

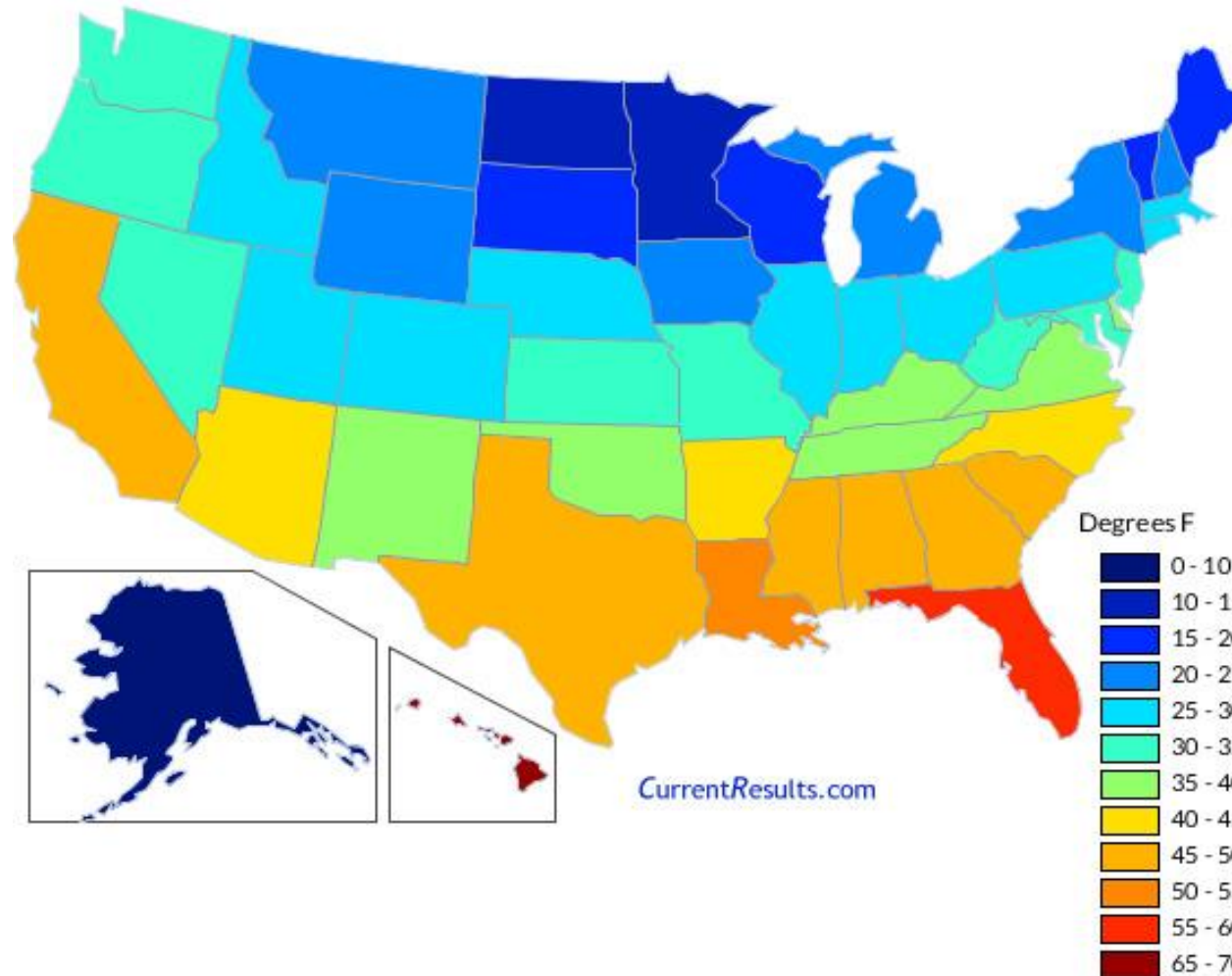
Winter Salt Out & Freezing issues

Presented by Terry Robinson
Scientist, Plant Nutrient Group
The Andersons

Winter State Temperature Averages supplied by NOAA National Climatic Data Center



Winter State Temperature Averages



What to do when winter arrives?



Masks were worn so we
didn't catch whatever the
geese caught.

Probably tetanus.



Methods of Determining Salt out Temperatures



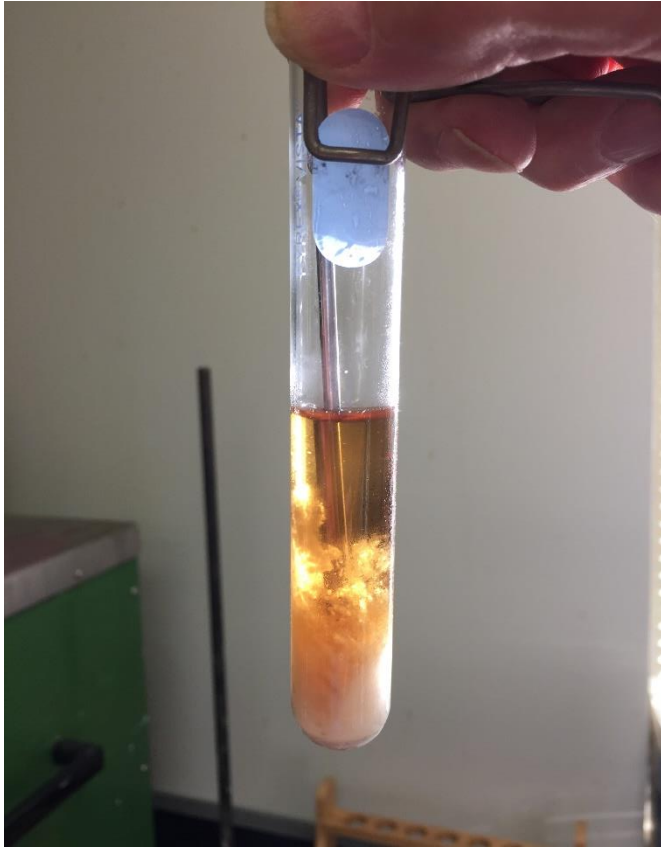
New ISO/DIS 23381 Determination of Salt Out (Crystallization) Temperature of Liquid Fertilizers

