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# A Cost Effective Technique for Chemical Wastes Reduction in Lime Water Softening Process

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**Abstract.** Lime softening is an established process for treating hard water where both the flow rate and the bicarbonate hardness of raw water are high. It is very important to keep a lime softener to run at optimum working conditions as its performance can affect on downstream purification processes such as sludge handling and outlet hardness. The performance of this process is highly depending on lime dosage. Control of lime addition rate is currently adjusted manually based on chemical tests aimed at maintaining the simple and total alkalinities in a certain range. However, the current method for regulating lime dosage is not often correct and finding an alternative technique. In this paper, a critical analysis of softening process was presented and it was shown that simple and total alkalinities method can not be principally an accurate control for lime dosage. Our experimental results showed that electrical conductivity (EC) can play as a valuable indicator for following the performance of lime softening process and accurate dosage of lime can be well detected by measuring EC of softened water. Therefore, in this work, a new application of EC as an alternative method has been developed for control of lime dosage to reduce a considerable amount of chemical wastes in softening process.

**Keywords:** Alkalinity, Control, Electrical conductivity, Softening process, Waste reduction.

## 1. Introduction

### 1.1. Water Softening

The calcium and magnesium (hardness) ions in water causes scaling in boilers, heat loss in heat exchangers and more problems in industrial applications. Water softening is a familiar process for solving hard water problems. Separation and removal of hardness ions is called softening. Water softening is almost a common unit operation in many industries and makes the water suitable for use in cooling towers or prepares it for additional purification. For large volume water softening, the traditional process is called cold/hot lime softening and no any alternative processes have not been yet success to abandon it [1]. In cold softening process the lime (either hydrated lime ($Ca(OH)_2$) or quicklime ($CaO$) is dissociated into $Ca^{2+}$ and $2\,OH^-$. Some of the $OH^-$ will react with bicarbonate ($HCO_3^-$) in the water, to yield carbonate ($CO_3^{2-}$), which will combine with the original $Ca^{2+}$ hardness in the water, and the $Ca^{2+}$ introduced via dissolved lime to form $CaCO_3$, which precipitates out. The $OH^-$ can also react with $Mg^{2+}$ to form $Mg(OH)_2$, which precipitates out too.

Although lime softening, for decreasing water hardness, is a traditional and voluminous process in the water utilities, it is still remained as a cost-effective and favorite process in some conditions.[2]. This technique requires high capital cost nevertheless is recommended especially where both the flow rate and the bicarbonate (temporary) hardness of raw water are high due to its lower operating cost.

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## 1.2. Lime Softening Control

Upsets in lime softening process can occur frequently and quickly and it may take days to put it correct. Each process upset subsequently causes more problems in the operation of industrial water plant [3].

Having an accurate method for evaluating the performance of this process is highly important for a number of reasons. Firstly, the lime softening process is currently adjusted manually based on chemical tests aimed at maintaining the simple and total alkalinities in a certain range. These chemical tests not only waste water but also produce a considerable amount of chemical waste water during titration. Secondly, the current control method is often inaccurate and promotes rapid process upsets in lime softening whereas consistent quality of the treated water with minimum hardness is the most desirable. Thirdly, optimal control minimizes the resulting sludge waste that must be disposed of. Finally, it reduces the operating costs of water treatment.

Today, it is generally alkalinity (basicity) is controlled as an indicator for the optimum operating conditions [4]. This is usually achieved by regulating working conditions in softening clarifier such a way that the double *P*-alkalinity of treated water exceeds a little greater than the *M*-alkalinity [2].

However, the current inaccurate method for regulating lime dosage, in spite of its shortcoming, produces a considerable amount of chemical waste water during titration tests. Therefore, it is highly desirable to provide a more confident approach for guaranteeing the optimum performance (i.e. minimum hardness of treated water and less sludge) of lime softening process and this is the main object of this paper.

# 2. Theory

## 2.1. Lime/Soda Softening Reactions

By adding hydrated lime, the following reactions results in the precipitation of solid calcium carbonate and magnesium hydroxide [4]:

$$2CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2 \tag{1}$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \tag{2}$$

$$\left[Ca^{2+} + 2HCO_3^-\right] + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O \tag{3}$$

$$\left[Mg^{2+} + 2HCO_3^-\right] + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2(s) + 2H_2O \tag{4}$$

## 2.2. Current Control Based on Alkalinity

In the past, maximum reduction in the total hardness was the ultimate purpose of a softening process. Because calcium hardness is removed initially, the best control for evaluating lime softening process is to check the residual magnesium hardness concentration. Therefore, when lime-soda softening process was first introduced, there were no simple titration procedures for determination of magnesium hardness [5]. Thus, magnesium concentration was determined indirectly via phenolphthalein (*P*) and methyl orange (*M*) tests for alkalinity. This was accomplished by keeping a positive value for (OH) concentration about 5 ppm as $CaCO_3$, that is, 2P-M = 5 ppm. The procedure is still in use for more than a few decades. Even an accurate (2P-M) determination is only an indirect indication of magnesium hardness concentration not the minimum hardness. But today, with various ion exchange resins, excess lime only increases expenses for a water utility. Hence, a more logical approach for pledging minimum hardness in lime softening is needed.

