

Mercury: Real Problems...Not Roman Mythology

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ABSTRACT

Some crude oils can contain a variety of mercury compounds: elemental mercury; mercuric chloride; mercuric sulfide; mercuric selenide; dimethylmercury; diethylmercury, etc., which can be damaging to refinery equipment and the environment. Mercury can also be a chemical component of a variety of complex asphaltenic and sulfur-containing compounds. It is important to understand that several of these mercuric compounds are volatile and can be distributed to refined products that can potentially impact product quality. Furthermore, mercury and mercuric compounds will also transition into the water phase. Removal of mercury in both of these phases represents some difficulties particularly with environmental discharge limits becoming more stringent.

This talk will focus primarily on chemical agents and aspects of mercury removal in the water environment as well as examining the chemical mechanisms of mercury complexation techniques.

INTRODUCTION

Mercury in Roman mythology was a major god of trade, profit and commerce. The word *mercurial* is commonly used to refer to something erratic, volatile or unstable. Hat makers long ago used mercury to in their work to make particular designs the hat maker wanted. As the hat maker's career progressed, he became more erratic, volatile or unstable. These symptoms as a result of mercury poisoning, have led to the banishment of most elemental mercury applications today as this element is being heavily regulated as an environmental and human safety hazard.

Increasing environmental concerns about heavy metal discharge have continued to fuel tightening metals discharge limits for oilfield production and refineries. Meeting lower limits will necessitate making changes to existing wastewater treatment systems and plant operations. For oil production and refinery applications, mercury and selenium are two very problematic metals to remove in the purification of industrial wastewater due to the low limits being specified, 50 parts per billion (ppb) or less.

Regulatory issues include the following for water, air and solid waste: Clean Water Act (CWA, Section 304), Total Maximum Daily Load (TMDL), Clean Air Act of 1990 (CAA, Section 112), National Emission Standards for Hazardous Air Pollutants, (NESHAP), Maximum Available Control Technology (MACT), and Resource Conservation and Recovery Act (RCRA).

The amount of mercury (1,2) in crude oil varies for 0.1 ppb to 3 parts per million (ppm) and when crude oil comes into contact with water, an entry of mercury into water-phase is introduced. Production of crude and natural gas also produces water. At most production sites, there are facilities for the separation of gas, oil and water. This "produced" water will have a variety of contaminants, including oil, sand, inorganic materials such as iron, sodium chlorides, hydrogen sulfide, and other salts and heavy metals such as nickel and mercury. Depending on the EPA, State and Local regulations, the produced water will have to be purified before being discharged in the environment. Wilhelm and Kirchgessner (2) have a review concerning discharging produced water for both onshore and offshore production facilities.

A second entry of mercury into water comes from refinery processes. In desalting applications, a small percentage of water (from 3 to 6% of the crude charge) is mixed with the crude feed slate of the desalter. Resolution of the emulsion is accelerated through the use of temperature (up to 275°F), an electric field (16,000 to 20,000 volts), and chemical demulsifier. With the water and crude oil being thoroughly mixed, this allows mercury to be transferred into the water phase. The mercury must then be removed before being discharged into the environment.

WHY TREAT METAL BEARING WASTE STREAMS?

Metals do not degrade readily in the environment and, therefore, are highly persistent. A number of heavy metals are human carcinogens and also have adverse effects on animals. Furthermore, metals can bioaccumulate in aquatic organisms and plants, posing a threat throughout the food chain. Some metals, such as arsenic, chromium and mercury, are readily transformed among various oxidation states, increasing their mobility in the environment. Human exposure pathways for metals include inhalation of dusts and fumes and ingestion of contaminated food, soil, ground water or surface water.

The metals occurring in waste streams that are listed as hazardous are:

Antimony	Chromium	Nickel
Arsenic	Cobalt	Silver
Barium	Copper	Selenium
Beryllium	Lead	Vanadium
Cadmium	Mercury	Zinc

PARTICULATE METALS REMOVAL

All discharge permits are based on total metals in the plant effluent. However, for treatment purposes, it is important to determine soluble and insoluble, or particulate, metals in the waste stream for treatment. In most applications, both particulate and soluble metals are present and must be removed at the same time.

