounds/gallon) and the weight of the MRC housing. In order to maintain efficient recovery and meet low silver discharge limits, MRCs are typically changed prior to exhaustion. However, frequent replacement can result in considerably lower silver yield. Improper operation and maintenance can also cause lower silver yield.

KODAK SILVER-RECOVERY AGENT (KODAK SRA) PRECIPITATE

Silver recovery by precipitation using TMT (tri-mercapto-s-triazine), produces an insoluble silver compound. The precipitate can range in color from light green to a bright yellow. The bright yellow indicates a higher silver content. The precipitate is collected using filtration. The bright yellow precipitate is typically 50–70% silver by dry weight.

Silver-Bearing Materials from Recovery Operations

Silver-Bearing Materials	Physical Appearance	Typical % of Silver (by dry weight)
Flake Silver	Grayish–Brown Solid	>90%
Metallic Replacement Cartridge Sludge	Dark Liquid/Sludge	20-40%
TMT-Silver Precipitate	Light Green to Yellow Sludge	50-70%

Silver-Bearing Materials from Washwater Treatment Operations

Silver-Bearing Materials	Physical Appearance	Typical % of Silver (by dry weight)
Ion-Exchange Resin (In-Situ Regeneration)	Black Swollen Beads	40-60%
Ion-Exchange Resin (Elution Regeneration)	Green Wet Sand	2-4%

SILVER-BEARING MATERIALS FROM WASHWATER TREATMENT

Ion-exchange technology is typically used to remove silver from washwaters when you must meet stringent discharge requirements.

There are two ion-exchange resin regeneration methods—in-situ regeneration and elution regeneration. The amount of silver found in ion-exchange resins depends on the method of regeneration.

ION-EXCHANGE RESIN (IN-SITU REGENERATION)

Ion-exchange resin that is regenerated using an in-situ technique collects precipitated silver during its use. Once the capacity of the resin begins to drop, it can no longer be used for washwater treatment. The resin is removed from the ion-exchange column and sent for refining. The resin will appear as black, swollen, and fractured beads. A resin that is completely exhausted and has been regenerated using an in-situ technique is typically 40–60% silver by dry weight.

ION-EXCHANGE RESIN (ELUTION REGENERATION)

Ion-exchange resin that is regenerated using an elution technique does not retain appreciable amounts of silver following regeneration. The exhausted ion-exchange resin is rinsed with a thiosulfate solution that elutes the silver off the resin and carries it from the column. This resin has the consistency of wet sand and is green in color. A resin that has been regenerated using an elution technique is typically 2–4% silver by dry weight.

PHOTOGRAPHIC FILMS AND PAPERS

Silver is recoverable from most unprocessed photographic films and papers, as well as processed black-and-white films and papers. Processed color photographic films and papers do not contain appreciable amounts of silver. The silver content of Kodak photographic films and papers is available from Kodak Environmental Services at (716) 477-3194.

COLLECTING SILVER-BEARING MATERIALS

Once you have removed silver from photographic processing solutions or washwaters, you will need to remove it from the silver-recovery or treatment equipment and prepare the material to be shipped to a refiner.

Observe safety precautions when removing silver-bearing materials from silver-recovery or treatment equipment. Refer to the manufacturer's recommended operating procedures, and always use the proper personal protective equipment.

FLAKE SILVER

Once the plated silver on the cathode of an electrolytic silver-recovery unit has reached a thickness of greater than 5 mm, you can remove it and ship it to the refiner. Prior to collecting the flake silver, make sure that the power to the electrolytic unit is off. Rinse the plated silver to remove any residual photographic processing solution before removing the silver from the cathode.

If your unit has a cathode that is replaced after each use, remove the cathode, rinse, and package it for shipping. The most commonly used units have permanent cathodes from which the plated silver must be removed. Remove the silver-laden cathode and place it on a sheet of plastic. Break the bead around the top and bottom of the cathode using a wooden or rubber mallet. Do not use a hammer which could damage the cathode. Score the cathode so the silver will fall away in large pieces. Carefully pry the silver away from the cathode using a paint scraper or similar tool. Rinse the cathode before returning it to the unit. You can spray the cathode with a lubricant to make the silver easier to remove. Break the removed flake into small pieces and allow to dry prior to shipping to the refiner.

