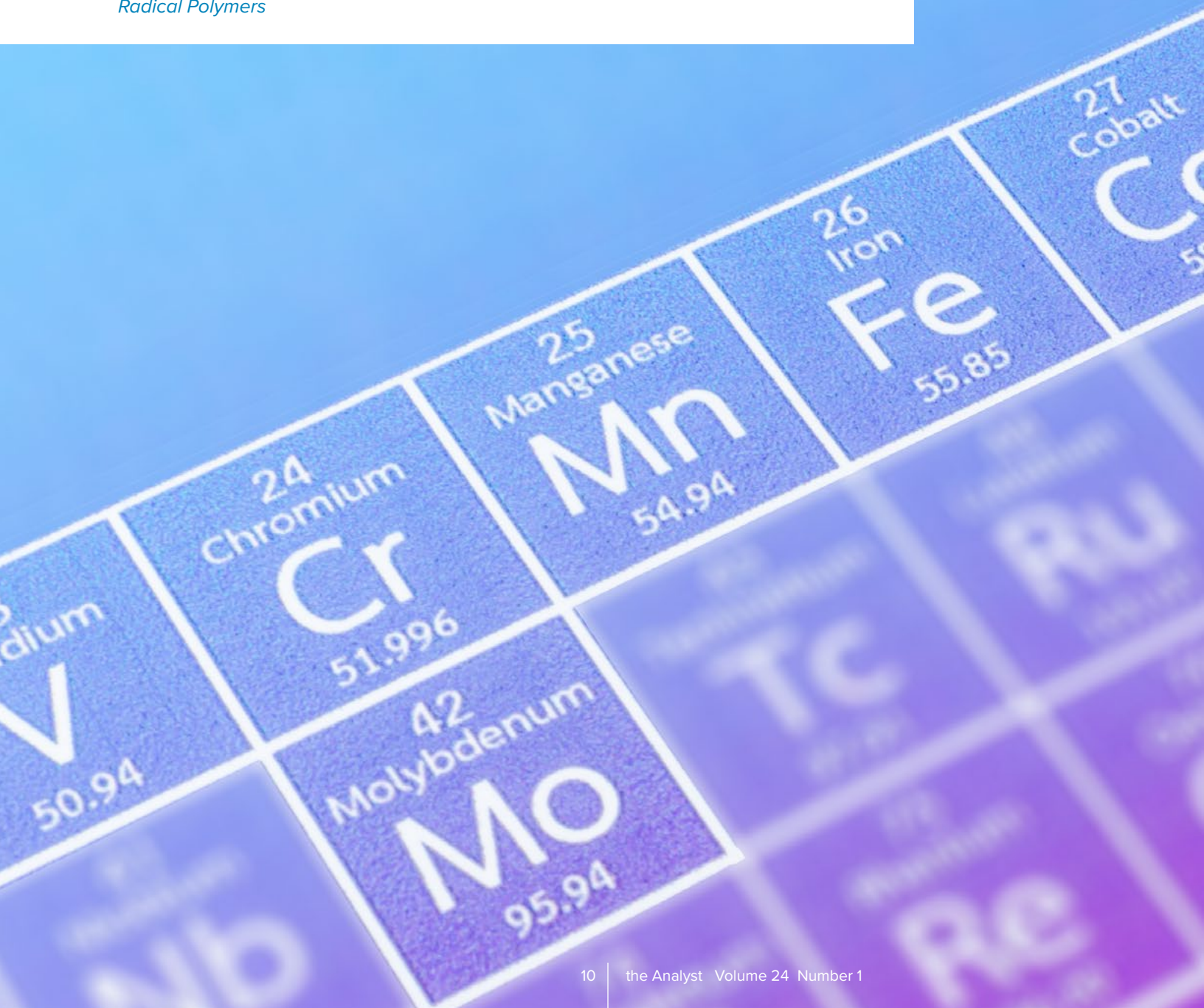


Comparing Common Metal Precipitating Agents: A Close Look at DTC, TTC, and Polymeric Choices

*By Dean Schmelter, Water Specialists Technologies, and Mike Standish,
Radical Polymers*



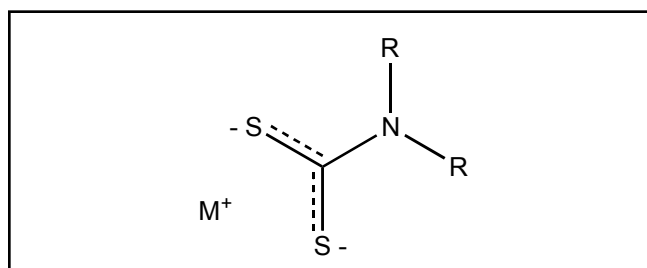
Abstract

The intent of this article is to provide a thorough review of the many choices for solving the common issue of heavy metal removal in wastewater applications. This goal is accomplished by presenting a direct and unbiased laboratory comparison of sodium dimethyldithiocarbamate, sodium trithiocarbonate, sodium polythiocarbonate and a polymeric dithiocarbamate. Further, a comprehensive study of each material's chemical properties, technical and use data, patents, toxicity profiles, and methods of destruction have been collected and are provided for the reader's consideration.

