Volume 2: Edition 3 – Precipitation Control for Feed water to RO & ZLD to Avoid Scaling *Mar 31, 2022*

Dear Water Warriors,

With majority of projects now shifting to Zero Liquid Discharge from mere Wastewater Treatment, Science of Precipitation comes back in existence.

Ca Mg & SiO_2 now need to be removed either during Reverse Osmosis or before Thermal Evaporation to control scaling and reduce CIP of MEE/MVR.

SSr our CTO accepted this invitation to simply the subject to educate beginners as subject appears quite complicated in handbooks and internet.

CIPs through a new challenge in managing salts as well as NO_3 as mostly HNO_3 is used for CIPs.

This issue of 'Waughter', let's focus on Precipitation.

Nidhi Jain – Civil Engineer

The Softening Tool in XLS

While we cover the theory of softening as well as explain the reactions in simple forms, for day-to-day operations you may need a quick calculator.

Please download the file

Waughter V2 E3_Lime & Soda Ash Estimates.xls

From www.aktionconsultancy.com

And you can estimate

Lime Dose
Soda Ash Dose
Sludge Concentration

In further versions we will also cover the XLS for estimation of $Mg(OH)_2$ for SiO_2 precipitation.

The XLS also includes though the $Mg(OH)_2$ & SiO_2 ratio required to be maintained for a feed water SiO_2 to achieve 15 ppm Final SiO_2 in treated water. Wait for the XLS tool in subsequent editions of Waughter.

What if not Removed ?

Ca in presence of alkalinity with precipitate as $CaCO_3$ and deposit on membranes. If high SO_4 is available $CaSO_4$ precipitation on membranes is also a concern.

Mg usually do not create a problem in RO as the pH control allows for Alkalinity to be free of OH.

SiO_2 above 300 ppm in RO reject can cause serious scaling on membranes and even Antiscalant are not able to solve the issue.

Even if RO is managed, the invers solubility associated with Ca Mg and SiO_2 means that their concentrations shall be reduced before feeding to MEE to avoid frequent CIPs.

SiO_2 removal needs co-precipitation with $Mg(OH)_2$, which can be precipitated only if all Ca is precipitated First.

Project Background – Case Study

Our customer here is well known group in Ahmedabad and some of the data are changed here to suit confidentiality and make the learning complete.

Sr No	Parameter	Unit	Value
1	pH		7
2	Turbidity	NTU	10
3	Total Suspended Solids	ppm as such	10
4	Total hardness	ppm as $CaCO_3$	225
5	Calcium	ppm as $CaCO_3$	150
6	Magnesium	ppm as $CaCO_3$	75
7	Chlorides + F	ppm as $CaCO_3$	1058
8	M.Alkalinity	ppm as $CaCO_3$	140
9	P.Alkalinity	ppm as $CaCO_3$	0
10	Sulphates	ppm as $CaCO_3$	1
11	Nitrates	ppm as $CaCO_3$	1
12	Silica	ppm as SiO_2	15
13	Sodium (By difference)	ppm as $CaCO_3$	975.0

Additionally, Ammonia is present from treated WWTP and calculated as NH_4Cl of 5 ppm as $CaCO_3$

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The Lime $Ca(OH)_2$ and Soda Na_2CO_3 Precipitation

CO_2 present is water consumes lime so to estimate lime dose, Equation is always used.

The Ca and Mg Present in water Consume Lime to convert to $CaCO_3$ and $Mg(OH)_2$ as precipitates as long as Ca & Mg are bonded with HCO_3. This form of Ca & Mg are also referred as Temporary Hardness. So, conclusion is for temporary hardness removal we only need lime. Apply Equation 2 & 3 below.