In wastewater treatment applications, chemical treatment is used to remove oils, solids, and other contaminants. These chemicals have a cationic charge to neutralize the anionic charges on the surface of the contaminants. When there are heavy solids loading and/or hydrocarbons in wastewater, a large demand for cationic charge by the anionic surfaces of the particles is usually warranted. Since heavy metal removal agents are usually cationic in nature, they may be consumed by the solids and not be available to remove soluble metals. Thus, in applications with high solids and/or hydrocarbons, it is often more cost effective, first, to remove the solids and particulate metals with a coagulant (cationic) product, and then second, use the metal removal agent for soluble metal ion precipitation.

Other interferences for heavy metal removal operations include emulsion-stabilizing agents such as detergents and other water-soluble organics requiring a high cationic charge demand. Again, it may be necessary to pre-treat the water to remove charge demand before removing the heavy metals with a metal removal agent.

Table 1 gives a quick comparison of available precipitation technologies commonly employed today for soluble metal removal.

PRECIPITATION

The most widely used process for the removal of heavy metals from waste streams is chemical precipitation. This method is used by approximately 75 percent of the facilities that treat aqueous metal-bearing wastes. Chemical precipitation exploits the low solubility of certain metal complexes in solution that can be described by the following mathematical expression:



where $n = 2, 3, 4$, etc., the brackets indicate molar concentrations, M is the metal species, L is the ligand, and K_{sp} is the solubility product. The smaller the K_{sp} , the greater the tendency for the metal-ligand complex to be insoluble. The precipitation reaction involves the alteration of the ionic equilibrium of the metal ion to produce an insoluble metal complex.

Chemical precipitation treatment depends upon one or more of the following variables: 1) maintenance of an alkaline pH through the precipitation reaction and subsequent settling; 2) addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion; 3) addition of an adequate supply of sacrificial ions (such as iron or aluminum) to ensure precipitation and removal of specific target ions; and 4) effective removal of precipitated solids.

Precipitation techniques currently being practiced on aqueous metal wastes include hydroxide (e.g. caustic or lime), sulfide, and carbonate precipitation processes. Hydroxide precipitation is effective in removing arsenic, cadmium, chromium III, copper, iron, manganese, nickel, lead and zinc. Sulfide precipitation is highly effective in the removal of cadmium, cobalt, copper, iron, mercury, manganese, nickel, silver, tin and zinc. Carbonate precipitation is effective in removing cadmium, nickel, and lead at a slightly lower pH than either hydroxide or sulfide techniques. Each of these processes has been reviewed in the literature (3).

SMALL ORGANIC PRECIPITANTS

Small molecule organic precipitants such as alkyl dithiocarbamates (DTC), trimercaptotriazines (TMT) and trithiocarbonates (TTC) are used extensively in the metal finishing and electronics industries in the U.S. These precipitants react stoichiometrically with metal ions and show similar characteristics in use. In our discussion, we will use DTC as an example, keeping in mind that TTC and TMT show similar characteristics.

In treating dilute rinse waters containing low concentrations of metals, say below 50 ppm (mg/L), the resulting metal-DTC complexes form colloidal particles in suspension, i.e. particles that will not settle in a reasonable period of time. In some wastewaters, these particles are so small that they appear only as color, carrying metal ions into the effluent. Thus, sufficient removal of metal ions from plant effluent necessitates the practice of appropriate coagulation/flocculation techniques for colloidal suspensions.

Small organic molecule precipitation is difficult to optimize. This is because most wastewaters contain dispersants such as dissolved oils, organics and surfactants. These dispersants inhibit the aggregation of particles, increasing the dosage requirements for coagulants and sometimes, flocculants. Since these precipitants are negatively charged molecules, product overfeed tends to disperse the precipitate particles. In applications where the initial metals levels are less than 5 ppm, it is more difficult to achieve discharge limits using small molecule precipitants.

