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Puffing as a totally green method for monitoring of hot/cold lime softening process

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ABSTRACT

Hot/cold lime softening process (LSP) is an established process for water conditioning. LSP is currently monitored with various chemical analyses such as measuring simple and total alkalinities, pH, and hardness of softened water. The current monitoring is a labor-intensive task, which consumes various chemicals and generates a considerable amount of chemical wastewater during daily routine tests. Experiences in many industrial softeners show that the results of the traditional chemical method are not often conclusive. In this work, the weakness of the current chemical method for LSP monitoring has been experimentally verified and the effectiveness of an eco-friendly clean technology, based on puffing, has been introduced. The new method functions via comparing the measured electrical conductivities of softened water before and after puffing. As a totally green method, it has several advantages such as lack of need for any chemical reagent, easy and reliable testing, significant reduction in test costs, and chemical wastes compared to the conventional chemical method.

Keywords: Lime softening process; Monitoring; Chemical method; Puffing method; Totally green method

1. Introduction

1.1. Lime softening process

Lime water softening is a key process in many industries for separation of hardness ions**,** mainly consisted of calcium Ca^{2+} and magnesium Mg^{2+}, to make the water suitable for use in cooling towers, or to prepare it for additional purification, or as a reverse osmosis pretreatment [1–3].

Lime causes a reduction in the temporary hardness [4], i.e. the calcium and magnesium associated with the bicarbonate alkalinity [5]. The following chemical equations, lime softening reactions, illustrate the reaction between hydrated lime and bicarbonate hardness [6]:

$$CO_2 + Ca(OH_2) \rightarrow 2CaCo_{3(s)} + H_2O \quad (1)$$

$$Ca(HCO_3)_2 + Ca(OH_2) \rightarrow 2CaCo_3(s) + 2H_2O \quad (2)$$

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$$\mathrm{Mg(HCO_3^-)_2 + 2Ca(OH)_2 \rightarrow 2CaCo_{3(s)} + Mg(OH)_{2(s)} + 2H_2O} \tag{3}$$

The solubility products of $CaCO_3$ and $Mg(OH)_2$ are [4]:

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 5 \times 10^{-9}$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 9 \times 10^{12}$$

The calcium carbonate and magnesium hydroxide are insoluble and simultaneously remove the calcium, magnesium, and bicarbonate ions from the solution [7,8]. Currently, many lime clarifiers use only lime instead of lime-soda ash because the other methods, such as cationic ion exchangers, for removing non-carbonate (permanent) hardness are more feasible [7,9].

Monitoring of a softening process is important for a number of reasons. First, consistent quality of the softened water with minimum hardness is most desirable. Second, optimal-monitoring results with minimum sludge must be disposed off. Finally, it reduces the operating costs of water conditioning. Therefore, lime softening process (LSP) must be monitored multiple times every day in many cases.

1.2. Current practice for LSP monitoring

Regulating pH, simple (P) and total (M) alkalinities, and measuring total hardness (TH) are generally suggested for monitoring of lime clarifiers performance [10,11].

Softening reactions are highly sensitive to pH as solubility of magnesium hydroxide decreases in pH more than 10, but the solubility of calcium carbonate increases at such high pH [12].

As the monitoring of lime process by pH is not practically accurate, currently measurement of P and M alkalinities are utilized as an indicator for optimum operating conditions. This is usually achieved by regulating working conditions in such a way that $(2P–M) \geq 5$ ppm as $CaCO_3$, where P and M are simple and total alkalinities of softened water, respectively [9]. However, as the control based on alkalinities is not conclusive enough, many operators prefer to measure simultaneously hardness and pH as a complementary test. The current monitoring is a labor intensive task which consumes chemicals and generates chemical wastes. Consequently, developing an effective method for LSP monitoring is highly desirable for both environmental and operating expense points of view.

2. Innovation on monitoring of LSP

2.1. Concurrency of electrical conductivity with hardness in LSP

Electrical conductivity (EC) can play a vital role in understanding the microscopic reactions in the LSP as it closely probes the progress of softening reactions.

Our tests showed that with lime addition to water, both, TH and EC of softened water decrease to a minimum value, due to the precipitation of insoluble products but then increase gradually as a result of excess lime. In addition, the bench-scale tests demonstrated clearly that the minimum hardness in the LSP is concomitant with minimum EC.

