



GEOCHEMICAL STUDY OF FLUORIDE IN GROUND WATER OF JHALAWAR DISTRICT AND METHODS OF DEFLOURIDATION

R. K. GANGAL* and ZAIBA ALAM

Department of Chemistry, M.L.V.Govt.College, BHILWARA–311001 (Raj.) INDIA
E:mail gangal_rkg@yahoo.co.in

ABSTRACT

An extensive study of 40 villages of district Jhalawar have been done. 70% of villagers have been suffering from dental fluorosis, gut fluorosis and skeletal fluorosis. The fluoride concentration is varying from 0.4 to 8.4 ppm. The problem of fluoride is so severe that younger generation is likely to be affected adversely. Activated aluminum is an excellent deflourodating material, which is available in plenty and low cost. Its deflouridation efficiency at neutral pH is commendable. The use of activated aluminum reduces the fluoride concentration from 8.5 ppm to 1.5 ppm. The natural ground water samples having fluoride concentration 1.36 ppm was reduced to 0.9 ppm using marble slurry.

Key words : Fluoride, Deflouridation.

INTRODUCTION

Rajasthan is the largest state in the country in terms of geographical spread with 56.4 million population (5% of the country's population). Rajasthan shows only 1.9% of ground water resources of the country. About 95% of the population is dependent upon ground water as Rajasthan has limited pool of surface water due to scanty rainfall averaging 55 cm per annum and droughts are frequent. Management and sustenance of ground water resources is a critical challenge in Rajasthan. The problem of excess fluoride in ground water is more than 1.5 ppm covering about 70% villages, out of 40 villages (affecting 20000 people) in the Jhalawar district of Rajasthan. The extent of fluoride in ground of 40 villages of Jhalawar district were analyzed. Analysis report show that 70% of the villages contains higher concentration of fluoride than the prescribed limit.

EXPERIMENTAL

Samples were collected from the wells and hand pumps (H.P.) of 40 villages of Jhalawar district as shown in October 2004. The inhabitants of the district Jhalawar are using this water from the wells and hand pumps (H.P.). The samples were collected according to the specification of APHA. Analysis of fluoride was made by solid electrode method (ion selective

electrode) having a doped single crystal membrane. The electrodes are frequently characterized by low restivity and doping reduces this in future. The LaF_3 electrode is one of the most useful solid-state electrode. This single crystal membrane electrode responds to fluoride ion and virtually no other anion or cation.

Minerals containing fluoride

Mineral	Chemical composition	Rocks in which these minerals are present
Fluorite	CaF_2	Pegmatic, Pneumatolitic Deposit as Vein deposit
Fluorapatite	$\text{Ca}_5(\text{FCl})\text{PO}_4$	Pegmatite and Metamorphosed Limestone
Micas		
(a) Biotite	$\text{K}(\text{MgFe}^{+2})(\text{AlSiO}_{10})(\text{OHF}_2)$	Basalt
(b) Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OHF}_2)$	Pegmatites Amphibolities
(c) Lepidolite	$\text{K}_2(\text{Li,Al})_5(\text{Si}_6\text{Al}_2\text{O}_3)(\text{OHF})_4$	Gabbro, Dolevi
Amphiboles		
(a) Hornblende	$\text{Ca}_2(\text{MgFe}^{+2})(\text{AlFe}^{+3})(\text{SiAl})_8\text{O}_{22}(\text{OHF}_2)$	Genesis Schists, Shales Clay, Alkaline rocks etc.
(b) Tremolite	$\text{Ca}_2(\text{MgFe}^{+2})_5(\text{Si}_8\text{O}_{22})(\text{OHF})_2$	
Actinolite		
Topaz	$\text{Al}_2\text{SiO}_4(\text{OHF})_2$	Acid igneous rock, Schists
Rock Phosphate	$\text{NaCa}_2(\text{MgFe}^{+2})_4(\text{AlFe}^{+3})(\text{SiAl})_8\text{O}_{22}(\text{OHF})_2$	Lime stone

A typical cell employing the saturated calomel electrode (SCE) and the fluoride electrodes containing an Ag/AgCl reference can be represented as:



The potential of the cell

$$E_{\text{cell}} = \frac{\text{AgCl} - E_{\text{SEC}} - 2.303 \log a^+}{F} + E_{\text{a}} + E_{\text{j}}$$

Spectrophotometric method : The fluoride content in water is determined by using zirconium oxychloride and alizarin red-S monosulphate reagent at 520–550 nm.