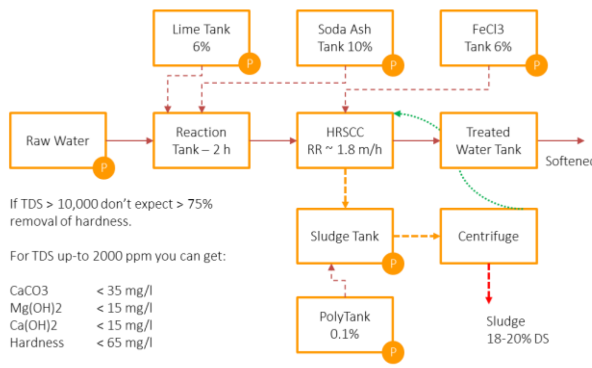
Sequential Understanding of Precipitation Chemistry									
Neutralization of CO2 gas and Precipitation as $CaCO_3$									
Equation 1	CO_2	+	$Ca(OH)_2$	=	$CaCO_3$	+	H_2O	+	
gm as Such	44		74		100				
gm as $CaCO_3$	100		100		100				
My Case	31.74		31.743		31.74	S			
Precipitation of Ca bonded with Alkalinity (Temporary Hardness) as $CaCO_3$									
Equation 2	$Ca(HCO_3)_2$	+	$Ca(OH)_2$	=	$2CaCO_3$	+	$2H_2O$	+	
gm as Such	162		74		200				
gm as $CaCO_3$	100		100		200				
My Case	140		140.00		280.00	S			
Precipitation of Mg bonded with Alkalinity (Temporary Hardness) as Mg(OH2) and Ca of Lime as $CaCO_3$. This Equation will only be valid if Ca is < Alkalinity.									
Equation 3	$Mg(HCO_3)_2$	+	$2Ca(OH)_2$	=	$2CaCO_3$	+	Mg(OH)2	+	H_2O
gm as Such	146.3		148		200		58.3		
gm as $CaCO_3$	100		200		200		100		
My Case	0		0.00		0.0	S	0.0	S	
Precipitation of Ca bonded with Chloride (Permanent Hardness) as $CaCO_3$ (Use Similar Equation if Ca Bonded with SO_4 or NO_3)									
Equation 4	$CaCl_2$	+	Na_2CO_3	=	$CaCO_3$	+	2NaCl	+	
gm as Such	111		106		100		117		
gm as $CaCO_3$	100		100		100		100		
My Case	89.0		89.00		89.0	S	89.0		
Precipitation of Mg bonded with Chloride (Permanent Hardness) as $CaCO_3$ (Use Similar Equation if Mg Bonded with SO_4 or NO_3), $CaCl_2$ produced would need Eq 4 to be repeated.									
Equation 5	$MgCl_2$	+	$Ca(OH)_2$	=	$Mg(OH)_2$	+	$CaCl_2$	+	
gm as Such	95.3		74		58.3		111		
gm as $CaCO_3$	100		100		100		100		
My Case	75		75.00		75.00	S	75.0		
Precipitation of excess Alkalinity (Bicarbonates bonded with Na) (in this case all hardness would be temporary only, Permannet Hardness will be Zero)									
Equation 6	$NaHCO_3$	+	$Ca(OH)_2$	=	$CaCO_3$	+	NaOH	+	H_2O
gm as Such	84		74		100		40		
gm as $CaCO_3$	50		100		100		100		
My Case	0		0.00		0.00	S	0.0		
Presence of Ammoniam Ion will Consume more lime and produce $CaCl_2$ that would need Equation 4 to be repeated.									
Equation 7	$2NH_4Cl$	+	$Ca (OH)_2$	=	$2NH_3$	+	$CaCl_2$	+	$2H_2O$
gm as Such	107		74		34		111		
gm as $CaCO_3$	100		100		200		100		
My Case	5		5.00		10.00		5.0		
Lime needed as $Ca(OH)_2$		mg/l	186.29			S	Sludge Estimation		
Soda Ash needed as Na_2CO_3		mg/l	89.00						
Sludge Formed Auuming 100% Reaction		mg/l	444.47						

If permanent Hardness is present Soda Ash Na_2CO_3 comes in process, and one need to apply equation 4 & 5 as well.

Equation 6 is rarely used and is of academic significance. Equation 7 is used to correct dose of lime if Ammonia is present, mainly in recycle water from a ETP where nitrification is poor.

The Role of HRSCC Clarifier or Settler

While chemistry is the DNA of process optimization, the role of Reaction Tank, pH and Addition Point of Na_2CO_3 and $Ca(OH)_2$ is important as well. The design of Reaction Tank can not generalized as optimum pH of $CaCO_3$ precipitation is 8.3 and that for $Mg(OH)_2$ is 10.4.



Dumping Lime or Soda does not help either, the right concentration of Lime Slurry to be dosed is ~ 6% and that of Soda Ash ~ 10%.

$FeCl_3$ is not required for the case most often, but system shall be engineered to dose ~ 10 mg/l $FeCl_3$ of 6% concentration.

Polyelectrolyte used shall be not only flocculating but dewatering in nature. It's often a better practice to use Flocculant on settled sludge or in Core of HRSCC post Reaction Tank as dosing flocculant in Reaction Tank disturbs natural Coagulation of $CaCO_3$ and $Mg(OH)_2$ flocs as they have opposing charges during nucleation.

For SiO_2 Precipitation Mg Precipitated to SiO_2 ratio can be from 2.5 to 1.35 from feed SiO_2 varying from 20 – 120 mg/l. The treated water SiO_2 is possible upto ~ 15 mg/l in lab experiments but in real plant the guarantee shall not be < 25 mg/l.

HRSCC if used shall be designed for an upwards rise rate of 1.8 $m^3/h.m^2$. In case plant flow rate is small say < 7 m^3/h use simple clarifier or just a settling tank with slopping bottom, never a plate clarifier or Tube settler.

