Ortho vs Poly and Salt Index

Fluid Technology Roundup

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Everything you need to know

- http://www.fluidfertilizer.com/PastArt/pdf/33P8-11.pdf
- http://www.fluidfertilizer.com/PastArt/pdf/35P17-19.pdf

by Dr. Raun Lohry

Ortho Vs. Poly

Author takes a look at the history and behavior of ortho and polyphosphates.

Summary: Reports covering nearly 40 years of research present strong evidence of the rapidity of phosphate hydrolysis. Whether hydrolysis is complete in a few days or weeks, the process is fast enough to supply plants and roots with sufficient orthophosphate.

Phosphorus is required for life. It is the main component of ATP—the compound essential for energy transfer. It is part of a myriad of functions. Plants are generally thought to consume only the phosphate in the ortho form. Why then are our modern-day high polyphosphate fertilizers effective in overcoming soil phosphorus (P) deficiencies when they contain large portions of their phosphate in the condensed forms – principally pyrophosphate and tri-polyphosphate? It's a question we get asked more and more, especially with the increased interest in the use of in-furrow starter fertilizers.

Liquid fertilizer began its growth with orthophosphates. Early in the sixties, the Tennessee Valley Authority (TVA) researched methods to make a more concentrated liquid phosphate. Growers appreciated many of the benefits of liquid fertilizers but there was a desire to provide more plant food per gallon of fertilizer. TVA found that removing bound water from phosphoric acid boosted the phosphate content from 54% to 70%. This 30% increase reduced freight costs and made a whole new series of products possible. Super acid was born. Reacting super acid with ammonia under controlled conditions resulted in highly concentrated, easy to handle, neutralized liquid ammonium polyphosphates (APP). The polyphosphates (PP) sequestered magnesium, iron, and aluminum which pose problems in orthophosphates. These new phosphates could accept non-chelated zinc.

Soil reactions

There is a normal hydrolysis of concentrated APP that is strongly temperature related. Many know first hand the problem of hydrolysis that occurs if APP is left to "cook" all summer in a tank. Poly content is reduced and sequestered metals may fall out leaving residue in the tank (and cloudy product). And, once the polys are hydrolyzed, the product may not be able to sequester added micronutrients such as zinc. Dilute APP solutions may hydrolyze to orthophosphate but water dilution does not appear to accelerate the normal hydrolysis process.

Adding APP to soil is quite a different matter. Research studies examining the conversion of condensed phosphates to orthophosphate report half-lives of less than one day to as long as 100 days. A half-life is the time it takes to convert half of the polyphosphate to orthophosphate. Some conditions that influence conversion rate are temperature, pH, aerobic status, biological activity, and minerals. Liquid polyphosphate converts more quickly than dry. Water-soluble polys convert quicker than acid-soluble. Researchers have had to take extra care with soil sample storage since polyphosphates convert more rapidly in field-moist soils than air-dried.

Sodium phosphate research

Sutton and Larsen (1964) studied the hydrolysis rate of radioisotope-labeled sodium pyrophosphate in pot and water cultures. They surmised that hydrolysis to orthophosphate was largely enzymatic and reported half-lives ranged from 4 to 100 days with the average being 18. Rates were higher at higher soil pH values. Hydrolysis proceeded more quickly with higher biological activity (as measured by CO_2 evolution). Pyrophosphate was not converted rapidly in the water culture and plants absorbed 2.4 times more orthophosphate. Subsequently, Sutton, et al. (1966) found that pyrophosphatase level, CO_2 evolution, temperature, and uptake were loosely correlated. Low temperatures restricted hydrolysis and therefore P uptake in barley. Gilliam and Sample (1968) studied hydrolysis rates in soils with different chemical properties to assess the relative importance of chemical and biological influences. They found a significant chemical contribution to hydrolysis rate. All the observed changes could not be attributed solely to biological factors. Coarse-textured soils appeared to hydrolyze PP faster than fine. Hons et al. (1986) also found texture to significantly interact with other factors to influence rate. Significant interactions expressed were: texture x organic matter content, texture x pH, texture x time, organic matter x time, pH x soil moisture, pH x time, and temperature x time.

Dick and Tabatabai (1986) demonstrated hydrolysis rate differences in four soils at three temperature regimes (Figure 1). Rates were lower at 50° than at 68° or 86° F. The amount of P hydrolyzed in the three acid soils (Clarion, Webster, Muscatine) decreased with increasing chain length although there were no significant differences between pyro- (P_2) and tri-polyphosphate (P_3).

Chang and Racz (1977) quantified temperature effects on sodium pyrophosphate hydrolysis (Figure 2). Rates increased linearly and increased about two- to three-fold from 68° to 95° F. Tri-polyphosphate hydrolysis was greater than pyrophosphate and both rates were higher in the non-calcareous soil. About 40-70% of the phosphate hydrolyzed in 120 hours at 68° F whereas about 80-95% hydrolyzed in 120 hours at 95° F

Minerals may also affect hydrolysis rate. Dick and Tabatabai (1987) showed Ca_2^{+}, pH, and non-buffered phosphatase activity to be positively correlated with hydrolysis rate while percentage of clay, extractable Al^{3+}, and water soluble Mg^{2+} were negatively correlated.

APP

The most commonly applied polyphosphate is ammonium

Dr. John J. Mortvedt

Calculating Salt Index

Salt content is one of the most critical characteristics of fertilizers that should be considered when fertilizers are applied, especially with seed-row or "in furrow" placement.

Summary: Salt index (SI) of a fertilizer is a measure of the salt concentration that fertilizer induces in the soil solution. SI does not predict the exact amount of a fertilizer material or formulation that could produce crop injury on a particular soil, but it does allow comparisons of fluid formulations regarding their potential salt effects. As we all know, placement of some formulations in or near the seed may decrease seed germination or result in seedling injury.

Fluid fertilizers containing potassium phosphate as the source of K have lower SI values than those containing KCl. When applied near the seed, fertilizers with lower SI values generally cause fewer problems in seed germination or seedling injury. SI of any fluid formulation can be calculated using the SI values of the most common fertilizer sources. Dealers or growers then can select those formulations with lower SI values that best fit their needs.

Banding of nutrients has received much attention over the years. Usually, the fertilizer is placed at a depth greater than that of the seed to allow root interception of the fertilizer band as roots grow outward and downward in the soil.

Band vs broadcast

Regions showing the greatest improvement in efficiency from banding over broadcasting lie in the northern U.S. and Canada, where colder soil conditions are experienced during spring seeding of row crops and small grains. Higher P rates are generally recommended if growers broadcast instead of band their fertilizers.

Banded P tends to be more efficient on very acid soils, highly calcareous soils, and those soils with very low levels of available soil P. Band applications also are usually more efficient when low P application rates are used.

Early planting dates, large amounts of crop residues on the soil surface, and soil compaction may subject plants to more stress. Banded nutrients are usually more effective for crops under these stress conditions. Vegetables respond well to banded fertilizers because they require a relatively large percentage of their total nutrients early in their growth period, and their rooting volume in the soil usually is restricted.

As extra equipment has been installed on planters over the years, it has become more difficult to have enough room to include the coulters required to open the soil for fertilizer placement below and to the side of the seed row. Some growers have quit applying starters because of this limitation and also because of the weight of openers for very large planters. Others have applied starters directly to the seed furrow, which does not require extra openers.