Introduction to Dithiocarbamates and Thiocarbonates

Dithiocarbamates (DTC) were first reported in literature in 1850 by Debus, where he wrote about the synthesis of dithiocarbamic acids in *Leibig's Annalen der Chemie*.¹ Dithiocarbamic acids are the reaction products of various amines with carbon disulfide. Dithiocarbamates are the resulting salt created when the acid is reacted with either an earth metal, such as sodium, potassium, or calcium, or a transition metal, such as copper, nickel, or zinc. Group 1A earth metal salts of dithiocarbamates have the basic chemical structure shown in Figure 1.

Figure 1: Discrete (single dithiocarbamate functional group, non-polymeric) Dithiocarbamate Structure



Note that each sulfur atom carries a partial negative charge (δ^-).

Since their discovery in the 19th century, dithiocarbamates have been recognized for their strong chelation properties and highly limited water solubility when formed as transition metal salts (Groups IIIB–IIB). Figure 2 provides a basic structure of a divalent transition metal, such as copper, nickel or zinc complex, with a alkylamine dithiocarbamate, such as dimethyldithiocarbamate.

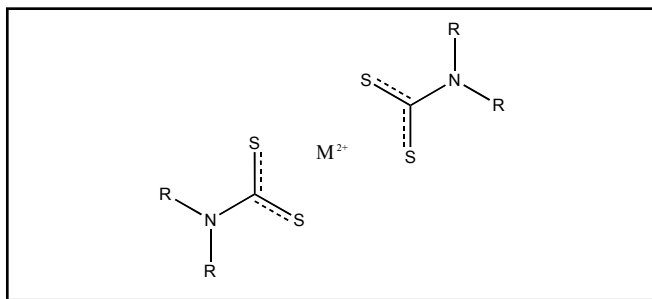
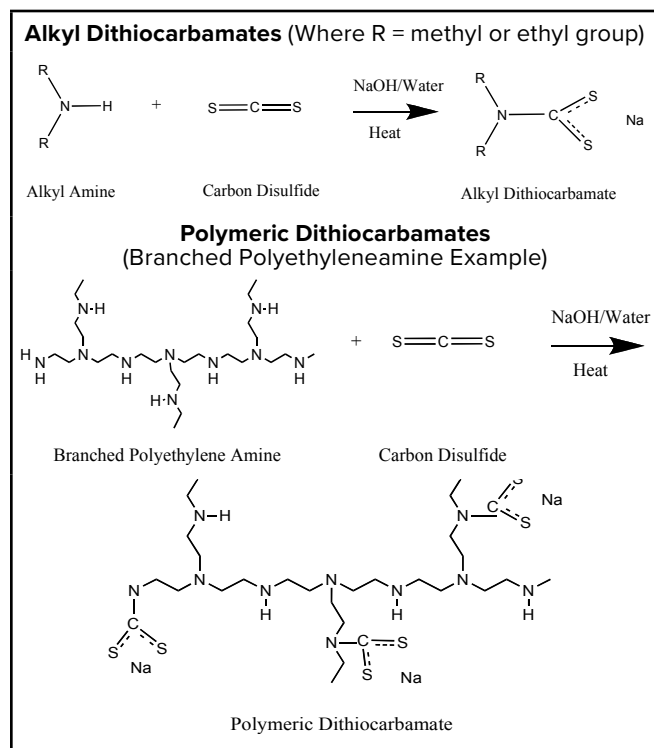
Figure 2: dithiocarbamate complex with divalent transition metal

Figure 2 shows a discrete (single dithiocarbamate functional group, non-polymeric) dithiocarbamate complex with divalent transition metal. Note that each sulfur atom carries a partial negative charge (δ^-).

Commercially, two primary types of dithiocarbamates are routinely utilized for heavy metals removal in wastewater applications. These are 1) Alkyl-amine derivatives such as dimethyl and diethyl dithiocarbamate and 2) Polyamine derivatives, which are formed from ethylene diamine and ammonia and subsequently reacted with carbon disulfide², or branched polyethylenimines (PEI) that are reacted with carbon disulfide to form the polymeric dithiocarbamate (PDTC).³ The basic reaction processes for preparing these materials are found in Figure 3.

