Chelates, Complexes & Salts of Multivalent Cations in Aqueous Solutions

Presented by: Brian Haschemeyer

Interactions with Water

Hydrolysis of Multivalent Cations

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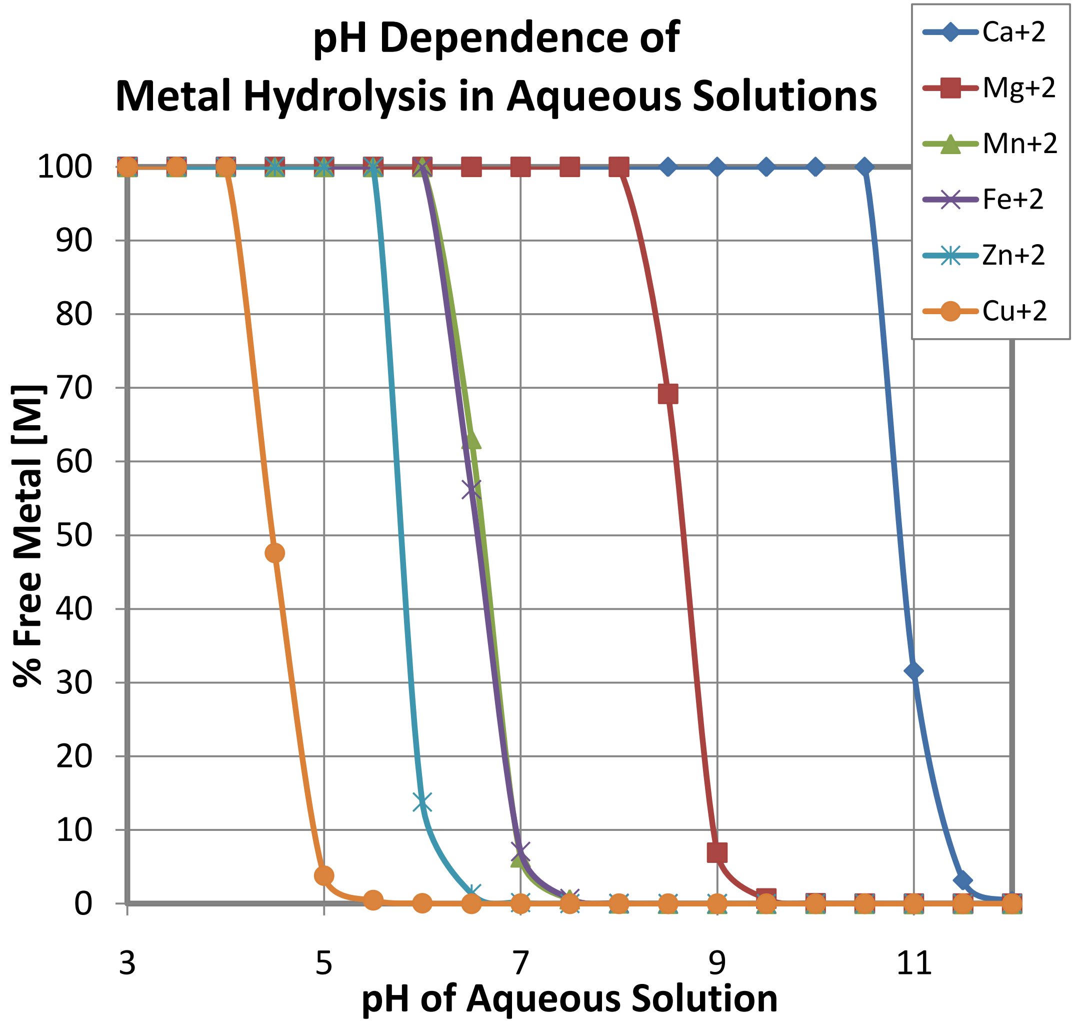
Hydrolysis Reaction

$$Zn(OH)_{2(s)} \Leftrightarrow Zn^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$[M]^{+n}$	Form	Ksp	mol	%M
Ca+2	$Ca(OH)_2$	$5x10^{-6}$	1	4.1
Mg+2	$Mg(OH)_2$	$5x10^{-12}$	1	2.5
Mn+2	$Mn(OH)_2$	$2x10^{-13}$	1	5.5
Fe+2	$Fe(OH)_2$	$5x10^{-17}$	1	5.6
Zn+2	$Zn(OH)_2$	$3x10^{-17}$	1	6.6
Cu+2	$Cu(OH)_2$	$5x10^{-20}$	1	6.4

- Most micronutrients react with water with increasing alkalinity (pH)
- Calcium and Magnesium are stable in mild alkaline conditions
- Most all others react with water to form hydroxide salts.



