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TESTING OF A DEFLUORIDATING FILTER USING MgO-CaO-$CaCl_2$ FOR USE IN RURAL RAJASTHAN

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ABSTRACT

A Magnesium Oxide based defluoridation technique using MgO–CaO-Calcium Chloride and pH adjustment by Sodium Bisulphate has been suitably modified for use with fluoride contaminated local groundwater having high alkalinity. Taking into consideration the high bicarbonate concentration in raw ground water the proportion of the lime has been changed. It was found that sodium bisulphate was not suitable for pH adjustment due to high concentration of sulphate in the pH adjusted water. Therefore dilute HCl was used instead. Six trials of the adapted defluoridation technique have been carried out in the laboratory successfully at 50 liter scale.

KEY WORDS: Defluoridation, Defluoridating Filter, MgO, CaO, Calcium Chloride

RESUMO

Uma técnica de defluoretação usando MgO-CaO-Cloreto de Cálcio e ajuste de pH com bisulfato de sódio foi modificada com éxito para água contaminada com fluoreto e com alcalinidade elevada. Considerando a alta concentração de bicarbonato na água natural, a proporção de CaO foi modificada, O bisulfato de sódio não foi adequado para ajuste do pH devido à alta concentração resultante de sulfato. Consequentemente, HCl diluído foi usado. Os resultdos experimentais com amostras de 50 litros de água foram satisfatórios para remover o fluoreto.

PALAVRAS CHAVE: Defluoretação, Filtro para Remoção de Fluoreto, MgO, CaO, Cloreto de Cálcio

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INTRODUCTION

The desert state of Rajasthan in India primarily depends upon groundwater for meeting its drinking water requirements. The groundwater in Rajasthan[1] has fluoride in excess of the permissible limit set by WHO of 1.5 ppm[2]. Flouride is known to be beneficial if present in the desirable concentration of 1 ppm and has adverse impacts on human health if present in excess[3 4]

Magnesium Oxide is known to remove fluoride from water since 1940's[5]. Since then various researchers have studied this process[6 7 8 9 10 11]. MgO being non-toxic, relatively easily available and cheap is a suitable adsorbent for F^- removal.

A new method of defluoridation based on MgO-CaO-$CaCl_2$ and pH adjustment using $NaHSO_4$ has recently been reported from the Indian Institute of Science, Bangalore, India[12 13 14]. The ratio of various chemicals used depends on fluoride concentration and bicarbonate concentration in the raw water. The ground water in Rajasthan has very high concentration of bicarbonates. A project supported by the Water Technology Initiative of the Department of Science and Technology, Govt. of India, New Delhi involves the testing and field trials of this filter in the fluoride affected Lakshmangarh Tehsil (subdivision), in the Sikar District of Rajasthan. Due to higher alkalinity of the local fluoride contaminated ground water, the defluoridation technique had to suitably be modified, and in this paper we report the preliminary findings of our study.

MATERIALS AND METHODS

Fabrication and Testing of the Filter

Food grade drums (50 liters capacity) were purchased from Time Technoplast (New Delhi). Plastic taps were fixed 2.5cm above the base of the containers Fig. 1. Calcium oxide (Mahalaxmi Traders, Ajmer) was purchased locally from Laxmangarh in 5 kg plastic sacks.

Fig. 1 Photograph of Testing of the Fluoride Filter in Laboratory.

Technical grade magnesium oxide, (light) was purchased from R/S Enteprises, Jaipur. Calcium Chloride Dihydrate (AR), conc. HCl (AR) was purchased from CDH (India) and Rankem (India), respectively.

Fluoride contaminated ground water was brought from village Shola 30km away from the Institute in mini water tankers and transferred to 500 liter drums in the laboratory.

Fixed volumes of 7.5% $CaCl_2$ solution in demineralised water was added to 50 liters fluoride contaminated water and stirred using plastic PVC pipes. Weighed amounts of MgO and CaO were added to it, and the water stirred vigorously using a PVC plastic pipe. The water was left overnight undisturbed. MgO and $Ca(OH)_2$ flocks settled down to the bottom of the container in form of white sludge. The supernatant water was filtered through six layers of cotton cloth tied to the mouth of the tap into another food grade container fitted with plastic tap Fig. 1. Hydrochloric acid (0.38 N) in demineralised water was added with constant stirring to the filtered water till the pH of the treated water was in between 6.5 to 8.5, and fit for the human consumption.

Water Testing

Fluoride was measured by using a Fluoride Ion Selective Electrode (Orion Thermo Scientific) using TISAB Buffer. Total Hardness, Calcium Hardness was determined by EDTA method. Carbonate and Bicarbonate was determined by titrating with H_2SO_4. For chloride, titration with silver nitrate was used. Duly calibrated pH, TDS meter was used for determining pH and TDS. Sodium and Potassium was determined by Flame Photometer (ESICO). Nitrate was measured by measuring the absorbance at 220nm and 270nm. Sulfate was determined by turbidity method using a colorimeter.