Other considerations. Banding away from the seed row is recommended over seed-row application under most conditions when applying higher nutrient rates, especially N, K, and S. Plants can efficiently use nutrients banded away from the seed row without adversely affecting seed germination or seedling emergence.

Recommendations for fertilizer placement in direct seed contact vary with crop. For many years maximum recommendations ranged from 10-20 lbs/A of N + K_2O in direct seed contact with corn and sorghum. These applied to formulations using KCl as the K source and would not be accurate if potassium phosphate was used as the source of K instead of KCl. This is because of the lower SI value of potassium phosphate compared with KCl (Table 1).

Crop tolerance to increased osmotic pressures (salt content) of the soil solution in the vicinity of the seed varies considerably. For example, wheat is more tolerant of high salt conditions than is grain sorghum, while corn is intermediate. Tolerance of most oil-seed crops (soybeans and cotton) to seed-row application of nutrients is very low, and seed-row application of fertilizer for these crops should be viewed with caution.

Fluid fertilizers may produce a lower osmotic pressure in the soil solution than granular products of a similar grade. Fewer problems generally are encountered using fluids as seed-row fertilizers when compared to granular, since less soil water is required and salts are mainly dissolved in fluid formulations.

Seed-row application

This method refers to placement of relatively lower rates of nutrients in direct seed contact, usually for row crops. It also has been called "pop-up" or "in-furrow" application, but "seed-row" is more descriptive. Seed-row placement increases the possibility of early root interception by nutrients.

Problems. Major concern of this practice is decreased seed germination or seedling injury caused by high salt concentrations in the soil solutions around germinating seeds.

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Dr. John G. Clapp

Let's Be Careful When Defining Salt Index

Original data and definition of salt-index predate many current fertilizers.

Summary: *The original data and definition of salt index come from a time before many of the current fertilizer products, especially fluids after the 1940s, were developed. In recent years, some have adopted a method that measures electrical conductivity (EC) and not the original osmotic pressure approach. A few products may have widely different salt index values, depending on methodology used. Salt index, by itself, does not tell us how much of a given product is safe when applied with the seed. It only provides relative differences among products. Many other factors such as soil temperature, soil moisture, and potential free ammonia formation may all impact germination and/or seedling root development.*

In the 1940s, dry fertilizer materials available at that time were evaluated for changes that occurred in the soil solution osmotic pressure upon application. In 1943, Rader et al. reported salt index values for 45 dry fertilizer materials based on the osmotic pressure of the soil solution when applied to Norfolk sand. This method involved mixing fertilizer materials with air-dried soil and then spraying with water to bring the moisture content to 75 percent of its moisture equivalent. After five days, the soil solution was removed and evaluated for conductivity and freezing point. The resulting freezing point values were then converted to osmotic pressure by tables developed for vegetable saps. A salt index value was then expressed relative to the increase in osmotic pressure as compared with that obtained with the same weight of sodium nitrate. During this time, three nitrogen (N) containing solutions were evaluated, but they could not be urea-ammonium nitrate solution (UAN) since the N content ranged from 37 to 40.8 percent. A laboratory method was later published by W.L. Jackson in 1958 where salt index of a fertilizer was measured by electrical conductance, rather than by osmotic pressure, relative to sodium nitrate. However, this method generally results in significantly higher salt index readings than the original method and data derived from this laboratory method did not correlate well with earlier soil-applied applications. Fluid fertilizers such as UAN, ammonium polyphosphate (APP), ammonium thiosulfate (ATS), potassium thiosulfate (KTS), calcium nitrate (CN9) and others were not available until after the original study. Data from these materials have been added to data from the original study in the fertilizer salt index reference tables being used today.

Recent studies

Method comparison. In 2004, Murray and Clapp compared several potassium (K) sources for salt index values, as determined by the Jackson method, with the original data published by Rader.

As noted in Table 1, salt index values from the two methods do not directly correlate. Some minor differences are noted as a result of differences in the K_2O concentration because Rader used chemically pure material for K_2SO_4 and KNO_3. In this study, a

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Two Distinct Fluid Starter Types

Ammonium polyphosphates

and

100% orthophosphates

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Polyphosphates

What are they?

How they are produced?

What they do and advantages to having *"polys"*?

Precautions

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Phosphoric Acid Sources



Wet

Thermal

KilnProcess Acid

PPA

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What is a polyphosphate?

- Polyphosphates are molecules containing more than one phosphorus atom
  - Prior to the advent of the TVA pipe reactor process they were very difficult to make
  - *Only source lay in "high poly"* superacids (which are very corrosive)
    - **Required high heat and high vacuum conditions**
    - **50% poly was about the most that could be achieved**

