Chelating Agents

Chelating agents are an extensive, but important subject to cover in some detail. Although reference to the chelate bond dates back as far as 1893, it wasn't until in 1920 two scientists, G. Morton and H. Drew, coined the word "chelate", derived from the Greek term *chela*, meaning "great claw" of the lobster or other crustaceans. The term chelate suggests the way in which an organic compound "clamps" onto the cationic element, which it chelates.

There are plenty of books, reviews and technical papers dealing with in depth chemistry of chelating compounds and their functions. The purpose of this manual is to supply information about chelation related to practical agricultural issues. One such issue is the different terms applied to chelated minerals:

1) Chelated
2) Sequestered
3) Complexed

In order for a compound to be called a true chelating agent, it must have certain chemical characteristics. This chelating compound must consist of at least two sites capable of donating electrons (coordinate covalent bond) to the metal it chelates. For true chelation to occur the donating atom(s) must also be in a position within the chelating molecule so that a formation of a ring with the metal ion can occur.

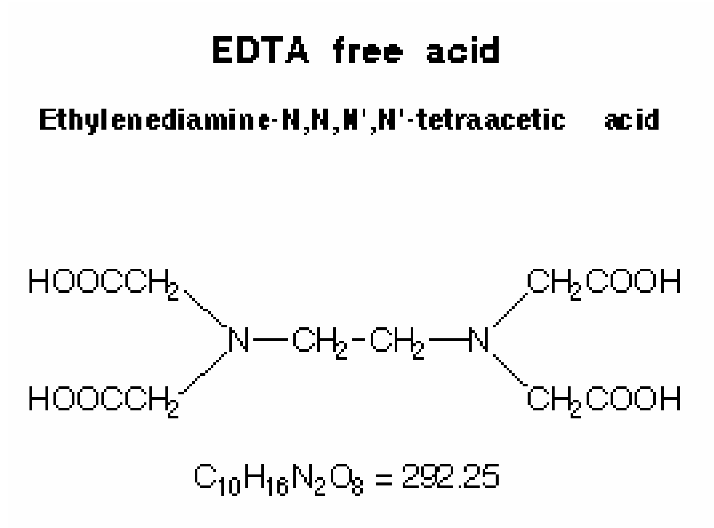
The term sequestered deals more with the action of chelation or complexing, not the actual chemical arrangement or definition. The term "complexed" originates from combinations of minerals and organic compounds that do not meet the guidelines of a true chelate.

There are five categories of compounds that are commonly mixed with minerals and used in agricultural foliar and soil applied applications:

1) Synthetic Chelates
2) Ligno Sulfonates
3) Humic or Fulvic Acids
4) Organic Acids
5) Protein (Amino Acids)

Each group of chelating agents will be briefly covered in the following pages to illustrate their respective basic functions relating to commercial agriculture. Although we could publish an entire book on this subject alone, the following information serves as a general guideline to help you understand some advantages and disadvantages of each type.

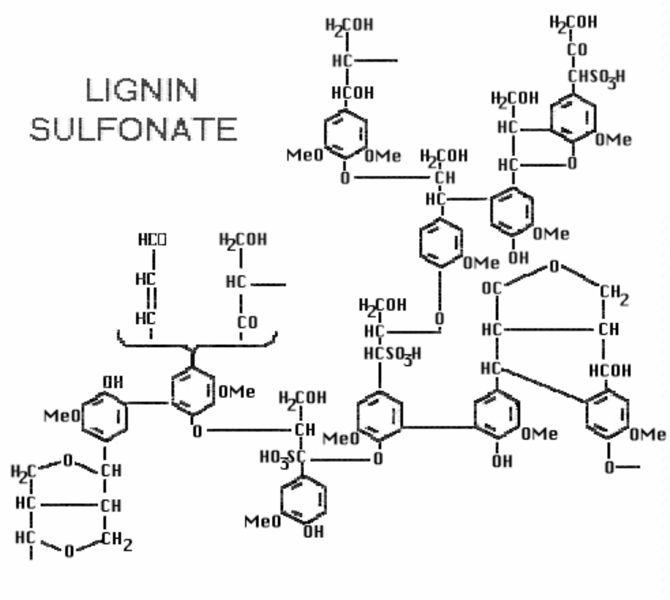
1. Synthetic Chelating Agents -- The most common form is EDTA that is usually used in agricultural mineral formulations as the disodium salt of EDTA. Synthetically chelated minerals among the strongest forms of chelation used in commercial agricultural applications. Here is a picture of pure EDTA:



Commonly used forms of minerals are; calcium EDTA, magnesium EDTA, zinc EDTA, manganese EDTA and Copper EDTA. Forms of synthetic iron chelates vary somewhat, according to the condition in which they are utilized. One popular form is iron EDDHA (ethylenediamine [di (o-hydroxyphenylacetic) acid]).
Although some may debate the effectiveness of synthetic chelating agents for foliar application, it is known that in a nutrient solution it is essential to have an excess of total mineral in relation to chelating agent so that the chelating agent does not compete for the mineral with the plant. This is one reason why soil applications of synthetic chelating agents are effective; there is plenty of non-chelated minerals present.