Nitrates & Chlorides

Highly Soluble Sources

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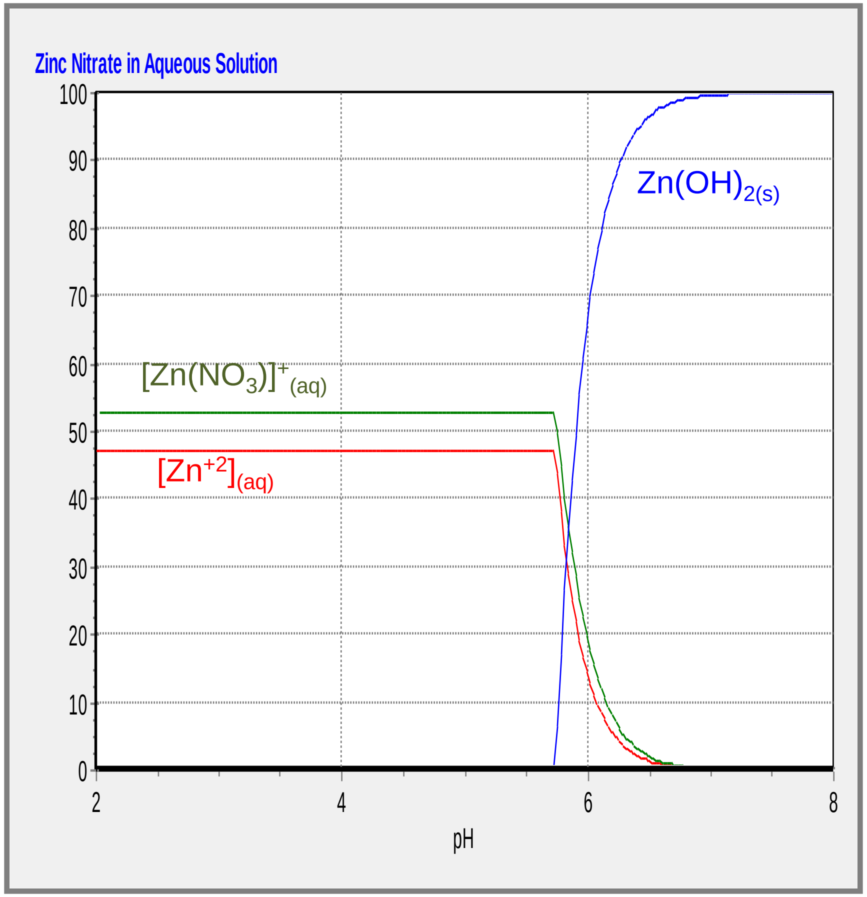
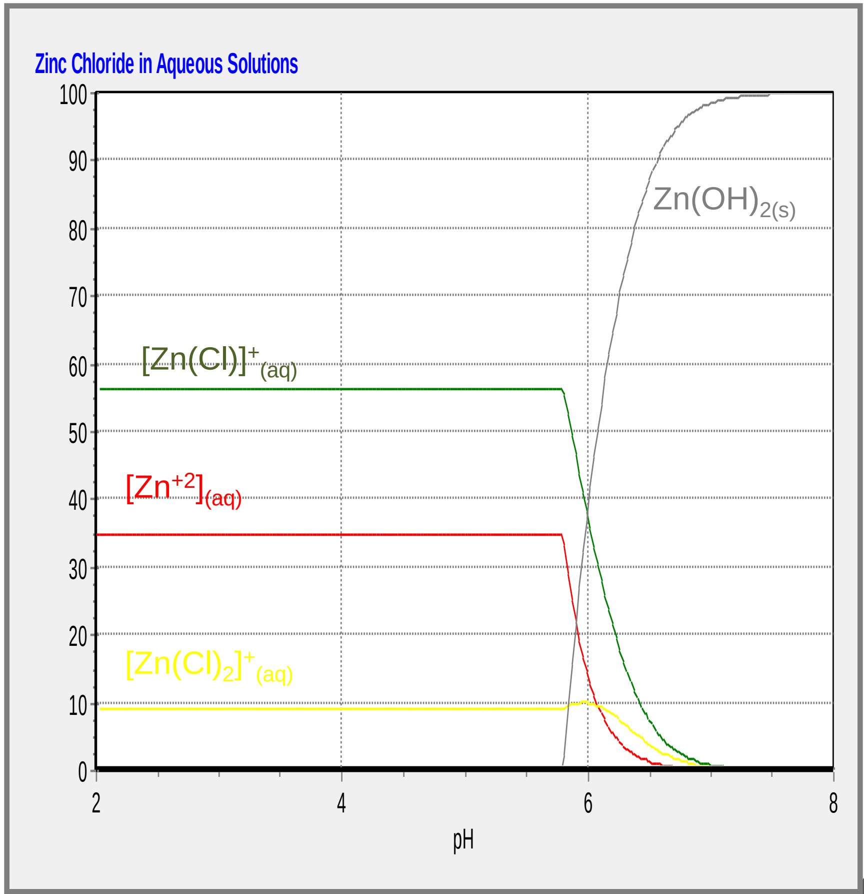
$$Zn(NO_3)_{2(s)} \Leftrightarrow Zn^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}$$

$$Zn(Cl)_{2(s)} \Leftrightarrow Zn^{2+}_{(aq)} + 2Cl^-{}_{(aq)}$$

$[M]^{+n}$	Form	Equil const.	mol	%M
Zn+2	$Zn(NO_3)_2$	Log K -0.12	1	5.5
Zn+2	$Zn(Cl)_2$	Log K 0.8	1	5.5





Phosphate Interactions

pH Dependence of Phosphate binding

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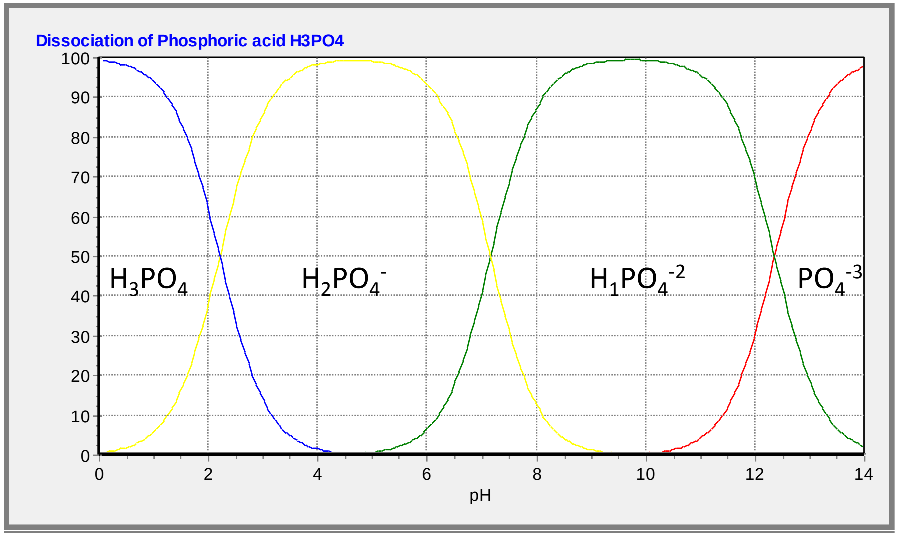
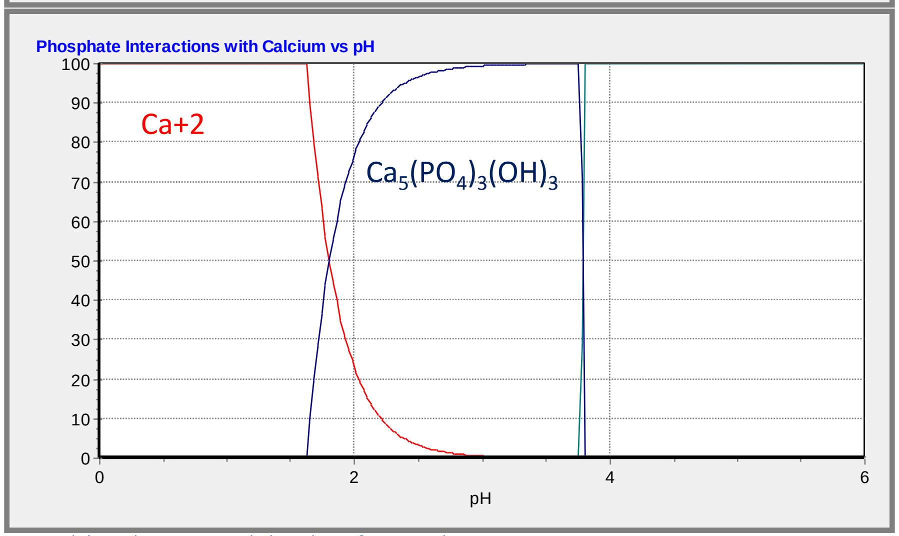




Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations

Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations

Acid	Mol. Form	pKa
H_3PO_4	$H_2PO_4^-$	2.2
	$H_1PO_4^{-2}$	7.2
	PO_4^{-3}	12.3

Can I mix phosphate with CN9 (Calcium Nitrate) and other divalent cations??