To summarize, disadvantages are:

1. Difficult to optimize coagulation/flocculation
2. Not effective for low-level metal removal.

POLYMER PRECIPITATION – NALMET®⁶ 8702

A polymeric precipitant (Figure 1) reacts with soluble metals to form insoluble complexes with the same mechanism as the small molecule organic precipitants (Figure 2). However, because the metal binding groups are bound to a polymer (4), simultaneous metal precipitation and clarification occurs. Using this class of chemicals allows good solids/liquid separation and may not require optimization of a second chemical. This is dependent on the wastewater equipment in the system (typically clarifiers) as well as adequate retention time. In some applications, the clarifier effluent is sent to filters before discharge.

The NALMET product line is designed to react and remove a variety of heavy metals from wastewater, as shown in Table 2. More importantly, mixed metal contamination is not a problem using NALMET due to the chemical's ability to complex at pH as low as 7 to and as high as 9. This is vastly different than hydroxide precipitation where the solubility of the different metal hydroxides varies with pH, as shown in Figure 3. For example, a wastewater contains 10 ppm Cu, 5 ppm Ni, and 4 ppm Zn. The calculated theoretical dosage for NALMET 8702 is: $(10 \times 19.0) + (5 \times 20.7) + (4 \times 18.5) = 367.5$ ppm.

NALMET removes the monovalent metals first, followed by divalent, as shown below. The metals are removed in descending order. Some overlap in selectivity does occur, especially when one metal is predominant in a waste stream.



Mercury, in its various forms, has a great affinity for certain minerals, as well as protein and non-protein molecules in the body. Mercury (I) or (II) have a great attraction to the sulfhydryls or thiols. The mercury atom or molecule will tend to bind with any molecule present that has sulfur or a sulfur-hydrogen combination in its structure (5). For these reasons, NALMET reacts more rapidly with Hg (I) and Hg (II) than with other soluble metals, as shown in the list above.

Mercury in Refinery Wastewater

Most, if not all, of the mercury in refinery wastewaters is derived from crude oil (1). In desalter applications, water is mixed with the crude to help remove inorganic chlorides from the crude. If chlorides are not removed, then in downstream processes, gaseous hydrogen chloride is formed leading to severe corrosion. Furthermore, more than just chlorides are moved from the oil phase to the water phase. Other contaminants include oil from poor oil/water separation, solids, inorganic salts, inorganic mercury compounds, elemental mercury, as well as other heavy metals such as iron or lead. The spent desalter washwater called "brine" is then sent to the refinery's wastewater treatment plant.

The wastewater treatment plant (WWTP) must now remove the contaminants not only from the desalter brine, but also from all other wastewater sources such as cooling water blowdown, tank bottoms, stormwater runoff, etc. However, in nearly all cases, the refinery's largest contaminant in the water is crude oil. Desalter operations are optimized to limit the amount of oil in the wastewater. However, 5% washwater for 200,000 barrels of crude is still 420,000 gallons of water per day, not including any other process water streams. If the oil level in the desalter brine is 1000 ppm (0.1%), this is still **420 gallons of oil to the WWTP per day!**

Based on experimental data from our laboratory, agitation between the water and oil phases in the desalter is necessary to remove not only chlorides **but** also mercury compounds. Thus, the WWTP will not only have to remove the oil, but also mercury before discharging to the environment.

The effect of mercury being transferred from the oil phase to the water phase was examined in the laboratory to simulate the effects of the mixed valve in the desalter crude unit. As agitation is increased, the amount of total mercury in the water phase also increased, as shown in Table 3. Even very gentle agitation "rolls" removed one-third of the mercury from the oil

phase. As the agitation becomes more severe, up to two-thirds of the mercury is transferred. Based on these results, it is important for the refinery to optimize the removal of chlorides as well as mercury from the crude oil. However, it must be acknowledged that deionized water was used, and that different sources of washwater may limit mercury transfer.