EDTA - Advantages	EDTA - Disadvantages
• EDTA chelates are very stable and can be mixed with just about any phosphate containing fertilizer at basically any pH. • EDTA is very resistant to microbial degradation; therefore it remains quite stable in soils.	• EDTA is a synthetic compound, **not** produced by plants. • Synthetic chelating agents can compete with the plant for a mineral. EDTA is known for its strong affinity towards calcium, and although debatable, some think that because of its persistence in a plant, it is possible that a zinc EDTA foliar applied, could be effective for zinc, but the EDTA could compete for calcium once in the plant.

2. Ligno Sulfonates -- Considered to be a water soluble, non-toxic polymer. Polymer usually means that the molecule is quite large. Here is a picture of part of a molecule:

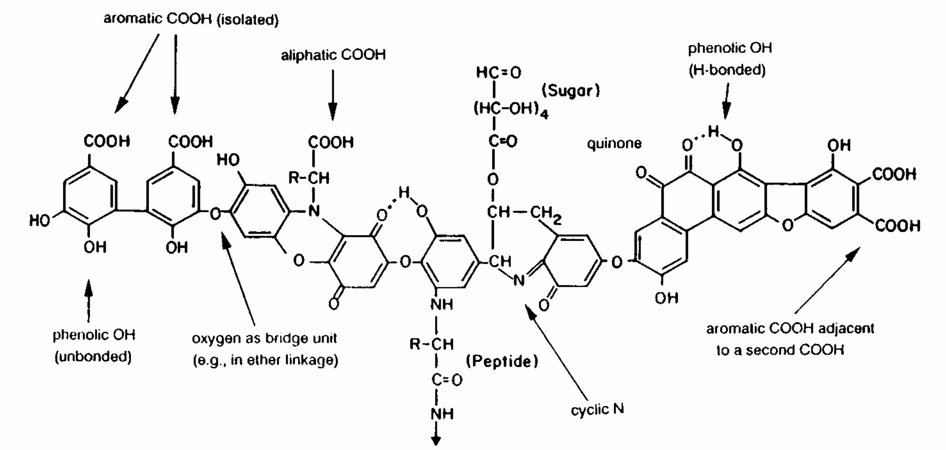


Lignin, a major polymeric component of woody tissues in higher plants, is composed of repeating phenyl propane units and usually amounts to 20-30% of the dry weight of wood. It is a by product of the pulp and paper industry. The lignin derived from soft woods is different that that from hardwoods, therefore, their reactivity differs somewhat.

Ligno sulfonates and mineral combinations are quite often referred to as sequestered or complexed. With all the available sites on the ligno sulfonate molecule, it is very possible that there would be 2 or 3 available to make a true chelate, however, the size of molecule to number of potential chelate sites makes this molecule an inefficient chelator. Although it is possible to make very effective mineral formulations from ligno sulfonates, most commercially utilized sources of this material are not formulated for effective foliar uptake.

Ligno Sulfonates - Advantages	Ligno Sulfonates - Disadvantages
• The best advantage of ligno based minerals is its lower cost. • Another advantage is the polymer is biodegradable and supportive of soil microorganisms. • Ligno sulfonate also has surfactant properties. (Soil applications)	• The main disadvantage of ligno sulfonate for foliar application is the size of the molecule. There are many different grades of lignin and thus different molecular weights. Some are as high as 21,000. • With proper sulfonation, lower MW lignin sulfonates do exist.

3. Humic or Fulvic acids -- There are thousands of published papers on the subject of humic and fulvic acids. Many debate the actual structure of these molecules, however, one commonly acceptable hypothetical structure is presented as follows:[4]

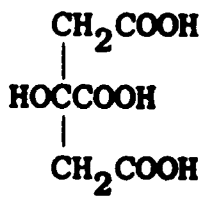


However, before one assumes that this is actually a "picture" of a humic acid molecule, let us do some calculations. The approximate molecular weight of the above pictured compound (excluding potential "R") is less than1,800. This would mean that the above picture is more representative of a fulvic acid molecule. Some in the humic acids industry try to peddle this structure as a humic molecule, however, one would have to "paste" a great number of this "pictured" compound together to get a true view of a large humic acid molecule. Especially some those molecules extracted from lignite or leonardite.

In foliar applications, the fulvic acids in NUE Amino Minerals may not play a direct role in availability and movement of minerals in the plant. However, they do act as plant stimulants and possibly precursors to plant hormones.

Humic & Fulvic Advantages	Humic & Fulvic Disadvantages
• Humic and fulvic acids are cost effective compounds to add to foliar & soil applied minerals. • When they are "small" enough to effectively move into the plant, they can supply a beneficial source of precursors to important plant chemicals.	• In foliar applications humic has a definite disadvantage of being too large in size. • In trace mineral mixtures humic molecules tend to settle out in the container, largely due to their molecular size and of their poor suspension of these complex colloids in water at lower pH.

