Treatment of Spent Chemical Oxygen Demand Solutions for Safe Disposal

Thomas R. Holm
University of Illinois
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Treatment of Spent Chemical Oxygen Demand Solutions for Safe Disposal

by

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ABSTRACT

The chemical oxidation demand (COD) test is used in numerous laboratories to characterize wastewater and effluent. The COD reagent contains high concentrations of \( \text{H}_2\text{SO}_4 \) and \( \text{Hg}^{2+} \) and \( \text{Cr}_2\text{O}_7^{2-} \) salts. All treatment methods must first neutralize the \( \text{H}_2\text{SO}_4 \) and, if necessary, reduce the \( \text{Cr}_2\text{O}_7^{2-} \) to \( \text{Cr}^{3+} \). Neutralizing the acid and adjusting the pH to \( \text{pH} > 5 \) causes the precipitation of \( \text{HgO} \), which removes 96% of the \( \text{Hg} \). This agrees very well with the amount of precipitation predicted by chemical equilibrium calculations. Adjusting the pH to a value greater than 7 causes \( \text{Cr(OH)}_3 \) precipitation, which reduces the soluble \( \text{Cr} \) concentration to less than 100\( \mu \text{g L}^{-1} \) (a reduction of greater than 99.99%), in fair agreement with chemical equilibrium calculations. A method for precipitating the \( \text{Hg} \) as \( \text{HgS} \) is reported. Excess \( \text{Na}_2\text{S} \) is added to precipitate \( \text{HgS} \), then excess \( \text{Zn}^{2+} \) is added to precipitate the excess \( \text{S}^{2-} \). The \( \text{Hg} \) concentration in the filtrate is reduced to less than 3\( \mu \text{g L}^{-1} \) (a reduction of greater than 99.999%). There is no detectable odor of \( \text{H}_2\text{S} \). The mixed precipitate (\( \text{HgS} \), \( \text{ZnS} \), and \( \text{Cr(OH)}_3 \)) can be sent to a commercial \( \text{Hg} \) reprocessor.
INTRODUCTION

The chemical oxygen demand (COD) can be empirically related to the biochemical oxygen demand (BOD) for many waste streams or effluents. If the correlation can be established, then it is usually more convenient to measure COD than BOD because the COD test is much more simple and rapid than the BOD test (Greenberg et al. 1992). The BOD test simulates the effect of biodegradable wastewater or effluent on receiving water. It is an estimate of the amount of oxygen that would be consumed after the wastewater or effluent is discharged to a receiving stream. The COD test is also used to monitor the performance of wastewater treatment systems (Rich 1973).

The COD test involves adding a reagent containing sulfuric acid (H_2SO_4), dichromate (Cr_2O_7^{2-}), silver (Ag^+), and mercury (Hg^{2+}) to a wastewater or effluent sample, refluxing, and determining the Cr_2O_7^{2-} remaining by titration with Fe^{2+} or by colorimetry. The Cr_2O_7^{2-} in the COD reagent oxidizes most organic substances nearly quantitatively under the conditions of the test (high temperature, concentrated acid). However, Ag^+ is necessary to catalyze the oxidation of straight-chain aliphatic compounds, such as fatty acids. Chloride interferes with COD measurements by precipitating Ag^+ and catalyzing the oxidation of any ammonia. For chloride concentrations up to 2000mg/L, the interference can be largely overcome by adding a large excess of mercuric ion (Hg^{2+}) to complex the chloride (Cripps and Jenkins 1964, Burns and Marshall 1965, Dobbs and Williams 1963).

In the open reflux COD method, the concentrations of H_2SO_4, K_2Cr_2O_7, Ag_2SO_4, and HgSO_4 after mixing the COD reagent and sample are 9.0M, 0.0139M (0.72g Cr/L), 010163M (3.5g Ag/L), and 0.0225M (4.5g Hg/L). The waste from the COD determination is hazardous because it contains concentrated acid and high concentrations of the toxic metals Hg, Cr, and Ag. (Silver has been removed from the U.S.E.P.A. priority-pollutant list. However, it is still regulated in wastewater. For example, the Urbana-Champaign Sanitary District (UCSD) discharge standard for Ag is 0.3mg/L.) Because of its toxic properties, discharge standards for Hg are typically stringent. For example, the discharge standard for the Urbana-Champaign Sanitary District is 3 μg/L. The disposal options for COD testing waste, therefore, are to store the waste and have a hazardous-waste service dispose of it or treat it as it is generated.

If the COD procedure used involves determination of the excess Cr_2O_7^{2-} concentration by titration with Fe^{2+}, then the COD testing waste contains only Cr^{3+}. If the excess Cr_2O_7^{2-} is determined photometrically, then the Cr_2O_7^{2-} can be reduced to Cr^{3+}, which is not considered hazardous, by adding Fe^{2+}. There are several options for lowering the dissolved Hg concentration. Neutralization of the H_2SO_4 is necessary for all of them. The dissolved Hg concentration can be reduced to very low levels by precipitating the insoluble salt HgS.

The goal of the project was to develop an effective and convenient method to treat COD testing waste for safe disposal. The effectiveness and convenience criteria were a Hg concentration less than 3μg/L and no intermediate separation steps such as filtration (a "one
Precipitation of HgS was the basis of the procedure. Chemical equilibrium modeling and experiments were used to develop the treatment procedure. The modeling was used to design the experiments while the experimental data were used to test the model.

Clearly, if HgS precipitation is used to remove Hg, then an excess of sulfide over Hg must be added to attain the minimum dissolved Hg concentration. However, excess sulfide presents problems of its own. At high pH values, Hg^{2+} forms soluble complexes with the bisulfide ion (HS^-), the predominant form of sulfide, which greatly increases Hg solubility. At low pH values, Hg^{2+} complexation by HS^- is negligible, but the predominant form of sulfide is hydrogen sulfide (H_2S), which is volatile, toxic, corrosive, and has a strong, objectionable odor. It is difficult to adjust the pH to a value that minimizes both Hg and H_2S. However, as the present work shows, it is possible to add a metal ion that precipitates the excess sulfide after HgS precipitation. As a result, both Hg and H_2S are minimized.

