A Non-toxic Alternative to Metal Precipitation

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Faced with the proposed MP&M standards, many finishers may have to consider new technologies to treat various waste streams in order to meet lower soluble metal limits in effluent. Chemical treatment beyond the standard hydroxide precipitation steps using metal precipitants may provide a viable option. Many of the precipitating agents on the market have been used effectively for many years, however, the toxicity and handling of these compounds must be considered when choosing the best precipitant for metals removal. Some recent, well-publicized spills show the potential hazards associated with some of these commonly used compounds. TMT (trimercapto-s-triazine, trisodium salt) is a non-toxic metal precipitant that effectively precipitates most metals, even metal complexes, in acidic or alkaline solutions. It is presently being used in many industries, including waste incineration, photochemical, mining, chemical synthesis, and metal finishing. This paper will discuss the characteristics of TMT and TMT metal precipitates, the relative benefits over other metal precipitants, as well as the best applications of this product.

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The removal of heavy metals from effluents before discharge to the environment has long been a requirement for virtually all industries, and for good reason. Many of these metals, such as mercury, lead, cadmium, copper, nickel, zinc and silver, found in metal processing effluents are toxic and pose a potential threat to the environment. Most of these metals, especially the more common nickel, copper and zinc, can be efficiently removed by the traditional addition of alkali followed by the removal of the resulting insoluble metal hydroxide salts. However, the presence of complexing agents may require the use of other metal removal processes to achieve the desired soluble metal limits. Also, the reduction of the permissible heavy metal concentration in the effluent may force the use of precipitating agents to produce more stable precipitates.

By producing more stable and less soluble precipitates, the use of sulfide based precipitating agents can keep the insoluble heavy metal salts from redissolving, even in the presence of chelating compounds, thereby meeting the low limits required for discharge. This can be done in addition to a hydroxide precipitating stage or separately. The relative stability of TMT metal precipitates over hydroxides is shown in Figure 1. The solubility products for many sulfur based precipitating agents are in the same range.

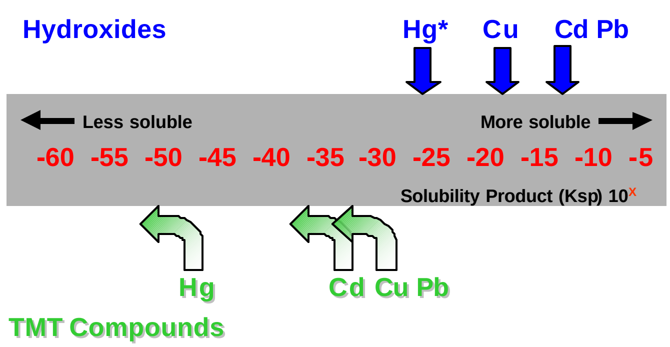


*Figure 1. -Solubility Product, Ksp (Ksp = $[Cations]^A$ x $[Anions]^B$ where A,B are the stoichiometric factors for the anion, cations, respectively) for hydroxide and TMT metal salts. *Hg does not form a hydroxide*

Other processes can be used such as ion exchange, electrolysis and the use of strong oxidizers to treat complexing agents. However, these processes may not be economically feasible for many effluents, and may require substantial capital investment.

Commonly used sulfide based precipitating agents include:

- Sodium sulfide, Na_2S
- Dithiocarbamates, DTC
- Trithiocarbonates, Na_2CS_3
- Trimercaptotriazine, TMT

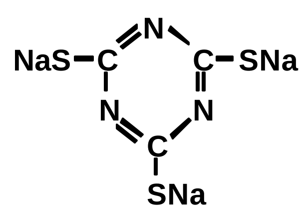
When choosing a precipitation agent, there are a number of factors that one must consider:

1. Effective and economical removal of metals
2. Stability of the precipitate produced
3. Toxicity of the precipitating agent

TMT works economically and efficiently over a broad pH range, producing an easily removed and stable precipitate. Because TMT is not toxic, it does not require treatment before discharge to the environment.

