



HARDNESS IN WATER
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Portable Well Company 2022

HARDNESS IN WATER

Introduction

“Softening” of water is as old as the written word.

The principle process that allows this purity to be achieved is ion exchange and just to illustrate that there is little new in the world, a examples of ion exchange can be found in the Bible, in the Book of Exodus 15:22-25 and also in the Book of Numbers 19:5-17. Sir Francis Bacon writing in the sixteenth century in New Atlantis and in Sylva Sylvarum also alludes to ion exchange.

Of course, these references are not explained as ion exchange, but as “sweetening bitter water with a tree” (oxidized cellulose) and “salt water being made fresh on passing through earth in twenty vessels” (Zeolites: being a naturally occurring ion exchange medium that exchanges hardness for softness). We follow illustrious footsteps.

Key Words

Total Hardness	Temporary Hardness	Permanent Hardness
Non Carbonate Hardness	Hardness Leakage	Hardness Breakthrough
Alkalinity	Sodium Bicarbonate	Base Exchange
Lime Soda Softening	Base Exchange Softening	Ion Exchange
SAC (Strong Acid Cation)	WAC (Weak Acid Cation)	Monovalent Ions
Divalent Ions	Calcium Sulphate	Magnesium Sulphate
Gypsum	Epsom Salt	Sodium Chloride
Backwash	Regeneration Concentrations	Regeneration
Operating Capacity	Linear Flow Rate	Brine
TDS (Total Dissolved Solids)		Backwash

Classification of `Hardness`

In water, certain materials react with soap yielding a precipitation that appears as `scum`. Until enough soap has been consumed to react with all such materials no lather will be formed. These types of water are classified `hard`. Synthetic detergents used in lieu of soap largely overcome this since the detergents do not cause precipitation of the hardness compounds (scum).



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

However, in other terms hardness is to be discouraged for its scaling tendencies in particular any process where heat is applied, kettles, steam raising, heating, power generation etc. This is principally due to hardness compounds being precipitated to form a scale on the heated surface. The portion of the **Total Hardness** deposited when water is boiled is called **Temporary Hardness** while the balance is called **Permanent Hardness** or more precisely **Non-Carbonate Hardness**.

Hardness Compounds

Temporary Hardness

Calcium Bicarbonate $\text{Ca}(\text{HCO}_3)_2$
Magnesium Bicarbonate $\text{Mg}(\text{HCO}_3)_2$

Permanent Hardness

Calcium Sulphate CaSO_4
Magnesium Sulphate MgSO_4
Calcium Chloride CaCl_2
Magnesium Chloride MgCl_2

From this it can be seen the principal cause of hardness are the bicarbonates producing **Temporary Hardness** and the sulphates and chlorides producing **Permanent Hardness**.

To simplify, **Temporary Hardness** is removed by **'boiling'** **Permanent Hardness** is not.

Total Hardness is always measured as mg/lCaCO_3 and an indication of 'Hardness' is commonly accepted as:

0 ~ 50 mg/l	Soft
50 ~ 100 mg/l	Moderately Soft
100 ~ 150 mg/l	Slightly Hard
150 ~ 200 mg/l	Moderately Hard
>200 mg/l	Hard
>300 mg/l	Very Hard

Waters extracted from underground sources are largely 'Hard' while such waters derived from chalk and limestone deposits are a major concern due to the carbonate



HARDNESS IN WATER Green paper Bulletin 06 Portable Well Company 2022

hardness resulting from the reaction of the calcium and magnesium carbonates with carbon dioxide. This accounts for the presence of `Alkalinity`.

Alkalinity is the presence of bicarbonates, carbonates and hydroxides of calcium, magnesium, potassium and sodium. Of these calcium bicarbonate is the most usual compound causing alkalinity.

There is confusion as to the use of the term **Alkalinity** due to Chemists giving two distinct meanings to the word. Firstly it is used to describe any solution with a $\text{pH} > 7.1$. Secondly, (and much more commonly) it is used to describe the total amount of the substances listed as contributing to Alkalinity present in the water. Taking the second concept analyses are quoted `alkalinity as CaCO_3 ` derived by titration at 4.5pH of the total constituents as listed above expressed as the equivalent weight in calcium carbonate.