Strategy for mitigation of fluoride:

Fluoride uptake capacity (FUC) method: Mechanism of fluoride removal by activated alumina in contact with water assumes the formulation of bohumia. Fluorine is the most electronegative of all the elements and it is very likely the main reason for the selectivity of activated alumina towards fluorine. Aluminum with three positive charge strongly attracts the electronegative fluoride ion. This attraction is even much stronger than between aluminum chlorine. It is probably a kind of ion exchange process, where hydroxyl ions are substituted by fluoride ions.



The effect of hydroxyl ion concentration or the pH on the exchange process becomes clear from the above equilibrium equation. When the hydroxyl ion concentration is increased, the equilibrium reaction moves towards the left and fluoride ions are mobilized. From the above mechanism, two points emerge,

- (a) pH of activated alumina as supplied should not exceed 8.0 (10% w/w suspended in water), and
- (b) Defluoridation capacity of activated alumina decreases with increasing pH or total alkalinity of the influent water.

This also explains the different defluoridation capacities observed with water at different places in the country using activated alumina.

Methods of testing FUC

The procedure for testing involves the determination of fluoride using either SPADNS Method or Ion Selected method using Orion meter. The method used for the determination of FUC is as follows:

- (i) **Washing of activated alumina (AA) :** 1 kg of AA, taken in the nylon bag (300 mesh) was dipped in a plastic bucket containing 10 L of raw water. AA in the bag was manually agitated. This procedure was repeated thrice with fresh raw water. Activated alumina was then transferred to a PVC column for determining FUC. Heat is liberated, when activated alumina comes in contact with water. This may lead to disintegration of activated alumina particles. Further AA samples can also have very fine particles. This may lead to very high aluminum in treated water in the first defluoridation cycle. This washing procedure is to minimize aluminum level in treated water.
- (ii) **Experimental setup :** 1 kg of AA was taken in a PVC columns having following specification: Height = 60 cm and I.D. = 6.00 cm.
- (iii) **Raw water characteristics :** Natural ground water spiked with 10 mg/L as CaCO_3 Sulphate = 55 mg/L.

- (iv) **FUC determination** : 10 L of raw water was taken in a 12 L plastic bucket with a flow control device. Raw water was passed through the column containing 1 kg of AA at a flow rate of 40 mL/min. The flow rate gave an approximate empty bed retention time of 25 min. About 30 L of raw water was passed through the column during the day. Minimum of two-hour rest period was given between each run (i.e. after passing 10 L raw water). This is to stimulate the field conditions, as domestic defluoridation unit is expected to be used under similar conditions. Treated water samples were collected after every 20 L for the analysis of fluoride.
- (v) **Fluoride analysis**: Fluoride concentration in raw water as well as treated water was analyzed by using Orion fluoride specific electrode with Orion meter.
- (vi) **Aluminum analysis** : Aluminum was determined by colorimeter using Eriochrome cyanide R as per usual the procedure described in standard methods.
- (vii) Column was operated till the treated water fluoride level was 1.5 ppm. Volume of the raw water passed through the column up to this point was noticed. Average concentration of the fluoride in treated water up to this volume was taken, as 0.75 mg/L. volume as initially treated water fluoride concentration will be low.

Calculation of FUC

$$\text{FUC} = \frac{(\text{FCI} - \text{FCT}) \times V}{W}$$

Where FCI = Fluoride concentration in inlet (Raw water),

FCT = Fluoride concentration in treated water,

V = Volume of water passed through the column up to the fluoride concentration of 1.5 mg/L, and

W = Weight of activated alumina

$$\therefore \text{FUC} = \frac{(10.5 - 0.75) \times 280 \text{ L}}{1 \text{ kg}}$$

$$= 2730 \text{ mg/kg AA}$$

Aluminum: With the washing procedure described above, aluminum concentration was below 0.1 mg/L through out the defluoridation cycle. Hence activated alumina is so far the best option for defluoridation of drinking water. In our samples, the fluoride concentration was reduced from 8.0 to 1.5 ppm with help of FUC method.

RESULTS AND DISCUSSION

Tables 1–3 show the fluoride concentrations in different villages of Jhalawar district. The fluoride concentration is increasing in Jhalawar district. Most of villagers told us about joint

pain, teeth changing from yellow to brown. They also experienced a thrust or desire to drink more water. Some of the them complained that they are unable to stand suddenly from sitting position. Children too have yellow teeth.