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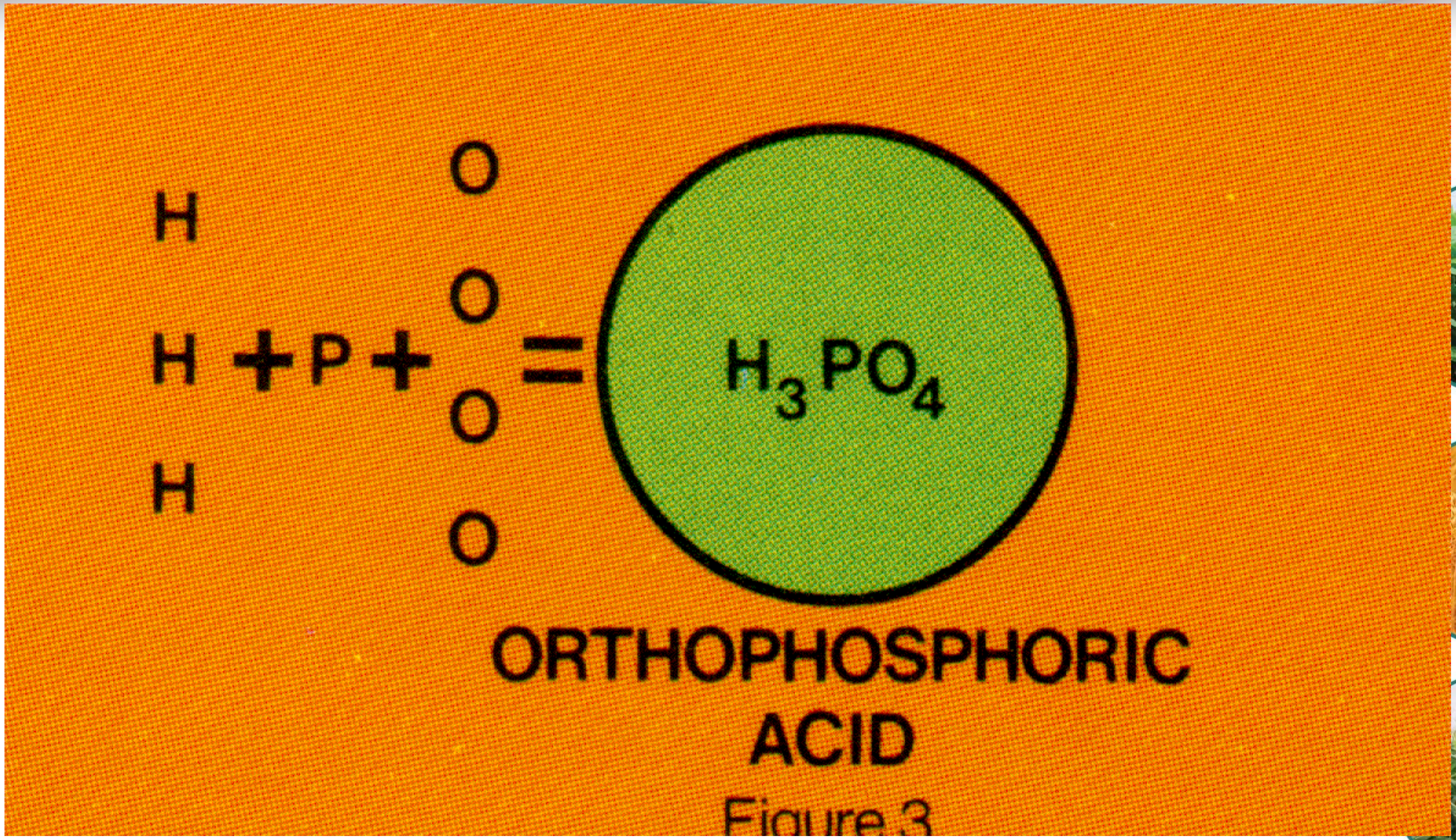
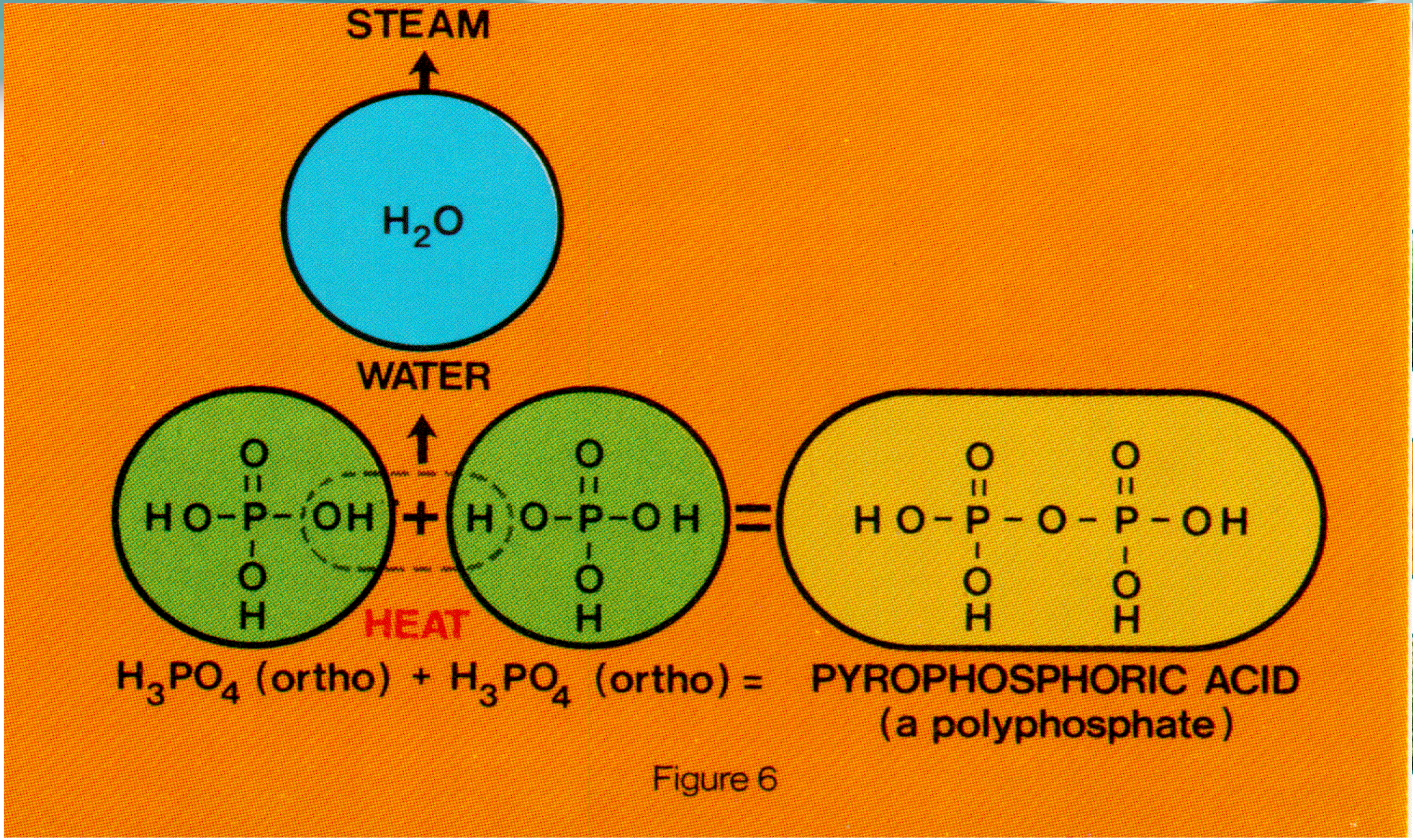
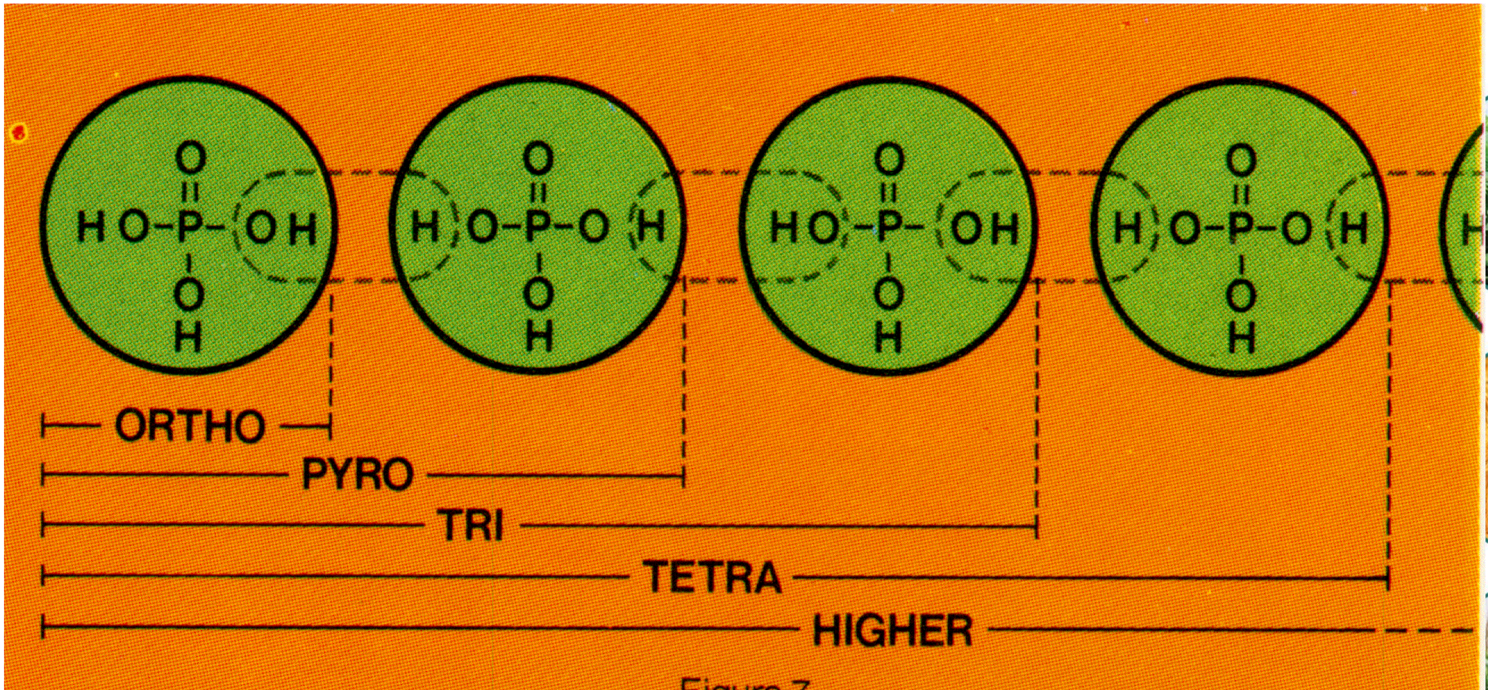


