TREATING CITRATE-CHELATED METALS

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As many scientists and engineers have discovered in recent years, the treatment of citrate-chelated metals may not be as complicated as some researchers originally believed.

Citric acid is a tri-basic organic acid that is only weakly dissociated in solution. It is present in large quantities in citrus and other fruits and is commercially manufactured by the bacterium, Aspergillus niger, during the fermentation of sugar. At room temperature, citric acid is a white crystalline powder.

Citric acid is widely used in food, beverages, pharmaceuticals, water softening, soap, shampoos and detergents. It is increasingly being used in the passivation of steel, in place of hazardous nitric acid, and as an etchant in metal finishing.

Citrate is often used in large quantities in industrial applications involving dissolved metals. Cleaners are increasingly being formulated with citric acid/citrate to enhance dissolution and the removal of rust, scale and other debris from metallic surfaces. Such cleaners are particularly used to remove metal oxide scale from heat transfer surfaces in boilers and nuclear reactors. Consequently, significant amounts of citrate and other chelated metals enter aquatic systems through industrial and municipal discharges.

Citrate forms 1:1 metal chelates with metals, as shown in **Figure 1**.

Metal Ion + CITRATE ⟶ Metal-CITRATE

$$M^{2+} + C_6H_5O_7^{3-} \longrightarrow [M(C_6H_5O_7)]^-$$

Figure 1: Chelation

Citric acid tends to react with heavy metals, such as Cd, Cu, Cr, Fe(II), Fe(III), Ni, Pb and radionuclides such as U and Pu to form water soluble complexes, many of which are recalcitrant. Coordination through terminal and central carboxylate groups leads to mononuclear bidentate species (depicted in **Figure 2**), whereas coordination involving the central hydroxyl group, in addition to terminal and central carboxyls, leads to mononuclear tridentate species, as shown in **Figure 3**. With radioactive elements such as U, Np, Pu and Am, which exist in the dioxo ion (MO_2^{2+}), citric acid forms binuclear tridentate species. This is illustrated in **Figure 4**.

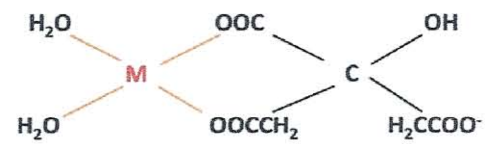


Figure 2: Monoonuclear Bideentate Complex

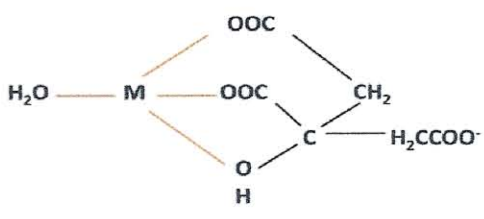


Figure 3: Monnonuclear Tridentate Complex

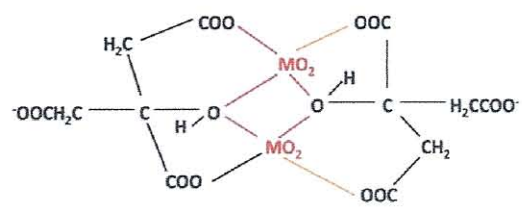
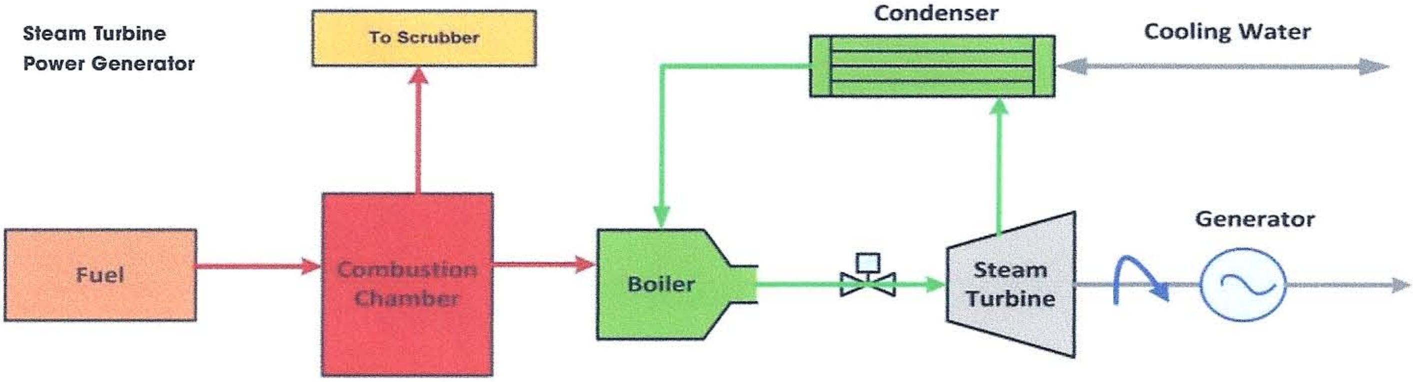


