Project Completion Report

Title of Project:

Laboratory study of fluoride removal from groundwater using acid-enhanced limestone defluoridation technique

File No. DST/TDT/WTI/2k7/24

Name of PI:

Dr. Robin Kumar Dutta

Professor, Department of Chemical Sciences

Tezpur University, Tezpur 784 028

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1. Title of the project: **Laboratory study of fluoride removal from groundwater using acid-enhanced limestone defluoridation technique**

2. Principal Investigator:

Dr. Robin Kumar Dutta
Professor, Department of Chemical Sciences
Tezpur University, Tezpur 784 028, Assam
Ph: 03712 267007/8/9 Extn 5055 (O), 9435006674 (M),
Fax: 03712 267005/6
E-mail: robind@tezu.ernet.in

Co-Investigator:

Dr. Tarun Kumar Maji
Professor, Department of Chemical Sciences
Tezpur University, Tezpur 784 028, Assam
Ph: 03712 267007/8/9 Extn 5053 (O), 9435381087 (M),
Fax: 03712 267005/6
E-mail: tkm@tezu.ernet.in

3. Implementing Institution:

Tezpur University (A Central University)
Napaam, Tezpur 784 028, Assam

Other Collaborating Institutions: None

4. Date of Commencement: 18/7/2008

5. Planned Date of Completion: 17/7/2011

6. Actual Date of Completion: 17/7/2011

7.(a) **Objectives as stated in the project proposal:**

Overall Development Objectives

- Development of the defluoridation process by optimization of quantity, strength of acid, etc., w.r.t. the quantity of water and concentration of fluoride.
- Optimization of chip size of crushed limestone, column size, etc., w.r.t. the quantity of groundwater and concentration of fluoride.
- Optimization of retention time.

Intermediate Objectives

- Study of the mechanism of fluoride removal from water by acid-enhanced limestone defluoridation with fluoride containing distilled water and groundwater.
- Treatment of used limestone for reuse.
- Examination of quality, e.g., pH and other contaminants, of treated water w.r.t. its potability. Removal of color if appears in the treated water.

7.(b) Objectives met:

The overall objectives of the project have been met as stated in the proposal which have been described below.

Overall development objective 1.

- *Development of the defluoridation process by optimization of quantity, strength of the acid, etc., with respect to the quantity of water and the concentration of fluoride:*

The present work. Any method that is to be used by common people in the rural areas of a state or country must be at affordable cost, since water is a primary daily requirement of human as well as animal. To get a method for defluoridation after fulfilling all these conditions is a very tough work. In our work of defluoridation, we have tried to execute all these conditions and a defluoridation method, viz., acid enhanced limestone defluoridation (AELD) has been evaluated which is low-cost and effective. During the course of the project we have chosen four acids, viz., acetic acid (AA), citric acid (CA), oxalic acid (OA) and phosphoric acid (PA) and fixed bed crushed limestone column reactors for the defluoridation and come out with very encouraging results.

The acids chosen: The acids are used to increase Ca^{2+} activity *in situ* in crushed limestone reactor. AA and CA have been chosen because they are of low cost and not only nontoxic unlike nitric acid, formic acid, etc., but are also common food additives. The familiarity of AA and CA to common people may be an advantage. They will form calcium acetate (soluble) and calcium citrate (insoluble) salts after reaction with limestone, which are not hazardous. OA is stronger acid than AA and CA and it will form an insoluble salt calcium oxalate after reaction with limestone. So, no OA should remain in the treated water. Solid form of OA can also be an advantage for rural application. PA is a recommended water treatment chemical and used in detergent preparation, metal treatment, refining of sugar and vegetable oils etc. Its calcium salt is also insoluble and which may help in the defluoridation process as calcium phosphate has been already used in this field.

Some of the expected benefits of the method were: its simplicity, which can be used by laymen; no need of electrical, thermal power, or pressure and reusability of the limestone. Most importantly, the overall cost may be lower than the other methods, since AA, CA, OA and PA are cheap and limestone is also naturally available in the fluoride affected areas.

Limestone defluoridation in presence of acetic acid

Acetic acid was chosen for the acid enhanced limestone defluoridation (AELD) due to the wide use of this acid in food industry and the low cost of the chemical. AA is widely used for preparation of pickle and it is also used in confectionery goods and flavourings. Due to its bacteriostatic properties it has considerable importance as a preservative. The results of the experiments performed for defluoridation in presence of AA has been presented below in detail.

Batch Study

Batch tests in plastic bottles were performed to determine the amount of the acid required for the AELD process and to determine the residence time required during the treatment. Different quantities of the acid were added to the fluoride water and treated with the limestone for different residence time. The results of this experiment have been discussed here.

Effect of acid concentration

The results of the batch experiments with AA and crushed limestone are shown in Fig. 3.1 and Table 3.1. The initial F⁻ concentration from 10 mg/L was reduced to below 2 mg/L with an initial AA concentration of 0.03 M.

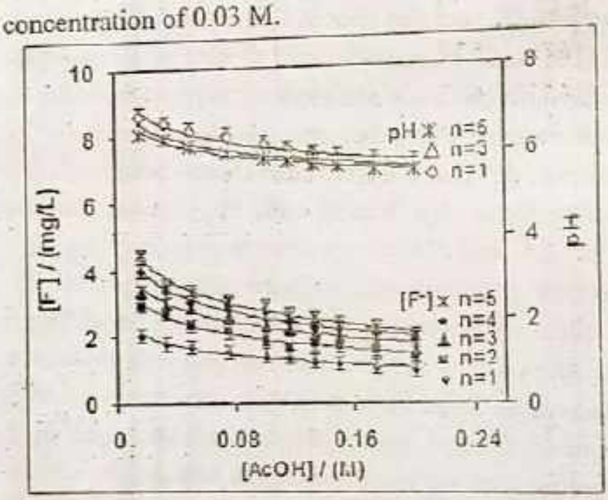

Figure 3.1. Concentration of F⁻ and pH of the treated water with crushed limestone of size 3-4 mm for 12 h *vs.* concentration of AA added to F⁻ containing distilled water in batch test. Initial [F⁻] = 10 mg/L. n = no. of repeated use of same limestone.

Moreover, one can see from Table 3.1 that the remaining F⁻ concentration can be further reduced to 1 mg/L on increasing $[AA]_o$ to 0.2 M. This suggests that for efficient fluoride removal, the AA concentration should be more than 0.03 M. A low concentration of the acid in the experiment is desirable, since higher concentration can influence the taste and odour of the treated water and the total treatment cost. Therefore, the concentration of the acid may be selected from a range of 0.03 to 0.1 M for the defluoridation experiments in fixed bed column.

The observed fluoride removal by this process may be attributed to an *in situ* generation of high concentration of Ca^{2+} ions by dissolution of limestone in presence of AA. It can be observed from the figure that the F⁻ removal ability of the crushed limestone chips gradually decreased with the number of repeated use of the same limestone (n). This may happen due to the decrease in adsorption sites of limestone, which become saturated by gradual adsorption of fluoride on repeated use of the same limestone.

Table 3.1. Remaining $[F^-]$ and pH of the treated water with crushed limestone of size 3-4 mm for 12 h with different amount of AA (Molar) added to F^- containing distilled water in batch test. Initial $[F^-]$ = 10 mg/L. n = no. of repeated use of same limestone.

	AA (M)										
n	0	0.01	0.03	0.05	0.07	0.1	0.11	0.13	0.15	0.17	0.2
	Remaining Fluoride (mg/L)										
1	3.77	2.08	1.80	1.71	1.55	1.45	1.40	1.27	1.20	1.08	0.98
2	5.62	2.96	2.74	2.37	2.18	1.95	1.64	1.78	1.72	1.59	1.45
3	6.66	3.40	3.01	2.88	2.63	2.37	2.24	2.11	2.02	1.83	1.63
4	8.47	4.01	3.40	3.05	2.98	2.72	2.44	2.22	2.21	2.13	1.93
5	8.52	4.48	3.56	3.37	3.08	2.96	2.66	2.55	2.38	2.28	2.02
	pH of the water after treatment										
1	6.92	6.89	6.70	6.53	6.40	6.18	6.05	5.95	5.85	5.78	5.72
2	7.29	6.73	6.55	6.35	6.18	6.05	5.92	5.83	5.84	5.74	5.63
3	7.37	6.64	6.47	6.28	6.07	5.94	5.84	5.78	5.72	5.69	5.62
4	7.28	6.52	6.36	6.21	6.13	6.00	5.92	5.85	5.82	5.70	5.63
5	7.11	6.47	6.35	6.17	6.00	5.85	5.76	5.68	5.65	5.57	5.52

Column Study

The batch test of AA enhanced limestone defluoridation shows that, minimum 0.03 M concentration of the acid will be required to bring down the fluoride level to 2 mg/L from an initial concentration of 10 mg/L. The results were best when the residence time was 12 h. Therefore, in this column study, the performances of the 0.03, 0.06 and 0.1 M concentrations of the acid have been investigated and the results of 0.1 M AA has been compared with the defluoridation by same procedure without adding acid to the water. The results of this column study have been described here with reference to different factors that affect the removal process.

Effect of acid concentration

A comparison between the fluoride removal capacity of the crushed limestone column in absence of the acid and in presence of the acid reveals that in presence of acids the removal capacity increased from 40 % (without acid) to 90 % (Fig. 3.3). There was a gradual decrease in the percent removal in both cases but the decrease was less in presence of the acid. To choose the optimum concentration of acid for the removal process and also to see the effect of residence time, a series of experiments with varying residence time has been done using the three concentrations of the AA *viz.*, 0.03, 0.06 and 0.1 M. The results of the experiments have been presented in the Fig. 3.4 and Table 3.2.

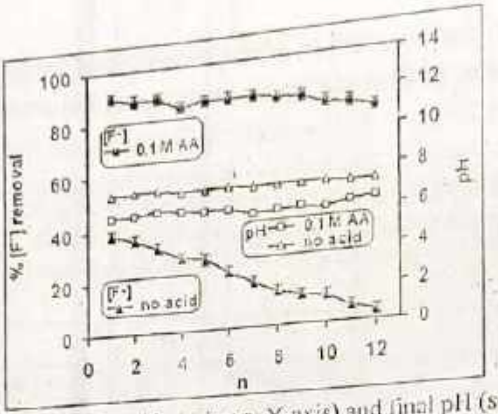

Figure 3.3. Percent removal of fluoride (primary Y-axis) and final pH (secondary Y-axis) *vs.* n (no. of repeated use of the same limestone bed), after treatment with 2-3 mm size of limestone particle for 12 h with initial [F⁻] of 10 mg/L prepared in distilled water without any acid and with 0.1 M of AA.