Of the most common substances found in waters causing **Alkalinity** being calcium and magnesium carbonates are also the cause of **Temporary Hardness** so, when the alkalinity and hardness values are equal all the hardness is **Temporary** and is then termed **Carbonate Hardness**. When **Total Hardness** is greater than **Alkalinity** then the excess is **Non Carbonate** better known as **Permanent Hardness**.

If, as is sometimes the case the **Total Hardness** is less than the **Alkalinity** the difference indicates **Sodium Bicarbonate** that increases the **Alkalinity** but not **Hardness**. This is almost always due to **Base Exchange** softening of the water supply but can also be due to natural softening in deep underground strata.

Removal of `Hardness`

In water treatment there are two common methods of treating `Hard` water. **Lime Soda** and **Base Exchange Softening**.

Lime Soda Softening

This form of softening changes the hardness compounds (including carbonates) causing them to become insoluble and precipitate. Precipitation followed by sedimentation and filtration completes the process.

Base Exchange Softening

Here, the nature of the hardness compounds is changed, that is the calcium, and magnesium ions predominantly are exchanged for sodium ions.



HARDNESS IN WATER

Green paper Bulletin 06

Portable Well Company 2022

Difference

The difference between these two methods is important.

In lime softening the hardness compounds are **removed**, in Base Exchange they are **exchanged**, resulting in that in lime softening **total dissolved solids (TDS)** are reduced but not in base exchange softening.

This is an important difference.

Since base exchange softening is the most common process used outside of municipal application this is the technology to be considered further.

Base Exchange Softening

Hardness of water is the cause of scale formation in pipes, kettles, sauce pans, boilers and that all too familiar ring around the bath. It is commonly accepted that the term “hardness” originated from the hard scale formed by calcium and magnesium. When this “hardness” has been removed the water is known as “soft”.

Thus, hardness of water is the combined amount of calcium (Ca^{++}) and magnesium (Mg^{++}) present in the water.

For the majority of ion exchange applications it is necessary to know what ions and their concentrations are present but for water softening generally just knowing the hardness present i.e. calcium and magnesium is sufficient. However, if it is known iron, manganese, strontium or barium are present it is prudent to consider these. If the water to be softened has a high sodium chloride content then it is necessary to obtain a complete ionic analysis.

Of all the ion exchange processes softening is largest volume user. In base exchange softening two versions of resin are used. Predominant is SAC (Strong Acid Cation) resin although WAC (Weak Acid Cation) is being increasingly used for waters with a high TDS (Total Dissolved Solids)

Here we have one of the water treatment industries anomalies. When considering reverse osmosis TDS refers to the sum of all ions both cation and anion while in ion exchange it refers to the sum of cations while considering cation exchange and anions while considering anion exchange.



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

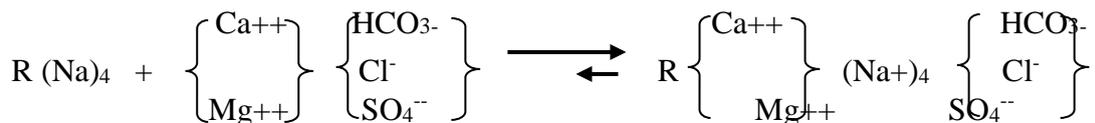
SAC resins can be used in both softening and deionising systems. When regenerated with brine (salt) they soften water operating in the sodium (Na⁺) form with sodium ions exchanging for divalent ions calcium and magnesium. When regenerated with acid either Hydrochloric (HCl) or sulphuric (H₂SO₄) and operating in the hydrogen (H⁺) it splits salts forming acid.

WAC resins for softening of waters with high TDS operate in conjunction with SAC resins operating in the acid form to split alkaline salts and hence demineralising. However, regeneration is initially by acid followed by conversion to the sodium form.

Softening Reaction

By its very name ion exchange describes its function. To provide the mechanism ions to be exchanged are “fixed” onto an insoluble base and exchanged for ions in solution. In practice an insoluble bead basically polystyrene is “loaded” with sodium ions that then exchange for calcium and magnesium ions until there are no longer any sodium ions available. At this point the resin is said to be “exhausted”.