Figure 4: Binuclear Tridenntate

Free, uncomplexed citric acid is biodegradable. However, the biodegradation of citrate complexes depends on the nature of the complex formed between the metal and citric acid. Bidentate complexes (chellates) of $Fe(III)^-$, Ni^-, and Zn^- citrate are readily biodegraded by Pseudomonas fluorescens, whereas tridentate complexes of $Fe(II)^-$,



Cd⁻, Cu⁻, Pb⁻, and U⁻ citrate are not. Fe (II)⁻ citrate must be oxidized, first, to Fe(III)citrate in order to undergo biodegradation. Alone, or combined with ammonia or ammonium bifluoride, NH_4F_2, citric acid is increasingly employed in the removal of metal oxide scale from heat transfer surfaces and in boiler water treatment systems for steam production.

Case study

A utility company located on the East Coast currently operates a fossil-fueled boiler that generates electric power. The high pressure, high temperature steam from the boiler passes at an elevated speed through a turbine equipped with propeller blades. The steam drives the blades and forces the turbine shaft to rotate at a high speed, which powers the electric generator. Steam that exits the turbine then will pass through a condenser and returned to the boiler. The warm water (cooling water circulating around the condenser's tubes) is returned to its source, a pond, where heat is released through evaporation.

Wastewater at the power plant is a mix of spent cleaners and rinses from cleaning operations, scrubber effluent, boiler blowdown and cooling water. The primary metals in the waste are those of boiler construction material, steel and condenser, along with minor constituents from chemicals used in boiler feed water treatment. Such metals will form stable complexes with citric acid and ammonia, which render the waste less amenable to conventional hydroxide precipitation treatment. Data in **Table 1** reveal concentrations of metal in raw water.

The challenge

The current wastewater treatment employs lime, dithiocarmate (DTC) and flocculent to meet discharge requirements with respect to metals. The facility anticipated they would need to meet the new discharge guidelines with much lower limits for metals as shown in Table 1. The current treatment system could not meet the new requirements for metals, especially, copper, iron, and nickel, and, therefore, a new technique was required.

The solution

A proprietary chemical that was formulated to remove metals from wastewater was added to the waste stream. The reaction produced large floc that settled efficiently, producing very clear supernatant that was free of particulates or suspended solids. The treatment eliminated all caustic, dithiocarbamate (DTC), and flocculent, and significantly reduced the amount of sulfuric acid needed for final pH adjustment. Table 1 contains the analytical data for raw water, treated effluent and discharge limits.

With environmental regulations becoming increasingly more stringent, industries and businesses continue to face rising costs regarding water, energy, labor and POTW surcharges. More effective and improved treatment techniques are constantly needed to maintain pace with the changing regulatory requirements. ***PE***

Parameter	Discharge Limits, mg/L	Before Treatment, mg/L	After Treatment, mg/L
Chromium	0.5	2.95	0.269
Copper	0.5	20.5	0.167
Iron	4.0	1390	2.22
Lead	0.4	0.57	ND
Nickel	2.0	5.48	1.35
Zinc	1.0	3.39	0.056

Table I

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