CHAPTER 6 - SILVER RECOVERY EQUIPMENT

A. GENERAL

1. The DRMO will not be a central recovery site for generators. Ideally, each generator should be set up with the proper equipment and return desilvering to the source of the waste stream. PMMs may provide this section to generating activities participating in the silver recovery program.

2. Some of the fundamental principles of the silver recovery program are:

a. Proper identification of expended hypo solution. Activities that process both x-ray and photographic film must be advised against mixing the solutions since they may be incompatible for recovery.

b. The quantity of silver in expended hypo solution will vary dependent on the ratio of exposed area to non-exposed area in the film or paper being processed. This may affect the yield of recovered silver.

c. The DRMS-DE/DW/DRMSI Operations Monitor evaluates the quantity and type of hypo solution being generated to determine the size and type of recovery equipment required.

B. INSTALLATION AND MAINTENANCE OF EQUIPMENT

1. Locate electrolytic units and passive silver cells in a designated processing area.

a. The designated processing area should be in an area with limited access that can be locked and secured during non-duty hours. Fit electrolytic units with a locking device. Adhere to security regulations of the appropriate Military Service.

b. Areas selected for recovery equipment must be located so that a spill or rupture can be readily confined to the immediate area and run-offs are prevented from entering any sewage or drainage system.

c. The processing area should be kept clean and free of debris at all times.

2. The DRMS-DE/DW/DRMSI Operations Monitor assists in training personnel in the installation, operation and maintenance of silver recovery equipment.

3. Fit the holding tank with a flow restrictor/cut-off valve to control the flow of the hypo solution. The holding tank must be installed to permit gravity feed of the hypo solution into the equipment.

4. Generators are responsible for preventive maintenance of equipment, e.g., day-to-day adjustments, replacement of fuses, gaskets, etc. Contact the DRMS-DE/DW/DRMSI Operations Monitor to arrange for any repair and/or other maintenance services as may be required.

5. If, for any reason, recovery equipment is inoperative, the generator should retain generations of hypo solution until equipment is repaired or replaced. Contact the assigned operations monitor if storage restraints preclude retention of hypo solution, to arrange processing of the hypo solution by other activities operating recovery units.

C. PROCEDURES FOR OPERATING ELECTROLYTIC SILVER RECOVERY UNITS

1. General. Electrolytic silver recovery units remove silver from hypo solutions by passing a controlled, direct electrical current between two electrodes (a cathode and an anode), which are suspended in the hypo

solution. Silver is deposited on the cathode in the form of nearly pure metallic silver. The plated silver (silver flake) is removed periodically from the cathode. Electrolytic units are available in varying sizes and capacities so that equipment can be matched to the needs of the user depending upon the amount of hypo solution being processed. Unit must be completely cleaned if it has been sulfiding.

2. Operation of the Unit. Regular monitoring of the system is required to insure efficient recovery of silver.

a. Fill the holding tank with expended hypo solution, open the flow control valve and slowly fill the electrolytic unit.

b. Turn the electrolytic unit on and set the current flow according to the manufacturer's instructions. Adjust the rate of hypo flow so that no silver remains in the effluent (the solution that has passed through the electrolytic unit). Test the effluent with silver estimating test paper (see paragraph E below) to determine whether or not effluent has been de-silvered. If no silver appears in the effluent, and the recovery unit is not sulfiding, the system is operating properly. If a rotten egg smell is coming from the electrolytic unit, the unit is sulfiding. Sulfiding occurs either when the unit is left on after all the silver has been removed from the hypo solution or when the unit is operating on too high a power setting. Sulfiding may be corrected by turning the unit off when not actually processing solution or by lowering the power setting during processing.

c. Next, note the number of gallons of hypo solution in the holding tank and the rate of flow, and estimate the number of hours required to process the hypo solution. Check the electrolytic unit occasionally and shut it off at the close of business.

d. When the holding tank is empty, turn off the unit to prevent sulfiding.

e. Unless the silver is thick enough to warrant removal, it is not necessary to harvest (remove) the silver from the cathode after each processing cycle. Silver flake should be harvested whenever silver reaches the thickness specified in the manufacturer's instructions.

3. Harvesting the Silver

a. When silver thickness has reached the manufacturer's recommended removal level, turn the unit off and remove the cathode. The flake may be removed from the cathode wet or left to dry on the cathode. If the flake is left to dry on the cathode, then flake removal should be accomplished inside of a plastic bag to reduce the loss of silver dust. The wet flake/silver-laden cathode should be put into a container in a secured area during the drying process. The drying area should be adequately ventilated since fumes given off during the drying process are quite corrosive. The drying process varies according to the thickness of the silver flake. At least 24 hours drying time is required.

b. Weigh harvested (removed) silver flake, place in plastic bags and store securely pending disposition. To reduce any possibility of weight loss through further evaporation, silver flake should be tightly sealed and immediately reported for disposition.

c. After harvesting the silver flake, clean the electrolytic unit, both inside and outside, by wiping with a rag dampened with a household cleaner. Clean off any hypo solution spilled on the unit and reinstall the cathode. You should add any silver bearing residue removed to the flake. Place used wiping rags in a separate bag and periodically turn in to the DRMO for disposition as SCL P8B.

