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Defluoridation Technique Based on Optimization of CaCl₂ Dosage

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Abstract : Based on an MgO-CaCl₂-CaO-HCl defluoridation system, and series experiments were performed to determine the optimum dosage of CaCl₂ by Groundwater fluoride removal from local fluoride contaminated water filter. The permissible limits of various water quality parameters have within the limits while determining the best possible dose. Using 6 ml of 7.5 % CaCl₂ /lit produce a residual F⁻ concentration of 0.53 ppm in the HCl treated pH adjusted water, this is lower concentration of residual F⁻. However, lower dosage of CaCl₂ at 3 ml/lit. CaCl₂ was chosen to reduce the cost of operation. Notice, that the TDS value of HCl treated pH adjusted water at the optimum dosage of 3.0 ml of 7.5 % CaCl₂ soln. is 1380.0 ppm, an increase of 170.0 ppm as compared to 1210.0 ppm in raw water.

Key words : Groundwater, Fluoride, CalCl₂, Defluoridation

Introduction

Fluoride is essential for the development of bones, dental and tooth enamel. It is harmful when it exceeds the permissible limit of 1.5 mg l–1in water¹.According to UNICEF estimates 25 countries around the world are suffering from fluorosis².In India, nearly 200 districts in 17 states with more than 6 million people are seriously affected by fluorosis ³. Initially enamel gets damaged and teeth become yellow⁴⁵. High concentration of fluoride occurs naturally in ground water and causes fluorosis⁶⁷ which primarily affect the teeth and bones in the body⁸.The most affected states in India are Andhra Pradesh and Rajasthan. These methods are commonly adopted for fluoride removal from water includes adsorption, coagulation, membrane, ion exchange, electrochemical ⁹⁻¹⁴. All of above mentioned methods have their own merits and demerits and have been extensively reviewed in the literature ^{15 16}.We have reported the initial results of field and laboratory trials of a MgO-CaCl₂-CaO-HCl based filter. Also we have reported MgO and CaOoptimization successfully reduced the fluoride from ground water^{19 20}. These method is based on a delfluoridation technique developed in India few years ago^{21 22 23}, using MgO-CaCl₂-Lime-NaHSO₄, which has seen successful field trials in several, places this country. Sludge obtained from defluoridation filters based on MgO, CaCl₂, CaO and HCl have been used to make cement stabilized mud blocks using local soil with high sand content²⁴

Experimental

Technical grade MgO, (light) waspurchased from Konoshima Chemical Co. Japan, CaO was purchased locally from Lakshman garh (R a j a s t h a n) in 5 kg plastic sacks. CaCl2.2H2O(AR), conc.HCL(AR) was purchased from CDH(India) and Rankem (India). respectively.

Six 1.0 lit. fluoride contaminated ground water samples from (Manish T.W.) were treated with 2.0, 3,0, 4.0, 5.0, and 6.0 ml of 7.5% CaCl₂ solution (in DM water) with constant stirring. Next, 0.8 gmMgO and 0.75gm CaO were added to each sample and the mixture stirred vigorously for 5 min and left overnight (16 hr.). Next day it was observed that white colored flock had settled at the bottom. The clear supernatant water was filtered using a Whatman 42 filter paper and 400 ml of the filtrate was treated with 0.38 N HCl (prepared in DM water) till the final pH was 8.0.The different volumes of HCl which were required in each case. The results of the experiments are discussed in section fig1.

The chemically treated water after 16 hand pH adjusted water after HCl treatment were analysed as follows. The Fluoride concentration was measured using an Ion Selective Electrode (Orion-Thermo Scientific, USA) using TISABIII as buffer.pH, TDS were measured using Hannap Hand TDS meter (USA). Calcium and magnesium hard ness was determined by EDTA method using Pand Rindicator. Alkalinity was determined by titrating with dil H₂SO₄. Chloride was determined by titrating with AgNO₃ solution. Sulphate was determined by a colorimeter (Instruments India Ltd) using Turbidity method.