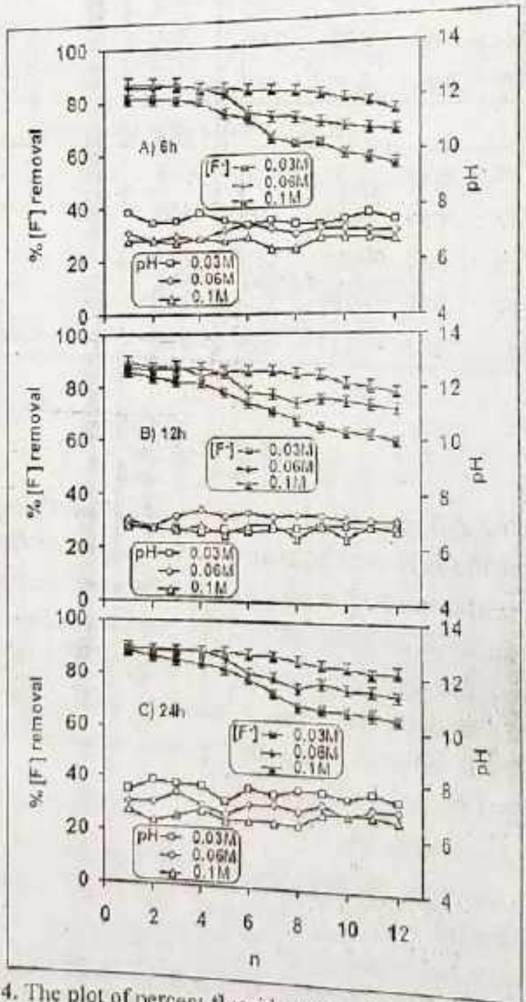

Figure 3.4. The plot of percent fluoride removal (primary Y axis) and pH (secondary Y axis) *vs.* no. of repeated use after addition of 0.03, 0.06 and 0.1 M AA before filtration to the feed water after treatment for (A) 6 h, (B) 12 h and (C) 24 h. Initial [F⁻] = 10 mg/L in distilled water.

One can see from the figure and the table that the fluoride removal is improved significantly with increase in the acid strength but gradually decreased with the number of repeated use of the same limestone column, n. With 6 h of residence time, 0.1 M AA brings down the fluoride concentration from 10 mg/L to below 1 mg/L up to n = 7, whereas, an AA concentration of 0.06 M reduces the fluoride level to below 2 mg/L up to n = 5. From the results, it can be seen that 0.03 M concentration is insufficient for the purpose while 0.06 M and 0.1 M both reasonably increase the removal capacity of the limestone.

Fluoride removal from groundwater

The suitability of this column treatment for defluoridation from groundwater amended with fluoride has been examined in comparison to the fluoride solution prepared in distilled water. Results of the experiments for F^- removal at lower concentrations of the acid 0.03 M $[AA]_o$ with distilled water as well as with groundwater have been presented in Fig. 3.5. The fluoride removal from distilled water was slightly better than that from groundwater for small values of n. However, with increase in n, the fluoride removal in the case of distilled water decreased slightly more rapidly than that in the case of groundwater.

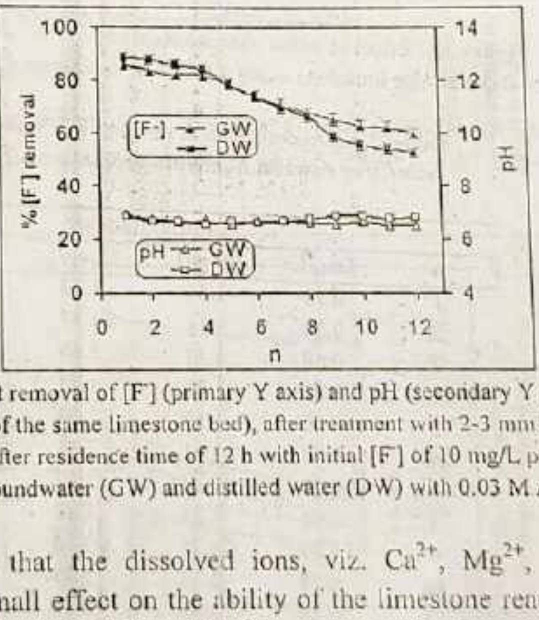

Figure 3.5. Percent removal of [F] (primary Y axis) and pH (secondary Y axis) *vs.* n (number of repeated use of the same limestone bed), after treatment with 2-3 mm size of limestone particle after residence time of 12 h with initial [F] of 10 mg/L prepared in groundwater (GW) and distilled water (DW) with 0.03 M AA.

The results indicate that the dissolved ions, viz. Ca^{2+}, Mg^{2+}, SO_4^{2-} present in the groundwater had a small effect on the ability of the limestone reactor in the presence of the acids to remove fluoride. Ca^{2+} and Mg^{2+} are reported to have negative correlation with F^-. The presence of sulfate or phosphate is known to inhibit fluoride removal by calcite.

Effect of initial fluoride concentration

The fluoride removal ability of limestone was also measured using different initial fluoride concentrations, viz. 5, 10, 15, and 20 mg/L to investigate the influence of initial concentration of fluoride on fluoride removal by the acid enhanced limestone defluoridation. The results of these experiments on the percent fluoride removal in the presence of different initial fluoride concentrations have been shown in Fig. 3.6 and the remaining F^- concentrations have been given in the Table 3.3.

It can be observed from the figure and the table that there is significant fluoride removal with all the initial concentrations; however, at lower initial concentration the percent removal is better. For example, with initial 5 mg/L concentration, the fluoride concentration was found to decrease to below 0.5 mg/L. Another observation is that initially the percent removal is very good but with increasing the number of repeated use of the same limestone the percent removal decreases. The figure reveals that the effect of initial concentration is not significant up to n = 5, whereas, after n = 5 the removal efficiency decreases with increase in the initial

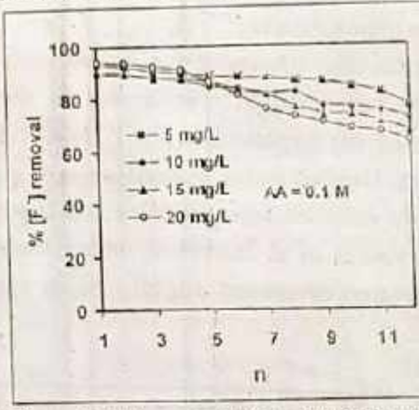

Figure 3.6. Effect of initial concentration of fluoride on fluoride removal by 2-3 mm size limestone using 0.1 M AA, to activate Ca^{2+} from limestone.

Table. 3.3. Concentration of remaining [F$^-$] in the treated water after removal from different initial concentration.

	Initial fluoride			
n	5mg/L	10mg/L	15mg/L	20mg/L
1	0.33	1.04	1.28	1.18
2	0.38	1.11	1.37	1.32
3	0.49	1.17	1.69	1.53
4	0.51	1.26	1.71	1.83
5	0.56	1.53	1.83	2.78
6	0.58	1.61	2.41	3.78
7	0.62	1.83	2.62	4.82
8	0.66	1.75	3.42	5.41
9	0.69	2.31	3.78	5.84
10	0.78	2.35	3.79	6.34
11	0.89	2.46	4.19	6.62
12	1.15	2.73	4.77	7.26

concentration but still the removal remains within 65-80 %. These results indicate precipitation to be the dominating mechanism of the fluoride removal in the present method since the final concentrations of Ca^{2+} and F$^-$ depends only on the solubility product in the presence of excess Ca^{2+} and not on the initial concentration of F$^-$. The results also indicate that arrangement of more than one limestone reactors in series and re-introduction of the acids before the water enters to the successive reactors may result in better fluoride removal for highly fluoride containing water.

Limestone defluoridation in presence of citric acid

Citric acid has diverse uses, e.g. in foods, beverages, personal care, pharmaceuticals, cleaning, dyeing, construction chemicals, photography, etc. Biologically, it is present in different forms in human as well as animal body. In this work CA has been used in defluoridation of groundwater with limestone. In order to systematic study of the use of CA in this water treatment process some batch and fixed bed column studies have been carried out, the results of which are presented below.

Batch study

The batch tests for defluoridation of water by using CA has been carried out following the same procedure as AA, to determine the quantity of CA needed for the limestone defluoridation process and the contact time required for the treatment. Different concentrations of acids were added to the fluoride water and treated with the crushed limestone for different time intervals in plastic bottles.

Effect of acid concentration

The results of batch experiments of F^- removal with crushed limestone chips of 3-4 mm size, as a function of initial concentrations of CA up to 0.1 M are shown in Fig. 3.8 and Table 3.4.

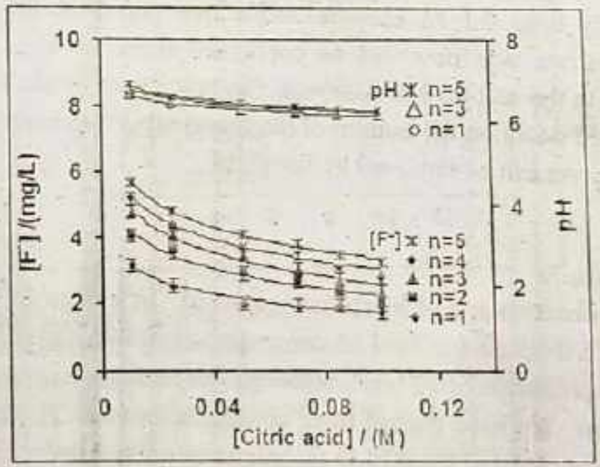

Figure 3.8. Concentration of F^- and pH of the water after treatment with crushed limestone of size 3-4 mm for 12 h *vs.* concentration of CA added to F^- containing distilled water in batch test. $[F]_o$=10 mg/L. n = no. of repeated use of same limestone.

It can be seen from the figure that addition of the acid to the water before treatment with crushed limestone lowers the F^- concentration from its initial value of 10 mg/L to below 2 mg/L, which is again much better compared to the fluoride removal by limestone filtration alone. The ability of the crushed limestone chips to remove F^- increased with increasing the acid concentration. However, the removal became poorer gradually with increase in the number of repeated use (n) of the same amount of limestone chips, which can be attributed to saturation of adsorption sites of the limestone chips.

Table 3.4. Remaining $[F^-]$ and pH of the water after treatment with crushed limestone of size 3-4 mm for 12 h with different concentration of CA added to F^- containing distilled water in batch test. $[F^-]_o$=10 mg/L. n = no. of repeated use of same limestone.

	CA (M)					
n	0.01	0.025	0.05	0.07	0.085	0.10
Remaining Fluoride (mg/L)						
1	3.18	2.53	1.98	1.90	1.91	1.74
2	4.07	3.58	2.91	2.67	2.43	1.97
3	4.77	4.07	3.48	3.04	2.70	2.34
4	5.19	4.36	3.82	3.54	3.16	2.80
5	5.67	4.81	4.07	3.80	3.44	3.25
pH of the water after treatment						
1	6.65	6.43	6.29	6.23	6.19	6.16
2	6.71	6.45	6.30	6.26	6.23	6.17
3	6.83	6.55	6.40	6.32	6.28	6.23
4	6.87	6.57	6.41	6.36	6.28	6.24
5	6.91	6.60	6.45	6.37	6.33	6.27

It can be observed from the Table 3.4 that, an initial CA concentration of 0.05 M is required to bring the F^- concentrations from 10 to less than 2 mg/L when the crushed limestone chips sample was used for the first time with contact time of 12 h. CA was added only upto 0.1 M because above that concentration, excessive precipitation of calcium citrate was observed as confirmed from IR and XRD data which has been described in the section 3.5. Although this precipitate makes the water turbid, the particles were settled down on the bottom of the container on standing for 2-3 h. Thus the turbidity of the solution can be removed by filtration.