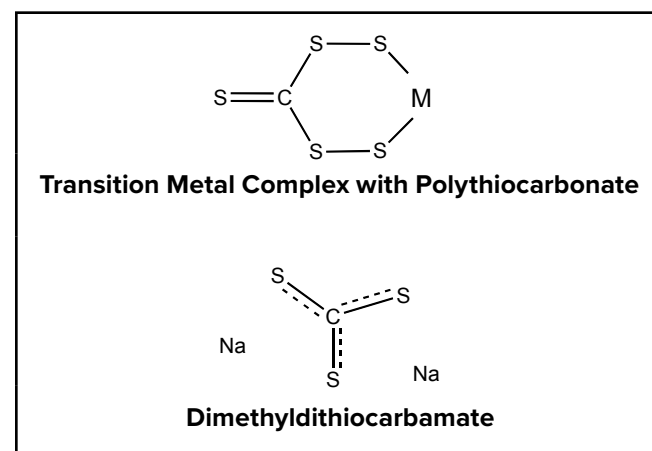
Figure 3: Common Dithiocarbamate Types

Trithiocarbonates and Polythiocarbonates

Trithiocarbonates and polythiocarbonates are inorganic sulfur compounds that are essentially the sulfur-based analogs to CO_3^{2-} . As with their oxygen-based cousins, trithiocarbonates carry a negative 2 charge and react with both earth metals and transition metals. Unlike CO_3^{2-} , thiocarbonates tend to have relatively good solubility with common group 1A and 2A metals such as calcium, magnesium, and barium at common concentrations found in most industrial waters. Additionally, thiocarbonates form very highly insoluble complexes with most all commonly found transition metals in wastewater applications.

Trithiocarbonate (TTC) and Polythiocarbonate (PTC) have been used successfully for the removal of heavy metals in waste treatment for decades. Their use has gradually increased due to new product developments, restrictions on the use of dithiocarbamates, and increased market awareness.

Whereas dithiocarbamates are formed from the reaction of amines with carbon disulfide, trithiocarbonates and polythiocarbonates are formed from the reaction of carbon disulfide and other sulfide sources. A primary difference between TTC/PTC and dithiocarbamates is the anionic charge found for each functional group. Dithiocarbamates carry a single negative charge, whereas TTC/PTC carry a charge of minus two per functional group. Common structures for thiocarbonates and polythiocarbonates are found in Figure 4.

Figure 4: Common Structures of TTC and PTC⁴

Note: Disodium Trithiocarbonate structure reflects equal distribution of the negative charges along all three sulfur atoms.

Functionality of Materials Across the Periodic Table

Across the range of dithiocarbamates and thiocarbonates mentioned in this article, reaction with metals and non-metals is relatively consistent between the various chemistries.

It is true that situational differences exist, but general trends are common. For instance, all the chemistries within these ranges are highly water soluble as the sodium and potassium salts. This is evidenced by the commercial materials, which are sold at concentrations of greater than 20%. The calcium salts are somewhat soluble at several percent in water but have much less solubility than their sodium and potassium analogs. It is important to note that the calcium salt solubility of all of these materials is greater than what would be found in even the most severe process water conditions. As such, dithiocarbamates and thiocarbonates are not useful for prevention of mineral scales such as calcium carbonate or calcium sulfate.

In the context of removal of transition metals from water systems, Figure 5 shows the typical metal complexes that are highly water insoluble as dithiocarbamate and trithiocarbonate salts. It is reported that the solubility of metal dithiocarbamates follow the order of Tl^{+1} , As^{+3} , Zn^{+2} , Fe^{+3} , Ni^{+2} , Cd^{+2} , Pb^{+2} , Co^{+3} , Cu^{+2} , Ag^{+1} , and Hg^{+2} in decreasing order of solubility.⁵ This follows a similar trend to that of metal sulfides.

Product stoichiometry reactions of alkyl dithiocarbamates are known to behave strictly relative to the calculated stoichiometry. This fact is supported by the extensive work conducted in the 19th and early 20th centuries, where alkyl dithiocarbamates were utilized as analytical reagents for the determination of metal concentrations. This property of common alkyl dithiocarbamates continues to be important in today's use in waste treatment applications, as it allows for proper calculation of product dosage and determination of residual dithiocarbamates in discharged waters. Figure 6 shows the stoichiometric derived ratios necessary for metal complexation with dimethyldithiocarbamate. Similar tables can be prepared for other alkyl dithiocarbamates by calculating the ratio of metal to

dithiocarbamate based on the valence of the metal, atomic mass of the metal, formula weight of the dithiocarbamate, and number of moles of dithiocarbamate required to satisfy the positive charge of the metal.

Figure 5: Typical Metal Complexes with Dithiocarbamates and Thiocarbonates

Typical Metal Complexes (Water Insoluble)

Non-Metal Complexes (Rarely Effective)

Periodic Table

Typical Commercial Product Forms (Water Soluble)