RESULTS AND DISCUSSION

MgO hydrates in water to form $Mg(OH)_2$ [6 13]

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad \text{(eq.1)}$$

Since the ionic radii of fluoride and hydroxide are similar, OH^- ions in the crystal lattice $Mg(OH)_2$ gets substituted by F^- [15 11 12].

$$Mg(OH)_2 + F^- \rightarrow Mg(OH)_{2-y}F_y \qquad \text{(eq.2)}$$

For defluoridation using MgO-CaO-$CaCl_2$-$NaHSO_4$ [12 13], the concentration of bicarbonate in raw water is the critical parameter. A preliminary sampling of the ground water of village Shola, a fluorosis affected village in Lakshmangarh indicated a very high HCO_3^- concentration of 937 ppm and high fluoride concentration of 2.15 ppm (Table 1). The ratio derived for MgO-CaO–$CaCl_2$ treatment method as given in the application notes[16] are only up to 700ppm HCO_3^{2-} concentration. Since the bicarbonate concentration in raw water sample was very high, we increased the lime dosage from the maximum dosage of 0.5 gm to 0.75 gm (Table 1). This is to ensure the presence of enough Ca^{2+} ions in the solution, as in the basic medium Ca^{+2} ions react with HCO_3^- ions to form $CaCO_3$ as precipitate .

$$HCO_3^{-1} + Ca^{2+} + OH^{-1} \rightarrow CaCO_3\downarrow + H_2O \qquad \text{(eq.3)}$$

The concentration of bicarbonate ions has to be low in the raw water to be treated by this process, otherwise it will get converted to carbonate ions when a mixture of MgO-CaO-$CaCl_2$ is added and the pH of water become basic

$$HCO_3^- + OH^{-1} \rightarrow CO_3^- + H_2O \qquad \text{(eq.4)}$$

Moreover in the pH adjustment step by 5% $NaHSO_4$ solution, one equivalent more of $NaHSO_4$ would be consumed by the CO_3^{2-} ions that are generated above.

$$CO_3^{2-} + HSO_4^{-1} \rightarrow HCO_3^- + SO_4^{2-} \qquad \text{(eq.5)}$$

The MgO dosage was kept at minimum (1.0 gm/lit) since the F^- concentration in the raw water as not very high (MgO dosage 1.0 →1.5 for F^- concentration 1.5 to 7 ppm).

In a preliminary experiment, 1.0 liter sample was treated with 1.0 gm MgO, 0.75gm CaO, 4.0 ml of 7.5% of $CaCl_2$ (in demineralised water) and stirred for five minutes. The solution was left overnight undisturbed. Next day it was filtered through Whatman 42 filter paper, 500 ml of this filtered water required 6.0 ml of 5% $NaHSO_4$ (in demineralised water) for neutralization to

Table 1 Analysis and Treatment of Water Sample of Village Shola (Pilaniyon Ki Dhani).

Date of Sampling 7th May 2012	Water 1 lit., MgO 1gm, CaO 0.75 gm, $CaCl_2$ (7.5 %) 4 ml				Sampling Site: Pilaniyon ki Dhani (Vill. Shola)	Date of Treatment 15th May 2012
S.No.	Parameter	Raw water	After 16 hrs.	After pH adjustment with 5% $NaHSO_4$	Desirable limits[17]	Permissible limits[17]
1	pH	8.53	11.02	7.45	6.5-8.5	No relaxation
2	TDS by meter	1527	1637	2109	500	2000
3	Chloride	262	393	399	250	1000
4	Carbonate	0	384	0	-	-
5	Bicarbonate	937	149	512		
6	Ca Hardness	19.3	1.594	2.561	75	200
7	Mg Hardness	20.2	2.903	3.241	30	100
8	Fluoride	2.15	0.472	0.432	1	1.5
9	Sulphate	61	64	425	200	400
10	Na^+	477	460	522		
11	K^+	4.5	5.8	5.92		
12	Total alkalinity ($CaCO_3$ eqv.)	750	426	410	200	600

pH 7.45 (Table 1). We found that the fluoride concentration reduced from 2.15 in raw water to 0.47 ppm in pH adjusted water (Table 1). To our expectation, we found that Total Alkalinity had decreased from 750 to 426 ppm (Table 1), as (HCO_3^{-1} had precipitated as $CaCO_3$).

However, it was observed that SO_4^{2-} concentration increased considerably from 61ppm in raw water to 425 ppm in pH adjusted water (Table 1), beyond the permissible limit of 400 ppm[17]. Therefore the pH adjustment with $NaHSO_4$ was not suitable. pH adjustment with H_2SO_4 was ruled out for the same reason (it would have increased the sulphate concentration).