The basic building block for polyphosphates



Using heat to drive out chemically bound water and link the phosphate molecules



With more heat additional links can be made each time removing another molecule of chemically bound water

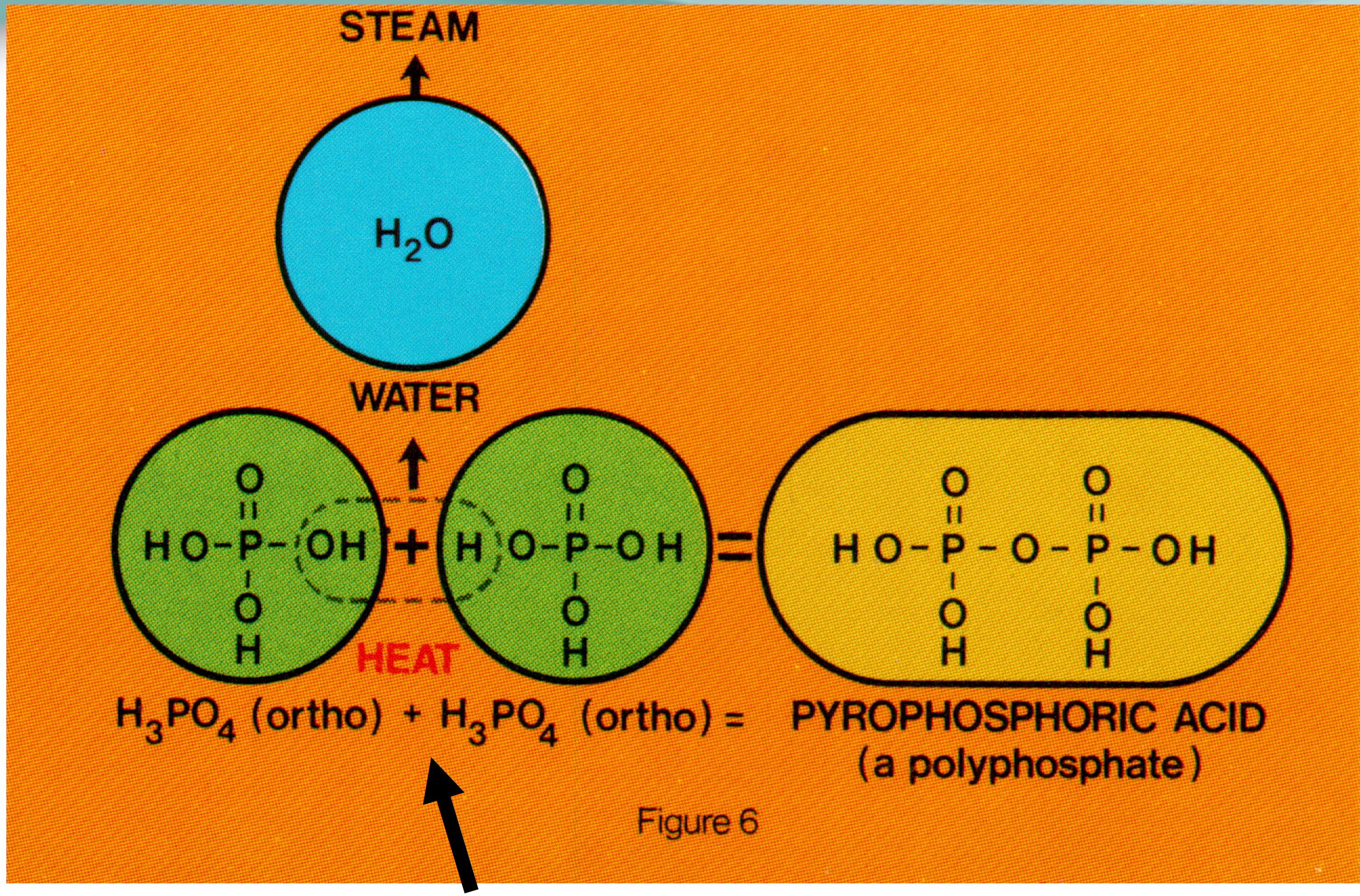


Figure 6

Where does the heat come from?

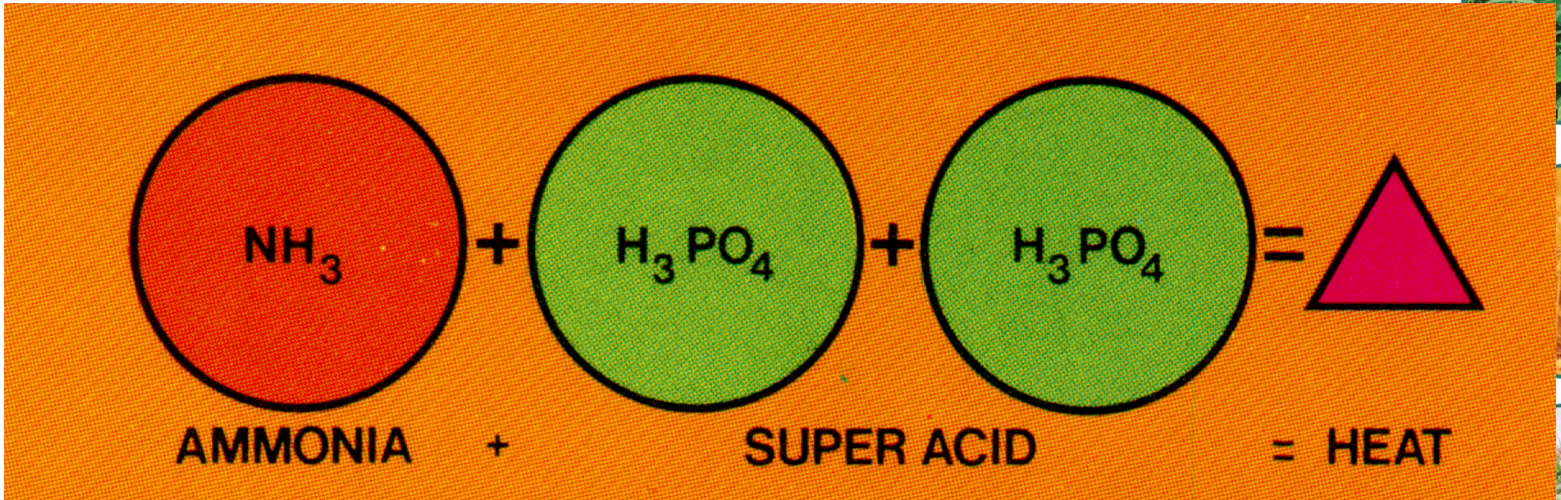


Figure 4

Ah-ha!

