Simplified Removal of Chelated Metals

Sultan I. Amer, AQUACHEM INC.

Metal Finishing, April 2004, Vol. 102 No. 4

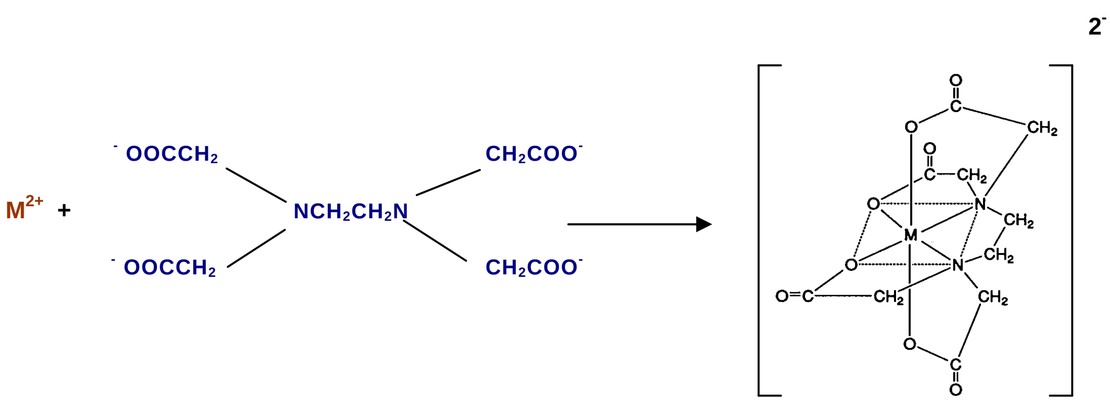
Chelating agents are used in large quantities in industrial applications involving dissolved metals. Significant amounts of these compounds enter aquatic systems through industrial activities and waste discharges. Ammonia, alkanolamines, and organic acids such as oxalic acid and ethylenediaminetetraacetic acid (EDTA) are widely used in electroless plating processes to enhance homogeneous deposition of metals.

Because of their sequestering effects, chelating agents are widely used in cleaning formulations. Most cleaners, especially alkaline cleaners used in plating baths and metal processing products, are formulated with such compounds to enhance their ability to dissolve and remove rust, scale and other debris from metallic surfaces. They are particularly commonly used to remove metal oxide scale from heat transfer surfaces in boilers and nuclear reactors and to remove toxic metals from contaminated soils.

Chelating agents most widely used in industrial applications are ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). Other commonly known chelates are compounds such as hydroxyethylenediamine-triacetic acid (HEDTA), diethylenetri aminepentaacetic acid (DTPA), etc. These compounds form 1:1 complexes (chelates) with many metals, as shown in Figure 1.

Figure 1: Chelation

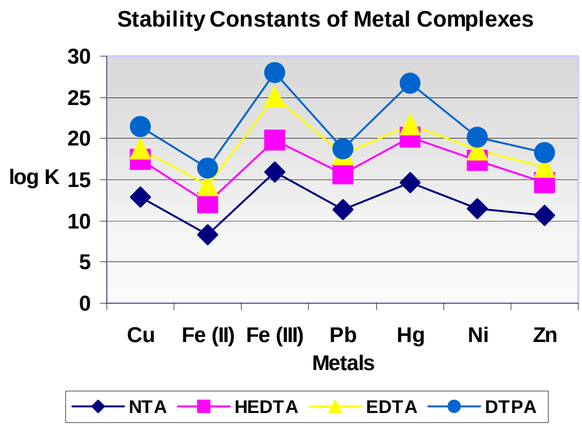
Metal Ion + **EDTA** ⟶ **Metal EDTA Complex**



Proposed Metal – EDTA Complex

Metal chelates form over a broad range of pH and are highly soluble and extremely **stable**.
Figure 2 below shows stability constants*, K, of some metal chelates, expressed in logarithmic values. These values are indicators of stability of metal chelates; the higher the value the more stable the metal chelate and the harder it is to break and remove the metal.

