Silver Management for Small Photoprocessing Operations

In 1993, an initial study of the economic impact resulting from silver pretreatment standards, the Silver Council identified more than 500,000 facilities throughout the U.S. that process photographic films and papers containing silver. More recent estimates suggest there are approximately 360,000 facilities. The majority of these facilities are small both in size (fewer than 10 employees) and in volume of discharged wastewater (typically less than 1,000 gallons per day - GPD). An EPA study of the photographic processing industry, published in 1981, indicated that more than 99 percent of these facilities discharged to POTWs. This continues to reflect accurately the current status of photographic processing discharges. Today, many POTWs do not have adequate resources to regulate and monitor the large numbers of small facilities, nor to assist them with improving the efficiencies of their silver recovery systems.

Some examples of city discharge limits (parts per million – ppm) for silver are listed in the Table below.

<table>
<thead>
<tr>
<th>City</th>
<th>Discharge Limit</th>
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<tbody>
<tr>
<td>Ardmore</td>
<td>2.370 ppm</td>
</tr>
<tr>
<td>Chickasha</td>
<td>0.290 ppm</td>
</tr>
<tr>
<td>Norman</td>
<td>0.080 ppm</td>
</tr>
<tr>
<td>Oklahoma City</td>
<td>0.240 ppm</td>
</tr>
<tr>
<td>Okmulgee</td>
<td>0.052 ppm</td>
</tr>
<tr>
<td>Tulsa</td>
<td>3.0 ppm</td>
</tr>
</tbody>
</table>

During processing of photographic films or paper, a silver-rich solution is generated. A silver-rich solution is defined as a solution containing sufficient silver that cost-effective recovery could be done either onsite or offsite. These solutions include:

- Used fix and bleach-fix solutions
- Low replenished (low-flow) washes following a fix or bleach-fix solution
- Stabilizers for the washless minilab film and paper processes

Low-silver solutions include:

- Used developers
- Stop baths
- Stabilizers following washes
- Bleaches
- Pre-bleaches
- Wash waters

Typical silver-rich and low-silver volumes for some processors of particular interest are listed in Table 1.

Small-size and medium-size photographic processors represent about 90 percent of the total number of photographic processing facilities. These include: small hospitals, doctors, dentists, veterinarians and chiropractors offices, neighborhood clinics, schools, portrait studios, minilabs, custom lab, professional processing labs, small microfilm facilities, printers, motion picture processors, and a large number of municipal, state, and federal facilities where some in-house photographic processing is done.
Several technologies are available to control silver in photographic effluent. The two most common technologies generally available to the photographic processor for recovering silver from silver-rich photographic processing solutions are electrolysis and metallic replacement (CRC). Precipitation, is a third, less common technology, that is also available for silver recovery. These three technologies have been in use in the industry for many years and are the subject of considerable research to improved recovery efficiencies, ease of use and economics.

Small photographic processing facilities that produce on average less than 2 GPD of silver-rich processing solution and discharge less than 1,000 GPD of process wastewater should use one of the following equipment options capable of recovering or managing at least 90 percent of the silver. The options are listed in order of increasing cost:

- One or two CRCs with manufacturer-specified flow control. Very small photographic processing facilities that generate less than 0.5 GPD of silver-rich processing solution require only one recovery cartridge. A second recovery cartridge used in these circumstances would oxidize and channel by the time the first cartridge was exhausted, resulting in higher waste and added costs with no additional silver recovery. For all other processing facilities it is strongly recommended to use two CRCs in series to reduce the potential of silver breakthrough.
- One electrolytic unit — It is strongly recommended that an additional CRC be used after electrolytic recovery to ensure consistent recovery.
- One precipitation unit
- One evaporation or distillation unit
- Alternative technology providing at least 90 percent recovery or management

The following procedures should be used in small photographic processing facilities:
- Processing and holding tanks for silver-rich solutions and the silver recovery or management system maintained in a manner that protects the material from accidental release to the POTW.
- The facility should have a spill plan to ensure spills of silver-rich solutions are not accidentally released to the POTW.

Analytical and recordkeeping requirements for facilities using a batch operation for silver recovery:
- The silver concentration should be checked weekly after the recovery or management system to ensure proper system operation.
- The test can be performed with silver test papers, an analytical test kit or a lab analysis. This test will identify problems or failures with the recovery/management system.
- Test results should be recorded in a silver recovery log.

Analytical and recordkeeping requirements for facilities using a continuous operation for silver recovery and management are listed below.
- The silver concentrations in effluent should be checked weekly.
- The test can be performed using silver test papers, an analytical test kit or a lab analysis. This test will identify problems or failures with the recovery system.
- Test results should be recorded in a silver recovery log.
To verify at least 90 percent recovery, all facilities should have a silver analysis done on the influent and effluent to the recovery system at least every 12 months by an analytical laboratory acceptable to the POTW. The facility should retain the analytical records for a period of time acceptable to the POTW.

### Estimated Process Volumes in Gallons Per Day (GPD)

<table>
<thead>
<tr>
<th>Facility Type (Size)</th>
<th>Silver-Rich Solution</th>
<th>Low-Silver Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dental Office (Small)*</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>Dental Office (Medium)*</td>
<td>0.2</td>
<td>10</td>
</tr>
<tr>
<td>Dental Office (Large)*</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>Hospital (Small)</td>
<td>20</td>
<td>2,600</td>
</tr>
<tr>
<td>Hospital (Medium)</td>
<td>40</td>
<td>5,200</td>
</tr>
<tr>
<td>Hospital (Large)</td>
<td>80</td>
<td>10,400</td>
</tr>
<tr>
<td>Medical Professional (Small)</td>
<td>0.2</td>
<td>100</td>
</tr>
<tr>
<td>Medical Professional (Medium)</td>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>Medical Professional (Large)</td>
<td>5</td>
<td>1,000</td>
</tr>
</tbody>
</table>

* This volume does not include wastewater containing silver from dental chairs.

DEQ’s Pollution Prevention Program is a non-regulatory program. It assists Oklahoma business and industry in identifying opportunities and implementing options for waste reduction and management. Services are confidential and provided free of charge.

For additional information & assistance contact:

**Department of Environmental Quality**  
Pollution Prevention Program  
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Oklahoma City, OK 73101-1677

Phone: (405) 702-9100 or (800) 869-1400  
Fax: (405) 702-9101

Much of the information in this article was adapted from the “Code of Management Practices for Silver Dischargers” published by the Association of Metropolitan Sewerage Agencies (AMSA) and the Silver Council.

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