The utilization of EC to oversee the chemical process in liquid phase is itself not new. EC has been utilized in the past as a means of controlling other processes such as for regulating the rate of blow down in power plants [9] or for characterization of colloidal gas aphrons [13]. However, there is no report in the scientific literature to show that EC of treated water can be utilized for the monitoring of LSP.

2.2. Puffing method

From a fundamental chemistry perspective, the most direct way to identify the optimal lime dose to achieve water quality objectives is to measure the calcium concentration as a function of consumed lime dose [14]. The optimum lime dose is the lowest dose at which the TH becomes minimized. For many types of water, the minimum TH may be achieved by examining a wide range of lime doses; a quick grab sample measurement of effluent TH is insufficient to determine operational efficiency [10].

Based on concurrency of EC with hardness in softened water, a simple and reliable technique, called puffing method, has been developed here to determine operational efficiency of LSP with detecting EC. Detailed description of the puffing method has been outlined in the US patent, US 20130098842 A1 [15,16]. The most interesting aspect of the puffing method is that the correct dose of lime can be checked by only a sample of softened water.

The method is based on the EC measurements of a treated water sample before and after puffing. If EC of the treated water after puffing is lower than EC of the treated water, the softening process is unsatisfactory and the lime dosage must be decreased. If EC of the treated water after puffing is higher than EC of the treated water, then the lime dosage is not enough and must be increased. If EC of the treated water after puffing is roughly equal to EC of the said treated water, then the lime dosage is optimum and water softener works in optimum condition.

Compared to the conventional method, the puffing method is a quick, reliable, and very low-cost test. No chemical waste is generated and no chemical material is needed for test in this very cost-effective technique.

3. Materials and methods

Hardness and alkalinities were measured by titration method. Detailed protocols for all chemical tests including alkalinities and hardness measurement (by titration method), EC, and total dissolved solid (TDS) measurements were based on the standard methods for examination of water and wastewater [17]. All analysis tools and chemicals reported in this paper were supplied by the central lab of Esfahan oil refinery company (EORC). EORC is a well-established company located in the central part of Iran, it can soften 180 $m^3 h^{-1}$ hard water from the Zayandeh-rood river or a metropolitan source. All on-site analysis data recorded or reported in this paper were obtained in the local central lab of EORC.

EORC utility section uses four hot lime clarifiers and also two ion-exchange units for generation of soft water, but only the performance of lime clarifiers has been considered in this paper.

For bench-scale tests, feedwater from Zayandeh-rood river and a metropolitan source have been used.

The jar tests were executed with a conventional apparatus having four one-liter beakers. An increasing quantity of lime was added to each beaker and stirred at 200 rpm for 5 min. After turning off the mixers and allowing the containers to settle for 15 min, the analyses of clear supernatants for hardness, calcium, alkalinities, EC and pH were performed. The Jenway 4310 was used for measuring EC.

4. Results and discussion

4.1. Weakness of current LSP control based on chemical analysis

Table 1 shows the analysis results of feed-water samples for hot and cold LSP at EORC.

Fig. 1 shows the relationship between TH and (2P–M) of softened water as a function of added lime for a typical hot lime softening condition at 90 ℃ at EORC clarifiers. It shows that the TH of softened water initially decreases to a minimum value and then increases while the curve of (2P–M) always progressively increases with addition of lime.

Fig. 1 shows a unique feature of TH curve vs. added lime dosage. Residual hardness curve in a softening process has a concave shape.

This figure clearly demonstrates that the current chemical control for a softening process, i.e. (2P–M) ≥ 5 ppm as $CaCO_3$, has no meaningful affiliation with quality of softened water as the value of (2P–M) cannot probe correctly the minimum hardness in softened water.

The similar inconsistency between the current chemical methods of control with quality of softened water can be seen in Fig. 2 for a feedwater sample with a high hardness.

This discrepancy of the current chemical monitoring of softening process has also been occurred in the cold softening process shown in Fig. 3.

