Waughter

AKTION CONSULTANCY

Volume 2 : Edition 5 – Softening & De alkalization for Ca, Mg Removal and Metal Removal *May 31, 2022*

Dear Water Warriors,

With zero liquid discharge being increasingly mandatory, the salts must be separated from Water. Bi-valents and SiO_2 therefore need to be precipitated before Final evaporation. But can we separate them in first place itself?

Ca & Mg if removed from water will solve all scaling woos and a view thus is to deal with them as early as we can.

The issue of '**Waughter**', let's understand Ca & Mg removal with or without Alkalinity Removal.

Nidhi Jain – Civil Engineer

Why Ca Mg with HCO_3 (Alkalinity) is a problem?

Ca & Mg in water tend to precipitate at elevated temperatures and concentrations as:

$CaCO_3$ & $Mg(OH)_2$ respectively.

If SO_4 content is high they can also precipitate as $CaSO_4$ in RO reject. Remember during RO process salt concentrate.

The scaling caused by $CaCO_3$ in water circuit leads to:

1. Loss of Heat Transfer and thus poor Heat Exchange
2. Under Deposit Corrosion
3. Reduction in Pipe Diameter and reduction in flow

Water Engineers can remove this hardness by precipitation method as discussed in previous editions. This time we address IX Process (Ion Exchange) to remove the hardness.

Ion Exchange Resin – Refresh it again.

The Ion Exchange Resins are solid globules in size like "Mustered", with typical size of 0.3-1.2 mm.

IX Resins are produced by "Copolymerization" of Styrene with DVB. This forms the "Matrix" (core) of the resin. The sulphonation of this Matrix results in Strong Acid Cation Exchange Resin.

$R\text{-}SO_3H$

Here $-SO_3H$, is know as functional group and H is the mobile ion willing to exchange other Cations.

For softening application, the resin is converted to Na form and appears as R-SO3Na, where Na is replaced with Ca & Mg and Na is released into water. This is softening Process.

Ion Exchange Resin - Fouling

Ions like Fe or other metal if available in water, will be exchanged by resin $R\text{-}SO_3Na$ in same way the Ca & Mg is exchanged. The Total Exchange Capacity of the Resin expressed as kg $CaCO_3$ per m^3 means the total Na Sites available for exchange. This is of academic significance and a manufacturing and QC related term.

Once resin is used in a process, it will lose it's capacity and at one time, it would not be able to exchange any further Ca & Mg and release Na in return. This state of Resin is termed as "Exhaustion". Once Resin is Exhausted, it needs "Regeneration". Since idea of Regeneration is to Provide Na and elute Ca & Mg any Na based salt can be used. NaCl, $NaHCO_3$, Na_2CO_3 etc.

Since, NaCl is the lowest cost. It's always preferred over rest.

Since Fe can not be replaced from R-SO3Fe during NaCl injection, Fe Fouls the Resin. So does other metal Ions.

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IX Softening Reactions

To simplify the understanding, we are now dealing with Ca only when we see equations. One can easily write the same with Mg.

Process is as below:

$$R\text{-}SO_3Na + Ca \begin{matrix} HCO_3^- \\ SO_4^{--} \\ 2Cl^- \end{matrix} \rightarrow R\text{-}SO_3Ca + Ca \begin{matrix} HCO_3^- \\ SO_4^{--} \\ 2Cl^- \end{matrix}$$

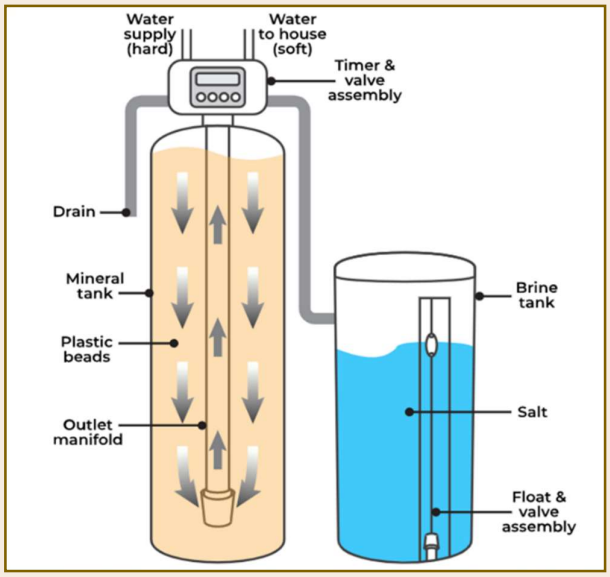
Regeneration is as below:

$$R\text{-}SO_3Ca + Na\ Cl^- \rightarrow R\text{-}SO_3Na + Ca\ 2Cl^-$$

As we can see that the Brine (NaCl) is used for regeneration.

Typically, 10-15% NaCl solution in injected into an Ion Exchange Softener for 20-30 mins for complete regeneration.

Resin can never be regenerated back to it's Total Exchange Capacity and returns back to a level of Na ions that is referred as "Operating Exchange Capacity", which is always lower then the "Total Exchange Capacity". The Operating Exchange Capacity of Softening Resin $R\text{-}SO_3\text{-}Na$ depends upon the Quantity of salt used per m^3 of Resin in the IX column.



