

Water softening using caustic soda: privileges and restrictions

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The aims of the current study is to investigate the constraint of using caustic soda in water treatment and evaluating its performance in water softening, compared to the other chemical group, including lime and sodium carbonate. Based on mass balance of reactants in the caustic softening process, a mathematical relation for expressing the constraint of using caustic soda in water softening was derived. To evaluate caustic soda performance in water softening and prove the derived relation as well, some experimental works on some water sources including well water and clarifier's inlet water in two oil refineries were performed. The results showed that compared to lime-sodium carbonate, the caustic soda is the best choice for water softening; however, using caustic soda in water softening, while restrictive mathematical relation does not verify the chemical characteristics of water, could lead to an extreme increase in alkalinity.

Keywords: water softening, lime, sodium carbonate, caustic soda.

INTRODUCTION

Applying untreated and impure water in industries for some applications such as steam generation, and cooling purposes could lead to serious problems like the formation of deposits and corrosion in related equipment. While hardness (calcium and magnesium hardness) and silica in water are the most significant impurities that result in forming deposits, dissolved oxygen and some other impurities that cause low pH in water are responsible for the formation of corrosion in equipment that use water as an operating fluid. The main technologies for the treatment of water are: precipitation softening, Ion exchange and reverse osmosis (RO). In precipitation technology the hardness (CO_2 as well) is precipitated by means of using chemicals such as lime, sodium carbonate, and caustic soda while silica is removed through adsorption on formed or added $\text{Mg}(\text{OH})_2$. The precipitation reactions, using lime and sodium carbonate are shown in Table 1¹.

Table 1. Precipitation reactions, using lime and sodium carbonate

$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$
$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + 2\text{CaCO}_3 + 2\text{H}_2\text{O}$
$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCO}_3 + \text{Na}_2\text{SO}_4$
$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCO}_3 + 2\text{NaCl}$
$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$
$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$
$\text{Mg}(\text{OH})_2 + \text{SiO}_2 \rightarrow \text{Mg}(\text{OH})_2 \cdot \text{SiO}_2$

As reactions show, in softening technology all kinds of salt aren't precipitated and only temporary hardness (bicarbonate salts) can be precipitated in reaction with lime; furthermore permanent hardness (noncarbonated) is converted to sodium salts in reaction with lime and sodium carbonate. As sodium salts are soluble, softening technology can not eliminate all kinds of salt and for their thorough elimination, other technologies must be applied.

In ion exchange technology water is demineralized using two ion exchange resin columns, which include a strong

cation unit and a strong anion unit. The cation resin exchanges hydrogen ions for cations and anion resins exchange hydroxide ions for anions. The demineralization reactions are shown in Table 2.

Sulfuric acid at a concentration of 2 to 6 percent regenerates the cationic resin bed and a caustic solution at a concentration of 4 percent is applied for regeneration of anionic resin bed. As demineralization reactions show, all kinds of salt are eliminated when raw water is passed through two cationic and anionic resin beds.

RO technology is another technology for thorough elimination of salts, which uses membranes for desalination of raw water.

In general, economic considerations will determine the using of either exchange or RO technologies².

Table 2. Demineralizations, using cation and anion exchange resins

$\begin{pmatrix} \text{Ca} \\ \text{Mg} \\ 2\text{Na} \end{pmatrix} \begin{pmatrix} \text{SO}_4 \\ 2\text{Cl} \\ 2\text{HCO}_3 \\ 2\text{NO}_3 \end{pmatrix} + 2\text{HZ} \rightarrow 2\text{Z} \begin{pmatrix} \text{Ca} \\ \text{Mg} \\ 2\text{Na} \end{pmatrix} + \begin{pmatrix} \text{H}_2\text{SO}_4 \\ 2\text{HCl} \\ 2\text{H}_2\text{CO}_3 \\ 2\text{HNO}_3 \end{pmatrix}$
$\begin{pmatrix} \text{H}_2\text{SO}_4 \\ 2\text{HCl} \\ 2\text{HNO}_3 \end{pmatrix} + 2\text{ZOH} \rightarrow 2\text{Z} \begin{pmatrix} \text{SO}_4 \\ 2\text{Cl} \\ 2\text{NO}_3 \end{pmatrix} + 2\text{H}_2\text{O}$
$\begin{pmatrix} \text{H}_2\text{CO}_3 \\ \text{H}_2\text{SiO}_3 \end{pmatrix} + \text{ZOH} \rightarrow \text{Z} \begin{pmatrix} \text{HCO}_3 \\ \text{HSiO}_3 \end{pmatrix} + \text{H}_2\text{O}$

