CCS Pipeline

CHELATION INFORMATION

Chelate – An organic chemical with at least two or more functional groups that can bind with metals to form a ring structure. Organic material in the soil can form chelates with some transition metals, however, most metal binding in the soil does not involve chelation. Chelates can increase the soluble fraction of some metals. Sugars and amino acid compounds can form chelate complexes with metals.

Chelation – To form a heterocyclic ring that contain at least one metal cation or hydrogen ion on the ring. Organic compounds are used as chelating agents. Chelate is Greek for claw or talon. The organic molecule wraps around the metal and bonds to all available positive charges.

Heterocyclic compound - A compound in which the ring structure is a combination of more than one kind of atom; ie. Pyridine - C_5H_5N.

Sequester – To set apart or bind and protect charges on metals or ions. With sequestering agents the chemical structure does not wrap around the metals, rather, the metals are bound in the structure of the sequestering agent. Large organic molecules have these properties for some metals. Humic and fulvic acid can sequester metals away from the soil solution. These large organic soil molecules have very high CEC, and can hold onto large quantities of metals and other materials with charges. Hydrogen bonding also occurs in these large molecules with metals and other positively and negatively

Foliar absorption – Foliar absorption of nutrients is dependent upon several factors, including; length of contact of the nutrient solution with the leaf surface, the degree of wetting of the surface and the physical properties of the leaf surface. Nutrients applied to leaf surfaces gain access into the plant by penetration of the surface or through stomata openings. The uptake of nutrients by foliar tissue differs from uptake by roots due to the resistance imposed by the outer coating or cuticle layer. Once nutrients have crossed the cuticle into the plant cells absorption into the cells is similar to that of roots. The movement of ions and organic materials across the cuticle physical barrier is by the physical process of diffusion. The diffusion of molecules through the cuticle is directly proportional to concentration, increased with temperature and lipophilicity of the compound or carrier. Urea increases the permeability of ions and organic molecules through the cuticle when applied simultaneously with the materials. The urea induces changes (increases permeability) of cuticle structures.

The solubility of a solute in a lipid membrane is dependent on the polarity of that compound. Ions are charged particles, therefore, polar, and are relatively insoluble in membranes. Carrier molecules can shuttle specific ions across thermodynamic barriers towards lower chemical potentials – can carry the ions through cuticle material and through lipid cell wall layers. Active (energy requiring mechanisms) is essential for uptake of most charged – unprotected – ions. Carrier molecules can facilitate diffusion movement of charged ions across biologic membranes. Some carrier molecules have selective affinities for various ions. pH, ionic concentration and water content also can facilitate movement.

All polyvalent cations are capable of forming chelates, but each metal differs in the ease with which it chelates. The stability of metal chelates or the replacing power of the elements in decreasing order is:
$Fe^{+3} > Cu^{+2} > Zn^{+2} > Fe^{+2} > Mn^{+2} > Ca^{+2} > Mg^{+2}$. Ferric iron chelates are more stable than any of the other metal chelates essential for plant growth. The solution of ferric ions could be expected to replace equal concentrations of any of the other metals from the chelation ring.

Each chelating agent (ligand) also differs in its ability to combine with a particular cation and render it to the chelated state. The ability of the chelating agent to bind the cation is indicated by its stability constants [Table 1]. Stability constant tables provide relative strength of different chelating (proton-ligand complexes).

Stability constants for proton-ligand complexes			Table 1		
Ligand	**Log K1***	**Log K2***	**Log K3***	**Log K4***	**Log K5***
Acetate	4.70				
Ammonia	9.40				
Citrate	5.80	4.48	2.96		
DCTA	11.78	6.20	3.60	2.51	1.70
DTPA	10.55	8.59	4.30	2.66	1.82
EDTA	10.34	6.24	2.75	2.07	
EGTA	9.47	8.85	2.66	2.00	
Ethylene-diamine	10.11	7.30			
Glycine	9.52	2.35			
Oxalate	3.64	1.22			
Tartrate	3.96	2.80			

* The constants selected refer to 25º C or in some cases to 20ºC, and ionic strength of 1.