YES - If and only if the ph is dropped to 2.2 or below; depending on concentrations long term storage may not be good

How much do I need add to get to pH 2?
~ 0.9% (w/w) solution of 54% Phos acid
~ 1.3% (w/w) solution of PekAcid

$[M]^{+n}$	Form	Ksp
Ca+2	$Ca_3(PO_4)_2$	$1x10^{-26}$
	$Ca_2(PO_4)_2(OH)_2$	$1x10^{-27}$
	$Ca_5(PO_4)_3(OH)_3$	$1x10^{-57}$

Sulfates

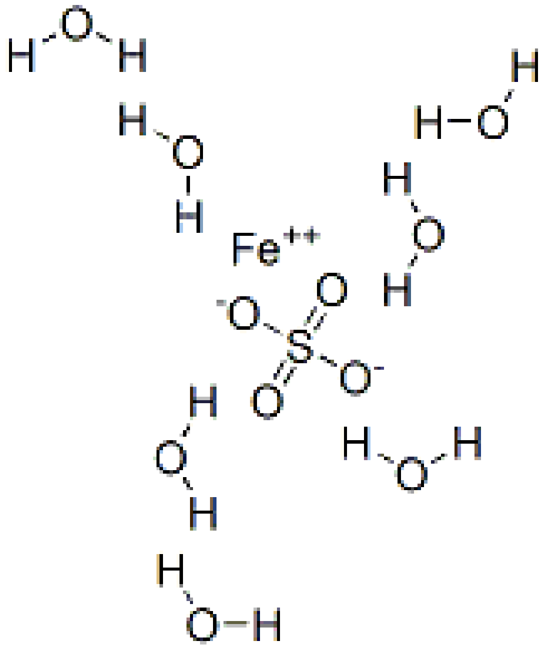
Do they complex????.....

Stability Constants (Log K Values)

Sulfate $(SO_4)^{-2}$

	[ML]/[M][L]
H+	1.98
Fe +2	2.20
Mg +2	2.25
Mn +2	2.30
Zn +2	2.28

There are stability constants for sulfate salts of divalent cations. Does this mean sulfate can complex??