METALLIC REPLACEMENT CARTRIDGE (MRC) SLUDGE

The silver-bearing MRC sludge is contained in the housing of the MRC. Typically, the housing is sealed and the entire unit is shipped to the refiner. Prior to sealing, you should rinse any residual photographic processing solution from the MRC. You can do this by connecting the new MRC in series after the MRC that you are removing. Run water through the cartridges at a slow rate until you have passed three times the volume of the old cartridge through the MRCs. Do not empty the rinsed MRC; wet steel wool exposed to air will rust, creating heat which may cause combustion.

TMT PRECIPITATE

TMT (tri-mercapto-s-triazine) precipitate is collected using filtration. The collected material can be air dried or shipped damp to the refiner. The precipitate does not require rinsing prior to shipping.

TMT precipitate that is generated using the semi-continuous unit is collected in the filter. Silver-containing filters should have the inlet and outlet caps secured. It is not necessary to remove the precipitate from the filter or to dry the material. The filters should not leak; however, you can pack the filters in plastic bags as extra protection during transportation.

ION-EXCHANGE RESINS

Consult the manufacturer's operating procedure for instructions on removing ion-exchange resins from the column. Once you remove and collect the resins, you do not need to rinse them prior to shipping them to the refiner.

WASTE CHARACTERIZATION

High purity flake silver from electrolytic silver-recovery units is considered to be a product by the United States Environmental Protection Agency (USEPA) and is not regulated as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) when sent for refining.

MRC sludge, precipitate, and ion-exchange resins that are destined for refining are considered characteristic sludges being reclaimed and are not regulated as a hazardous waste by USEPA under RCRA. If these silver-bearing materials are not sent for refining, they may be classified as a hazardous waste if they contain leachable silver.

Representative samples of rinsed silver-bearing MRC sludge, rinsed flake silver, TMT precipitate, and silver rich ion-exchange resins from properly maintained and operated silver-recovery or wastewater treatment equipment were tested using the Toxicity Characteristic Leaching Procedure (TCLP). The samples did not leach silver at greater than 5 parts per million (ppm). Therefore, these materials would not be classified as a hazardous waste for silver under RCRA by USEPA.

Representative samples of processed and unprocessed photographic films and papers were also tested using the TCLP. The samples did not leach silver at greater than or equal to 5 ppm. Therefore, these materials would not be classified as a hazardous waste (for silver) under RCRA by USEPA.

Some states may choose to regulate materials from silver recovery under their own hazardous waste program more stringently than USEPA. Check with your state for any additional hazardous waste requirements.

SHIPPING AND TRANSPORTATION OF SILVER-BEARING MATERIALS

Silver-bearing materials that are not classified as a hazardous waste do not require manifesting during transportation to a refiner. A hazardous waste transporter is not required and you can ship the material using a carrier such as United Parcel Service (UPS) or Roadway Package Service (RPS).

In states where these materials are more stringently regulated, manifesting or transportation by a licensed carrier may be required. Check with your state for any additional transportation requirements.

REFINING SILVER MATERIALS

Refining the silver-bearing materials from a photographic processing facility requires several different processes. The complexity of these processes accounts for the difference in the costs associated with refining.

FLAKE SILVER

Flake silver is dried and directly melted. The material is then sampled and assayed to determine silver content.

METALLIC REPLACEMENT CARTRIDGE (MRC) SLUDGE

Silver-rich sludge is removed from the MRC and any residue is rinsed. The removed materials are dried and milled to provide a consistent mixture. The dried material is sampled and assayed to determine silver content. The material is then heated to remove any residual water and organic compounds. A smelting process is then used to melt the material and separate the metallic components

TMT PRECIPITATE

TMT precipitate is removed from the filter housing or bag filter. The precipitate is slurried, sampled, and assayed to determine silver content. The material is then heated to remove any residual water and organic compounds and then introduced into a smelting process.