## 2.3. A Novel Approach Based on EC Measurement

Softening reactions produce solid components (calcium carbonate and magnesium hydroxide) that finally will be removed from aqueous phase by precipitation. Therefore *TDS* in aqueous phase decrease by precipitation of $CaCO_3$(s) and Mg $(OH)_2$(s). Reduction in total ions due to removing calcium, magnesium and bicarbonates can be detected by measuring the conductivity of aqueous phase. It is a quick reliable and relatively of low cost test. Thus *EC* can play a vital role for understanding of microscopic reactions in the softening process. *EC* can really probe the progress of softening reactions and therefore, *EC* data should be used for evaluating the performance of softening process.

Compared to the current method, no chemical waste is produced and no chemical materials or water is needed for titration in this very cost effective alternative technique.

## 3. Experimental

Detailed protocols for the experiments, including titration and calculation methods, were based on the standard methods [6]. Sample water was obtained from a local river. The jar test was executed with the conventional apparatus with a six 1-liter beakers. An increasing quantity of commercial hydrated lime was added to each beaker and stirred at 50 rpm for 10 minute. After turning off the mixers and allowing the containers to settle for 15 minutes, the analyses of clear supernatants for total hardness, calcium, simple and total alkalinities, EC and pH were performed. The Jenway 4310 was used for measuring EC. Generated solid (mg/L) was measured by gravimetric method, i.e., evaporation of the samples.

## 4. Results and Discussion

Fig.1 shows changes of TH and (2P-M) as $CaCO_3$ of treated water as a function of added lime dosage. It shows that the total hardness first decreases in concentration to a minimum value and then increases with addition of lime. Fig. 1 shows a unique aspect of total hardness curve.

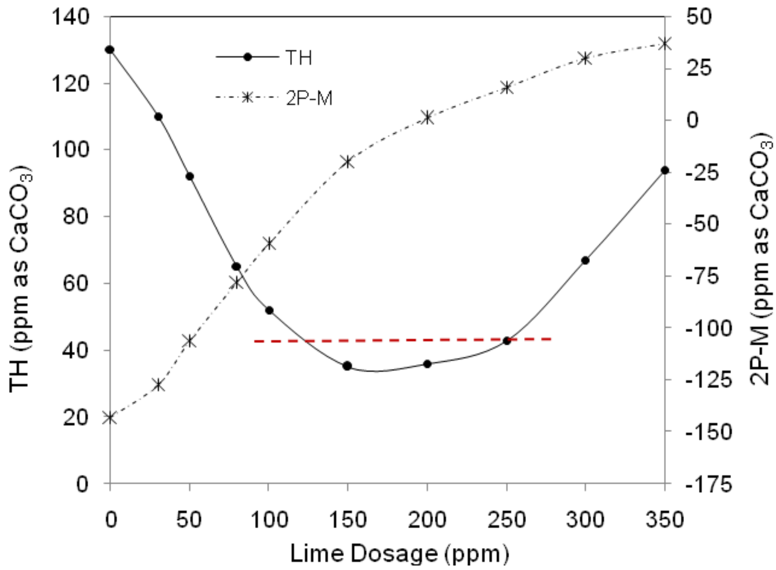


Fig. 1: Changes of TH and (2P-M) of treated water versus added lime dosage

Residual hardness has a concave shape with very low slope in minimum region. Therefore, the quality of treated water remains almost the same, either with 125 ppm or 250 ppm lime is added to the feed water.

It can be seen that the value of (2P-M) can not probe the minimum hardness in treated water. Accordingly, this general belief that a positive value of this parameter is a good signal for efficient performance of softening clarifiers is not correct.

Other operating parameters were also checked for finding a decisive parameter for proper evaluation of the performance of the lime clarifier.

Changes in total hardness (TH) and electrical conductivity (EC) of the treated water as a function of lime dosage have been shown in Fig. 2. It clearly shows that how accurately the minimum hardness in treated water can be probed by EC. This is the main discovery of this work. This idea was validated by many more experimental tests and it was found that the workability of *EC* analysis is a rule not an exception.