Copper sulfate crystals

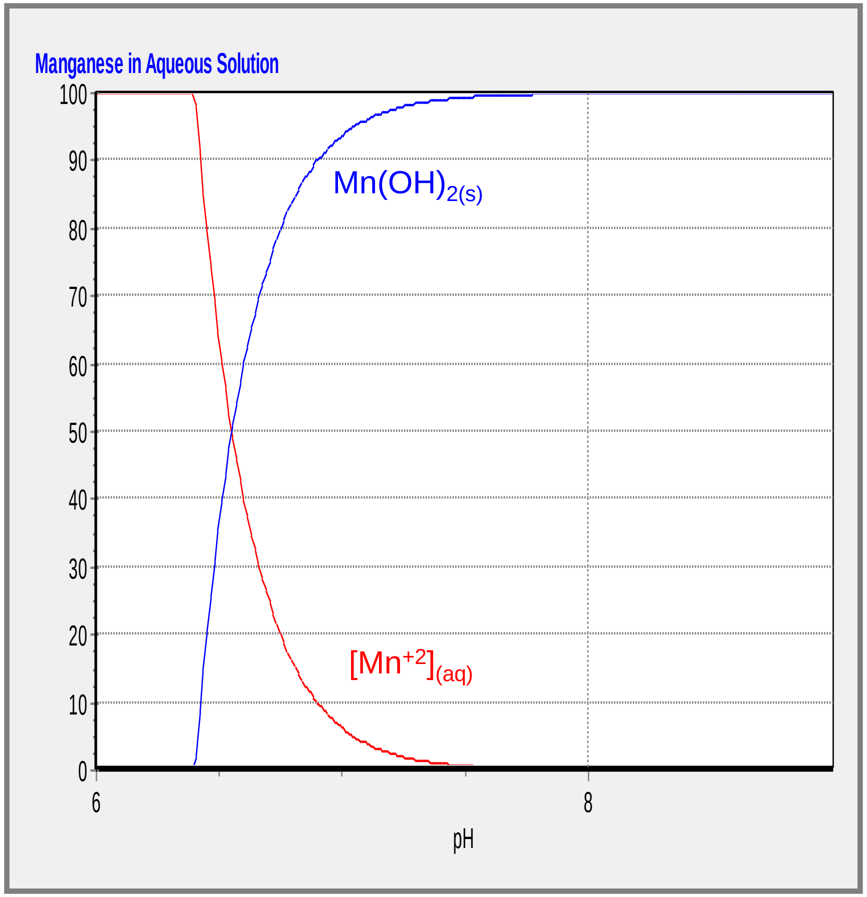
Ferrous sulfate crystals

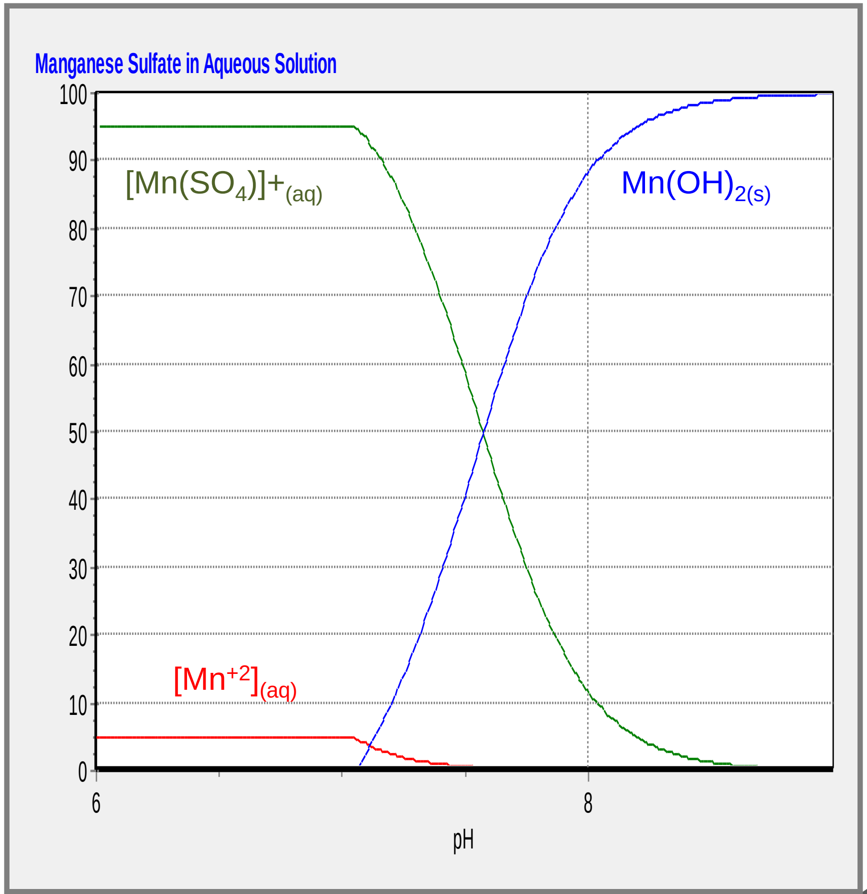
Sulfates

Do they complex????..... To some extent yes…

Sulfate Coordination Suppressed Alkaline Hydrolysis of Mn+2 in aqueous solutions

$[M]^{+n}$	Form	Equil const	mol	%M
Mn+2	$MnSO_4$	Log K 2.2	1	5.5
Mn+2	$Mn(OH)_2$	Ksp $2x10^{-13}$		



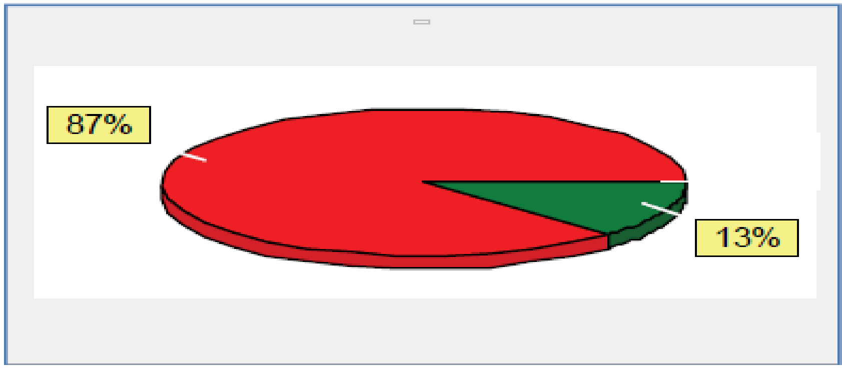


Glyphosate Micro Compatibility

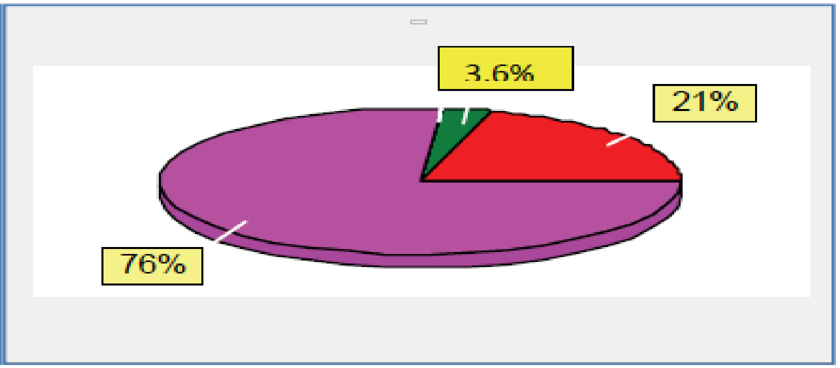
Glyphosate vs Mn^{+2} with and without AMS

pH of Spray Solution = 5.5

No AMS

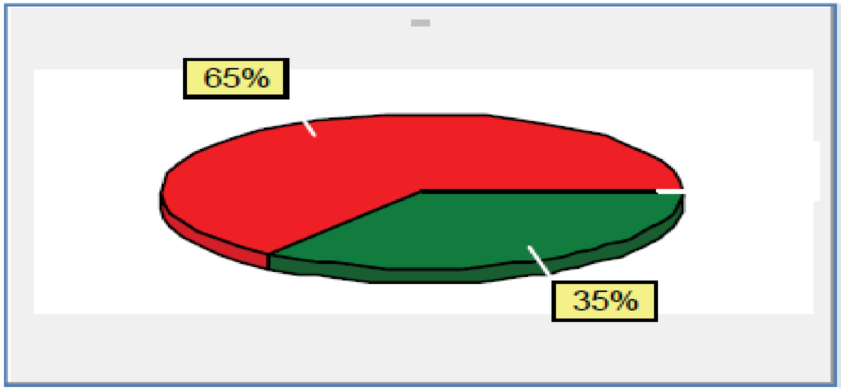


8lbs of AMS per 100 gallons

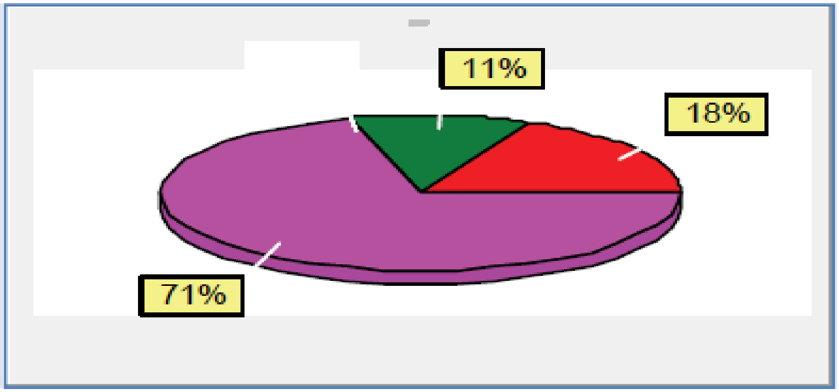


pH of Spray Solution = 6

No AMS



8lbs of AMS per 100 gallons



Thiosulfates

Calcium and Magnesium Solutions

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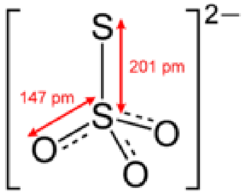
A Liquid Sulfur product with Calcium and Magnesium, this is great.