The process is illustrated by (were R represents the resin):-



Equation #1

Note that a balanced equation is present, this is necessary requirement for all ion exchange processes. Four monovalent sodium ions (Na⁺) on the resin (R) are exchanged for one divalent calcium ion (Ca⁺⁺) and one magnesium ion (Mg⁺⁺) in solution on the left side of the equation while on the right side of the equation calcium and magnesium are now on the resin (R) with sodium now in solution.

An important point is the direction and scale of the arrows. The longer arrow shows that the reaction predominantly progresses to the right hand side but there is a tendency for the reaction to reverse or reach an equilibrium. What this shows is that if the resin and water were allowed to stand the reaction would over time reach an equilibrium were there would be sodium ions on the resin with calcium and magnesium ions in the water.

Hardness Leakage

There are limits to water quality achieved by softening using SAC resin with hardness leakage being effected by the TDS of the water being treated.



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022



Note the effect of TDS represented by sulphate (SO_4^-) balanced on both sides of the equation increasing the salt concentration resulting in a shift to the left side and an equilibrium in the ion exchange reaction.

In practical terms a hardness leakage $<1\text{mg/l}$ is achievable with a well regenerated system with feed water TDS $<5000\text{mg/l}$.

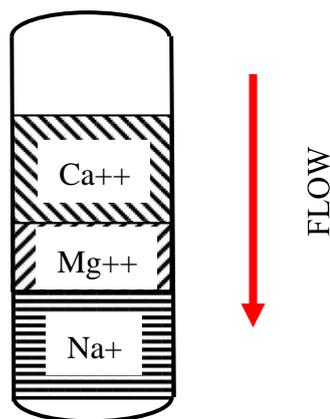
What then is Hardness Leakage?

As water flows through the ion exchange resin bed calcium and magnesium is exchanged for sodium. However, there is a “ranking” in the affinity for calcium and magnesium for the sulphonated sites that hold the sodium ion on the resin.

Consider the sulphonated sites as sulphuric acid and calcium as the sulphate salt calcium sulphate (CaSO_4) and magnesium as the sulphate salt magnesium sulphate (MgSO_4) then consider the solubility of these salts. CaSO_4 commonly known as gypsum has a low solubility while MgSO_4 commonly known as Epsom Salt has a much higher (>100 times) solubility. Relating this to bond strength or selectivity calcium has a stronger affinity for the SAC exchange site. Or another way less likely to dissolve or hydrolyse off the resin than magnesium.

So, even though calcium (Ca^{++}) and Magnesium (Mg^{++}) are both divalent ions there is a different selectivity or attractiveness for ion exchange.

In practice during service this selectivity establishes a stratified resin bed:





HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

Fig #1 Exhaustion Bands in Softening

As the service continues the stratification continues until all sodium is displaced and magnesium leaks or “breakthrough” as hardness. This is known as “**Hardness Leakage**”.

Of course it’s not quite as straightforward as this. In practice the stratification zones are rarely closely defined being effected by velocity, flow distribution and degree of exhaustion of the resin. Temperature has limited effect unless very low when all ion exchange becomes sluggish.

A common fault in softener operation is caused by improper backwash. Water tends to flow through ion exchange resin uniformly or along the path of least resistance. In service a resin bed becomes compacted while in regeneration the initial backwash aims to restore uniformity but improper backwash effects this leaving areas compacted that a) are not expanded and therefore not regenerated and b) being exhausted and hence heavier than regenerated resin will sink to the lower bed during brine displacement rinsing. All of these will cause early hardness breakthrough.

A well operated softener with a feed water <5,000mg/l TDS can easily achieve a hardness leakage of <1mg/l during service.

Note **Hardness Leakage** not **Hardness Breakthrough**. What is the difference?

No ion exchange process is 100% efficient, very efficient but there is always a margin. Table #3 illustrates this:

Item	mg/l as	Feed	Softened
Calcium	CaCO ₃	1000	<1
Magnesium	CaCO ₃	2000	<1
Sodium	CaCO ₃	22000	25000
Bicarbonate	CaCO ₃	2000	2000
Carbonate	CaCO ₃	0	0
Sulphate	CaCO ₃	3000	3000
Chloride	CaCO ₃	2000	2000
Nitrate	CaCO ₃	0	0
TDS	CaCO ₃	2500	2500

Fig #3 WAC Water Softening Hardness Leakage



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

The two practical limitations for hardness leakage are Raw Water TDS (as CaCO_3) and regeneration level expressed as g/l NaCl brine solution. This is illustrated in Fig #4.