Figs. 1–3 show clearly the inadequacy of the current performance control based on the alkalinities, because the minimum hardness was occurred where (2P–M) is less than zero for all three water samples. They also demonstrate this main point that measuring

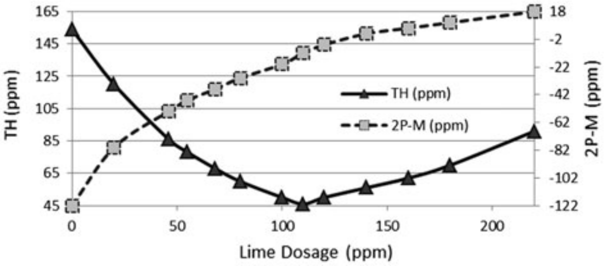

Fig. 1. Changes of TH and (2P–M) of softened water vs. lime dosage in hot LSP for a water sample with moderate hardness.

Table 1
Analysis of feedwater samples for the hot and cold LSP

Water sample hardness	TDS (ppm)	TH (ppm as $CaCO_3$)	P (ppm as $CaCO_3$)	Permanent hardness (ppm as $CaCO_3$)	Temporary hardness (ppm as $CaCO_3$)	pH	EC (μS/cm)	M (ppm as $CaCO_3$)	2P–M (ppm as $CaCO_3$)
Moderate	160	154	0	32	122	8.12	310	122	−122
High	738	370	0	170	200	7.9	1,640	200	−200
High	677	545	0	243	302	7.38	1,378	302	−302

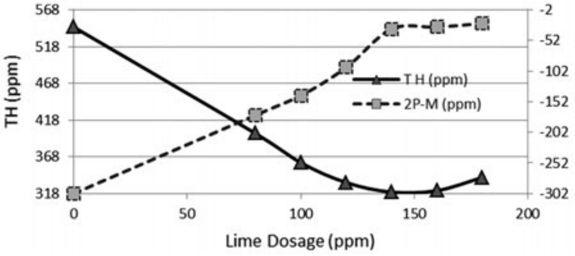

Fig. 2. Changes of TH and (2P–M) of softened water vs. lime dosage in a hot LSP for a water sample with a high hardness.

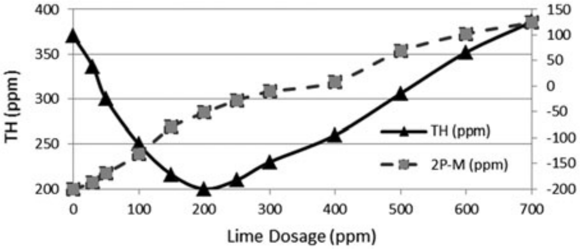

Fig. 3. Changes of TH and (2P–M) of softened water vs. lime dosage in the cold LSP for a water sample with a high hardness.

only the TH is not enough to ensure probing the optimum operating conditions in the softening process because of the concave nature of TH curve.

Therefore, regulating the performance of a hot or cold LSP based on measurement of P and M alkalinities is not only inaccurate, but it may lead the operator to make an incorrect action.

4.2. Concurrency of EC with hardness in softened water

Changes in TH and EC as a function of lime dosage have been shown in Fig. 4 for a typical water sample with a moderate hardness in the hot lime softening condition at 90 ℃ at EORC clarifiers.

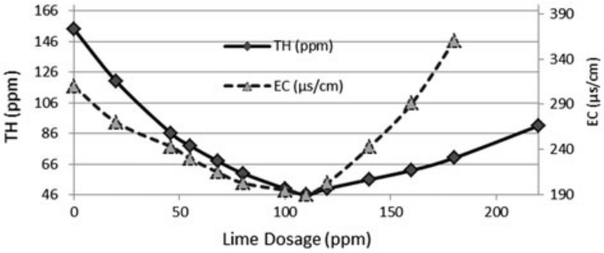

Fig. 4. Changes in TH and EC as a function of lime dosage in hot LSP for a water sample with a moderate hardness.

It shows clearly that the minimum hardness in softened water can be probed accurately by EC as the minimum EC follows exactly the minimum hardness. Fig. 5 shows the corresponding results for a typical water sample with a high hardness.

The idea was validated by many more experimental tests and it was found that EC can monitor the trend of residual hardness in the softened water even in the cold LSP as shown in Fig. 6.

