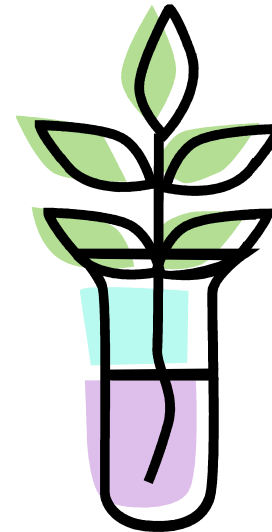


Dry/Liquid Fertilizer Formulation Issues

Bill Easterwood
Yara North America, Inc.



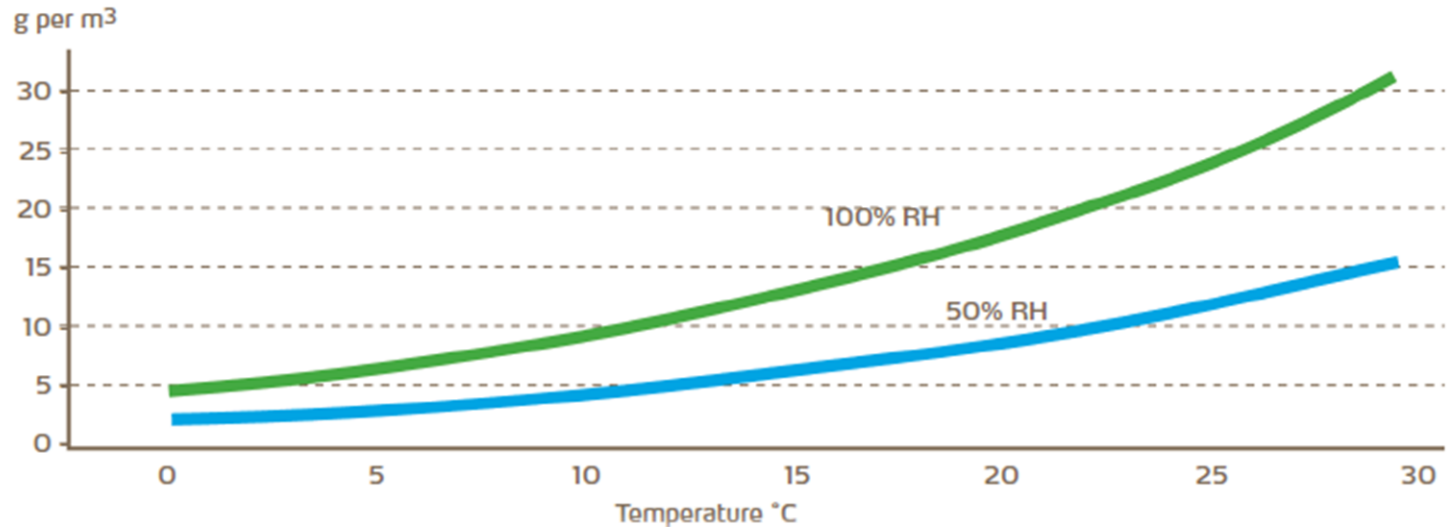
Important Dry Fertilizer Properties for Handling, Storage & Spreading

- **Hygroscopicity**
- **Caking**
- **Compatibility (Chemical & Physical)**
- **Particle Shape and Size Distribution**
- **Particle Strength**
- **Segregation**
- **Tendency to generate dust & fines**

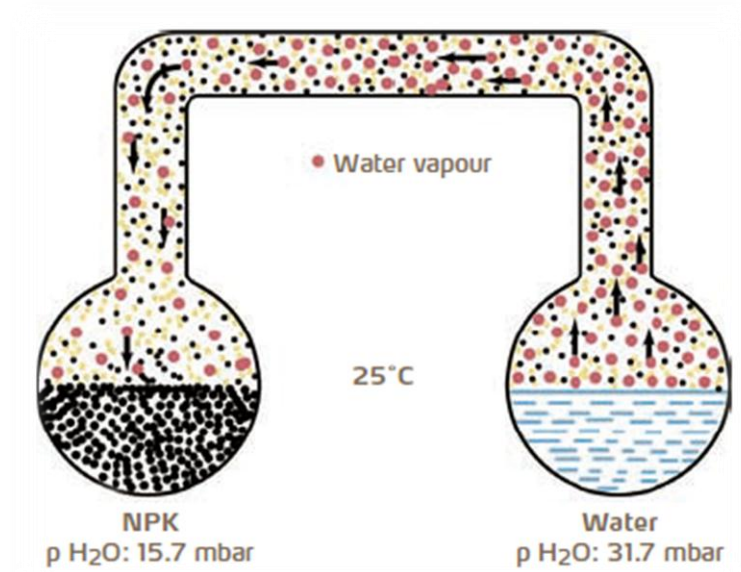
Hygroscopicity

- Air contains moisture as water vapor
- Exerts a water vapor pressure (p_{H_2O}) via humidity/temperature
- Water vapor pressure varies with humidity/temperature of air
- Hot air contains more water than cold air
- Water content is expressed as relative humidity (RH)