Generally, the precipitation softening technology has the lowest cost of operation among other technologies³, though it has some flaws such as, incomplete desalination. Despite some flaws, precipitation softening technology is widely used for pretreatment or intermediate treatment of water in RO plants⁴, in order to increase the water recovery of RO desalting. Also, when there is no obligation for using ultra pure water, in some applications, such as waste water softening to use as make-up water

for closed circulation cooling systems, the precipitation softening technology could be the best choice for water treatment.

In general lime and sodium carbonate are used for precipitation softening but some problems such as handling difficulties of chemicals, health problems, caused by lime, and also some operating upsets, including blocking the lines and injection equipment, arise during handling such chemicals. To overcome such problems, caustic soda could be a good choice for replacing lime and sodium carbonate. Caustic soda has no handling difficulties similar to those of lime and sodium carbonate and can be used easily for water softening.

The use of caustic soda, as a superior alkaline reagent in water softening is discussed in many references. Abdessemed et al.⁵ have studied the optimum conditions for decarbonation by mixture of lime and caustic soda and represented the softening results as a function of pH. Anditya Rahardianto et al.⁶ and Christopher et al.⁷ integrated RO desalination system with an inter-stage softening process, using caustic soda for high-recovery reverse osmosis desalination. They noticed only economic considerations about choosing alkaline reagent for inter-stage softening. Also, El-Manharawya & Hafezb⁸, Alabdula'aly & Al-Rehaili⁹ and Benefield & Morgan¹⁰ found caustic soda, as an efficient alkaline reagent in water softening, compared to lime and sodium carbonate, which can be used over a wide variation of feed water quality but they didn't mention the feed water quality that caustic soda could be suitable for water softening.

Overall, in different studies, the economical considerations have had the major role in choosing caustic soda but the restrictions and limitations of using caustic soda in water softening have not yet been studied. In the current study, the constraint and conditions for using caustic soda in water softening are investigated and the limitations of caustic usage, expressed in a mathematical relation, are evaluated through experimental works.

WATER SOFTENING USING CAUSTIC SODA

The precipitation reactions of caustic soda with hardness are shown in Table 3¹¹. As reactions show, contrary to lime softening, sodium carbonate (Na_2CO_3) is produced along with CaCO_3 and $\text{Mg}(\text{OH})_2$, as the products of temporary hardness precipitation. As a result, when there is no enough reactant(s) to consume the produced sodium carbonate, the alkalinity (P, M)¹ of water could extremely increase, due to an increase in carbonate ions. Permanent calcium hardness, such as calcium sulfate and calcium chloride are the best sources to consume the formed sodium carbonate. Consequently, if water contains enough permanent calcium hardness, the produced sodium carbonate will be consumed and the alkalinity of treated water will be controlled. Alkalinity relationships are shown in Table 4.

As Table 4 shows, for water source which contains temporary hardness (bicarbonate), the amount of bicarbonate can be considered as (M-2P) (truncated to M when P=0). In some cases for which the amount of temporary Mg.H (magnesium hardness) is negligible, compared to temporary Ca.H (calcium hardness), then the term (M-2P) represents the amount of calcium bicarbonate

Table 3. Precipitation reactions, using Caustic soda

$\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
$\text{Ca}(\text{HCO}_3)_2 + 2\text{NaOH} \rightarrow \text{CaCO}_3 + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$
$\text{Mg}(\text{HCO}_3)_2 + 4\text{NaOH} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$
$\text{MgSO}_4 + 2\text{NaOH} \rightarrow \text{Mg}(\text{OH})_2 + \text{Na}_2\text{SO}_4$
$\text{MgCl}_2 + 2\text{NaOH} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{NaCl}$
$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$
$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$
$\text{Mg}(\text{OH})_2 + \text{SiO}_2 \rightarrow \text{Mg}(\text{OH})_2 \cdot \text{SiO}_2$

