ANALYSIS OF FLUORIDE CONTENT IN BRINE SOLUTIONS, SALT AND PAN SOIL OF THOOTHUKUDI SALT PANS, THOOTHUKUDI DISTRICT (INDIA)

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ABSTRACT

Fluoride is widely distributed in nature, and occurs in continental rocks of earth's crust. Fluoride level in saline water has been given wider importance than any other naturally occurring inorganic constituent. The level of fluoride in saline water samples, salt and pan soil of Thoothukudi salt pan were analyzed. The presence of fluoride in brine solutions were supported by electrical conductance values. For the analysis of fluoride, Zirconyl alizarin method was followed. The concentration of fluoride in the brine samples varied from 0.9 mg/l to 1.2 mg/l. The concentration of fluoride in the successive samples increased gradually, and then started to decrease during salt formation. During the process of crystallization, considerable amount of fluoride got deposited into the pan soil. Similarly, electrical conductance values also increased to a certain limit (176 dS/m), and then decreased during the formation of salt.

Keywords: ***Concentration, Crystallization, Electrical conductance, Saline water.***

I.INTRODUCTION

Fluorine is a diatomic gas having an atomic number 9, and atomic mass 19. It is the most electronegative element, and is much more reactive than oxygen and chlorine and are known both metallic and non metallic fluorides. As on date more than a hundred fluorine containing minerals have been identified. Commercially, the important ones have been fluorspar or fluorite, cryolite, fluorapatite and calcium fluoride. Fluorine and its compounds have been extensively used in industries. Fluorine compounds play an important role in semi conductors, fertilizers, production of high purity graphite, electrolysis of alumina and in nuclear applications [1].

Depending on its status co, fluoride can cross cell membranes, and enter the soft tissues causing impairment of their function. Fluoride being noxious to the environment, affects the health of humans, animals as well as plant life. Humans consume considerable amount of fluoride from drinking water, thus accounting for the extensive amount of human tooth and bone deformities [2]. The maximum tolerance limit of fluoride in drinking water as specified by WHO ranges from 0.5 mg/l to 1.5 mg/1 [3]. Fluoride is recognized as essential element in human diet. Skeletal and dental problems can be prevented by maintaining the fluoride concentration to 1ppm in the dietary intake. However, when the fluoride concentration is above this level it leads to many bone diseases, mottling of teeth and lesions of the endocrine glands, thyroid, liver and other organs. It is necessary to supplement diet with fluoride in low fluoride areas and it is essential to reduce the fluorine levels in areas where fluorine poisoning takesplace by both natural and human activities [1]. Chronic exposure to fluoride

in groundwater causes adverse health problems not only in humans, but also in various species of domestic animals in the form of fluorosis. The primary manifestations are dental fluorosis (Fig.1), and osteosclerosis of skeleton (skeletal fluorosis). Besides these maladies, non skeletal fluorosis or toxic effects of chronic fluoride exposure in soft tissues, viz., gastrointestinal discomforts, neurological disorders, impaired endocrine and reproductive functions, teratogenic effects, apoptosis, genotoxic effects, excitotoxicity, etc., have also been reported in man as well as in domestic and laboratory animals [4].

Fig 1: Dental fluorosis in humans

The mortality of the zebra mussels or mollusks rose with the increase of both fluoride concentration and exposure time. No mortality occurred in the first 24 hours at fluoride concentrations up to 360 mg /l, while in the same period, 60 % of animals exposed to 720 mg F/1 died [5].

The effects of 600 ppm NaF (271 ppm fluoride ion) in the drinking water of the rats for one week significantly decreased the serum levels of the thyroid hormones thyroxine (T4) and triiodothyronine (T3) to 0.95 ± 0.076 µg/ml and 88 + 1.64 ng/dl, respectively. Treatment intraperitoneal for one week with 20 mg curcumin/kg body weight actually increased the serum total T4 level to 5.25 ± 0.089 µg/ml, which was significantly higher ($p<0.05$) than in normal control level and highly significantly higher ($p< 0.001$), and greater than in the NaF control [6]. The broilers grew much slower in all high fluoride groups than those in control groups. Meanwhile, broilers in high fluoride groups showed decreased feed intake and depression. The Malondialdehyde content increased significantly in high fluoride groups when compared with that of the control group [7].