Column study

From the observations of batch test results of CA enhanced limestone defluoridation it is clear that, a minimum of 0.01 M concentration of the acid can be used for F^- removal from initial concentration of 10 mg/L although the performance of the acid in this concentration is quite low. We have chosen three concentrations of CA *viz.*, 0.01, 0.05 and 0.1 M for a comparative study of the AELD technique in a fixed bed column after different treatment time viz., 6, 12 and 24 h. The findings of this experiments using fluoride containing distilled water have been presented here (Fig. 3.10 & Table 3.5).

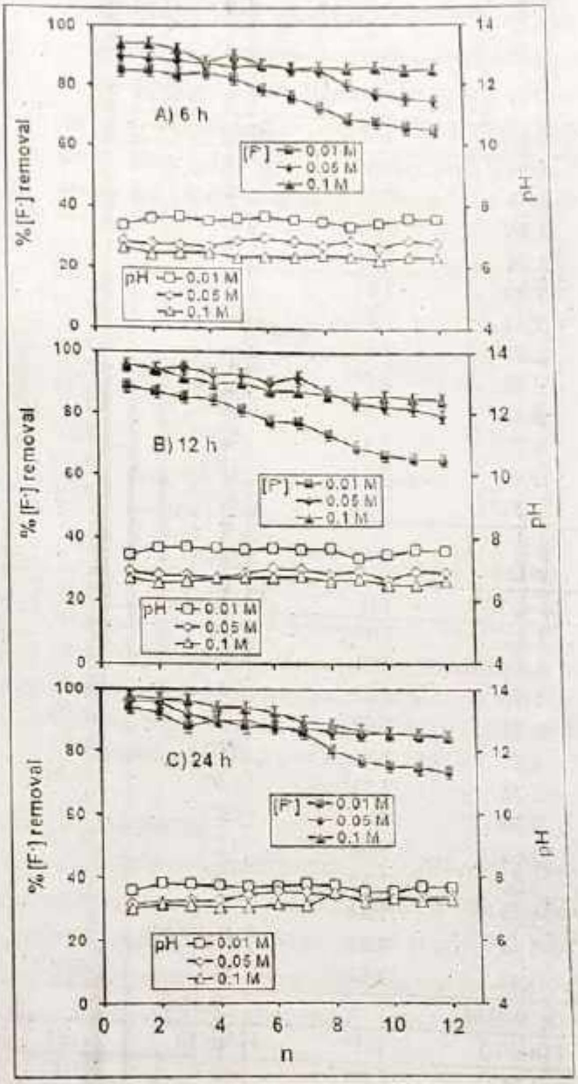

Figure 3.10. The plot of percent fluoride removal (primary Y axis) and pH (secondary Y axis) *vs.* no. of repeated use after addition of 0.01, 0.05 and 0.1 M CA before filtration to the feed water after treatment for (A) 6 h, (B) 12 h and (C) 24 h. Initial concentration of fluoride is 10 mg/L.

The effect of initial concentration of F^- solution on this defluoridation process, the final pH and the effect of other ions have also been discussed here.

Effect of acid concentration

The acid concentrations as well as the treatment time determine the fluoride removal capacity of the limestone column. As in the case of AA here also the fluoride removal is improved with increase in the acid strength and gradually decreased with the number of repeated use of the same limestone column, n (Fig. 3.10 & Table 3.5).

Table 3.5. Remaining [F^-] and pH of the water after treatment of 0.01, 0.05 and 0.1 M CA containing 10 mg/L fluoride water, using 2-3 mm size limestone chips

column for (A) 6 h, (B) 12 h and (C) 24 h treatment time.

(A) 6hr	0.01M		0.05M		0.1M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	1.49	7.38	1.01	6.85	0.59	6.65
2	1.51	7.62	1.09	6.78	0.58	6.45
3	1.64	7.68	1.14	6.76	0.76	6.49
4	1.56	7.54	1.22	6.68	1.20	6.48
5	1.74	7.61	1.35	6.88	0.96	6.32
6	2.12	7.68	1.32	6.98	1.28	6.36
7	2.38	7.59	1.45	6.85	1.38	6.34
8	2.82	7.50	1.52	6.73	1.40	6.42
9	3.12	7.34	1.97	6.87	1.42	6.36
10	3.22	7.45	2.31	6.64	1.40	6.26
11	3.41	7.61	2.45	6.88	1.50	6.34
12	3.51	7.58	2.52	6.78	1.46	6.32

(B) 12hr	0.01M		0.05M		0.1M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	1.12	7.44	0.45	6.94	0.41	6.73
2	1.31	7.71	0.57	6.82	0.54	6.58
3	1.47	7.72	0.51	6.83	0.82	6.62
4	1.51	7.69	0.72	6.76	1.02	6.74
5	1.87	7.65	0.72	6.91	0.98	6.75
6	2.24	7.71	0.97	7.05	1.24	6.77
7	2.26	7.66	0.79	7.01	1.26	6.79
8	2.65	7.68	1.24	6.88	1.38	6.65
9	3.06	7.38	1.65	6.97	1.44	6.71
10	3.32	7.48	1.75	6.69	1.42	6.54
11	3.44	7.65	1.82	6.96	1.48	6.52
12	3.49	7.61	2.05	6.92	1.52	6.64

(C) 24hr	0.01M		0.05M		0.1M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	0.58	7.58	0.33	7.15	0.23	7.01
2	0.76	7.82	0.43	7.25	0.29	7.15
3	1.20	7.78	0.89	7.28	0.34	7.12
4	0.96	7.74	1.01	7.27	0.56	7.06
5	1.20	7.71	1.02	7.45	0.59	7.05
6	1.15	7.73	1.27	7.54	0.72	7.16
7	1.40	7.79	1.36	7.51	1.06	7.11
8	1.97	7.75	1.40	7.42	1.12	7.51
9	2.31	7.54	1.45	7.32	1.34	7.21
10	2.45	7.55	1.46	7.34	1.42	7.32
11	2.52	7.71	1.50	7.35	1.43	7.25
12	2.64	7.68	1.54	7.39	1.51	7.29

Fluoride removal from groundwater

The suitability of this column treatment for defluoridation from groundwater amended with fluoride has been examined in comparison to that from distilled water (Fig. 3.11).

Initially at low n, the fluoride removal from groundwater was found to be better than that of distilled water. However as n increases over 7, the removal for groundwater decreased more rapidly than that from the distilled water. This trend is just opposite to that observed with AA. The results of the groundwater experiments show that the process is effective also for removal of fluoride from groundwater containing fluoride. The presence of different ions present in the groundwater has a little affect on the removal process.

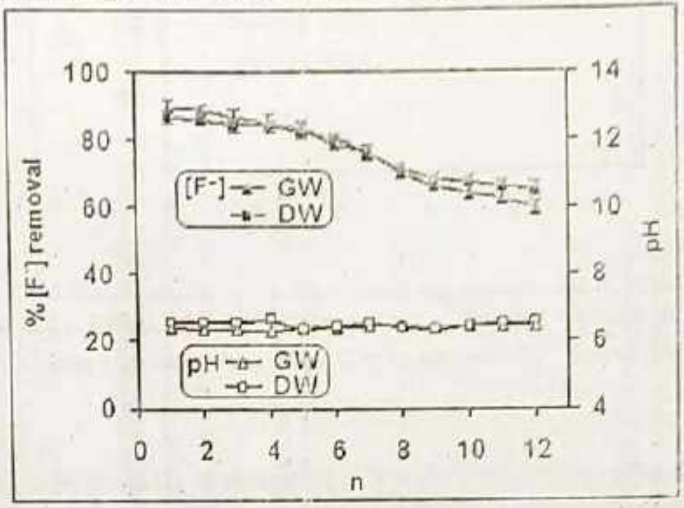

Figure 3.11. Percent removal of $[F^-]$ (primary Y axis) and pH (secondary Y axis) vs. n (no. of repeated use of the same limestone bed), after treatment with 2-3 mm size of limestone particle after residence time of 12 h with initial $[F^-]$ of 10 mg/L prepared in GW and DW with 0.01 M CA.

Effect of initial fluoride concentration

Since, fluoride is present in different concentrations in different groundwater sources, the fluoride removal capacity of limestone has been examined using different initial fluoride concentrations, viz. 5, 10, 15, and 20 mg/L with initial [CA] = 0.1 M and residence time of 12 h. The results of these experiments have been shown in Fig. 3.12 and Table 3.6. It can be seen from the figure and the table that the F^- removal capacity of the limestone is satisfactory starting with all initial concentrations.

The difference between the fluoride removal results obtained from this experiment and the results included in the Table 3.5 under similar conditions can be attributed to the difference in composition of the limestone samples used. Similar discrepancies have been observed in other cases also. However, this does not affect the evaluation of relative fluoride removal ability of a column. The removal percentage is better in case of lower initial concentration than the higher concentrations.

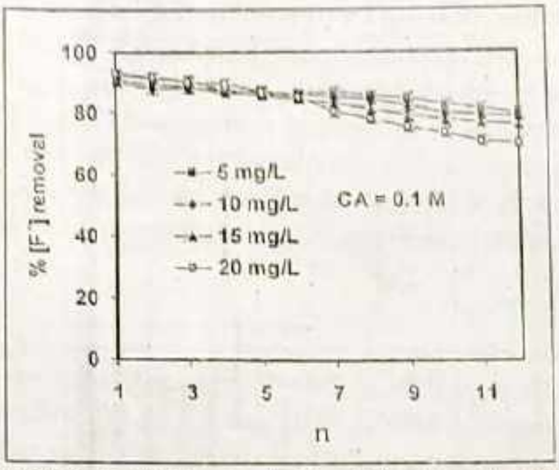

Figure 3.12. Effect of initial concentration of fluoride on fluoride removal by 2-3 mm size limestone using CA, to activate Ca^{2+} from limestone.

Table 3.6. Concentration of remaining $[F^-]$ in the treated water after removal from different initial concentration, [CA] = 0.1 M, residence time = 12 h.

	Initial fluoride			
n	5mg/L	10mg/L	15mg/L	20mg/L
1	0.45	0.97	1.03	1.41
2	0.53	1.21	1.13	1.68
3	0.56	1.18	1.25	2.02
4	0.61	1.33	1.74	2.12
5	0.64	1.38	2.01	2.58
6	0.68	1.39	2.18	2.92
7	0.65	1.46	2.41	3.92
8	0.71	1.56	2.62	4.36
9	0.75	1.75	3.01	4.91
10	0.86	2.02	3.18	5.24
11	0.92	2.06	3.35	5.84
12	1.01	2.14	3.52	6.02

For example, with initial 5 mg/L concentration, the fluoride concentration was found to decrease to below 1 mg/L upto n = 11 whereas with the 15 and 20 mg/L initial concentrations, even with n = 1 the remaining F^- concentration is greater than 1 mg/L. It can be observed from the data that with increasing the number of repeated use of the same limestone the percent removal decreases and after n = 5 the removal efficiency decreases with increase in the initial concentration. Thus, the acid enhanced limestone defluoridation technique is useful for treatment of high as well as low fluoride containing groundwater and the capacity of the technique should be improved by arrangement of more than one limestone reactors in series.

Limestone defluoridation in presence of oxalic acid

Oxalic acid is found in various source in the nature and is being used for different purposes like, cleaning or bleaching, extractive metallurgy, restoration of old wood etc. OA has higher acidic properties in comparison to acetic and citric acid, therefore, it may possess high fluoride removal capacity than that of AA and CA. The fluoride removal by OA has been studied directly with the fixed bed column tests without going for preliminary batch test. The results of the column experiment and interpretations have been presented here.