Using NALMET 8702 on water samples containing HgCl_2 and Hg_2Cl_2 blend (500 ppb each), it was found that 6.0 ppm of chemical can precipitate 80% or 800 ppb. Higher dosages of 12 ppm gave 90% removal (100 ppb), and 18 ppm, 98% removal, (20 ppb).

Mercury Removal Experience

Currently Nalco is treating two solid waste incinerators in Europe and the quench water contains 720 ppb and 210 ppb mercury. Applying NALMET 8702 at a pH between 7-8 gives the following results:

Unit No. 1	Inlet 720 ppb	outlet 16 ppb	NALMET 8702: 15 ppm
Unit No. 2	Inlet 210 ppb	outlet 12 ppb	NALMET 8702: 25 ppm

This water contains no oil and is fairly clear prior to treatment. NALMET 8702 is fed upstream of the clarifiers, passed through small mixing chambers and sent to clarifiers for settling. An anionic flocculant is used as needed to help settling the precipitate. The water is then sent to multimedia filters to remove any small particles. The water is discharged meeting the >25 ppb specification.

We have several oil platforms in Southeast Asia that are using NALMET 8702 to remove mercury from their wastewater stream.

SUMMARY

NALMET 8702 is used to remove +1 and +2 heavy metals from wastewater streams in a variety of industrial applications. In particular, oilfield production in Southeast Asia and refineries using crude oil from Southeast Asia can have difficulty with mercury in the oil and wastewater applications. Polymeric dithiocarbamates, NALMET 8702 can remove mercury from the wastewater by precipitation, meeting the discharge specifications and allowing for the treated wastewater to be discharged to the environment.

Table 1. Comparison of Commercial Metal Precipitant Chemistries

	NALMET 8702	OH	Na ₂ S	FeSO ₄	DTC	TTC	TMT	Ven Met
Chemical Cost	high	low	low	low	mod	mod	high	high
Sludge Disposal Cost	mod	high	high	high	mod	mod	mod	low
Treat Chelated Metals?	yes	no	no	maybe	yes	yes	maybe	yes
Low Levels?	yes	maybe	maybe	maybe	maybe	maybe	maybe	maybe
Mixed Metals?	yes	maybe	maybe	maybe	yes	yes	yes	maybe
Solid/Liquid Separation	easy	tough	tough	tough	tough	tough	tough	tough
Toxicity of product	mod	non toxic	human toxic	mod	high	mod	low	human toxic
Automation Available?	Nalmet 2000	pH	no	no	ORP	ORP	ORP	ORP
Ease of use	easy	easy	hard	hard	hard	harder	hard	hard

OH = hydroxide precipitation
DTC = alkyl dithiocarbamate
TTC = trithiocarbonate
TMT = trimercaptotriazine
Ven Met = sodium borohydride