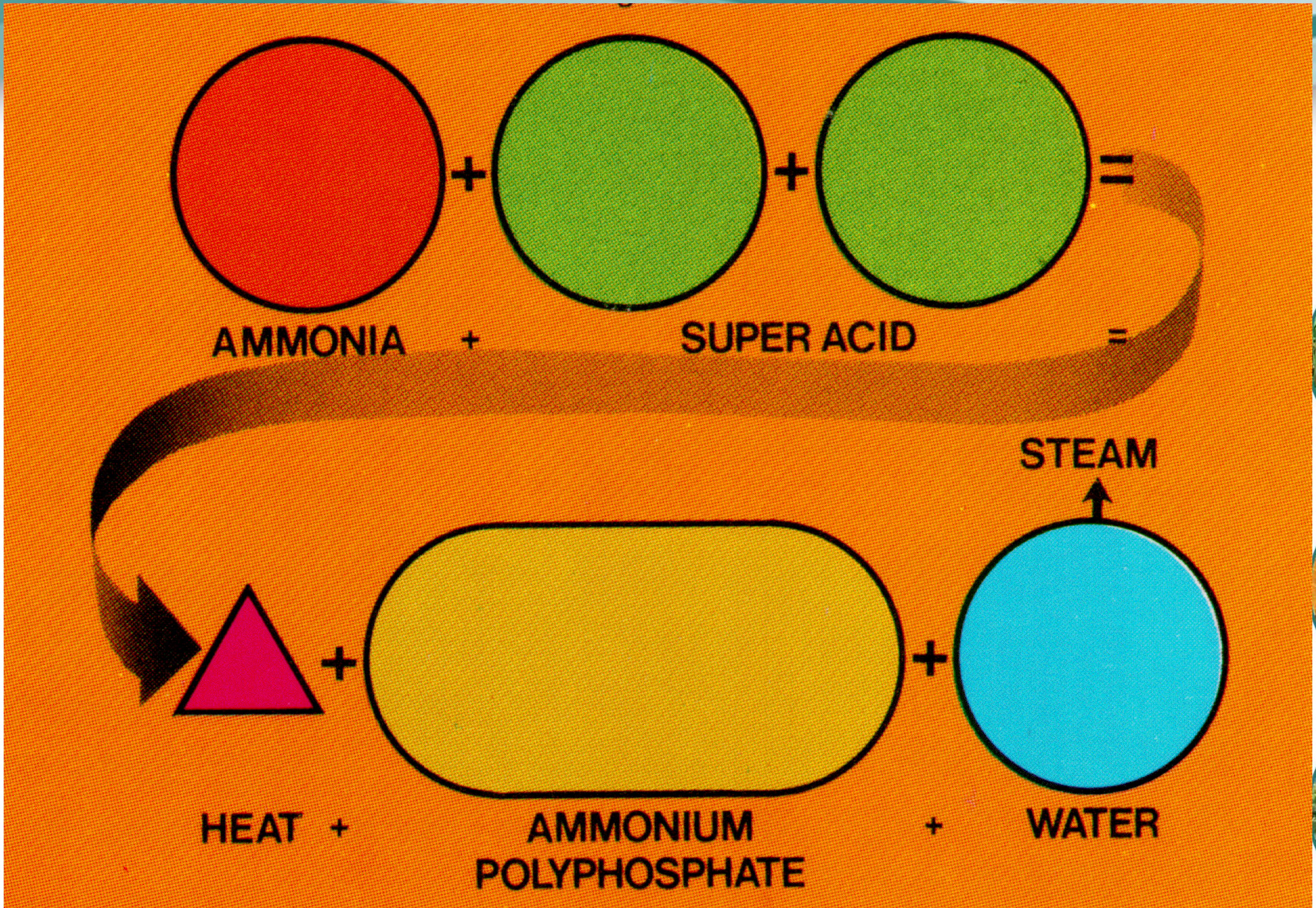


Figure 8

The overall process

Why Superacids?

- *It’s difficult to produce polyphosphates from* orthophosphoric acids because they contain so *much “free” water*
- Superacids *contain no “free” water (they are* anhydrous)