TMT: Product Description

Trimercapto-s-triazine trisodium salt, or TMT, is available as a 15% solution or a 55% salt. The structure is shown below:



Pertinent product data:

CAS #	17766-26-6
Molecular weight.	143.22 g/mol
Odor	Virtually none
TMT 15 pH	approx. 12.5
TMT 15 density	1.12 g/mL

The sulfur groups are the active sites that bond to the metal ions. For divalent metal ions, a 3:2 molar ratio of the metal(M) to TMT is required:

Equation 1: $3M^{2+} + 2TMT^{3-} \rightarrow M_3TMT_2$

For monovalent ions, a 3:1 molar ratio of the metal(M) to TMT is required:

Equation 2: $3M^{+} + TMT^{3-} \rightarrow M_3TMT$

Most transition metals form an insoluble TMT – metal complex. However, some trivalent metals, as shown in Table 1, do not.

Table 1. Application of TMT	
Metals that do precipitate	Metals that do not precipitate
Cadmium (Cd) Copper (Cu) Lead (Pb) Mercury (Hg) Nickel (Ni) Silver (Ag) Tin (Sn) Zinc (Zn)	Aluminum (Al) Chromium (Cr) Iron (Fe)

Figure 2 shows the addition rates of TMT for the various metals that form insoluble TMT complexes. The different addition rates are a function of the molecular weights of the metals, and are given in terms of liters of TMT 15 per kilogram of metal.

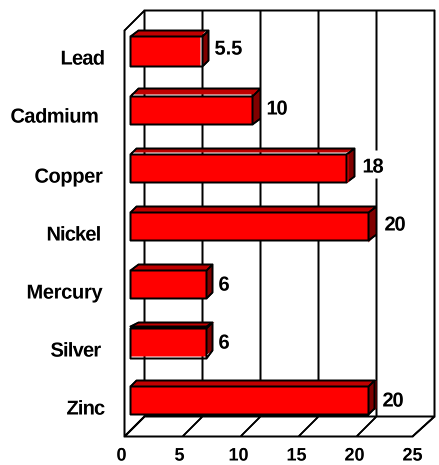


Figure. 2 –TMT addition requirements for various metals in terms of liters of TMT 15 per kilogram of heavy metal. For gallons TMT 15 per pound of heavy metal, multiply the number from the chart by 0.120.

TMT-metal sludges exhibit excellent chemical and thermal stability and may be acceptable for non-hazardous landfills[1]. Table 2 shows the TCLP, Toxic Characteristic Leaching Procedure, test results on sludge samples containing mercury, lead and cadmium. In all cases the TCLP limits are met.

Table 2. TCLP Results on Various TMT-Metal Sludges[2]

Metal	Content in Sludge Initially (ppm)	Content in TCLP Extract (ppm)	TCLP Limit (ppm)
Hg	17.29 27.69	0.004 0.003	0.2
Pb	13.43 24.24	0.22 0.22	5.0
Cd	11.51 11.57	0.21 0.13	1.0

TMT –metal sludges are typically coarse and easily flocculated with non-ionic or anionic polyacrylamides. The addition of iron or aluminum salts may be necessary for solutions containing only small amounts of heavy metals.
Other benefits include:

- Ease of use as liquid or solid
- Ability to precipitate metals in a wide pH range
- Handling ease: non-toxic, virtually no odor
- Excess product does not require detoxification

TMT Applications

For over 20 years, TMT has been used effectively in a variety of industries where the product benefits can be realized.

Combustion plants
Several hundred garbage incineration facilities and coal fired power generation plants presently use TMT primarily for the precipitation of ionic mercury and cadmium in the scrubber solutions. TMT is considered to be state-of-the-art for these applications. Hazardous waste treatment is another area where TMT is used.

Photographic industry
TMT is used to remove silver from photographic waste streams producing silver sludges that can be subsequently recycled. Batch processing can be done for the silver removal process.

Chemical synthesis
The removal of catalysts from chemical processes is another area where TMT is used. Due to the non-toxic nature of the product, pharmaceutical companies use TMT for removal of copper and palladium[3].