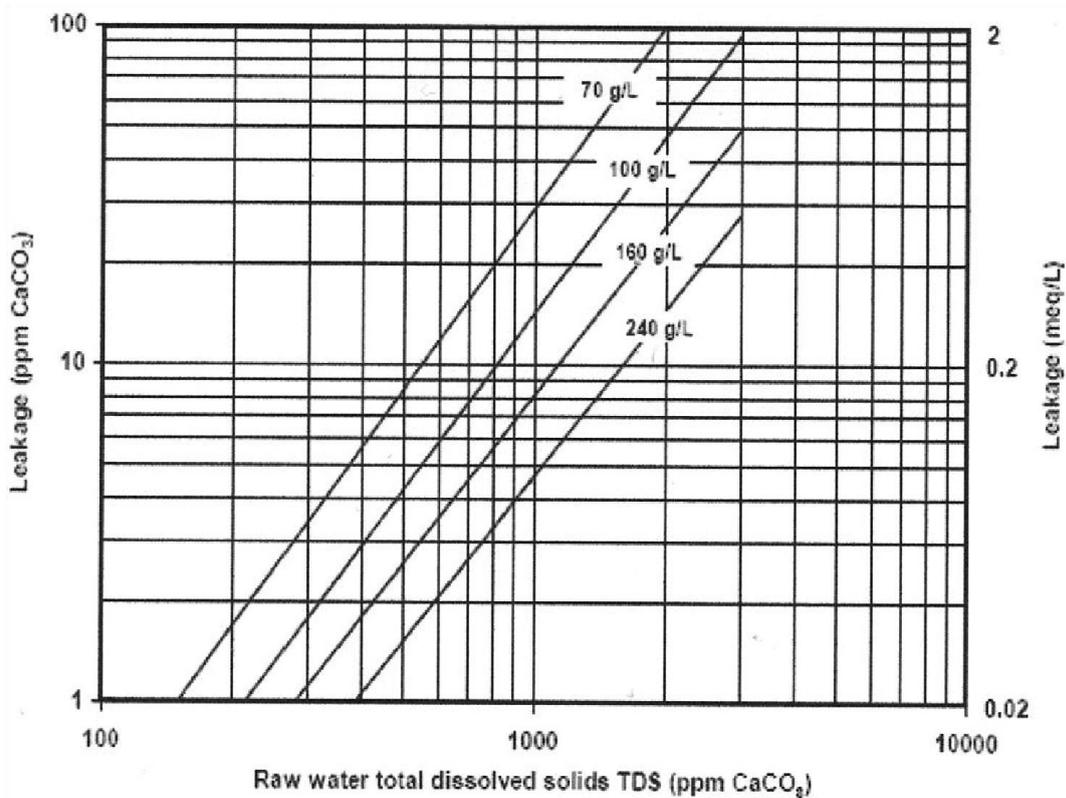


Fig #4 Hardness Leakage / Regeneration Levels

To achieve 1mg/l hardness leakage at 100g/l regeneration level raw water TDS can be no higher than 220mg/l (mg/l = ppm) while to achieve 1mg/l hardness leakage at 400mg/l raw water TDS a regeneration level of 240g/l is required.



HARDNESS IN WATER Green paper Bulletin 06 Portable Well Company 2022

Using Hardness Breakthrough to limit the softener say 3mg/l is considered a practical limit then 70g/l regeneration level has less capacity to 3mg/l breakpoint than 240g/l has. For visual comparison consider the area beneath the curve.

Regeneration Concentrations

The highest concentration of sodium chloride brine that can be achieved at normal temperatures is approximately 26% by weight however usage at this strength does cause

Osmotic shock to resin resulting in split beads. Consequently for softener application solutions in the range 8% ~ 12% are common.

Concentration of brine is checked by the use of a hygrometer with 8% solution by weight 1.58 SpG while 12% solution by weight is 1.09.

Consider brine at 10% concentration by weight having a SpG of 1.074 and having salt weight of 0.897lbs/us gallon or 107g/l. then for say 140g/l regeneration level 1.308 litres are required.

Operating Capacity

Fig #5 is the base starting curve for operating capacity of Dow Marathon C a common resin used in water softening. Note that kgr/ft³ is used almost exclusively only in the USA for resin calculations multiply by 2.29 for mg/l.