Figure 2:



EDTA is, by far, the most widely used chelating agent in industrial applications due its excellent sequestering performance and low cost. Significant quantities of EDTA -containing waste have been released into the environment and, once in the environment, it is extremely difficult to remove.

Note: I) *Data was obtained from Akzo Chemicals' Product Brochure on Chelates
ii) Cu – Copper, Fe – Iron, Pb – Lead, Hg – Mercury, Ni – Nickel, Zn – Zinc

Removal of chelated metals is a problem facing most metal related industries. Removal of chelated metals involves:

- Removal of the metal chelate species as is the case with ion exchange, reverse osmosis, and nanofiltration. These techniques generate concentrates from which the metal must be removed/recovered prior to disposal, or
- Breaking the metal-chelate into free metal and free chelating agent, followed by separation of the metal in an insoluble form. The chelating agent is discharged with the treated effluent.

Chelated metal-bearing waste streams treated with conventional hydroxide precipitation alone most likely do not meet discharge requirements. Consequently, the industries will have to employ ion exchange, reverse osmosis or add a polishing step to existing treatment.

Most common chemical separation practices for metals in chelated form involve treatment with dithiocarbamate (DTC), hydrosulfite, sulfide, iron salts or combinations thereof. These chemicals are often effective in lowering metal concentrations in effluents and achieving compliance. However, they are toxic, hazardous, harmful to the environment, and generates waste that may require further treatment in order to render it suitable for disposal.

Techniques such as ion exchange, reverse osmosis, and nanofiltration can effectively remove chelated metals from wastewater. However, generated concentrates will require further treatment. Additionally these techniques are costly in comparison to chemical separation processes.

Unfortunately, the *more effective the chelating agent, the more difficult it is to remove the metal in wastewater treatment*. Difficulties encountered in treating electroless waste, where the chelating agents are normally present along with ammonia, amines, alkanolamine or combinations of these, are examples of situations that frequently produce difficult-to-treat waste streams.

AQUACHEM INC. • 4501 Cartwright Center Rd., Unit 605 • Missouri City, TX 77459-3541 • (832) 539-1020 • Fax (832) 539-1389

New Generation Products Offer New capabilities

The latest generation AQUASIL® products have been developed specifically to handle difficult-to- treat chelated metals from waste streams. As with the basic AQUASIL® products, the new products utilize the fast kinetics and synergistic effects of several functionalities which involve complex mechanisms. The products are stand-alone and applicable to wastewater with low to moderately high pH (about 2 to 10). They are also capable of simultaneously removing non-chelated metals, oil and grease, organic matters, and suspended solids and can be used in both batch and continuous processes. Furthermore, generated sludge is stabilized and passes the Toxic Characteristic Leaching Procedure (TCLP) test.

Early Real World Results

The following case studies are examples where the wastewater contains chelating agents.

Manufacturing and Plating

A Midwest manufacturer generates a stream of chelated wastewater. The waste stream is a combination of acid rinses, degreaser, and copper plating waste. Previously, the waste stream was treated with ferric chloride, caustic and polymer in a continuous setup. The facility needed a new chemistry to consistently bring the concentrations of copper and nickel to 1 ppm or less.

TABLE I

Parameter	Daily Max. (mg/L)	Before (mg/L)	After (mg/L)
Cadmium	**0.26**	**0.037**	**< 0.004**
Chromium	**1.71**	**0.348**	**0.010**
Copper	**1.0**	**106**	**0.382**
Lead	**0.43**	**1.07**	**< 0.004**
Nickel	**1.0**	**123**	**0.121**
Zinc	**1.48**	**3.19**	**< 0.010**
pH*	**6.5 – 11.0**	**1.93**	**9.1**

The wastewater is treated without pH adjustment. Analytical data shown in Table I indicate that the facility is meeting the set limit of < 1 ppm for both copper and nickel.

