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WATER-SOLUBLE FERTILIZER DILUTION

Feeding from bulk tanks:

Water-soluble fertilisers can be directly diluted into the irrigation water in bulk tanks, spray tanks, bowsers, etc. In this situation the required amount per litre is applied directly into the tank, with good agitation. Where a feed of 1 gram per litre is required add 1 kilo (1000g) of fertiliser per 1000 litres ($1m^3$) of water.

For Feeding via an injector from a concentrated stock of fertiliser:

The standard 10% stock solution is made from 10 kg of fertiliser diluted into to 100 litres of water or multiples of this. Stronger stock can be made up with warm water, but the standard stock mixes well with water at 10^0C and will not crystallize out at normal temperature.

The constituent components of the stock will separate into layers over a few days, so agitation of the stock is required.

Dilution of the 10% stock solution to produce the final strength feed

Feed strength	Dilution ratio	$g \, l^{-1}$ of fertigation	E.C. $mS \, cm^{-1}$ (+ water EC)
Weak feed (e.g. for young plants)	1:200 (0.5%)	0.5	0.5 to 0.6
Normal feed	1:100 (1.0%)	1.0	1.0 to 1.2
Strong feed	1:66 (1.5%)	1.5	1.5 to 1.8

The nutrient applied can be easily calculated from the dilution rate:

At a weak strength of $0.5 gl^{-1}$ simply multiply the stated analysis by 5 to obtain the ppm of each nutrient given. EG: 13+04+42 will give N 65ppm; P_2O_5 20ppm; K2O 210ppm.

At a normal strength of $1.0 \, gl^{-1}$ simply multiply the stated analysis by 10 to obtain the ppm of each nutrient given.
EG: 13+04+42 will give N 130ppm; P_2O_5 40ppm; K_2O 420ppm.

(Note that ppm = $mg \, l^{-1}$. and the term $mg \, l^{-1}$ means milligrams per litre)

The ideal pH for irrigation water is pH 5.5 to 6.0. Use the lower value for calcifuges. Within this range the Dissolved inorganic carbon (DIC) is in the form of carbonic acid with some bicarbonate and very little carbonate.

Below this pH range there is a danger of acidification of the growing media with toxic effects, particularly in peat substrates. Above this pH range there is a danger of raising the pH of the growing media and locking up nutrients, plus blocking of drippers etc with calcium carbonate deposits.

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Acidification of Hard water.

There is frequent confusion between alkaline water and hard water.

Alkaline water has a pH of over pH 7, pH 7 is neutral and values below 7 are acidic. The pH is statement of the number of H^+ ions present in the liquid expressed as a negative logarithmic value.
High concentrations of H^+ ions give a low pH value so acid conditions and conversely high pH values arise when the number of H^+ ions present in the liquid is low.

H^+ ions are buffered by carbonates in solutions (H^+ ions react with carbonates and bicarbonates). Where carbonate concentration is low then a little acid rapidly alters the pH, giving an acid solution. Where carbonate concentration is high a lot of acid is needed to react with the carbonate and lower the pH.
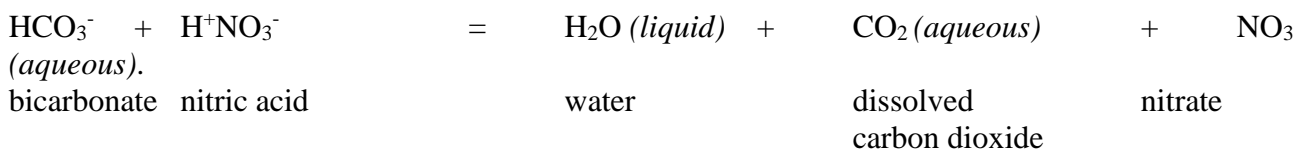
Hard water has a high content of carbonate (CO_3^{2-}) bicarbonate (HCO_3^-) that enters the water as the anion from dissolved calcium carbonate ($CaCO_3$), magnesium carbonate ($Mg.CaCO_3$) and sodium carbonate (Na_2CO_3). The CO_3^{2-} reacts with H^+ (acid) ions in the water, these occur naturally from carbonic and organic acids, to form bicarbonate predominantly (HCO_3^-) anions. As the water evaporates in the compost, or at the tip of the drippers, or on the foliage of plants, the Ca_2^+ cation and the HCO_3^- anion reform, as $CaCO_3$, calcium carbonate evaporite.