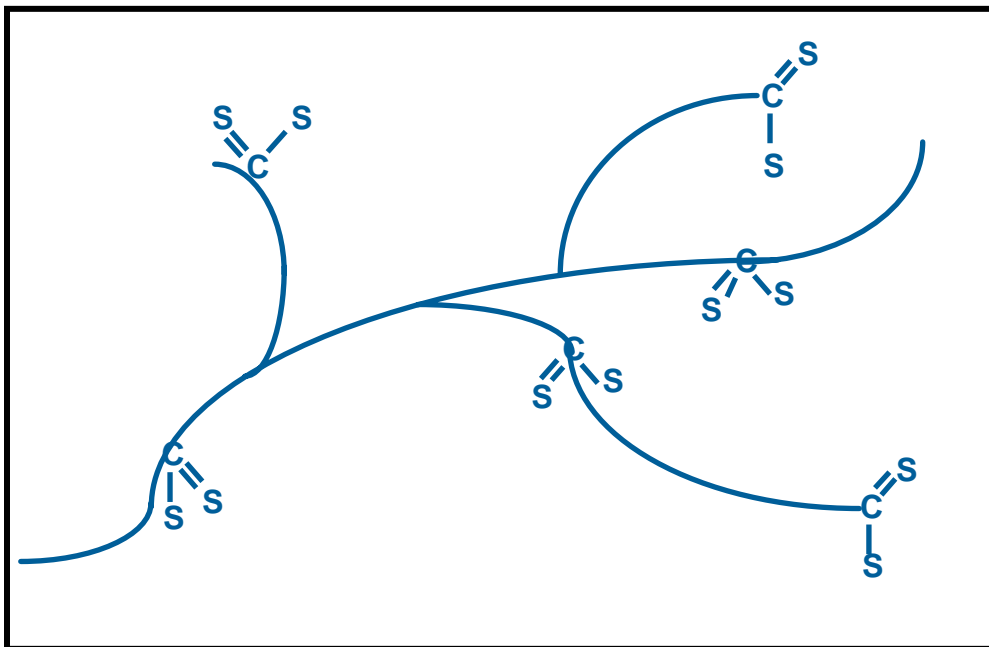


Figure 1. CS₂ Modified Polymer Backbone

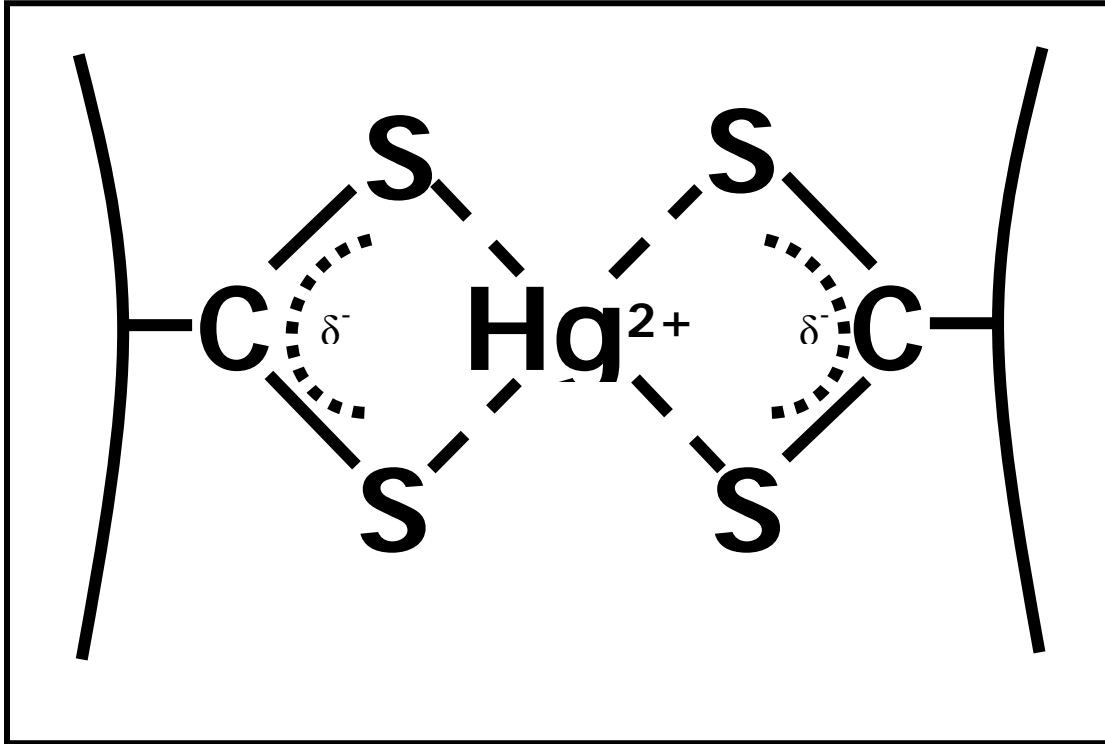


Figure 2. Metal Complex Schematic of Small Molecule and Polymeric Dithiocarbamates

