Considerations on the Use of Dithiocarbamates for the Removal of Metals from Water

by:

Peter S. Zisson

&

Dr. Thomas E. McNeel

Buckman Laboratories International, Inc.
1256 North McLean Blvd.
Memphis, TN 38108

ABSTRACT

As discharge restrictions become stricter and sludge disposal costs rise, traditional technologies for the removal of metals from plating shop wastewater such as lime and ferric chloride become increasingly less attractive. One technology that is of increasing interest is the use of dithiocarbamates to complex the soluble metals in the wastewater stream. Dithiocarbamates form a highly insoluble, dense sludge, resulting in high quality effluent water and greatly reduced sludge volumes. Despite the benefits available from dithiocarbamate technology, certain practical problems to the implementation of a dithiocarbamate treatment program exist. This paper examines some of these problems and offers potential solutions, including some case histories.

Introduction

Before it was necessary to remove metal ions from wastewater it was known that most metals were less soluble in water at higher pH. This fact led to the first technique used for treatment of metal-bearing waste. By adding an alkalinity building agent such as caustic soda (NaOH), hydrated lime ($Ca(OH)_2$), or magnesium hydroxide ($Mg(OH)_2$) to the water, large amounts of soluble metals are precipitated as metal-hydroxide complexes. The precipitated metal can then be separated from the water, and the relatively clean water can be discharged. This technique has been used successfully for several decades.

In recent years the advent of increasingly stringent environmental regulations has resulted in problems for hydroxide precipitation. The most immediate problem is the reduction in compliance levels for many of the metals commonly used in plating operations. In many areas hydroxide technology alone does not produce effluent water of sufficiently low metal content to comply with local discharge regulations. Consequently, the tighter regulations have spurred the development of adjuncts to, or replacements for, hydroxide technology.

One of the earliest adjuncts to hydroxide technology involves the use of iron as a precipitant. The iron is fed to the system in the form of ferric chloride ($FeCl_2$) or ferric sulfate ($FeSO_4$). When the pH is raised using a hydroxide donor like caustic soda the iron coprecipitates with the other metals as ferric hydroxide ($Fe(OH)_2$) and acts to reduce the regulated metals in the effluent water. This is often sufficient to achieve an effluent that is in compliance with the local discharge requirements.

As with all technologies, however, there is a drawback to iron precipitation technology. Compared to the actual quantities of target metals to be removed from the water, the amount of iron required for successful operation is extremely high. The net result is a marked increase in the volume of sludge that must be disposed of when compared to hydroxide technology.

Disposal of the sludge generated from the precipitation of metals from plating line operation waste is another area where more stringent regulations has created problems for operators of these plants. Under federal regulations, any solid waste generated by a plating facility is, by definition, a hazardous waste. Disposal of hazardous waste is becoming more and more expensive as the number of facilities willing to accept the waste falls.

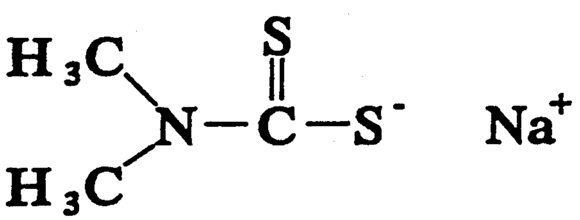
This increased cost associated with the increased sludge volume incurred as the result of a switch to iron precipitation technology can be prohibitive. It certainly has a negative impact on the profitability of surface finishing operations, resulting in interest in alternative technologies.

Dithiocarbamates

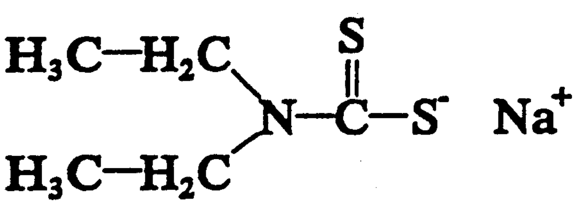
One technology that has become popular is the use of dithiocarbamates

(DTC) as precipitants. Dithiocarbamates are organic sulfide compounds that offer the advantage of the sulfide ion's strong reducing and metal-complexing power while minimizing the hazards associated with the use of plain sulfide. DTC technology offers the metal finishing operator the ability to meet today's more stringent discharge requirements while keeping sludge volume to a minimum.

There are two dithiocarbamate species currently in use as metal precipitating agents, sodium dimethyldithiocarbamate (DMDTC) and sodium diethyldithiocarbamate (DEDTC). These molecules are shown below.



