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Abstract Sodium borohydride treatment systems for control of heavy metal discharge offer several advantages to the photographic industry. Chemical reduction with sodium borohydride is rapid and results in low residual metal content; in addition, the reduced metals can be recovered with minimum expense. Sodium borohydride reduction is now being used to recover high purity silver from spent fixers more completely than alternative methods. Also, sodium borohydride treatment is an effective, economical method for removing low level heavy metal contamination from effluent streams.

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Introduction

The discharge of heavy metals is obviously a concern of both government regulatory agencies and the photoprocessing industry. The most significant metal discharge from the photoprocessing industry is silver in the effluent streams. Since the loss of silver represents, not only a potential environmental concern, but also a very real economic loss, most photoprocessors have installed a variety of systems to minimize such silver losses.

The purpose of this presentation is to review the use of sodium borohydride to minimize the discharge of heavy metal,[1–4] in particular silver from photoprocessing sources. This paper will discuss the chemistry and overall advantages of the borohydride system, specific examples/procedures for recovery of silver from various photographic fixers/solutions, and the use of sodium borohydride for effluent control of heavy metal discharges.

Chemical Aspects of Borohydride Reduction

In aqueous solution, sodium borohydride functions as a reducing agent for conversion of a soluble metal cation (or complexed metal cation) to the insoluble elemental metal:

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-$$

$$8M^+ + 8e^- \rightarrow 8M^\circ$$

$$NaBH_4 + 8M^+ + 8OH^- \rightarrow NaBO_2 + 8M^\circ + 6H_2O$$

Since one equivalent of sodium borohydride can reduce eight equivalents of metal ion, low-level borohydride usage results in substantial reduction of the dissolved metal. Table I shows the theoretical weight ratios of reduced metal per weight of sodium borohydride. In the case of silver, the weight ratio is 22.1, so that the sodium borohydride cost per kilogram of silver recovered is as low as $2.47/kg ($0.07/oz).

In actual practice, the borohydride:metal ratio may vary since other reducible compounds may react with borohydride making it unavailable for metal reduction. Therefore more efficient silver recovery is obtained when silver-bearing streams are segregated from other process effluents. Most users find that a 100% excess of borohydride generally ensures rapid and complete reduction. Since the dissolved borohydride ion maintains a strong reducing environment, resolubilization of the metal through oxidation by dissolved oxygen or through complex formation is prevented.

In addition to the chemical efficiency of sodium borohydride reduction, there are several other practical advantages for this treatment. The procedure is irreversible, extremely rapid, and results in high yields of the reduced metal even at low initial metal ion concentrations. In most cases, the metal can be obtained directly in high purity, so that additional processing is minimized. The by-product of the reduction is sodium borate; this treatment introduces boron at 3 ppm/100 ppm silver recovered. Under normal conditions of use, final boron level in the overall plant discharge would typically be less than 1 ppm. In fixer solutions containing 0.5% silver, for example, SBH treatment would introduce 150 ppm boron as boric acid.

Sodium Borohydride Based Recovery of Silver from Photoprocessing Solutions and Silver Halides

Sodium borohydride based treatment of various photographic fixers offers an excellent method for high yield, high purity silver recovery.[5] This process yields metallic silver typically at 96–98% purity. Recovery usually exceeds 99.9%; residual silver levels following recovery with sodium borohydride are generally in the range of 0.5–10 ppm. Therefore, this method can increase the return of silver by as much as 5–10% over existing methods.

Since sodium borohydride, formulated as a liquid caustic solution (SWS™)[6] can be added directly to the fixer, no special equipment is needed. This method requires only that the pH be adjusted to 5.5–6.5 during addition of the SWS solution. The silver metal precipitates as coarse, granular particles which settle rapidly, permitting the desilvered aqueous phase to be siphoned-off. Filtration is normally not necessary. Generally this process requires 3 hours to quantitatively recovery high purity silver, independent of batch size.