Effect of acid concentration

Fig. 3.14 (A,B,C) shows the percent fluoride removal from water containing 10 mg/L fluoride in the presence of 0.01, 0.05 and 0.1 M OA after limestone treatment using a column of 2-3 mm sized crushed limestone particles, after residence time of 6 h, 12 h and 24 h, respectively. In Table 3.7 (A,B,C) the remaining F^- concentrations and pH of the water after treatment have been given. It can be observed from the figures and the tables that the fluoride removal is improved significantly with increase in the acid strength but gradually decreased with the number of repeated use of the same limestone column, n. With 6 h of residence time, 0.1 M OA brings down the fluoride concentration from 10 mg/L to below 1 mg/L up to n = 13, whereas, an OA concentration of 0.05 M reduces the fluoride level to below 2 mg/L up to n = 8. The AELD process with OA has been found to be more effective than that with AA and CA (Section 3.1 and 3.2). However, the OA concentration of 0.01 M seems to be insufficient for the purpose. The results of these experiments reveal that 0.05 and 0.1 M OA concentrations are effective for the treatment process.

Effect of initial concentration of fluoride

The initial concentration of fluoride in the water is important in the acid enhanced limestone defluoridation process. It is difficult to remove fluoride from water containing low initial F^- concentration as it is hard to achieve supersaturation of F^- and Ca^{2+} at low initial concentration of F^-. So, it is difficult to lower the fluoride level from a concentration like 50 mg/L directly through precipitation without addition of a sufficiently high amount of Ca^{2+}. We have investigated the removal of fluoride by the present method with different low initial fluoride concentrations, *viz.* 5, 10, 15 and 20 mg/L. The results of these experiments performed in presence of 0.1 M OA and 0.05 M OA for 6 and 12 h of residence time have been shown in Fig. 3.15 and the remaining F^- concentrations have been presented in the Table 3.8.

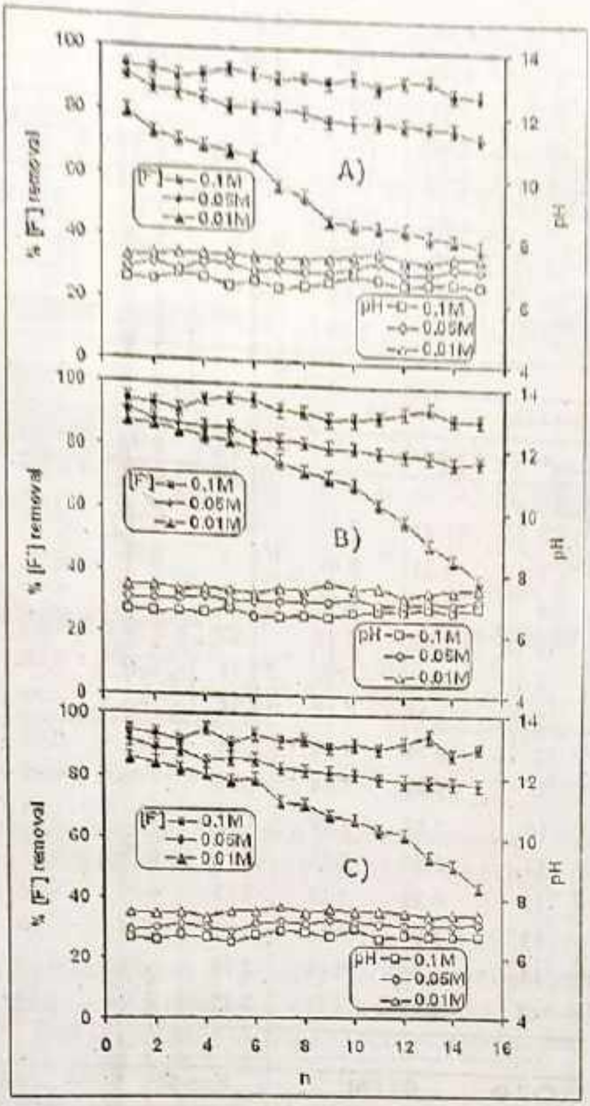

Figure 3.14. The plot of percent fluoride removal (primary Y axis) and pH (secondary Y axis) vs. no. of repeated use after addition of 0.01, 0.05 and 0.1 M OA before filtration to the feed water after treatment for (A) 6 h, (B) 12 h and (C) 24 h. Initial concentration of fluoride is 10mg/L.

Table 3.7. Remaining [F⁻] and pH of the water after treatment of 0.01, 0.05 and 0.1 M OA containing 10 mg/L fluoride water, using 2-3 mm size limestone chips column for (A) 6 h, (B) 12 h and (C) 24 h treatment time.

(A) 6h	0.01 M		0.05 M		0.1 M	
n	F (mg/L)	pH	F (mg/L)	pH	F (mg/L)	pH
1	2.04	7.35	0.88	6.99	0.59	6.63
2	2.66	7.45	1.26	7.15	0.68	6.6
3	2.88	7.48	1.38	6.96	0.88	6.83
4	3.06	7.51	1.52	7.2	0.83	6.73
5	3.23	7.48	1.81	7.15	0.64	6.47
6	3.38	7.41	1.82	6.99	0.78	6.63

7	4.31	7.38	1.85	7.02	0.91	6.4
8	4.62	7.38	1.94	6.96	0.9	6.5
9	5.43	7.41	2.21	6.99	1.02	6.63
10	5.51	7.51	2.24	7.12	0.85	6.86
11	5.56	7.64	2.22	7.32	1.17	6.76
12	5.62	7.38	2.29	6.96	0.95	6.57
13	5.85	7.35	2.34	6.99	0.91	6.63
14	5.92	7.48	2.41	7.15	1.32	6.67
15	6.12	7.48	2.67	7.09	1.36	6.57

(B) 12h	0.01 M		0.05 M		0.1 M	
n	F (mg/L)	pH	F (mg/L)	pH	F (mg/L)	pH
1	1.23	7.53	0.84	6.94	0.55	6.64
2	1.34	7.53	1.16	6.99	0.64	6.58
3	1.51	7.43	1.28	7.01	0.84	6.7
4	1.68	7.46	1.37	7.2	0.48	6.67
5	1.82	7.43	1.37	7.05	0.45	6.83
6	2.03	7.3	1.71	7.03	0.48	6.58
7	2.43	7.49	1.76	7.03	0.79	6.58
8	2.74	7.43	1.82	7.1	0.85	6.61
9	2.92	7.68	1.96	7.06	1.06	6.58
10	3.14	7.49	1.97	7.21	1.05	6.7
11	3.76	7.53	2.11	6.99	0.95	6.8
12	4.28	7.24	2.17	6.97	0.81	6.8
13	5.06	7.43	2.23	7.08	0.66	6.86
14	5.54	7.46	2.42	7	0.99	6.77
15	6.13	7.53	2.35	7.15	1.02	6.89

(C) 24h	0.01 M		0.05 M		0.1 M	
n	F (mg/L)	pH	F (mg/L)	pH	F (mg/L)	pH
1	1.42	7.53	0.83	6.93	0.54	6.52
2	1.57	7.46	1.09	7.02	0.63	6.61
3	1.77	7.56	1.18	7.12	0.83	6.77
4	1.93	7.37	1.5	7.02	0.48	6.55
5	2.13	7.61	1.4	6.87	0.95	6.43
6	2.05	7.6	1.44	7.18	0.62	6.77
7	2.8	7.72	1.72	7.24	0.83	6.9
8	2.87	7.53	1.76	7.18	0.77	6.87
9	3.23	7.65	1.84	7.28	1.04	6.74
10	3.39	7.6	1.92	7.24	0.94	6.99
11	3.7	7.62	2.03	7.12	1.05	6.65
12	3.86	7.56	2.11	7.09	0.85	6.77
13	4.61	7.43	2.13	7.09	0.65	6.71
14	4.88	7.47	2.17	7.09	1.26	6.71
15	5.6	7.47	2.21	7.12	1.04	6.55

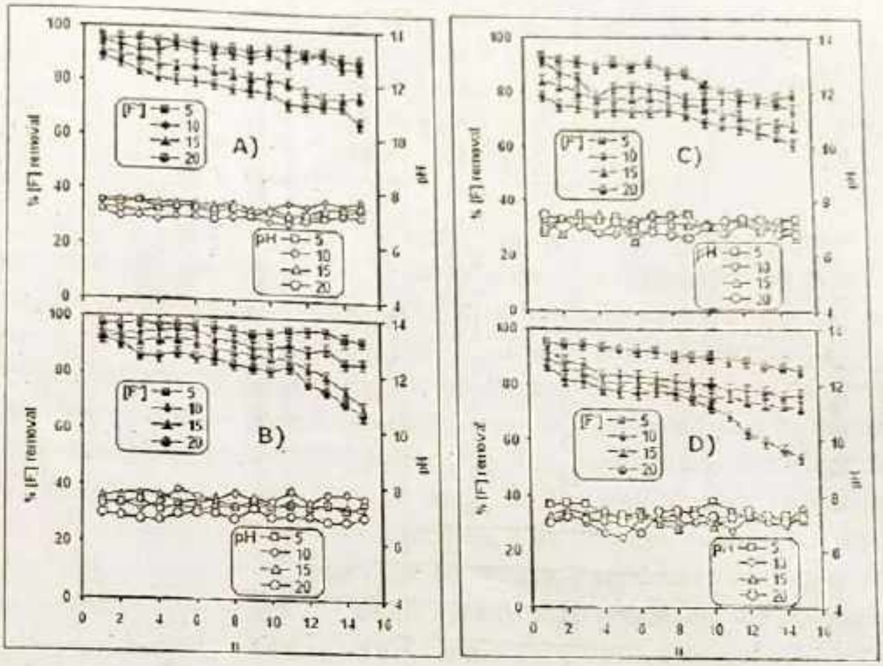

Figure 3.15. The percent removal of fluoride at initial concentrations of fluoride of 5, 10, 15 and 20 mg/L : 0.1 M OA after 6 h (A) and 12 h (B), 0.05 M OA after 6 h (C) and 12 h (D).

Table 3.8. Concentration of remaining F^- in the treated water after removal from different initial concentration. 0.1 M OA after 6 h (A) and 12 h (B), 0.05 M OA after 6 h (C) and 12 h (D) of treatment time.