Although removal of Hg from COD testing waste was the objective, some experiments using more dilute solutions were performed to test and validate the chemical equilibrium model. These experiments used 0.1M HNO_3 rather than 9M H_2SO_4 because activity coefficient calculations are generally valid only up to an ionic strength of 0.1M. Precipitation of HgO provided a useful test of the model because the equilibrium Hg concentration is in an easily measurable range. Precipitation of Cr(OH)_3 provided a useful test of the model, even though Cr^{3+} is considered non-hazardous. Even if the chemical equilibrium model were validated, experiments using synthetic COD testing waste were necessary because the effects of the high ionic strength and sulfate concentration on HgS precipitation kinetics were unknown.

Scope of the Problem

For wastewater known to have a low chloride content, Hg can probably be omitted from the COD reagent. However, most COD determinations probably use Hg to minimize any chloride interference. Discharge permits may specify the COD method and, therefore, the reagent composition. (Personal communication, J. Hall, Chairman, Subcommittee D19.06, Methods for Analysis of Organic Substances in Water, American Society of Testing and Materials, February, 1996). For example, some large food processing plants that discharge to the UCSD sewer system are required to perform daily COD testing and the COD reagent must contain Hg (Personal communication, J. Royer, UCSD, February, 1996).

The following information from two wastewater laboratories gives some indication of the amount of COD testing waste produced each year in the United States. The Los Angeles County Sanitation Districts (LACSD) use COD to characterize industrial wastes; sewer fees are based in part on the COD of waste streams. The LACSD laboratory performs approximately 10,000 COD determinations per year. Roughly one third of the samples are analyzed by the open-reflux method (Personal communication, R. Baird, Laboratory Director, February, 1996), for which the final volume (water plus reagents) is 150mL. The rest of the
LACSD COD determinations use the closed reflux method, for which the final volume is 7.5-30mL. Therefore, the total volume of COD testing waste generated by the LACSD laboratory in one year is 500-650L. The UCSD laboratory performs approximately 500 COD determinations per year using the closed-reflux method (10mL ampules), generating 5L of COD testing waste per year.

Previous Research on Treatment of Mercury-Containing Laboratory Wastes

Some papers on the treatment of laboratory wastes to remove Hg have been published, but few of them dealt specifically with COD testing waste. One paper on treating COD testing wastes was by Dean et al. (1971). They recommend sodium thiosulfate (Na$_2$S$_2$O$_3$) as a source of sulfide for treating Hg-containing laboratory wastes. They state that sodium sulfide (Na$_2$S) "should not be used [to treat COD testing waste] because the precipitate may redissolve in excess alkaline sulfides." Dean et al. (1971) listed several companies that would accept HgS for reprocessing. The ASTM (1987) method for treating Hg-containing wastes is essentially identical to that of Dean et al. (1971).

The procedures for total Kjeldahl nitrogen determination use HgSO$_4$ as a catalyst. Standard Methods (Greenberg et al. 1992), AOAC Official Methods of Analysis (Helrich 1990), and the Annual Book of ASTM Standards, Volume 11.01, Water (1987) all specify thiosulfate to precipitate HgS in the distillation step. Dillon et al. (1972) used "either Na$_2$S or Na$_2$S$_2$O$_3$" to precipitate HgS. They did not treat the excess sulfide. Mima (1974) used alkaline Na$_2$S to precipitate HgS from Kjeldahl nitrogen waste. The excess sulfide was oxidized by hydrogen peroxide. Hautala and McDonald (1978), found that neither Mima’s nor Dillon et al.’s methods could reduce the Hg concentration below the effluent standard of their state (50 µg/L). However, it is not clear whether the methods themselves were inadequate. They found that the pH for minimum soluble Hg concentration was in the range of 7-7.5. Gajda (1979) adapted the method of Hautala and McDonald (1978) to large volumes (100L) of laboratory wastewater.

Pragay (1975) suggested that Hg could be removed by pH adjustment and precipitation of mercuric oxide (HgO), although the Hg removal by this method is "far from quantitative". Pragay(1975) also suggested powdered zinc (Zn) could remove more than 99% of dissolved Hg$^{2+}$ by amalgam formation. However, for the pH suggested (6.0), much of the Hg$^{2+}$ in COD waste would be precipitated as HgO before addition of the Zn. The dissolved Hg concentration would therefore be determined by the relative rates of HgO dissolution and incorporation of the dissolved Hg in the Zn amalgam.

Lunn and Sansone (1994) recommend ion exchange using a strongly acidic resin in batch mode (suspending the resin and then filtering) for Hg removal from solution. They state that ion exchange in batch mode lowers dissolved Hg concentrations to approximately 1 mg L$^{-1}$. However, for ion exchange with a strongly-acidic resin, the pH must be greater than 4. ("Strong"-acid resins have pKa values in the range 3<pKa<4.) As shown in this report,
most of the Hg precipitates as HgO at pH 4. Therefore, ion-exchange treatment necessarily
involves HgO precipitation and filtration as a pretreatment step.

Metallic iron reduces Hg\textsuperscript{2+} to elemental Hg (Lunn and Sansone 1994). Passing a dilute
(<2.5 mg/L) Hg\textsuperscript{2+} solution through a column packed with powdered Fe lowers the Hg\textsuperscript{2+}
concentration to less than 5 \mu g/L. However, elemental Hg is slightly soluble in water (0.28
\mu M, 56 \mu g L\textsuperscript{-1}) (Windholz et al. 1983). Therefore, water treated with metallic Fe can be
aerated to remove the elemental Hg. But this is essentially changing a water pollution
problem into an air pollution problem. A Hg trap could be used in conjunction with aeration.
Proprietary absorbents for Hg vapor are commercially available.
METHODOLOGY

Equipment

Most of the experiments involved precipitation of HgS, HgO, or Cr(OH)₃. The general procedure involved pH adjustment, filtration, adding acid to preserve samples for later analysis, and determination of the dissolved Hg or Cr concentration. The equipment used for determination of dissolved metals depended on the specific experiment.