Furthermore, the treatment generates less sludge and enhances filter press operation.
Generated filter cake passes the TCLP test. Caustic has been reduced and ferric chloride and polymer eliminated.

Circuit Board

A circuit board manufacturer generates about 7,500 gal of wastewater daily. The waste stream is acidic (pH = 1.8) and contains mainly copper and lead, with tin and nickel as minor metallic components. Additionally, the waste stream also contains cleaners that have chelating agents, ammonia and ethanolamine. The treatment employs hydroxide precipitation along with dithiocarbamate (DTC). The facility was looking for an alternative technology that can eliminate the use of DTC.

TABLE II

Parameter	PSES Daily Max. (mg/L)	Before (mg/L)	After (mg/L)
Copper	4.5	200	ND
Lead	0.6	2.02	ND
Nickel	4.1	NA	ND
Tin	-	NA	-
pH*	6.5 – 9.5	1.81	7.5

Note: - NA – Not available

Again, the acidic waste stream was treated without any pH adjustment. Analytical data shown in Table II indicate that the treatment brought the concentrations of copper and lead to the non-detectable levels. Moreover, the treatment eliminated DTC, caustic and polymer. The treatment also generates less waste, which passes the TCLP test.

Traditional Plating Shop

A plating shop in the Midwest generates two waste streams, chrome rinses and zinc-cyanide waste. After cyanide destruction and chromium reduction, the two streams are combined. This combined waste stream has a pH > 12, high concentrations of metals and suspended solids. Due to the presence of chelated metal, the facility is experiencing difficulties in meeting discharge requirements, especially for cadmium and zinc.

TABLE III

Parameter	Daily Max. (mg/L)	Raw water (mg/L)	Treated water (mg/L)
Cadmium	0.12	65	ND
Chromium	25	110	< 0.5
Copper	2.5	4.1	ND
Zinc	7.3	128	0.55
pH	5 – 11.5	> 12	9

The pH of the raw water was adjusted to about 6 – 7 prior to the AQUASIL® treatment. As shown in Table III, the new treatment is achieving almost 100% percent removal of heavy metals. Furthermore, the new technique simplified the entire process, replacing all treatment chemicals, minimizing operator intervention, and generating less sludge.

Treatment of chelated metal waste is a daunting undertaking, especially in light of the continued development of new and more efficient chelating agents. The lack of information about the nature and concentration of chelating agent(s) used in industrial formulations adds to the difficulty encountered in wastewater treatments programs. Care and diligence must be exercised in dealing with chelated wastewater, as the treatment chemistry and its results vary from one case to another. There are still many challenges to overcome in developing new products to deal with some extremely difficult-to-treat chelated metal wastes.

REFERENCES

1. Wall E., Henke K., Matlock M., and Atwood D., "Aqueous Leaching Properties and Environmental Implications of Cadmium, Copper, Lead, and Mercury Dimethyl-dithiocarbamate Compounds," Symposium Paper Presented Before the Division of Environmental Chemistry, American Chemical Society, April 2001.

2. Hering, J.G. and F.M. Morel, "Kinetics of Trace Metal Complexation: Ligand-Exchange Reactions," Environ. Sci. Techn., Vol. 24, pp242-252 (1990).

3. Huang, Y. C. and S. S. Koseoglu, "Separation of Heavy Metals from Industrial Waste Streams by Membrane Separation Technology," Waste Management, Vol. 13, p481 (1993).

4. Schwarzenbach G., COMPLEXOMETRIC TITRATIONS, Interscience Publishers Inc., N.Y., 1957

5. Pankow J.F., AQUATIC CHEMISTRY CONCEPTS, Lewis Publishers, Chelsea, MI, 1991.

Sultan Amer, Ph.D. is President of AQUACHEM, INC. AQUASIL® is Registered Trademark of AQUACHEM INC.

For more information on Aquasil Technology, contact:
AQUACHEM, INC.
Tel.: 832-539-1020
Fax: 832-539-1389
E-Mail: info@aquachem-inc.com