(A) 0.1 M	F (mg/L)			
6 h	5	10	15	20
1	0.35	0.59	0.64	2.14
2	0.40	0.68	0.54	2.19
3	0.42	0.87	0.85	3.24
4	0.49	0.82	0.85	3.72
5	0.54	0.63	1.21	3.89
6	0.73	0.58	1.64	3.93
7	0.89	0.91	2.15	4.13
8	0.92	0.89	2.87	4.38
9	0.94	1.02	3.32	4.50
10	1.12	1.12	3.87	4.62
11	1.22	1.17	4.12	5.43
12	1.29	0.94	4.89	5.51
13	1.36	0.91	5.13	5.56
14	1.42	1.32	5.43	5.62
15	1.46	1.36	5.87	6.85

(B) 0.1M	F (mg/L)			
12h	5	10	15	20
1	0.34	0.55	0.52	1.21
2	0.38	0.64	0.59	1.34
3	0.41	0.84	0.89	1.56
4	0.48	0.48	0.83	2.23
5	0.52	0.44	1.13	2.57
6	0.71	0.47	1.01	2.34
7	0.84	0.79	1.65	2.61
8	0.79	0.84	2.16	2.78
9	0.93	1.06	2.70	2.63
10	1.08	1.05	2.94	3.04
11	1.11	0.95	3.24	3.45
12	1.17	0.81	3.95	4.12
13	1.24	0.66	4.76	4.56
14	1.20	0.99	5.49	5.89
15	1.26	1.02	6.56	6.78

(C) 0.05M	F (mg/L)			
6h	5	10	15	20
1	0.33	0.88	0.82	1.40
2	0.39	1.26	1.10	1.70
3	0.42	1.48	1.70	2.30
4	0.53	2.15	2.10	2.80
5	0.45	1.81	1.20	3.01
6	0.73	1.82	1.64	3.14
7	0.43	1.85	0.98	2.90
8	0.92	1.94	2.87	3.38
9	0.63	2.21	2.10	3.60
10	1.12	2.24	3.87	4.62
11	1.20	2.22	4.12	4.77
12	1.27	2.29	4.25	5.02
13	1.21	2.34	4.65	5.18
14	1.35	2.41	4.73	5.37
15	1.41	2.67	4.87	5.48

(D) 0.05M	F (mg/L)			
12h	5	10	15	20
1	0.27	0.84	0.81	1.20
2	0.38	1.16	1.00	1.40
3	0.43	1.28	1.30	1.80
4	0.53	1.65	1.36	2.30
5	0.45	1.66	1.41	2.81
6	0.77	1.71	1.45	3.10
7	0.40	1.76	1.52	2.90
8	0.88	1.82	1.56	3.11

9	0.91	1.96	1.62	3.30
10	1.04	1.97	1.66	4.12
11	1.09	2.11	1.82	4.62
12	1.14	2.17	1.89	4.96
13	1.20	2.23	2.14	5.06
14	1.25	2.42	2.22	5.21
15	1.28	2.35	2.35	5.32

It can be seen from the figures and the tables that with OA also the percent fluoride removal increases with decrease in the initial concentration of fluoride. The fluoride from initial concentration of 5 mg/L is removed within 6 h to below 1 mg/L upto 15th repeated use of the same limestone column with 0.1 M OA. The percent fluoride removal decreased with increase in the initial concentration. The results however clearly show that the present method can remove fluoride from a low initial concentration which may be attributed to adsorption of fluoride along with precipitation. Fig. 3.15 indicates also that a repeatation of the present process in series, say twice or thrice, for the same fluoride containing water should reduce high initial fluoride concentration, e.g., 20 mg/L to below 1 mg/L, with moderate acid concentration of about 0.05 M, with 6 h residence time, using the same limestone column for more than n = 15, which seems to be reasonable and practical.

Limestone defluoridation in presence of phosphoric acid

Phosphoric acid, known as green acid has been used in versatile fields *viz.*, water treatment, detergent preparation, fertilizer production, metal treatment, ceramics, enamels, paper, flame retardants, paints, glass fibre, biofuels, yeast and fermentation, textiles, refining of sugar and vegetable oils, pharmaceuticals applications and various food applications. In water treatment it has been used for Lead (Pb) precipitation, corrosion inhibition, control of red and black waters, source of nutrients, scale inhibition-softening agents, pH control, sequestration and precipitation of metal ions etc. PA is approved for use in drinking water treatment by the US EPA (Environmental Protection Agency). The idea of using PA in the AELD process came from the earlier works related to the use of calcium phosphate and HAP for defluoridation. Both of these materials are known to have good fluoride removal ability. In limestone column, in presence of PA containing F^- water, formation of calcium phosphate hydroxide or HAP are expected to take place which should add to the fluoride removal already taking place by precipitation and adsorption in the limestone column. Therefore, the F^- removal should be increased in presence of HAP in the limestone column. The results of the experiments performed on using PA enhanced limestone defluoridation have been presented here.

Effect of acid concentration:

Limestone defluoridation in presence of 0.1 M PA

A column filled with 2-3 mm size limestone has been used for the F^- removal experiment with 0.1 M PA. It was presumed that limestone starts to react with PA forming calcium phosphate and HAP as soon as the PA containing F^- water is added to the column. Fluoride should be precipitated by limestone as CaF_2 as well as adsorbed simultaneously by limestone and HAP. Therefore, it was expected that the removal of fluoride may start immediately after the addition of the water to the limestone column. In this experiment, the treated water has been collected after different residence times from 1 min of residence time up to 24 h to observe the remaining F^- concentration and pH as a function of residence time.

Figure 3.18 (A) illustrates the percent removal of the fluoride from initial 10 mg/L in presence of 0.1 M PA using 2-3 mm size of the limestone for 3 h and 12 h of residence time. In Table 3.10 the remaining fluoride concentrations of the treated water along with pH after 3, 6, 9 or 12 h of treatment time have been presented. It can be clearly observed from the figure and the table that there is a little difference between the remaining F^- concentrations after 3, 6, 9 and 12 h as was observed in Fig. 3.17. The fluoride removal with $n = 1$ were found to be 0.73 mg/L (at $t = 3$ h) and 0.52 mg/L (at $t = 12$ h) with final pH of 4.85 and 6.12, respectively. The fluoride removal further improved up to n equal to 7-8 and the decreased gradually with n.

It may be noted that the fluoride was removed excellently to below 0.1 mg/L, more than 99 % between about 5 to about 30 times repeated use of the same limestone. This excellent increase in fluoride removal may be due to the precipitation and adsorption by fresh limestone and newly produced HAP within the limestone column. Limestone is fresh initially and HAP begins to form resulting in very good fluoride removal between n = 5-30. With n = 330, the remaining fluoride after 3 and 12 h were recorded as 2.65 and 2.04 mg/L with final pH of 4.70 and 4.93, respectively. The observed slow neutralization of the acid in the limestone column may be attributed to slow diffusion of the acid into the limestone across a less permeable HAP or FAP surface which will be discussed with the help of XPS, X-ray, IR, etc. latter. The pH of the water increases slightly towards the neutral side with increase in the residence time. Thus the performance of PA in the AELD method is remarkable.

The capacity of the limestone for defluoridation was determined by using the same limestone chips repeatedly until the remaining fluoride concentration of the water was less than 2 mg/L. It is an interesting observation of this work that, the same limestone bed can be repeatedly used for about 330 times. The capacity of 600 gm 2-3 mm size limestone flakes for defluoridation of 10 mg/L of fluoride water is almost 66 liter.

Limestone defluoridation in presence of 0.05 M PA

Use of lesser amount of acid in the water treatment process is always desirable; therefore, the defluoridation of water using PA has been tried by adding 0.05 M PA to the water before filtration through the limestone column. The results of this experiment have been presented in Fig. 3.18 (B) for 3 and 12 h residence time and in Table 3.11 for 3, 6, 9, 12 h of residence time. As was observed in the case of 0.1 M PA, there is a very small increase in F^- removal as well as the pH of the water with increasing treatment time. As in case of the 0.1 M PA, there is increase in fluoride removal to below 0.1 mg/L after 2-3 times repeated use of the same limestone to n = 24 which may be due to precipitation and adsorption by fresh limestone and newly produced HAP within the limestone column.

The capacity of the 600 g limestone in this treatment process to remove fluoride from 10 mg/L to 2 mg/L (up to n = 315) has been calculated to be 63 liter. The capacity of limestone with 0.05 M PA has been found to be slightly smaller than that with 0.1 M PA. The formation of HAP and subsequent precipitation and adsorption by both limestone and HAP probably contribute to the overall good fluoride removal capacity with 0.05 M PA.

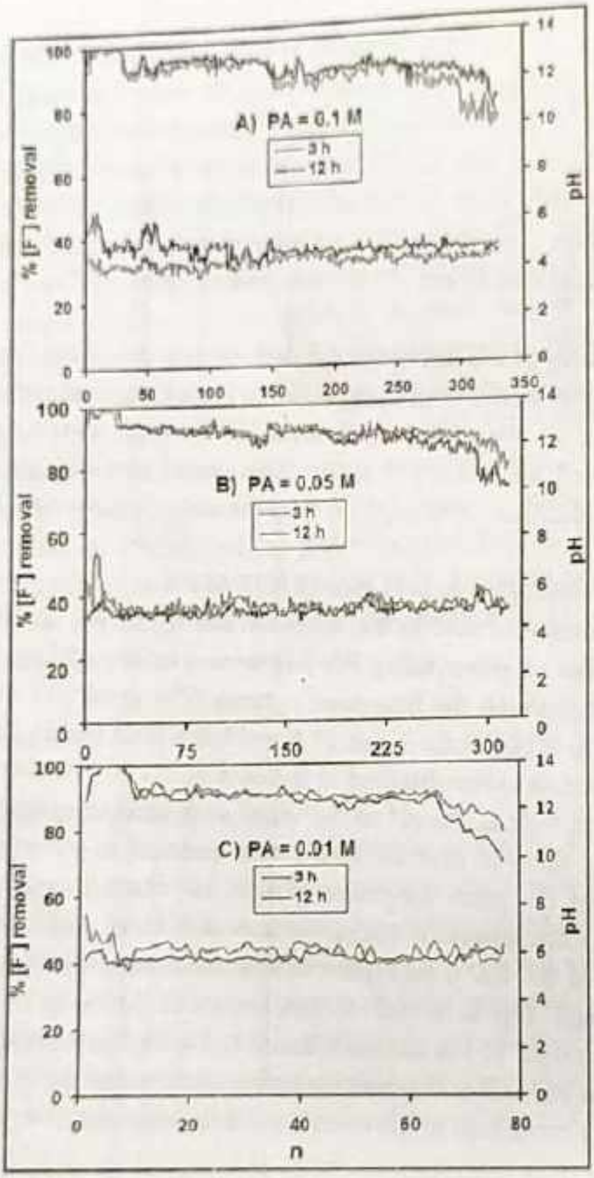

Figure 3.18. The plot of percent $[F^-]$ removal (primary Y axis) and pH (secondary Y axis) *vs.* number of repeated use of the same limestone (n) after addition of (A) 0.1M (B) 0.05 M and (C) 0.01 M PA to the initial 10 mg/L fluoride water before treatment using the limestone column for 3 h and 12 h.