Adopted Andersons Methods for determining Salt out temperatures

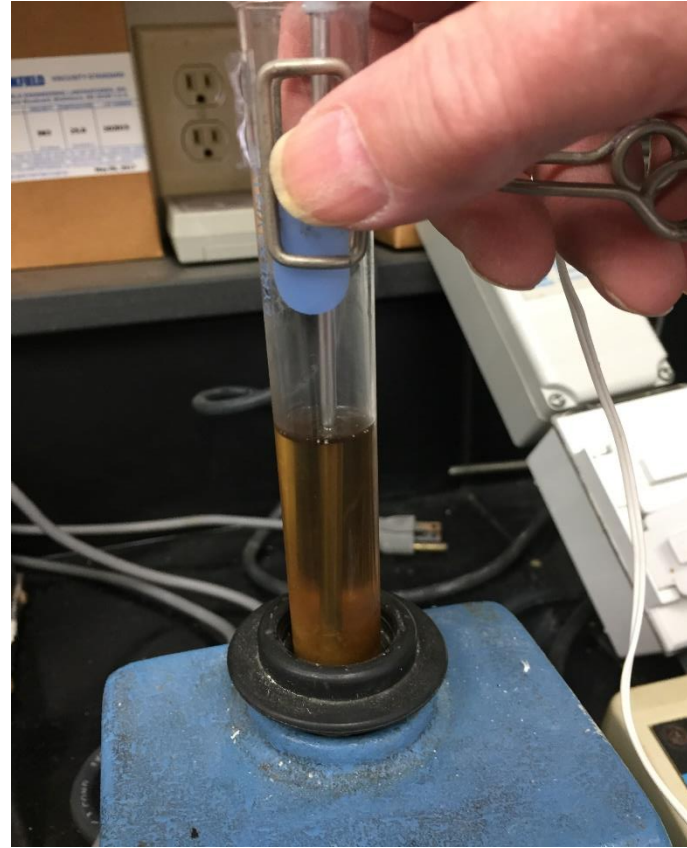
- 1) **Quick Chiller Method:** Maintain Chiller at about -24 F. Expose sample to chiller via clear test tube and record temperature and type of solids that form. Remove sample from chiller and stir vigorously with test tube stirrer at room temperature. Record temp when solution is clear and free of solids. Repeat if needed. This is the salt out temperature reported. This is a quick test and since you are using the temperature when the sample warms up to clear, This value represents the ISO/DIS 23381
- 2) **Slow Cooling/thawing method:** Subject samples to slow incremental temperature decreases and record temperature and type of solids that form. Then slow incremental increases to temperature until samples is clear. Repeat 3 cycles. Record this temperature when sample is clear as the Salt out temperature. We have seen some salt out temperatures increase by 15-20 F because of freeze thaw concentration effects.



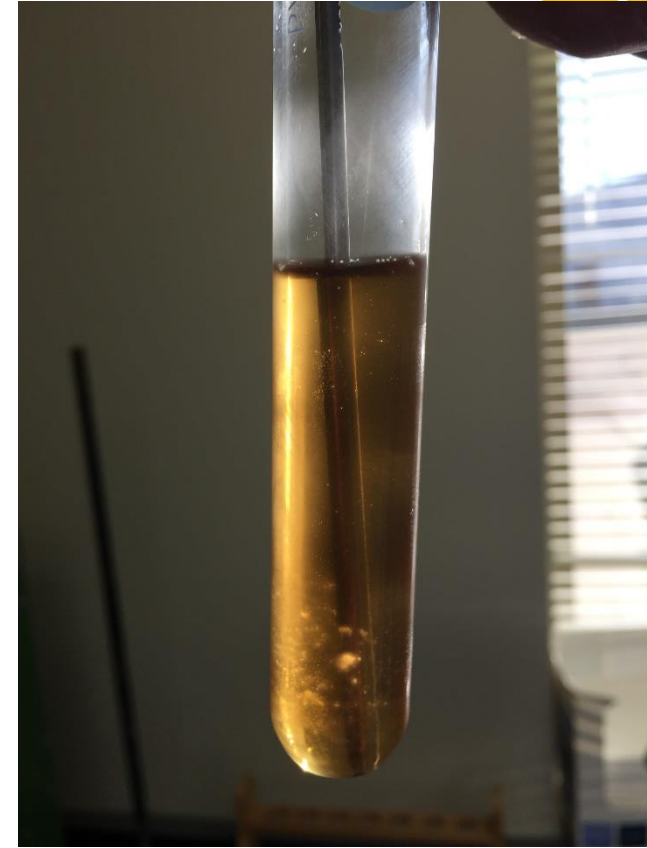
Salt Out Determination Chiller Method



Sample exposed to -25 °F until solids start to appear & temperature recorded as start temperature. Then exposed another 2-3 minutes longer.



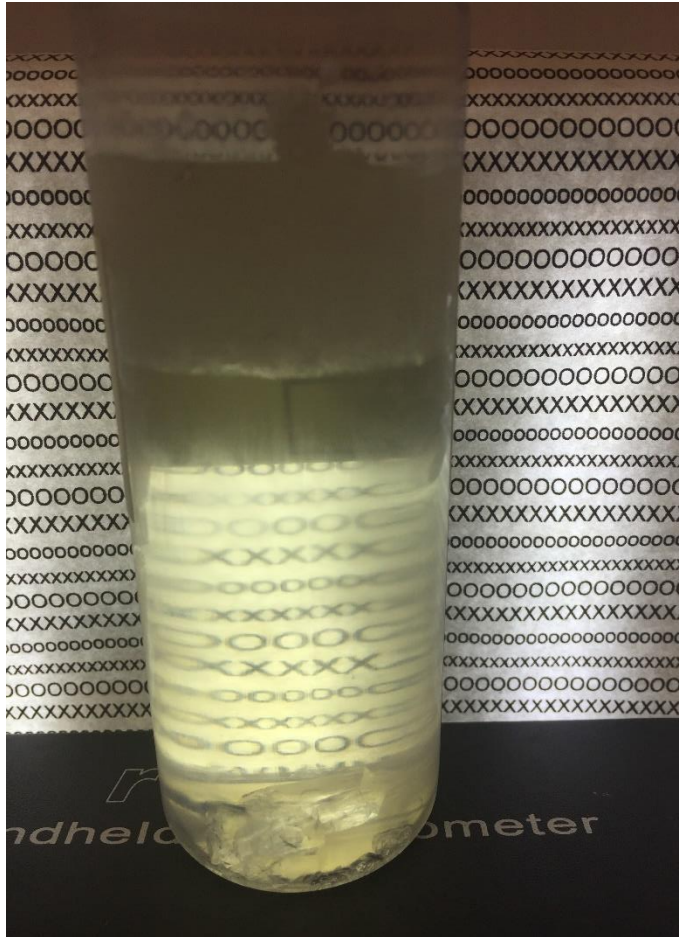
Sample is then stirred with test tube stirrer and temperature probe. Solids are observed as they slowly re dissolve.



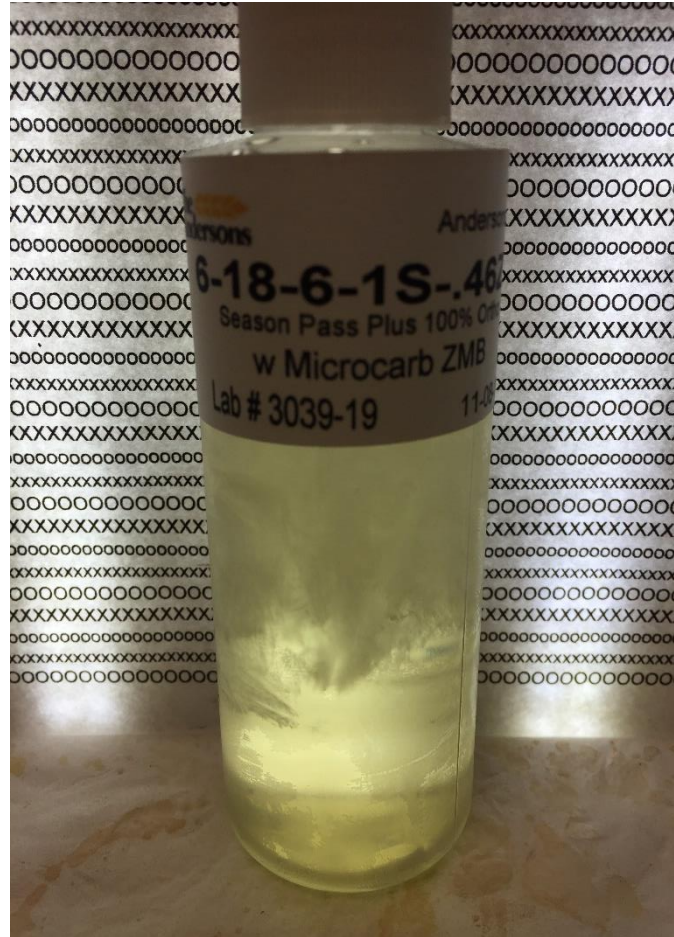
Sample right before the salt out temperature is recorded. You can see a small amount of ice phase still present.