Electroplating/ metal finishing
A variety of applications for TMT can be found in the "metal working" industry which includes printed circuit board producers and electroplaters.
Generally, the treatment of these galvanic waste streams require the following steps:

1. Pretreatment stages to treat cyanide or reduce chromium with oxidation processes, for example, using hydrogen peroxide.

2. Precipitation of the uncomplexed metals as hydroxides using lime or caustic.
3. Precipitation of the complexed metals with precipitation agents, such as TMT.

The flow diagram[5] shown in Figure 3 provides a more detailed process using TMT.

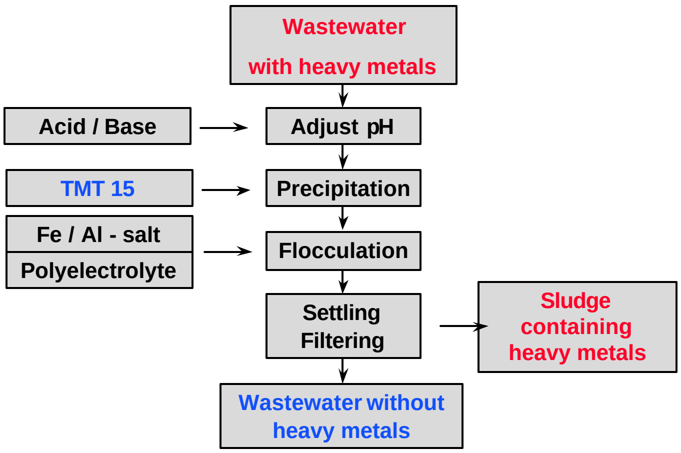


Figure 3. –General flow diagram for treating galvanic effluents containing metals.

Other steps may be required to accommodate a hydroxide recycling stage, or for metals bound with strong complexing agents like EDTA.

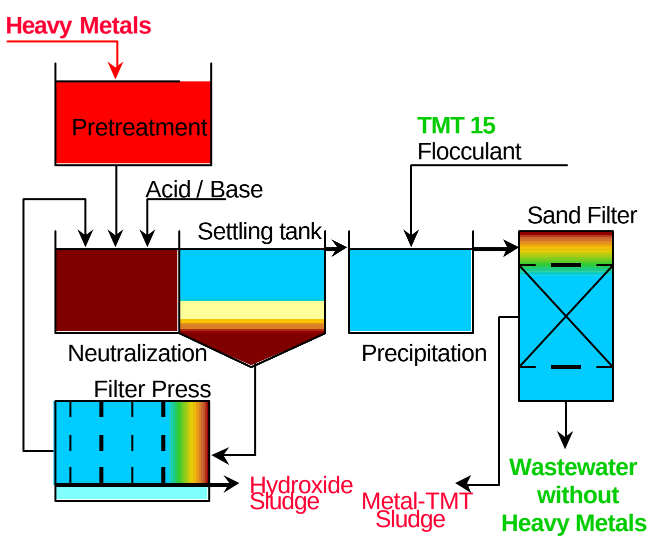


Figure 4 .-Schematic diagram of waste treatment for galvanic effluents containing heavy metals.

In Figure 4, the bulk of the metals are precipitated as hydroxides, while the remaining complexed metals contained in the settling tank overflow are treated with TMT in a polishing step. This allows for the recycling of the hydroxide salts after filtration with, in this case, a filter press. The metal TMT sludge can be sent to a landfill. By precipitating the uncomplexed metals with relatively cheap reagents such as lime or caustic, the more expensive sulfur based precipitating agents, in this case TMT, can be used only where needed, thereby optimizing the treatment costs.

Case Study #1

Problem: An electroplating shop creates a process rinse water effluent containing 24 ppm copper at a pH of 2. It was determined that some of the copper was complexed.

Solution: Using a process design similar to that represented in Figure 4, a two stage process was implemented to meet their copper treatment targets.