Water content of humid air



Water Vapor will move from high to low Water Vapor Pressures



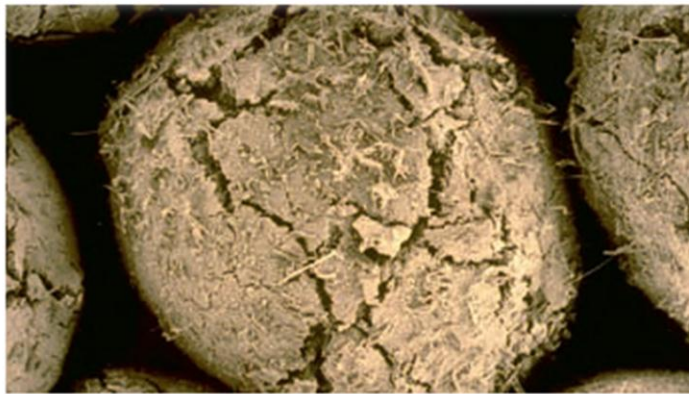
***All fertilizers are hygroscopic and start absorbing moisture
at a specific humidity or water vapor pressure***

Hygroscopicity

Some very hygroscopic fertilizers attract moisture more readily and at lower humidity than others.

Water absorption takes place if the water vapor pressure of the air exceeds the water vapor pressure of the fertilizer.

Absorption of moisture during storage and handling will reduce the physical quality of the fertilizer. By knowing the air temperature, humidity and surface temperature of the fertilizer, we know if water absorption will occur or not.

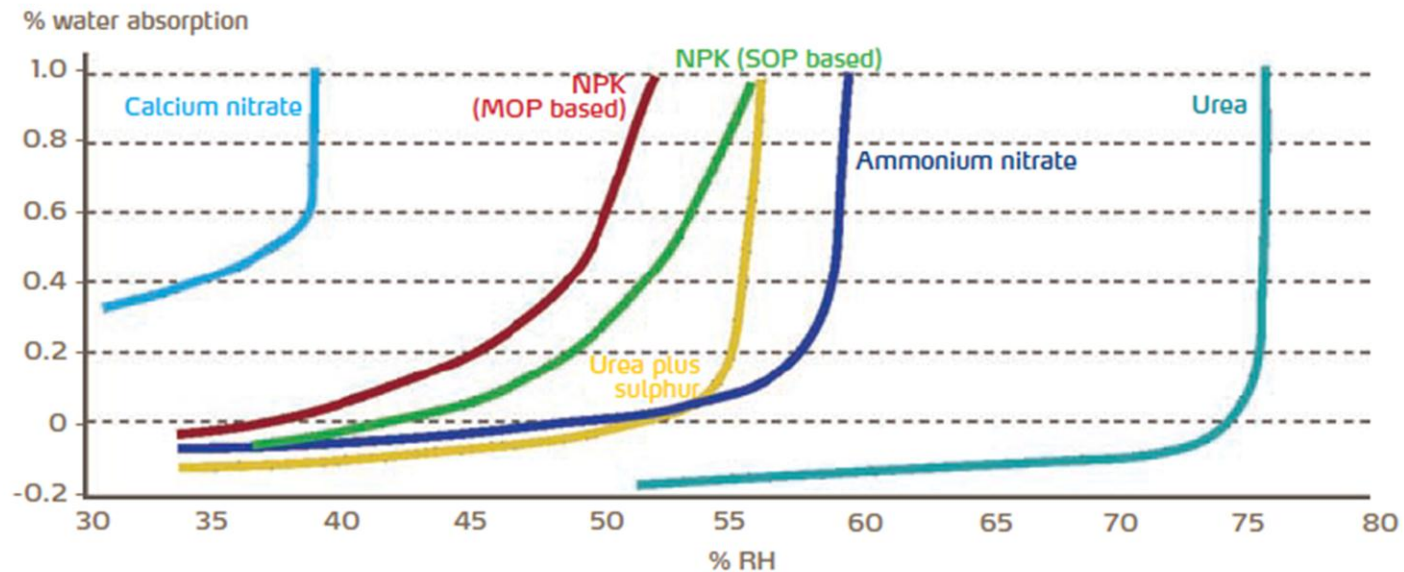


Disintegrated fertilizer due to water absorption

Hygroscopicity

Water absorption is low at low humidity but can increase drastically when a certain humidity is attained at a specific temperature. This humidity is called the Critical Relative Humidity (CRH) of the fertilizer. CRH decreases as temperature increases.

Critical relative humidity of fertilizers at 25°C



Hygroscopicity

Significant water uptake has undesirable consequences for fertilizer products:

- **Particles gradually become soft and sticky**
- **Caking tendency increases**
- **Formation of dust and fines increases**
- **Warehouse floors become damp and slippery**
- **Spreading quality can be significantly decreased**

Caking

Most fertilizers cake during storage due to the formation of strong crystal bridges and adhesive forces between granules.