Chelates can be used to prevent or correct micronutrient deficiencies. They can be used as foliar spray and well as in soil application. Table 2 below shows characteristics of chelates for these applications.

The strength of the ligand to bind the metal cations affects the availability of the mineral to the plant. A weak chelating agent is not able to protect against hydrolysis, especially in high pH environments. When synthetic chelates are used the metal cations must be released either within the plant or at the surface of the roots. A strong chelating agent may tightly bind the metal and not release it to the plant.

Characteristics of chelates used as foliar spray or soil application. Table 2	
Foliar Application	**Soil Application**
1 Easily absorbed by plants.	1 Should not be easily replaced by other polyvalent cations in the soil.
2 Translocated readily within the plant.	2 Must be stable against hydrolysis.
3 Easily decomposed so the metal becomes available.	3 Has to be resistant to microbial decomposition.
4 Must be compatible with other materials in the spray.	4 Should be soluble in water.
5 Must not damage the cuticle.	5 Should not easily precipitate by ions or colloids in the soil.
	6 Must be available to plants either at root surfaces or within the plant.
	7 Must be nondamaging to plants at concentrations required to prevent deficiencies.

Strongest complexing agents (synthetic materials) are used mainly in soil applications. Their stability must withstand high soil pH and other soil properties may affect their activity (ie: EDTA is not good supplier of Fe and Mn in high organic soils). Fe-EDDHA should only be used in high pH soils.

Chelates in Table 3 are categorized according to their chelating (complexing) strength. The strongest chelate may not be the ideal chelate if the bond with the metal ion is too strong.

Metal chelating (complexing) agents grouped by chelating (complexing) strength. Table 3

STRONGEST (Synthetic)	Intermediate (Long-chain natural organics)	Weakest (Short-chained or small organics)
EDTA	Polyflavonoids	Citric Acid
HEEDTA	Ligand sulfonates *	Ascorbic Acid
DTPA	Humic & Fulvic Acids	Tartaric Acid
EDDHA	Amino Acids	Adipic Acid
NTA	Glutamic Acid	
CDT	Polyphosphates **	

* Some companies make these synthetically

** Polyphosphates are not organic, however, they behave like organic chelate molecules

Foliar application of some synthetic chelate materials can cause a phytotoxic reaction, especially at high rates. Synthetic materials are often used for soil applications. The intermediate chelating agents are generally safer for foliar application and are more often used foliarly than for soil application. A general rule is, chelating agents that easily decompose are safer for foliar application. Foliar use of chelates is often much cheaper than soil application because of the lower rates. Foliar application of chelates is more efficient than soil use. The weakest chelation agents are generally used in special situations or when materials are placed adjacent to the root zone.

Organic chelates generally provide better metal uptake and translocation within the plant. Inorganic materials may become toxic, especially if the plant can not metabolize them.

CHEMICAL NAMES AND ABBREVIATIONS FOR SOME COMMON CHELATES

BPDS	Bathophenanthrolinedisulfonic acid
CIT	Citric acid
CDTA (DCTA)	trans-1,2-Cychlohexylenedinitrilotetraacetic acid
DTPA	Diethylenetrinitrilopentaacetic acid
EDDHA (EHPG, APCA)	Ethylenediiminobis(2-hydroxyphenly)acetic acid
EDMA	Ethylenediaminemonoacetic acid
EDDA	Ethylenediamine-N, N'-diacetic acid
EDTA	Ethylenedinitrilotetraacetic acid
ED3A	Ethylenedinitrilotriacetic acid
EGTA	Ethylenebis(oxyethylenetrinitrilo)tetraacetic acid
HBED	N,N'-Bis(2-Hydroxyethyl)ethylenedinitrilotriacetic acid
HEDTA (HEEDTA)	N-(2-Hydroxyethyl)iminodiacetic acid
IDA	Iminodiacetic acid
NTA	Nitrilotriacetic acid

Ranking of chelation agents for metals under High, Moderate and Slightly REDUCED soils at pH 7.0 (As soil becomes more reduced metals become less available for roots.)