Figure 6: Stoichiometry of Dimethyldithiocarbamate and Transition Metals

<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: right; margin-right: 10px;">Formula Weight</div> <div>143.19</div> <div style="margin: 0 20px;"> </div> <div style="text-align: left; margin-left: 10px;"> Na^+ sodium dimethyldithiocarbamate </div> </div>				
Metal	Oxidation State	Atomic Weight	Molar Ratio	Weight Ratio
Chromium	3	52.00	3 to 1	8.26
Manganese	2	54.94	2 to 1	5.21
Iron	2	55.85	2 to 1	5.13
Iron	3	55.85	3 to 1	7.69
Cobalt	2	58.93	2 to 1	4.86
Nickel	2	58.69	2 to 1	4.88
Copper	2	63.55	2 to 1	4.51
Zinc	2	65.39	2 to 1	4.38
Palladium	2	106.40	2 to 1	2.69
Silver	1	107.90	1 to 1	1.33
Cadmium	2	112.40	2 to 1	2.55
Tin	4	118.70	4 to 1	4.83
Antimony	3	121.80	3 to 1	3.53
Platinum	4	195.10	4 to 1	2.94
Gold	3	197.00	3 to 1	2.18
Mercury	2	200.60	2 to 1	1.43
Lead	2	207.20	2 to 1	1.38

It should be noted that disodium trithiocarbonate also follows the rules of stoichiometry relative to its solubility calculations. However, trithiocarbonate can tend to form water insoluble complexes that are colloidal and well dispersed throughout the water phase. This property can incorrectly lead to the conclusion that more trithiocarbonate is needed relative to the predicted stoichiometry.

There are exceptions to the use of stoichiometry as a dosage calculator for dithiocarbamates and trithiocarbonates. Two specific instances are uses where the soluble water concentration is less than 1 mg/L and with some polymeric dithiocarbamates. In the former instance, empirical observation suggests that a dosage as much as 2–3 times that predicted may be required to effectively reduce low part per million concentrations of metals to low part per billion concentrations. It is likely that this observance is both related to chemical and physical aspects of the reaction. Chemically, dithiocarbamates have limited hydrolytic stability in water.

That is, the material decomposes over time in aqueous solutions. The rate of decomposition is impacted by a number of factors, including the pH and temperature of the water, composition of the dithiocarbamate, and a series of complex aqueous reactions. The primary point is that, as the degradation occurs, less dithiocarbamate is available for metal complexation, thus affecting the stoichiometry.

Polymeric dithiocarbamates also do not always behave according to predicted stoichiometry. The primary reason for this is that these materials have the dithiocarbamate functional groups spread across the backbone of the polymer. This is important for two reasons. First, it is possible that not all of the dithiocarbamate functional groups are required to be complexed with the metal to render the total molecule as water insoluble. Additionally, it is possible that two polymers can complex with the same metal ion in order to satisfy the charge neutralization process.

Comparative Laboratory Studies

At this point in the article, we have a theoretical view of many of the properties of dithiocarbamates, polymeric dithiocarbamates, thiocarbonates, and polythiocarbonates. To begin to develop a practical comparison, a series of laboratory tests were conducted to directly compare the efficacy of commercially available metal precipitating agents. The tests were conducted in side-by-side comparisons using the same laboratory-prepared waters and treatment conditions. The primary objective of the evaluations was to provide an unbiased and direct comparison of the materials under common use conditions. The following provides details of the experiments conducted.

Materials evaluated:

- Sodium dimethyldithiocarbamate (SDDC)
- Disodium trithiocarbonate (TTC)
- Sodium polythiocarbonate (PTC)
- Proprietary polythiocarbonate blend (PTC blend)
- Polymeric dithiocarbamate (PDTC)

Scope of Experiments

A total of five experimental conditions were evaluated. Within the experiments, both chelated and unchelated copper (Reagent-Grade— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was examined

with and without the use of an inorganic coagulant (Industrial-Grade—Aluminum chlorohydrate (ACH)). Chelated copper samples were prepared using reagent-grade disodium EDTA as specified.

The selected parameters of each test were as follows:

1. 5 mg/L Cu^{2+} , No chelate, with and without ACH coagulant
2. 20 mg/L Cu^{2+} , No chelate, ACH coagulant addition
3. 5 mg/L Cu^{2+} , No chelate, ACH coagulant addition (pre- and post-treatment)
4. 5 mg/L Cu^{2+} , 1:1 Stoichiometric addition of EDTA, ACH coagulant addition (pre- and post-treatment) – 1X treatment
5. 5 mg/L Cu^{2+} , 1:1 Stoichiometric addition of EDTA, ACH coagulant addition (pre- and post-treatment) – 1.5X treatment

Experimental Procedure

Prepare 5-gallon water sample containing copper and EDTA if indicated.

1. Measure and record copper solution pH and ORP.
2. Volumetrically transfer 1 L of copper solution to four separate glass vessels.
3. Place glass vessels on four place gang stirrer and adjust paddle speed to ~ 30% power.
4. Quantitatively add precipitating agents as indicated to each stirring vessel.
5. Add coagulant if indicated.
6. Continue stirring for ~ 5 minutes.
7. Document visual observations via digital photography.
8. Measure treated solution pH and ORP.
9. Filter samples using 50 cc syringe and 0.45 μm nylon disc membrane.
10. Place filtered samples in clean 50/mL polyethylene sample containers.
11. Label sample containers numerically to provide blind analysis.
12. Send samples off site for copper analysis via ICP.