During shutdown it's a good idea to do CIP of HRSCC using Citric Acid to clean shaft and bottom sludge scraper. Use HCl or H_2SO_4 to reduce pH < 7.5 for subsequent feed in RO or MEE.

If you wish to use NaOH Instead of $Ca(OH)_2$

During Lime softening Ca available in lime need to be precipitated as $CaCO_3$. This means excess sludge!!

NaOH Can be handy in some situations to manage the sludge volumes.

Sequential Understanding of Precipitation Chemistry									
Neutralization of CO_2 gas and Precipitation as $CaCO_3$									
Equation 1	CO_2	+	2 NaOH	=	Na_2CO_3	+	H_2O	+	
gm as Such	44		80		106				
gm as $CaCO_3$	100		100		100				
My Case	31.74		31.743		31.74				
Precipitation of Ca bonded with Alkalinity (Temporary Hardness) as $CaCO_3$									
Equation 2	$Ca(HCO_3)_2$	+	NaOH	=	$CaCO_3$	+	$NaHCO_3$	+	H20
gm as Such	162		40		100		84		
gm as $CaCO_3$	100		50		100		100		
My Case	140		70.00		140.00	S	140		
Precipitation of Mg bonded with Alkalinity (Temporary Hardness) as Mg(OH2) and Ca of Lime as $CaCO_3$. This Equation will only be valid if Ca is < Alkalinity.									
Equation 3	$Mg(HCO_3)_2$	+	4 NaOH	=	$Mg(OH)_2$	+	$2Na_2CO_3$	+	$2H_2O$
gm as Such	146.3		160		58.3		212		
gm as $CaCO_3$	100		200		100		200		
My Case	0		0.00		0.0	S	0.0		
Precipitation of Ca bonded with Chloride (Permanent Hardness) as $CaCO_3$ (Use Similar Equation if Ca Bonded with SO_4 or NO_3)									
Equation 4	$CaCl_2$	+	Na_2CO_3	=	$CaCO_3$	+	2NaCl	+	
gm as Such	111		106		100		117		
gm as $CaCO_3$	100		100		100		100		
My Case	9.0		9.00		9.0	S	9.0		
Precipitation of Mg bonded with Chloride (Permanent Hardness) as $CaCO_3$ (Use Similar Equation if Mg Bonded with SO_4 or NO_3), $CaCl_2$ produced would need Eq 4 to be repeated.									
Equation 5	$MgCl_2$	+	2 NaOH	=	$Mg(OH)_2$	+	2 NaCl	+	
gm as Such	95.3		80		58.3		117		
gm as $CaCO_3$	100		100		100		100		
My Case	75		75.00		75.00	S	75.0		
Precipitation of excess Alkalinity (Bicarbonates bonded with Na) (in this case all hardness would be temporary only, Permannet Hardness will be Zero)									
Equation 6	$NaHCO_3$	+	NaOH	=	Na_2CO_3	+	H2O		
gm as Such	84		40		106				
gm as $CaCO_3$	50		50		100				
My Case	140.00		140.00		280.00				
Presence of Ammoniam Ion will Consume more lime and produce $CaCl_2$ that would need Equation 4 to be repeated.									
Equation 7	NH_4Cl	+	NaOH	=	NH_3	+	NaCl	+	$2H_2O$
gm as Such	53.5		40		17		58.5		
gm as $CaCO_3$	50		50		50		50		
My Case	5		5.00		5.00		5.0		
Alkali needed as NaOH	mg/l	257.39				S	Sludge Estimation		
Soda Ash needed as Na_2CO_3	mg/l	-302.74							
Sludge Formed Auuming 100% Reaction	mg/l	192.73							

In NaOH use however be aware that $Mg(OH)_2$ precipitation would mean that all $NaHCO_3$ produced should first be converted to Na_2CO_3 and then only free OH ion would be available for $Mg(OH)_2$ precipitation.

The negative value of Soda ash above indicate here that use of NaOH would not be beneficial as enough $CaCl_2$ is not available to consume the produced Na_2CO_3.

Quick Calculations –

If Only Lime is used:

Approximate if you do not wish to go in detailed calculations:

$Ca(OH)_2$ Dose in ppm = 0.8 to 1 ppm / ppm of removed Alkalinity or Carbonate Ca Hardness as $CaCO_3$

Quantity of Carbonates sludge formed in Carbonate Ca Hardness removal with lime:

$CaCO_3$ sludge (g/m^3) = 2 to 2.1 ppm / ppm of removed Alkalinity or carbonate Ca Hardness as $CaCO_3$

Using soda:

Use of caustic soda increases the quantity of sodium in the treated water. The quantity of sodium added is :

Na in ppm = NaOH in ppm x 23 / 40 (i.e. 57,5 % of the load)