II.EXPERIMENTAL

2.1 Collection of samples

The brine samples were collected from the salt pan of Thoothukudi. The total area of the salt pan was 23500 acres. The chief source of saline water was from the Bay of Bengal. The samples were collected daily for a period of 1 week. The collection of samples were made in 1 liter capacity sampling polythene bottles. The sample bottles were initially washed with water, rinsed with de-ionized water and for two or three times before collecting the brine solution for analysis. Due to evaporation the concentration of the saline water in the salt pan gradually increases and finally salt is formed. After allowing the saline water to pass into the condenser and

crystallizer ponds, the salt water got crystallized on the seventh day. The perfect crystallized salt and pan soil were also collected for analysis. For the analysis of the salt, the salt was made into a saturated solution by dissolving 390 g salt in 1 liter of the de-ionized water. The pan soil was collected by a suitable technique by inserting a PVC pipe of 2 feet length into the soil. Analysis of pan soil was made by dissolving 470 g of the pan soil in 1 litre of the de-ionized water.

2.2 Preparation of the reagent

70 mg of alizarin red S was dissolved in 50 ml of distilled water. 300 mg of zirconyl chloride octahydrate was dissolved in 50 ml of distilled water. The alizarin red S solution was poured slowly into zirconyl chloride octahydrate solution. After a few minutes the solution became clear. This was called as the first solution. To a little amount of distilled water 101 ml of concentrated hydrochloric acid was added, and the volume was made upto 400 ml. To this 33.3 ml of the concentrated sulphuric acid was added. The solution was cooled. The first solution was mixed with the second solution. This mixture was made upto 1000 ml in a standard measuring flask.

2.3 Analysis of Fluoride

100 ml of sample or a portion of sample was taken, and diluted to 100 ml in a Nesslers tube. 5 ml of acid – zirconyl alizarin reagent was added, and kept in dark. The colour standards were compared after one hour . The volume of standard fluoride which was used for comparing the colours were noted [8] and the fluoride content calculated using the formula,

$$\text{Fluoride (ppm)} = \frac{\text{Standard fluoride in ml x 50 x 100}}{\text{Sample in ml}}$$

2.4 Determination of electrical conductance

Electrical conductance of the water samples were carried out using a conductivity meter (Systronics). The conductivity meter was calibrated using 0.01 N KCl solution at 25ºC. The conductivity cell was washed free of KCl solution by distilled water and finally with the respective samples. The electrical conductance of the different saline water samples were measured at 25ºC, and the result was tabulated.

III.RESULTS AND DISCUSSION

In all kinds of samples such as saline water, crystallized salt and pan soil along with other ions fluoride ion is also present in considerable amount. The fluoride ion concentration and electrical conductivity of the collected samples were estimated, and tabulated in Table -1.

The amount of fluoride ion present in the various brine samples of salt pan were analyzed till the crystallization stage, and are plotted in Fig.2. From the graph it is clear that during the initial stage, the concentration of fluoride ion was low and with the progression of days it increased gradually, and attained the maximum value (0.9 ppm to 1.2 ppm). This higher concentration of fluoride gradually decreased with the formation of salt (1.2 ppm to 1.0 ppm).