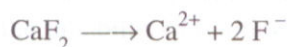
Table 1. Tehsil Jhalrapatan of District Jhalawar

Villages/Sources	Fluoride (ppm)
Tanda/H.P.	2.0
Khedla/H.P.	0.4
Badi Manpura/H.P.	1.0
Tadi-Sohanipura/H.P.	4.5
Pipliya-Gujraon/H.P.	3.0
Rang-Patan/H.P.	1.8
Kheriya H.P.2	1.0
Kheriya H.P.2	1.0
Khedala (Well)	0.4
Nala	0.8
Bhoomadi	0.8

Note: The samples were collected on 15.10.04 at 10.00 A.M.

Causes of fluoride

Since the source of fluoride is the minerals present in the rocks. This may be due to a specific fluoride mineral such as mica (thin shining flakes and amphiboles, elongated thin minerals common in many hard rock). Fluoride containing minerals, react with water to dissociate calcium fluoride into its ions; thus releasing F^- ion in H_2O



Geological Survey of India has studied the lietology of the area and reported the presence of fluorite mineral in the Jhalawar District. Biotic (Mica rich mineral) is also available in this area and shows high value of fluoride. Analysis data of present study illustrate the distribution of fluoride levels in various sub surface water samples in Jhalawar district.

Table 2. Tehsil Jhalrapatan of District Jhalawar

Villages/Sources	Fluoride (ppm)
Pipliya Gujaroan/Well	3.0
Rang patan 2/H.P.	3.0
Badi Manpura/H.P.	1.0
Dungar Gaon H.P.4	4.0
Gadiya Mahar	3.0
Dungar Gaon H.P.	3.5
Rupawaldia/H.P.	1.0

Note: Samples were collected on 24.10.2004 at 1.00 P.M.

Table 3. Tehsil Aklera of District Jhalawar

Villages/Sources	Fluoride (ppm)
Kotra/H.P.	5.5
Kohri/H.P.	1.0
Dhaba/H.P.	2.5
Kangari/H.P.	4.5
Goriya Khera	4.5
Kangari/H.P.2	1.5
Devkaka Dhar/H.P.	4.0
Dhaba/H.P.2	3.0
Gora Khera/ H.P.	3.5
Punya Kheri/ H.P.	1.0
Gorya Kheri/ H.P.	8.2
Gopal Pura	2.5
Pipliya	2.5
Tukadiya	2.0

Note: Samples were collected on 26.10.2004 at 1.00 PM

Table 4. Tehsil Aklera of District Jhalawar

Villages/Sources	Fluoride (ppm)
Narhera	3.0
Dungargaon/H.P.	2.6
Gulkheri	4.4
Narhera 2/H.P.	2.2
Khejra/H.P.	3.0
Goriya Khera/H.P.	2.6
Dhaba/H.P.	8.0
Khori/H.P.	3.0
Lesuria Shna/H.P.	0.8

Note : Samples were collected on 28.10.2004 at 11 A.M.

It can be seen from the data in the tables that the locations of highest fluoride level (in ppm) as well as lowest level (in ppm) do not follow any pattern. In the same village, the adjoining wells and hand pumps. May show different values of fluoride. Fluoride no doubt is essential up to 1 ppm but it is harmful beyond 1.5 ppm as per W.H.O. and E.P.A. guidelines. The interaction of fluoride and biotic system is striking through reaction such as



This indicates the incorporation of some of the amount of fluoride in bones along with phosphorous. Since it gives an excellent fit in nature also, a reaction similar to bone fixation is followed. When water with excess fluoride is used, then it starts replacing the phosphorous in bones leading to weakening of the bones and as a result fluorosis occur. Since most phosphate minerals such as appetite contain some amount of fluoride, the use of phosphate fertilizer leads to the accumulation of excess of fluoride in soils, which may get into the ground water as well as soil run off to surface water. This eventually ends up the foods chain through agriculture activities where the suitability of fluoride rich water may be restricted. The figure indicates that a substantial part of the region is not really suitable for agriculture based simply on fluoride contents of the source water that is the sub-surface water. Surface run off do not pose any fluoride problem due to the dilution factor of the large volume of water in a river and presence of low levels of dissolved phosphorous. Removal of excess of fluoride is by the reaction:



Since aluminum and fluoride has great affinity.

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