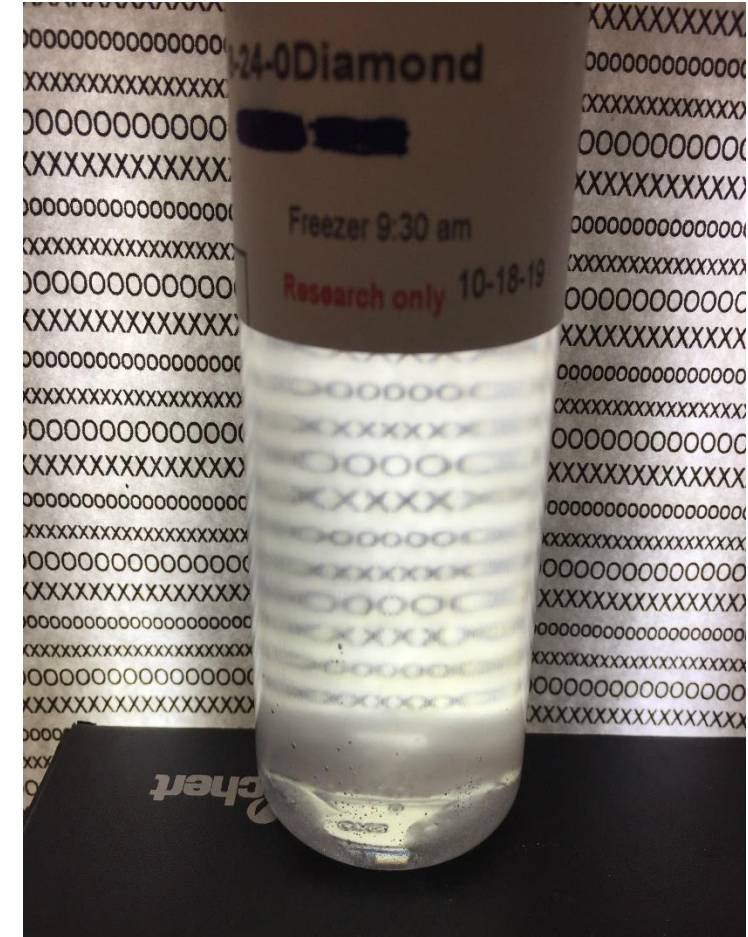
100% Ortho Phosphate fertilizers exposed to freezer 4 °F



Ice phase on top and
MAP & DAP on the bottom.



Ice phase that floated to the
top

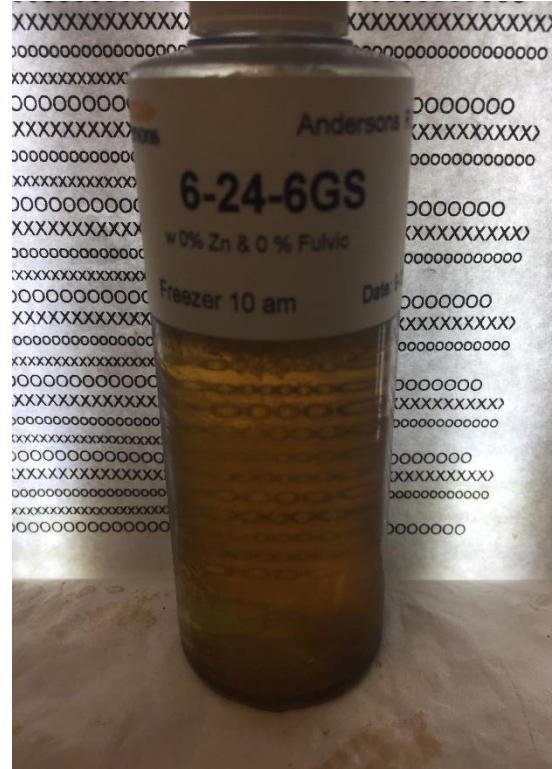


Sample was in freezer 5 days
then sat idle (68 °F) 5 days. MAP
& DAP crystals still not dissolved.

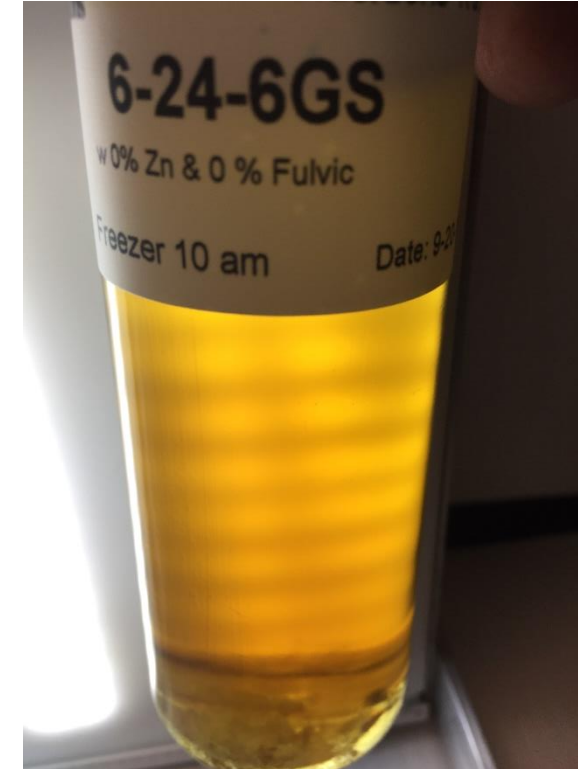
80% Ortho Phosphate fertilizers exposed to freezer 4 °F



6-24-6 80% Ortho
Phosphate
In freezer 4 °F for 2 weeks.
Note the ice on top and
MAP & DAP crystals on the
bottom.



Same sample as on the left.
Clear liquid in the middle
with ice on top and crystals
on the bottom



Same sample as on the left.
Exposed to 68 °F for
10 days no agitation. Note
the MAP & DAP crystals
still on the bottom.



Observations when Fertilizer Salts Out



- Ice phase usually forms first and floats to the top. Since the ice is primarily water, this process concentrates the other components in the fertilizer thus changing the physical characteristics of the system.
- With this increase in concentration of the liquid portion, the formation of MAP & DAP crystals becomes more possible. You now have a product that is non-homogeneous and will behave differently than before it salted out.
- **Solution after Salt out:** Heat of some kind is necessary to re-dissolve the MAP & DAP crystals as well as the Ice. With heat alone, the process will take an extended amount of time and the final product will be stratified with low concentration fertilizer on the top and high concentration fertilizer on the bottom, leaving the solution susceptible to further salt out episodes.
- Along with heat, one must also introduce some type of agitation/re-circulation. This helps the fertilizer return to the original concentration throughout the vessel before the salt out occurred.