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

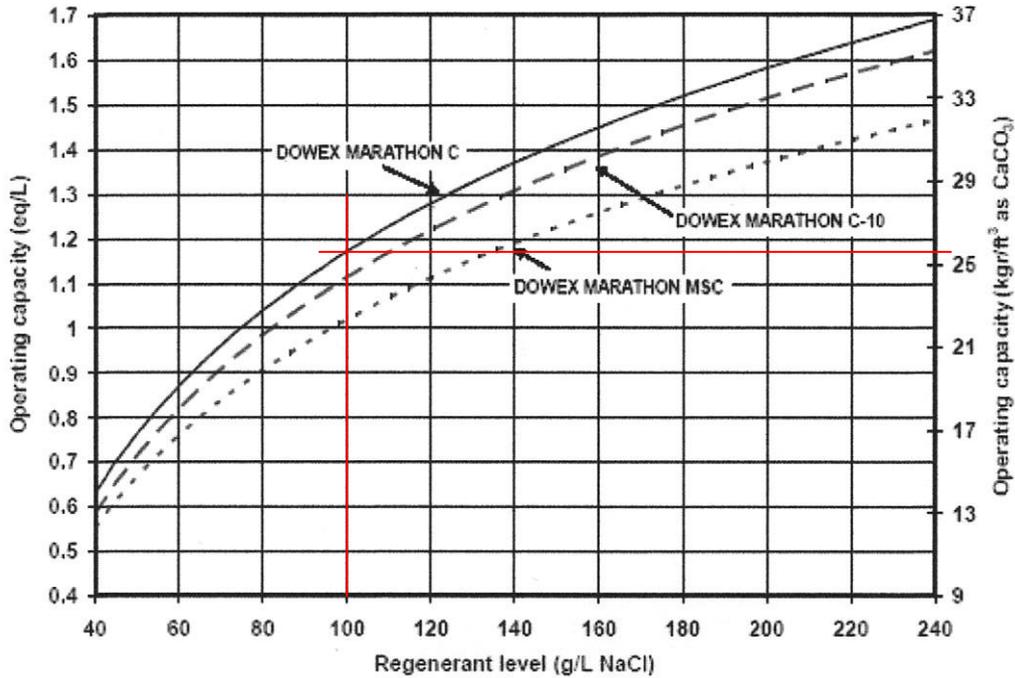


Fig #5 Operating Capacity

For a regeneration capacity of 100g/l NaCl the resin has an ion exchange capacity of say 26kg/ft³ or 59.54g/l. However allowances must be made for other factors:

Fig #6 Correct for Feed TDS

Assuming a raw water TDS of 1,000 then the capacity would be reduced to 95.7%



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

Figure 8. Correction of operating capacity for %Na in feed.

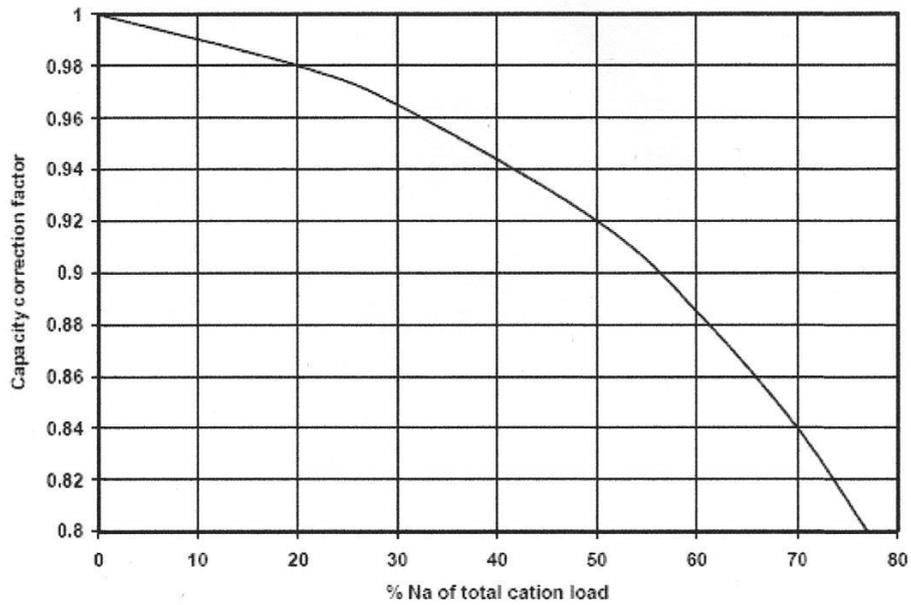


Fig #7 Correct for % Na

The higher the sodium (Na) % against total cations in the feed water the greater the correction in resin capacity. Thus, for say 50% Na resin capacity is reduced 92%



