ELECTROCHEMICAL REMOVAL OF IRON AND FLUORIDE FROM WATER

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Removal of fluoride (defluoridation) and iron (deferration) of water are carried out simultaneously in the same electrolytic cell. Aluminium and graphite (or TSI) anodes and aluminium cathode area employed. The results indicate that it is possible to bring down the F^- from 90 ppm or more to less than 0.8 ppm and Fe^{++} from 10 ppm to almost negligible quantity in about 2 to 3 hours and with an energy consumption of 3–6 KWh m^{-3} of water depending on the contents of F^- and Fe^{++}.

INTRODUCTION

In some parts of India, the ground water is heavily contaminated with dissolved fluoride and ferrous iron. The presence of fluoride ion in drinking water may be beneficial or detrimental to public health depending upon its concentration available in water. In recent years, scientific reports have been appearing on the harmful effects of fluoride, especially when fluoride is ingested above 1 ppm. Consumption of fluoride bearing water leads to several ailments [1,2]. The tolerable limit of Fe^{++} iron in drinking water is 0.3 ppm [3] and the consumption of water containing above 0.5 ppm of soluble iron leads to ulcer and constipation, in addition to its staining the fabrics.

Two distinct methods of treatment are available for the removal of fluoride from water, viz. (i) chemical treatment and (ii) exchange process. The former process employs $AlCl_3$ [4] alum and lime and is known as 'Nalgonda process' [5,6]. In the exchange process, ion exchange resins are employed [7–12], where F^- is exchanged by a suitable ion like OH^- or Cl^-. Electrodialysis was also tried with 80% efficiency for the defluoridation of ground water [13]. Electrocoagulation of F^- by electrochemically generated $Al (OH)_3$ was attempted [14–18]. Activated alumina has been used successfully as a defluoridation medium in a down flow column [19,20].

Air oxidation and CO_2 stripping followed by filtration is one of the methods suggested for the removal of soluble iron [21,22]. Deferration was also carried out by ozonization, followed by diatomaceous earth filtration [23].

In this paper, the defluoridation and deferration of drinking water have been carried out simultaneously by electrolysis in the same cell, based on the principles of electroflocculation and oxidation respectively. Aluminium content in water after the removal of F^- and /or Fe^{++} has also been estimated, since there are reports that kidney patients are at risk from bone disease and anaemia caused by the aluminium in water.

EXPERIMENTAL

The cell assembly consisted of a two litre glass beaker acting as a container and fitted with a PVC cell cover having slots for introducing electrodes and thermometer. Two aluminium sheets (7.5(b) × 15(h) cm with immersion height of 12 cm), having an interelectrode distance of 1 cm, acted as anode and cathode

for the removal of fluoride alone. However, when iron also had to be removed along with fluoride, the anode consisted of aluminium plate (4 (b) × 15 (h) cm) and graphite plate (4.2(b) × 15(h) cm with immersion height of 12 cm) and fixed to the same busbar. While the cathode was same as described above. The interelectrode distance was maintained at 1cm.

Electrolyte was prepared by dissolving known quantities of sodium fluoride (~ 2 - 90 ppm F^-) and/or ferrous sulphate (~ 4 to 10 pm Fe^{++}) in tap water. From the stock solution, 2 litres of the same was used for each experiment after the initial analyses of F^- and Fe^{++}.

Electrolysis was started after taking the water containing F^- or Fe^{++} or both in the cell container by passing d.c. from a rectifier. Effects of initial concentration of F^- and/or Fe^{++}, current density and temperature with duration have been studied. At the end of electrolysis, the water was stirred and the precipitate was allowed to settle for 15 minutes. Water samples, after filtration, were collected for the estimation of F^- and Fe^{++} The presence of free aluminium, if any, was also estimated.

ANALYSIS

Fluoride: The fluoride content in the water before and after electrolysis was determined using ion selective electrode (Or ion). Citrate was included as a chelating agent in the buffer for adjusting the total ionic strength and to avoid interference by fluoride-bonding metal ions such as Al, Ca and Fe as well as boric acid [24].

Ferrous iron: The soluble Fe^{++} in water before and after electrolysis was determined by colorimetric method [25] using 1–10 orthophenanthroline.