Treatment procedure:

- Stage 1
  1. Lime was added to adjust pH from 2 to 9 using 1.0 kg $Ca(OH)_2$ per $10m^3$ (8.3 lb/10,000 gal) of effluent.
  2. Agitated for 30 minutes in reaction tank.
  3. Hydroxide sludge removed with filter press.
- Stage 2
  1. To filtrate from stage 1, 0.61 L TMT 15 per 10 m^3 (0.61 gal/10,000 gal) was added to treat the remaining 3.4 ppm copper (see Figure 2).
  2. 0.1 kg $FeCl_3$ was added per $10m^3$ (0.83 lb/10,000 gal) as a coagulent for the relatively small amount of metals present.
  3. Non-ionic flocculent was added at a rate of 20 L as a 0.05% solution per $10m^3$ (20 gal/10,000 gal).
  4. Metal TMT precipitate was removed via settling and filtration.

Result: The residual copper concentration in the effluent was 0.03 ppm, well below targeted levels.

Case Study #2

Problem: A wire drawing plant needs to treat draw emulsion effluent containing 274 ppm copper and 168 ppm zinc. Due to the presence of ammonia, precipitation using lime or caustic was not successful.

Solution: A single stage circuit using TMT was implemented to treat the effluent in 1 m^3 batches, similar to that shown in Figure 5. No pH adjustment was necessary since the effluent was already at a pH of 7.3.

Treatment procedure:

1. Based on the reagent requirements described in Figure 2 for copper and zinc, 8.1 L of TMT 15 per m^3 (8.1 gal/1,000 gal) was added.
2. A strong anionic flocculent was added at a rate of 40 L as a 0.05% solution per m^3 (40 gal/1,000 gal).
3. Metal TMT precipitate was removed via settling and filtration.

Result: The residual copper and zinc concentrations were 0.03 and 1.4 ppm, respectively.

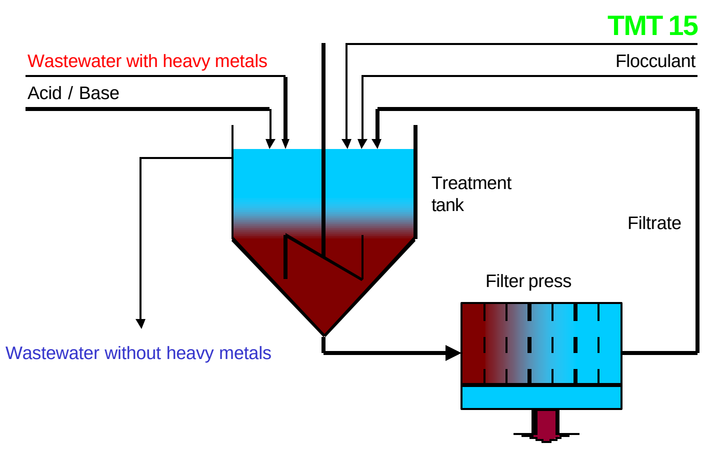


Figure 5. -Batch treatment flowsheet for galvanic effluents containing heavy metals using TMT alone.

Comparison of Sulfur Based Precipitation Agents

When considering which precipitation agent to use, the specific application must be well understood. Table 3 describes some of the relative advantages and disadvantages between these products. Factors such as the pH of the effluent, the metal content, the presence of chelating agents among others, must be taken into account. The all important treatment costs will have to be factored in with handling and disposal costs.

The equipment and the circuit design will also be dependent upon which agent is chosen. For example, if sodium sulfide was chosen, the materials of construction for the reaction tanks, piping, pumps and venting must be able to handle the corrosive nature of the product. For DTC and trithiocarbonates, a residual treatment circuit may be necessary to properly detoxify the effluent. The hazardous nature of some of these products will also dictate the equipment required for the health and safety of the operators.

Table 3. Application of Various Precipitation Agents Advantages and Disadvantages

Precipitating Agent	Advantages	Disadvantages
Sodium Sulfide (Na_2S)	-Sludge stability. -Tried and tested -Costs: very low	-Elevated pH only -Floc. Problems -Corrosive -Odor -Difficult handling -Residual treatment probable -Ecology/ toxic properties: poor
Dithiocarbamates (DTC) Trithiocarbonates ($NaCS_3$)	- Proven effective even for strongly chelated metals -DTC frequently used. -Costs: average	-Effective at pH >7 -Odor -Residual treatment likely -Ecology/ toxic properties: poor
Trimercapto-triazine (TMT)	-Ease of handling -Odorless -Sludge stability -Works in wide pH range -No residual treatment required -Ecology/ toxic properties: good -No reaction with ferric flocs	-Strongly chelated metals may require extra stages -Difficulty with Zn and chelated Ni -Costs: above average

Table 4 focuses on the toxicologic and ecological properties of sodium sulfide, trithiocarbonate, dithiocarbamate and TMT. These properties are expressed in terms of acute toxicity and lethal concentration data, as well as the products of decomposition and whether or not they are mutagenic.