Result and Discussion

Water samples brought from the village Pilaniyon Ki Dhani (Manish T.W.) with various dosage of 7.5% CaCl₂ solution while keeping the dosage of MgO and CaO constant, at 0.8 gm/lit. and 0.75 gm/lit. and analysing the water after 16 hrs. and after pH adjustment with HCl, we found that on increasing CaCl₂ dosage, the volume of HCl consumption decreases from 9.9 to 8.3 ml (fig. 1). This may be due to increased formation of HCl from hydrolysis of CaCl₂.



Fig. 1 Optimization of CaCl₂ Dosage: Variation of Vol. of 0.38 N HCl required to bring the pH of 400 ml of 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln., treated water to a final pH of 8(water: PKD, Manish T.W.)

The pH of the water after 16 hrs. was basic with an avg. pH of 10.9 due to the addition of CaO, MgO and CaCl₂. The pH was reduced to 8.0 (fig. 2) on treatment with 0.38 N HCl.



Fig. 2Optimization of $CaCl_2$ Dosage: Variation of pH in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW pH = 8.5 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

We found that using 3.0 ml of 7.5 % $CaCl_2$ /lit. dosage, produced water with least residual F⁻ conc. of 0.733 ppm, this was chosen to be the optimum dosage of 7.5 % $CaCl_2$ solution (fig. 3). Using 6 ml of 7.5 % $CaCl_2$ /lit. produce a residual F⁻ conc. of 0.53 ppm in the HCl treated pH adjusted water, this is lower concentration of residual F⁻. However, lower dosage of $CaCl_2$ at 3 ml/lit. $CaCl_2$ was chosen to reduce the cost of operation.



Fig. 3 Optimization of CaCl₂ Dosage: Variation of F^- conc. in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW F^- = 2.32 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

When the dosage 7.5 % CaCl₂ solution varied from 2.0 ml to 6.0 ml the TDS of both water, after 16 hrs.and HCl treated pH adjusted water increased from 1270.0 to 1330.0 ppm and 1360.0 to 1460.0 ppm respectively (fig. 4). Notice, that the TDS value of HCl treated pH adjusted water at the optimum dosage of 3.0 ml of 7.5 % CaCl₂ soln. is 1380.0 ppm, an increase of 170.0 ppm as compared to 1210.0 ppm in raw water. This is within the permissible limit of 2000 ppm for drinking water.



Fig. 4 Optimization of CaCl₂ Dosage: Variation of TDS in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW TDS = 1210 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

The Cl⁻ conc. was found to continuously increase, in water after 16 hrs. from 332.0 ppm to 427.0 ppm (fig. 5).



Fig. 5 Optimization of CaCl₂ Dosage: Variation of Cl⁻ in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW Cl⁻ = 212 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

This is because of increasing dosage of 7.5 % $CaCl_2$ soln. being added in each of the water samples in the experiment. Notice, that the Cl⁻ conc. in HCl treated pH adjusted water is more than the water after 16 hrs. because of the addition of HCl. The Cl⁻ conc. at optimum dosage of 3.0 ml of CaCl₂ soln. is 617.0 ppm. This value is within the permissible limit of 1000 ppm. Notice, that the Cl⁻ conc. increased by 405.0 ppm in this process as compared to raw water which had a Cl⁻ conc. of 212.0 ppm.

There is no consistent trend in Mg^{2+} Hardness on increase CaCl₂ dosage for both water after 16 hrs. and HCl treated pH adjusted water. The Mg^{2+} Hardness value of the HCl treated pH treated water at the optimum dosage of 3.0 ml of 7.5 % CaCl₂ soln. is 68.0 ppm (fig. 6), an increases of 32.6 ppm as compared to 35.4 ppm in raw water is within the permissible limit of drinking water.



Fig. 6 Optimization of CaCl₂ Dosage: Variation of Mg^{2+} Hardnessin water after 16 hrs. and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW $Mg^{2+} = 35.4$ ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

The Ca^{2+} Hardness increases from 20.0 to 24.0 ppm on increasing $CaCl_2$ dosage for water after 16 hrs. and 18.0 to 24.0 ppm for HCl treated pH adjusted water (fig. 7).



