

Optimization of MgO Dosage in MgO-CaCl₂-Lime-HCl Based Defluoridation Technique

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Abstract: A series of experiments were performed to determine the optimum dosage of MgO for fluoride removal from local fluoride contaminated groundwater based on a MgO-CaCl₂-Lime-HCl defluoridation system. Since the defluoridation process is to be utilized in a fluoride filter, the permissible limits of various water quality parameters have also to be met while determining the best possible dose. An optimum dosage of 0.8 g/L MgO was found. This dosage achieves at the same time the maximum fluoride removal, minimum concentration of residual Total Hardness and TDS in the defluoridated water.

Keywords: Defluoridation, Fluoride removal, Magnesium oxide

Introduction

Intake of excess fluoride from drinking water with excess of 1.5 ppm^{1,2} causes fluorosis which primarily effects the teeth and bones in the body³. Initially the teeth become yellow and then the enamel gets damaged permanently^{4,5}. The joints start paining while the bones become brittle and in severe cases symptoms of knock knee appear^{6,7}. Acidity, constipation are also common complains. The various health effects of fluoride have been well documented in the literature⁸⁻¹². According to UNICEF estimates 25 countries around the globe are suffering from fluorosis¹³ and forefront among them being India, China, Mexico, Argentina and Kenya. According to Hydrology and Water Resources Information System for India¹⁴, 90 million people in India in 15 states including 6 million children are affected by fluoride. The most fluoride affected states in India being Andhra Pradesh and Rajasthan.

The techniques commonly adopted for fluoride removal from water include adsorption^{15,16}, ion exchange^{15,17,18}, coagulation¹⁹, membrane based or electrochemical ones²⁰. Each of them have their own merits and demerits and have been extensively reviewed in the literature^{21,22}.

We have recently reported the initial results of laboratory and field trials of a MgO-CaCl₂-Lime-HCl based filter^{23,24}. The method is based on a defluoridation technique developed in India few years ago²⁵⁻²⁷ using MgO-CaCl₂-Lime-NaHSO₄, which has seen successful field trials in several, places this country. Since this method is sensitive to bicarbonate concentration, the chemical dosage has to be carefully fine-tuned so as to meet the drinking water quality parameters. Using dosage guidelines as rough indicators from the parent technique²⁸⁻³¹, a chemical dosage of 1.0 g MgO, 0.75 g CaO, 4.0 mL CaCl₂ (in demineralised water) was arrived at and used in laboratory²³ and field trials reported earlier²⁴. In order to be able to treat large volumes of fluoride contaminated local ground water it was decided to fine tune the dosage of the various chemicals used for the process and in this paper we report the dosage optimization study of MgO for this new defluoridation system.

Experimental

Technical grade MgO, (light) was purchased from Konoshima Chemical Co. Japan. CaCl₂.2H₂O (AR), conc. HCL (AR) was purchased from CDH (India) and Rankem (India) respectively. CaO (Mahalaxmi Traders, Ajmer) was purchased locally from Lakshmanagarh in 5 kg plastic sacks.

Eight 1.0 L raw water samples from (Pilaniyon kin Dhani, main tube well) were treated with 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2 g MgO with constant stirring. Next, 0.75 g CaO and 4.0 mL of 7.5% CaCl₂ (in demineralised water) was added to each sample and the mixture stirred vigorously for 5 min and left overnight (16 h). On the next day it was observed that the white coloured floc 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 demineralised water) till the final pH was 8.0. Different volumes of HCL were required in each case (Figure 1).

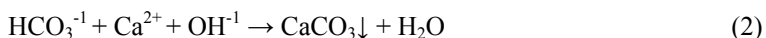
The raw water, chemically treated water after 16 h and pH adjusted water after HCl treatment were analysed as follows. The Fluoride concentration was measured using an Ion Selective Electrode (Orion-Thermo Scientific, USA) using TISAB III as buffer. pH, TDS were measured using Hanna pH and TDS meter (USA). Calcium and magnesium hardness was determined by EDTA method using P and R indicator. Alkalinity was determined by titrating with dil H₂SO₄. Chloride was determined by titrating with AgNO₃ solution. One representative sample of raw was analysed for nitrate using a Shimadza 1800 UV-VIS Spectrophotometer by measuring the absorbance at wavelengths at 220 nm and 270 nm. Na⁺ and K⁺ were measured using a flame photometer (ESICO). Sulphate was determined by a colorimeter (Instruments India Ltd) using Turbidity method.