For the HgO precipitation experiments, the dissolved Hg concentration was determined by anodic stripping voltammetry (ASV) (Perone and Kretlow 1965, Luong and Vydra 1974). The equipment included a BAS-100 potentiostat (Bioanalytical Systems, West Lafayette, IN), EG&G-PAR 303A static mercury drop electrode system equipped with an EG&G-PAR glassy carbon electrode, and an EG&G-PAR 305 magnetic stirrer (EG&G Princeton Applied Research, Princeton, NJ).

For the HgS precipitation experiments, the dissolved Hg concentration was determined by cold-vapor atomic absorption spectrophotometry (CVAAS) (Hatch and Ott 1968). The equipment included a TJA Video-22e atomic absorption spectrophotometer and a TJA 440 vapor generation accessory (Thermo-Jarrell Ash, Franklin, MA).

Dissolved Cr³⁺ was determined by differential pulse voltammetry using the BAS-100 and EG&G-PAR 303A described above. The working electrode was a hanging Hg drop. The supporting electrolyte was 0.2M sodium thiocyanate and 0.2M acetate buffer (pH 3.2). The method of standard additions was used to determine Cr(III) concentrations.

The pH was determined using an Orion model 920 pH meter and a combination pH electrode (Orion model 8165BN). Solutions of Na₂S and Pb(NO₃)₂ were standardized by potentiometric titrations using Orion Ag⁺/HS⁻ and Pb²⁺ ion-selective electrodes (models 34117-077 and 948200). The Pb(NO₃)₂ solution was standardized with EDTA, while the Na₂S solution was standardized with the Pb(NO₃)₂ solution.

Procedures

Precipitation experiments were performed using synthetic COD testing waste or 0.1M HNO₃. The synthetic COD testing waste (9M H₂SO₄, 0.028M K₂Cr₂O₇, 0.02M HgO) was prepared using deionized water and reagent grade chemicals. The 0.1M HNO₃ solutions contained either 0.02M HgO or 0.028M Cr(NO₃)₃.

The pH was adjusted to approximately 10 for HgS precipitation and 7 for HgO and Cr(OH)₃ precipitation. For the dilute HNO₃ experiments, the pH electrode was calibrated using commercial buffers traceable to National Institute of Standards and Technology buffers.
For the synthetic COD experiments, the pH electrode was calibrated by measuring the potential in a 1.5M Na₂SO₄/0.001M HNO₃ solution and the electrode slope was assumed to be 58 mV per decade (Nernstian value at 20°C). For example, for a pH electrode potential in 1.5M Na₂SO₄/0.001M HNO₃ of 160 mV (typical value), the potential would have to be less than -72mV for pH>7.

Neutralization of COD testing waste (18M H⁺) by concentrated NaOH produces a large amount of heat. The standard enthalpy change for the reaction of aqueous H⁺ and OH⁻ to produce liquid H₂O is -13.343 Kcal/mol. With a 6-fold dilution of COD waste, the resulting temperature increase is approximately 40°C. However, boiling was observed when the NaOH was added too quickly, probably because mixing was not sufficiently rapid and there were large gradients in H⁺ and OH⁻ concentrations. Adding the NaOH over a 5-minute period avoided boiling. A large flask suspended in an ice bath was used for HgS precipitation. It was removed from the ice bath when the suspension of HgS cooled to 20°C. A jacketed beaker with cold tap water circulating in it was used for HgO precipitation from synthetic COD testing waste. Cooling by either method took 10-20 minutes. The pH electrode was inserted only after almost all of the H₂SO₄ had been neutralized. The first appearance of turbidity was a convenient indicator of neutralization.

For the HgO and Cr(OH)₃ precipitation experiments, the samples were filtered using 0.2μm cellulose-acetate syringe filters (Gelman) and a polycarbonate filter pump (Schleicher and Schuell). The syringe filters and filter pump were cleaned by filtering 50 mL of 1M HCl and three 50-mL volumes of deionized water. A filter blank (30 mL of deionized water filtered by the acid-cleaned assembly) was taken with every set of samples.

In the HgO precipitation experiments, two 30-mL samples were filtered immediately after pH adjustment and two more samples were filtered one hour after pH adjustment. The samples were acidified after collection by adding 0.5mL 10% Ultrex II HNO₃. The Hg concentrations in the filtrates were determined by ASV. A 0.5mL aliquot of sample was added to 4.5mL 0.1M NaSCN/0.01M HCl in the ASV cell. Quantitation was accomplished by the method of standard additions with correction for dilution. Small volumes of filtrate were required for ASV(0.5 mL per replicate), so the final suspension volume after NaOH addition in the HgO precipitation experiments was approximately 150 mL.

The sample collection procedure in the Cr(OH)₃ precipitation experiments was similar to that of the HgO experiments. One 30-mL sample was filtered immediately after pH adjustment and one more sample was filtered one hour after pH adjustment. The samples were acidified after filtration. The Cr(III) concentrations in the filtrates were determined by DPV. A 4mL aliquot of sample was added to 1 mL 1M NaSCN/1M acetate buffer (pH 3.2) in the ASV cell. Quantitation was by standard additions with correction for dilution.

After HgS precipitation, the suspensions were filtered through 0.2 μm polycarbonate filters (Nuclepore 111106) held in an acid-cleaned glass filtration assembly (Millipore XX10 047 00). The filtrates were preserved with 0.05% (by weight) K₂Cr₂O₇ and 5% (by volume)
HNO₃ (Feldman 1974). The Hg concentrations in the filtrates were determined by CVAAS. Large volumes of filtrate (50 mL per replicate) were required for CVAAS, so the final suspension volume in the HgS precipitation experiments was 1000 mL.

In the experiments involving synthetic COD waste, the waste was diluted by a factor of 6 (i.e., the final volume was 6 times the original volume) to avoid precipitation of Na₂SO₄·10H₂O (Glauber’s salt). (The reason for this is given in the results and discussion section.) The solubility of Na₂SO₄·10H₂O is 1.9M (Harvie and Weare 1980), while neutralization/dilution of COD waste by a factor of 6 gives a Na₂SO₄ concentration of 1.5M. The procedure of Dean et al. (1971, ASTM 1987) involves dilution by a factor of only 3.5-3.8.