Table 3.10. The amount of remaining fluoride and pH of the treated water starting with initial 10 mg/L F^- containing 0.1 M PA before filtration through limestone column after different time intervals.

n	$[F^-]$ 10 mg/L				pH = 1.7			
	3 h	6 h	9 h	12 h	3 h	6 h	9 h	12 h
1	0.73	0.84	0.63	0.52	4.85	5.55	5.62	6.12
2	0.71	0.65	0.53	0.47	4.69	5.56	5.61	5.87
3	0.74	0.62	0.43	0	4.71	5.52	5.45	6.16

4	0.24	0.21	0.20	0.25	4.96	5.62	5.64	6.4
5	0.18	0.20	0.25	0.26	4.86	5.32	6.11	6.39
6	0.19	0.21	0.22	0.23	4.56	5.22	5.95	6.77
7	0.19	0.19	0.03	0.02	4.37	4.88	4.78	5.91
8	0.23	0.18	0.12	0.01	4.73	5.05	6.05	6.17
9	0.24	0.24	0.22	0.06	4.62	5.24	6.02	6.86
10	0.02	0.02	0.03	0.03	4.45	4.67	4.84	6.42
11	0.06	0.03	0.03	0.02	4.87	5.01	5.54	6.14
12	0.03	0.03	0.04	0.04	4.22	4.40	5.92	6.29
13	0.03	0.02	0.02	0.01	4.24	4.69	4.86	5.85
14	0.03	0.02	0.02	0.02	4.23	4.76	4.84	5.66
15	0.03	0.02	0.02	0.01	4.40	4.48	4.58	5.12
16	0.16	0.13	0.09	0.11	4.12	4.38	4.45	5.13
17	0.17	0.16	0.02	0.16	4.41	4.78	4.87	5.21
18	0.12	0.10	0.09	0.08	4.42	5.10	5.24	5.38
19	0.08	0.07	0.07	0.07	4.35	4.62	4.78	4.91
20	0.06	0.09	0.09	0.09	4.47	4.65	4.76	5.16
21	0.06	0.06	0.07	0.07	4.45	4.71	4.79	5.18
22	0.06	0.05	0.04	0.05	4.62	4.85	4.96	5.21
23	0.06	0.05	0.05	0.03	4.54	4.78	4.92	5.43
24	0.03	0.02	0.02	0.04	4.38	4.67	4.78	5.62
25	0.03	0.02	0.01	0.03	4.51	4.86	4.96	5.17
26	0.04	0.03	0.03	0.02	4.62	4.76	4.91	5.32
27	0.07	0.06	0.05	0.04	4.56	4.87	4.93	5.41
28	0.07	0.06	0.05	0.05	4.38	4.67	4.81	5.46
29	0.07	0.06	0.05	0.04	4.38	4.71	4.84	5.38
30	0.46	0.04	0.35	0.27	4.56	4.71	4.82	5.14
31	0.77	0.66	0.52	0.46	4.28	4.73	4.76	5.16
32	0.78	0.85	0.62	0.58	4.54	4.68	4.86	5.22
33	0.84	0.85	0.80	0.72	4.37	4.57	4.82	5.67
34	0.86	0.89	0.84	0.91	4.36	4.51	4.75	5.68
35	0.95	1.00	0.91	0.85	4.49	4.57	4.72	5.19
36	1.00	0.92	0.86	0.73	4.43	4.50	4.78	5.24
37	0.94	0.86	0.77	0.75	4.22	4.62	4.82	5.25
38	0.89	0.86	0.82	0.84	4.40	4.59	4.67	5.46
39	0.84	0.78	0.78	0.72	4.34	4.43	4.47	4.83
40	1.00	0.89	0.87	0.85	4.22	4.51	4.61	4.43
41	0.97	0.94	0.82	0.74	4.36	4.51	4.77	5.22
42	0.90	0.81	0.81	0.79	4.52	4.71	4.87	5.28
43	0.80	0.72	0.69	0.68	4.41	4.62	4,92	5.29
44	0.74	0.71	0.70	0.58	4.35	4.61	4.87	5.26
45	0.60	0.58	0.62	0.52	4.36	4.57	4.86	5.31
46	0.52	0.45	0.35	0.26	4.85	5.55	5.62	6.12
47	0.56	0.48	0.35	0.29	4.69	5.56	5.61	5.87
48	0.67	0.58	0.43	0.35	4.71	5.52	5.45	6.16
49	0.87	0.73	0.52	0.35	4.96	5.62	5.64	6.31
50	0.84	0.76	0.77	0.71	4.86	5.32	5.97	6.34
51	0.71	0.76	0.62	0.62	4.56	5.22	5.95	5.88
52	0.88	0.72	0.67	0.64	4.37	4.88	4.78	5.91
53	0.94	0.86	0.82	0.81	4.73	5.05	6.05	6.17
54	0.93	0.82	0.81	0.77	4.62	5.24	6.02	5.65
55	1.00	0.94	0.91	0.82	4.45	4.67	4.84	6.38
56	0.97	0.86	0.74	0.68	4.69	5.01	5.54	6.14

57	0.89	1.10	0.89	0.92	4.22	4.40	5.92	6.29
58	0.87	0.74	0.69	0.56	4.24	4.69	4.86	5.85
59	0.74	0.72	0.65	0.61	4.23	4.76	4.84	5.66
60	0.73	0.66	0.54	0.49	4.40	4.48	4.58	5.12
61	0.78	0.62	0.59	0.42	4.12	4.38	4.45	5.13
62	0.73	0.71	0.64	0.48	4.41	4.78	4.87	5.21
63	0.58	0.54	0.53	0.52	4.42	5.10	5.24	5.38
64	0.87	0.64	0.61	0.52	4.35	4.62	4.78	4.91
65	0.64	0.52	0.53	0.48	4.47	4.65	4.76	5.16
66	0.73	0.64	0.52	0.46	4.45	4.71	4.79	5.18
67	0.82	0.72	0.61	0.51	4.62	4.85	4.96	5.21
68	0.88	0.74	0.62	0.46	4.54	4.78	4.92	5.43
69	0.69	0.53	0.50	0.42	4.38	4.67	4.78	5.62
70	0.74	0.62	0.54	0.48	4.51	4.86	4.96	5.17
71	0.45	0.42	0.46	0.47	4.62	4.76	4.91	5.32
72	0.72	0.63	0.51	0.46	4.56	4.87	4.93	5.41
73	0.56	0.46	0.42	0.44	4.38	4.67	4.81	5.46
74	0.67	0.54	0.51	0.47	4.38	4.71	4.84	5.38
75	0.45	0.42	0.41	0.46	4.56	4.71	4.82	5.14
76	0.65	0.58	0.49	0.46	4.28	4.73	4.76	5.16
77	0.63	0.47	0.42	0.41	4.54	4.68	4.86	5.22
78	0.62	0.54	0.48	0.45	4.37	4.57	4.82	5.30
79	0.53	0.48	0.43	0.44	4.36	4.51	4.75	5.33
80	0.51	0.52	0.48	0.45	4.49	4.57	4.72	5.19
81	0.51	0.48	0.49	0.45	4.43	4.50	4.78	5.24
82	0.69	0.57	0.62	0.46	4.22	4.62	4.32	5.25
83	0.49	0.47	0.48	0.50	4.40	4.59	4.67	5.46
84	0.59	0.49	0.45	0.48	4.14	4.21	4.32	4.27
85	0.49	0.45	0.46	0.47	4.22	4.51	4.61	4.43
86	0.57	0.46	0.52	0.46	4.18	4.28	4.54	4.67
87	0.52	0.42	0.47	0.37	4.52	4.71	4.87	5.28
88	0.52	0.48	0.45	0.36	4.41	4.62	4.92	5.29
89	0.48	0.45	0.42	0.37	4.29	4.64	4.76	4.97
90	0.67	0.54	0.48	0.46	4.36	4.57	4.36	5.31
91	0.69	0.55	0.47	0.34	3.89	4.74	4.38	4.59
92	0.56	0.53	0.58	0.51	3.96	4.38	4.64	4.78
93	0.54	0.49	0.48	0.45	3.92	4.59	4.67	4.76
94	0.58	0.54	0.48	0.42	4.21	4.46	4.54	4.81
95	0.62	0.57	0.54	0.48	4.24	4.76	5.55	4.52
96	0.61	0.55	0.52	0.38	4.26	4.56	4.67	4.83
97	0.39	0.36	0.32	0.38	4.51	4.22	4.34	4.67
98	0.67	0.52	0.46	0.34	4.14	4.27	4.67	5.12
99	0.88	0.48	0.46	0.48	4.54	4.87	4.61	5.18
100	0.69	0.42	0.42	0.45	4.38	4.67	4.54	5.21
101	0.74	0.48	0.48	0.48	4.51	4.71	4.87	5.43
102	0.45	0.45	0.47	0.49	4.62	4.71	4.92	5.17
103	0.72	0.52	0.58	0.46	4.56	4.73	4.76	5.17
104	0.56	0.64	0.49	0.37	4.38	4.68	4.86	5.32
105	0.67	0.72	0.58	0.36	4.38	4.57	4.38	5.41
106	0.45	0.74	0.52	0.98	4.56	4.51	4.64	5.46
107	0.65	0.53	0.61	0.56	4.28	4.57	4.67	5.07
108	0.63	0.62	0.62	0.57	4.54	4.50	4.81	5.14
109	0.71	0.42	0.41	0.38	4.37	4.62	4.84	5.16

110	0.51	0.56	0.54	0.71	4.36	4.59	4.82	5.19
111	0.69	0.52	0.46	0.56	4.49	4.21	4.76	5.24
112	0.49	0.54	0.51	0.47	4.43	4.51	4.86	5.25
113	0.63	0.66	0.42	0.46	4.73	4.28	4.82	5.46
114	0.64	0.57	0.51	0.46	4.62	4.71	4.75	4.27
115	0.73	0.60	0.41	0.41	4.45	4.74	4.72	4.43
116	0.82	0.82	0.80	0.45	4.71	4.38	4.78	4.67
117	0.88	0.42	0.81	0.46	4.22	4.59	4.82	5.31
118	0.62	0.68	0.91	0.34	4.24	4.46	4.67	4.59
119	0.74	0.71	0.74	0.52	4.23	4.76	4.32	4.78
120	0.60	0.58	0.56	0.45	4.40	4.56	4.61	4.76
121	0.52	0.46	0.37	0.34	4.14	4.22	4.54	4.84
122	0.56	0.48	0.82	0.46	4.22	4.27	4.84	4.52
123	0.72	0.68	0.67	0.62	4.25	4.21	4.32	4.41
124	0.75	0.72	0.66	0.60	4.31	4.36	4.36	4.52
125	0.77	0.71	0.68	0.66	4.62	4.4	4.70	4.72
126	0.64	0.62	0.60	0.59	4.70	4.74	4.84	4.73
127	0.62	0.60	0.59	0.52	4.92	5.23	4.30	4.91
128	0.59	0.56	0.52	0.51	4.51	4.71	4.90	5.11
129	0.64	0.63	0.62	0.61	4.95	4.98	4.99	5.12
130	0.61	0.60	0.59	0.57	4.97	5.12	5.12	5.14
131	0.63	0.62	0.61	0.59	4.74	4.77	4.87	4.89
132	0.56	0.53	0.52	0.51	4.21	4.52	4.81	4.93
133	0.68	0.66	0.64	0.62	4.63	4.66	4.75	4.77
134	0.57	0.55	0.53	0.51	4.44	4.47	4.52	4.56
135	0.62	0.58	0.56	0.55	4.32	4.44	4.48	4.49
136	0.59	0.54	0.52	0.51	4.53	4.56	4.58	4.60
137	0.61	0.59	0.57	0.55	4.59	4.60	4.63	4.65
138	0.52	0.53	0.51	0.50	4.38	4.41	4.45	4.48
139	0.63	0.63	0.62	0.61	4.36	4.41	4.41	4.45
140	0.65	0.64	0.62	0.63	4.41	4.48	4.51	4.56
141	0.67	0.64	0.63	0.62	4.51	4.53	4.57	4.59
142	0.66	0.65	0.64	0.63	4.63	4.69	4.71	4.73
143	0.68	0.66	0.64	0.62	4.75	4.79	4.81	4.83
144	0.67	0.65	0.64	0.54	4.79	4.81	4.83	4.86
145	0.69	0.67	0.66	0.54	4.85	4.87	4.89	4.92
146	0.79	0.77	0.76	0.74	4.95	4.98	4.99	5.10
147	0.84	0.83	0.82	0.81	5.21	5.22	5.24	5.26
148	0.95	0.94	0.92	0.91	5.23	5.26	5.31	5.35
149	0.98	0.97	0.95	0.93	5.31	5.35	5.41	5.45
150	1.02	0.98	0.96	0.94	4.89	4.91	4.95	4.98
151	1.31	1.21	1.12	1.11	4.76	4.81	4.82	4.85
152	1.43	1.32	1.22	1.13	4.81	4.85	4.87	4.89
153	1.12	1.09	1.11	1.10	4.84	4.88	4.89	4.91
154	1.32	1.23	1.21	1.13	4.78	4.82	4.81	4.85
155	1.52	1.42	1.30	1.21	4.80	4.83	4.88	4.92
156	1.34	1.22	1.13	1.12	4.92	4.93	4.96	4.99
157	1.42	1.31	1.21	1.23	4.89	4.91	4.92	4.93
158	1.63	1.51	1.42	1.42	4.84	4.86	4.87	4.89
159	1.51	1.32	1.41	1.41	4.74	4.77	4.78	4.80
160	1.62	1.51	1.42	1.32	4.77	4.78	4.79	4.81
161	1.61	1.52	1.41	1.42	4.75	4.79	4.81	4.82
162	1.42	1.35	1.21	1.13	4.81	4.83	4.85	4.87

