Waughter

AKTION CONSULTANCY

Volume 1 : Edition 9 – Internal Conditioning : Chemicals & additives in Water Management *Sep 30, 2021*

Dear Water Warriors,

Green Chemistry is a dream. Chemicals may have their risk but are very important to our objectives and thus friend of a process designer to achieve treatment objectives.

Boilers and other heat transfer equipment need protection from the wrath of Pure water; Hungry to eat anything. Knowledge of Langlier Saturation Index thus essential to know it's mood.

This issue of '**Waughter**', we discuss the Chemistry Integration with Mechanical know-how.

Nidhi Jain
Editor Waughter

In this edition we cover up the Chemicals and additive water management which include following points:

Q. Is physical treatment enough to treat Water?

Q. Do you know physical impurity has a charge?

Q. Choice of Coagulant

Q. Oxidation and Cl_2 Chemistry

Q. Boiling Water Treatment: Internal Conditioning?

Q. Cooling Water – Chemistry Integration

LSI and its significance, explained by my colleague Ms Vaishali Singh a fresh engineer from college turning pro from an Intern.

Q. Is physical treatment enough to treat Water?

Water from different sources is drawn to industry for different purposes but is this water safe for industrial use; the answer is NO.

Feed water treatment is focused on protecting downstream equipment from scaling, fouling, corrosion, and other forms of damage or premature wear due to contaminants present in the source water.

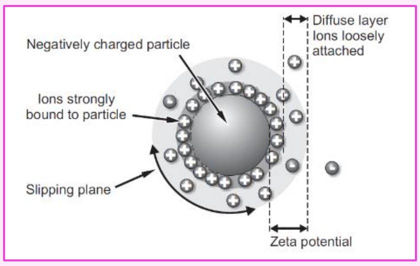
After physical treatment let's move forward to Chemical treatment. The processes include Neutralization, disinfection, chelation, dispersion, crystal growth modification, sequestration etc.

Chemicals are wonderful !! they add value to the CAPABILITY of a water treatment engineer and therefore this competence is a must in the armoury of all water and wastewater professionals.

Q. Do you know physical impurity has a charge?

A physical impurity is made out of Cations and Anions. Imagine at t=0 , $CaHCO_3$, $NaNO_3$ or $CaSO_4$ etc that are part of a "Physical Impurity" start dissolving in water. Once Dissolved Cations (Ca^{++}, Na^{+}, Mg^{++} are free to move and also $SO4^{--}$, $NO3^{-}$,$HCO3^{-}$).

A detailed chemistry look will suggest that the dimensions of Anions are much larger the Cation, effecting their mobility.



The Cation go out of Particle (very close) and block Anions that as a combination make particle Negative.

As a unit they are still electroneutral because Cation are just near the bulk of the particles. Its natural that Anions would then make another layer after cation. This double layer creates a problem in any +Ve charge reaching particle core and thus the similar negative particle repel each other.

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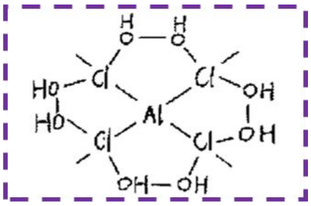
Choice of Coagulants

Many metal salts can be used as coagulants for water and wastewater process objectives of Colloid, Turbidity & TSS removal

Alum

$FeCl_3$

$FeSO_4$



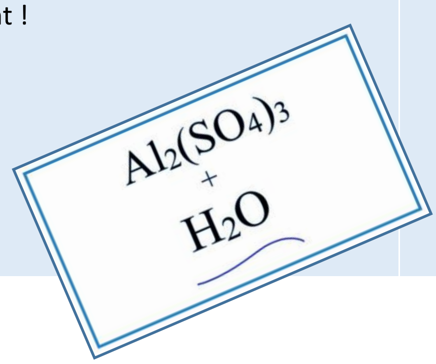
PAC

When Alum is dosed into water we have below reaction.

$Al_2 (SO4)_{3.} 14H_2O + nH_2O$ <--> $2Al (OH)_3 + 8H2O + 3H2SO4^{-2}$

H_2SO_4, must be neutralized or else it will stop reaction moving forward. Alkalinity present in water assumes this role. Thus Lime or NaOH must be added in water if alkalinity is not sufficient.