Salt Out vs Precipitation



- Salt out : When a liquid fertilizer is exposed to low temperatures for an extended time. These temperatures vary and the results can be ice or ice and crystalline salt complexes. Usually re dissolve with heat and agitation.
- Precipitation: Solids that form from incompatible mixing of products, pH change, hydrolysis of polyphosphates releasing insoluble metals. To mention a few causes. These solids typically don't re dissolve. Identification of the precipitate and possible cause of precipitate can lead to a solution of further prevention.



Salt out vs Precipitation



These samples precipitated at room temperature and will not re dissolve unless the chemistry is changed. Prime examples of precipitation failures.

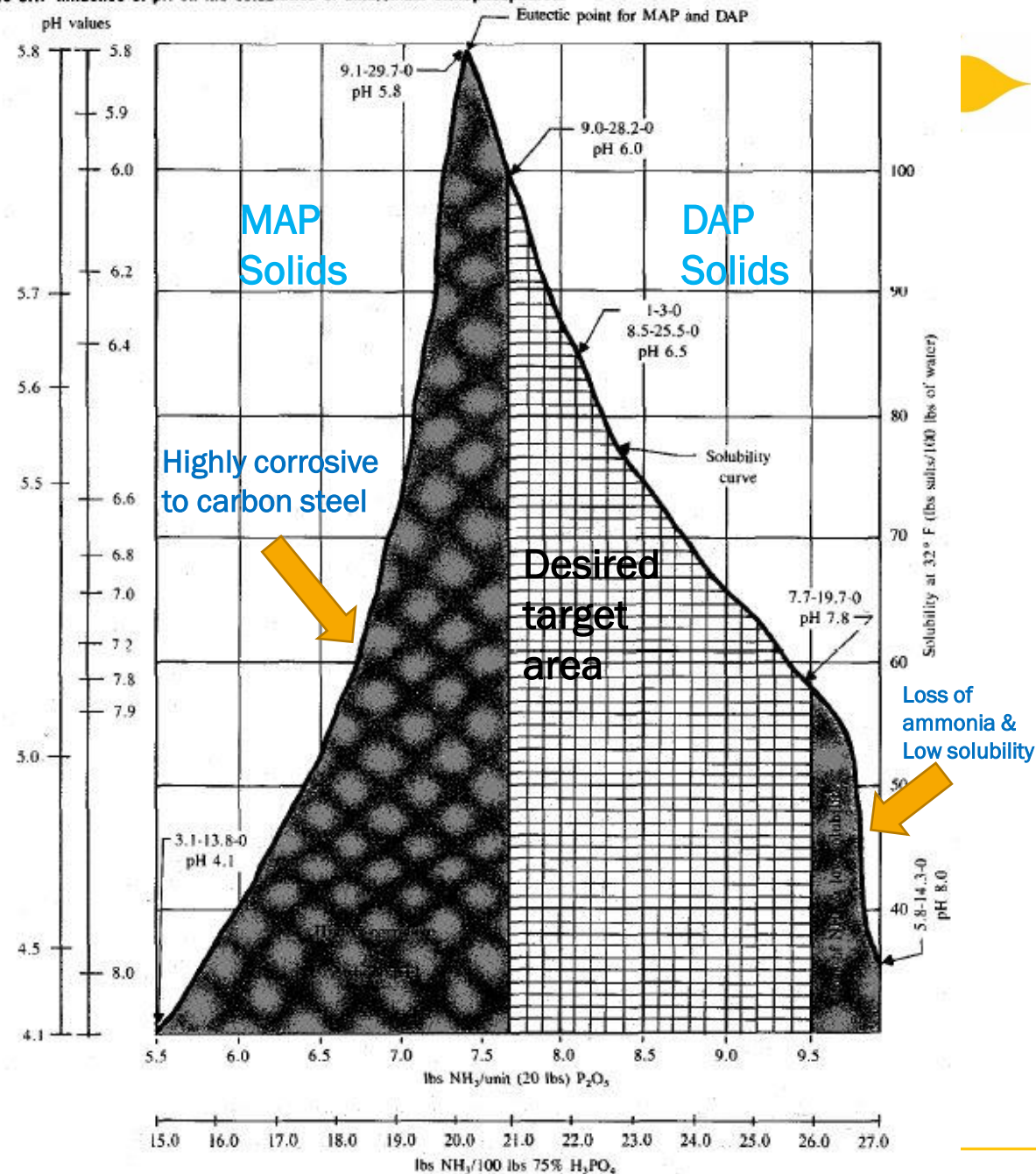


Solubility of Ammonium Ortho Phosphates

The diagram located on the right has been in circulation for many years after being developed by TVA. The scale on the right is related to the total concentration (Solubility of Ammonium Phosphates 100% Ortho Salt lbs/100 lbs Water)

The scale on the left is related to the pH. 5.8 to 8.0 relates to the cross hatched section with the “Desired target area” of the diagram on the right hand side. The scale to the left pH 5.8 to 4.1 relates to the left side of the diagram. This area also has a lower pH and products that fall into this area can be corrosive to steel storage tanks.

Figure 3.1: Influence of pH on the solubilities of ammonium orthophosphates.