Nitric acid is a <u>strong acid</u> in <u>aqueous</u> <u>solution</u>, it completely <u>ionizes</u> into the <u>nitrate</u> <u>ion</u> NO_3^- and a <u>hydrated proton</u>, known as a hydronium ion, H_3O^+.

HNO_3 +	H_2O	$\rightarrow$	H_3O^+ +	NO_3^-
nitric acid	water		hydronium	nitrate

Hydronium quickly dissociates into	H^+	+	H_2O
	hydrogen ions		water

Nitric acid (HNO_3) added to hard water reacts with part or all of the bicarbonate, depending on the amount of acid added. The form the dissolved inorganic carbon (DIC) takes in the water is pH dependant on the number of H^+ ions in the water. The H^+ ions are supplied by the nitric acid and buffered by the bicarbonate.

HCO_3^- +	$H^+NO_3^-$		=	H_2O *(liquid)* +	CO_2 *(aqueous)*	+	NO_3
(aqueous).							
bicarbonate	nitric acid			water	dissolved carbon dioxide		nitrate

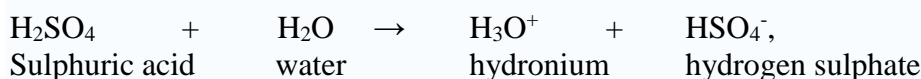Phosphoric and Sulphuric acid are also used to reduce hardness of irrigation water.

Phosphoric acid, also known as **orthophosphoric acid** or **phosphoric (V) acid**, is a mineral (inorganic) acid having the chemical formula <u>H_3PO_4</u>. Orthophosphoric acid is a non-toxic, inorganic, rather weak triprotic acid with slower dissociation and reaction than nitric acid. More acid is needed to react with the hardness and more time is needed for the reaction.

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Phosphoric acid is also applied as urea phosphate in crystalline form. This is a common fertiliser component of feed solutions and is the acidic P source in Scotts Excel products.
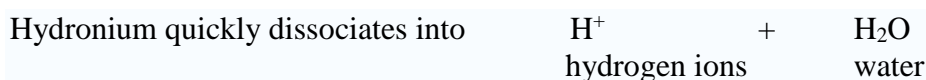
Urea phosphate is an organic compound of carbon, hydrogen, nitrogen, oxygen and phosphorus. Its formula is $CO(NH_2)_2.H_3PO_4$. It is made by reacting urea with phosphoric acid. It used as a fertilizer; as such, its NPK formula is 17-44-0. It is soluble in water, and produces a strongly acidic solution (pH 1.0). Urea phosphate is sometimes added to blends which contain calcium nitrate and magnesium nitrate to produce water-soluble formulas such as 15-5-15, 13-2-20, and 13-2-13. The acidity of urea phosphate allows Ca, Mg and P to co-exist in solution. Under less acidic conditions, there would be precipitation of Ca-Mg phosphates. Urea phosphate is often used in Drip irrigation to clean the pipe system.

Sulphuric acid, H_2SO_4, is a strong mineral acid. It is soluble in water at all concentrations. The hydration reaction of sulfuric acid is highly exothermic. If water is added to concentrated sulfuric acid, it can boil and spit dangerously.

The reaction is best thought of as forming hydronium ions, by:

$$H_2SO_4 \quad + \quad H_2O \quad \rightarrow \quad H_3O^+ \quad + \quad HSO_4^-,$$
Sulphuric acid   water   hydronium   hydrogen sulphate

and then

$$HSO_4^- \quad + \quad H_2O \quad \rightarrow \quad H_3O^+ \quad + \quad SO_4^{2-}.$$
hydrogen sulphate   water   hydronium   sulphate

Hydronium quickly dissociates into H^+ + H_2O
     hydrogen ions   water

Citric acid $C_6H_8O_7$ is a weak acid that is also used in crystalline form as a safe acidifier in fertiliser compounds, e.g. Scotts Universal. The acidic reaction of citric acid is very weak and is ineffective at neutralising carbonates. The product is a strong chelating agent of metallic elements and is effective as a water softener from actively chelating of Ca^{2+} and Mg^{2+} ions so removing them from the carbonate compounds. Citric acid is not used alone as an acidifier of water for irrigation use.