DMDTC



DEDTC

DMDTC has a much lower use cost than DEDTC, and consequently is the product of choice in most applications. Both products are made by the reaction of carbon disulfide (CS_2) with a secondary amine. The principle cost differential comes as the result of the differing cost of the two amines, which is substantial. Dimethyl amine currently costs $0.39/#, while diethyl amine costs about $1.40/#. Additionally, DEDTC has a higher molecular weight than DMDTC, so more material is required for a given quantity of metal. Since both products are similar in their ability to complex metals, the economics of DMDTC offer a distinct advantage in most systems.

Advantages of DTC Technology

Just as iron technology offers advantages over hydroxide technology, so does DTC technology. The initial, and still most compelling reason for using DTC technology is the quality of the final effluent water. In most cases, DTC can produce effluent water with significantly lower levels of toxic metals than can hydroxide treatment. As discharge restrictions tighten, DTC allows plants to remain in compliance with local regulations.

There are two techniques by which a plant can use DTC technology to improve metals removal efficiency. The most economical technique, from the standpoint of chemical cost, is to use DTC to scavenge any metals remaining after hydroxide precipitation. This approach is often referred to as "polishing" with DTC. Polishing allows a plant to achieve compliance with minimal changes to the existing wastewater treatment operation. The case history below illustrates a successful polishing operation.

Case 1: Polishing with DTC

A zinc plating operation in Southern

California had trouble meeting their effluent limits for zinc and chrome. The plating operation uses zinc with chrome brighteners to plate file cabinet parts prior to final assembly. They have a continuous plating line which treats 40,000 pieces per day. Failure to meet the limits set by the State of California and the local sewer authority resulted in fines and threats of plant shut-down.

In the past, rinse water from the zinc and chrome rinse tanks was collected in separate sumps. The hexavalent chrome in the chrome rinse sump was reduced, and all of the waste water was mixed and treated in two thousand gallon batches. The pH was increased to 9.5 with caustic soda, and the chrome and zinc precipitated as metal hydroxides. The water/sludge mixture was dosed with an anionic polymer and pumped to a clarifier. The supernatant was sent to the sewer, and the sludge was further concentrated in a plate and frame press. The filtrate from the press was sewered, and the sludge was sent to a hazardous waste landfill.

Because the hydroxide precipitation was not efficient enough to meet discharge limits, DTC was recommended as a polishing step prior to settling and filtration. The dose of DTC recommended was based on a residual of 4 ppm each of zinc and trivalent chrome in the water after hydroxide precipitation. This calculated out to 127 ppm of a 40% DMDTC solution, or about a quart of DTC solution per 2000 gallon batch.

The DTC is added to the reaction tank 30 minutes after the pH is adjusted with the sodium hydroxide. Mixing is continued for an additional 15 minutes before resuming treatment, which then proceeds as in the past. Since starting the DTC polishing treatment, the chrome and zinc levels in the effluent have not exceeded 1 ppm, and are typically less than half that level, well within discharge limits. The plant personnel consider the cost of the DTC to be cheap insurance against fines for being out of compliance.

An alternative technique is to complex most or all of the metals with DTC, replacing hydroxide or iron technologies almost entirely. This approach can be very successful, but can also be costly. Since DTC reacts stoichiometrically with metals, treatment of waters with high metal content can be cost prohibitive. Hydroxide also reacts stoichiometrically, but the cost of hydroxide sources is very low compared to DTC. The increased cost of treatment, however, is often offset by a significant reduction in sludge volume, especially in the case of iron technology.

The cost of sludge disposal, especially hazardous waste sludge disposal, continues to rise. Five years ago the cost savings resulting from the reduction in sludge volume offered by total precipitation with DTC would probably not have been enough to offset the cost of the treatment chemicals. Today total precipitation with DTC is much more likely to be economically viable, as demonstrated by the case history below.

Case 2: DTC as the Main Precipitant
A plating facility on the West Coast was using ferric chloride to precipitate electroless copper from its effluent wastewater. While the plant was able to achieve acceptable wastewater quality using ferric chloride, the volume of sludge generated was extremely high.

Treatment with hydroxide technology alone had proven unacceptable, with copper levels in the effluent exceeding compliance levels.