The Na₂S solution was standardized by titrating with Pb(NO₃)₂, which was, in turn, standardized by titrating with standardized Na₂EDTA solution. The titrations were monitored with Ag⁺/HS⁻ and Pb²⁺ ion-selective electrodes with a double junction reference electrode (Orion). The endpoints were determined by the method of Gran (1952).

In experiments involving neutralized COD waste, the pH electrode was calibrated by measuring the potential of 0.0010M HNO₃/1.5M Na₂SO₄. The H⁺ concentration was then estimated by measuring the pH-electrode potential and assuming a slope of 58 mV/(log [H⁺]) (the theoretical value at 20°C).

**Modeling**

Chemical-equilibrium calculations were performed using the computer program Titrator (Cabaniss 1987). The stability constants for Hg²⁺-HS⁻ complexes were taken from Dyrsen (1988) and Dyrsen and Wedborg (1989). The solubility product of Cr(OH)₃ and the stability constants for Cr(III) species were taken from Rai and Zachara (1988). All other equilibrium constants were taken from Martell and Smith (1974).
RESULTS AND DISCUSSION

HgO Precipitation

Figure 1 shows the solubility of HgO as a function of pH for ionic strength 0.1M. The Hg solubility decreases by approximately 90% between pH 3 and pH 4. The total soluble Hg concentration (the sum of concentrations of all soluble Hg species) is essentially constant for pH values greater than 4, so fine adjustment of pH should be unnecessary for HgO precipitation.

![Graph showing solubility of HgO as a function of pH](image)

**Figure 1. Total soluble Hg in equilibrium with HgO as a function of pH.**

The solubility of HgO in 1.5M Na₂SO₄ (neutralized COD waste) is expected to be slightly less than in dilute solutions. The predominant Hg species for pH>4 is the neutral complex Hg(OH)₂⁰ (Figure 2). Combining the equations for HgO dissolution

\[ HgO(s) + 2H^+ \rightarrow Hg^{2+} + H_2O \quad (1) \]

and formation of the aqueous Hg(OH)₂⁰ complex
\[ Hg^{2+} + 2H_2O \rightleftharpoons Hg(OH)_2^0 + 2H^+ \quad (2) \]

gives the net equation for HgO dissolution for pH>4.

\[ HgO(s) + H_2O \rightleftharpoons Hg(OH)_2^0 \quad (3) \]

In equations 1-3 and all subsequent equations, the s in parentheses indicates a solid phase, \(H_2O\) is liquid water, and all other species are aqueous species. (Equation 3 describes the overall reaction, but not the intermediate steps.) Because \(Hg(OH)_2^0\) is uncharged, its activity coefficient is assumed to be 1.0 regardless of ionic strength (Stumm and Morgan 1981). The mass-action equation corresponding to equation 3 is given by equation 4, where braces indicate activities and

\[ K_s = \frac{[Hg(OH)_2^0]}{[H_2O]} \quad (4) \]

and \(K_s\) is the solubility product constant. The activity of pure \(H_2O\) is 1.00 by definition and is assumed to be 1.00 in dilute aqueous solutions. It is less than 1.00 in concentrated salt solutions. For example, the activity coefficient of water decreases from 1.00 in pure water to 0.62 in 1.5M \(Na_2SO_4\) (Robinson and Stokes 1959). Therefore, the concentration (equal to the activity) of \(Hg(OH)_2^0\) is expected to be approximately 38% lower in 1.5M \(Na_2SO_4\) than in 0.1M \(NaNO_3\).

![Diagram showing Hg speciation as a function of pH.](image)

Figure 2. Hg speciation as a function of pH.
Table 1 presents the results of the HgO precipitation experiments. For HgO precipitation from 0.1M HNO₃, the model calculation was very close to the experimental result. There was essentially no change in dissolved Hg after one hour, so the precipitation kinetics were rapid. The HgO solubility in diluted, neutralized COD waste was less than in 0.1M NaNO₃, in qualitative agreement with expectations.

### Table 1. Results of HgO precipitation experiments

<table>
<thead>
<tr>
<th>Initial Solution</th>
<th>Final pH</th>
<th>Dissolved Hg (mM) t = 10 minutes</th>
<th>t = 1 hour</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M HNO₃</td>
<td>6.9</td>
<td>0.43</td>
<td>0.40</td>
<td>0.44</td>
</tr>
<tr>
<td>0.1M HNO₃</td>
<td>7.3</td>
<td>0.55</td>
<td>0.52</td>
<td>0.44</td>
</tr>
<tr>
<td>COD*</td>
<td>7.1b</td>
<td>0.10</td>
<td>0.12</td>
<td>0.28</td>
</tr>
<tr>
<td>COD*</td>
<td>7.4b</td>
<td>0.14</td>
<td>0.13</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Notes:  
*a*Simulated COD waste.  
b*Estimated pH. See text.

Although HgO precipitation reduces the dissolved Hg concentration in treated COD waste by more than 99%, the amount precipitated is approximately 96% because of dilution. HgO could be precipitated from undiluted COD waste using concentrated NaOH (9M). This was tried and the result was a large volume (approximately half of the original sample volume) of needle-like Na₂SO₄·10H₂O crystals. The amount of Hg-contaminated solid material to dispose of would be much greater by this method than by precipitation of HgO alone. Dillon et al. (1972) advocate heating to avoid Na₂SO₄·10H₂O precipitation in treated Kjeldahl waste. They found that heating to 28°C prevented Na₂SO₄·10H₂O precipitation. However, if COD waste were neutralized with 9M NaOH without dilution, the final Na₂SO₄ concentration would be 3M. The enthalpy of dissolution of Na₂SO₄·10H₂O at 298°C is 19.987 Kcal/mol (Robie and Waldbaum 1968). Assuming the enthalpy is independent of temperature (van’t Hoff approximation, Moore 1962) and neglecting activity corrections, that solution would have to be heated to 39°C to avoid Na₂SO₄·10H₂O precipitation. Therefore, dilution seems to be more convenient than heating to avoid Na₂SO₄·10H₂O precipitation from COD waste.