Benefits of the TVA pipe reactor process

(Developed in the mid-*60’s)*

1. Allowed production of High poly ammonium phosphate solutions
2. Eliminated the need for high poly superacids

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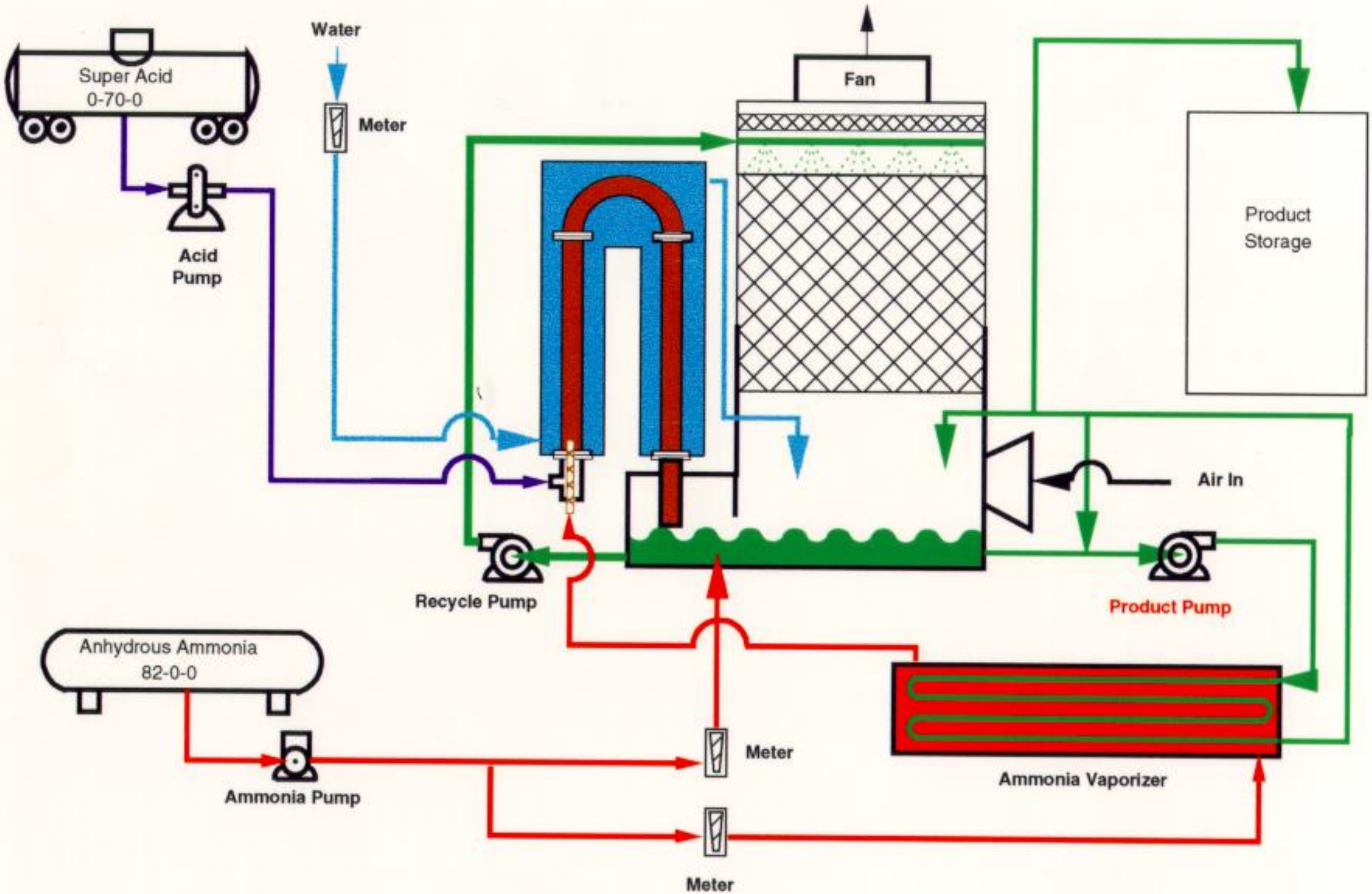
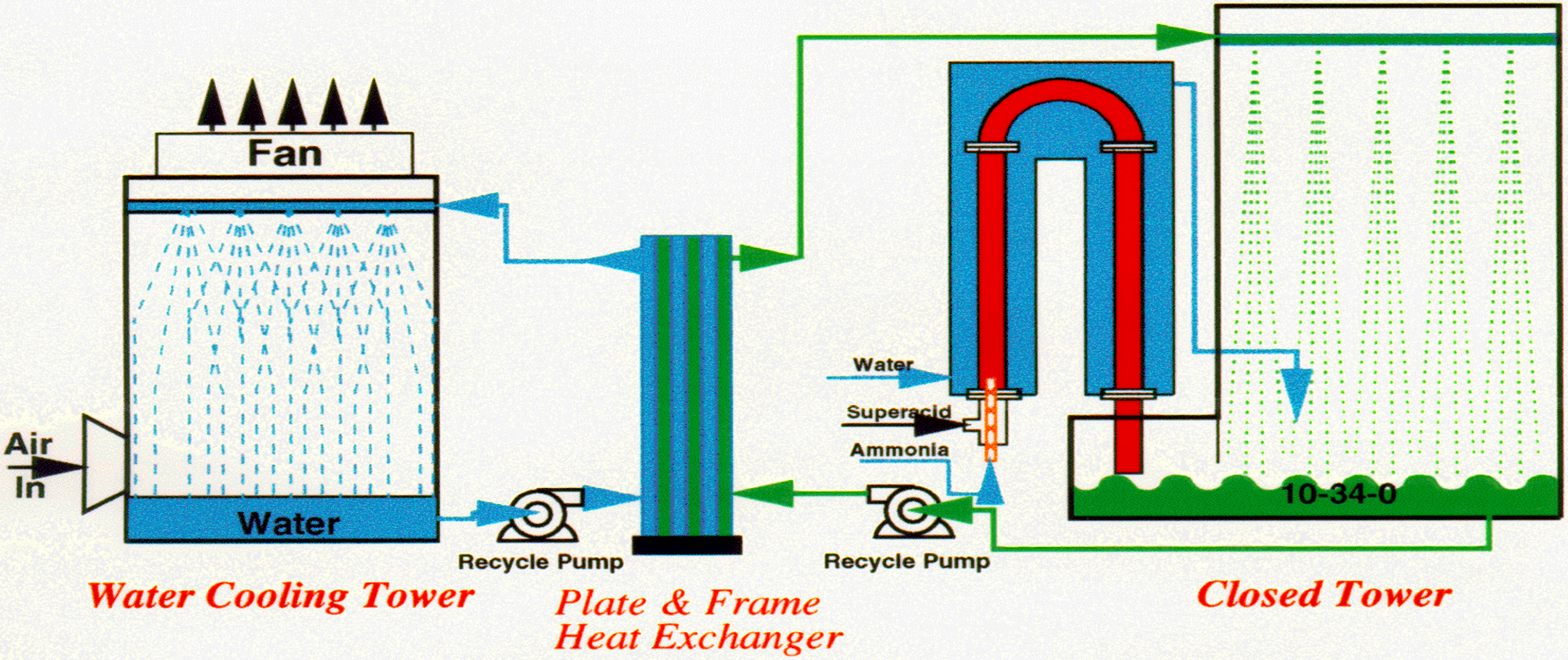
The TVA Reactor