IX Softening Design

To understand IX Colum design for softening one has to go through the table below in sequential order.

Parameter	Unit	Value	Explaination
Soft Water Requirement	m3/d	500	The quantitity of Soft water needed per day
Cycle per day	-	2	No of Times Softner need regeneration in a day. That time will be lost
Hours Available per day	h	24	It's Plant or Factory working hours =(9*2+2*2+2)
Operation	h	9	Softener Performing hours, Production of Soft water
Regenration	h	2	Softener Regeneration hours for Brin Injection, Rinse and be ready again
Idle, Free time	h	2	Time available for any maintenance etc. Can be Zero if one wishes
Output between Regeneration	m3	250	Soft water to be produced
Flow rate	m^3/h	27.8	OBR/Op Hours
Load (Hardness)	mg/l	200	It's the sum of Ca & Mg present in Water. Also referred as "Load"
Work Done	kg $CaCO_3$/Cycle	50	Load * OBR/1000
Resin Selected	-	R-SO_3Na	Strong Acid Cation Exchange Resin in Na form
Regeneration Level Selected	kg/m^3	130	Kg of Salt per m^3 of Resin
Operating Exchange Capacity	Kg $CaCO_3/m^3$	55	This is selected from the characteristics Curves of Resin from Resin Supplier.
General Deration Factor	-	0.9	10% reduction in capacity fom Lab based Curve to Site Coditions
Corrected Exchange Capacity	Kg $CaCO_3/m^3$	55	Operating Exchange Capaity X General Deration Factor
Resin Volume, Nett	m3	0.909	Quantity of Resin Required in IX Column
Salt Required per Regeneratio	kg	118.1818	
Salt Concentration - Injection	15%	6.5	Can be 10-15%
Ejector Type	-	1::1	1 Part water sucks 1 part salt during Injection
Brine Concentration in BMT	%	30%	
BMT Volume	l	394	Add 20% as gross capacity and round to nearest standard Size

Once you have the Resin Volume, Flowrate and Brine measuring tank size. You have two choices:

1. Use standard available Vessels in FRP and check how much Resin can be filled keeping at least 50% Free Board (*The empty volume above Resin Surface*) and use Multiport Valves or Individual valves.

2. Size a MS Tank with Epoxy painting Inside. Brine is injected during regeneration (corrosive) and keep bed depth of Resin > 750, < 1500 mm up-to 2000 mm Dia vessels and up to 2500 mm for vessels > 2000 mm Dia up-to 3200 mm dia. Beyond that Dia, its preferred to split the flow in multiple vessels.

3. In some special cases one can go for CCR regeneration of softener. Usual regeneration is Co Flow.

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Is Soft Water Good enough?

Removal of Ca & Mg from Water is at a Cost. It introduces the equivalent amount of Na in water and thus the TDS remains the same.

Further the Alkalinity (HCO_3) is in the water so on Anion side no change is noticed by simple SAC-Na based softening.

This gives a new concept that was popular a lot before "Reverse Osmosis", ***DEALKALIZATION,*** that aims at:

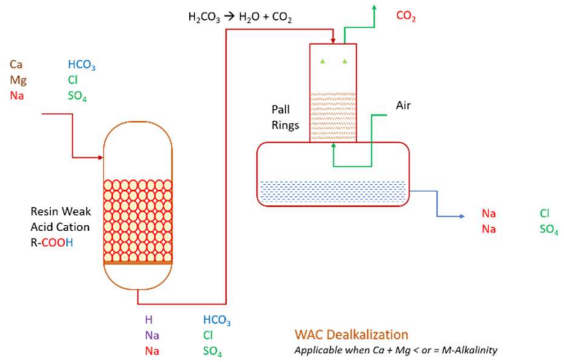
a. Removal of Ca & Mg by Resin
b. Removal of HCO3 by Degasification.

This means the Dealkalizations removes Cation as well as Anion and thus the TDS is reduced in this process to an extent of Temporary Hardness (Alkalinity + Ca, Mg). This Process is also known as "Partial De-ionization" and can be achieved by various methods:

1. Weak Acid Cation Resin based Softening + De-gasification

2. Split Stream DE alkalization followed by DG

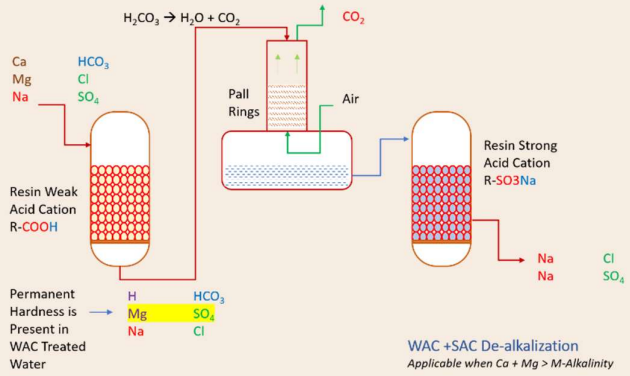
Depending upon the Water analysis, Level of Temporary hardness and Permanent Hardness and treated water quality required, the engineer may wish to design any of the below processes.