4. Removing Sludge. During periodic servicing, remove silver-laden sludge from the bottom of the unit. You may accumulate and dry sludge according to instructions in paragraph D3 above; however, the drying process for silver-laden sludge is much longer than that for harvested silver flake***. Once the sludge is dry, place in plastic bags and turn in to the DRMO for disposition as SCL VSF.***

D. PROCEDURES FOR USING PASSIVE SILVER RECOVERY CELLS (PSC)

1. General. The passive silver recovery cells remove silver from used fixer solutions. PSCs are designed to remove silver from the effluent streams of automatically replenished processing equipment as well as with batch replenishment and hand-processing equipment.

2. **Types of Passive Systems**. DRMS is currently using four types of passive systems; Mini McKays, ***single/dual/tandem, and silver sure unit(s) with replaceable cores/cells. The cores/cells on these units are removed when exhausted (filled up with silver), drained, dried and placed in plastic bags and usually a second container (bag/box/carton) and turned in to the DRMO as SCL PSC.***

a. The Mini McKay is a small cylindrical unit designed for use at dental labs due to the usually small amount of used hypo generated.

b. The single cell units with replaceable cores/cells are permanent pieces of equipment. They have a 6 pound wire mesh screen core/cell that can be removed when exhausted and turned in for recovery.

c. The **dual/tandem** units are permanent pieces of equipment and have two cores in a side by side configuration for larger applications. One core acts as the primary recovery system with the second core in place to remove silver to an even lower level. Dual/tandem units have either 4 or 6 pound wire mesh screen cores that can be removed when exhausted and turned in for recovery.

d. The silver sure units with replaceable cores/cells are permanent pieces of equipment. There is a variety in sizes of silver sure cores/cells, the general description is they are long and tubular, and as in the other types of passive systems, the cores/cells are removed when exhausted and turned in for recovery. Names associated with this type of units are silver sure, MTS, MPS, SS100, SS125, SS200, SS250, etc.

3. Operating Principles

a. The passive silver cells actually operate through a combination of two principles. Electrolytic plating and metallic displacement. The passive units do this without the use of electricity, hence the name passive. Silver is recovered electrolytically based on a combination of three factors: 1) a cathode - negative charge, 2) an anode - positive charge, 3) agitation. The passive units incorporate each of these factors without the use of electronics by using the natural laws of chemical reaction and gravity. Units must be installed with incoming hose attached to the inlet at least 1 inch lower than the processor outlet. The effect created by a chemical reaction between two unlike metals, the steel in the wire screen and the silver in the used fixer solution, act together in the acid fixer solution to create an electrical charge. This charge coupled with the movement of the fixer through the wire mesh core causes the silver to plate from the solution onto the core. While this is taking place, the metallic replacement principle is also in effect where some of the silver in the solution is being replaced by the iron in the core. As the solution enters the PSCs it falls into the bottom of the chamber/bucket and to exit the unit it must flow through the core and exit through the top by way of the outlet tube. By forcing the solution to flow from bottom to top, the core is permeated by silver laden fixer and the plating/metallic displacement process can work at an optimum level. Ph should also be taken into consideration when using PSCs. The ph level of used fixer solution should be in the 4.5 - 6.5 range. Too high or too low of a ph will prevent silver recovery.

b. Maximum flow rate for PSCs is 125 milligrams per minute (ml/min). A flow rate faster than this may result in lost silver which in turn may exceed the Federal, state and local limits on effluents containing silver. A flow rate that is too slow may result in the disintegration of the wire mesh core. A passive silver cell needs movement of fixer through the core to work effectively.

c. PSCs may also be used as tailing units to other PSCs and electrolytic units. Care must be taken to ensure that enough silver is present in the solution to enable the PSC to function properly. Too little silver present in solution has the same effect as a too slow flow rate. Core disintegration may result due to the core trying to process too little silver in an acidic solution. Although some cores have been known to disintegrate, this does not mean that it has ceased to function. The effluent from disintegrated cells should be tested to ensure the cell is still working.

d. PSCs work very well with most chemistries. Black and white chemistries may be processed directly through the PSCs. Color chemistries must be mixed with black and white with a ratio of 5 parts black and white to 1 part color. Bleach chemistries should not be processed at all by PSCs.

4. ***Core/Cell Replacement. When the core/cell is exhausted, the generator should take the following actions to replace the cell/core for turn in to the DRMO.***

a. On bucket types only, disconnect the unit from the film processor. (Tank types do not require disconnection for core/cell changing.

b. Remove the lid/cap from the container and drain excess fluid from the core/cell back into the unit.

c. Allow the core/cell to air dry by placing it on absorbent toweling or paper for 48 or more hours.

d. Prepare the core/cell for turn in to the DRMO by placing it in two layers of plastic bags.

e. Replace removed core/cell with new core/cell.

5. Connecting the PSCs to the Used Fixer Source. Connect the hose from the film processer or batch holding to the inlet elbow located on the side of the PSC bucket or unit. If elbows are not already attached, simply apply teflon tape to the threads of the elbow or connection and screw in or on until elbow is snugly secured. Do not over tighten. Attach a hose in the same manner to the outlet on the bucket/unit and run it to the drain.