So why not Thiosulfate formulations of Zinc, Manganese, Copper, etc. ??

Not for sure …. it may be possible if thiosulfate is stable in pH's lower than 6.

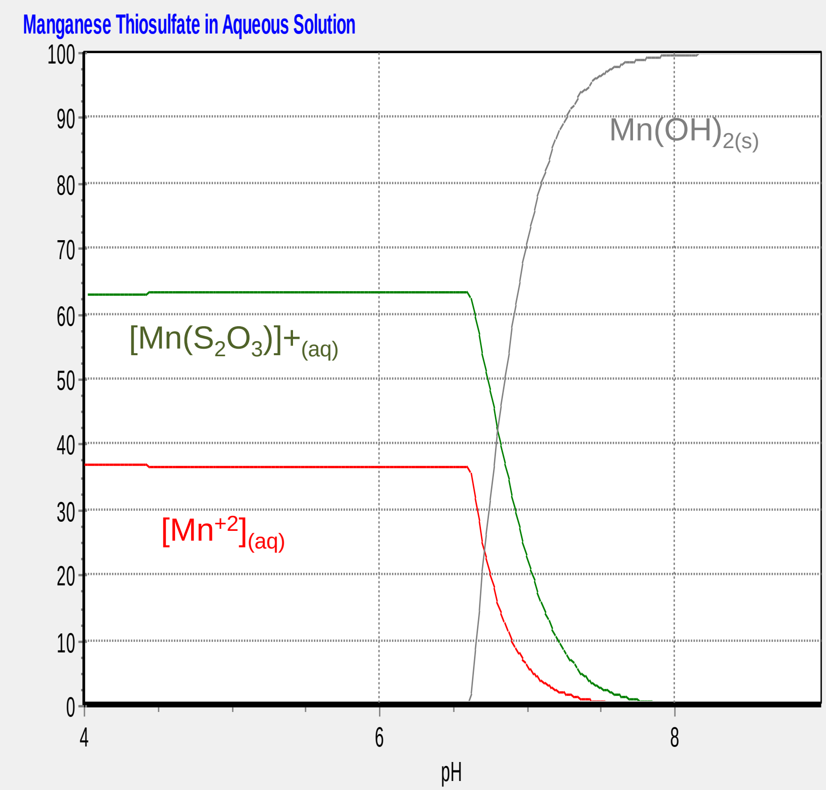


Thiosulfates are stable only in neutral or alkaline solutions, but not in acidic solutions, due to decomposition to sulfite and sulfur.

$S_2O_3^{2-}$ (aq) + 2 H^+ (aq) → SO_2 (g) + S (s) + H_2O

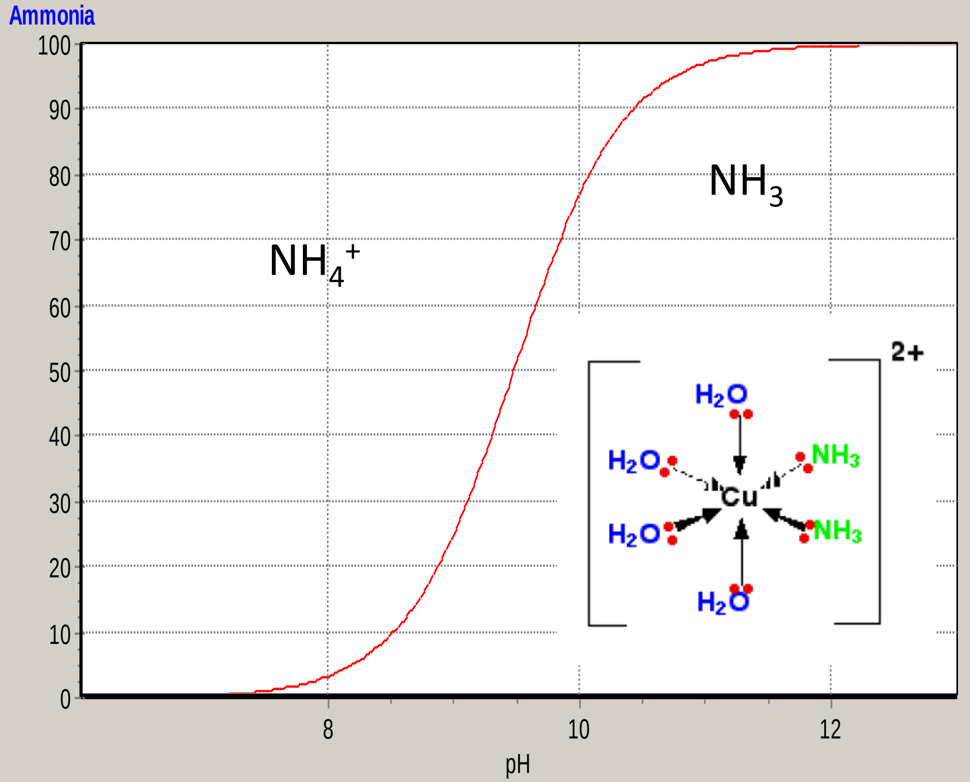
How low can you go with the pH and how long with it stay stable???

$[M]^{+n}$	Form	Equil const.	mol	%M
Mn+2	$MnSO_4$	Log K 0.7	1	5.5
Mn+2	$Mn(OH)_2$	Ksp $2x10^{-13}$		



Ammonium

Ammonium (NH4+) is deprotinated to ammonia (NH3) in alkaline conditions so solutions need to be sufficiently alkaline (pH's >9) to allow ammonia to complex metal.   Common for use in polyphoshate solutions. Ammonium is often used to complex metals in conjunction with other organic acids such as citric acid.