Soil Redox Status	Metal	Strength (ranking > > > >)								
Slight	Cu^{+2}	EDDHA	HEDTA	DTPA	HIDA	EGTA	NTA	EDTA	CDTA	CIT
High		HEDTA	DTPA	HIDA	EDTA	NTA	EGTA	EDDHA	CDTA	CIT
Moderate		HEDTA	DTPA	EDTA	HIDA	EGTA	NTA	CDTA	EDDHA	CIT
Slight	Fe^{+2}	HEDTA	CDTA	DTPA	EDTA	HIDA	NTA	CIT	EGTA	EDDHA
High		HEDTA	CDTA	DTPA	EDTA	HIDA	NTA	CIT	EGTA	EDDHA
Moderate		HEDTA	CDTA	EDTA	DTPA	HIDA	NTA	CIT	EGTA	EDDHA
Slight	Mn^{+2}	EDTA	EGTA	DTPA	NTA	CDTA	HEDTA	HIDA	CIT	HBED
High		EDTA	HEDTA	DTPA	CDTA	EGTA	NTA	HIDA	CIT	HBED
Moderate		EDTA	HEDTA	DTPA	CDTA	EGTA	NTA	HIDA	CIT	HBED
Slight	Zn^{+2}	HEDTA	NTA	EDTA	DTPA	HIDA	CDTA	EDDHA	EGTA	CIT
High		HEDTA	EDTA	DTPA	NTA	HIDA	CDTA	EGTA	CIT	EDDHA
Moderate		HEDTA	EDTA	DTPA	NTA	CDTA	HIDA	EGTA	CIT	EDDHA

Ranking of chelation agents for metals under Acid, Neutral and Basic soils at pH 4 - 9.

METAL	pH 4	pH 5	pH6	pH 7	pH 8	pH 9
Cu^{+2}	HIDA	EGTA	HEDTA	HEDTA	DTPA	DTPA
	EGTA	HIDA	EGTA	DTPA	HEDTA	HEDTA
	HEDTA	NTA	NTA	EDTA	CDTA	CDTA
Fe^{+2}	HIDA	HIDA	HEDTA	HEDTA	CDTA	CDTA
	HEDTA	HEDTA	NTA	CDTA	DTPA	DTPA
	EGTA	NTA	HIDA	EDTA	HEDTA	HEDTA
Fe^{+3}	EDDHA	EDDHA	EDDHA	EDDHA	EDDHA	EDDHA
	HEDTA	HEDTA	HEDTA	HEDTA	DTPA	DTPA
	EGTA	EDTA	EDTA	EDTA	CDTA	CDTA
Mn^{+2}	EGTA	EGTA	EGTA	EDTA	DTPA	DTPA
	HIDA	HIDA	HEDTA	DTPA	CDTA	CDTA
	NTA	NTA	EDTA	CDTA	EDTA	EDTA
Zn^{+2}	HIDA	HEDTA	HEDTA	HEDTA	DTPA	DTPA
	HEDTA	HIDA	NTA	EDTA	HEDTA	EDTA
	NTA	NTA	EDTA	DTPA	CDTA	HEDTA

GENERAL INFORMATION

EDDHA AND HBED FORM EXTREMELY STABLE Fe^{+3} CHELATES (HBED was not plotted and was ~ EDDHA).

Competition for chelates from Al^{+3}, Ca^{+2} & Mg^{+2} at high pH may cause differences in soils depending upon the level of these cations, especially calcareous soils.
Anaerobic conditions can influence chelation properties at any soil pH.

When using any chelation material always follow the manufacturers usage guidelines and blending requirements.

Information contained in this pipeline should be used for general planning purposes only. Specific soil conditions and soil nutrient levels will have an impact on chelation with different materials and metals (cations). A soil test and irrigation suitability test should be taken before any soil chelate is used. Foliar use of chelation agents can result in better nutrient uptake by leaves and improved internal translocation. If irrigation water quality is poor (high calcium, sodium and bicarbonates) foliar chelates should be considered.

For information on soil and fertility considerations, call Creech Crop Services, LLC.

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