Table 4. Alkalinity relationship¹

Criteria	Hydroxide	Carbonate	Bicarbonate
P=0	0	0	M
P=M	P	0	0
2P=M	0	2P	0
2P<M	0	2P	M-2P
2P>M	2P-M	2(M-P)	0

P (ppm as CaCO_3) = $\text{OH} + \frac{1}{2} \text{CO}_3$

M (ppm as CaCO_3) = $\text{OH} + \text{CO}_3 + \text{HCO}_3$

and the term (Ca.H-M+2P) represents the amount of permanent calcium hardness in water source. As each mole of calcium bicarbonate produces one mole sodium carbonate then the validity of the following relation ensures that the produced sodium carbonate can be consumed, completely, by permanent calcium hardness.

$(\text{Ca.H-M} + 2\text{P}) \geq (\text{M}-2\text{P})$ or $\text{Ca.H} \geq 2(\text{M}-2\text{P})$;

while temporary $\text{Mg.H} = 0$ & $2\text{P} < \text{M}$ (1)

Conversely, when the amount of temporary calcium hardness is negligible, compared to temporary magnesium hardness then the term (M-2P) represents the amount of magnesium bicarbonate and Ca.H, alone represents the amount of permanent calcium hardness in water source. As each mole of magnesium bicarbonate produces two moles sodium carbonate then the validity of following relation ensures that the produced sodium carbonate can be consumed, completely, by permanent calcium hardness.

$(\text{Ca.H}) \geq 2(\text{M}-2\text{P})$;

while temporary $\text{Ca.H} = 0$ & $2\text{P} < \text{M}$ (2)

Relations of (1) and (2) are the same and this means that regardless of the type of temporary hardness, the criteria for water softening with caustic soda can be shown as follows:

$(\text{Ca.H}) \geq 2(\text{M}-2\text{P})$; while $2\text{P} < \text{M}$ (3)

The validity of relation (3) ensures that water can be treated with caustic soda without any extreme increase in alkalinity.

Economical and Environmental Considerations

Comparison of the lime-sodium carbonate system with caustic softening system shows that the amount of produced CaCO_3 in case of using caustic soda is significantly less than the other case. Decrease in produced CaCO_3 reduces the environmental problems of landfill of precipitation products. Additionally, the caustic softening process produces 0.5 mole sodium carbonate per mole of consumed caustic soda which can be considered as an economical alternative for water softening, compared to lime and sodium carbonate.

EXPERIMENTAL WORKS

To prove relation (3) two series of precipitation softening tests were performed on two water sources which had different hardness characteristics. The first source was well water in Tehran Oil Refinery (Iran). This water is feed water to hot lime softening plant which produces treated water for steam generation. The typical analysis of well water in Tehran Refinery is shown in Table 5. According to relation (3) the amount of calcium hardness in well water is insufficient ($\text{Ca.H} < 2(\text{M}-2\text{P})$) and softening with caustic soda would result in increase in M alkalinity. To prove this, some precipitation softening tests were performed on well water, using lime and caustic soda.

Table 5. The Typical Analysis of Raw Water (well water) in Tehran Refinery

pH	TH	Ca.H	P	M
	ppm, as CaCO_3			
7.7	678	450	0	338

The second water source was feed water to the clarifier section of waste water treatment plant at Tabriz oil refinery (Iran). This water was the combination of some effluents such as, boiler blow-down and cooling water blow-down and was being treated in the clarifier, using lime (cold lime softening). Due to the presence of plenty of permanent hardness in the inlet stream to the clarifier some sodium carbonate was being added to the clarifier to improve the softening process and some polyelectrolyte for flocculation of formed sediments, as well. The treated water was being sent to the cooling towers as make-up water. The typical analysis and operating parameters of the feed water into the clarifier are presented in Table 6. According to relation (3) the amount of calcium hardness in feed water is sufficient ($\text{Ca.H} > 2(\text{M}-2\text{P})$), which means that the inlet stream into the clarifier can be softened, using caustic soda rather than lime and sodium carbonate without any extreme increase in M alkalinity. To prove this, a field test was conducted on the clarifier, using caustic soda with same dosage of lime, while the injection of lime and sodium carbonate were stopped and injection of polyelectrolyte with the same flow rate was continued. Field test continued for ten days and 66 softening results of this period were compared to 110 softening results

of lime-sodium carbonate softening (before field test) within 20 days.