Employing EC as an alternative technique for monitoring of lime clarifiers has many advantages over the current method, including: no expensive chemical reagents is used, no waste water is generated and above all of them, accurate probing of this novel physical technique guarantees minimizing the amount of sludge is generated in this chemical precipitation process.

Table 1 shows the analysis and relevant experimental data for a sample of water. The first row of table 1 shows the characterization data of feed water. The changes of TH, EC and (2P-M) as a function of lime dosages are shown at the second, third and last column respectively. They show clearly that detection of minimum hardness by EC is much more accurate than the current method based on (2P-M). The 6th column of table 1 shows the amount of solid that is generated during various steps of lime addition. It can be seen that quality of treated water remains almost the same, either with 125 ppm or 250 ppm lime is added to the water sample but using lime dosage of 250 ppm may cause to waste about 50% and produce 440 mg/L solid waste instead of 300 mg/L in practice. Therefore, the operation of the lime clarifier results in 50% extra lime consumption and producing 140 mg/L more sludge in this case if control is based only on hardness of treated water.

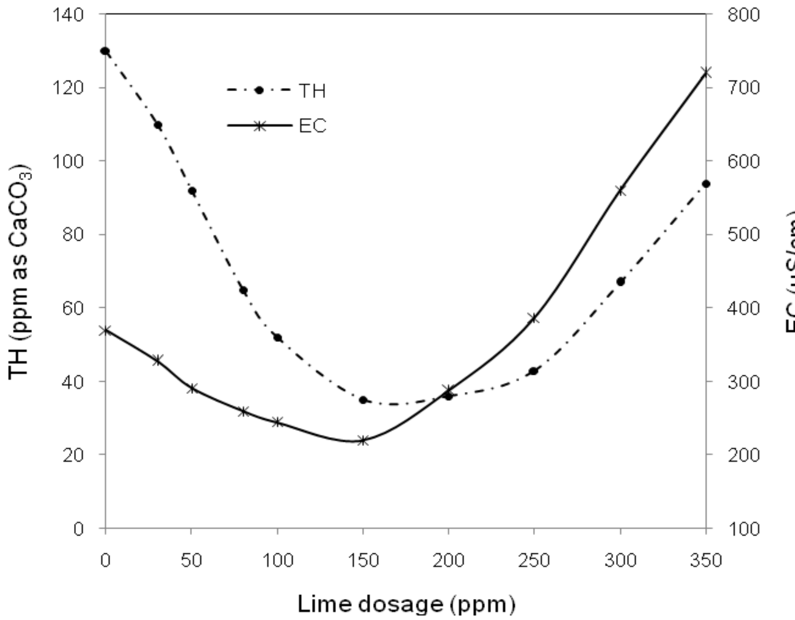


Fig. 2: Changes of TH and EC versus lime dosage at ESC clarifier feed water

Table 1: Analysis and relevant experimental data for a sample of water

| Lime dosage (ppm) | TH (ppm as $CaCO_3$) | EC (µS/cm) | P (ppm as $CaCO_3$) | M (ppm as $CaCO_3$) | Generated solid (mg/L) | 2P-M (ppm as $CaCO_3$) |
|---|---|---|---|---|---|---|
| 0 | 130 | 370 | 0 | 143 | 0 | -143 |
| 30 | 110 | 328 | 0 | 127 | 75 | -127 |
| 50 | 92 | 291 | 0 | 106 | 125 | -106 |
| 80 | 65 | 260 | 0 | 78 | 191 | -78 |
| 100 | 52 | 245 | 1 | 61 | 244 | -59 |
| 150 | 35 | 220 | 10 | 40 | 351 | -20 |
| 200 | 36 | 289 | 23 | 45 | 400 | 1 |
| 250 | 43 | 387 | 36 | 56 | 440 | 16 |
| 300 | 67 | 560 | 56 | 82 | 491 | 30 |
| 350 | 94 | 720 | 72 | 107 | 530 | 37 |

## 5. Conclusions

Analysis of experimental data obtained from a full scale lime clarifier showed that evaluating the lime clarifier performance based on P and M alkalinities is not accurate. A new monitoring method based on EC measurement has been developed for control of softening processes. This is a new approach and it has the following advantages:

(a) No chemical waste is produced in this new technique and no chemical is needed.

(b) The cost of tests is reduced to less than twenty percent.

(c) The volume of sludge and also treated hardness are usually reduced during lime softening process.

(d) It is an eco-friendly alternative technique for routine tests for optimizing the performance of lime clarifier.

## 6. Acknowledgement

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