Results and Discussion

The role of MgO in the water defluoridation process is based on the removal of fluoride in the lattice of Mg(OH)₂ formed by the hydrolysis of MgO.



The lowering of bicarbonate concentration in the raw fluoride contaminated water is crucial in the fluoride removal process. This is because the presence of bicarbonates would consume an equivalent more of HCl in the last pH adjustment step. For the above reason, more addition of lime in the process helps to provide adequate OH⁻¹ and Ca⁺² so that the following reaction reduces bicarbonate ions from fluoride contaminated water.



Since the solubility of lime in water is limited³¹, it is necessary to add an aqueous solution of Ca^{+2} salt, in this case CaCl_2 , to provide enough Ca^{+2} ions for the above reaction. Lime is also known to play a role in the fluoride removal process as some fluoride is precipitated as CaF_2 . However when lime alone is used it leaves a residual fluoride^{32,33} of 8-10 ppm CaCl_2 .

The dosage of all other parameters except HCl required for neutralization was kept constant during the experiments. It was observed that as more MgO was added the amount of HCl required was larger (Figure 1), this is understandable due to more OH^- furnished from the $\text{Mg}(\text{OH})_2$ formed. When the dosage of MgO is varied, notice that the maximum fluoride removal (67.5%) is obtained with a dosage of 0.8 g/L MgO (Figure 2).

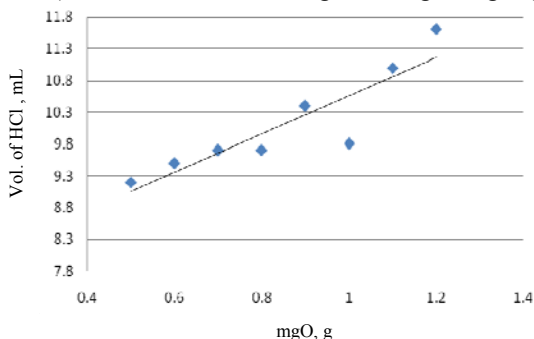


Figure 1. Variation of Vol. of 0.38 N HCL required to bring the pH of 400 mL of 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution, treated water to a final pH of 8

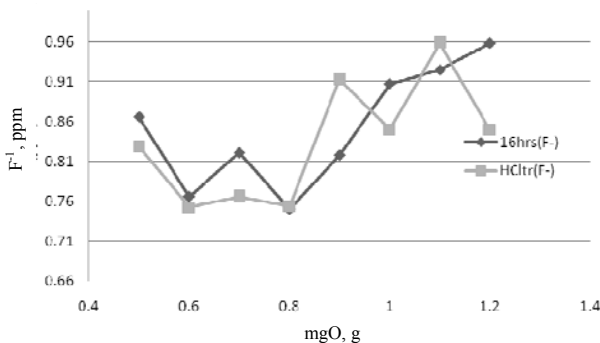


Figure 2. Variation of F^- conc in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW $\text{F}^- = 2.32$ ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

The TDS values of the residual water is also minimum at this dosage (30 ppm increase from raw water, Figure 3). The TDS of 1240 ppm in pH adjusted water is well within the permissible limit of 2000 ppm. Apparently, complex multiple equilibria are occurring simultaneously, an analysis of which is not the aim of the present study.

There was not much change in the chloride concentration on varying dosage of MgO. However a net increase in the concentration of Cl^- was observed on treatment with $\text{MgO} + \text{CaCl}_2 + \text{Lime}$ (by an average of 182 ppm) and further (453 ppm) on HCl treatment increase as compared to the chloride concentration of raw water (Figure 4). This is due to addition of Cl^- from CaCl_2 and HCl. However the Cl^- conc in HCl treated water is 665 ppm value is well within the permissible limit of 1000 ppm.