The mechanism of water acidification:

When H^+ ions population is high then the pH is low (below 5) the DIC takes the form of carbonic acid in the water: $(H^+ \ HCO_3^-)$

When H^+ ions population is medium, then the pH value is also medium (5 to 6.0), the DIC takes the form of carbonic acid and bicarbonate in the water: $(H^+ + HCO_3^-) + (H^+ + CO_3^{2-})$, with increasing bicarbonate as the pH rises, so less H^+ ions are available to form carbonic acid.

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When H^+ ions population is low then the pH is higher (above 7.5) the DIC takes the form of bicarbonate and carbonate in the water: $(H^+ + CO_3^{2-}) + (CO_3^{2-})$.

When H^+ ions population is very low then the pH is very high (above 9) the DIC takes the form of carbonate in the water: (CO_3^{2-}).

Enough acid needs to be added to reduce but not remove all of the bicarbonate. A little buffer must be left in the water (50 to 150 ppm) to ensure that no free H^+ ions enter the growing media and cause acidification of it. The water is normally reduced in pH from 7.5 or more to between 5.5 and 6. This gives the correct reduction in bicarbonate and carbonate. The actual bicarbonate remaining should be checked. The calculation below shows the acid input required.

We need to react with 150 to 200 ppm bicarbonate from typical groundwater for use in irrigation. This will reduce the typical bicarbonate level of 250 ppm down to an acceptable 50 ppm to 100 ppm.
100ppm HCO_3^- contains 1.64×10^{-3} mol l^{-1} HCO_3^- and ppm = g $l^{-1} \times 10^{-3}$.

100 g $l^{-1} \times 10^{-3}$ HCO_3^- / 61 (relative atomic mass of HCO_3^-) = 1.64×10^{-3} moles HCO_3^- .

$1.64 \ 10^{-3}$ moles of HNO_3 is required to neutralize the $1.64 \ 10^{-3}$ moles of HCO_3^-.

64 (relative atomic mass of HNO_3) $\times 1.64 \ 10^{-3}$ moles = 1.05×10^{-1} g

The strength of the acid is usually 60%(w/w) so we need 1.05×10^{-1} g $\times$ 100/60 g = 1.72×10^{-1}g.

HNO_3 is a liquid so is more conveniently measured by volume. The specific gravity of the HNO_3 (60% w/w) is 1.31 so 1.72×10^{-1}g / 1.31 = 0.13 ml l^{-1} of HNO_3 (60% w/w).

To make up a stock of 100 litres that is to be diluted at 1:100 to produce 10 000 litres of fertigation and neutralize 100 ppm HCO_3^-, the acid needed is 0.13 ml l^{-1} of HNO_3 (60% w/w) x 10000 = 1300 ml or 1.3 litres.

In approximate terms, 1.3 litre of HNO_3 (60% w/w) will neutralize 100 ppm of bicarbonate. Many water samples are very hard and need more acid to bring them into the acceptable range. Water with 250 to 300 ppb bicarbonate is common from chalk aquifer areas. For this hard water we need to add enough acid to react with 150 ppm to 200 ppm bicarbonate, this requires 1.9 to 2.6 litres of acid per 100 litres of stock.

It is worth noting that Calcium is not removed by the acidification. This is available to the crop as a vital nutrient. The pH of the media can rise, even when the water has been acidified. The basic cations of $Ca^{2+,}$ $Mg^{2+,}$ K^+, Na^+ are all still present and will attach to the media and be available to the crop through cation exchange. Only where the bicarbonate in the water has been totally reacted with the acid and H^+ are free in the water will acidification of the media occur. This is dangerous and usually undesirable. This is why a buffer of HCO_3^- is left in the water.

Citric acid chelates the Ca^{2+} and Mg^{2+} ions in solution. These ions are no longer able to associate with carbonate so hardness is reduced. They can be taken in by plant roots as chelates so remain available as nutrients.

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Nitrogen contribution from Nitric Acid

NO_3 contains 14% N from the calculation:

$$\frac{\text{Atomic mass of N (14g)}}{\text{Molecular mass of } HNO_3 \text{ (63g)}} \times 100 = 22.2\% \text{ N at 100\% strength}$$

22.2% x 60% = 13% N

This applies 20ppm N per litre of the diluted solution per 1 litre acid added to the 100 litres of stock diluted at 1:100.

OR

25 ppm N per 100 ppm bicarbonate reduced by the acid.