Since nitrate concentration in raw water was found to be 161 ppm, one and half times the permissible limit of 100 ppm[17], pH adjustment with nitric acid would not be suitable. Therefore dilute HCl was tried for pH adjustment.

$$CO_3^{2-} + HCl \rightarrow HCO_3^{-} + Cl^{-} \qquad \text{(eq.6)}$$

Next, 1.0 liter raw water sample was treated with, 1.0 gm MgO, 0.75gm CaO, 4.0 ml $CaCl_2$ (in demineralised water) and left overnight. Next day this water was filtered and, 400 ml of the filtrate was titrated pH metrically to determine the volume of 0.38 N HCl required for neutralization. The variation of pH with volume of 0.38 N HCl added is shown in Fig. 2. Notice that the $CO_3^{2-} \leftrightarrow HCO_3 \leftrightarrow H_2CO_3$ equilibrium is apparent. We found 5.6 to 9.6 ml of 0.38 N HCl was required to reduce the pH between 8.5 to 6.5 (within the potable limits) at 927 ppm HCO_3^{-1} conc. in raw water. This translates to 630 to 1008 ml of 0.38 N HCl for 45 liters of filtered MgO-CaO-$CaCl_2$ treated water.

Dilute HCl of 0.38 normality was considered to be adequate for pH adjustment, as it would not be prudent to handle highly concentrated HCl solution when the filters are put to field trails and possible use in the villages. If too dilute HCl solution is used the volume of HCl required would be more. As 1 liter food grade plastic containers are easily available therefore this volume of HCl solution can be easily dispensed.

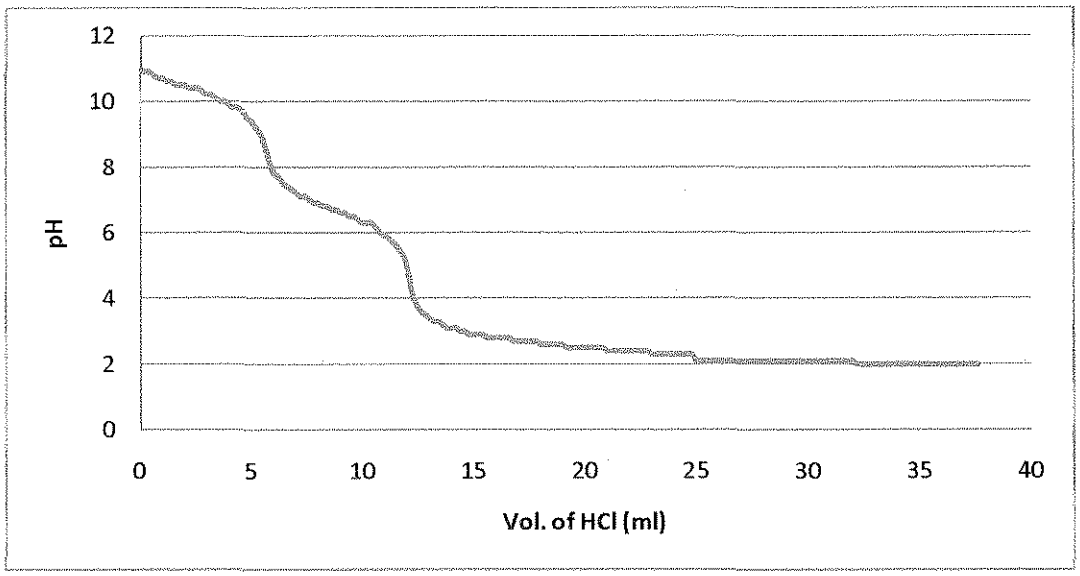

Fig. 2 Variation of pH of CaO-MgO-$CaCl_2$ treated water (400ml) from Pilaniyon ki Dhani (Village Shola) on addition of 0.38 N HCl

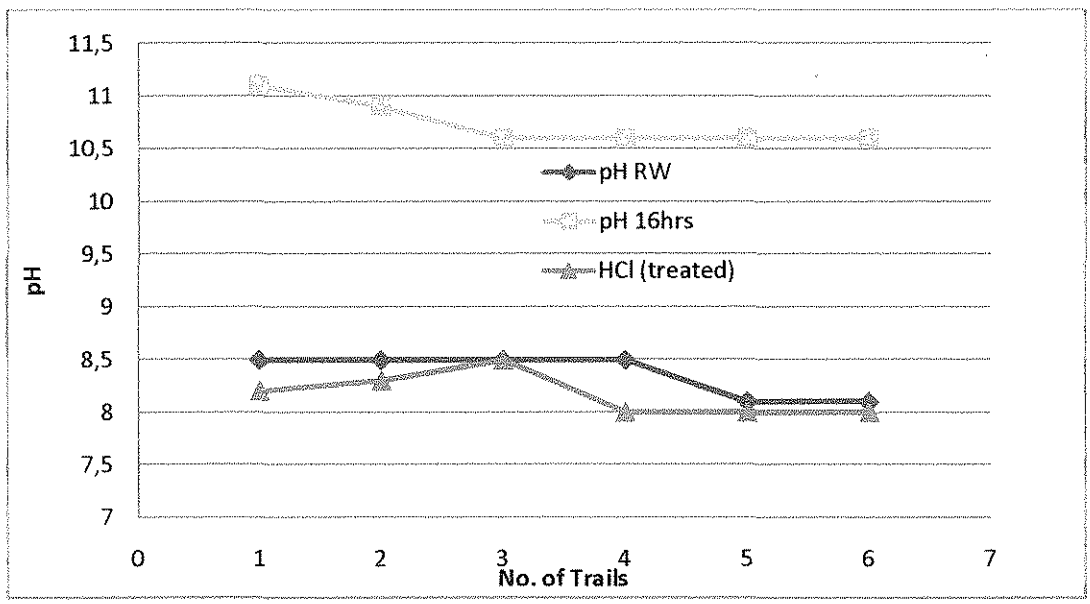

Fig.3 Variation of pH during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