Fig. 7 shows the change of EC and (2P–M) vs. TH for a water sample with a high hardness. It shows that the minimum hardness and the minimum EC exactly coincide, while there is no meaningful affiliation between (2P–M) and the minimum hardness. Changes

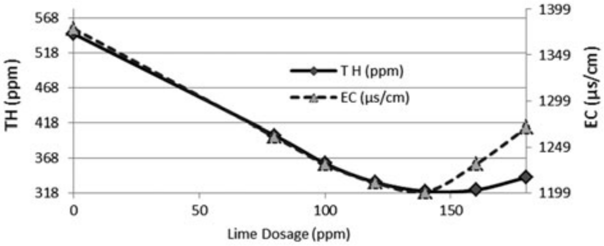

Fig. 5. Changes in TH and EC as a function of lime dosage in hot LSP for a water sample with a high hardness.

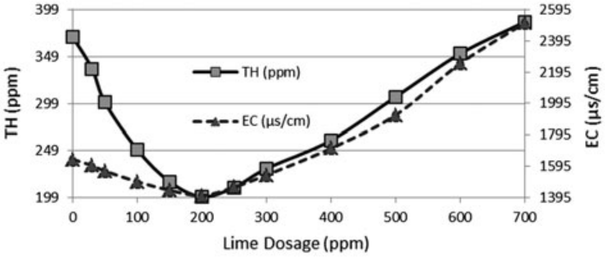

Fig. 6. Changes in TH and EC as a function of lime dosage in the cold LSP for a water sample with a high hardness.

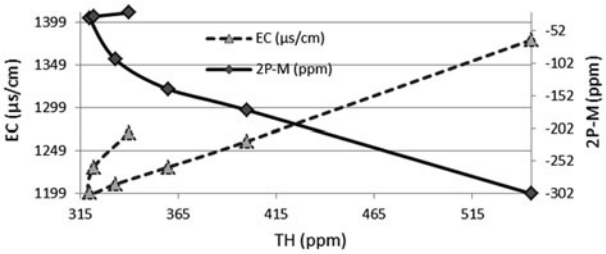

Fig. 7. Change of EC and (2P–M) vs. TH for a water sample with a high hardness.

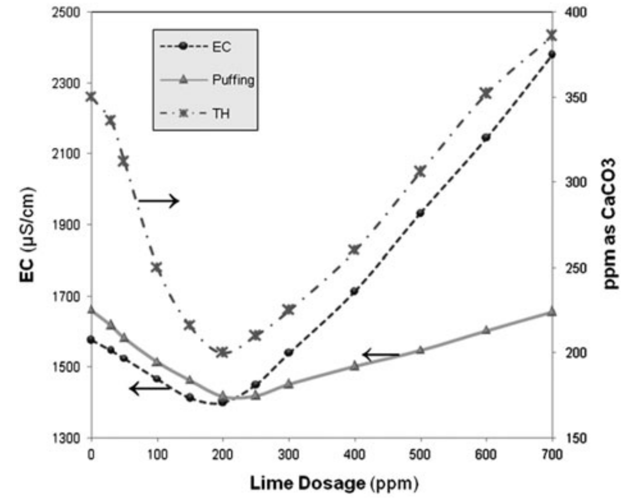

Fig. 8. Changes in EC, TH, and puffing test as a function of lime dosage.

of EC and (2P–M) vs. TH for other water samples for the hot or cold lime process are similar to Fig. 7.

4.3. Validity of the puffing method for monitoring the performance of lime softening

As outlined in Section 2.2, the puffing method is based on measurement of EC of treated water sample before and after puffing. Changes in EC of treated water sample, TH and EC of treated water sample after puffing (the puffing test) as a function of lime dosage have been shown in Fig. 8. There is a minimum value for the puffing test that exactly corresponds to the minimum hardness of softened water and minimum EC of softened water before puffing. Therefore, Fig. 8 shows clearly that the optimum lime dosage can be probed accurately with measuring the EC of softened water sample before and after puffing, since the minimum ECs follow exactly the minimum hardness. The technique was validated by many more experimental tests and it was found that the puffing method can monitor correctly the performance of the hot/cold LSP.

This novel physical technique has been applied for the first time in performance monitoring of hot lime clarifiers at EORC. The results have been so successful that it has replaced the conventional (current) chemical analyses at EORC.

5. Conclusion

The current monitoring and evaluating the performance of LSP, based on chemical analyses, is often not correct. An effective technique based on EC measurement has been introduced to monitor properly the performance of LSP.

This novel technique has several advantages—such as being safer, lack of need for any chemical reagent, being a very straightforward and reliable test—resulting in significant reduction in operating costs and a considerable reduction in wastes during LSP handling compared to the current chemical method.

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