Picture above Depicts how one can achieve Temporary Hardness removal along with Alkalinity Removal.

What if We have Permanent hardness Present?

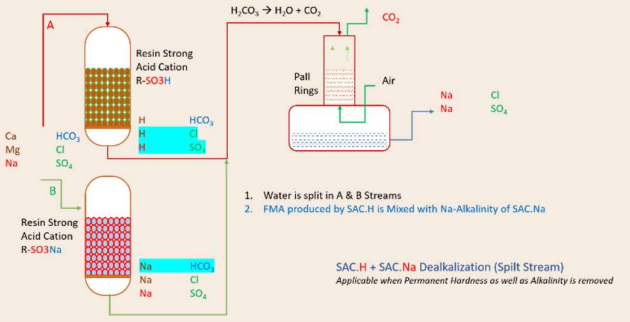
If permanent Hardness is present, it can be removed by providing a simple softener post WAC Exchanger and Degasification.



During such design be aware that Hardness is reduced a lot so Na/TC ratio post Degasser is quite high. High Na/TC ration means majority of Cations are Na and this means the Operating Exchange capacity of *R-SO3Na* is compromised. Please refer Resin Characteristics Curves for Correction Factor applicable for Na/TC Ratio. One need not consider it, if Na/TC < 22%.

Split Stream Dealkalization?

WAC resins are 3X price in comparison to SAC resin, their operating exchange capacity though 75-80% more if operated for 24 h Cycle.



If one wishes for 2 regeneration a day, it makes sense to go for split stream dealkalization where FMA produced by SACH Exchanger reacts with Alkalinity of SACNa Exchanger and results in De-alkalization when mixed and sent to degasification.

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Metal Removal by WAC Exchanger

Heavy metals like Fe, Zn, Ni etc can be exchanged by WAC resins R-COONa.

The WAC Resin exhibits a unique advantage of Volume expansion. The Resin can be either in H form or Na Form. The H to →Na expansion of Resin is 120% and this means this resin can have a Squeezing Action.

This property of Resin is used to trap the metals and elute them from resin bed by regeneration. During regeneration with HCl First resin converts exhausted resin in H Form from predominant Na Form. And then regenerating with NaOH is to convert the entire resin to R.COONa form, ready for next cycle to arrest Ca, Mg and Off-course Metals.

To enhance the Performance of Metal removal, the feed can be acidified using HCl to keep the pH to around 6.00. This ensures majority of metals are in Dissolved state (exchangeable).

In a ZLD Projects, where the regeneration waste also needs treatment; in most cases the Regenerant HCl and NaOH self-neutralize each other.

Excess NaOH or $Ca(OH)_2$ may be added to this effluent to raise pH to 9.5, a pH where most metals will exhibit least solubility and thus precipitated. The slurry then passed though filter Press shall remove all the precipitated metals and the Filtrate of the Filter press can be mixed directly into the concentrated stream, either at last RO or the MEE Feed tank.

Key to above regeneration technique is:

1. Stoichiometric Quantity of HCl as per the Op Exchange Capacity of WAC Resin in Kg $CaCO_3/m^3$ of Resin.

2. Equivalent amount of NaOH Injection to Convert R.COOH to R.COONa

Remember, H to → Na, is 120% expansion so while you design the exchanger keep 150% free board above the Quantity of Resin filled in the WAC Exchanger.

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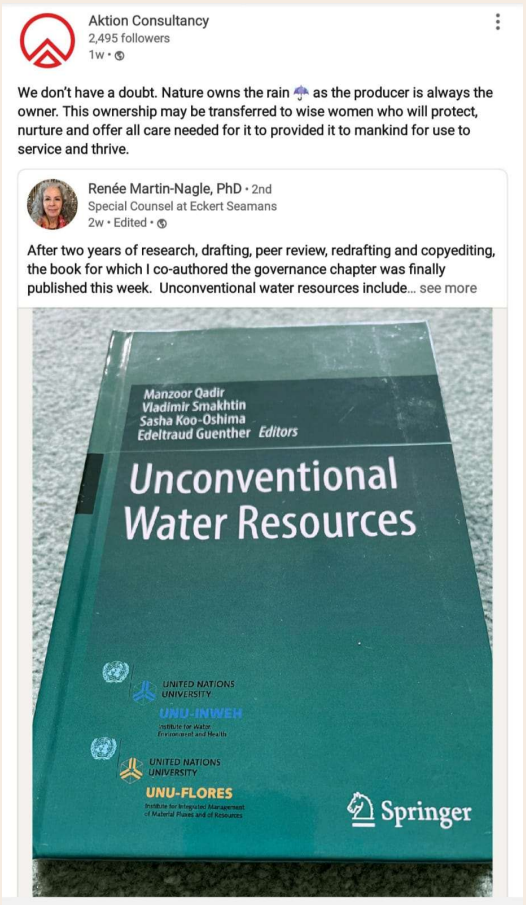

Our world is Waughter

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: "Reverse Osmosis Design from Software and Pre-treatment Significance"

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