6. Multiple PSC Installation. For multiple installation of units for large volume users or used fixer with very high concentrations of silver PSCs may be installed in series. All that is required is to run the outlet hose from one unit to the inlet of the next unit in the series ensuring that each subsequent unit attached is approximately 1 inch lower than the previous unit.

7. Maintenance of the System. Passive silver recovery systems installed correctly operate nearly maintenance free. Periodic checks to ensure plating action, core exhaustion evaluation and effluent checks are all that is really necessary for proper operation. Practice normal housekeeping measures to ensure cleanup of small spills and splashes on a day-to-day basis.

8. PCS Evaluation. To determine the life of a core, a number of methods may be used.

a. When the silver level of effluent increases to a level that is determined to be unworkable with a PSC, it may be time to change the core. Care must be taken to insure that the increase is not just a fluctuation caused by processing used fixer with a higher level of silver concentration or the flow rate has inadvertently increased.

b. Most cores may be checked by using a screwdriver, or pencil to check the life of the cell. Insert the screwdriver or pencil through the view port and into the core. The core is about 6 inches high. If the screwdriver or pencil will push fairly easily into the core an inch deep, there is about 5 inches of core left. If the object penetrates the core 5 inches, there is about 1 inch of the core left for processing. This method may be used for estimating how much life is left.

c. Determine the silver concentration of used fixer with silver estimating paper using the instructions in paragraph E. The life of the core may be approximated by comparing the silver concentration of the fix to the chart below and determining the total gallons the core will process.

Example:

If your silver estimating test paper shows 1/3 T.O. per gallon, the core should be changed once you have used approximately 270 gallons of fixer. If the processor averages 30 gallons a month, 270 divided by 30 equals 9. The core should be changed in 9 months. At 100 gallons a month, 270 divided by 100 equals 2.7. The core should be changed in 11 weeks.

ESTIMATED PLATING CAPACITY FOR DUAL/TANDEM WITH 6 LB CORES

Maximum Flow Rate	Silver Content T.O./Gallons	Total Gallons	Silver Content GM/Liter	Total Liters
125 ml/min	1/4	360	2.05	1365
125 ml/min	1/3	270	2.71	1033
125 ml/min	½	180	4.11	681
125 ml/min	1	90	8.22	341

ESTIMATED PLATING CAPACITY FOR DUAL/TANDEM WITH 4 LB CORES

Maximum Flow Rate	Silver Content T.O./Gallons	Total Gallons	Silver Content GM/Liter	Total Liters
125 ml/min	1/4	280	2.05	1060
125 ml/min	1/3	210	2.71	795
125 ml/min	½	140	4.11	530
125 ml/min	1	70	8.22	265

E. SILVER ESTIMATING TEST PAPER

1. Silver estimating test paper is impregnated with a chemical substance which changes color depending on the amount of silver present in the solution. The papers are supplied with a color step chart for estimating, by comparison, the approximate silver concentration of a solution. This test paper is used to determine the silver content of spent fixer solutions and to check the efficiency of cartridge or electrolytic recovery units. Test paper is also used to determine when a cartridge may be reaching the exhaustion point. Silver estimating test paper is not intended as a substitute for chemical analysis. It is, however, a quick, easy-to-use method for estimating silver content.

a. PSCs should be tested on a regular basis (weekly as a minimum and more frequently as a PSC nears exhaustion point) by immersing a piece of test paper in the effluent discharged. Shake the strip to remove any excess liquid and place the strip on a clean, white card. After about 15 seconds, compare the color of the moistened strip with the chart furnished. If the solution being tested contains bleach fix (fixer generated from color process), the dyes from the fixer may cause an inaccurate reading. (To obtain a proper reading the test paper should be rinsed with clear water after immersion in the effluent.) After about 15 seconds, compare the color of the moistened strip with the chart furnished with the test paper. This is best done under incandescent lighting. The PSC may be exhausted and should possibly be replaced when the color of the strip approximates the color on the chart indicating one gram per liter. If the paper color is darker, silver is passing through the PSC and is being lost. Test only the effluent discharged from the system during normal operation. Depending on the chemicals used and the degree of exhaustion, the effluent may require testing several times a week or every few hours.

b. Electrolytic units should also be tested on a regular basis. When unit is first turned on, effluent should be tested each hour to ensure that the controls of the unit are properly set. Immerse a piece of test paper in the effluent discharged from the electrolytic unit. Shake the strip and place it on a clean white card. If the color of the moistened strip is darker than the color on the chart indicating one gram per liter, silver is being lost; this indicates that the unit's controls are not properly set.

2. Test papers are also useful for determining the approximate silver concentration of spent hypo prior to processing for silver recovery. Simply dip a strip of test paper into the solution and compare it with the chart furnished with the test books to determine very roughly what the silver concentration is. However, at high silver concentration, the test paper readings tend to indicate a higher silver concentration than is actually present.

3. In order to retain effectiveness, test papers should be stored in a cool, dark and dry area removed from exposure to the hypo collection area if possible.