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Experiment 1: 5 mg/L Cu²⁺, No Chelate, With and Without ACH Coagulant

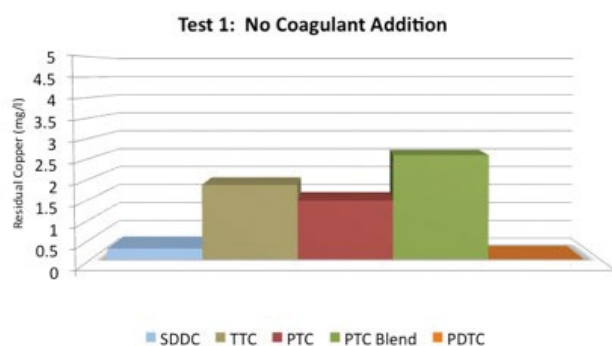
Starting Solution

- 5mg/L solution Cu²⁺ using CuSO₄ • 5H₂O
- No EDTA added
- pH ~ 7.43
- ORP ~ +140 mV

Treatment Conditions

- Precipitant added
- Rxn time <10 min
- Filtration via 0.45µm membrane
- Analysis via ICP

Product	ACH (mg/L)	Product (mg/L)	Soln. pH After Treatment	Solution ORP (mV)
SDDC	0	60	8.0	+51
TTC	0	50	7.9	+38
PTC	0	50	7.4	+107
PTC Blend	0	80	7.5	-280
PDTC	0	60	6.5	-56



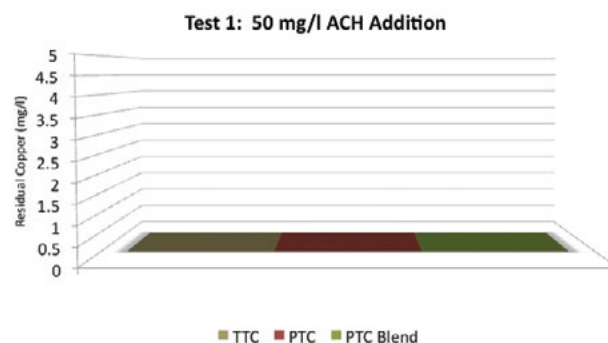
Starting Solution

- 5mg/L solution Cu²⁺ using CuSO₄ • 5H₂O
- No EDTA added
- pH ~ 7.43
- ORP ~ +140 mV

Treatment Conditions

- Precipitant added
- Coagulant addition
- Rxn time <10 min
- Filtration via 0.45µm membrane
- Analysis via ICP

Product	Initial ACH (mg/L)	Product (mg/L)	Soln. pH After Treatment	Solution ORP (mV)
TTC	50	50	7.1	-149
PTC	50	50	6.7	-152
PTC Blend	50	80	6.9	-149



Photographs from Test 1:

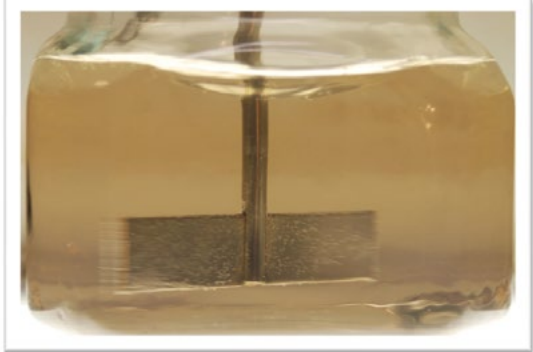
SDDC – No Coagulant Addition



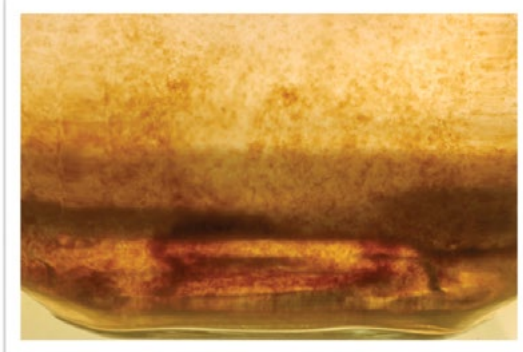
TTC – No Coagulant Addition



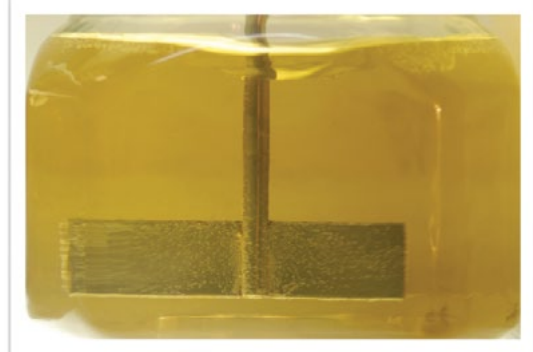
PTC – No Coagulant Addition



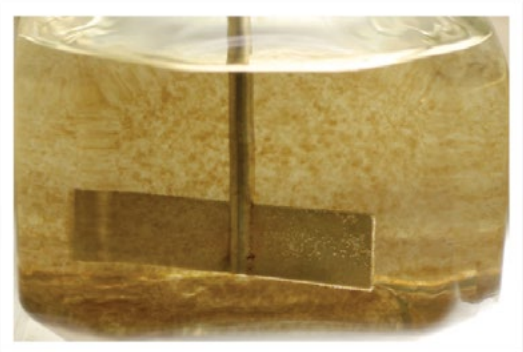
TTC + ACH Coagulant Addition



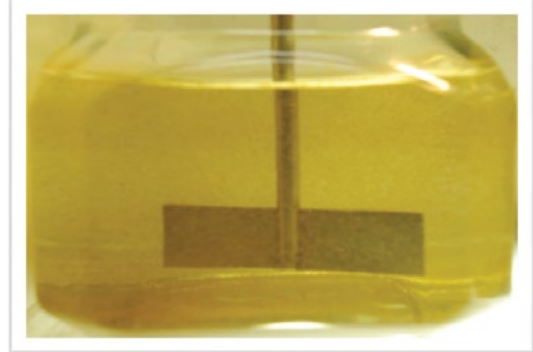
PTC Blend – No Coagulant Addition



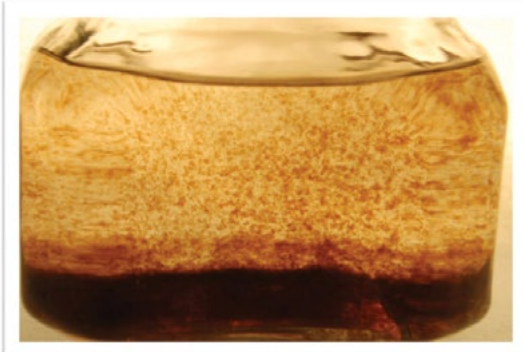
PTC + ACH Coagulant Addition



PDTC – No Coagulant Addition



PTC Blend + ACH Coagulant Addition



Experiment 2: 20 mg/L Cu^{2+} , No Chelate, ACH Coagulant Addition

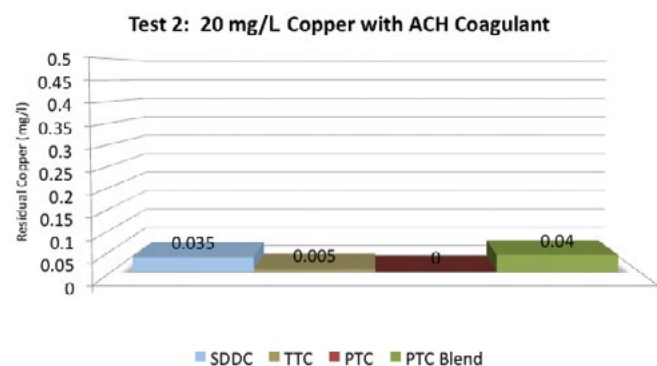
Starting Solution

- 20 mg/L solution Cu^{2+} using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- No EDTA added
- No coagulant addition
- pH ~ 7–8
- ORP ~ +200 mV

Treatment Conditions

- Precipitant added
- Coagulant addition
- Rxn time <10 min
- Settling time ~ 12 hours
- Filtration via 0.45 μm membrane
- Analysis via ICP

Product	ACH (mg/L)	Product (mg/L)	Soln. pH After Treatment	Solution ORP (mV)
SDDC	280	192	8.1	-200
TTC	280	210	7.9	-170
PTC	280	228	7.5	-164
PTC Blend	280	168	7.5	-149



Photographs from Test 2:

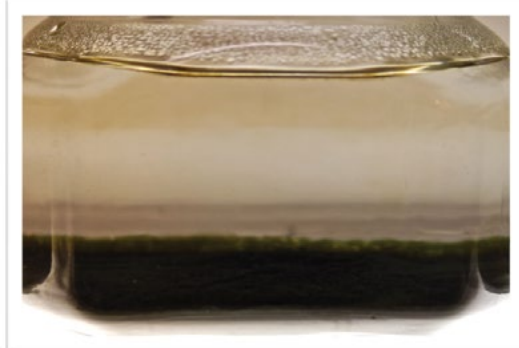
SDDC + ACH Coagulant



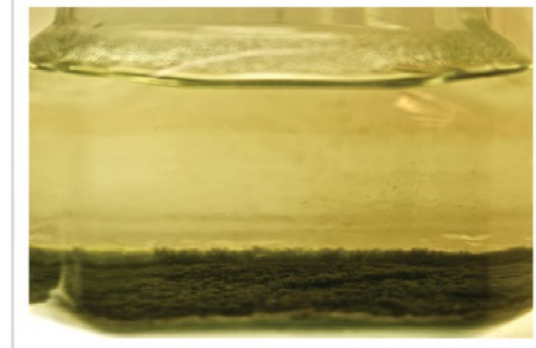
TTC + ACH Coagulant



PTC + ACH Coagulant



PTC Blend + ACH Coagulant



Experiment 3: 5 mg/L Cu²⁺, No Chelate, ACH Addition (Pre- and Post-Treatment)