Solubility of Ammonium Ortho Phosphates

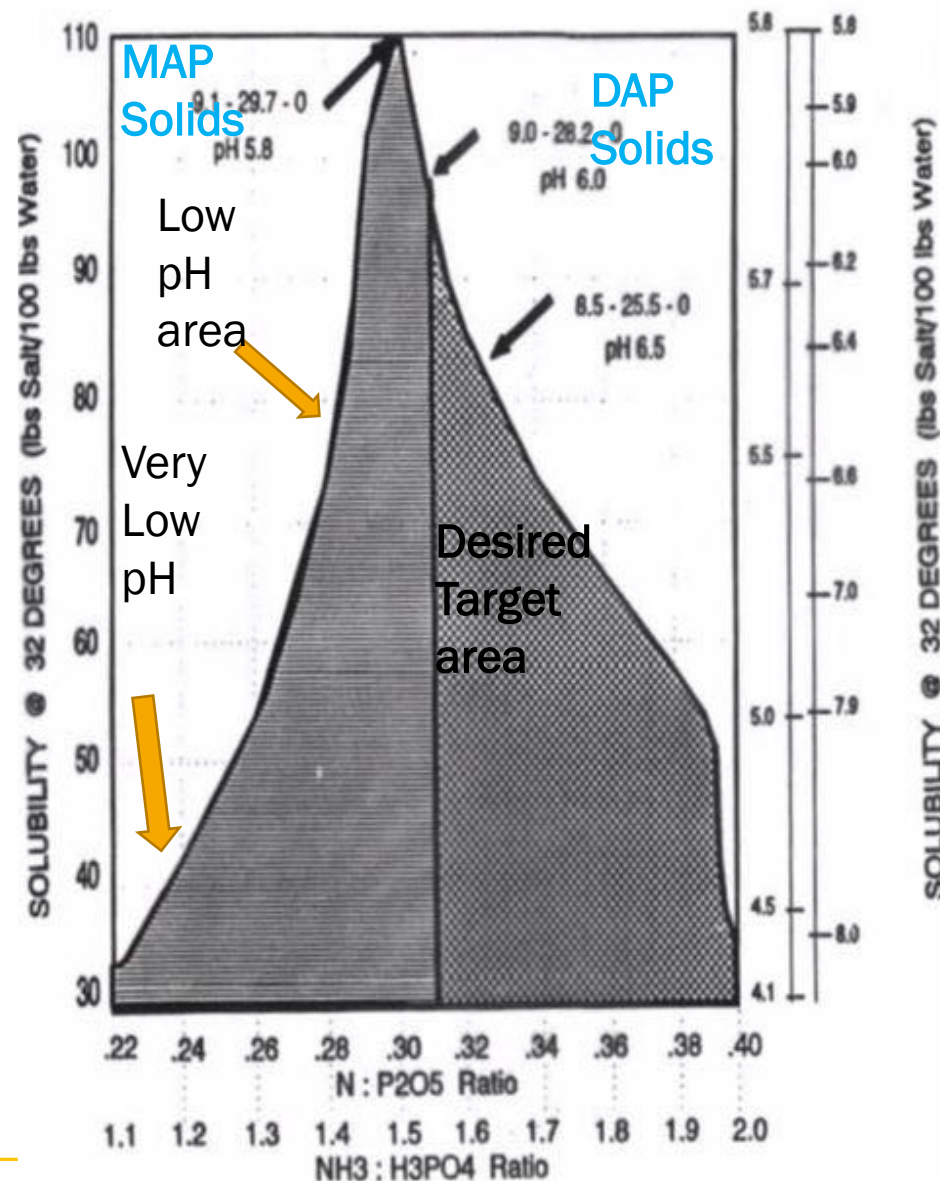


Same diagram as previous but with N:P2O5 ratio shown on the bottom scale of the diagram. This converted scale is much easier to work with when developing formulas. The key scale is the N:P2O5 Ratio. The N value is only counted for non neutralized N components ie: Aqua ammonia or Anhydrous ammonia.

The P2O5 value is only counted for Non neutralized P2O5 sources ie: Ortho phosphoric acid.

This diagram can also be used with some success with NPK systems that include (KOH). Accounting for the K2O from KOH, by subtracting that K2O value from the P2O5 then using that new P2O5 value to obtain the N:P2O5 ratio.

Ammonia and KOH are both bases and neutralize phosphoric acid but when KOH is in the system instead of KCl higher pH values can be obtained with lower salt out characteristics.



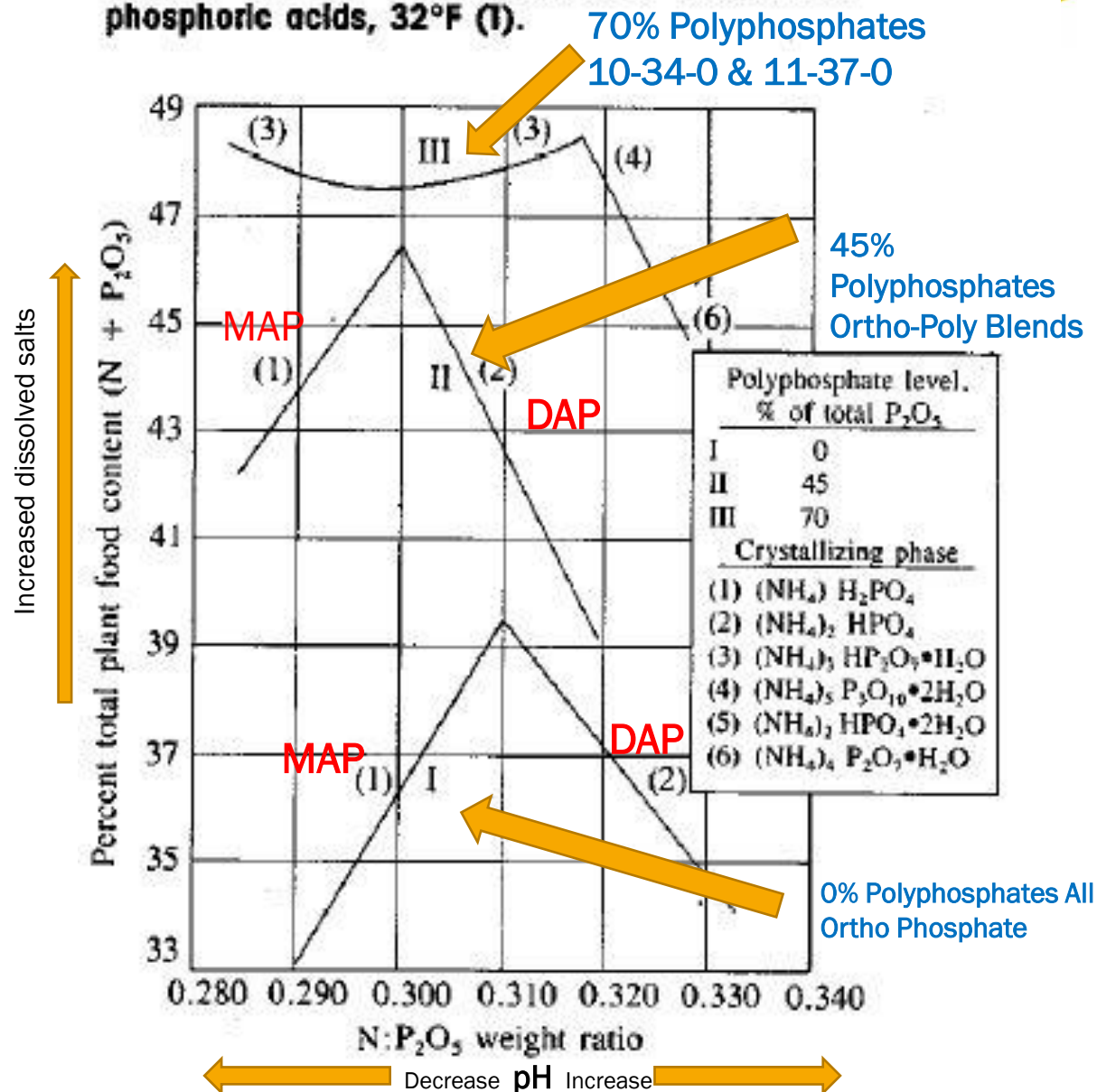
Effect of Polyphosphates on solubility of Ammonium Phosphate solutions

Scale from bottom to top shows an increase of dissolved salts NH_4 & P_2O_5
 Scale at bottom shows increase in N:P $_2\text{O}_5$ weight ratio (pH increase to the right)

This chart can give you a relative comparison of the solubility of ammonium polyphosphates versus Ortho phosphate. As you can see the higher polyphosphate are much more soluble and not so pH dependent. Notice the peak of the 45% Polyphosphate is representative of a 9-30-0 grade. The peak of the all ortho phosphate is representative of 7.5-24-0

Some work has been done to determine Potassium Phosphate solubility of 100% ortho products. Typically 0-20-23 will have a salt out of 20 F. Add a little ammonia in place of the K $_2\text{O}$, 1.4-20-20 and you will see a salt out of 0 F. We have found that pH plays a critical role in determining salt out values. TVA has limited data with NPK fertilizers containing KOH.

Figure 3.2: Effect of polyphosphate level and N:P $_2\text{O}_5$ weight ratio on solubility of ammoniated phosphoric acids, 32°F (1).