Aluminium: Aluminium was estimated using Atomic Absorption spectro photometer (AAS) Model. Perkin Elner 380)

RESULTS AND DISCUSSION

Figures. 1(a) & (b) show the variation of concentration of fluoride and cumulative efficiency for the removal of fluoride with duration for water containing different initial concentrations of fluoride. It is evident from the figure, that more than 60% of initial fluoride content is removed in the first 30 minutes, irrespective of initial fluoride concentration. The removal of F^- is very low after 60 minutes, leading to very poor efficiency. It is, however, possible to bring down the F^- to less than 1 ppm in about 120 to 160 minutes depending upon the initial concentration of F^- (6 to 90 ppm) present in the water.

Fig. 2: Variation of concentration of F^- with quantity of electricity at different current densities (A dm^{-2}).
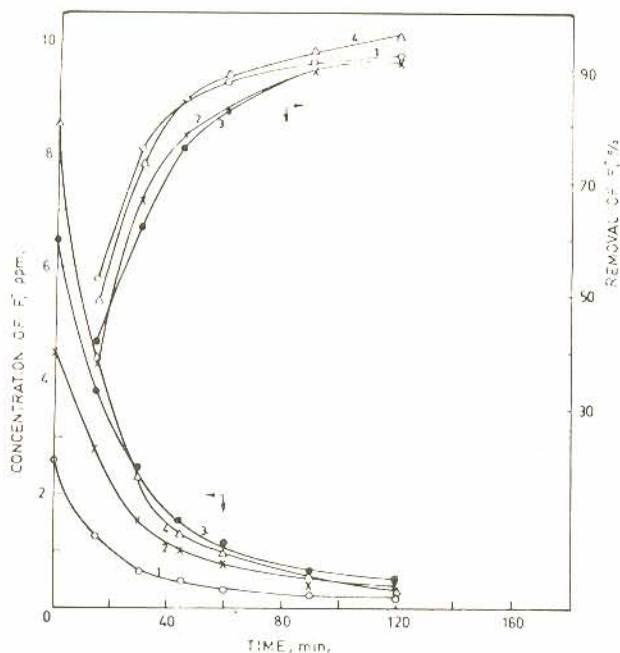(1) 0.1 (2) 0.25 (3) 0.5 (4) 1.0

Fig. 1(a) & (b): Variation of concentration of F^- and cumulative efficiency for removal of F^- with duration for different initial concentrations of F^- (ppm)
a) (1) 2.7 (2) 4.5 (3) 6.5 (4) 8.6 b) (1) 10.3 (2) 19.0 (3) 49.4 (4) 91.2

Fig. 3: Variation of concentration of F^- with duration at different temperatures.
(1) 303K (2) 313K (3) 323K.

Using about 6 ppm of initial concentration of F^- in water, the variation of concentration of F^- with quantity of electricity at different current densities is shown in Fig. 2. Though the removal of F^- is almost same at all current densities, it is evident that the removal of F^- has become less at higher current density (1 A.dm^{-2}).

Among the different temperatures studied as seen from Fig. 3, the maximum removal of F^- with duration is observed at 313 K.

It has been found that the addition of lime water (as is done in Nalgonda process) has no appreciable effect in F^- removal as is evident from Table I. The electrodes, especially the anode, needed a nitric acid dip at the start of every experiment to bring down the voltage of the cell. The change of polarity of the electrodes had no adverse or beneficial effect.

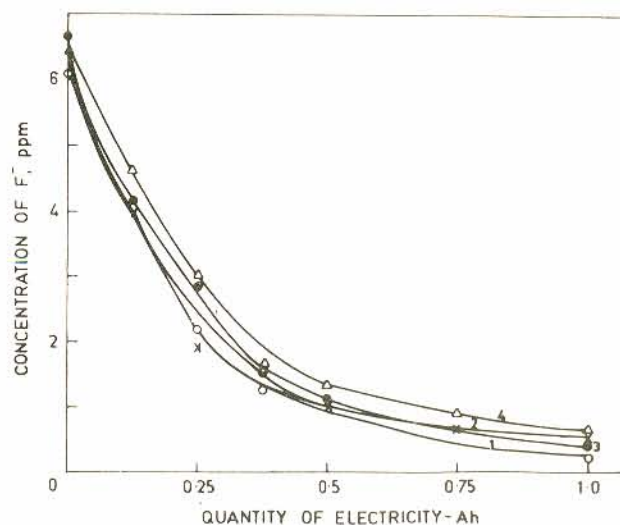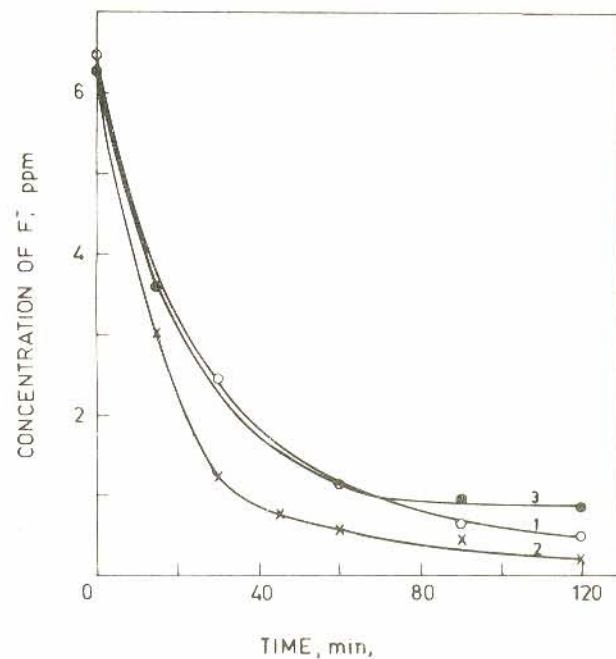Table II shows the removal of Fe^{++} at different durations both