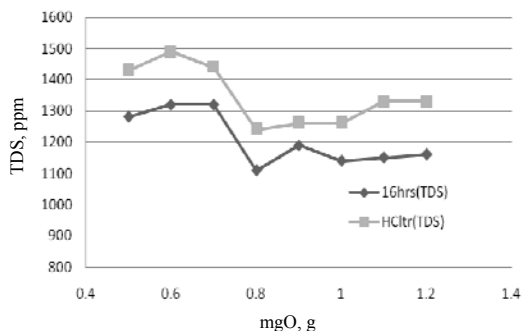


Figure 3. Variation of TDS in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW TDS = 1210 ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl₂ Solution)

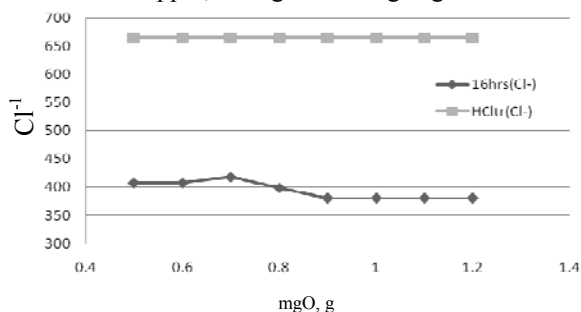


Figure 4. Variation of Cl⁻ in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW Cl⁻ = 212 ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl₂ Solution)

One would expect the concentration of dissolved Mg⁺² to have increased continuously on increasing MgO dosage. However, in the presence of Ca(OH)₂ and CaCl₂ and the various other ions present in ground water, the concentration of residual Mg⁺² was found to be minimum at 0.8 g/L. MgO (Figure 5). At 78 ppm Mg⁺² is within the permissible limit of 100 ppm¹.

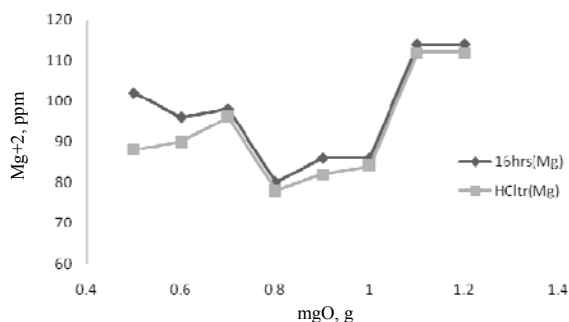


Figure 5. Variation of Mg⁺² in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW Mg⁺² = 35.4 ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl₂ Solution)

The Ca⁺² conc in MgO+Lime+CaCl₂ and HCl treated water is on an average ≈ 16 ppm more than raw water concentration (Figure 6). This is due to the added Ca⁺² from lime and CaCl₂. Since the amount of Ca⁺² added is constant in all the nine water samples, one would expect that the Ca⁺² conc. in water should be same for all the samples. However, notice that residual Ca⁺² in water is minimum at 0.7-0.8 ppm.

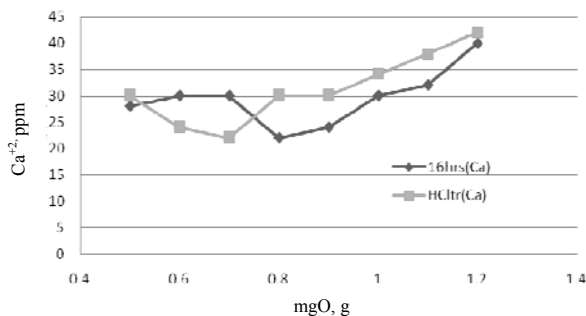


Figure 6. Variation of Ca^{+2} in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW $\text{Ca}^{+2} = 14.0$ ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

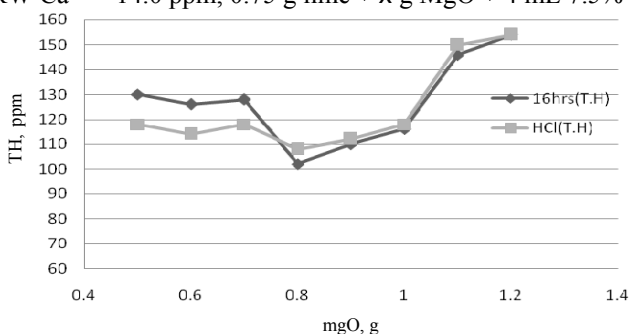


Figure 7. Variation of TH in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW TH = 49.4 ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

Due to the added Ca^{+2} and Mg^{+2} the total hardness value ($\text{Ca}^{+2} + \text{Mg}^{+2}$) is on an average ≈ 79 ppm higher than that of raw water (Figure 7). Notice that the total hardness value is also minimum at 0.8 g/L (108 ppm, max permissible limit 600 ppm) for both $\text{MgO} + \text{Lime} + \text{CaCl}_2$ and HCl treated water.