Table 4. Toxicological/Ecological Properties of Various Precipitating Agents

	Na_2S	Na_2CS_3	DTC	TMT
Acute Toxicity Rat LD_{50} mg/kg	208	n.a.	3,590	7,878
Lethal Conc. Fish LC mg/L	25 (LC_{50})	55 (LC_{50})	20 (LC_{50})	12,000 *(LC_0)
Products of Decomposition	H_2S	H_2S CS_2	CS_2	none
Mutagenic Yes/No	n.a.	n.a.	Yes	No

*Note: No fish mortality at 12,000 ppm, hence "LC_0"

Sodium sulfide(Na_2S) has a long track record for use as a precipitating agent. It is by far the cheapest of the four, and is still used today. When used on its own, the product produces fine particulates that do not settle easily. Furthermore, sodium sulfide can only be used for solutions with elevated pH levels. If acidified, it releases hydrogen sulfide gas which is extremely toxic. Both the rat and the fish toxicity data reveal why residual sulfide treatment steps may be mandatory. Handling of the product must be done with great care due to the potential release of H_2S and its corrosiveness.

Although sodium trithiocarbonate(Na_2CS_3) is not as frequently used as Na_2S or DTC, it is still an effective precipitating agent with similar application strengths as Na_2S. No acute toxicity or mutagenic property data are available. However, it is very toxic to marine life[6] and could require that any residual Na_2CS_3 be treated before discharge. The decomposition products, hydrogen sulfide and carbon disulfide, are both very hazardous toxins.

For treating strongly complexed metals, DTC is the most effective of the four products. Like sodium sulfide, it is frequently used in the metal finishing industry. However, it is far more expensive. Commonly available as an approximately 40% solution as sodium dimethyl or diethlyldithiocarbamate, it is relatively stable. On the downside, as past environmental exposure would indicate[9 & 10], DTC is the most detrimental to marine life of the four[7]. It is also known to have mutagenic properties[11]. Therefore, worker exposure must be limited. Carbon disulfide, a neurotoxin, is the main product of decomposition. In most cases, detoxification of any residual DTC is required.

TMT works well in effluents in a very wide pH range, and is the only one of the four precipitating agents that works effectively in acidic effluents. It is also the only one that does not produce hazardous products of decomposition. The sludges produced are stable and pass TCLP tests. Due to the product's lack of toxicity, transport and shipping risks are minimal. Handling and worker exposure problems are virtually eliminated, and residual treatment systems are not necessary. However, disadvantages include extra steps required for strongly chelated metals, difficulties in precipitating zinc and chelated nickel, as well as the higher costs of the product itself.

Summary

The treatment of heavy metal containing waste streams from plating operations is commonly accomplished by hydroxide precipitation. However, the presence of complexing agents and/or a reduction in the permissible discharge limits may force certain facilities to consider additional treatment options, such as sulfur based precipitating agents that produce far more stable precipitates than hydroxides. These chemicals can be used alone or together with hydroxide precipitating steps. When choosing a precipitating agent for a particular process, the performance and costs of the product are the most critical considerations. But the toxicity of some of these products must also be considered since these factors will affect the handling, use and potential treatment of the product as well.

Of the four sulfur based precipitating agents that were discussed in this paper, TMT shows by far the best toxicological and ecological properties. Although the product is more expensive than the others, when one considers other expenses such as those associated with handling and detoxification, TMT may actually be more economical to use. TMT is capable of precipitating heavy metals even in strongly acidic conditions, unlike most precipitating agents, and also produces stable TMT – metal sludges that will pass TCLP test conditions.

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