We wonder where is charge on $Al(OH)_3$. The pre-requisite of Coagulation of negative charge particle is a +ve (opposing) charge. In reality, we make a cloud of precipitate that has $Al(OH)_3$, $Al(OH)^+{}_2$, $Al(OH)^{++}{}_3$ that is a mass of flocs bound with each other and help in coagulation when mixed with -Vely charged Turbidity (Particulate Matter). Right !



Absolutely wrong. Nothing will happen as we need to break the Zeta potential barrier. Physics comes handy now - remember Flash mixers forces them to intermingle and achieve coagulation. Role of Alum, and similar coagulant is over as soon as coagulation (charge neutralization) takes place.

"Van der Waals Force of attraction", will help in agglomeration, a process by which, we need the particles to coalesce together be bigger and settle. But we do not have infinite time and wait for the weak Van der Waals Force of attraction help in water treatment so we look for a Flocculant that can bridge the gap between these particles and bind them together in a web/net so that the resultant floc is bigger and heavier.

All metal salts are excellent coagulants and moderate flocculants. They were in use till we intended a material called Polyelectrolyte. Before that era lignin and tannin played the role of natural flocculants.

Polyelectrolytes:

Polyelectrolytes are polymers with dissociating groups in their repeat units. They can be divided into *polycations* and *polyanions* and *polysalts*. Like ordinary electrolytes (acids, bases and salts), they dissociate in aqueous solutions (water) and bear one or more charges depending on the pH value.

The three most common anionic groups are carboxylate (–COO-), phosphonate (–PO3H-, –PO32-), and sulfonate (–SO3-) and the most common cationic groups are primary, secondary and quaternary ammonium (–NH3+, =NH2+ & ≡N+)

Poly Acrylic Acid (PAA), Poly Methacrylic Acid (PMAA) and Poly Acrylamide PAM are widely used as flocculating agent (Settling) and dewatering applications (Sludge dewatering)

Oxidation and Cl2 Chemistry

Water structures open to sun may have Algal growth due to various nutrients like nitrogen, phosphorus. Bacteria present in water are in search of suitable media for growth and nutrition. The algae bacterium is facilitated by the presence of dead organisms, Sunlight, and high temperature.

Chlorine (Cl_2) is a gas, an excellent oxidizing agent that provides properties desirable in disinfection usage as well as algae control in Clarifiers and Cooling Towers. It also oxidizes Fe and other metal ions and e.g Ferrous to Ferric encouraging them to become $Fe(OH)_3$ precipitate.

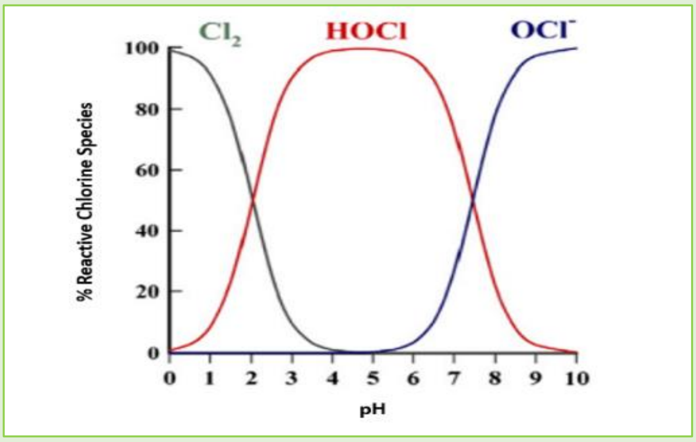
Chlorine is available in one of three forms: sodium hypochlorite, calcium hypochlorite and liquid chlorine.

$Cl_2 + H_2O = HOCl + HCl$

When a Na-hypochlorite is added to water, it also reacts to form hypochlorite ion and hydroxide:

$NaOCl + H_2O = HOCl + NaOH$

To kill bug we need HOCl and not OCL^-, and that is the relevance of below curve.



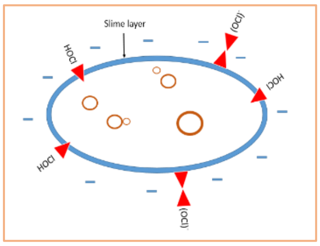
These forms can exist together and the relative concentration of each depends on the pH of the solution and not on whether chlorine gas or bleach was added:

$HOCl \leftrightarrow OCl^- + H^+$

Be aware use of NaOCl produces NaOH and increases pH so be careful and never dose it in high pH environment as we will not achieve disinfection.