ION-EXCHANGE RESINS

Ion-exchange resins are thoroughly mixed to ensure consistency. The material is sampled and assayed to determine silver content. The resin is often dried, milled and sampled again to verify silver content. The material is heated to remove any residual water and organic compounds and then introduced into a smelting process.

PHOTOGRAPHIC FILMS AND PAPERS

Silver is recovered from photographic films in two ways:

1. Some photographic films may initially be washed to remove the silver-bearing emulsion from the film base, allowing the base to be recycled. The removed silver-bearing emulsion is heated to remove water and any organic compounds, and is then introduced into a smelting process.
2. When film base recycling will *not* be performed, photographic films are directly heated to remove water and organic materials (including the film base); they are then introduced into a smelting process.

Photographic papers are generally not separated for recovery of the paper base. These materials are also heated to remove water and organic materials (including the paper base), and introduced into a smelting process.

REFINING COSTS

Refining costs are the combination of the charges assessed to you by a refiner to process your silver-bearing materials. Charges may vary from refiner to refiner; there are generally three types of charges you will be assessed for refining.

1. Retainment or Accountability Charge. This is typically a small percentage of the total silver found; the refiner uses this to compensate for any inaccuracies in the sampling and analytical method of the assay.
2. Treatment or Handling Charge. This is the cost assessed to cover the receiving and processing of your material prior to refining. The more labor intensive refining processes, such as with MRC sludge, will be assessed a higher charge.
3. Refining Charge. This is the cost assessed to you for actually operating the refining process.

The silver value returned to you will be the overall net value of the silver minus these charges. The refiner may also include a charge for shipping the silver-bearing materials from your facility if the refiner provides the transportation. MRCs that are not operated correctly or are frequently changed, and ion-exchange resins that have been regenerated using an elution process, may contain so little silver that the refining costs exceed the value of the silver.

CHOOSING A SILVER REFINER

It is important to choose a reputable refiner to process your silver-bearing materials. You may want to request references or visit the refining operations to ensure that your material will be handled in an environmentally sound manner. Consult your state regulatory agency to review the refiner's history of regulatory compliance and to make sure that the refiner has all of the required regulatory permits. Review the refiner's silver accounting system to be sure that you will receive the maximum return from your materials.

If you need assistance in locating a refiner, call Kodak Environmental Services at (716) 477-3194.



MORE INFORMATION

If you have environmental or safety questions about Kodak products or services, contact Kodak Environmental Services at 1-716-477-3194, between 9 a.m. and 7 p.m. (Eastern time) or visit KES on-line at www.kodak.com/go/kes.

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 1-716-722-5151.

For questions concerning the safe transportation of Kodak products, call Kodak Transportation Services at 1-716-722-2400.

Additional information is available on the Kodak website and through the U.S.A./Canada faxback systems.

The products and services described in this publication may not be available in all countries. In countries other than the U.S., contact your local Kodak representative, or your usual supplier of Kodak products.

The following publications are available from Kodak Customer Service or from dealers who sell Kodak products.

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| J-210 | <i>Sources of Silver in Photographic Processing Facilities</i> |
| J-211 | <i>Measuring Silver in Photographic Processing Facilities</i> |
| J-212 | <i>The Technology of Silver Recovered for Photographic Processing Facilities</i> |
| J-214 | <i>The Regulation of Silver in Photographic Processing Facilities</i> |
| J-312 | <i>Personal Protective Equipment Requirements in Photographic Processing Facilities</i> |

For more information about Kodak Environmental Services, visit Kodak on-line at:
www.kodak.com/go/kes

Many technical support publications for Kodak products can be sent to your fax machine from the Kodak Information Center. Call:
U.S. 1-800-242-2424, Ext. 33 / Canada 1-800-295-5531
—Available 24 hours a day, 7 days a week—

If you have questions about Kodak products, call Kodak.
In the U.S.A.:
1-800-242-2424, Ext. 19, Monday–Friday
9 a.m.–7 p.m. (Eastern time)
In Canada:
1-800-465-6325, Monday–Friday
8 a.m.–5 p.m. (Eastern time)



EASTMAN KODAK COMPANY • ROCHESTER, NY 14650

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KODAK Publication No. J-213

CAT No. 816 0418

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Revised 4/99
Printed in U.S.A.