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

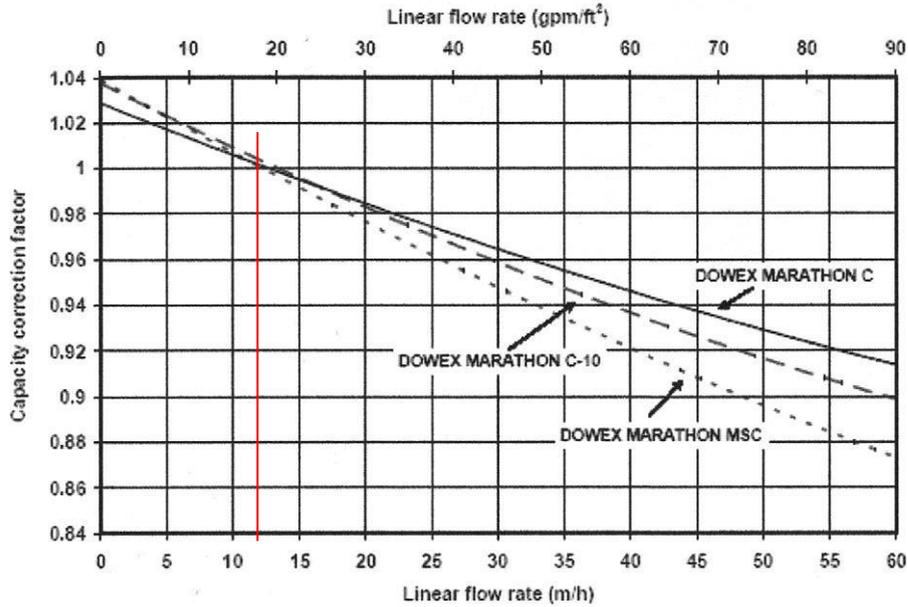


Fig #8 Correction for Linear Flow Rate

Assuming linear flow rate of 12 m/hr as commonly experienced in softener application a correction factor of 1 is applicable.