HOCl Availability & Importance

OCl- has a negative charge and thus can not penetrate into the bacteria 's body but HOCl enters the cell wall and release Ö and that oxidises the DNA materials and kills bacteria. See figure below:



The pH of the water is important relative to the varying proportions of the hypochlorous acid and hypochlorite ions. In a solution with pH rising over 6.0 the proportion of hypochlorous acid declines from virtually 100% down to almost 0 at pH 9.0.

Therefore, when the goal is disinfection, the pH of water shall be preferably ~ 7.0 for lowest dose of Disinfectant e.g. in cooling towers.

Chlorine demand is the difference between total chlorine added in the water and residual chlorine. It is the amount which reacts with the substances in water, leaving behind an inactive form of chlorine. Chlorine demand can be caused in a water body due to rain containing ammonia or the addition of fertilizers which can be oxidized by chlorine.

The possible reactions between HOCl and ammonia are as:

NH_3	+	HOCl	=	H_2O	+	NH_2Cl	Mono chloramine
NH_3	+	2HOCl	=	$2H_2O$	+	$NHCl_2$	Di chloramine
NH_3	+	3HOCl	=	$3H_2O$	+	NCl_3	Nitrogen Tri chloride

To sum chlorine is consumed for:

1. Oxidation of Metals
2. Form chloramines
3. Do Disinfection

And since the Disinfection is often the goal, we dose chlorine more than the demand to maintain free residual chlorine (FRC) of 0.3 ppm.

Chemicals at a Glance

Several chemicals are used in WTP & ETP applications, and we have tabulated their potential use. The designer must study a little more on each chemical as SAFETY is utmost concern when handling chemicals. Also, each chemical has it's specific compatibility with the metallurgy of equipment associated with WTP, ETP unit operations.

Name	Chemical Formula	Availability	Conentration	Use	Solution Strength
Salt	$NaCl$	Solid	100%	Softener	10-15%
Hydrochloric Acid	HCl	Liquid	33%	DM Plant, pH Control	5%
Caustic	$NaOH$	Lye	48%	DM Plant, pH Control	5%
Sulphuric Acid	H_2SO_4	Liquid	98%	DM Plant, pH Control	30%
Alum	$Al_2(SO_4)_3$	Solid	100%	Coagulation	10%
Ferric Chloride	$FeCl_3$	Solid	100%	Coagulation	10%
Ferrous Sulphate	$FeSO_4$	Solid	100%	Coagulation	10%
Poly Aluminium Chloride	$Al_2(OH)nCl_6$-n]m	Solid	100%	Coagulation	10%
Sodium Hypochlorite	$NaOCl$	Liquid	11%	Disinfection	As Available
Sodium Meta Bisulphite	$Na_2S_2O_5$	Solid	100%	FRC removal, RO	5%
Sodium Hexa Meta Phosphate	$(NaPO_3)_6$	Solid	100%	Scale Control, RO	5%
RO Antiscalant	Brand Specific	Liquid	Brand Specific	Scale Control, RO	As Supplied
Polyelectrolyte	Brand Specific	Liquid/Solid	Brand Specific	Flocculation	0.1-1%
Ammonia (aq)	NH_4OH	Liquid	88%	BWT pH Boost	10%
Tri Sodium Phosphate	Na_3PO_4	Solid	100%	BWT Hardness Scale Control	10%
Hydrazine hydrate	N_2H_4	Liquid	24-35%	BWT Oxygen Scavenger	10%
Citric Acid	$C_6H_8O_7$	Solid	100%	RO Cleaning - Scale	Membrane Guide
Sodium Lauryl Sulfate	$C_{12}H_{25}NaSO_4$	Solid	100%	RO Cleaning - Organics	Membrane Guide
Urea	$CO(NH_2)_2$	Solid	100%	Aeration Tank - ETP/STP	5%
Di Ammonium Phosphate	$(NH_4)_2HPO_4$	Solid	100%	Aeration Tank - ETP/STP	5%

Some Tips:

H_2SO_4 dilution is a RISK as the reaction is exothermic. Always have water first and then add H_2SO_4 slowly. The best thing is to practice this Water First with all chemicals. $FeSO_4$, $FeCl_3$ are highly corrosive: Use only artificial material. No SS 304 or 316. So is HCl, has fumes and avoid as much as possible.