RESULTS AND DISCUSSION:

The well water softening results in Tehran refinery, using lime and caustic soda are shown in Table 7.

The softening results for the clarifier at Tabriz refinery, using lime-sodium carbonate (before field test) and caustic soda are shown in Figures 1 to 3.

Precipitation softening results on well water in Tehran Refinery (Table 7) show that softening, using caustic soda results in efficient decrease in total hardness, compared to lime, however, the alkalinity (P, M) increases dramatically. This increase in alkalinity is due to built-up produced carbonate ions in treated water, as a result of precipitation reactions (Table 1).

According to Table 4 where $2\text{P} > \text{M}$, the amount of carbonate ions is $2(\text{M}-\text{P})$. Accordingly, based on precipitation results (Table 7) the amounts of carbonate ions in softening tests are 28 and 260 ppm, as CaCO_3 for lime and caustic soda, respectively. This means that although caustic soda has a good performance in softening but due to increase in alkalinity, it is not a good choice for Tehran Refinery's well water softening.

So the experimental results support relation (3). Applying relation (3) for Tehran Refinery's well water with the characteristics stated in Table 5 results in $450 > 676$, which represent that caustic is not a good choice for water softening in Tehran Refinery.

But the condition and the results of softening tests on the clarifier at Tabriz Refinery were different. The tests were conducted under real conditions, where the inlet and outlet streams and chemical injections, as well were almost continuous, but there were some fluctuations in test results, because of the change in steady-state condition such as, change in chemical characteristics of inlet stream. Then we had a series of softening results, recorded during the field test, using caustic soda, which lasted for 10 days. The softening test results, including, total hardness (TH) decrease, P and M alkalinity and pH for outlet stream are shown in Figures 1 to 3, respectively. To compare, the results for lime-sodium carbonate softening (before field test) are represented in the relevant figures. The Figure1 shows that caustic soda has better performance than lime-sodium carbonate and

Table 6. The typical analysis and operating parameters of inlet stream into clarifier

Temp.	Total Flow	Lime Dosage	Sodium carbonate dosage	Poly electrolyte dosage	pH	TH	Ca.H	P	M
$^{\circ}\text{C}$	M^3/hr	ppm as total flow				ppm, as CaCO_3			
45	120	125	125	0.7	8.6	620	450	8	120

Table 7. Precipitation softening results, using lime on raw water in Tehran refinery

Chemical	Dosage ppm	Temperature $^{\circ}\text{C}$	pH	TH	Ca.H	P	M
				ppm, as CaCO_3			
$\text{Ca}(\text{OH})_2$	250	90	7.8	300	110	4	150
$\text{Ca}(\text{OH})_2$	313	90	8.4	240	60	10	110
$\text{Ca}(\text{OH})_2$	375	90	8.9	210	80	14	40
$\text{Ca}(\text{OH})_2$	500	90	9.2	100	90	16	30
NaOH	250	90	9.45	120	18	46	224
NaOH	313	90	10.4	28	8	84	216
NaOH	375	90	10.4	26	7	90	256
NaOH	500	90	10.8	18	6	170	300