TVA PIPE REACTOR PROCESS SCHEMATIC



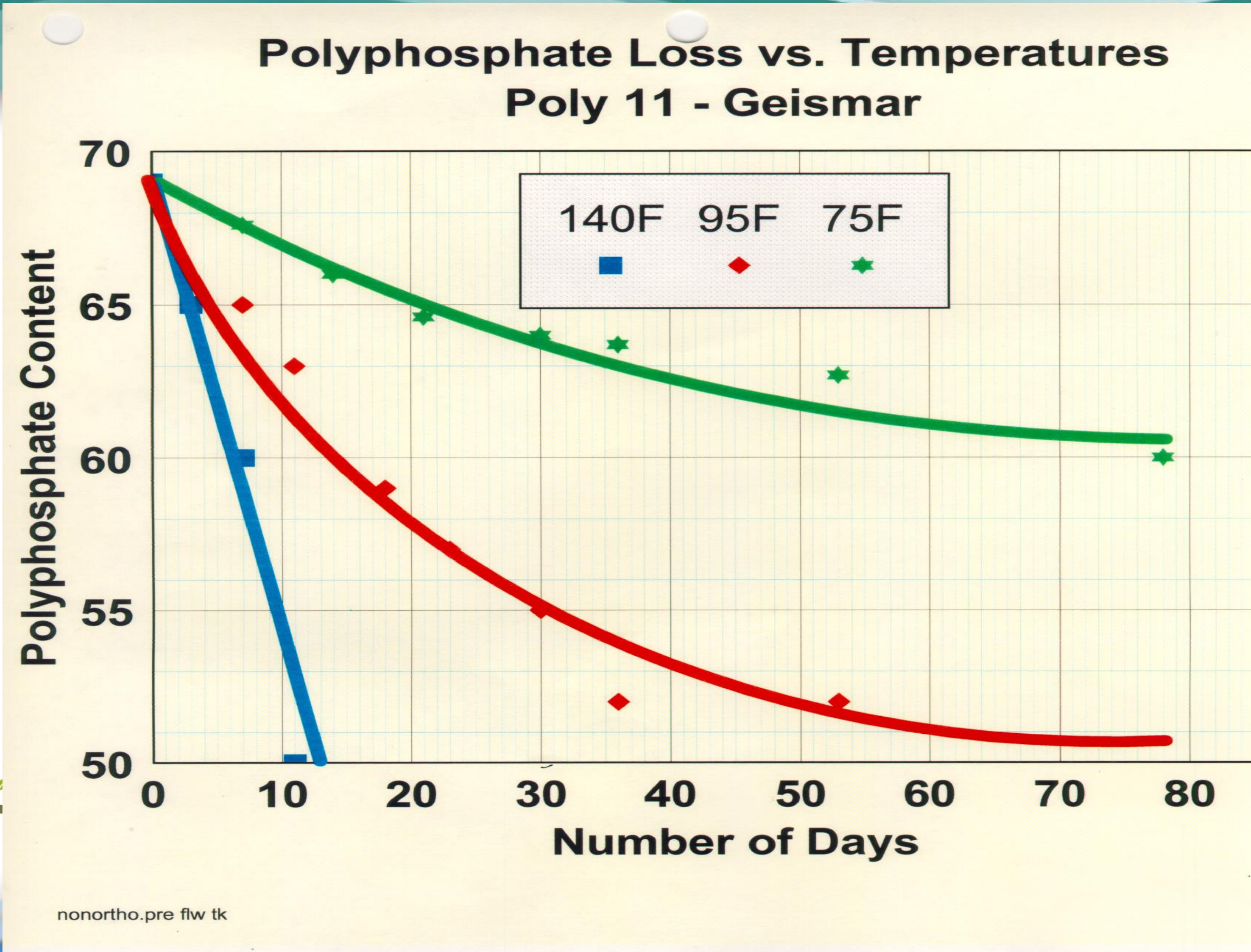
Modifications Required

Add a plate & frame heat exchanger

Add a pump - 50 hp - to recyle water

Add cooling system for the water - evaporative tower or chiller

Close in current tower - remove packing and fan



Polyphosphate Loss vs. Temperatures
Poly 11 - Geismar
140F 95F 75F
Polyphosphate Content
70
65
60
55
50
0 10 20 30 40 50 60 70 80
Number of Days
nonortho.pre flw tk

High Ortho

- N from ammonia, urea
- P from high grade orthophosphoric acid
- K from KOH
- S from ATS
- Micros from EDTA chelated sources

High Poly

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High Ortho

- N from ammonia, urea
- P from high grade orthophosphoric acid
- K from KOH
- S from ATS
- Micros from EDTA chelated sources

High Poly

- N from ammonia, UAN
- P from polyphosphate (converted from super acid)
- K from KCl
- S from ATS + other
- Micros from ammoniated complexes, sulfates, chlorides and chelates

Plant Food Madness

The market is becoming more diverse with blends

30/70 ortho/poly—typical high polyphosphate

50/50 ortho/poly

60/40 ortho/poly

70/30 ortho/poly

80/20 ortho/poly

100/0 ortho/poly

We're no longer "purists"

Blends are the growth area.

K source can be KCl or KOH.

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Ortho Benefits

- Plants use only ortho phosphate
- Immediately available phosphorus
- Higher ortho = lower viscosity for uniform flow rates over a wide range of temperatures
- Fewer contaminants to settle out
- 100% ortho—virtually no contaminants
- Excellent storability

Ortho Cons

- Does not sequester micronutrients
- Must use completely chelated micros
- Usually more expensive per unit of phosphate

Poly Benefits

- Concentrated P
- Sequesters micros (important for zinc)
- Cheaper acid raw material source
- *So called "Contaminants" include micronutrients* at no extra charge

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Poly Cons

- Often not recommended for in-furrow placement depending on K source
- Polyphosphate chains need to break down (hydrolyze) for bio availability
- Higher Viscosity (due to concentration)
- Storability problems if Poly converts in the tank before use

Ortho vs Poly.pdf

Seed Safety

- High orthos tend to be built with monopotassium phosphate as raw material. (ortho acid + KOH) = low salt index
- Safer on the seed – Corn seed $300+/bag (better be safe on the seed!!!)
- Ask about the salt index if seed placed



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- Safer on the seed – Corn seed $300+/bag (better be safe on the seed!!!)
- Ask about the salt index if seed placed
- High poly fertilizers are usually built with potassium chloride for the K source. Lowest cost, but higher salt index. Avoid seed placement. Economical for other placements

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Corrosiveness

- Important for equipment, especially planters
- Spend a quarter million dollars on a planter and what becomes the main concern if used for fertilizer application? Rust and corrosion!
- Foliar application gets fertilizer on equipment
- Generally, low salt index fertilizers made with monopotassium phosphate are also least corrosive to mild steel



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Salt Index Basics

- The salt index (SI) is a ***relative*** measure of a fertilizer to draw moisture and compete with roots and plants for water
- The higher the fertilizer SI the greater the risk of injury to the plant.
- Germinating seeds are especially sensitive to fertilizer mixtures with a high SI
- SI values are based on sodium nitrate = 100

SI Basics (Cont'd)

- Each component of a mixture has its own SI
- The SI of fluid mixtures can be calculated from the SI values of its components
- The SI permits the comparison of fluid formulations using different components
- SI tables are available from a number of sources (Farm Chemicals Handbook; Professional Dealers Manual – ARA; Publications of the FFF)



SI Basics (Cont'd)

- Again, the SI of a mixture is the sum of the SI values contributed by each of its components
- *The SI for a "high analysis" NPK mixture may be greater than for a "low analysis"* one --- however, the SI ***per unit of plant nutrient*** may be lower for the higher analysis product!
- Thus must compare mixtures on the basis of per unit of plant nutrient

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Calculating Salt Index Values

- Step 1. Determine the SI ***per unit of plant nutrient*** of each raw material
- Step 2. Calculate the total units contributed to the final mixture by each raw material
- Step 3. Multiply the above value (total units contributed) by the value found in Step 1
- Step 4. Repeat Steps 1,2 and 3 for each raw material
- Step 5. Sum the contributions from each of the raw materials to find the SI of the total blend



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Salt Index Values of Fertilizer Materials

Material and analysis	Salt Index: Per equal wts of materials	Salt Index: Per unit of nutrients*
NITROGEN/SULFUR		
Ammonia, 82% N	47.1	0.572
Ammonium nitrate, 34% N	104.0	3.059
Ammonium sulfate, 21% N, 24% S	68.3	3.252
Ammonium thiosulfate, 12% N, 26% S	90.4	7.533
Urea, 46% N	74.4	1.618
UAN, 28% N (39% a. nitrate, 31% urea)	63.0	2.250
32% N (44% a. nitrate, 35% urea)	71.1	2.221
PHOSPHORUS		
APP, 10% N, 34% P_2O_5	20.0	0.455
DAP, 18% N, 46% P_2O_5	29.2	0.456
MAP, 11% N, 52% P_2O_5	26.7	0.405
Phosphoric acid, 54% P_2O_5		1.613[a]
72% P_2O_5		1.754[a]
POTASSIUM		
Monopotassium phosphate, 52% P_2O_5, 35% K_2O	8.4	0.097
Potassium chloride, 62% K_2O	120.1	1.936
Potassium sulfate, 50% K_2O, 18% S	42.6	0.852
Potassium thiosulfate, 25% K_2O, 1 7% S	68.0	2.720

[a] Salt index per 100 lbs of H_3PO_4 *One unit equals 20 lb.