Several mechanisms are involved:

- **Chemical reactions in the finished product**
- **Dissolution and re-crystallization of fertilizer salts on particle surfaces**
- **Adhesive and capillary forces between surfaces**



Crystal bridges between fertilizer particles cause caking

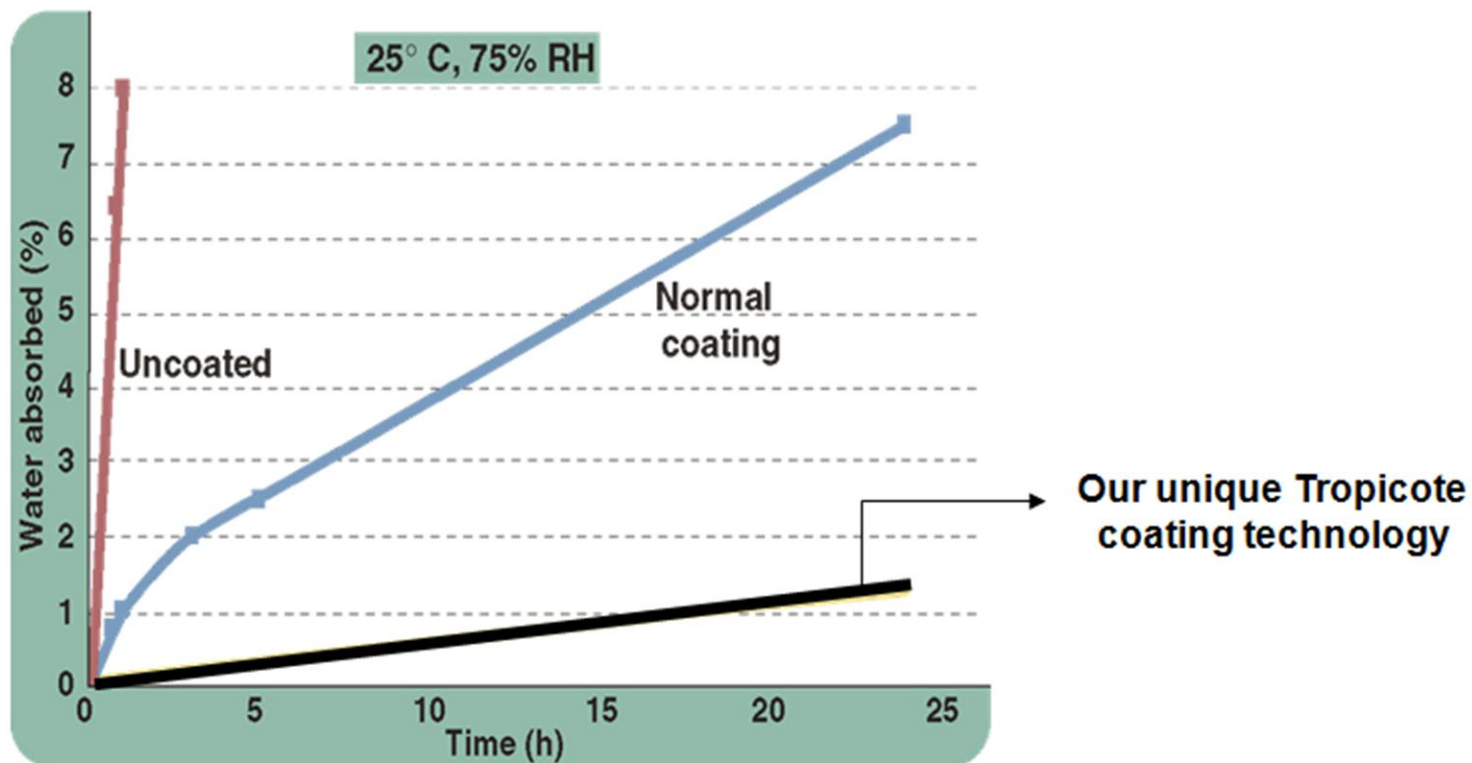
Caking is affected by several factors

- Air humidity
- Temperature and ambient pressure
- Moisture content of product
- Particle strength and shape
- Chemical composition

Caking tendency remains low if these parameters are controlled. Also, application of an anti-caking agent is often needed. Otherwise...

How does Tropicote™ coating perform.

Calcium Nitrate at



Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



0 h

after exposure to humidity

Tropicote™ is an effective protection against atmospheric moisture pick-up in the handling chain

Tropicote™ technology: Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



0,25 h

after exposure to humidity

Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



0,5 h

after exposure to humidity

Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



0,75 h

after exposure to humidity

Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



1 h

after exposure to humidity

Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



1,25 h

after exposure to humidity

Tropicote™ technology:

Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



1,5 h

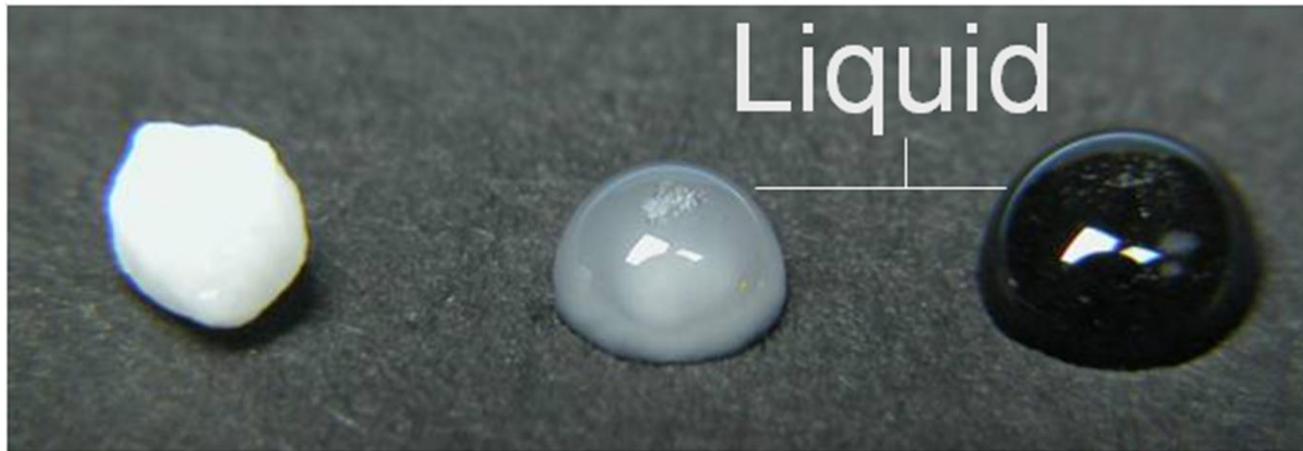
after exposure to humidity

Tropicote™ technology: Superior quality during storage and handling

Yara Tropicote

Competitor A

Competitor B



2,5 h

after exposure to humidity

Tropicote is an effective protection against atmospheric moisture pick-up during the handling chain



Severe caking

TAKE HOME MESSAGE!!!!

Minimize water uptake potential by your fertilizers

- Cover product with plastic sheeting
- Minimize outside air infiltration into the warehouse
- If possible, use coated products that reduce water uptake
- For coated products, minimize abrasion to coated products during blending – Blend them as the last addition to the blend

Remember, water in the air moves from a high potential to a low potential like water flowing downhill. Reduce the flow.

Fertilizer Flowability Testing – 30°C & 80% RH Test against known fertilizer standards