163	1.72	1.62	1.50	1.42	4.85	4.86	4.88	4.91
164	1.62	1.51	1.41	1.31	4.86	4.88	4.89	4.93
167	1.73	1.62	1.54	1.52	4.89	4.91	4.91	4.95
168	1.52	1.41	1.31	1.21	4.92	4.97	4.98	4.99
169	1.30	1.22	1.10	1.05	4.87	4.88	4.92	4.96
170	1.21	1.11	1.05	0.98	4.76	4.78	4.76	4.82
171	0.72	0.69	0.67	0.65	4.63	4.68	4.72	4.75
172	0.61	0.60	0.58	0.56	4.54	4.55	4.56	4.57
173	0.68	0.66	0.64	0.62	4.62	4.64	4.69	4.72
174	0.71	0.71	0.69	0.69	4.64	4.68	4.70	4.71
175	0.79	0.76	0.75	0.73	4.72	4.78	4.82	4.86
176	1.12	1.02	0.98	0.96	4.75	4.85	4.87	4.92
177	1.21	1.10	1.08	1.10	4.71	4.72	4.75	4.76
178	1.42	1.31	1.21	1.12	4.75	4.78	4.82	4.83
179	1.20	1.12	1.10	1.16	4.78	4.82	4.85	4.87
180	1.31	1.21	1.11	1.14	4.81	4.83	4.85	4.88
181	1.41	1.31	1.22	1.15	4.88	4.89	4.92	4.93
182	1.31	1.22	1.21	1.14	4.73	4.74	4.76	4.77
183	1.21	1.12	1.03	1.12	4.82	4.84	4.87	4.89
184	1.33	1.21	1.12	1.11	4.89	4.92	4.95	4.93
185	1.42	1.31	1.21	1.12	4.84	4.86	4.87	4.88
186	1.61	1.51	1.43	1.31	4.91	4.92	4.93	4.95
187	1.22	1.21	1.10	1.21	4.74	4.79	4.80	4.81
188	1.21	1.12	1.09	1.12	4.78	4.81	4.85	4.87
189	1.33	1.21	1.10	1.12	4.75	4.78	4.80	4.81
190	1.41	1.21	1.12	0.98	4.85	5.55	4.83	4.89
191	1.32	1.11	1.13	0.99	4.69	5.56	4.89	4.80
192	1.22	1.02	0.98	1.13	4.71	5.52	4.99	4.81
193	1.20	0.98	0.94	0.91	4.96	5.62	5.24	4.82
194	1.23	1.10	1.07	1.02	4.86	5.32	5.30	4.87
195	1.12	0.96	0.94	0.92	4.56	5.22	5.41	4.91
196	1.11	0.98	0.96	1.10	4.37	4.88	4.95	4.93
197	1.30	1.21	1.12	0.97	4.73	5.05	4.82	4.95
198	1.23	1.01	0.98	0.92	4.62	5.24	4.87	4.99
199	1.20	1.11	0.97	0.94	4.45	4.67	4.89	4.96
200	1.31	1.21	0.98	0.95	4.87	5.01	4.81	4.82
201	1.20	1.14	1.06	0.93	4.22	4.40	4.88	4.75
202	1.11	1.01	0.97	0.89	4.24	4.69	4.96	4.57
203	0.98	0.96	0.94	1.10	4.23	4.76	4.92	4.72
204	1.10	1.03	1.10	1.04	4.40	4.48	4.87	4.71
205	0.96	0.94	0.92	0.91	4.12	4.38	4.78	4.86
206	1.00	0.98	0.96	0.92	4.41	4.78	4.79	4.92
207	0.97	0.94	0.89	0.84	4.42	5.10	4.81	4.76
208	1.21	1.10	1.02	0.96	4.35	4.62	4.85	4.83
209	1.23	1.01	0.97	0.92	4.47	4.65	4.88	4.87
210	1.12	1.02	1.10	0.95	4.45	4.71	4.89	4.88
211	1.34	1.10	1.32	0.93	4.62	4.83	4.91	4.93
212	1.24	0.98	0.95	0.89	4.54	4.78	4.98	4.77
213	1.42	1.21	1.12	1.04	4.38	4.67	4.92	4.89
214	1.33	1.20	1.11	0.97	4.51	4.86	4.76	4.93
215	1.24	1.10	1.07	0.97	4.62	4.76	4.72	4.88
216	1.22	1.01	0.98	0.94	4.56	4.87	4.56	4.95
217	1.11	1.03	0.97	0.96	4.38	4.67	4.69	4.81

218	1.34	1.21	1.12	0.98	4.38	4.71	4.70	4.87
219	0.96	0.94	0.91	0.84	4.56	4.71	4.82	4.81
220	1.13	0.98	0.94	0.86	4.28	4.73	4.87	4.89
221	0.97	0.95	0.92	0.84	4.54	4.68	4.75	4.80
222	0.94	0.92	0.91	0.83	4.37	4.57	4.82	4.81
223	0.89	0.86	0.87	0.81	4.36	4.51	4.85	4.82
224	1.12	0.98	0.71	0.66	4.49	4.57	4.85	4.87
225	1.20	0.96	0.91	0.86	4.43	4.51	4.92	4.91
226	1.31	1.10	0.94	0.92	4.22	4.62	4.76	4.93
227	0.95	0.94	0.92	0.85	4.41	4.59	4.87	4.95
228	0.73	0.72	0.69	0.62	4.34	4.43	4.95	4.99
229	0.85	0.81	0.78	0.71	4.22	4.51	4.87	4.96
230	0.71	0.65	0.62	0.58	4.36	4.51	4.93	4.82
231	1.02	0.94	0.95	0.87	4.52	4.71	4.80	4.75
232	0.94	0.92	0.91	0.90	4.41	4.62	4.85	4.57
233	0.97	0.92	0.87	0.84	4.35	4.61	4.80	4.72
234	0.98	0.93	0.89	0.86	4.36	4.57	4.83	4.71
235	0.92	0.85	0.81	0.82	4.85	5.55	4.89	4.86
236	1.10	0.96	0.93	0.91	4.69	5.56	4.99	4.92
237	0.98	0.96	0.92	0.93	4.71	5.52	5.24	4.76
238	1.21	1.10	1.06	0.98	4.96	5.62	5.30	4.83
239	1.32	1.12	1.04	0.85	4.86	5.32	5.41	4.87
240	1.12	1.01	0.96	0.92	4.56	5.22	4.95	4.88
241	1.02	0.98	0.94	0.89	4.37	4.88	4.82	4.93
242	0.96	0.95	0.91	0.87	4.73	5.05	4.87	4.77
243	0.98	0.92	0.89	0.88	4.62	5.24	4.89	4.89
244	0.99	0.94	0.92	0.84	4.45	4.67	4.81	4.93
245	0.87	0.81	0.78	0.72	4.69	5.01	4.88	4.88
246	0.98	0.93	0.92	0.85	4.22	4.40	4.96	4.95
247	0.86	0.82	0.81	0.78	4.24	4.69	4.92	4.81
248	0.96	0.92	0.92	0.94	4.23	4.76	4.87	4.87
249	0.94	0.91	0.89	0.86	4.40	4.48	4.78	4.81
250	0.87	0.82	0.81	0.76	4.12	4.71	4.79	4.89
251	1.01	0.92	0.91	0.90	4.41	4.73	4.81	4.80
252	1.32	1:10	1.20	0.98	4.42	4.68	4.85	4.81
253	0.94	1.21	1.12	1.10	4.35	4.57	4.88	4.82
254	1.12	1.01	0.98	0.96	4.47	4.51	4.89	4.87
255	1.21	1.02	0.97	0.95	4.45	4.57	4.91	4.91
256	0.96	1.10	0.99	1.12	4.62	4.50	4.98	4.93
257	1.13	1.12	0.98	0.96	4.54	4.62	4.92	4.95
258	1.04	0.98	0.96	0.95	4.38	4.59	4.76	4.99
259	1.61	1.62	1.54	1.41	4.51	4.43	4.72	4.96
260	1.31	1.21	1.13	1.05	4.62	4.51	4.56	4.82
261	1.62	1.41	1.24	1.16	4.56	4.51	4.69	4.75
262	1.73	1.40	1.35	1.21	4.38	4.71	4.70	4.57
263	1.41	1.31	1.25	1.16	4.38	4.62	4.82	4.72
264	1.32	1.21	1.14	1.13	4.56	4.61	4.87	4.71
265	1.41	1.31	1.22	1.12	4.28	4.57	4.75	4.86
266	1.23	1.12	1.02	0.96	4.54	5.55	4.82	4.92
267	1.61	1.51	1.21	1.12	4.37	5.56	4.85	4.76
268	1.52	1.41	1.32	1.12	4.36	5.52	4.85	4.83
269	1.33	1.22	1.21	1.12	4.49	5.62	4.92	4.87
270	1.41	1.31	1.12	1.05	4.43	5.32	4.76	4.88