Stepwise Formation Constants

ion	K_n	log K_n
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	4.25
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	3.61
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	2.98
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_4	2.24
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_f	13.08

Equilibrium Reaction	Log K_f
$Cu^{2+} + 4NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$	13.0
$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$	8.6

Citrate

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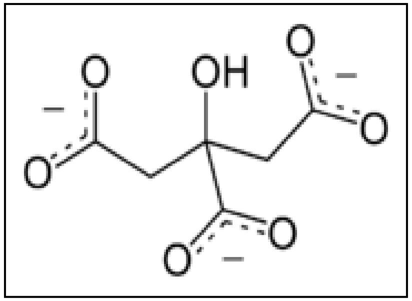
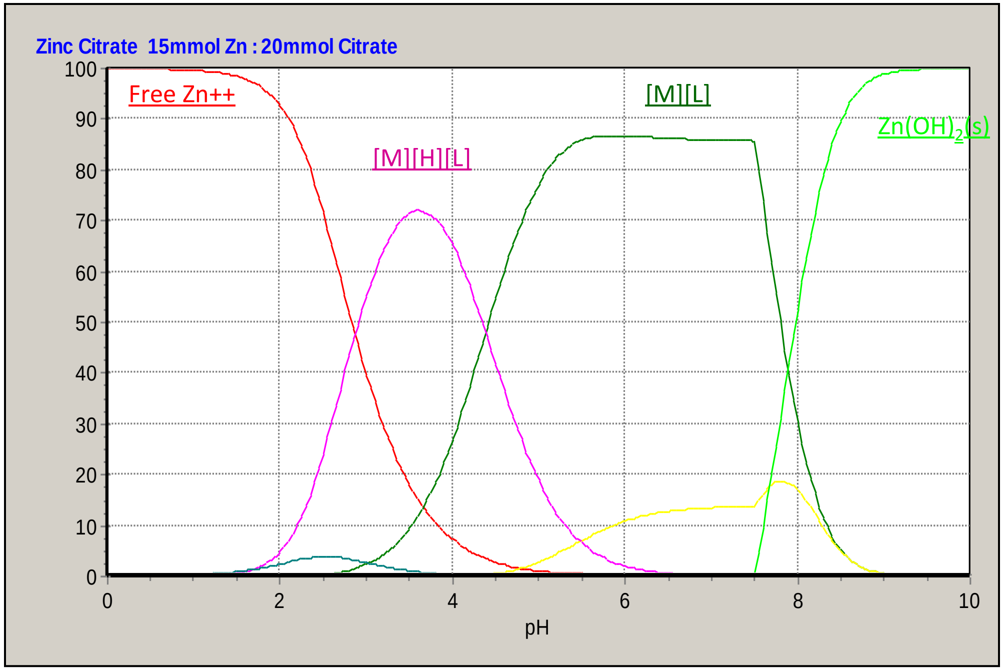
Citric acid is natural biodegradable chelator. Because of its carboxyl groups, citric acid chelates / complexes metals in the acidic environment. Often used for formulation stability and foliar applications



Citrate	pKa	Log Kf
pK_3	6.1	6.1
pK_2	4.6	10.7
pK_1	3.1	13.8



Stability Constants (Log K Values)[1]

CITRATE

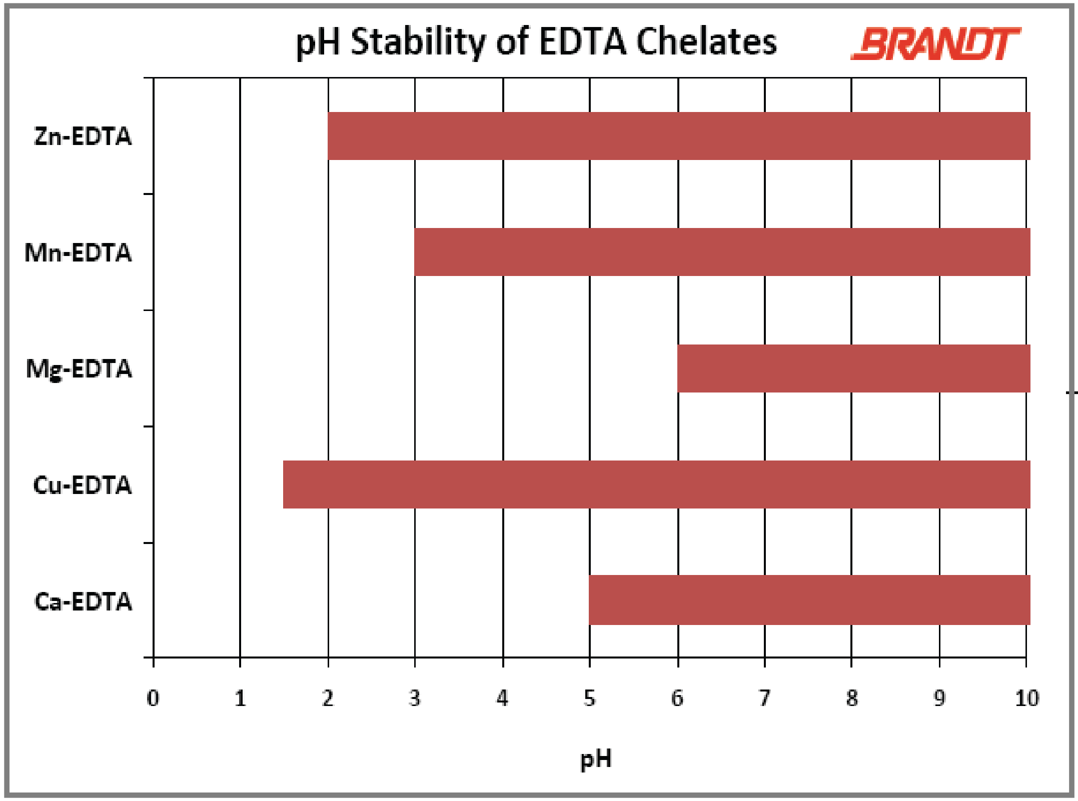
	[MHL]/[M][H][L]	[ML]/[M][L]
Al +3	11.8	8.1
Ca +2	7.6	3.4
Cu +2	9.5	6.7
Fe +2	8.7	4.5
Fe +3	12.4	11.2
Mg +2	7.2	3.2
Mn +2	7.1	3.7
Zn +2	8.7	5.0

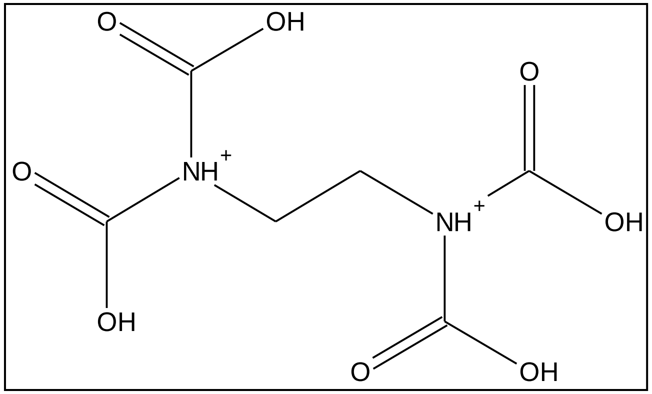
[1] R.M Smith; A.E. Martell, Crtical Stability Constants, Plenum Press, New York and London, 3rd Edition.