HgO precipitation may be useful as the first step of a multi-step method to treat COD testing waste. Neutralizing the acid and precipitating most of the Hg may lower the price charged by a hazardous waste service to dispose of the treated waste.
Other bases besides NaOH can be used to neutralize the H₂SO₄ in COD waste. The use of surplus or technical-grade chemicals may lower the overall treatment cost. Carbonates or bicarbonates should be used with extreme caution because of the bubbling or foaming. Calcium hydroxide (lime) should not be used because of the precipitation of CaSO₄·2H₂O (gypsum). Lime was tried briefly in the present project because it is available in an inexpensive technical grade. However, the precipitate had nearly the volume of the waste and the consistency of whipped cream. It was nearly impossible to filter.

HgS Precipitation

Figure 3 shows the soluble Hg and H₂S concentrations in equilibrium with HgS for an excess of sulfide. The Hg concentrations are very low for pH<10. For pH>10, the Hg concentrations are high due to sulfide complex formation. The H₂S concentrations are fairly high for pH<9. It may be possible to achieve low concentrations of both Hg and H₂S by carefully optimizing the pH. However, if Zn²⁺ is added to precipitate the excess sulfide, then the system is insensitive to both pH and Zn (Figures 4, 5). When there is excess Zn, the predominant Hg species is Hg(OH)₂, so the dissolved Hg concentration is expected to be somewhat lower in COD waste than in dilute NaNO₃ as discussed in the section on HgO precipitation. Both Hg and H₂S are very low when Zn is in excess.

![Graph showing H₂S and Hg concentrations as a function of pH](image)

*Figure 3. Total soluble Hg and H₂S in equilibrium with HgS as a function of pH, total sulfide concentration 3mM.*
Figure 4. Total soluble Hg in equilibrium with HgS as a function of pH and total Zn, total sulfide concentration 3mM.

Figure 5. Concentration of H$_2$S in equilibrium with HgS and ZnS as a function of pH and total Zn, total sulfide concentration 3mM.
Table 2 presents the results of the HgS precipitation experiments. The Hg concentration was less than 5 μg L⁻¹ in all cases. The Hg concentration was essentially unchanged after one hour, so the precipitation kinetics were rapid. The filtrate was not analyzed for sulfide, but two facts indicate the sulfide concentration was very low. First, there was no detectable H₂S odor. Second, the recoveries of Hg spikes were nearly 100%. Sulfur compounds interfere in the determination of Hg by CVAAS (Kopp et al. 1972), so quantitative spike recoveries indicate low sulfide concentrations.

Table 2. Results of HgS precipitation experiments

<table>
<thead>
<tr>
<th>Initial Solution (0.0225M Hg)</th>
<th>Hg Concentration (μg/L)</th>
<th>Detection Limit</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t = 10 minutes</td>
<td>t = 1 hour</td>
<td></td>
</tr>
<tr>
<td>0.1M HNO₃</td>
<td>1.6</td>
<td>2.5</td>
<td>0.36</td>
</tr>
<tr>
<td>0.1M HNO₃</td>
<td>5.2</td>
<td>3.3</td>
<td>0.21</td>
</tr>
<tr>
<td>COD*</td>
<td>2.5</td>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>COD*</td>
<td>0.6</td>
<td>0.2</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Notes: 10<pH,11 in all experiments

*Simulated COD testing waste

bSamples were lost in a lab accident

The Hg concentration predicted by chemical equilibrium modeling was 2x10⁻¹⁶M (4x10⁻¹⁴g/L), while the measured Hg concentrations were approximately 1x10⁻⁸M. Clearly, agreement between theory and experiment was not as good as for HgO precipitation. Filtration blanks were collected along with and were treated identically to the samples. The filtration blanks, thus, were used to estimate the contribution of the overall process of filtration, preservation, and analysis to the observed Hg concentrations. The measured Hg concentrations were significantly greater than the detection limits estimated from the filtration blanks. (The detection limit is estimated from the standard deviation of the blank. (Anon. 1980). The variation of detection limits in Table 2 is the result of variability in the filtration blank.) Therefore, the Hg concentrations were “real”, i.e., not entirely an artifact of sample handling and analysis.

There are several possible explanations for the differences between predicted and measured Hg concentrations. The stability constants for Hg²⁺-HS⁻ complexes may be inaccurate. Dyrsen (1988) estimated the stability constants from Ag⁺-HS⁻ stability constants and correlation with Hg²⁺-dithizone extraction constants. The system may not have reached equilibrium. Even though the Hg concentrations were the same after one hour of stirring as
after a few minutes, much longer times may be necessary to reach equilibrium. A metastable amorphous HgS phase may have precipitated, which would have slowly recrystallized to the stable (and more insoluble) HgS phase. Amorphous, metastable precipitates are known for some metal ions (e.g., Fe(OH)₃) and the amorphous precipitates are more soluble than the well crystallized precipitates, but amorphous HgS is not mentioned in the available compilations of solubility products. Filtration may not have removed all of the solid HgS. Particles of HgS smaller than 0.2 μm in diameter may have passed through the filter. Regardless of the difference between predictions and results, the soluble Hg concentration was reduced by several orders of magnitude by HgS precipitation.

Using HgS precipitation followed by precipitation of the excess sulfide as ZnS, it may be possible to satisfy stringent Hg discharge standards. (The chemist should check with the local wastewater authority before discharging the filtrate to the sanitary sewer.)

**Cr(OH)₃ Precipitation**

Figure 6 shows the soluble Cr concentration in equilibrium with Cr(OH)₃ as a function of pH. Cr(OH)₃ precipitation reduces the Cr concentration by almost 5 orders of magnitude. Figure 7 shows Cr(III) speciation as a function of pH. The predominant Cr species for 7<pH<11 is the neutral complex Cr(OH)₃⁰. (It is interesting to note that the activity of the free Cr³⁺ ion corresponds to concentrations less than one ion per liter at high pH values. The total soluble Cr concentration, however, is much higher than that.)