Table - 1

Fluoride ion concentration (ppm) and electrical conductivity (dS/m) in brine samples, salt and pansoil

Sample No.	Sample Collection	Concentration of Fluoride(ppm)	Electrical Conductance(dS/m)
S1	First day	0.9	142
S2	Second day	1.0	158
S3	Third day	1.1	165
S4	Fourth day	1.1	169
S5	Fifth day	1.2	176
S6	Sixth day	1.1	163
S7	Seventh day	1.0	149
S8	Tenth day	1.0	181
S9	Tenth day	0.6	141

S1 – S7 indicates brine samples

S8 – indicates salt sample

S9 – indicates pan soil sample

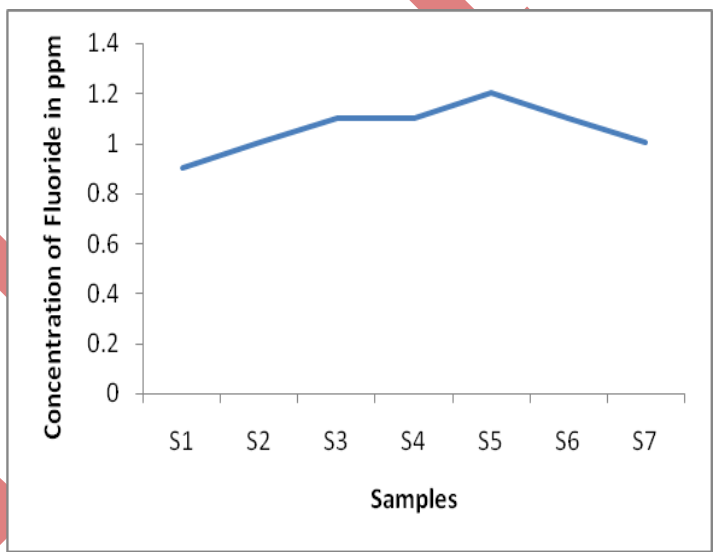

Fig 2: Fluoride ion concentration in brine samples during the crystallization stages.

S1 – S7 indicates brine samples

During the formation of salt, considerable amount of fluoride got settled in the pan soil, and it was estimated to be 0.6 mg /l. Mohammed Naji et al proved that the concentration of fluoride ranged between 1.4 mg/1 to 2.3 mg/1 during monsoon season and 1.1 mg/1 to 2.23 mg/1 in the post monsoon season [9]

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The electrical conductivity of the saline water samples were measured periodically. There was a gradual increase in the value of electrical conductivity, and it reached the highest value of 176 dS/m which later decreased accordingly, and reached the minimum value (149 dS/m).The electrical conductivity values are displayed in Fig 3. During the testing of pan soil, and EC value of 141 dS/m was observed due to the presence of cations and anions.

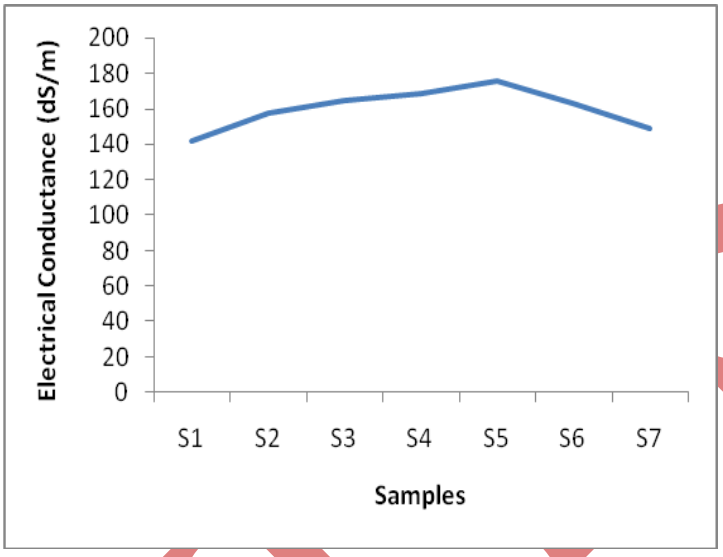

Fig 3: Electrical conductance of brine samples during the stages of crystallization

S1 – S7 indicates brine samples

IV.CONCLUSION

Initially, the salt pans of Thoothukudi contained less amount of fluoride during which the crystallization process increased to a maximum and finally declined. However, the amount of fluoride (1.0 ppm) was not harmful to humans. Thereby indicating that the salt of Thoothukudi salt pan was safe for human consumption.

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