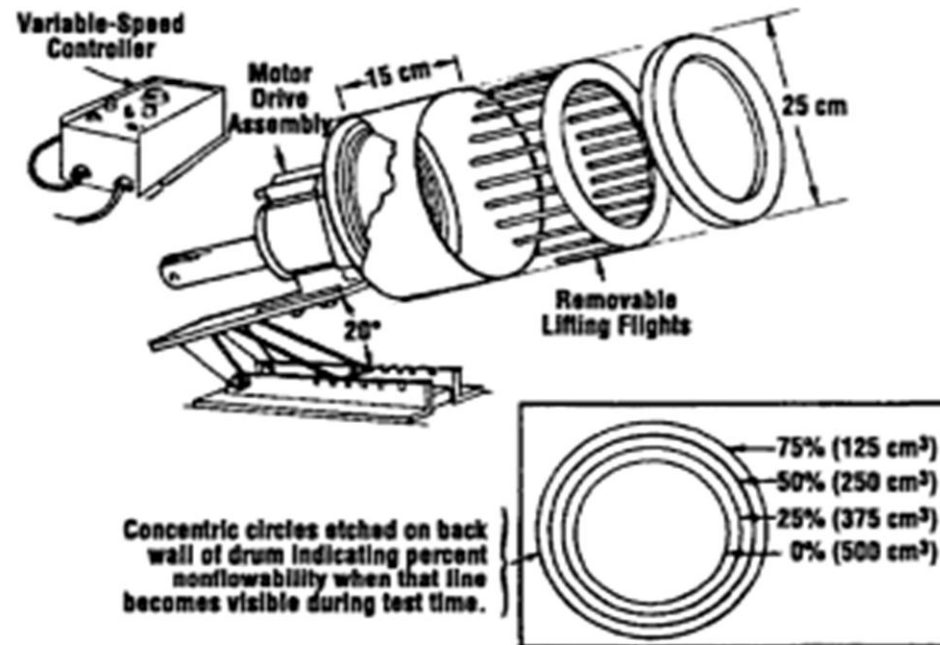


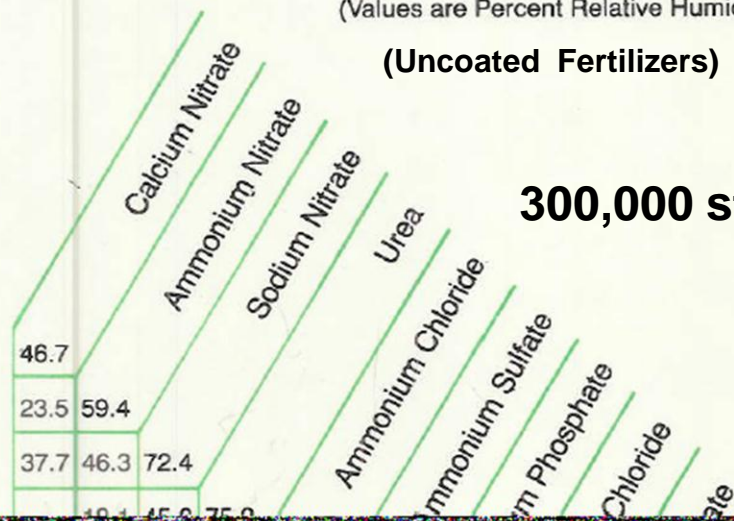
Figure 18.15. Rotary Drum for Measuring Flowability of Fertilizer When Exposed to Humid Conditions.

Product Flowability Testing at IFDC In Muscle Shoals, Alabama

Critical Humidities of Fertilizer Salts and Mixtures at 30°C. (86°F.)

(Values are Percent Relative Humidity)

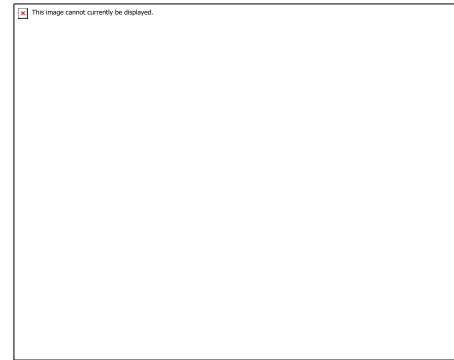
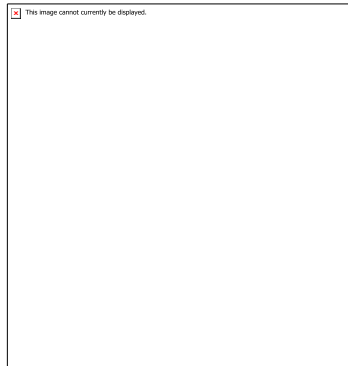
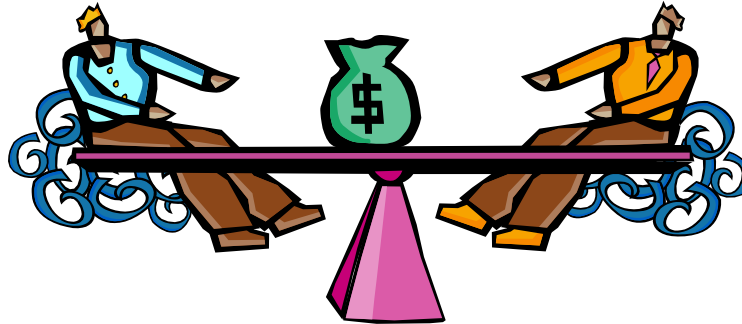
(Uncoated Fertilizers)



300,000 st of AN used in Florida

Liquid Fertilizer Formulation Issues

Liquid Fertilizer Formulation Topics (C³SAW)



Liquid Fertilizer Formulation Topics (C³SAW)

- Solubility
- Compatibility
- Common Ion Effect
- Order of Addition
- Chelates
- Water Quality

Fertilizer Solubility

Solubility of a fertilizer - The solubility of a fertilizer is defined as the maximal amount of the fertilizer, that can be completely dissolved in a given amount of distilled water at a given temperature.

What Fertilizer Grade Can I make with KNO_3 at 30°C (86°F)?

The solubility of KNO_3 at 30 degrees is 370 g/liter.

There are 1000 ml/l. Each ml = 1 gram

The total weight of water + KNO_3 is 1370 g.

$370/1370 = 27\%$ KNO_3 on a weight basis.

The analysis of the KNO_3 is 13-0-44.

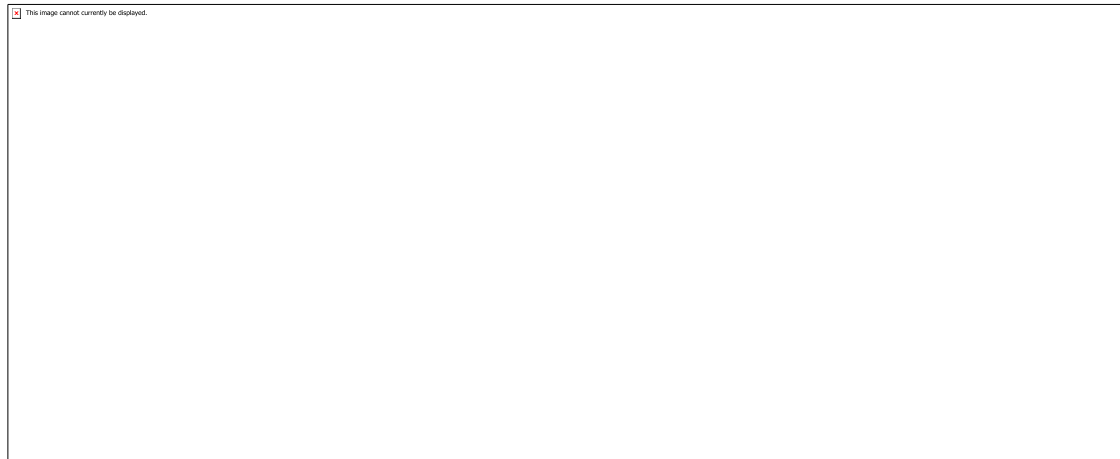
$13 \times 0.27 = 3.5$; $44 \times 0.27 = 11.9$