Temperature effects on conversion of 11-37-0

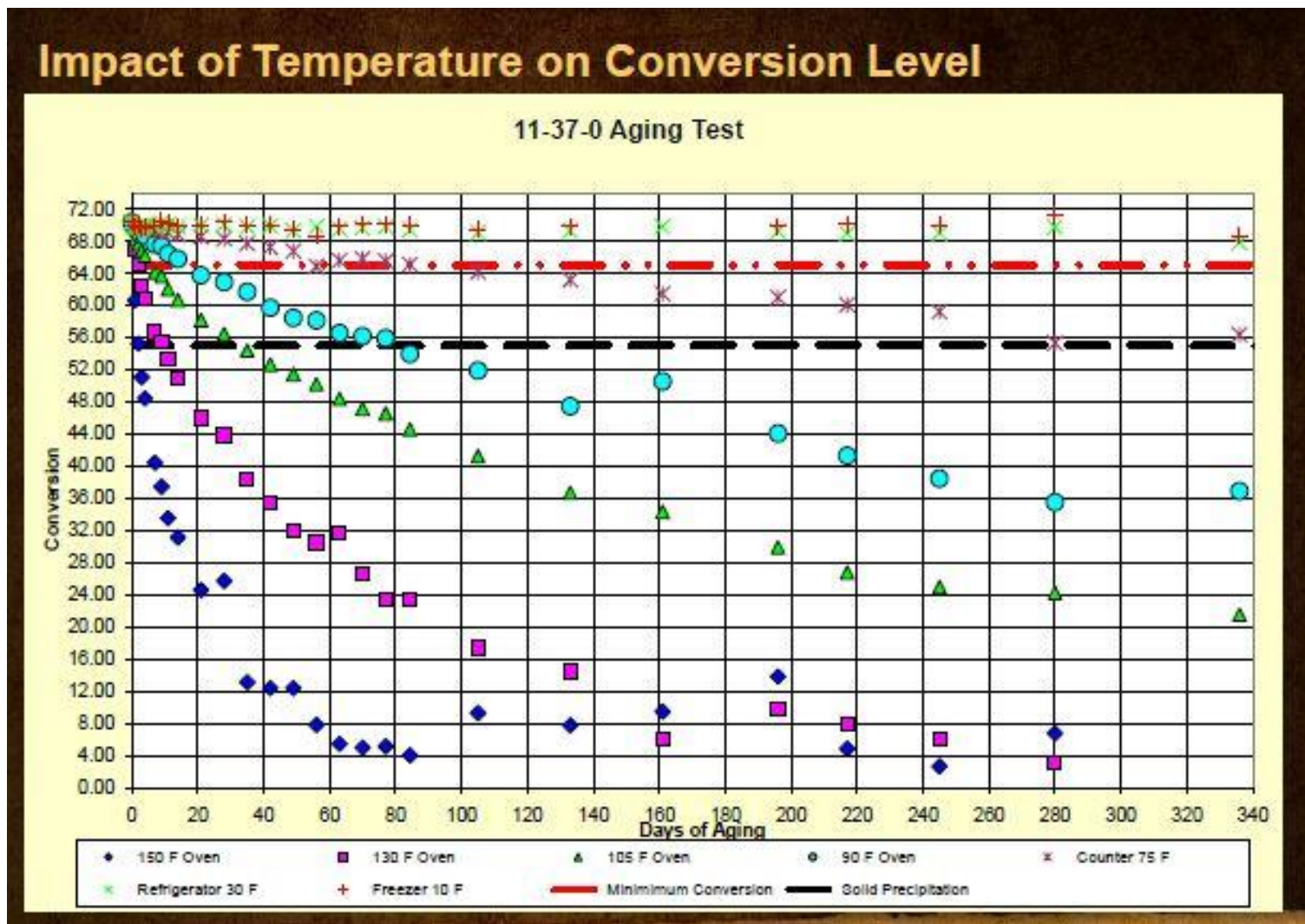
John Walker from Potash Corp



Left scale is conversion, or % Polyphosphates. The bottom scale is days of aging. The minimum conversion is shown at about 65%.

This will be slightly different depending on the tramp metal content of the wet process acid used.

Obviously temperatures above 90 F have a detrimental effect on the % Polyphosphate content.



Compatibility of Micronutrients: Fully Chelated vs Sequestered



Fully Chelated metals are determined by the ability of the metal to remain in solution (dissolved) for the life of the product it is dissolved in. Our verification is determined by the ability of the chelated metal solution to be added to a 100% Orthophosphate solution and remain dissolved, with no precipitate, for an extended period of time.

Chelated/Sequestered: There are many molecules that hold metals in solution. Some of the most popular are EDTA (Ethylenediaminetetraacetic acid), Di Sodium EDTA, HEDTA, MEA (Monoethanolamine), TEA (Triethanolmine), Glucoheptonate, Ammonium, Citrate, Acetate, Formate, Polyamino acids and polyphosphates etc.....

We prefer to work with the EDTA groups which we find have the strongest chelating capability for most metals.

When working with solutions containing tramp metals it is important to keep the Metal Chelate Selectivity (Displacement) series in mind. This chart on the right shows the preference of EDTA chelation based on the metals. Similar to the Noble Metals chart. Ex: Fe^{+3} must be chelated before attempting to chelate Cu^{+2} etc when both are present in an unchelated or sequestered form.

V^{+3}	Vanadium	
Fe^{+3}	Iron (Ferric)	
Hg^{+3}	Mercury	
Ti^{+3}	Titanium	
Cu^{+2}	Copper	
VO^{+2}	Vanadium Oxide	
Ni^{+2}	Nickel	
Pb^{+2}	Lead	
TiO^{+2}	Titanium Oxide	
Zn^{+2}	Zinc	
Cd^{+2}	Cadminum	
Co^{+2}	Cobalt	
Al^{+3}	Aluminum	
Fe^{+2}	Iron (Ferrous)	
Mn^{+2}	Manganese	
V^{+2}	Vanadium	
Ca^{+2}	Calcium	
Mg^{+2}	Magnesium	
Ba^{+2}	Barium	

First

last

Adding non EDTA metal micronutrients to poly phosphates



10-34-0 & 11-37-0 blends with a minimum of 70% polyphosphates can keep most metals in solution, up to about 1.5% wt total of the metals. This value is based on ignoring the tramps Mg, Al, Fe, & S contained in the wet process acid.

We found that non EDTA metals can be added to 50% polyphosphates and stay in solution, totaling about 0.5 to 0.75% depending on the metals

We have also found that non EDTA metals can be added to 20% polyphosphates and stay in solution, totaling 0.2 to 0.25% depending on the metals.

Those metals sequestered by acetate, citrate, nitrate, ammonium, etc will vary to the amount and length of stability in the above solutions. Stability tests can be performed to verify.