After pH adjustment by HCl, the pH of water was 8 to 8.5, (Fig. 3) with fluoride concentration ranging from 0.7 to 0.86 ppm with an initial fluoride in the raw water varying from 2.26 and 2.3 ppm (Fig. 4). The CO_3^{-2} in pH adjusted water varied from 30 to 34 ppm when the concentration varied from 30 to 42 ppm (Fig. 5). The bicarbonate concentration in pH adjusted water was 305 to 420 ppm, while it was 934 to 1150 ppm in raw water (Fig. 6). The sulphate concentration was found to be low 40-80ppm (Fig. 7) and chloride concentration 470-581 ppm well within the permisible limit of 1000 ppm (Fig. 8). Also notice, that the method produces water of nearby constant total alkalinity of approximately 400 ppm though the total alkalinity of raw water various from 840 to 1000 ppm (Fig. 9). Thus there is a reduction of total alkalinity by 400ppm. Notice that the TDS of treated water increased by 1200 to 1400 ppm (Fig. 10), in treated water as compared to raw water, but is still very much within the permissible limit of 2000 ppm[17].

As the solubility $Mg(OH)_2$ in water is low (5.0×10^{-12})[18], therefore Mg^{2+} concentration in raw water and treated water does not vary appreciably (average concentration 38 ppm) (Fig. 11). The Calcium added in form of CaO and $CaCl_2$, gets precipitated in form of $CaCO_3$, and the concentration of Ca^{2+} decrease from 15 ppm in raw water to 4 to 5ppm in pH adjusted water (Fig. 12). For the above reasons the Total Hardness was also found to decrease (Fig. 13).

There is no significant change in Na^+ and K^+ values in raw and treated water which average 300-500 ppm in the various samples. It was found using six layers of cloth for filtering and one tap as outlet it took on an average 2.5 hrs for 45 liter of MgO-CaO-$CaCl_2$ treated water to filter through and the filter cloth had to removed and cleaned twice to remove the fine particles of sludge. Hence two taps were fitted 6 inches apart, after which it took only 45 minutes for filtration. It was observed the filter cloth did not choke in the new arrangement. Notice that the volume of filtered water is 45 liter in the second container which increased to 45.6 liters on addition of 600 ml 0.38 N HCl.

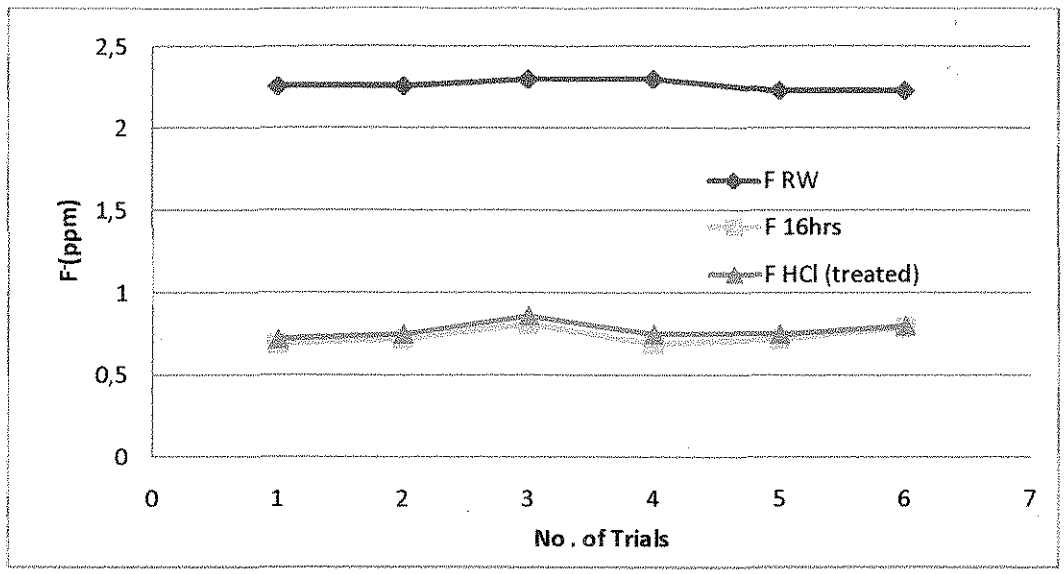

Fig.4 Variation of F^- during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water Pilaniyon ki Dhani (Village Shola)