4. Organic Acids -- These compounds are one of two groups of compounds that are essential for the transportation and solubility of divalent elements (2 positive charges: Zn^{++}, Mn^{++}, Fe^{++}, Cu^{++}) in plants. The organic acids can be called "anionic organic acids" because of their negative charge. One such popular organic acid in agriculture is citric acid:



Although organic acids do not directly chelate monovalent elements, (single positive charge: K^+, Na^+), they are associated in plant systems by loosely held ionic attractions.

In foliar applications, these anionic (negatively charged) organic acids play an important role in converting cationic (positively charged) minerals into nonionic (neutral) compounds for increased leaf penetration and movement into the plant. Plants have the ability to manufacture many types of organic acids such as: citric, malic, fumaric, succinic and others. Some of these acids are utilized to transport minerals in the plant. Others are excreted from the roots to solublize and take needed minerals into the plant system.

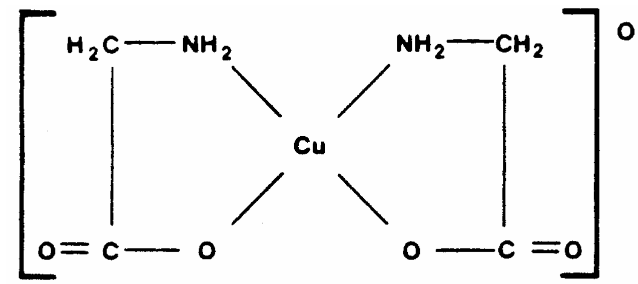
NUE Amine Minerals contain a group of these natural organic acids, derived from a fermentation process.

Organic Acids - Advantages	Organic Acids - Disadvantages
• Organic acids are one of the natural systems a plant utilizes to solublize and translocate minerals. • The groups of organic acids in NUE Amino minerals have been proven in field demonstrations to be more effective in correcting mineral deficiencies on some crops than mineral applications without these compounds. • By neutralizing the charge of minerals, organic acids make mineral uptake more effective.	• Commercially produced individual organic acids are quite expensive compared to some other chelating and complexing agents. • Compared to synthetic chelating agents and some amino acid chelating compounds, organic acid chelates form weaker bonds with minerals, especially at increasing pH levels.

5. Protein (Amino Acids) -- Amino acids are the second type of natural compounds that plants produce to solublize and translocate minerals.
Plants manufacture these compounds to make minerals biologically available in the cell. Even when unchelated or uncomplexed minerals are sprayed on plants (i.e. 10% zinc sulfate), the mineral must combine with an organic compound such as an amino acid before the plant can effectively utilize it.

As with organic acids, amino acid compounds also play a role in mineral uptake into plant tissue, because of the increase permeability effect of the amino acid on the cuticle.

Following is a diagram of an amino acid chelate of copper:



A dipeptide Chelate of Copper

Another important function of amino acid chelated minerals is that they are less phytotoxic to plants, especially during stress points in plant development.

Amino Acids - Advantages	Amino Acids - Disadvantages
• Amino acids are one of the natural systems a plant utilizes to translocate and utilize minerals. • The groups of amino acids in NUE Amino minerals have been proven in field demonstrations to be more effective in correcting mineral deficiencies on some crops than mineral applications without these compounds. • By neutralizing the charge of minerals, amino acids make mineral uptake more effective.	• Enzymatically hydrolyzed protein is expensive to produce. • The actual combination of properly prepared amino acid/peptide compounds and minerals is not 100% complete with simple tank mix procedures.

Chelating Agents -- Putting it all together

The description of the chelating or complexing compounds given in the previous 5 pages, is very basic. One could gather enormous amounts of information on each subject. However, the purpose of illustrating only the basic characteristics is to relay information that is useful in understanding and using NUE Amino Minerals in comparison to other products. Following is a summary of the key points:

NUE Amino Minerals are formulated to provide important benefits and advances in foliar feeding technology:

1) Better Tank Mixing Compatibility -- Although the organic acids and amino acids portion of NUE AMINO Minerals does not supply the chelating stability of EDTA (at high pH's), tank mixing NUE AMINO Minerals with phosphate fertilizers is now better. Properly mixed, N-P-K and mineral combinations (including calcium) will remain visually clear, indicating that no less water-soluble mineral-phosphates compounds have formed.
2) Superior Plant Uptake -- When minerals are blended with organic compounds that are negatively charged (anionic), the positively charged minerals (cationic) become neutral (nonionic) compounds.
3) Superior Translocation & Availability -- Under natural conditions when a plant becomes deficient of minerals, it has the ability to produce and excrete from its roots both organic acids and protein compounds. These root excretions solublize, chelate and translocate minerals from the soil to the plant very effectively. When foliar applying minerals, this natural mineral uptake system is bypassed by direct application to foliage. Therefore, it is important to apply the minerals with similar compounds the plant would take from the soil. When a mineral is sprayed on a plant in a purely chemically solublized form, the plant must first supply the necessary biological compounds to make this mineral useable. This takes both time and energy for the plant to make this transformation. Part of the NUE AMINO Mineral formulation is in a form that the plant can utilize immediately.