EDTA

	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6
	0.0	1.5	2.0	2.66	6.16	10.24
	Log Kf = 24.06	Log Kf = 22.56	Log Kf = 21.06	Log Kf = 19.06	Log Kf = 16.4	Log Kf = 10.24

Ion	[M][H][L]	[M][L]
Al +3	20.7	18.0
Ca +2	15.0	11.6
Cu +2	22.9	19.7
Fe +2	18.2	15.3
Fe +3	28.0	26.5
Mg +2	19.9	9.8
Mn +2	18.2	14.8
Zn +2	10.7	17.5





HEDTA

For Magnesium in acidic conditions

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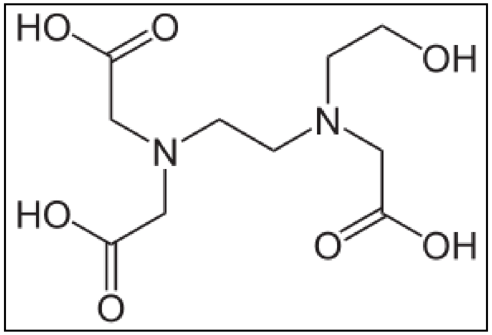
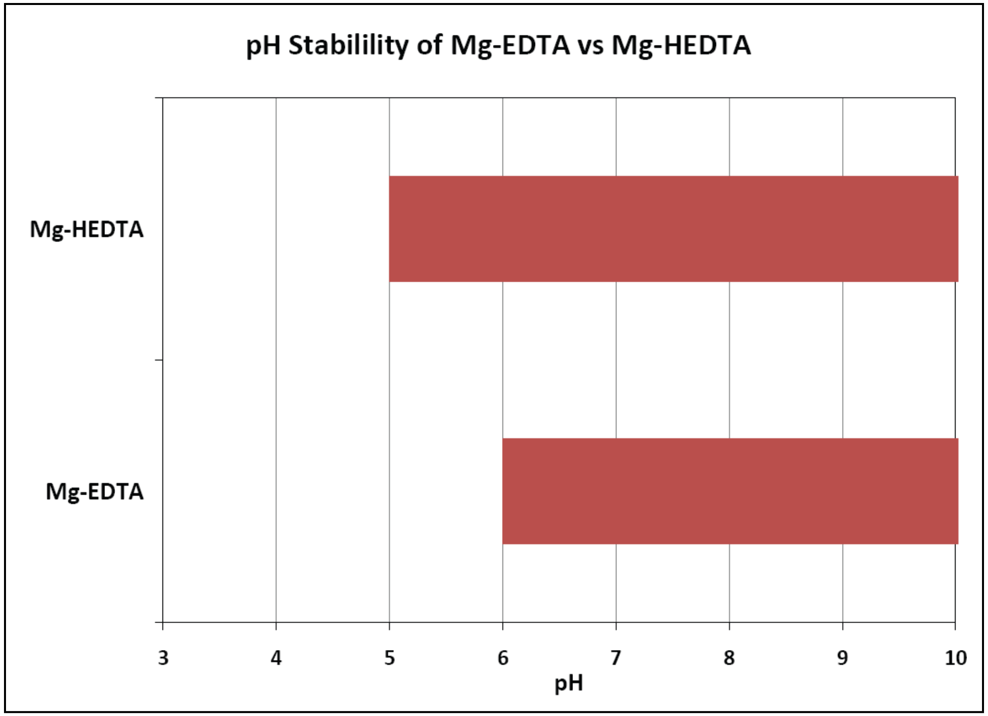
A Chelating agent that may have some advantage over EDTA for Iron in alkaline conditions and Magnesium in between pH 5 - 6



HEDTA	pKa	Log Kf
pK_3	10.3	10.3
pK_2	5.6	15.9
pK_1	2.8	18.7



Stability Constants (Log K Values)[1]

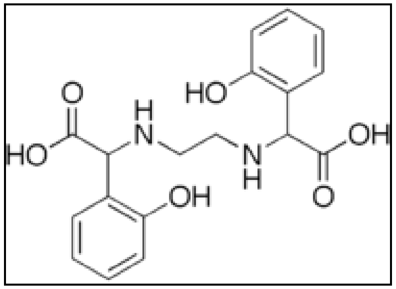
	HEDTA [MHL]/[M][H][L]	[ML]/[M][L]
Al +3	17.7	15.6
Ca +2	--	9.0
Cu +2	20.8	18.3
Fe +2	15.8	13.0
Fe +3	--	19.8
Mg +2	--	7.0
Mn +2		10.9
Zn +2	--	14.7

[1] R.M Smith; A.E. Martell, Crtical Stability Constants, Plenum Press, New York and

EDDHA

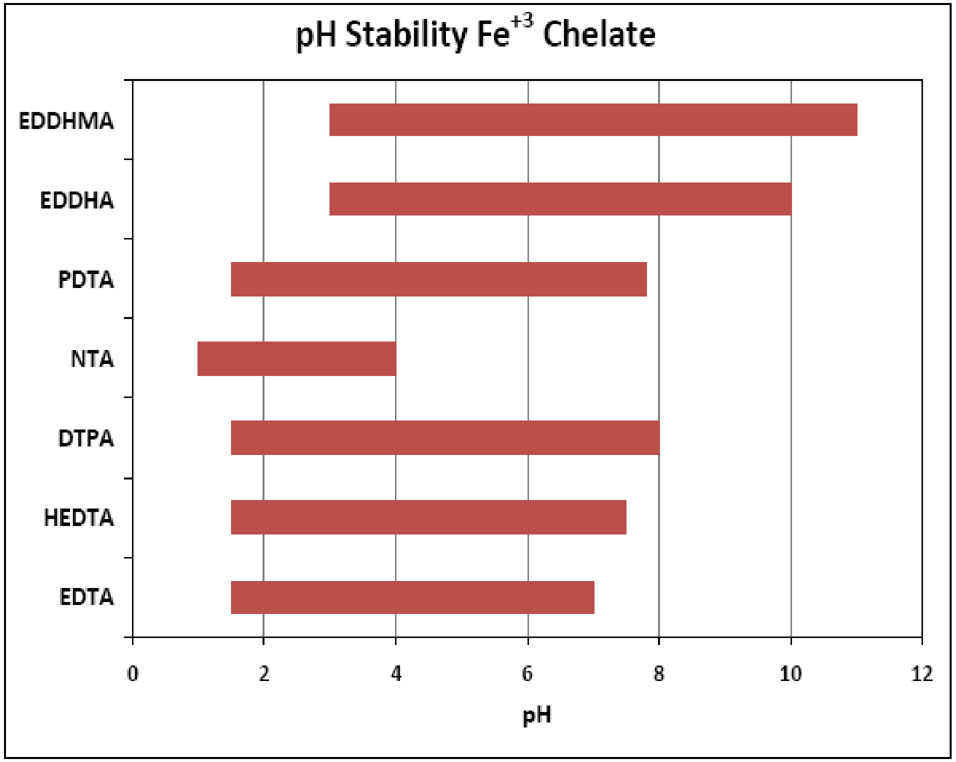
For Iron in alkaline conditions

A high-performance chelating agent used in Agriculture particularly with iron in alkaline soil conditions.