We can make a 3.5-0-11.9 at 30°C

Common Ion Effect

The Common Ion Effect - Solubility is also dependent on other fertilizers in the fertilizer solution. If a certain fertilizer is being dissolved in the same solution with another fertilizer that contains a common ion, the solubility of both fertilizers is reduced.

For example, Potassium Nitrate and Potassium Sulfate are compatible, and can be dissolved in the same solution. However, since both contain potassium, their solubility is reduced when mixed together.



Fertigation Fertilizers Compatibility Chart

	Urea	Ammonium Nitrate	Ammonium Sulphate	Calcium Nitrate	Potassium Nitrate	Potassium Chloride	Potassium Sulphate	Ammonium Phosphate	Fe, Zn, Cu, Mn Sulphate	Fe, Zn, Cu, Mn Chelate	Magnesium Sulphate	Phosphoric Acid	Sulphuric Acid	Nitric Acid
Urea	✓													
Ammonium Nitrate	✓	✓												
Ammonium Sulphate	✓	✓	✓											
Calcium Nitrate	✓	✓	X	✓										
Potassium Nitrate	✓	✓	✓	✓	✓									
Potassium Chloride	✓	✓	✓	✓	✓	✓								
Potassium Sulphate	✓	✓	R	X	✓	R	✓							
Ammonium Phosphate	✓	✓	✓	X	✓	✓	✓	✓						
Fe, Zn, Cu, Mn Sulphate	✓	✓	✓	X	✓	✓	R	X	✓					
Fe, Zn, Cu, Mn Chelate	✓	✓	✓	R	✓	✓	✓	R	✓	✓				
Magnesium Sulphate	✓	✓	✓	X	✓	✓	R	X	✓	✓	✓			
Phosphoric Acid	✓	✓	✓	X	✓	✓	✓	✓	✓	R	✓	✓		
Sulphuric Acid	✓	✓	✓	X	✓	✓	R	✓	✓	✓	✓	✓	✓	
Nitric Acid	✓	✓	✓	✓	✓	✓	✓	✓	✓	X	✓	✓	✓	✓

✓ = Compatible

X = Incompatible

R = Reduced Solubility

Mixability of fertilizers for preparation of concentrated solutions for Fertigation

	Amnitra™	YaraLiva™ CALCINIT™	Kristalon grades	Krista™ MAP	Krista™ MKP	Krista™ K	Krista™ SOP	Krista™ MAG	Krista™ MgS	Krista™ UP	Calci- MAG™	Urea	Phos- phoric Acid	Nitric Acid	Boric Acid	micronu- trientes based in sulphates
Amnitra™	-	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES 1	YES 1	YES	YES
YaraLiva™ CALCINIT™	YES	-	NO	NO	NO	YES	NO	YES	NO	NO**	YES	YES	NO	YES 1	NO	NO
Kristalon grades	Yes	NO	-	YES	YES	YES	YES	YES	YES	NO**	NO	YES	NO+	NO+	NO+	YES
Krista™ MAP	YES	NO	YES	-	YES	YES	YES	RS***	NO**	YES	RS***	YES	P	P	YES	YES
Krista™ MKP	YES	NO	YES	YES	-	YES	YES	RS***	NO**	YES	RS***	YES	YES 1	YES 1	YES	YES
Krista™ K	YES	YES	YES	YES	YES	-	RS*	YES	RS*	YES	YES	YES	P	P	YES	YES
Krista™ SOP	YES	NO	YES	YES	YES	RS*	-	RS	YES	YES	NO	YES	P	P	YES	YES
Krista™ MAG	YES	YES	YES	RS***	RS***	YES	YES	-	YES	YES	YES	YES	RS***	P	NO	YES
Krista™ MgS	YES	NO	YES	NO**	NO**	RS*	RS	YES	-	NO**	NO**	YES	NO**	YES 1	NO	YES
Krista™ UP	YES	NO**	YES	YES	YES	YES	YES	YES	NO**	-	NO	YES	P	P	YES	YES
Calci-MAG™	YES	YES	NO	RS***	RS***	YES	NO	YES	NO**	NO	-	YES	RS***	P	NO	NO
Urea	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	YES	-	YES 1	YES 1	YES	YES
Phosphoric acid	YES	NO	NO+	P	YES	P	P	RS***	NO**	P	RS***	YES	-	YES 1	P	YES 1
Nitric acid	YES	YES	NO+	P	YES	P	P	P	YES	P	P	NO	YES 1	-	P	YES 1
Boric Acid	YES	NO	NO+	YES	YES	YES	YES	NO	NO	YES	NO	YES	P	P	-	YES
micronutri- entes based in sulphates	YES	NO	YES	YES	YES	YES	YES	YES	YES	YES	NO	YES	YES 1	YES 1	YES	-

NO** Restricted mixtures, or high concentrations precipitations could turn out.