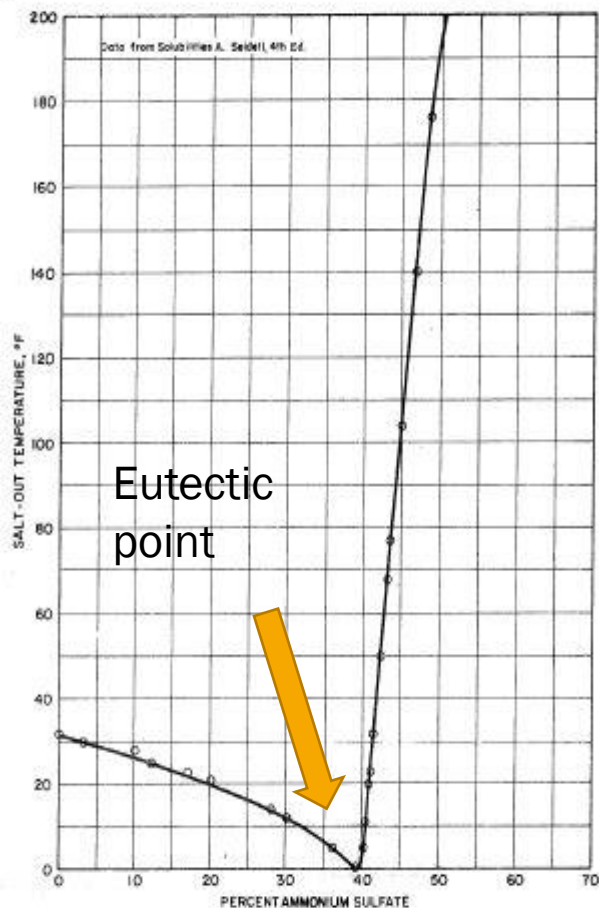
Some Nutrient Incompatibilities



- Sulfate, Nitrate, and Chloride based metals have very limited solubility's in low polyphosphate fertilizers.
- Low value phosphate fertilizers IE: 8-1-8 do not mix well with hard water. Phosphates will precipitate.
- We have found some solubility inconsistencies with the mixtures of Manganese EDTA and Boron MEA.
- Iron EDTA and Copper EDTA have been found to degrade in the presence of sunlight/UV light. The EDTA bond is broken/destroyed and Iron will take the place of copper leaving it to precipitate as a solid.
- Potassium mixed with UAN can cause the precipitation of potassium nitrate crystals at certain concentrations.
- Potassium mixed with Sulfur in the form of sulfate can cause potassium sulfate to precipitate.
- I am sure you know of other incompatible mixtures.



Aqua Ammonia & Ammonium Salts



Ammonium Sulfate Salt out diagram. Typical 8-0-0-9S solution falls in the eutectic point.

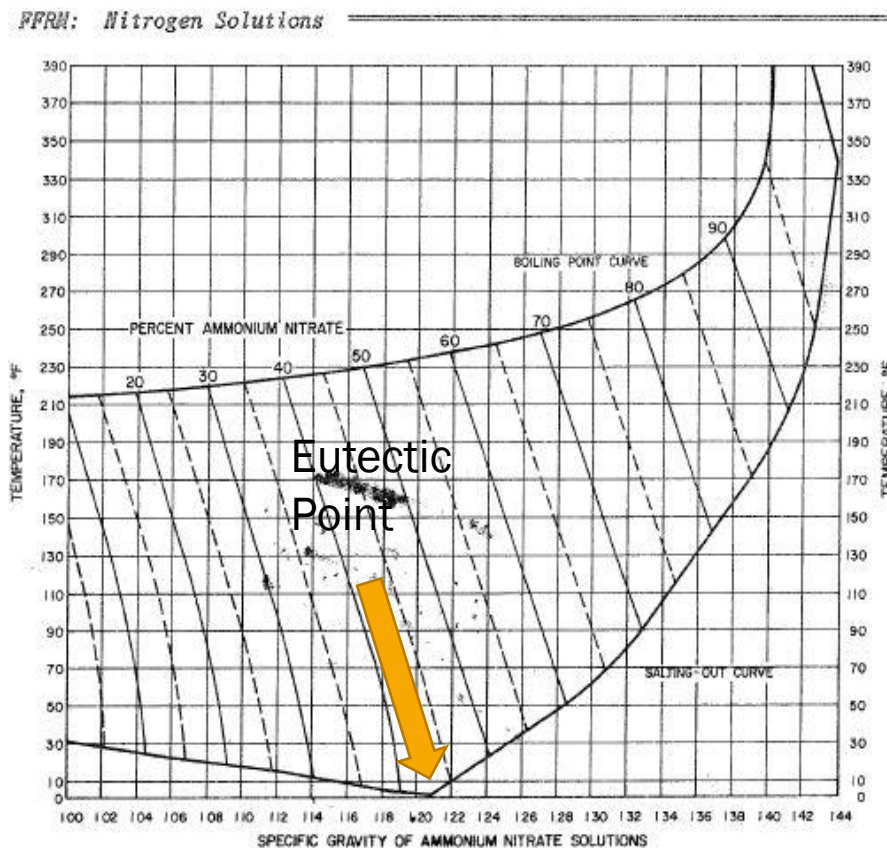


Figure 2-2. Physical Properties of Ammonium Nitrate Solutions

Ammonium Nitrate Salt out and boiling point curve. 45% Solution falls in the eutectic point.