EDDHA

	pKa	Log Kf
pK_4	12.2	12.2
pK_3	10.7	22.9
pK_2	8.9	31.8
pK_1	6.5	38.3



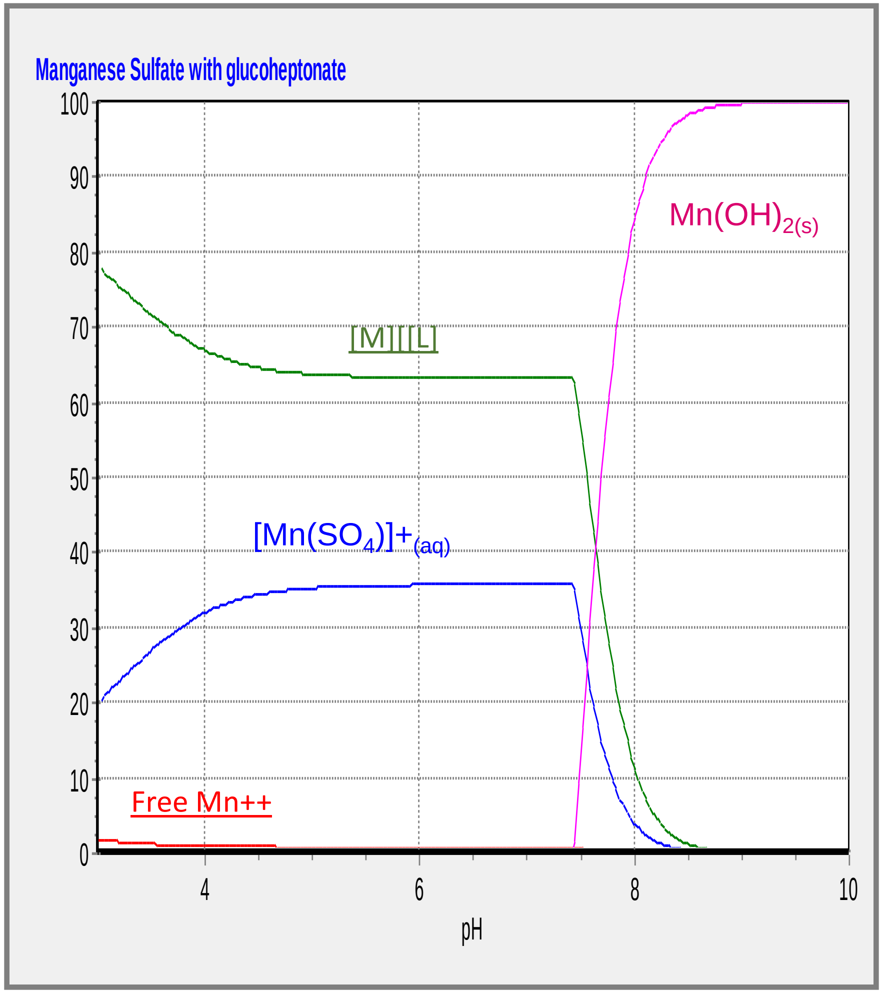
Stability Constants (Log K Values)[1]

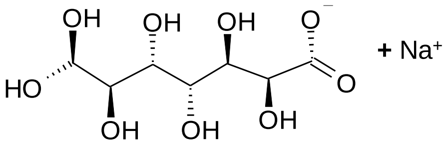
	EDDHA	
	[MHL]/[M][H][L]	[ML]/[M][L]
Al +3	-	-
Ca +2	17.7	8.2
Cu +2	33.2	25.0
Fe +2	-	15.3
Fe +3	-	35.4
Mg +2	18.2	9.0
Mn +2	-	-
Zn +2	25.8	17.8

[1] R.M Smith; A.E. Martell, Critical Stability Constants, Plenum Press, New York and London, 3rd Edition.

Glucoheptonate

Iron and Copper in alkaline conditions





Glucoheptonates and Gluconates are biodegradable complexes/chelates that is useful as an alternative for very high pH solutions, especially for Fe^{+3} and Cu^{+2}

Stability Constants (Log K Values)[1]

[ML]/[M][L]

	Glucoheptonate	Gluconate
Al+3	--	--
Ca+2	1.25	2.2
Cu +2	41.2	38.9
Fe+2	1.1	1
Fe+3	38.3	37.2
Mg+2	0.78	0.7
Mn+2	--	--
Zn +2	1.82	1.7

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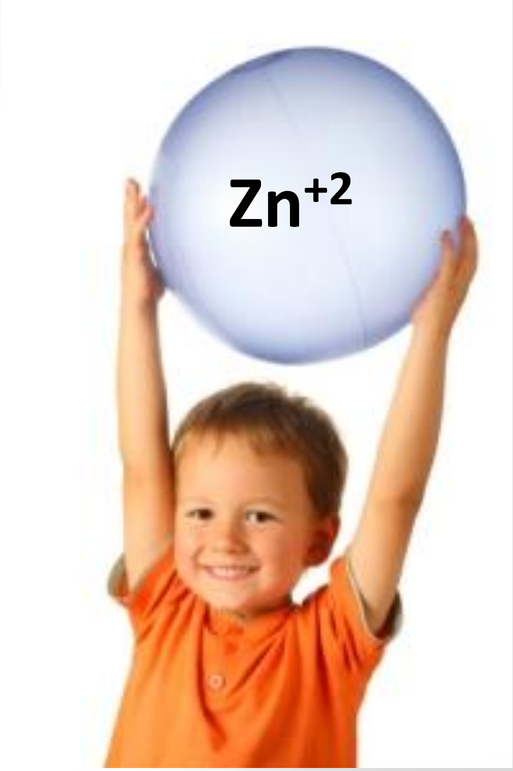
Butch here has a strong complex on the football!!!!



See, chelating is not that complicated. Even I can do it.

QUESTIONS??

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