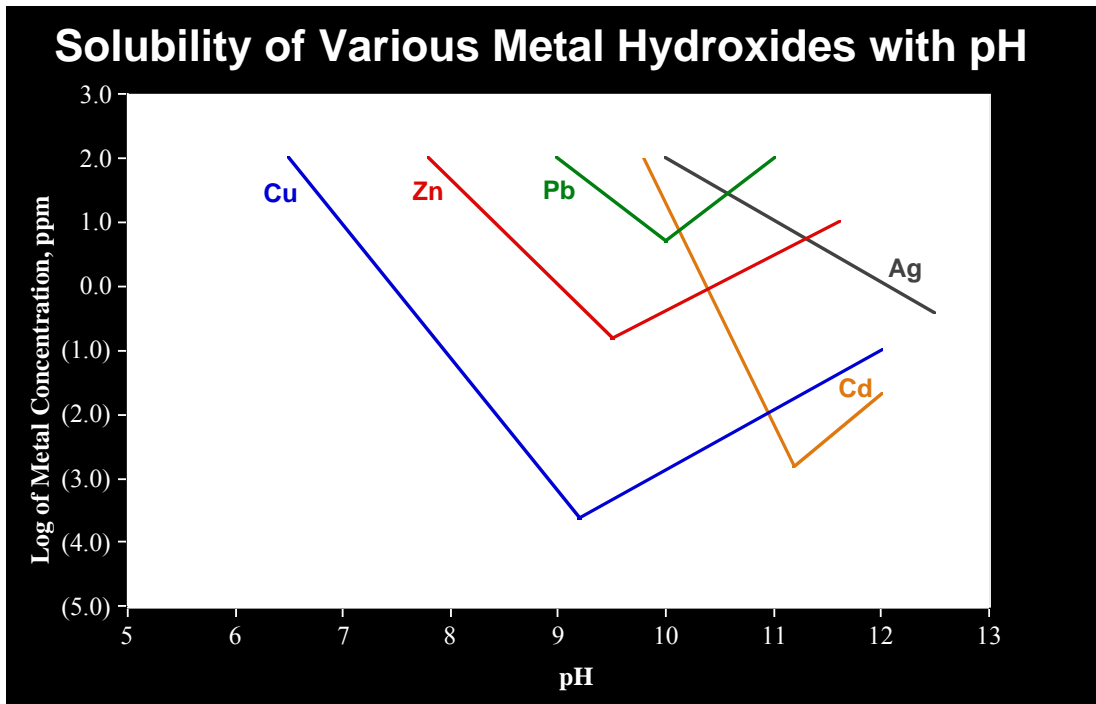


Figure 3. Solubility of Various Metal Hydroxides with pH (3)

Table 2. NALMET® Dosage needed to remove 1 ppm Metal.

Element	8702 ppm
Copper (Cu)	19.0
Lead (Pb)	5.9
Nickel (Ni)	20.7
Zinc (Zn)	18.5
Mercury (Hg (II))	6.0
Selenium (Se (II))	20.0
Silver (Ag)	5.6
Cadmium (Cd)	10.8
Iron (Fe(II))	21.7
Manganese (Mn)	22.0
Cobalt (Co)	20.6
Tin (Sb (II))	10.2

Table 3. Agitation studies for Mercury Removal from the Oil Phase

Hg ppb in Oil	Comments
1081.1	Raw Crude
607.7	20 very slow rolls
606.4	20 medium rolls
605.9	20 hard shakes
371.4	200 hard shakes
373.3	30 minutes on shaker "High"

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5. Oji, L.N. “Mercury Disposal Via Sulfur Reactions,” *Journal of Environmental Engineering*, **124**, 945-52 (1998).
6. NALMET is a registered trademark of Nalco Company.