Figure 6. Total soluble Cr³⁺ in equilibrium with Cr(OH)₃ as a function of pH.
The ionic strength is expected to have no effect on Cr(OH)$_3$ solubility for pH values between 7 and 11. In this pH range the predominant dissolved Cr species is the uncharged complex Cr(OH)$_3^0$ (Figure 7). Combining the equation for Cr(OH)$_3$ dissolution

$$\text{Cr(OH)}_3^{\text{solid}} + 3H^+ = \text{Cr}^{3+} + 3H_2O \quad (5)$$

with the equation for Cr(OH)$_3^0$ formation

$$\text{Cr}^{3+} + 3H_2O = \text{Cr(OH)}_3^0 + 3H^+ \quad (6)$$

gives the net equation for Cr(OH)$_3$ dissolution in the pH range $7 < \text{pH} < 11$.

$$\text{Cr(OH)}_3^{\text{solid}} = \text{Cr(OH)}_3^0 \quad (7)$$

The mass action equation corresponding to equation 7 is given by

$$K_{so} = [\text{Cr(OH)}_3^0] \quad (8)$$

The activity coefficient of Cr(OH)$_3^0$ is assumed to be 1.00 regardless of ionic strength because the complex is uncharged (Stumm and Morgan 1981). Therefore, Cr(OH)$_3$ solubility is assumed to be independent of ionic strength for $7 < \text{pH} < 11$. The solubility of Cr(OH)$_3$ increases somewhat at high pH due to the formation of Cr(OH)$_4^2$.

![Graph showing Cr$^{3+}$ species concentrations in equilibrium with Cr(OH)$_3$ as a function of pH.](image)

**Figure 7.** Cr$^{3+}$ species concentrations in equilibrium with Cr(OH)$_3$ as a function of pH.
Synthetic COD testing waste has a deep blue-green color which changed to green as the acid was neutralized (i.e., as the speciation changed from predominantly Cr$^{3+}$ to the hydroxo-complexes). (Figure 7) After Cr(OH)$_3$ precipitation and settling, the supernatant appeared to be colorless. After filtration and acidification, visible spectrophotometry confirmed that more than 99.9% of the Cr was precipitated, in qualitative agreement with the chemical equilibrium model. Table 3 presents the results of the Cr(OH)$_3$ precipitation experiments. Precipitation of Cr(OH)$_3$ from synthetic COD waste reduced the Cr concentration by at least four orders of magnitude. The exact reduction was less than in the 0.1M HNO$_3$ experiments, but it was hard to estimate because of analytical difficulties.

Table 3. Results of Cr(OH)$_3$ precipitation experiments

<table>
<thead>
<tr>
<th>Initial Solution (0.0139M Cr)</th>
<th>Cr concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
</tr>
<tr>
<td>0.1M HNO$_3$</td>
<td>10.0</td>
</tr>
<tr>
<td>0.1M HNO$_3$</td>
<td>10.2</td>
</tr>
<tr>
<td>COD$^a$</td>
<td>10.5$^b$</td>
</tr>
<tr>
<td>COD$^a$</td>
<td>10.1$^b$</td>
</tr>
</tbody>
</table>

Notes: $^a$Synthetic COD testing waste.
$^b$Estimated pH. See text.
$^c$See text.
$^d$Assuming no ionic strength effect. See text.

In differential pulse voltammetry (DPV), the potentiostat controls the potential of the working electrode relative to a reference electrode and measures the current flowing to or from the working electrode. The output is a plot of current as a function of potentials. If a reducible (or oxidizable) substance is present at a sufficiently high concentration, then DPV gives a peak-shaped output. The peak potential is characteristic of the substance being determined and the conditions of the determination (solution composition, temperature). The height of the peak is proportional to the concentration of the substance being determined (Bard and Faulkner 1980). DPV of Cr(III) in 0.1M NaNO$_3$ (produced by neutralizing a solution of Cr(NO$_3$)$_3$ in 0.1M HNO$_3$) was fairly straightforward, but synthetic COD testing waste proved to be problematic. Figures 8 and 9 show voltammograms of filtered samples from neutralized 0.1M HNO$_3$ and synthetic COD testing waste. Voltammograms are shown for the samples as taken and spiked with 2µM Cr(NO$_3$)$_3$ (104µg Cr/L). The difference between the spiked and unspiked peak currents was much greater for 0.1M HNO$_3$ than for synthetic COD testing waste, i.e., the sensitivity was much greater for HNO$_3$. For 0.1M HNO$_3$, the
peak potentials were in a relatively flat region of the baseline. Therefore, it was relatively easy to distinguish the peaks from the baseline. On the other hand, for synthetic COD testing waste, the peak potentials were in the curving part of the baseline. Therefore, it was difficult to pick small peaks out. There does not appear to be a detectable peak in the unspiked curve of Figure 9. The peak for the spiked curve is clearly higher than for the unspiked curve. Clearly, the Cr concentration in the treated synthetic COD testing waste was less than the spiked concentration of 104 µg/L. However, it is difficult to say how much less.

![Graph](image)

**Figure 8. Differential pulse voltammograms of Cr³⁺ in 0.1M NaNO₃.**

Determination of Cr in treated COD testing waste by inductively coupled plasma atomic emission spectrometry was attempted, but the concentrated salt extinguished the plasma. When the sample was diluted, the Cr was undetectable. High salt concentrations usually do not cause problems for electroanalytical methods such as DPV. The loss of sensitivity in treated COD testing waste was unexpected.

**Ag₂S Precipitation**

Like Hg²⁺, Ag⁺ forms complexes with HS⁻ and, as a result, the solubility of Ag₂S increases as pH increases in sulfidic solutions. Figure 10 shows that the addition of Zn²⁺ in excess of sulfide effectively limits the dissolved Ag concentration. The dissolved Ag concentration is relatively insensitive to pH or Zn as long as there is excess Zn. There were no experiments involving Ag. However, the chemical equilibrium modeling indicates that Ag concentrations in treated COD testing waste should be quite low.
Figure 9. Differential pulse voltammograms of Cr$^{3+}$ in neutralized synthetic COD testing waste.