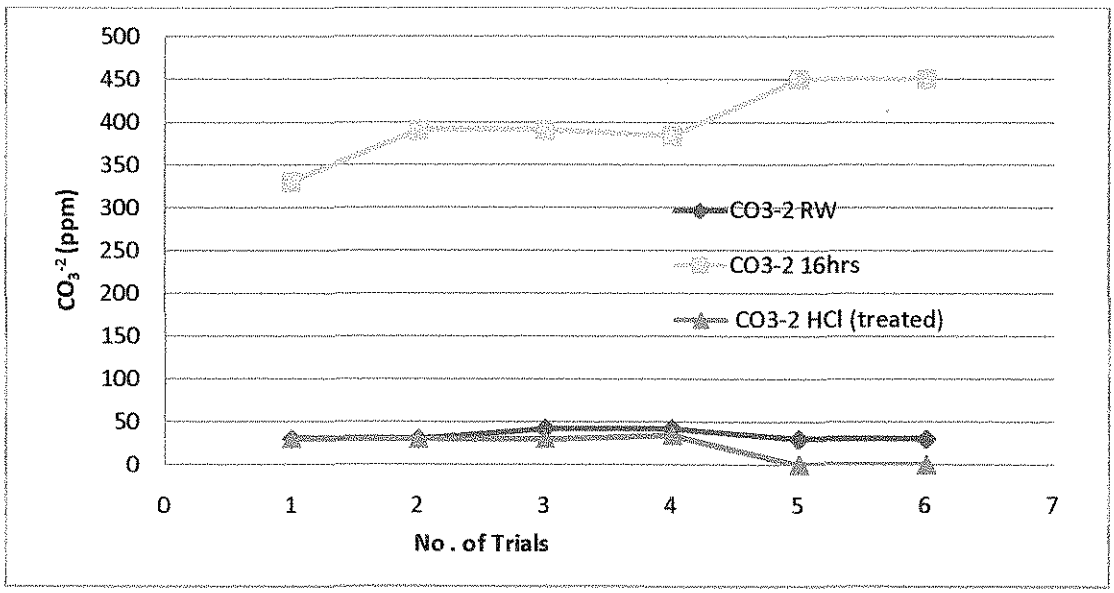

Fig.5 Variation of CO_3^{-2} during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

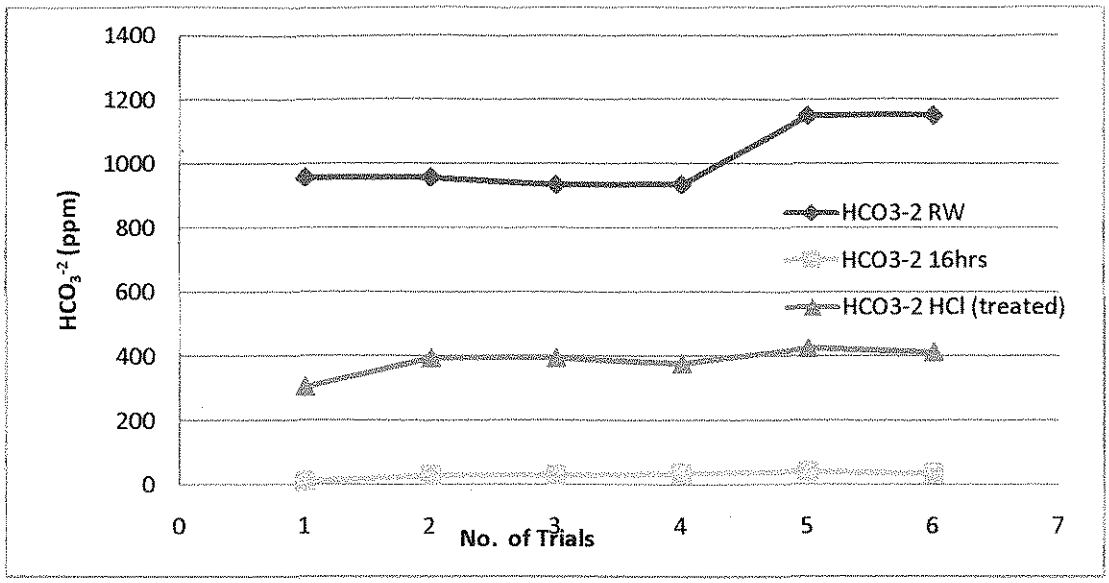

Fig.6 Variation of HCO_3^{-1}during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