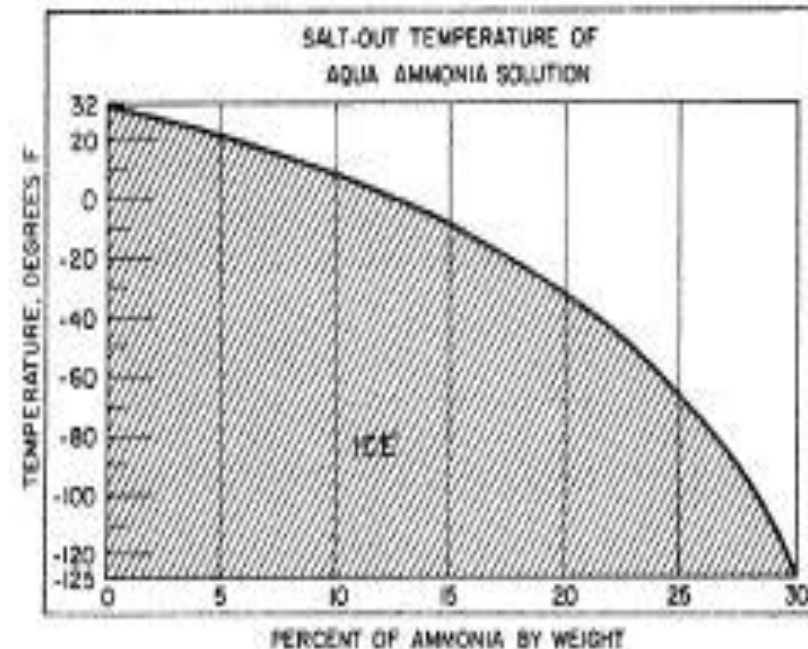


Figure 2-6. Salt-Out Temperature of Aqua Ammonia Solutions

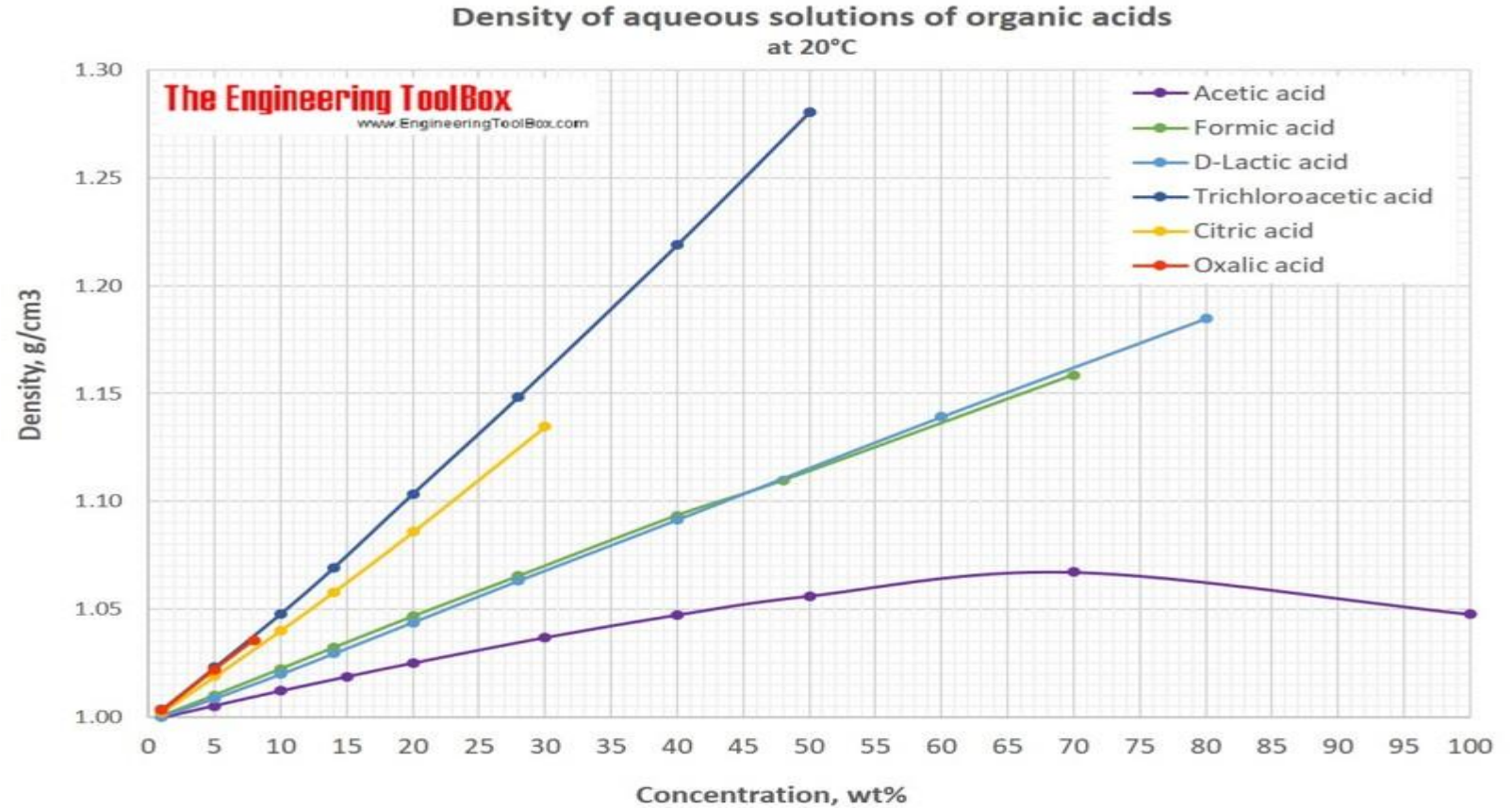
Typical Salt out diagram for Aqua Ammonia.



Acetic acid 45% or 100%?



The concentration curve for acetic acid (purple line) is another example of the reason for verification. The density is the very close to the same for 45% & 100%



Ammonium Sulfate pH curve

Data is not always what we expect.
That is why we need to verify!!

So when you expect the ammonium sulfate solution to have a pH of 7.0 don't be surprised if the meter shows a value of 4.0 or 5.0. All the same ..

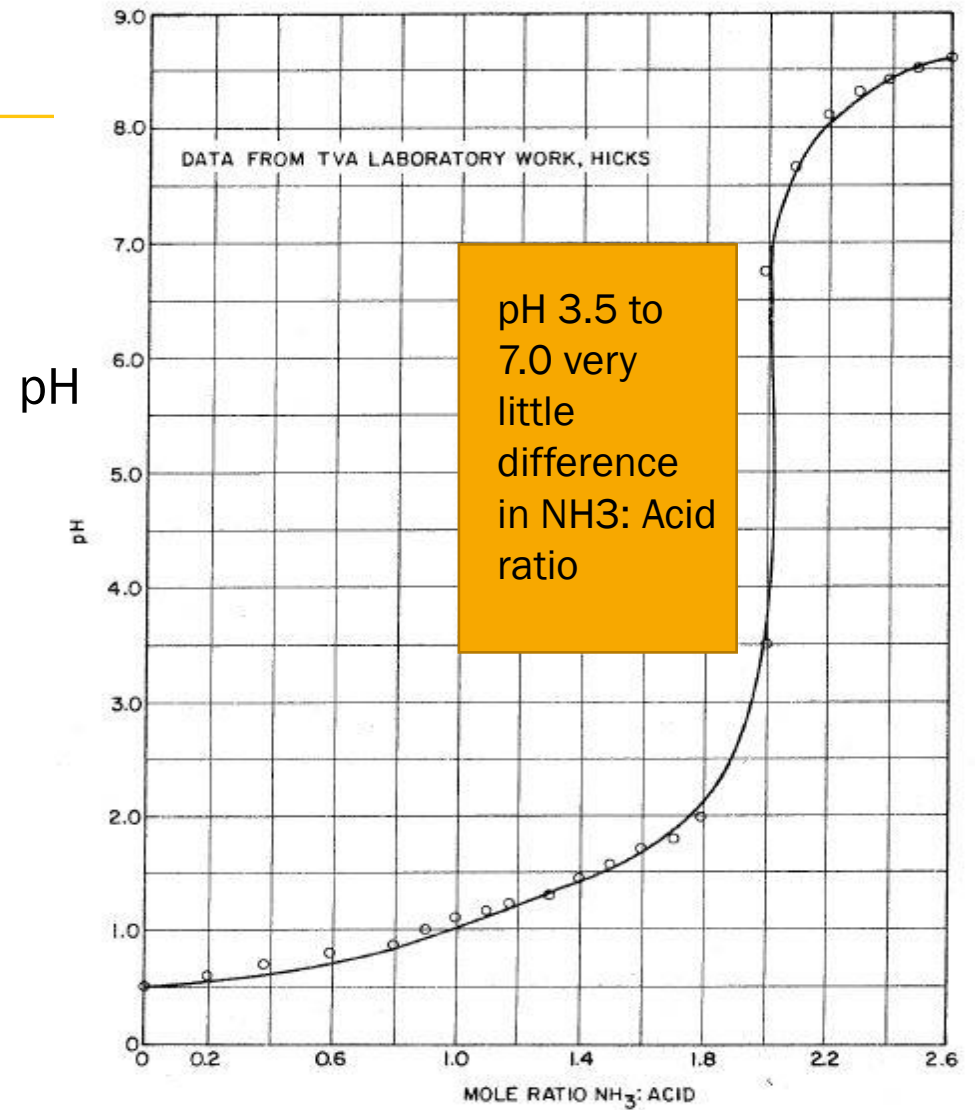


Figure 2-4. Effect of Adding Ammonia to Sulfuric Acid



Storage & Compatibility Properties of different formulations



- Know and/or verify salt out values for products to be stored. Internet can be a useful tool or a trap sometimes.
- If salt out value is undesirable then look at changing the chemistry, the location, or time of year, to obtain successful storage.
- One must also recognize that hot temperatures can be just as damaging to high polyphosphate products.





Questions? Comments ?