SMBS may cause fainting and nausea, be careful. Citric acid solutions shall be prepared 8-10 h in advance of use.

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Boiler Water Treatment – Internal Conditioning?

In addition to the water treatment and degasification, treatment chemicals, like trisodiumphosphate and sodium sulfite or film formers, are added to the feedwater.

If possible, residual hardness stabilizers and oxygen binding product should be added via two separate dosing pumps. Adapting exact chemical dosing rates for various operating conditions is made possible with this design.

At separate dosing points the alkalinity builder products, like trisodium phosphate, and the oxygen binding chemical, like sodium sulfite, are added to the feedwater tank at the boiler feed pump suction.

Food Grade Steam Generation - Hotel & Food Industry

Usually trisodium phosphate for alkalization and sodium sulphite for oxygen binding are used in this application. As mentioned, small quantities of bound carbonic acid can lead to corrosion in the condensate system. Therefore, the boiler feed water is often pre-treated by reverse osmosis.

The pH for boiler feedwater, as required by the boiler manufacturer, may not be maintained simply by dosing phosphate. It is possible to add caustic soda for alkalization of the boiler water, in addition to, or as an alternative to phosphate and sulfite.

Dosing for Salt Free BWT Operation:

By using the above-described dosing of phosphate and sulfite, the salt concentration in the boiler water is increased.

This, however, is not permitted for high pressure steam boilers. Ammonia does not concentrate in the boiler water. Ammonia can bind free carbonic acid in the steam condensate system as ammonium carbonate, alkaline condensate is achieved.

The quantity of ammonia to be dosed can be determined via the residual iron concentration in the condensate water.

Oxygen Scavenger

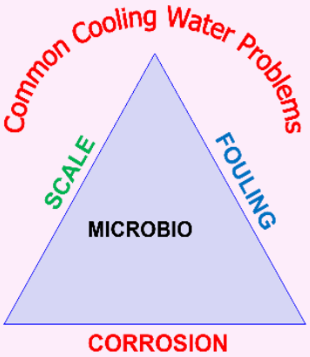
Primarily, dissolved oxygen in the feedwater has to be reduced by physical processes (thermal de-aeration) to 2 ppb level. If, in practical operation, this is not possible because of frequent shutdowns, an oxygen binding chemical is to be added.

Na_2SO_3 is a non-steam volatile oxygen binding media. It does not enter the steam condensate circuit. N_2H_4 is a steam volatile oxygen binding media that has an alkalizing effect. Hydrazine enters the steam circuit and the condensate. Unfortunately, though, hydrazine is carcinogenic.

During handling and dosing, the corresponding health and safety regulations must be maintained.

Cooling Water – Chemistry Integration

The efficiency of a cooling system depends on efficient heat transfer that can be inhibited by deposits on heat transfer surface. Further, in low velocity area the deposits may lead to accelerate under deposit and pitting corrosion.

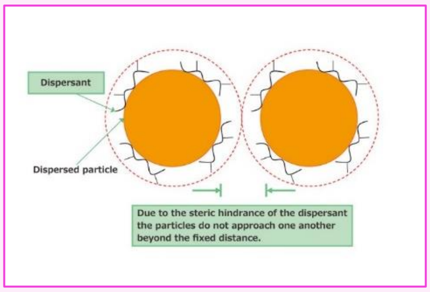


Thus we need to have a cooling water treatment program that shall address:

- Corrosion Control
- Scaling Control
- Fouling
- Microbial Issues – Algare growth etc.

Dispersants

Organic dispersants, include organophosphorus compounds and polyelectrolytes. If the applied dispersant is a charged molecule, such as a polyelectrolyte, it will disperse suspended solids by adsorbing to their surfaces, thus adding an electrostatic charge to each particle, causing mutual repulsion.



In other words, dispersants act oppositely from coagulants, augmenting the charge of suspended solids rather than neutralizing them.

$CaCO_3$ crystal distortion caused by various organic treatment reagent.