RS Reduced solubility

RS* Consider the Krista SOP solubility

P Precaution: should be mixed with precaution, follow the order: 1st water, 2nd specialty nutrient and 3rd acid

NO + Contain chelates which could be damaged with acids

RS*** Reduced solubility, is recommended to keep the pH below 5

Yes 1 Mix only with diluted solution



[illegible]

3/1/09

ic Acid

Nit			
Phospho			
Phospho			
Sulfuric Acid			

[illegible]

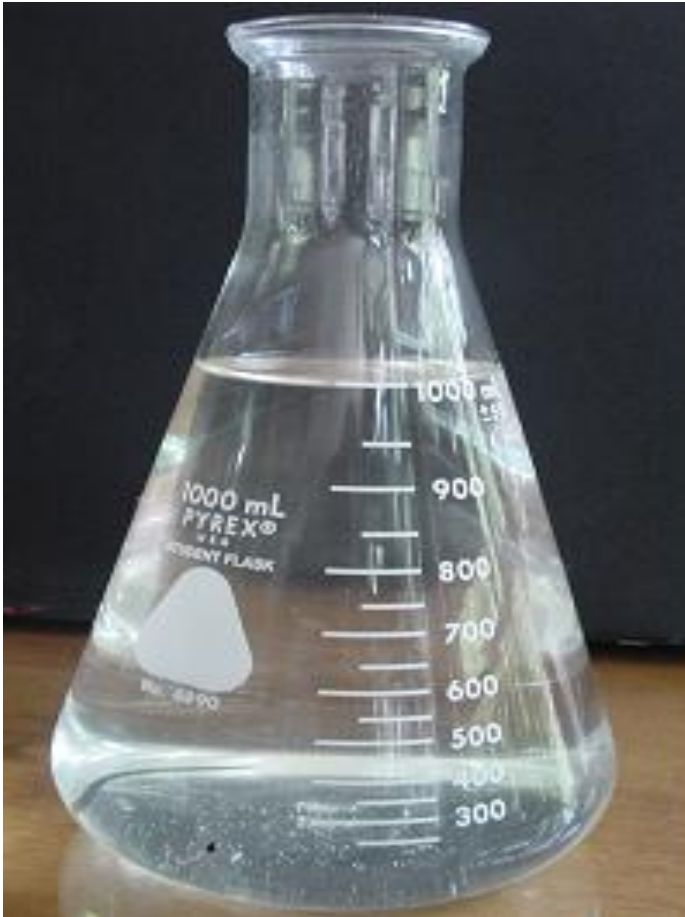
Order of Addition/Mixing Suggestions for Fluid Fertilizers

- Always check with the chemical information about
 - about insolubility and incompatibility
- Always fill the mixing container with 50-75% of the required water to be used if mixing dry soluble fertilizers
- Always add the liquid fertilizer materials to the water before
 - adding dry soluble fertilizers. The additional fluid will provide
 - some heat in case the dry fertilizers have the characteristics of
 - making solutions cold. [Temperature influences solubility]
- Always put acid into water and not water into acid
- To prevent precipitation, always add acid followed by hydroxides/carbonates and then neutral products to the water
- Always add the dry ingredients slowly with circulation or agitation to prevent the formation of large, insoluble or slowly soluble lumps

Order of Addition/Mixing Suggestions for Fluid Fertilizers

- **Do Not attempt to mix aqua ammonia directly with any kind of acid. The reaction is violent and immediate.**
- **Do Not mix a compound containing sulfate or phosphate with another compound containing calcium. The result will be a mixture of insoluble gypsum or calcium phosphate.**

Conduct a “Jar” Test of Your Formulation!



Chelated Metal Fertilizers

The word “Chelate” is derived from the Greek word for “Claw”. Metallic plant nutrients are completely bound, like a claw by distinct organic molecules [ligands] within specific chemical parameters to make them available for plant uptake by the roots and reduce nutrient deficiencies.

Ligands protect metal nutrients from high pH chemical environments and the formation of metal hydroxides.