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

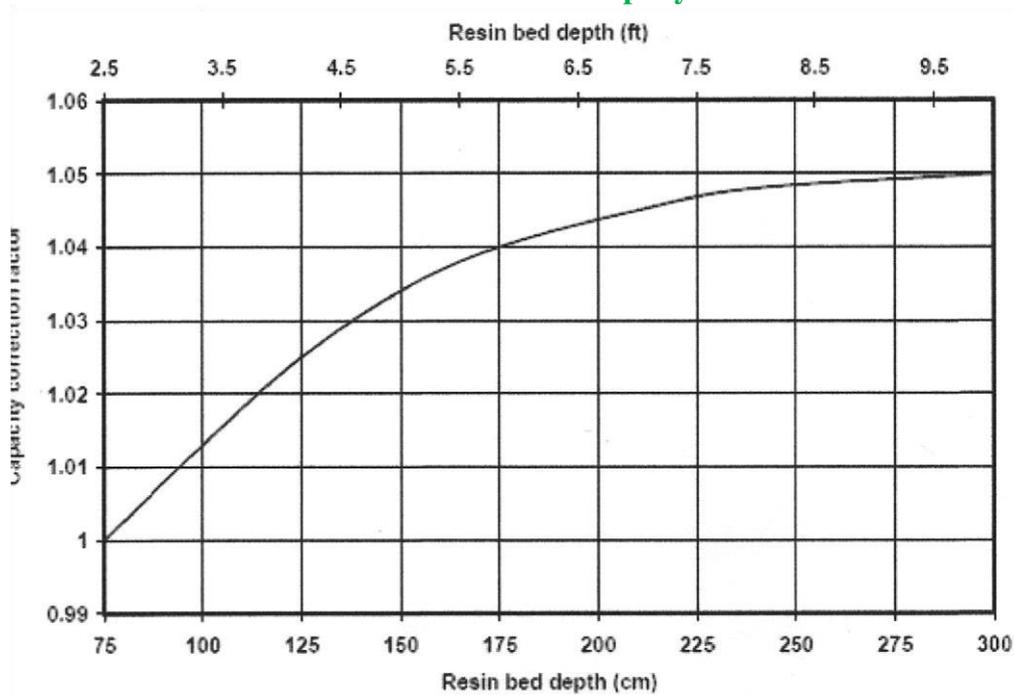


Fig #9 Correction Factor for Bed Depth

The data on which all the foregoing graphs are based is developed in the manufacturer's laboratory. 75cm is the minimum recommended bed depth for softeners using Marathon C resin. For this depth a correction factor of 1 is applicable

From an initial capacity of 59.4g/l by applying the above correction factors the actual operating capacity is:

$$59.54 \times 0.957 \times 0.92 \times 1 \times 1 = 52.42\text{g/l}$$

With a regeneration level of 100g/l that is an excess of 1.91 times.

Actual Capacity

Litres of resin x 52.42 / TDS = litres

Assume resin capacity of 25 litres and a feed TDS of 100mg/l then:

$$\text{Service Cycle} = \frac{25 \times 52.42 \times 1000}{120} = 10,92.83 \text{ litres (approx } 11\text{m}^3\text{)}$$



HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

Regeneration

Hydraulic performance of ion exchange resin is usually presented as flux, linear velocity or bed volume. Of these bed volume is probably the easiest to relate to especially in field operation as it directly relates to the volume of resin. Assuming 25 litres of resin then that is 1 Bed Volume (BV). Note that this applies to the total volume of the bed resin + water. A common error is to consider water content which is usually about 22% of the actual volume but no bed volume is quantity of resin.

Typical ion exchange resin operating parameters could be presented as:

Service Flow Rate	1 ~ 5gpm/ft ³	8 ~ 40BV/h
Linear Flow Rate	4 ~ 20gpm/ft ²	10 ~ 50m ³ /m ² /h
Regeneration	0.25 ~ 0.5gpm/ft ³	2 ~ 4BV/h
Backwash	1.5 x Service Flow	
Displace	Regeneration flow	
Rise	Service flow	

Note gpm is usgpm simply because all development and until recently the majority of ion exchange manufacture was USA based.

From the above the advantage of using bed volumes (BV) is clear.

Manufacturers datasheets will have recommended operating criteria such as service flow rate 6 ~ 40 BVh, regeneration flow rate 2 ~ 5 BVh. The actual criteria is selected by the designer and is often not available to the field person.

For softener application service flow is usually circa 12 BVh with regeneration brine flow rate 3 BVh.

Assume the following criteria:

Bed Volume	25 litres C100 IX Resin
Regeneration Level	120g/l
Brine 10% Concentration	107g/l

Amount of brine 25 x 120 = 3000 / 107 = 28 litres @ 10% NaCl by weight

Regeneration Flow Rate 3BVh = 3 x 25 = 75 litres
Time = 28 / 75 = 22.4 minutes.

Conclusion



**HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022**

Too often the phrase “its hard water so install a softener” is heard.

From the foregoing it can be seen that its not quite that simple.

There are many considerations to be balanced in softener selection and as always in water treatment all succeed or fail with the quality of the feed water analysis.

The above Green paper only deals with the basic selection procedure the presence of iron, manganese etc does rather complicate matters as does alkalinity all of which do make life interesting but as always please remember water treatment is an “art”, some even say a black art rather than a science.

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We look forward to hearing from you.

Terry Cummings
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HARDNESS IN WATER
Green paper Bulletin 06
Portable Well Company 2022

ABOUT AUTHOR

Since entering the industry, the author has now accumulated 60+ years of experience in design, engineering, execution and troubleshooting water and wastewater systems with experience in building services, power both fossil and nuclear, potable and municipal water and wastewater systems including desalination and tertiary, pharmaceutical, microelectronics, petro-chemical and general industry. He is the author of many published works including Green papers of which this document is one. While primary contact is via UK, involvement is and has been worldwide with ongoing international activities.