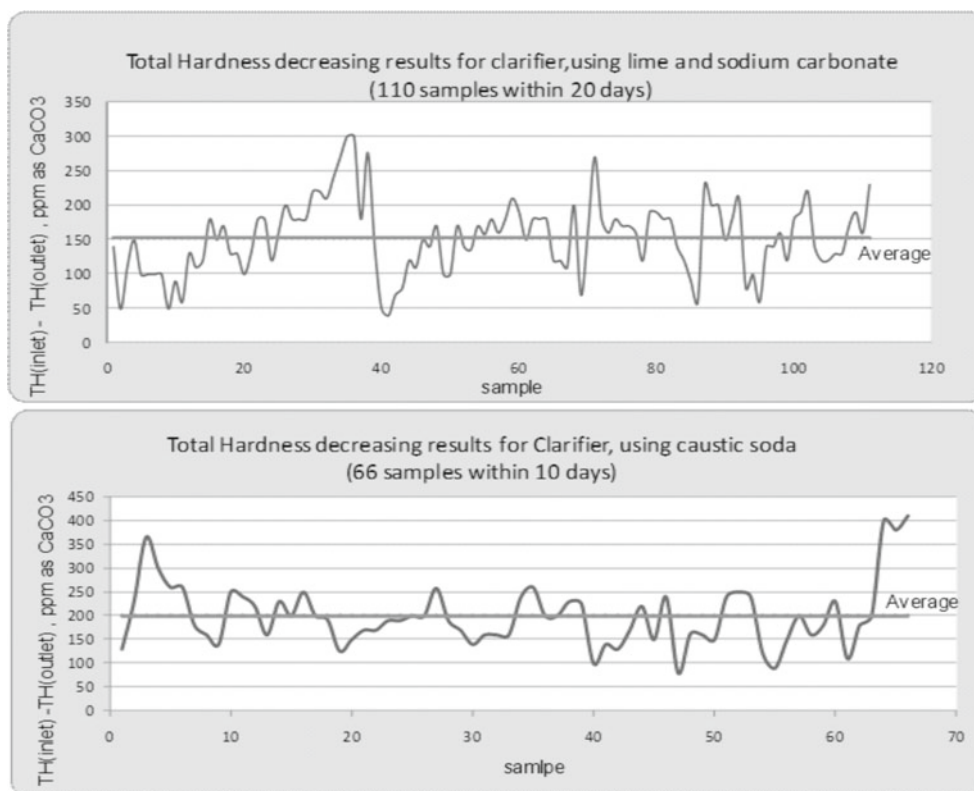


Figure 1. Total hardness decreasing results for the clarifier

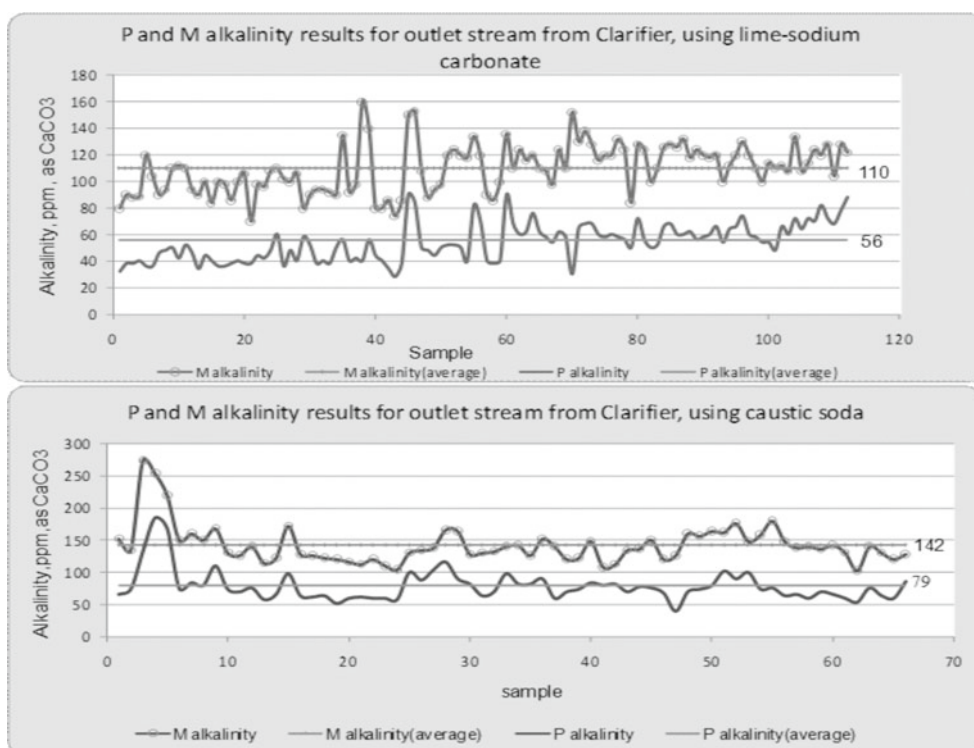


Figure 2. P and M alkalinity results for outlet stream from clarifier

the average decrease in total hardness are 150 and 200 ppm, as CaCO₃ for lime-sodium carbonate and caustic soda systems respectively. This is because, the amount of the produced sodium carbonate through softening reactions, using caustic soda is more than the amount of the injected sodium carbonate in the lime-sodium carbonates softening process. The softening reactions, using caustic soda (Table 3) show that the amount of produced sodium carbonate is 0.5 mole for each mole of consumed caustic soda. As the dosage of caustic soda during the field test was 125 ppm (3.125 moles/m³)

then the amount of the produced sodium carbonate is estimated 165.61 ppm (1.563 moles/m³), which is more than the injected sodium carbonate through lime-sodium carbonate softening process (125 ppm).