Alkalinity removal

NaOH in ppm = 0.8 to 1 ppm / ppm of removed Alkalinity as $CaCO_3$

Quantity of carbonates sludge formed in Alkalinity removal with caustic soda is:

CaCO3 sludge (g/m^3) = 2 to 2.1 ppm / ppm of removed Alkalinity as $CaCO_3$

Carbonate Ca Hardness removal using NaOH

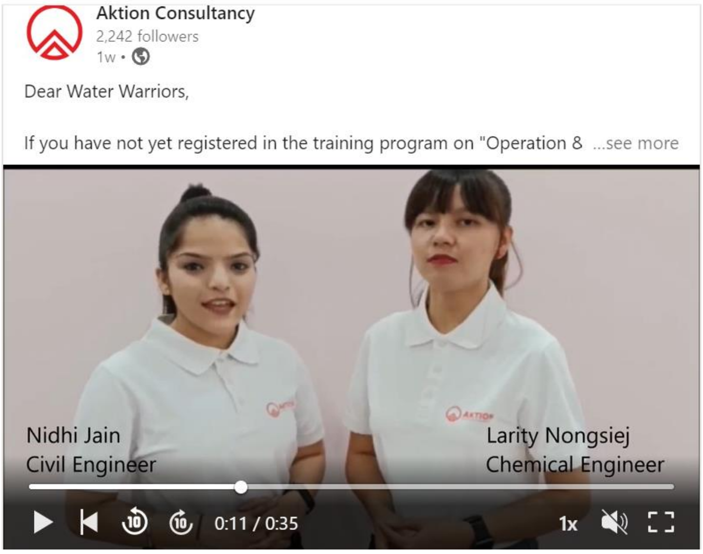
NaOH g/m^3 = 0.45 to 0.6 ppm / ppm of removed Alkalinity as $CaCO_3$

Quantity of carbonates sludge formed in carbonate Ca Hardness removal with caustic soda is:

$CaCO_3$ sludge (g/m^3) = 0.9 to 1.1 ppm / ppm of removed Ca Hardness as $CaCO_3$

World Waughter Day – 2022

What could be a better way then Training to celebrate world water day – 2022?

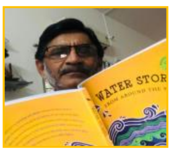


Our Sanjeev Srivastava, Nidhi Jain and Larity Nongsiej covered the subject of "Operation & Maintenance strategy for RO and WWTP". With 152 Registrations, 72 Participants and 38 participants answering the quiz, the program was a great success with announcement of prize for:

1. Panneer Selvam
2. Rohan Rachani
3. Anjali Kandala, Ms
4. Al Shaikh

With equal marks.



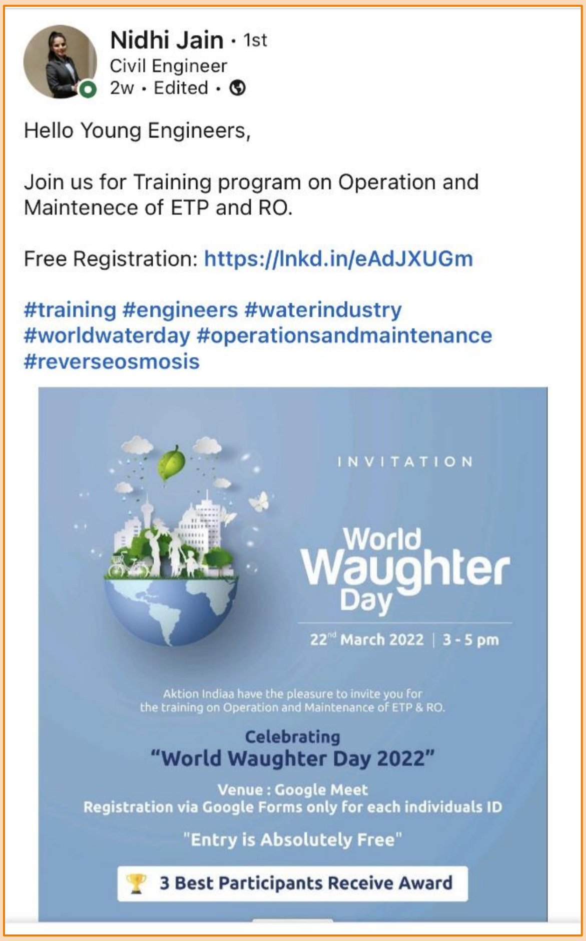



The Five levers of a successful O&M Covered in detail are repeated below:

- Flow Management
- Equipment Health
- Performance of Individual Unit Operation
- Data Logging and Sampling Protocols
- Data Analysis, Trends and Control

Aktion is committed to share "Knowledge".

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: "Softening & De alkalization for Ca, Mg Removal and Metal Removal"

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