Figure 10. Total soluble Ag in equilibrium with Ag$_2$S as a function of pH and total Zn, total sulfide concentration 3mM.
RECOMMENDED PROCEDURE

The recommended procedure for treatment of a small volume V (V ≤ 500 mL) of COD testing waste is as follows. Measure a volume 2V of water into an erlenmeyer flask large enough to contain 12V. Clamp the flask into an ice bath on a magnetic stirrer. Slowly pour the COD testing waste into the flask while stirring. Add 6M NaOH until the first sign of turbidity. The volume of NaOH used will be approximately 3V. (The NaOH concentration can be in the range 3-10M. The final volume of neutralized acid should be approximately 6V to avoid precipitation of Na₂SO₄.) The NaOH should be added over 5 minutes. Cool the mixture to 20-25°C and remove the flask from the ice bath. Insert a pH electrode. If necessary, add acid to adjust the pH to the range 2 < pH < 3. In a fume hood, add a two-fold molar excess of Na₂S over Hg. (The chemist should have a record of the Hg concentration if [s]he prepared the reagent. If a commercial reagent is used, then it is necessary to find out the Hg concentration.) Add NaOH to adjust the pH to a value greater than 10. Add a two-fold molar excess of ZnCl₂ over Na₂S. Allow the precipitates to settle. (Settling minimized the time spent filtering.) Decant, filter, and pour the filtrate down the drain (after checking with the local wastewater agency).

The recommended procedure is based on experience with precipitation and dissolution; dissolving a precipitate is often a slow process. The procedure is rationalized as follows. Adding Na₂S at low pH precludes HgO precipitation. If HgO were allowed to precipitate before Na₂S addition, then the rate of HgS precipitation may be limited by the rate of HgO dissolution. (It may be possible to combine the NaOH and Na₂S, which would simplify the procedure somewhat, but that was not tested.) Adding ZnCl₂ after Na₂S allows complete reaction of Hg²⁺ with HS⁻ before ZnS precipitation. Therefore, the HgS precipitation rate is not limited by the ZnS dissolution rate.
DISPOSAL OF MERCURY-CONTAINING PRECIPITATES

The mixed precipitate can be sent for reprocessing. Because of its volatility, Hg is readily separated from Cr(OH)₃ and ZnS. Dean et al. (1971) listed four companies that would accept HgS for reprocessing. One of them, Bethlehem Apparatus Company, has a new telephone number: 610-838-7034. Of the other companies, two could not be located and the other two no longer accept HgS in small quantities. Another company that currently accepts HgS is Advanced Environmental Recycling (610-797-7608). A chemical information line operated by the Chemical Manufacturers Association (800-262-8200) may provide leads to other companies that reprocess Hg.
ECONOMIC ANALYSIS

A recent price for the disposal of a 55-gallon drum of COD testing waste was $4,000 (P. Ashbrook, University of Illinois, Division of Environmental Health and Safety, personal communication). In this section an estimate of the cost of treating COD testing waste in the laboratory is presented. The method is intended for batches of 1L or less, so comparison of the price of treating small batches with the price of disposing of a large volume may not be valid.

The cost estimate (Table 4) includes chemicals, labor, and disposal/reprocessing costs. The chemical costs are from the Aldrich 1994-95 catalog. Some large organizations may have negotiated lower chemical costs with chemical vendors. Use of technical-grade or surplus chemicals may also reduce the chemical cost. The labor cost assumes a yearly salary of approximately $25,000. The time for allowing the precipitate to settle and to dry the precipitate is not included in the labor cost because the chemist can be doing other things. The reprocessing cost assumes a charge of $162. (Personal communication, Bethlehem Apparatus Co., February, 1996)

Clearly, it is more expensive to treat a large quantity of COD testing waste by the procedure described above than to have a commercial hazardous-waste handler take it away. The cost may not be strictly comparable to that of disposing of a large volume. Storing a drum of COD testing waste may have a cost, but it would be difficult to estimate it.

Continuous treatment may be more economical than batch treatment for large quantities of COD testing waste. Continuous treatment must neutralize the \( \text{H}_2\text{SO}_4 \), dilute to avoid the precipitation of \( \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \), dissipate heat, and precipitate HgS. Figure 10 shows how a system can be assembled using a peristaltic pump and condenser. If the COD testing waste flow rate is \( Q \), then the NaOH/Na\(_2\)S flow rate must be at least 5\( Q \) to achieve the minimum dilution of 1:6. The NaOH and Na\(_2\)S concentrations are 3.6M and 0.0075M. Zinc chloride can be added manually to the neutralized waste in the receiving vessel.

The use of a system like the one shown schematically in Figure 11 would reduce the labor cost of treating COD testing waste. The capital cost for new components is estimated to be $600 for the pump, tubing, condenser, ring stands, and clamps. Many of the components may be available in wastewater laboratories, which would reduce the capital cost. All of the components were available in the author’s laboratory. The system was tested by neutralizing 9M \( \text{H}_2\text{SO}_4 \) and was found to neutralize, dilute, and cool as expected.
### Table 4. Estimated cost of treating 55 gallons of COD testing waste in one-liter batches