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TABLE I. Weight Ratios of Reduced Metal Obtainable from Ionic Species/Theoretical Amount of Sodium Borohydride

Metal	Valence	Weight ratio[a]
Lead	Pb^{2+}	22
Cadium	Cd^{2+}	12
Mercury	Hg^{2+}	21
Copper	Cu^{2+}	7
Silver	Ag^{+}	22
Gold	Au^{3+}	14
Nickel	Ni^{2+}	6
Palladium	Pd^{2+}	11
Platinum	Pt^{4+}	10
Cobalt	Co^{2+}	6
Rhodium	Rh^{3+}	7
Iridium	Ir^{4+}	10

[a] Weight ratio = maximum kilograms of metal reduced per kilograms of sodium borohydride.

Since this process is inherently faster and more efficient than other methods, it is ideally suited for large-scale centralized recovery.

The procedure for recovery of silver using SWS is outlined below:

(*a*) Adjust pH to 5.5 – 6.5;
(*b*) Add diluted SWS solution [1 kg SWS/69 g (1 lb SWS/20 troy oz) silver, recommended dilution of 1 to 1 by volume with water] over 30 min, with good mixing
(*c*) Postagitation at slow to moderate speed
(*d*) Settle for 1 hr and decant desilvered aqueous phase;
(*e*) Wash recovered metallic silver and dry.

Specific procedures for various types of spent photographic fixer/developers have been developed (e.g., bleach fixer, x-ray fixer, graphic arts fixer, C-41 photo fixer, etc.). In solutions containing other reducible materials such as ferric ion or formaldehyde, the amount of SBH required should be based on the total reducible species in solution. Normally these materials do not interfere with the recovery or purity of the silver obtained by the SWS treatment as outlined.

In studies conducted on a C-41 fixer, we have demonstrated that the reuse of the fixer solution after silver removal presented no problems over five treatment cycles. In fixer solutions containing ferric ion (or complexed ferric ion), SWS must be added in sufficient quantities to reduce both the ferric ion (to ferrous ion) and silver ion (to silver metal) present. The resulting ferrous ion could then be reoxidized prior to reuse of the fixer solution. For economic reasons, SWS treatment may be practical only for spent fixers containing ferric ions not intended for recycle.

In cases where silver halide can be recovered (e.g., from green film or waste emulsions), sodium borohydride treatment can provide an efficient method for conversion to metallic silver.[7] This procedure involves forming an aqueous slurry of the silver halide: adjusting to pH 11 with caustic; maintaining a treatment temperature of 70–90°C; adding the calculated amount of SWS (diluted 5:1 with water) over 30 min; postagitation for 0.5–1 hr at 70–90°C (158–194°F); settling out silver metal, decanting the aqueous phase, washing, filtering and drying the resulting silver sludge. In the case of silver chloride, the reduction is exothermic and extremely rapid and should be done at 25°C (76°F) instead of 70–90°C (158–194°F). Yields of silver from this procedure are normally >95%; silver purity is on the order of 95–98%.

The process schematic for a typical SWS-based silver recovery system is shown in Fig. 1. No specialized equipment is required. Material of construction of the reactor tank may be either mild steel or low density polyethylene. The equipment costs of a treatment system with a 400-gal capacity would be approximately *$7000* to *$10,000* depending on which alternate is chosen for silver/wash/recovery step.

Chemical costs vary depending on the type of fixer but generally range from $4.80/kg ($0.15/oz) of recovered silver of x-ray fixers to $16.00/kg ($0.50/oz) for bleach fixers.

Sodium Borohydride Based Pollution Control Applications

Sodium borohydride based pollution control processes can reduce discharge of heavy metal to significantly under 1 ppm. Various metal ion impurities including lead,[8] cadmium, mercury,[9–12] silver, nickel, and cobalt can be reduced and removed from effluent streams. The free metal cation, weakly associated complexes, and many organometallic compounds are reducible by borohydride; strong complexes such as cya-