The alkalinity behaviors of both lime-sodium carbonate and caustic softening systems are shown in Figure 2 (P and M alkalinity) and Figure 3 (pH). These figures show that the alkalinity and the pH of the outlet stream for caustic soda softening is a little higher than lime-sodium carbonate softening. This can be considered as a result of caustic soda injection fluctuation and

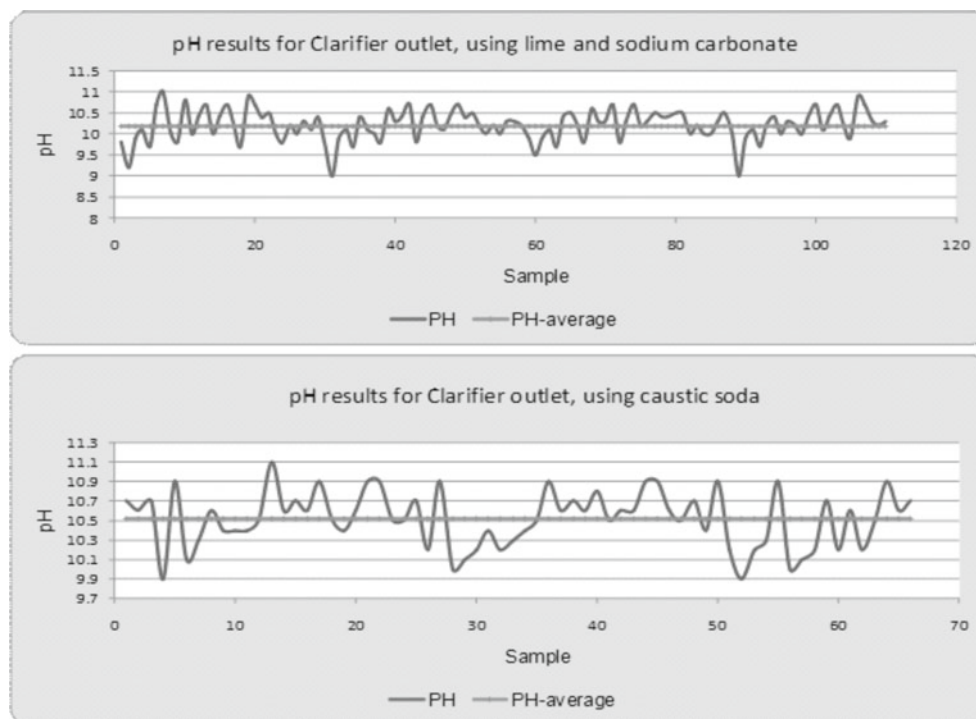


Figure 3. The pH results for softening, using lime and sodium carbonate

consequently, increase in caustic soda flow during the field test. The amount of carbonate ions in both cases can be estimated from Table 4. Figure 2 shows that the average amounts of P and M alkalinities for lime-sodium carbonate softening are 110 and 56 ppm, as CaCO_3 , respectively and therefore the amount of carbonate ions in effluent from clarifier are 108 ppm, as CaCO_3 (2(M-P); while $2P > M$). Similarly, for caustic softening (Fig. 2) the amount of carbonate ions are 126 ppm, as CaCO_3 . This shows that the difference between carbonate ions in two softening systems isn't significant. A small increase in ion carbonates during caustic softening can be considered as a result of increase in operating pH of caustic softening system. As Figure 3 shows the average