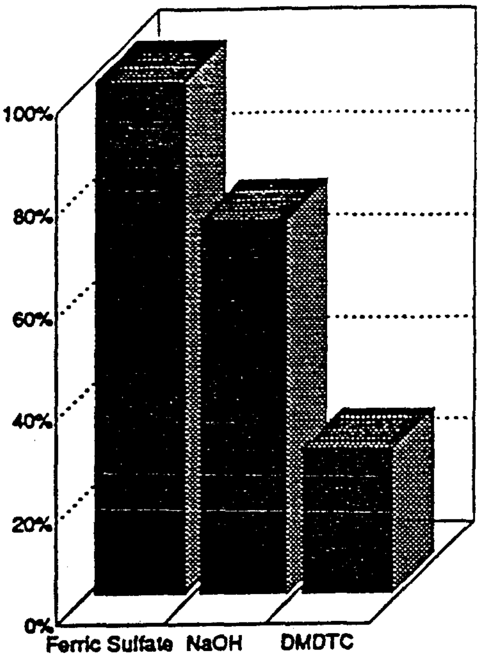
The plant produces approximately 8000 gallons of wastewater per day, with copper levels ranging from 6 - 40 ppm. When using ferric chloride to precipitate the copper, sludge disposal was costing $100,000 per year. Plant personnel were interested in reducing this cost, and DTC technology was recommended.

Wastewater was collected for batch processing daily. The copper content of each day's batch was analyzed prior to treatment. A 40% solution of DMDTC was dosed to the batch at the rate of 15 ppm per ppm of copper, or about 13 fluid ounces per ppm of copper, to the 8000 gallon batch.

The DTC treatment resulted in a sludge volume reduction of 78%, reducing sludge disposal costs by $78,000 per year. Offsetting the savings was a chemical cost for DTC of $25,000 per year, resulting in a net savings of over $50,000 per year.

The sludge volume reduction available from DTC technology is significant. DTC technology results in much less sludge than iron technology, and even offers reductions when compared to hydroxide technology. The graph at the right shows typical sludge volume reductions that can be achieved using DTC technology.

As shown in the graph, there is a distinct reduction of sludge volume when changing from hydroxide technology to DTC as well. While such a change is not currently as viable economically as the change from iron technology to DTC is, the cost of sludge disposal is rising much faster than the cost of DTC. Plants with high sludge disposal costs should periodically review the relative costs and savings available.



Relative Sludge Volume

Implementing a DTC Program

As with all technologies, DTC is not a panacea. A properly designed and implemented DTC program can reduce sludge disposal costs and soluble metals in the effluent streams, but proper design of the program is important. Changes in treatment technology involve more than simply swapping chemicals. Considerable testing, and trial and error, go into making the change, as illustrated below.

Case 3: Implementing a Program
A captive chrome plating line at a West Tennessee manufacturer produced about one cubic yard of solid waste per day using iron technology for precipitation. The management was looking for alternate precipitation technology to comply with the Federal mandate for sludge minimization. DTC technology was presented as a viable alternative.

The original procedure for waste treatment involved depressing the wastewater pH to 2.5, reducing chrome with sodium metabisulfite, adding ferric sulfate, and elevating the pH to 9 with caustic soda. An anionic polymer was added, and the wastewater was then pumped to a settler. The solids were concentrated in a plate and frame filter press. The pH of the effluent water was lowered to 7 and the water was discharged to a city sanitary sewer.

It was initially hoped that only a minor change in the treatment procedure would be needed to replace the ferric sulfate with DTC. The desired treatment would remain unchanged through the chrome reduction step. Instead of adding ferric sulfate and increasing pH to 9, only enough caustic soda would be added to bring the pH to 7. DTC would be dosed, followed by the anionic polymer, and the sludge separation would follow as before. This technique would eliminate dosing of the ferric sulfate and the acid required to reduce pH prior to discharge, while reducing the volume of sludge produced.

This treatment procedure was implemented at the start of operations one Monday morning. It soon became apparent that the procedure was not working. Floc formation in the settler was poor and solids were carrying over into the effluent. The old treatment procedure was reestablished, and a five gallon sample of the raw wastewater was taken to the laboratory for some bench studies.

After a few hours of lab work two possible treatment approaches were uncovered. When lime or magnesium hydroxide was used in place of caustic soda to increase the pH, floc formation improved and high quality effluent was produced. As an alternative, it was found that adding a cationic coagulant after the DTC and before the anionic flocculant also resulted in high quality effluent. The latter technique allowed continued use of caustic soda for pH adjustment and produced the least sludge. Due to the lower sludge volumes produced in lab testing, the plant chose to try the cationic coagulant.

A five gallon pail of the proposed coagulant polymer was shipped to the plant, and a trial was started. After some initial adjustments, floc formation was stabilized, good clarification was achieved, and the effluent water was well within the discharge limits set by the city. The plant elected to continue with this treatment procedure. Average sludge production dropped from one cubic yard per day to less than two cubic yards per week.