<table>
<thead>
<tr>
<th>Chemicals</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amount of acid</strong></td>
<td>$55\text{gal} \times 3.78\text{L/gal} \times 18\text{ mol/L} = 3,742\text{mol}$</td>
</tr>
<tr>
<td><strong>Amount of NaOH</strong></td>
<td>$3,742\text{mol} \times 40\text{g/mol} = 149,688\text{g} \approx 150\text{kg}$</td>
</tr>
<tr>
<td><strong>Cost of NaOH</strong></td>
<td>$150\text{kg} \times $92.00/12kg $= $1,150.00</td>
</tr>
<tr>
<td><strong>Amount of Hg</strong></td>
<td>$55\text{gal} \times 3.78\text{gal/L} \times 0.0225\text{mol/L} = 4.68\text{mol}$</td>
</tr>
<tr>
<td>**Amount of Na}_2\text{S}</td>
<td>$4.68\text{mol} \times 2 \times 78\text{g/mol} = 449.3\text{g}$</td>
</tr>
<tr>
<td>**Cost of Na}_2\text{S}</td>
<td>$449.3\text{g} \times $9.25/kg = $4.16</td>
</tr>
<tr>
<td>**Amount of ZnCl}_2</td>
<td>$4.68\text{mol} \times 4 \times 136.28\text{g/mol} = 2,551\text{g}$</td>
</tr>
<tr>
<td>**Cost of ZnCl}_2</td>
<td>$2,551\text{g} \times $25.40/500g = $129.60</td>
</tr>
<tr>
<td><strong>Total Chemical Cost</strong></td>
<td>$1,283.76</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Labor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number of batches</strong></td>
<td>$55\text{gal} \times 3.78\text{L/gal} = 208\text{L}$</td>
</tr>
<tr>
<td><strong>Time per batch</strong></td>
<td>Set-up 45min. Neutralize acid, cool 30min. Precipitate 5min. Decant, filter 40min. Total 2hr.</td>
</tr>
<tr>
<td><strong>Labor cost</strong></td>
<td>$2\text{hr/L} \times 208\text{L} \times $12.00/hr = $4,992.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disposal/Reprocessing</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>**Amount of Cr(OH)}_3</td>
<td>$55\text{gal} \times 3.78\text{L/gal} \times 0.0139\text{mol/L} \times 103\text{g/mol} = 298\text{g}$</td>
</tr>
<tr>
<td><strong>Amount of HgS</strong></td>
<td>$55\text{gal} \times 3.78\text{L/gal} \times 0.0225\text{mol/L} \times 233\text{g/mol} = 1,090\text{g}$</td>
</tr>
<tr>
<td><strong>Amount of ZnS</strong></td>
<td>$55\text{gal} \times 3.78\text{L/gal} \times 0.0225\text{mol/L} \times 97\text{g/mol} = 454\text{g}$</td>
</tr>
<tr>
<td><strong>Total solid material</strong></td>
<td>$1.842\text{kg} \times 2.205\text{Lb/kg} \approx 4\text{Lb}$</td>
</tr>
<tr>
<td><strong>Cost of Disposal/Reprocessing</strong></td>
<td>$162 \text{ for up to 25Lb}$</td>
</tr>
<tr>
<td><strong>Total Cost</strong></td>
<td>$6,437.76</td>
</tr>
</tbody>
</table>
Figure 11. Apparatus for continuous treatment of COD testing waste (schematic, not to scale).
CONCLUSIONS

The soluble Hg concentration in COD testing waste can be lowered to less than 3 \( \mu \text{g/L} \) by precipitation of HgS. There are two potential problems with HgS precipitation. At low pH, the excess sulfide is mostly in the form of H\(_2\)S, a toxic, malodorous, corrosive gas. At high pH, complexation of Hg\(^{2+}\) with HS\(^-\) dramatically increases Hg solubility. Addition of Zn\(^{2+}\) in excess of Na\(_2\)S precipitates the excess sulfide as ZnS. HgS is much less soluble than ZnS, so excess Zn\(^{2+}\) does not solubilize any Hg. Addition of Zn\(^{2+}\) reduces concentrations of H\(_2\)S at low pH values and of Hg at high pH values to very low levels. The HgS can be sent to a mercury reprocessor for recycling. The waste must be diluted by a factor of 6 to avoid precipitation of Na\(_2\)SO\(_4\)·10H\(_2\)O. If Na\(_2\)SO\(_4\)·10H\(_2\)O does precipitate, then a larger amount of Hg-containing solid material must be disposed of.

Chemical equilibrium calculations agreed qualitatively with the results of HgS precipitation experiments. The Hg concentration was reduced by several orders of magnitude and ZnS precipitation reduced the sulfide concentration to an undetectable value. However, the measured soluble Hg concentrations were greater than the predicted concentrations.

The amount of soluble Hg in COD testing waste can be reduced by 96% by precipitation of HgO. The Hg concentration is close to that predicted by chemical equilibrium calculations. The soluble Hg concentration should be independent of pH for pH>5. Therefore, careful adjustment of the pH is unnecessary. The HgO can be sent to a mercury reprocessor for recycling.

The amount of soluble Cr in COD testing waste is reduced by more than 99.99% by Cr(OH)\(_3\) precipitation. The pH range for minimum Cr solubility is 7<pH<11. There was fair agreement between chemical equilibrium calculations and Cr(OH)\(_3\) precipitation experiments.

Precipitation of HgO, HgS, and Cr(OH)\(_3\) is rapid. The treated waste can be filtered within minutes of pH adjustment or reagent addition.
ADDITIONAL CONSIDERATIONS

Before using the treatment method described above (or any other method), the chemist must determine whether such treatment is legal. Current federal regulations seem to allow on-site treatment and shipping the byproduct of the treatment to a Hg reprocessor. (Anonymous 1994) Most laboratories that do COD testing probably qualify as conditionally exempt small quantity generators. A laboratory “... is a conditionally exempt small quantity generator in a calendar month if [it] generates no more than 100 kilograms of hazardous waste in that month.” Such facilities may be allowed to treat hazardous wastes on-site. “A conditionally exempt small quantity generator may either treat or dispose of his acute hazardous waste in an on-site facility or ensure delivery to an off-site treatment, storage, or disposal facility, either of which, if located in the U.S., is ... [a] facility which [b]eneficially uses or reuses, or legitimately recycles or reclaims its waste ... .” Acid neutralization and HgS precipitation is the on-site treatment. The commercial Hg reprocessor is the facility that beneficially reclaims the waste. However, even if federal regulations allow on-site treatment of COD testing waste, state or local regulations may prohibit it.

Clearly, eliminating Hg from the COD determination is preferable to treating the COD testing waste. Baumann (1974) showed that the chlorine produced by the oxidation of chloride can be determined by distillation and titration with thiosulfate. The apparent COD can be corrected after determination of the chlorine. However, COD determinations would be more laborious by this method. Korenaga et al. (1993) developed a COD method that uses Ce(IV) as the oxidant rather than Cr_2O_7^{2-}. Their method tolerates high chloride concentrations (up to 30g/L) with no masking agent. It may be possible to use an instrumental method like total organic carbon instead of COD if a suitable correlation with BOD can be developed. If elimination of Hg from the COD reagent or using an instrumental method instead of the “wet-chemical” COD test are infeasible, then use of the closed-reflux COD method in place of the open-reflux method would reduce the volume of Hg-containing wastewater by a factor of 5-20.
REFERENCES


Anonymous. 1994. 40 CFR Chapter 1, Section 261.5.