The most common chelates used in agriculture are:

EDTA

DTPA

EDDHA

Chelated Metal Fertilizers

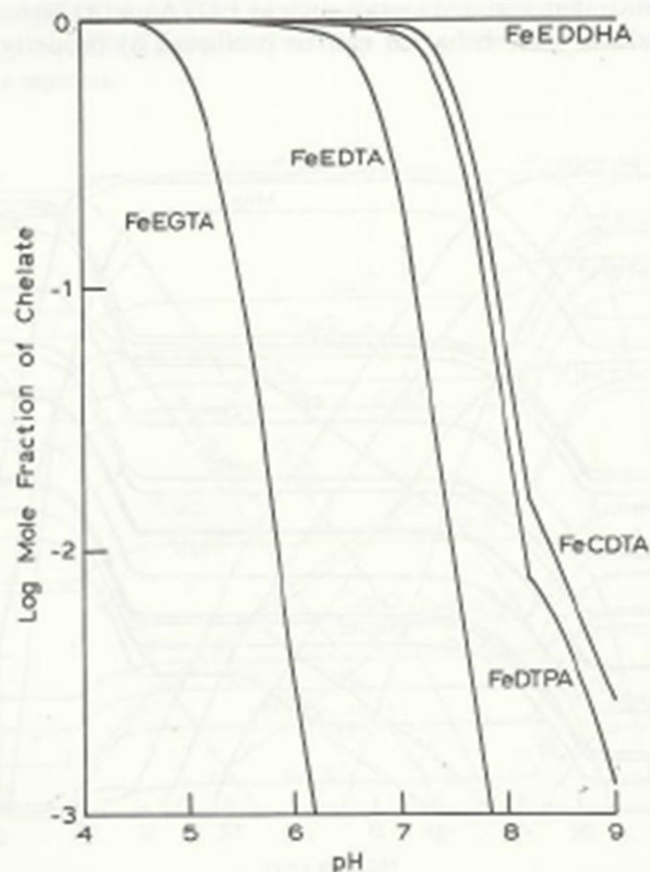


Fig. 15.11 Effectiveness of various metal chelating agents to hold iron in a modified Hoagland hydroponic solution (adapted from Halvorson and Lindsay, 1972).

The strength of bonding between the metal and the ligand depends on the type of ligand, metal ion and the pH. The stronger the bond, the more stable the metal ion-ligand.

Chelated Metal Fertilizers

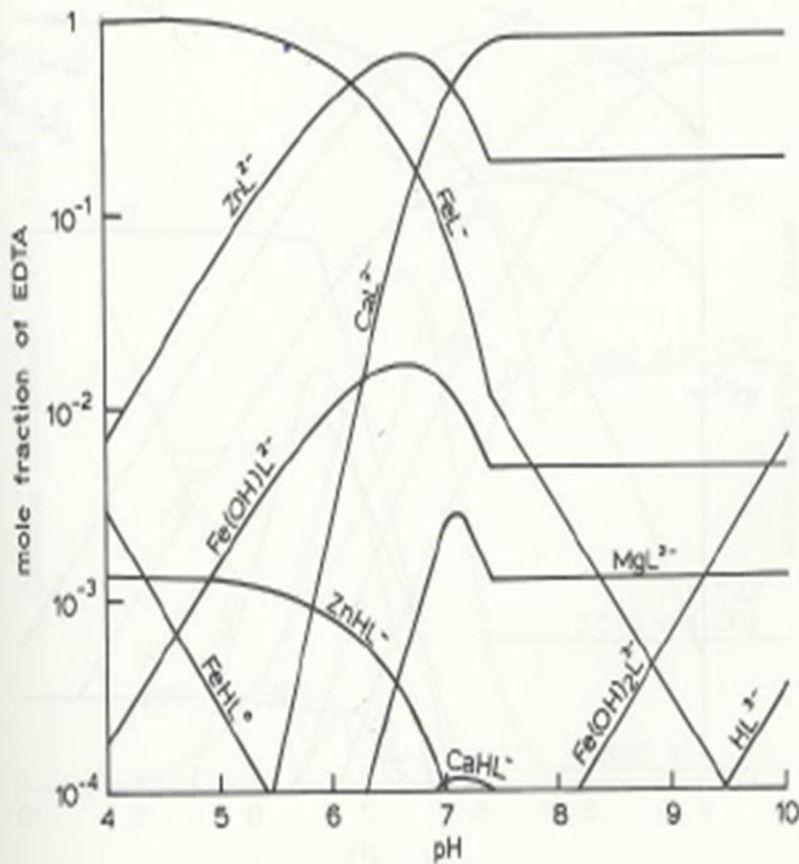


Fig. 15.4 The mole fraction diagram for EDTA in soils when Zn^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , and H^{+} are competing metal ions at 0.003 atm of $CO_2(g)$.

As the ligand stability decreases due to higher pH, other ions can replace chelate-bound ions. Here, calcium is replacing iron on EDTA as the pH nears 7.0

Water Quality

Water is the matrix/building block for fluid fertilizer manufacture

We have seen that:

- high salts can reduce fertilizer solubility
- high pH can undermine the stability of micronutrients, secondary nutrients and micronutrients, particularly chelates.

Use low salt, slightly acidic (pH 6.0-6.5) water for fluid manufacture



Conclusion: Fluid Formulation is enhanced with (C³SAW) and will produce a quality product for Growers with less headaches for all.

- Solubility
- Compatibility
- Common Ion Effect
- Order of Addition
- Chelates
- Water Quality

Thank you for your attention
Questions?