Mortvedt, "Calculating Salt Index"

Salt Index of Some Common Liquid Formulations

Formulation	Salt index	Salt index per unit of plant nutrient (20 lb)
2-20-20 [a]	7.2	0.17
3-18-18 [a]	8.5	0.22
6-24-6 [a]	11.5	0.32
6-30-10 [a]	13.8	0.30
9-18-9 [a]	16.7	0.48
10-34-0 [b]	20.0	0.45
7-21-7 [c]	27.8	0.79
4-10-10 [c]	27.5	1.18
28%UAN [c]	63.0	2.25

[a] These grades are formulated using potassium phosphate as the K source.
[b] Use in seed-row placement with caution.
[c] Not suggested for use in seed-row placement.

Why SI is Important Today



- Row placement easier with large planters
- Need more seed safety
- Fertilizer openers on large planters have disadvantages
  - Expensive
  - Take extra horsepower
  - Obstruct trash flow in high residue conditions
  - Disturb seedbed in no-till
  - Seed depth variable because moist soil kicked out by fertilizer opener sticks to seed depth control wheels

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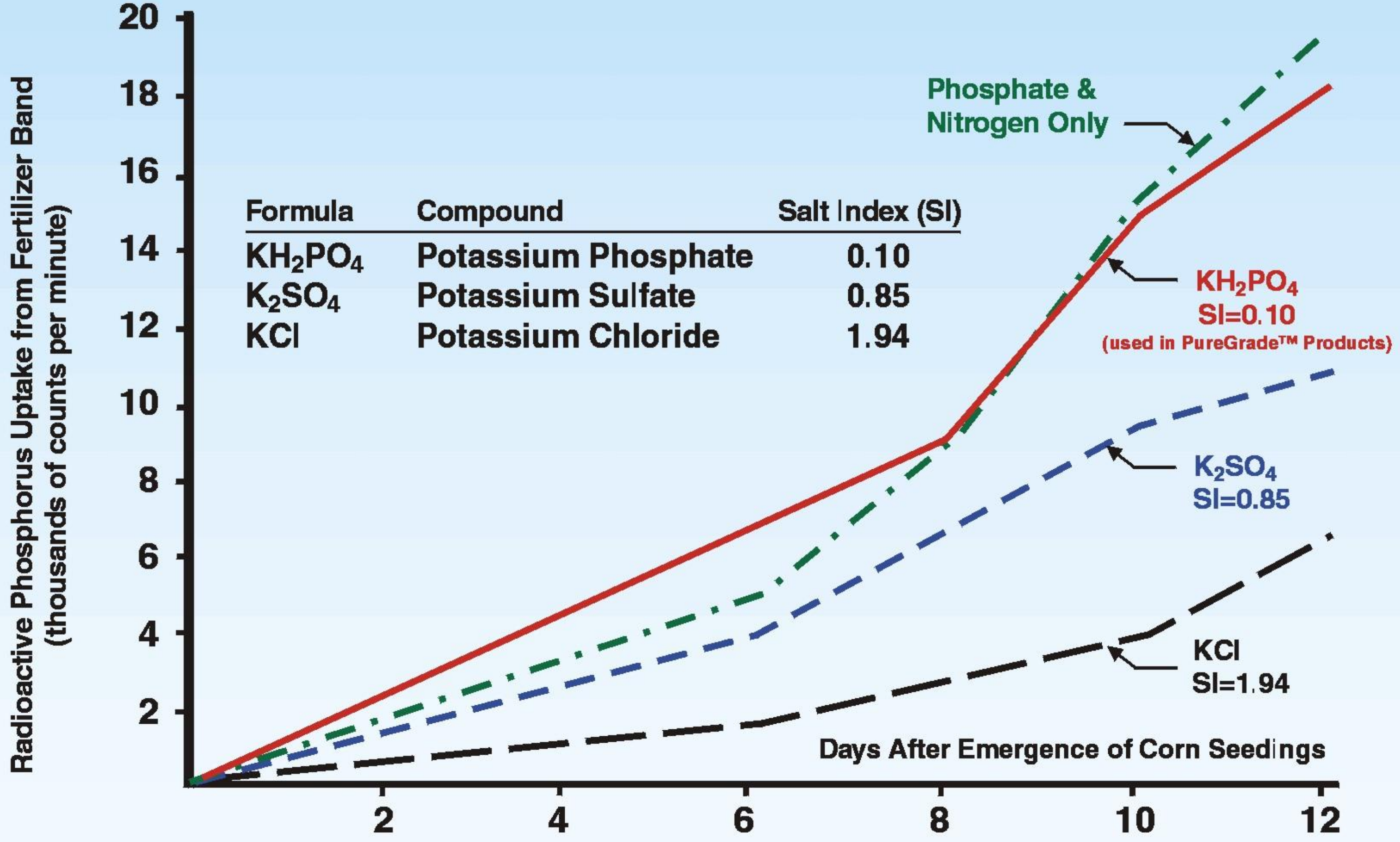
Phosphorus Uptake by Corn as Affected by the Potassium Salt Added to Phosphate-Nitrogen Mixture in Band



Source - How Roots Tap a Fertilizer Band by Prof .A.J. Ohlrogge
National Plant Food Institute, Washingtion, D.C.

Using Ortho and Poly in the field

- Rader said that salt index determines placement
- Far from seed—no concern about SI
- Strip-till: Poly P with high SI fertilizers applied preplant in subsurface band. Planter applied low SI 6-24-6 for safety in seed furrow
- Ammonia and 10-34-*0 applied together in "dual band." Plus planter applied low SI starter fertilizer* in seed furrow
- Liquid or dry surface broadcast + row placed liquid, low SI ortho at planting

Ortho vs Poly summing up

- Original liquid fertilizers were all ortho
- Plants use only ortho form
- High ortho products are typically more dilute
  - Flow better in cold temperatures
  - Lack sequestration power
- Polys naturally break down to form ortho P
- TVA pipe reactor process used concentrated acid and ammonia under high temperature to form high poly
- Most fertility programs include both.

Salt Index Summing up

- For seed placement (and foliar) or very close to the seed use low salt index products to protect expensive seed and leaf tissue
- *Don't want corrosion on equipment? Use low salt* index fertilizer made from monopotassium phosphate. No chloride or nitrate
- Broadcasting or banding several inches from seed furrow-- look for economical alternatives
- Successful fertilizer programs include both low SI *products and "conventional" fertilizers*

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Sulfur – common fluid sources

- ATS 12-0-0+26S (ammonium thiosulfate)
- KTS   0-0-25+17S (potassium thiosulfate)
- K-Row 23® 0-0-23-8S. Supplies K and S. A new product designed for blending with ammonium polyphosphate for seed safe application with pop-up fertilizers.



Micronutrients – common fluid sources

- Zinc: Chelates, ammoniated zinc complexes, *sulfates, nitrates, chlorides…*
- Manganese: Chelates, sulfates,
- Copper: Chelates, sulfates, chlorides
- Iron: Chelates, sulfates
- Boron: Boric acid, Solubor®

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Chelates and micronutrients

Chelating Agent	Micronutrients			
	Copper	Iron	Manganese	Zinc
EDTA	X	X	X	X
HEEDTA	X	X	X	X
NTA		X		X
DTPA		X		
EDDHA		X		

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Thank you

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