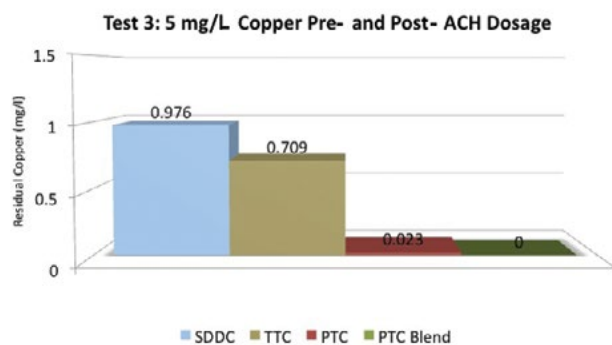
Starting Solution

- 5mg/L solution Cu²⁺ using CuSO₄ • 5H₂O
- No EDTA added
- No coagulant addition
- pH ~ 7.5
- ORP ~ +139 mV

Treatment Conditions

- Precipitant added
- Coagulant addition
- Pre-treatment – 160 mg/L ACH
- Post-treatment – 80 mg/L ACH
- Rxn time <10 min
- Filtration via 0.45µm membrane
- Analysis via ICP

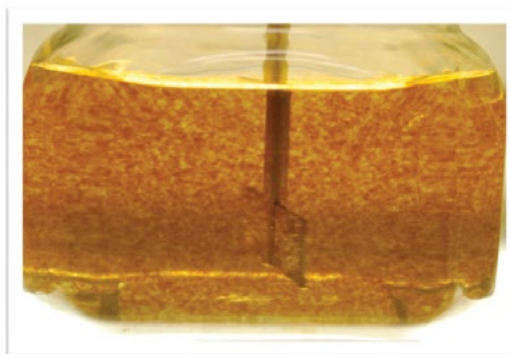
Product	ACH Pre Treatment (mg/L)	Product (mg/L)	ACH Post Treatment (mg/L)	Soln. pH	Solution ORP (mV)
SDDC	160	64	80	7.2	+50
TTC	160	70	80	7.2	+20
PTC	160	76	80	7.4	+37
PTCBlend	160	56	80	7.5	-149



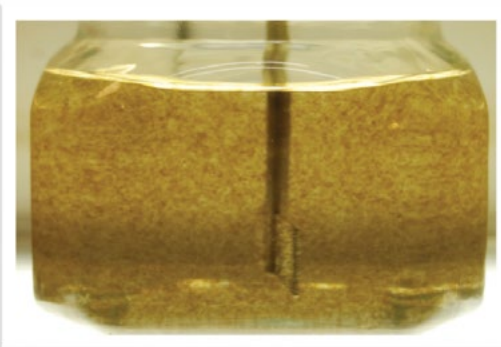
Photographs from Test 3: SDDC



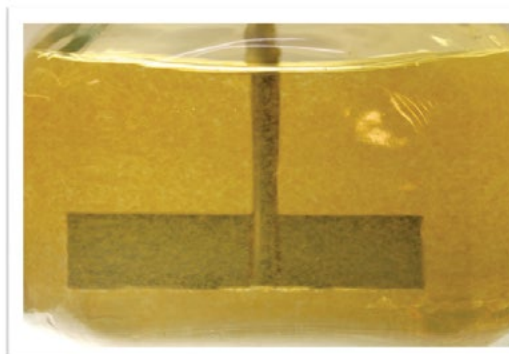
TTC



PTC



PTC Blend



Experiment 4: 5 mg/L Cu^{2+} , 1:1 Stoichiometric Addition of EDTA, ACH Coagulant Addition (Pre and Post Treatment) – 1X Stoichiometric Treatment

Starting Solution

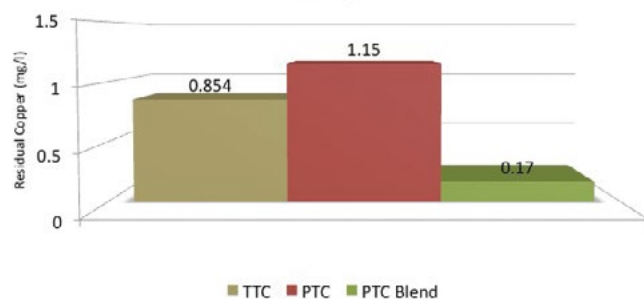
- 5mg/L solution Cu^{2+} using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- 1:1 Stoichiometric EDTA dosage added
- pH ~ 7.5
- ORP ~ +100–200mV

Treatment Conditions

- Precipitant added
- Coagulant addition
 - » Pre-treatment – 160 mg/L ACH
 - » Post-treatment – 80 mg/L ACH
- Rxn time <10 min
- Filtration via $0.45\mu\text{m}$ membrane
- Analysis via ICP