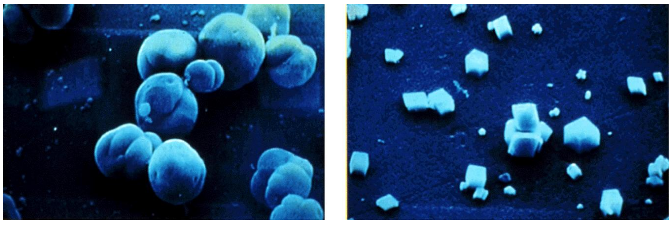
Microbiology

Variety of biocides are simple chlorination or bromination may be applied to control algae growth and prevention of biofilm.

The combination of dispersant with micro-biocides allows derbies (dead bio films) to be in suspension that can be removed via side stream filters.

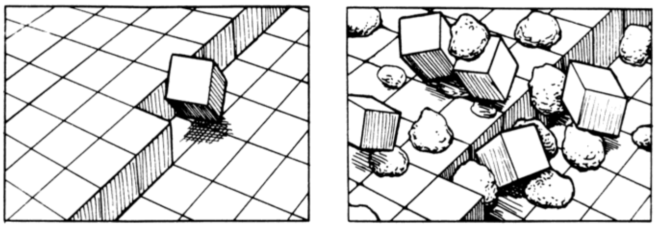
Threshold inhibitors

These are sequestering agents such as polyphosphates, Organo phosphorous compounds, and polymers (polyacrylates).



These exert a "threshold effect "reducing the potential for precipitation of calcium compounds, iron, and manganese.

Crystal Modifiers



Another group of control agents includes those chemicals used to modify the crystal structure of scale. Simply putting it means even if scale is formed, chemicals can penetrate it and clean it during CIP. Such products are more popular in non-heat transfer applications such as Reverse Osmosis.

Corrosion Control

Chemistry can be applied to protect either Anodic Side by use of Chromates, Nitrites, Orthophosphates, Silicates or Molybdates. The mechanism means inhibiting anodic site in a corrosion cell.

Care must be taken as Severe localized pitting attack can occur at an unprotected anodic site if insufficient inhibitor is present Bicarbonates, Polyphosphates, Polysilicates, Zinc based products on the other hand offer Cathodic protection by blocking the electrochemical reaction at the cathode.

The subject demands a complete Issue of Waughter on CW Chemistry in subsequent years.

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Langelier Saturation Index (LSI)

Ms Vaishali Singh came on board as summer intern during COVID-19, and subsequently decided to frow her career with us as water engineer. She has compiled this information on LSI.

LSI measures ability of solution to dissolve or deposit calcium carbonate, and helpful in indicating corrosivity of water. LSI Index is affected by presence of:

- Alkalinity (mg/l as CaCO3),
- Calcium hardness (mg/l Ca^{++} as CaCO3),
- The total dissolved solids (mg/l TDS),
- The actual pH,
- The temperature of the water (°C).

Parameters		Derived	
Temp(°C)	TDS	"A"	"B"
0	20	2.6	0.05
2	40	2.55	0.08
4	80	2.5	0.1
6	120	2.44	0.13
8	160	2.39	0.15
10	200	2.34	0.17
12	240	2.29	0.18
14	280	2.24	0.19
16	320	2.19	0.2
18	380	2.15	0.21
20	400	2.1	0.22
22	440	2.05	0.23
24	480	2	0.24
26	520	1.95	0.25
30	560	1.88	0.26
40	600	1.7	0.27

pa(Ca++) = Log(100000/Calcium Hardness)
p(Alk) = Log(50000/Total alkalinity)
A = 2.6045*EXP((-0.0108*Temperature))
B = 0.0144*TDS^0.4545
C = Log(1+((10^-(10.6-pH))*(1+Temp/30))*2)

Significance

To decide quality of water treatment chemicals

LSI predict about the nature of water as scaling or corrosion

Langelier Index = (pH-pHs), where,

pH = Actual pH of water
pHs = SUM (p(Ca++) : C)

LSI	Indication
Positive LSI	Scale Forming Water
Negative LSI	No Potential To Scale,
LSI Close to Zero	Non Scaling

जल जीवन जननी !!

Our world is Waughter

The technical knowledge share attempt of Aktion Consultancy and the contents in the magazine shall be qualified by Sanjeev Srivastava our Technology Lead.

Our next edition focuses on: Pocket Book for Service Technicians for day-to-day calculations

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