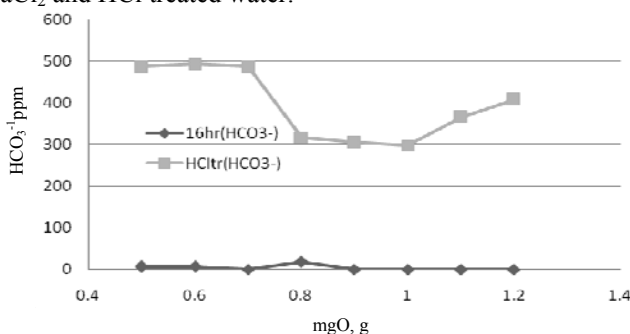


Figure 8. Variation of HCO_3^{-1} in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW $\text{HCO}_3^{-1} = 940$ ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

The HCO_3^{-1} conc in $\text{MgO} + \text{Lime} + \text{CaCl}_2$ treated water is reduced by to an average of ≈ 936 ppm as compared to that of raw water (Figure 8). This reduction of bicarbonate is attributed to the precipitation of CaHCO_3 in this step (Eq.1) and also due to the alkaline pH of this water conversion of HCO_3^{-1} to CO_3^{-2} takes place. However, on treatment with HCl and adjusting the final pH to 8 (within potable limits 6.5 to 8.5) the conc of HCO_3^{-1} increases

by 392 ppm as the CO_3^{2-} ions now changes to back bicarbonate. In the same line the CO_3^{2-} in the alkaline $\text{MgO} + \text{Lime} + \text{CaCl}_2$ treated water increases by ≈ 340 ppm as compared to raw water (Figure 9).

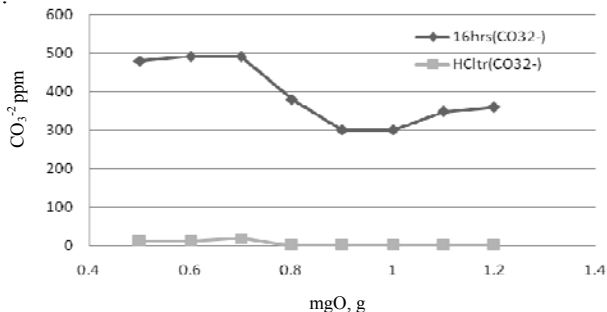


Figure 9. Variation of CO_3^{2-} in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW $\text{CO}_3^{2-} = 30$ ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

On treatment with HCl nearly all the CO_3^{2-} is again converted back HCO_3^{-1} and its concentration decreases by ≈ 389 ppm. The HCO_3^{-1} concentration in HCl treated water is minimum for a MgO dosage of 1 g/L. At 0.8 g/L MgO dosage, the total alkalinity value is 260 ppm well within the permissible limit of 600 ppm (Figure 10).

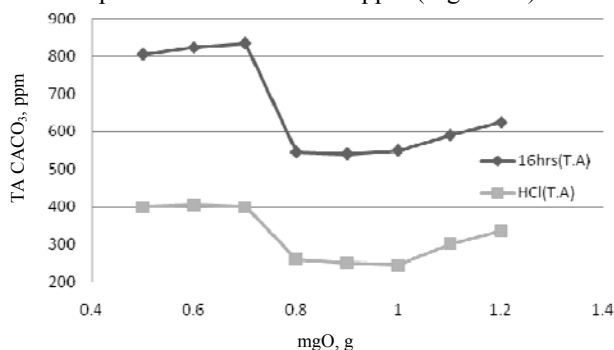


Figure 10. Variation of TA in (CaCO_3 eqv) in water after 16 h and pH adjustment with HCL conditions (Water: PKD, RW TA = 30 ppm, 0.75 g lime + x g MgO + 4 mL 7.5% CaCl_2 Solution)

As fluoride removal is maximum, Total Hardness and TDS is minimum at 0.8 g/L and HCO_3^{-1} is minimum at 1.0 g/L, an optimum dosage of 0.8 g/L MgO for defluoridation purposes may be considered for the ground water in the present case. In the 50 L scale defluoridation filters based on this technique which is undergoing field trials in the village Pilaniyon ki Dhani the dosage of MgO would be adjusted accordingly.

Conclusion

From the above experiments we can conclude that the 0.8 g/L of MgO is the most suitable dosage as it results in maximum fluoride removal using this technique. Next, the dosage of CaCl_2 and Lime also need to be optimized to arrive at the overall optimum dosage.

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