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Stoichiometry & DTC

Dear Advice & Counsel,

I am new to the field of treatment of metal finishing wastewater. We operate what I understand is a conventional treatment system that employs cyanide oxidation, chromium reduction, pH adjustment for rendering metals insoluble, and polishing with "DTC" prior to clarification. The manual that I have been given for the waste treatment system states that DTC should be added at up to 100–200% over the "stoichiometric" amount. I took chemistry more than 20 years ago and never needed it until now and I am not sure what this means. Can you elaborate?

Signed,
Unbalanced

Dear Unbalanced,

I'll give it a try.

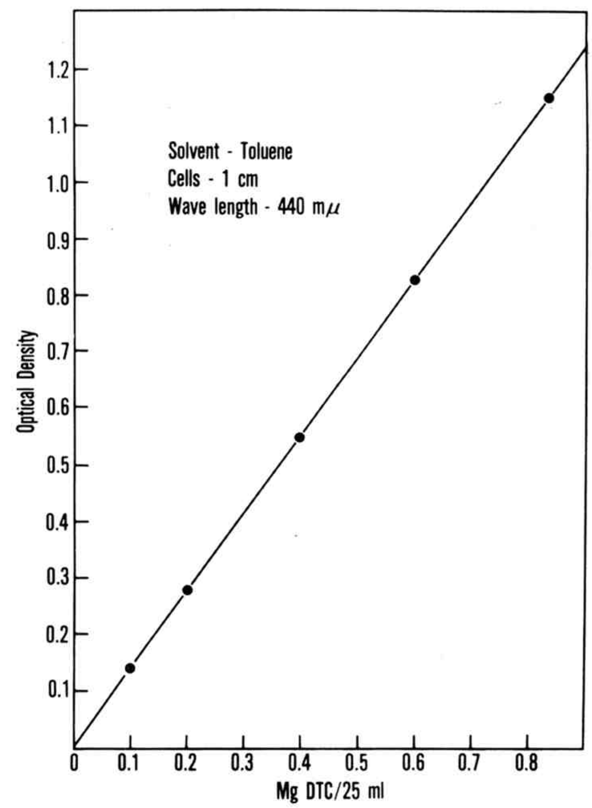
Stoichiometry is a fancy word used in chemistry for describing the "balancing" of reacting compounds or elements. Chemical compounds and elements that react with each other do so by ratios that is based upon molecular/atomic weights. The "stoichiometric" amount of a chemical required for a reaction is that amount which, theoretically, will react if all of the reacting compounds are totally consumed. I suppose this is still confusing so let's go over a basic example.

If we wanted to produce water by reacting oxygen and hydrogen, one thing we would need to know is how much of each to mix together. First we write a balanced chemical equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$4 \quad + 32 \rightarrow 36$$

Underneath the equation I have written the atomic weights of the reactants. This shows you that hydrogen reacts with oxygen in a 1:8 ratio. In other words, it would take 4 pounds of hydrogen to convert 32 pounds of oxygen to 36 pounds of water under ideal conditions (in the metric system, we would say it takes 4 grams of hydrogen to convert 32 grams of oxygen to 36 grams of water). The *stoichiometric* amount of hydrogen required per pound of oxygen is therefore 1/8 pound.

For your problem, we first need to know the exact chemical formula of "DTC." DTC is a commonly used acronym for a number of organic compounds that fall into a broad class of chemicals called carbamates. I will assume your DTC is actually sodium dimethyldithiocarbamate, which can be written as $Na[(CH_3)_2NC{=}S\text{-}S]$. If this is not what you are using, you will have



Typical calibration graph.

to get the right chemical formula from the MSDS or from the supplier. The molecular weight of $Na[(CH_3)_2NC{=}S\text{-}S]$ is obtained by adding all of the elements together. $Na[(CH_3)_2NC{=}S\text{-}S]$ contains 1 sodium, 2 sulfur, 3 carbon, 1 nitrogen and 6 hydrogen atoms, each with atomic weights of 23, 32, 12, 1, and 14, respectively. When each atom is multiplied by the atomic weight and totaled, the sum is 143.

Let's assume that the only metal you are precipitating is nickel. Nickel has an atomic weight of 58.7. We now write the chemical reaction of nickel and "DTC" as follows:

$$Ni^{+2} + 2[(CH_3)_2NC{=}S\text{-}S]Na = Ni2[(CH_3)_2NC{=}S\text{-}S] + 2Na^{+}$$
$$58.7 + 286$$

Note that because nickel is always a divalent ion (Ni^{+2}), while sodium is monovalent, it takes two molecules of sodium-DTC to react with one ion of nickel (the valences must add up to 0 for the reaction to be complete).

Stoichiometry based upon the above reaction predicts that for every 58.7 pounds (or grams or any other weight unit) of nickel that is in the water, you will need 286 pounds of "DTC." The ratio is 286/58.7 or 4.9 to 1, so for every gram of nickel you are trying to remove, you will need 4.9 grams of "DTC." That is the stoichiometry for this reaction. If you want a 100% excess, you would add 9.8 grams, *etc*.

Also, most DTC containing products are only about 40% by weight DTC. Based on a specific gravity of 1.2 a gallon of DTC would weigh 8.34 x 1.2 = 10 pounds. At 40% a gallon of DCT product would contain 4 pounds of DTC.

If you have other metals besides nickel, you will need to calculate the required amount of DTC for each of the other metals that DTC can react with. Common other metals that are precipitated with DTC are copper, zinc, cadmium. Lead, mercury, silver, cobalt, divalent manganese and ferrous iron. Note that DTC reacts only with divalent metals and is therefore not recommended for precipitation of trivalent chromium.

Now that we have covered the theoretical, let me state that most operators utilize jar testing to determine how much DTC gets the best results. If you are concerned about using too much DTC, Dr. Wing provided a procedure for determining residual DTC in treated wastewater (January 1982 issue of *P&SF*):

1. Take a known volume of wastewater (example 100 mL for 1–2 mg DTC).
2. Add 50 mL of toluene.
3. Transfer to a 250 mL separatory funnel.
4. Add 5 mL concentrated ammonium hydroxide and 10 mL of 2% copper sulfate solution. Shake thoroughly.
5. Allow for separation, draw aqueous layer into a beaker.
6. Filter the toluene into a 250 mL graduate.
7. Add 50 mL of toluene to the aqueous layer, shake separate and collect the toluene in the same graduate
8. Repeat until the toluene extract is colorless.
9. Transfer the colored toluene to a volumetric flask, rinse, dilute to volume.
10. Place aliquot in spectrophotometer using toluene as a reference. Note transmission. Convert percent transmission to optical density.
11. Use optical density to determine the mg/25mL (M value) from a calibration graph prepared with known standards.
12. Calculation:

$$\frac{(V \times M \times 1{,}000 \times 0.942)}{(25 \times S)}$$

= mg/L DTC, where

V= size of volumetric flask
M = value determined from calibration graph
S = sample size (mL).