in presence and absence of F^-. It is clear that the concentration of Fe^{++} is reduced to less than 1 ppm within 30 minutes irrespective of the presence or absence of F^-, by employing aluminium - graphite or aluminium - TSI anodes.

Analysis of water after the removal of F^- and Fe^{++} in all these experiments showed < 1 ppm Al^{+++}, as indicated by AAS.

When F^- alone is present, Al^{3+} ions from the aluminium anode dissolve and react with F^- ions to form the insoluble AlF_3, which will get coagulated by the gases evolved at the anode and cathode. However, where F^- and soluble Fe^{++} are present, both aluminium and graphite are used as anode. Aluminium anode removes the F^- by precipitation as AlF_3 as described above and Fe^{++} is oxidised to Fe^{+++} at graphite anode. The oxidised Fe^{+++} precipitates as $Fe(OH)_3$ since the pH is above 5. Aluminium cathode is employed

because the system will not be affected even if there is failure of electricity during electrolysis. This may lead even to the use of alternating current for electrolysis for F^- removal.

TABLE-I: Effect of addition of lime in electrolytic defluoridation of water

Electrolysis	Duration (mts)						
	0	15	30	45	60	90	120
With lime (ppm)	6.46	3.8	2.5	1.5	1.14	0.64	0.53
Without lime (ppm)	6.46	4.4	2.2	1.9	1. 7	1. 2	0.8

The economics of this process depends on the cheapness of electricity. Though the chemical process, especially the use of activated alumina, will be cheaper, the electrolytic removal of F^- can be resorted to certain processes where addition of chemicals will either spoil or hinder subsequent steps in the process.

CONCLUSION

A simple method of defluoridation and deferration of water by electrolysis in the same cell simultaneously, based on electroflocculation and oxidation, is described wherein the energy consumption is low (3.6 kWh m^{-3} water depending on the initial concentration of F^-) with no addition of chemicals. A current density of 0.5 A dm^{-2} and temperature of 313K are found to be optimum. In all the experiments after the removal of F^- and Fe^{++}, the Al^{3+} was < 1 ppm. It is also hoped that the treatment

of water by chlorine can also take place simultaneously, in case water contains more Cl^- in addition to F^- and Fe^{++}. Thus two (removal of F^- and Fe^{++}) or three (additionally chlorination of water) operations are possible in the same cell simultaneously.

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TABLE-II: Deferration in the presence of absence of F^- with different anodes

Anode	Iron removal with flouride (in ppm) Duration (mts)				Iron removal without fluoride (in ppm) Duration (mts)				Fluoride removal with iron (in ppm) Duration (mts)			
	0	30	60	120	0	30	60	120	0	30	60	120
Aluminium	6.5	0.65	0.59	0.48	6.5	0.59	0.56	0.56	6.08	2.66	0.76	0.58
Aluminium + graphite	3.8	0.22	0.16	0.16	4.6	0.2	0.09	0.09	6.27	3.99	2.28	1.44
	6.5	0.31	0.21	0.10	5.8	0.27	0.17	0.01	6.08	3.99	2.85	2.09
	9.7	0.47	0.29	0.29	10.7	0.37	0.27	0.27	6.27	4.18	2.66	1.9
Aluminium + TSIA	6.5	0.35	0.32	0.29	6.2	0.32	0.29	0.26	6.46	1.95	0.91	0.51

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