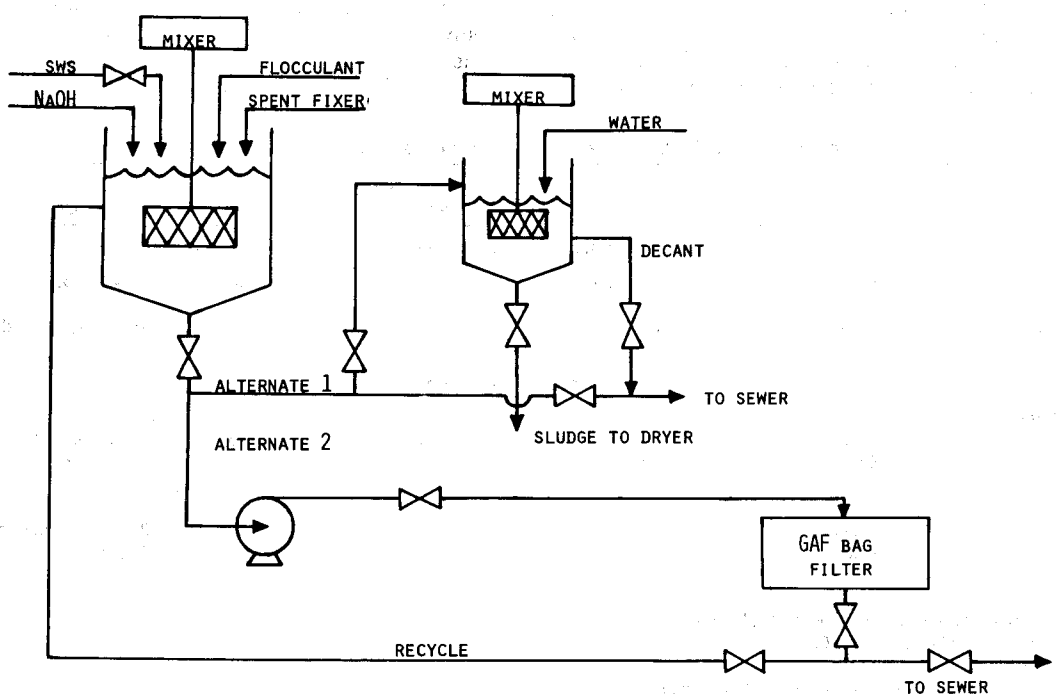

Figure 1. Silver recovery from spent fixer solution flow diagram.

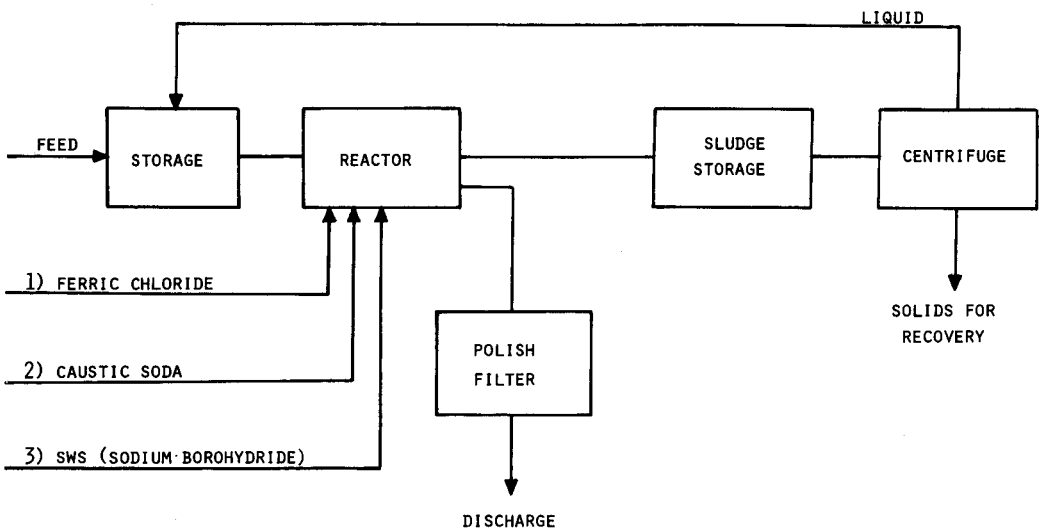

Figure 2. Flow diagram of Powers Chemco's effluent system.

nide are not generally reducible. In the latter cases, it is necessary to first destroy the complex prior to borohydride treatment. In general, the system is operated at pH 8–11 to assure efficient utilization of borohydride. Due to the low level of dissolved metal in the effluent to be treated, efficient mixing of the borohydride is essential.