Fig. 7 Optimization of CaCl₂ Dosage: Variation of Ca²⁺Hardness in water after 16 hrs. and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW Ca²⁺ = 14.0 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

Notice, that the Ca^{2+} Hardness value of the HCl treated pH adjusted water at optimum dosage of 3.0 ml/ lit of 7.5 % $CaCl_2$ is 16.0 ppm, an increase of 2.0 ppm from Ca^{2+} Hardness value in raw water. Though an increasing quantity of calcium is being added, the Ca^{2+} Hardness does not increase much because of precipitation of $CaCO_3$ by the following reaction.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \qquad (1)$$

$$Ca^{2+} + HCO_3^{-} + OH^{-} \rightarrow CaCO_3 \downarrow + H_2O \qquad (2)$$

The Total Hardness of both water after 16 hrs. and HCl treated pH adjusted water does not show any consistent trend on varying the dosage of CaCl₂ soln. (fig. 8).



Fig. 8 Optimization of CaCl₂ Dosage: Variation of Total Hardness in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW T.H. = 49.4 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

Notice that the Total Hardness of HCl treated pH water at the optimum dosage of $3.0 \text{ ml } 7.5 \% \text{ CaCl}_2$ soln. was 84.0 ppm, an increases of 34.6 ppm from the Total Hardness value in raw water. The HCO₃⁻ conc. (in CaCO₃eqv.) decreases 488.0 ppm to 372.0 ppm in water after HCl treated water (fig. 9).



Fig. 9Optimization of CaCl₂ Dosage: Variation of HCO₃⁻ in water after 16 hrs.and pH adjustment with HCl Conditions (Water: PKD, Manish T.W., RW HCO₃⁻ = 940 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

This is because on increasing $CaCl_2$ dosage, HCO_3^- is being removal from the soln. in water after 16 hrs. (refer to equation4). Also in HCl treated pH adjusted water most of the $CO_3^{2^-}$ changes to HCO_3^- . However, since increasing calcium dosage also removes $CO_3^{2^-}$ from the soln. (refer to equation 3). Therefore their HCO_3^- conc. in HCl treated pH adjusted water decreases, on increasing the dosage of $CaCl_2$ (fig. 10). Also notice that the $CO_3^{2^-}$ conc. in water after 16 hrs, decreases for the same reason.



Fig. 10 Optimization of CaCl₂ Dosage:Variation of $CO_3^{2^-}$ in water after 16 hrs and pH adjustment with HCl Conditions (Water: PKD,Manish T.W., RW $CO_3^{2^-} = 30$ ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

On increasing the CaCl₂ dosage it was found that the Total Alkalinity (in CaCO₃eqv.) decreases, from 400 to 380.0 ppm in HCl treated pH adjusted water, this is due to lowing of both CO_3^{2-} and HCO_3^{-} . Notice, that the Total Alkalinity (in CaCO₃eqv.) at the optimum dosage of 3.0 ml /lit. of CaCl₂ soln. is 375.0 ppm as compared to Total Alkalinity of raw water at 830.0 ppm (a decrease of 455.0 ppm) (fig. 11). This value is within the permissible limit of 600.0 ppm for the Total Alkalinity (in CaCO₃eqv.) in drinking water. After optimisation of CaCl₂ dosage, notice that all the values, are within the permissible limit.



Fig. 11Optimization of CaCl₂ Dosage: Variation of Total Alkalinity in (CaCO₃ eqv.) in water after 16 hrs. and pH adjustment with HCl Conditions (Water: PKD,Manish T.W., RW T.A. = 30 ppm, 0.75 gmCaO + 0.8 gmMgO + x ml 7.5% CaCl₂ soln.).

Conclusion

From the above experiments we can conclude using 6 ml of 7.5 % $CaCl_2$ /lit.produce a residual F⁻ conc. of 0.53 ppm in the HCl treated pH adjusted water, this is lower conc. of residual F⁻. However, lower dosage of CaCl₂ at 3 ml/lit. CaCl₂ was chosen to reduce the cost of operation. Notice, that the TDS value of HCl treated

pH adjusted water at the optimum dosage of 3.0 ml of 7.5 % $CaCl_2$ soln. is 1380.0 ppm, an increase of 170.0 ppm as compared to 1210.0 ppm in raw water.

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