Product	Initial ACH (mg/L)	Product (mg/L)	Post ACH (mg/L)	Solution ORP (mV)
TTC	160	70	80	-54
PTC	160	76	80	-68.5
PTC Blend	160	56	80	-270

Test 4: 5 mg/L EDTA Chelated Copper - 1X Stoichiometric Dosage



Time-lapsed Photographs from Test 4:



Experiment 5: 5 mg/L Cu^{2+} , 1:1 Stoichiometric Addition of EDTA, ACH Coagulant Addition (Pre- and Post-Treatment) – 1.5X Stoichiometric Treatment

Starting Solution

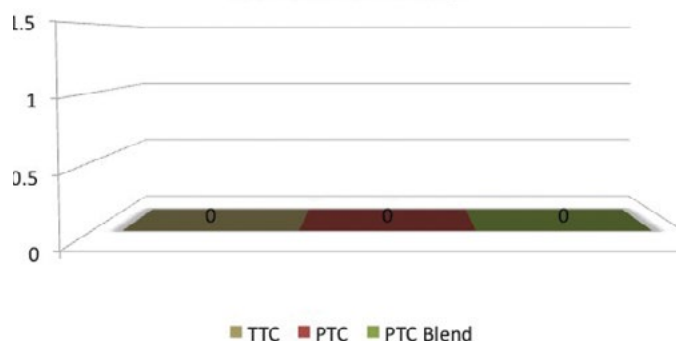
- 5mg/L solution Cu^{2+} using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- 1:1 Stoichiometric EDTA dosage added
- pH ~ 7.5
- ORP ~ +100–200mV

Treatment Conditions

- Precipitant added
- Coagulant addition
- Pre-treatment – 160 mg/L ACH
- Post-treatment – 80 mg/L ACH
- Rxn time <10 min
- Filtration via 0.45 μm Membrane
- Analysis via ICP

Product	Initial ACH (mg/L)	Product (mg/L)	Post ACH (mg/L)	Solution ORP (mV)
TTC	160	105	80	132
PTC	160	114	80	70
PTC Blend	160	84	80	32

Test 5: 5 mg/L EDTA Chelated Copper – 1.5X Stoichiometric Dosage



Time-lapsed Photographs from Test 5:

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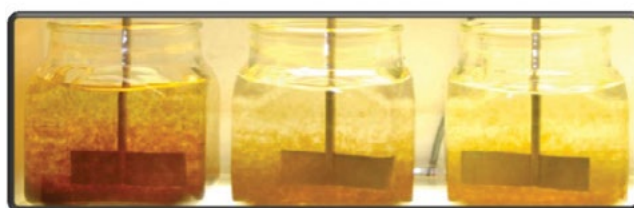


TTC

PTC

PTC Blend

01:01.5

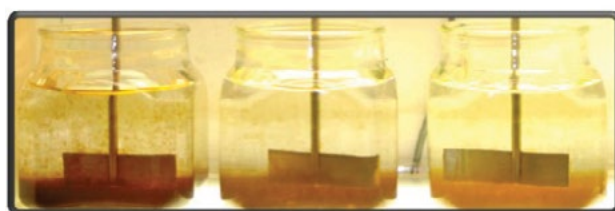


TTC

PTC

PTC Blend

02:08.7

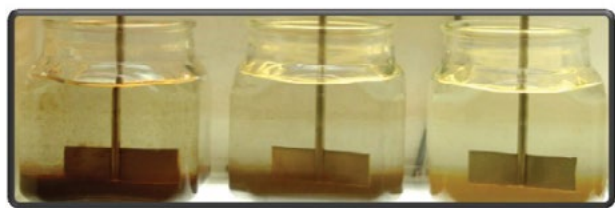


TTC

PTC

PTC Blend

03:42.7



TTC

PTC

PTC Blend

Conclusions from experimental work:

- All products effective across low, moderate, and high copper loadings.
- SDDC and PDTTC function better than TTC and PTC in absence of coagulant.
- ACH proved to be an effective coagulant in all circumstances.
- TTC and PTC w/ACH better than SDDC and PDTTC with or without ACH.
 - » Faster and more complete clarification.

- For EDTA chelated copper.
 - » The PTC blend performed at lower dosage than TTC or PTC.
 - » PTC and the PTC blend showed better clarification properties.
- Time.
- Clarity.
 - » All products effectively removed EDTA chelated copper.
- Overall
 - » PTC shows equivalent copper removal to TTC.
 - » PTC shows better copper removal efficiency than TTC, DTC, or PTDC.
 - » PTC and the PTC blend show better clarification properties to TTC. ⚗



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Dean Schmelter, Water Specialists Technologies, can be reached at (407) 321-7910 or dean@waterspecialists.biz.

Mike Standish, Radical Polymers, can be reached at (423) 316-9877 or mike.standish@radicalpolymers.com.