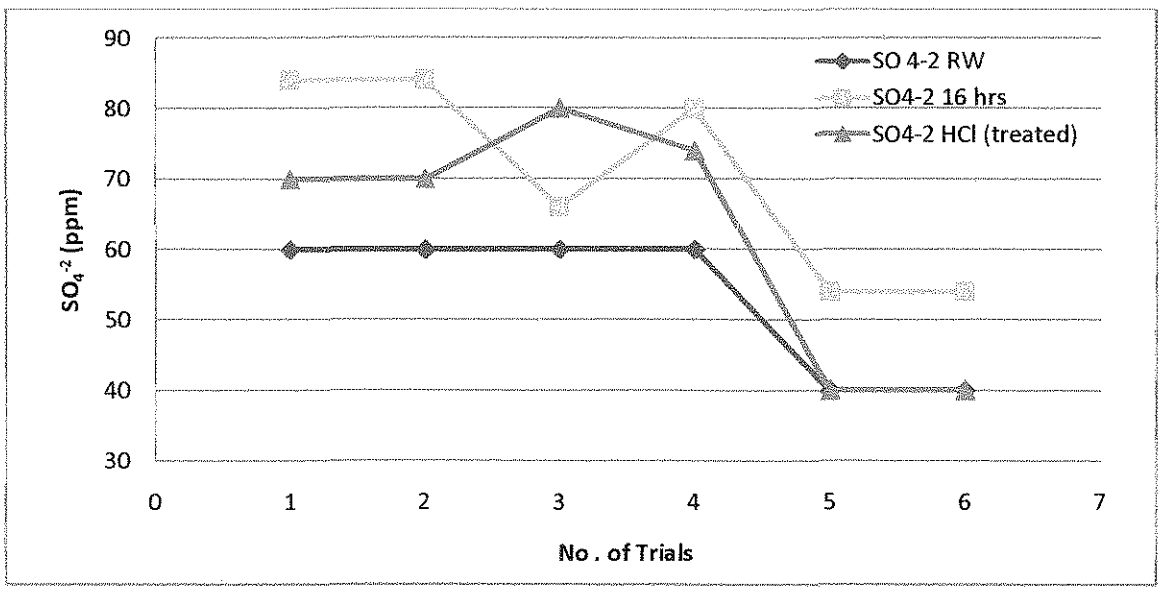

Fig.7 Variation of SO_4^{-2} during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water Pilaniyon ki Dhani (Village Shola)

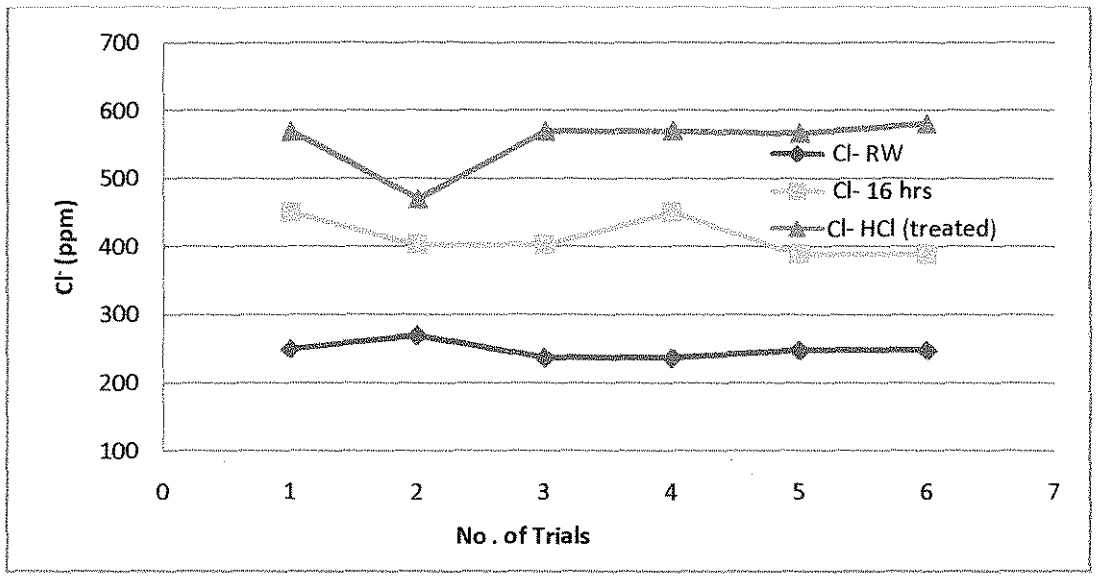

Fig.8 Variation of Cl^- during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

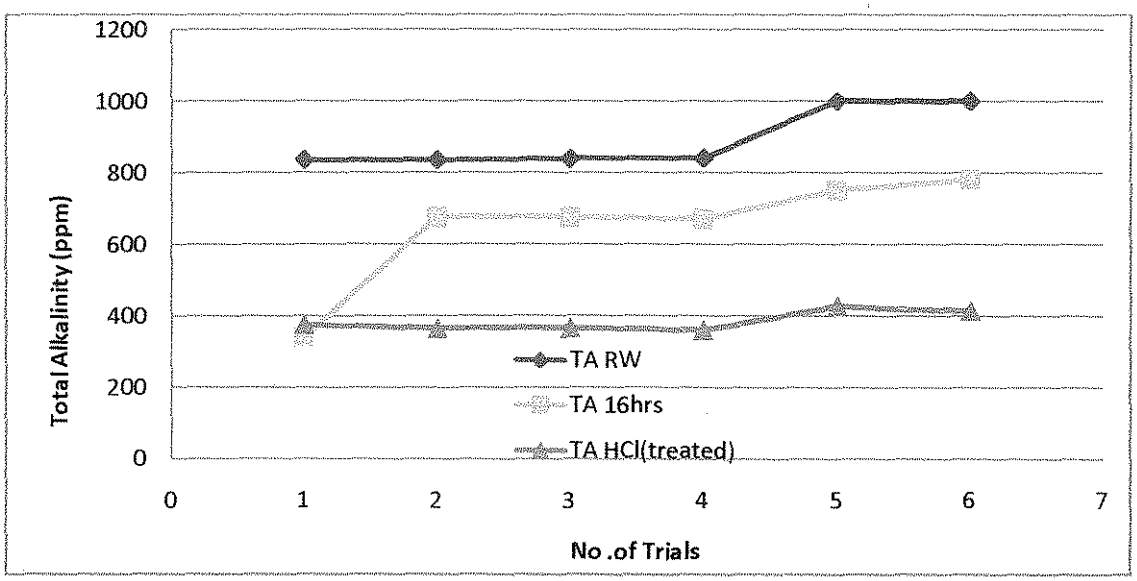

Fig.9 Variation of Total Alkalinity during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