In most cases, DTC technology can solve problems associated with tight discharge restrictions and sludge minimization requirements, but successful treatment is not automatic. Treatment techniques must be adjusted individually to each system for best results. Without the assistance of someone skilled in wastewater treatment with DTC it is often difficult to achieve good results. Initial program design is as important as consistent product dosing.

Potential Problems with DTC Treatment

As treatment programs become more effective, they tend to become more complex. This is a necessary evil of improved treatment technology. With this greater complexity comes a wider range of potential problems. DTC is no different from earlier treatments in this respect.

One of the greatest advantages of hydroxide treatment is its ease of control. A simple pH meter can be used to establish when enough caustic has been added to the wastewater to complex with all of the metals. This approach works in both batch and continuous treatment plants.

With iron treatment technology the level of iron salt is usually set a little higher than necessary to establish a safety margin. Since the excess iron will be precipitated by caustic, and the caustic dose will be regulated by pH, no excess iron will be discharged to the sewer. From the standpoint of chemical cost the extra iron salt and caustic are negligible, as both are low cost commodity chemicals. The most significant cost of iron overdosing is the extra sludge produced.

The costs escalate rather rapidly, however, when DTC is overfed to insure complete complexing. DTC chemicals are more expensive than commodities like caustic soda and ferric chloride. The higher cost offers a significant incentive for controlling the amount of DTC that is fed.

Controlling DTC dosage in batch treatment systems is relatively easy. The most accurate technique is to analyze for the metals in solution and calculate the quantity of DTC required. The appropriate quantity of DTC can then be added and mixed into the solution. After mixing the supernatant can be tested for remaining metals prior to clarification and discharge.

The residual of DTC remaining in the water after treatment can also be tested, albeit with difficulty. Techniques range from simple, but not very sensitive, turbidimetric methods to highly accurate HPLC (High Performance Liquid Chromatography) and IC (Ion Chromatography) instrumental procedures. The equipment required for the turbidimetric procedures can be obtained at reasonably low cost, but the HPLC and IC instruments typically cost more than $20,000. This type of analysis is only practical for the largest systems.

This type of testing applies only to grab sampling of the waste stream. It is most applicable to batch processing systems, where the efficacy of each treatment step can be verified before proceeding. These tests are not suitable for controlling continuous treatment systems unless the level of soluble metal in the wastewater is fairly stable. If there is significant variation in the metals content in the wastewater, treatment with DTC will be more difficult.

When using hydroxide technology, continuous flow systems can be controlled by automated pH sensing equipment. This equipment uses an electrode that measures the pH of the stream directly. A similar electrode, which can sense DTC directly, is under development.

It is possible, however, to use DTC technology in continuous treatment systems where the metal content varies. One effective technique is to feed the DTC at a rate suitable for the average level of metals, and follow it with low doses of iron salts. When the metals in the water are low the excess unreacted DTC will react with the iron and be consumed. When the metal levels are high the iron will act as a polishing step. Since only a little iron is used, the sludge volume remains low.

Another approach to treatment of continuous systems is to feed the DTC at a rate sufficient for the highest anticipated level of metals. Any excess DTC in the effluent water can be easily deactivated by chlorination of the water prior to discharge to the sewer. Oxidation of DTC molecules, which occurs very rapidly in the presence of hypochlorite or peroxide, results in insoluble thiuram disufide precipitation. These thiuram disulfides pose little problem for typical municipal sewer systems. Oxidation can be controlled automatically by standard ORP techniques, making the entire system automatic.

Conclusions

Environmental restrictions on discharge of soluble metals are becoming stricter every day. Disposal of hazardous waste sludges is becoming more expensive, and the number of available disposal locations is getting smaller. For these reasons, alternate technologies for the treatment of wastewater containing soluble metals are being given serious consideration in many plants.

One technology that offers many benefits is the use of dithiocarbamates to complex soluble metals. Metal-DTC complexes have extremely low solubilities. The use of DTC as a complexing agent, when properly applied, can result in very clean effluent water while forming relatively small amounts of sludge.

Suitable techniques exist for the determination of excess levels of DTC in water. These techniques can be used effectively to control product dosing in batch treatment systems, but do not lend themselves to automatic control. Research into automatic control of DTC dosing is currently underway and shows some promise. Automatic control will greatly facilitate the use of DTC as a precipitant.

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DTC - Aquatic Toxicant - Must be oxidized prior to biological treatment (Chlorine or Peroxide)

- Expensive
- Residuals difficult to measure. Measurement instrumentation expensive.
- Limited utility - batch process only at present.