pH of effluent from clarifier is 10.2 for lime-sodium carbonate system and 10.55 for caustic soda system. The relationship between pH and solubility of CaCO_3 is shown in Figure 4. As Figure 4 shows when the pH value falls in the range of 10 to 11 the solubility of CaCO_3 remarkably increases with increase in pH value. Considering that the average pH value of treated water in lime-sodium carbonate and caustic systems are 10.2 and 10.55, respectively, the increase of 15–20 ppm, as CaCO_3 in carbonate ions in caustic softening system seems to be acceptable. Consequently it is concluded that the softening process on inlet stream of clarifier, using caustic soda does not impose any extra-carbonate ions on treated water.

These results support relation (3) and it recommends that the caustic soda is a good choice to replace lime-sodium carbonate.

CONCLUSION

Water softening process, using lime is considered as an undesirable process because of some weaknesses, such as operating upsets, difficulties in lime handling, environmental problems and cost of operation. The caustic soda has no such problems but there is some restriction on its use in water softening. The restriction on using caustic soda was investigated and presented in the form of a mathematical relation, which determines water hardness characteristics, suitable for caustic soda softening. Based on this relation, when the hardness characteristics of water is so that $\text{Ca.H} \geq 2(\text{M}-2\text{P})$; while $2\text{P} < \text{M}$ (where Ca.H is calcium hardness, M and P are alkalinity) the caustic soda can be used for softening, else the alkalinity of water will increase, due to increase in carbonate ions of treated water. Furthermore the mathematical relation was evaluated through conducting two series of experimental works. The first experimental work was done on well water at Tehran Refinery, where the hardness characteristics of raw water didn't satisfy

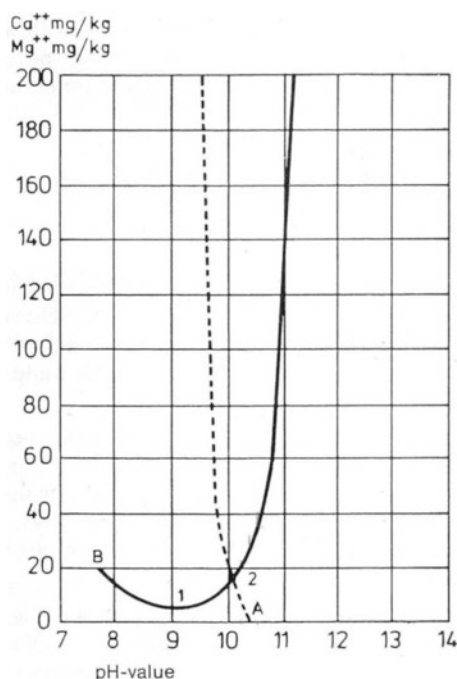


Figure 4. Solubility of $\text{Mg}(\text{OH})_2$ and CaCO_3 dependent on pH value¹². Curve A: $\text{Mg}(\text{OH})_2$ as Mg^{++} . Curve B: CaCO_3 as Ca^{++}

the restrictive mathematical relation and water treating, using caustic soda led to increase in alkalinity, due to increase in carbonate ions of treated water. The second experimental work was conducted on the clarifier (waste water softener) at Tabriz Refinery, where the clarifier's inlet stream hardness characteristics satisfied the restrictive mathematical relation. The field test on the clarifier showed that the caustic soda can be used for clarifier's inlet stream softening, rather than current lime-sodium carbonate chemicals, without any increase in alkalinity of treated water. Further, the field test results showed that the caustic soda has better performance than lime-sodium carbonate and it would be the best choice for water softening.

Acknowledgement

The authors would like to appreciate Ahar Branch, Islamic Azad University for the financial support of this research, which is based on a research project contract.

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