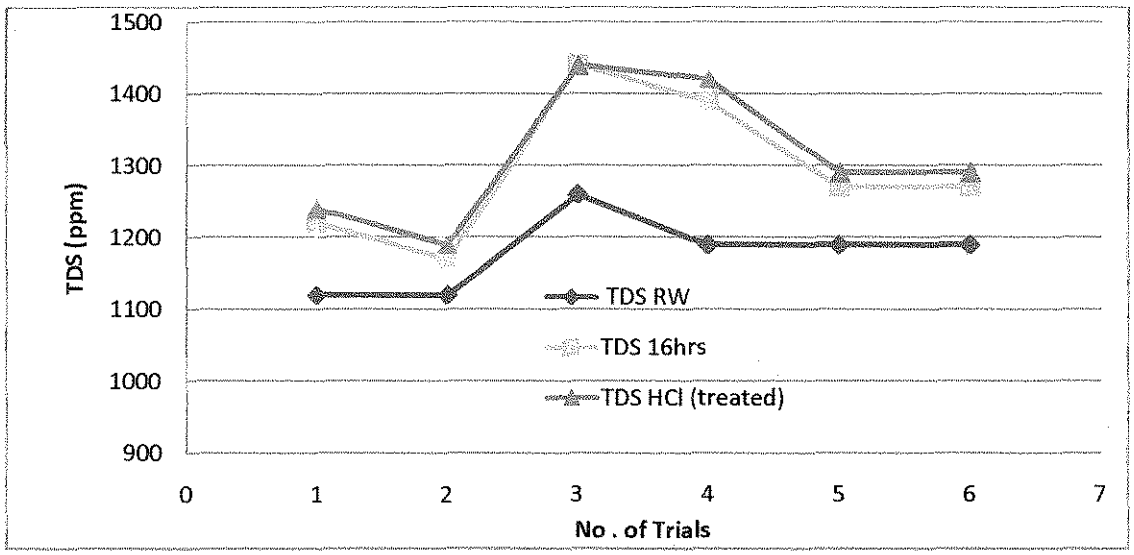

Fig.10 Variation of TDS during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

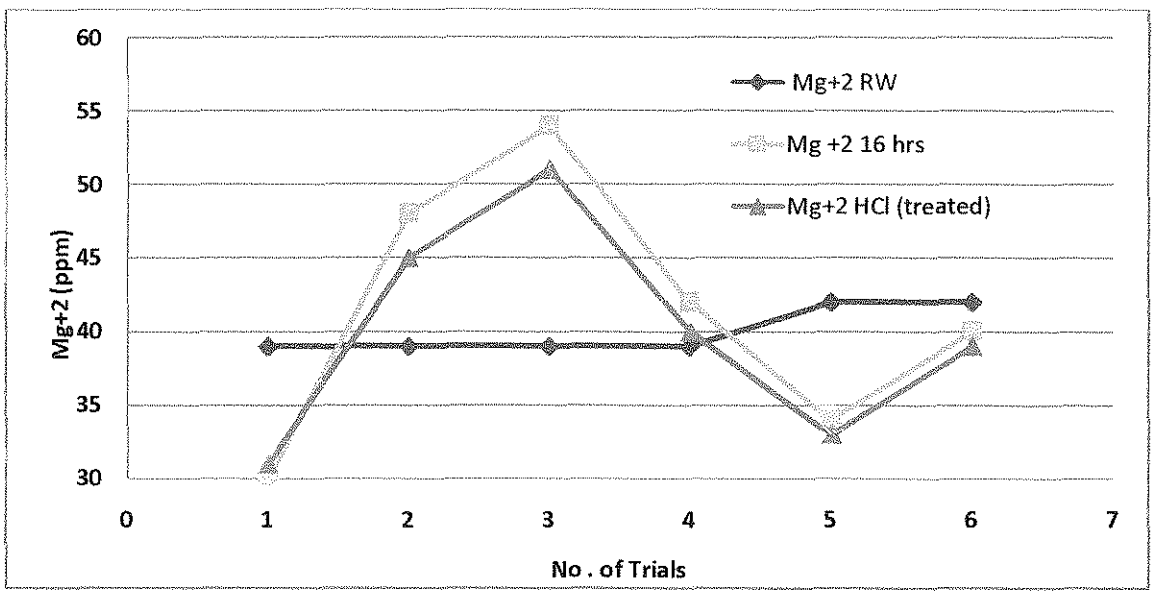

Fig.11 Variation of Mg^{+2} during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