With the exception of precious metals, SBH treatment generally serves as a final treatment following alkaline precipitation to remove the residual metal ion in the effluent (typically in the range of 10–150 ppm).

Presently 75–5700 l/min (20–1500 gal/min) treatment facilities based on this borohydride technology are operating to control lead, mercury, and silver/cadmium effluents having initial concentrations in the range of 2–120 ppm. Of particular interest to the photographic industry is the silver/cadmium control system at Powers Chemco in Glen Cove, N.Y.

Powers Chemco, a large manufacturer of lithographic film, has an effluent discharger of 95,000–378,000 l/day (25,000–100,000 gal/day). They have been successfully reducing an incoming stream containing 10–120 ppm Ag^+ and 5–60 ppm Cd^{+2} to meet discharge limits of less than 0.1 ppm Ag^+ and <0.2 ppm Cd^{+2} in the final effluent using a sodium borohydride pollution control system. Discharge over the most recent test period averaged 0.09 ppm silver and 0.09 ppm cadmium.

The Powers Chemco System uses ferric hydroxide flocculation to improve liquid solid separation of the resulting sludge. Figure 2 shows a schematic outline of this process. Chemical treatment cost for this effluent has been *ca.* $16.00/kg ($0.50/oz) of silver removed.

In order to improve the liquid-solid separation step in borohydride effluent treatment, we have recently completed an evaluation of various organic flocculents/coagulants. Some of these results are shown in Table II. Depending on the form of silver (e.g., complexed, halide), concentration, and reaction conditions (pH), the reduced silver will vary both in particle size and in the subsequent rate of agglomeration. In simple systems, a high molecular weight flocculent (e.g., American Cyanamid. 1561) can be used to agglomerate the particles. However, when the reduced silver is colloidal in nature, a low molecular weight primary coagulent (e.g., Nalco 8101) is used to neutralize the surface charge on the colloid and form a pinpoint flock. Subsequent treatment with a high molecular weight flocculent (e.g., Nalco 7120) agglomerates the particles and improves the settling rate.

The advantages of using organic flocculants include low silver levels in the discharge, eliminating the need for final neutralization, improved sludge characteristics and simplified silver refining techniques.

TABLE II. Summary of Flocculant Data for Liquid Solid Separation of Borohydride Reduced Silver

Flocculant	Type	MW	Residual Silver Decant	Residual Silver Filter	Comments
		Single-Polymer Systems			
American Cyanamid 1561	Cationic	Very high	4.1	2.3	Very viscous prior to dilution
Diamond Shamrock 216-L	Cationic	High	4.2	1.2	Very easy to handle
		Two-Polymer Systems			
American Cyanamid					
1. 507	Cationic	Low	4.7	3.5	40 ppm treat (pinpoint floc.)
2. 7120	Cationic	High			0.4 ppm treat
Nalco					
1. 8101	Cationic	Low	2.5	0.5	200 ppm treat (pinpoint floc.)
2. 7120	Cationic	High			2 ppm treat

Experimental
1. Starting material—soluble silver—100 ppm, pH_i – 4.8.
2. Reduce silver in large batch at pH 6.0.
3. Divided into small samples.
4. All flocculants added at 0.01% of concentration received.
5. Flocculant dosage was 0.4 ppm.

Because of the wide variety of available flocculents and operating conditions, a flocculent supplier should be consulted for empirical determination of the design parameters associated with each effluent system.

Summary

Sodium borohydride treatment offers the photoprocessing industry a chemical method of efficiently recovering silver from both spent fixer solutions and plant effluents. Such treatment of high silver bearing streams (e.g., fixer solutions) results in excellent recovery of silver metal, thus minimizing introduction into the effluent. Nonetheless, effluent treatment for removal of residual silver prior to discharge can also be accomplished with borohydride reduction.

Borohydride based systems are now operating commercially both for effluent control and metal recovery at chemical costs of \$4.80–\$16.00/kg (\$0.15–\$0.50/oz) of recovered silver. The design of these treatment systems is based on standard, readily available process equipment; and can be adapted to existing systems with modest additional capital cost. The overall efficiency of silver reduction using sodium borohydride results in an economical recovery system with minimal discharge of silver in the final effluent.

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