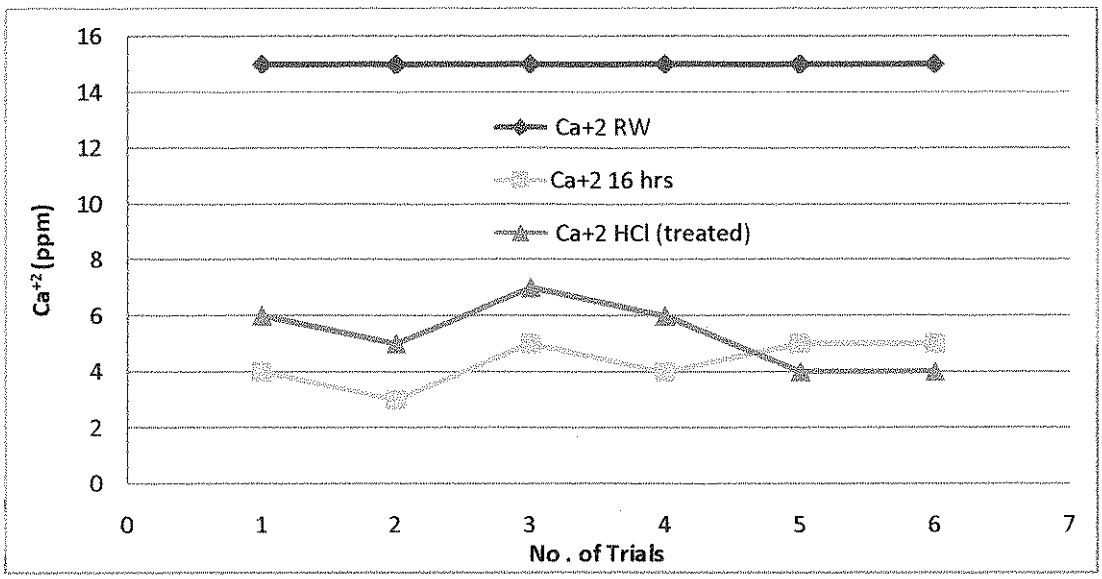

Fig.12 Variation of Ca^{+2} during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

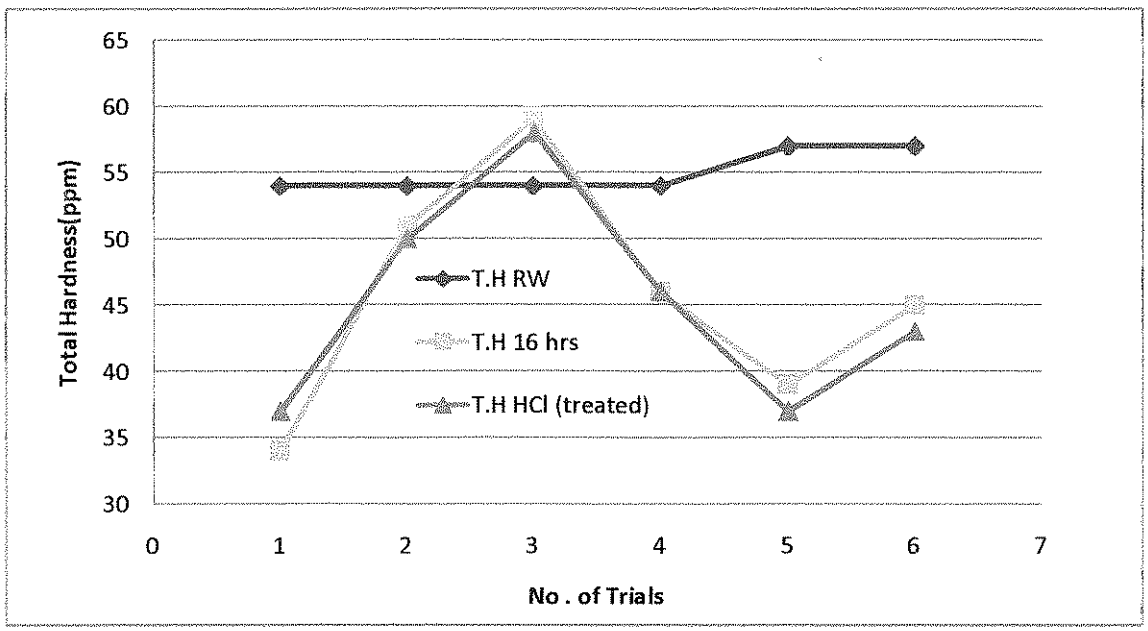

Fig.13 Variation of Total Hardness during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

CONCLUSION

We have determined that the MgO-CaO-$CaCl_2$ method of defluoridation can be adopted for water having high alkalinity. Since the local ground water contains high SO_4^{2-} concentration $NaHSO_4$ cannot be added for pH adjustment, instead 0.38 N HCl can be used . The final Cl^- concentration in treated water was found to be within the permissible limits, so were other parameters except nitrate which is very high in the raw water itself.

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