271	1.42	1.10	1.02	0.97	4.22	5.22	4.87	4.93
272	1.31	1.21	1.04	0.95	4.40	4.88	4.95	4.77
273	1.51	1.41	1.35	1.13	4.14	5.05	4.87	4.89
274	1.71	1.63	1.51	1.32	4.22	5.24	4.93	4.93
275	1.61	1.41	1.32	1.21	4.18	4.67	4.80	4.88
276	1.42	1.32	1.21	1.12	4.52	5.01	4.85	4.95
277	1.61	1.41	1.23	1.12	4.41	4.42	4.93	4.81
278	1.82	1.71	1.31	1.13	4.29	4.69	4.80	4.87
279	1.41	1.31	1.12	0.96	4.36	4.76	4.85	4.81
280	1.62	1.40	1.21	1.12	3.89	4.48	4.82	4.87
281	1.73	1.54	1.43	1.20	4.62	4.51	4.79	4.82
282	1.52	1.41	1.31	1.14	4.56	4.51	4.81	4.75
283	1.61	1.42	1.21	1.15	4.38	4.71	4.85	4.57
284	1.71	1.55	1.36	1.25	4.38	4.62	4.88	4.72
285	1.61	1.42	1.32	1.13	4.56	4.61	4.89	4.71
286	1.42	1.21	1.13	1.05	4.28	4.57	4.91	4.80
287	1.31	1.21	1.11	1.02	4.54	5.55	4.98	4.92
288	1.51	1.42	1.23	1.03	4.37	5.56	4.92	4.76
289	1.42	1.30	1.21	1.12	4.36	5.52	4.76	4.83
290	1.51	1.44	1.23	1.04	4.49	5.62	4.72	4.87
291	1.61	1.45	1.32	1.22	4.43	5.32	4.56	4.88
292	1.41	1.34	1.23	1.12	4.22	5.22	4.69	4.93
293	1.72	1.65	1.46	1.22	4.40	4.88	4.70	4.77
294	1.61	1.43	1.34	1.21	4.14	5.05	4.82	4.89
295	1.42	1.32	1.12	1.05	4.22	5.24	4.87	4.93
296	1.50	1.34	1.21	1.16	4.18	4.67	4.75	4.88
297	1.70	1.55	1.41	1.25	4.52	5.01	4.82	4.95
298	1.61	1.50	1.32	1.22	4.41	4.42	4.85	4.81
299	1.51	1.43	1.21	1.12	4.29	4.69	4.85	4.87
300	1.81	1.62	1.43	1.23	4.36	4.51	4.92	4.81
301	2.20	1.68	1.48	1.24	4.38	4.62	4.82	4.72
302	2.64	1.84	1.62	1.52	4.56	4.61	4.87	4.71
303	2.42	1.95	1.84	1.52	4.28	4.57	4.75	4.86
304	2.21	1..82	1.75	1.51	4.54	5.55	4.82	4.92
305	2.40	1.78	1.57	1.48	4.37	5.56	4.85	4.76
306	2.61	1.89	1.65	1.47	4.36	5.52	4.85	4.83
307	2.82	1.97	1.80	1.61	4.38	4.67	4.69	4.81
308	2.42	1.70	1.61	1.42	4.38	4.71	4.70	4.87
309	2.00	1.58	1.71	1.51	4.56	4.71	4.82	4.81
310	2.62	1.74	1.65	1.52	4.28	4.73	4.87	4.89
311	2.42	1.86	1.62	1.42	4.54	4.68	4.75	4.81
312	2.21	1.52	1.41	1.30	4.37	4.57	4.82	4.81
313	2.82	1.82	1.74	1.60	4.36	4.51	4.85	4.82
314	2.82	1.81	1.62	1.51	4.49	4.57	4.85	4.87
315	2.62	1.61	1.54	1.42	4.41	4.40	4.93	4.81
316	2.42	1.72	1.52	1.31	4.29	4.69	4.81	4.87
317	2.40	1.82	1.61	1.30	4.36	4.76	4.85	4.81
318	3.00	2.79	1.81	1.72	4.35	4.48	4.82	4.87
319	2.21	1.74	1.44	1.32	4.62	4.51	4.79	4.82
320	2.22	2.11	2.00	1.52	4.56	4.51	4.81	4.75
321	2.00	1.82	1.63	1.42	4.38	4.71	4.35	4.57
322	2.42	2.21	2.12	1.61	4.38	4.62	4.88	4.72
323	2.63	2.42	2.21	1.81	4.58	4.91	4.92	4.93

324	3.00	2.62	2.51	2.10	4.84	4.86	4.87	4.89
325	2.82	2.61	2.44	2.12	4.74	4.77	4.78	4.80
326	2.61	2.52	2.31	2.20	4.77	4.78	4.79	4.81
327	2.91	2.72	2.61	2.42	4.75	4.79	4.81	4.82
328	2.41	2.20	2.14	2.00	4.50	4.83	4.85	4.87
329	2.82	2.70	2.45	2.11	4.69	4.86	4.88	4.91
330	2.65	2.52	2.12	2.04	4.70	4.88	4.89	4.93

Table 3.11. The amount of remaining F^- and pH of the treated water starting with initial 10 mg/L F^- containing 0.05 M PA before filtration through limestone column after different time intervals.

	$[F^-]$ =10mg/L				pH=1.7			
n	3h	6h	9h	12h	3h	6h	9h	12h
1	0.52	0.42	0.04	0	4.79	5.14	5.62	6.37
5	0.02	0.02	0.02	0.02	5.12	5.21	5.26	5.29
10	0.27	0.46	0.35	0.22	5.37	5.83	6.73	7.40
15	0.01	0.01	0.03	0.02	5.08	5.67	5.59	5.57
20	0.03	0.06	0.04	0.09	4.76	4.92	5.02	5.30
25	0.24	0.52	0.47	1.10	4.98	4.75	4.78	5.12
30	0.56	0.65	0.34	0.53	4.88	4.48	4.93	5.11
35	0.66	0.61	0.60	0.54	4.73	4.90	4.87	5.21
40	0.58	0.46	0.69	0.47	4.92	4.87	4.91	5.17
45	0.67	0.38	0.54	0.68	4.89	4.91	4.79	4.78
50	0.73	0.61	0.61	0.70	4.69	4.84	4.85	4.84
55	0.84	0.67	0.67	0.68	4.84	4.97	4.76	4.94
60	0.62	0.41	0.66	0.58	4.97	4.78	4.96	4.85
65	0.71	0.62	0.53	0.61	4.78	4.78	4.91	4.78
70	0.82	0.76	0.74	0.76	4.93	4.95	4.89	4.84
75	0.93	0.91	0.81	0.84	4.87	4.69	4.69	4.94
80	0.76	0.72	0.68	0.68	4.82	4.72	4.74	5.10
85	0.88	0.84	0.81	0.76	4.67	4.84	4.90	5.03
90	0.75	0.69	0.65	0.65	4.96	4.97	4.79	4.92
95	0.84	0.81	0.75	0.71	4.82	4.72	4.76	5.10
100	0.99	0.76	0.74	0.76	4.93	4.95	4.89	4.84
105	0.75	0.71	0.67	0.68	5.12	5.21	5.26	5.29
110	0.85	0.83	0.79	0.73	5.37	5.83	6.73	7.40
115	0.97	0.91	0.87	0.82	5.08	5.67	5.59	5.57
120	0.95	0.89	0.86	0.82	4.76	4.92	5.02	5.31
125	1.31	1.26	1.12	1.20	4.98	4.75	4.78	5.12
130	1.42	1.32	1.21	0.98	4.88	4.48	4.93	5.10
135	1.21	1.31	1.23	1.10	4.73	4.90	4.87	5.21
140	0.67	0.62	0.59	0.55	4.92	4.87	4.91	5.17
145	0.91	0.89	0.92	0.88	4.89	4.91	4.79	4.78
150	0.78	0.73	0.65	0.62	4.69	4.84	4.85	4.84
155	0.86	0.83	0.78	0.74	4.84	4.97	4.76	4.94

160	0.78	0.74	0.73	0.71	4.97	4.78	4.96	4.85
165	0.87	0.84	0.81	0.78	4.76	4.78	4.81	4.85
170	0.89	0.84	0.82	0.78	4.91	4.9	4.82	4.92
175	0.91	0.86	0.83	0.82	4.75	4.87	4.74	5.24
180	0.97	0.94	0.89	0.86	4.67	4.72	4.78	5.01
185	1.21	1.16	0.96	0.93	4.69	4.89	4.76	4.87
190	1.33	1.24	1.12	0.99	4.88	4.69	4.75	4.92
195	1.21	1.16	1.12	0.97	4.67	4.72	4.76	5.01
200	1.22	1.18	0.97	0.95	4.65	4.93	4.69	5.17
205	1.21	1.13	1.11	0.98	5.23	5.05	5.17	6.12
210	1.22	0.98	0.94	0.92	5.52	7.51	7.54	7.59
215	1.12	0.95	0.92	0.87	5.05	5.45	5.64	5.57
220	0.93	0.86	0.81	0.76	4.82	5.34	5.02	5.41
225	1.21	1.13	0.97	0.94	4.87	5.46	5.14	5.04
230	1.12	1.10	1.11	1.00	4.67	4.82	4.82	5.09
235	1.21	1.13	1.21	1.16	4.86	4.94	5.02	5.14
240	1.22	1.12	1.10	0.92	4.95	4.89	4.94	5.10
245	0.95	0.92	0.91	0.84	4.69	4.85	4.90	5.03
250	1.31	1.31	1.21	1.15	4.88	4.89	4.74	4.92
255	1.22	1.14	1.07	0.96	4.83	4.92	4.96	5.21
260	1.62	1.42	1.21	1.20	4.82	4.89	4.98	5.12
265	1.42	1.31	1.22	1.12	4.69	4.94	5.02	4.92
270	1.33	1.23	1.14	1.09	4.78	4.87	4.95	5.17
275	1.62	1.41	1.22	1.11	4.86	4.94	5.02	5.14
280	1.52	1.43	1.21	1.00	4.95	4.89	4.94	5.13
285	1.72	1.62	1.42	1.21	4.69	4.85	4.90	5.03
290	1.62	1.51	1.33	1.21	5.37	6.73	6.74	6.92
295	2.62	1.71	1.63	1.51	5.08	5.81	5.85	6.61
300	2.63	1.85	1.56	1.45	4.76	5.53	5.67	5.52
305	2.23	2.12	2.11	1.51	4.92	4.95	4.69	4.83
310	2.82	2.61	2.43	2.11	4.48	4.75	4.89	5.24
315	2.84	2.63	2.41	2.10	4.86	4.94	4.90	4.92

Limestone defluoridation in presence of 0.01 M PA

In a similar way as the above experiments, limestone defluoridation has been tried using 0.01 M PA to observe the effect of further reducing the amount of the acid. In case of 0.01 M PA also good fluoride removal has been shown by the limestone column. The percent F removal and pH of the water after treatment have been presented in the Fig. 3.18 (C) for 3 and 12 h of residence time and concentration of remaining F^{-} along with pH values have been presented in the Table 3.12 for 3, 6, 9 and 12 h of residence time. From this plot it can be observed that limestone defluoridation in presence of even 0.01 M PA can reduce fluoride to below 2 mg/L up to 76 times of repeated use of the same limestone. Interestingly, with 0.01 M

Table 3.12. The amount of remaining F⁻ and pH of the treated water starting with initial 10 mg/L F⁻ containing 0.01 M PA before filtration through limestone column after different time intervals.

n	[F] = 10 mg/L				pH = 2.25			
	3h	6h	9h	12h	3h	6h	9h	12h
1	1.00	0.67	0.48	0.06	5.83	5.92	6.92	7.75
2	0.26	0.01	0.02	0	6.14	6.23	6.55	6.68
3	0.21	0.01	0	0	6.12	6.14	6.92	7.06
4	0.01	0	0	0	6.23	6.27	6.39	6.54
5	0.01	0	0	0	5.66	5.19	6.56	6.63
6	0.01	0	0	0	5.73	5.16	5.84	6.96
7	0	0.01	0.01	0.02	5.56	4.38	5.23	5.64
8	0.05	0.04	0.02	0.19	5.84	5.87	6.34	5.58
9	0.36	0.31	0.02	0.27	5.76	4.98	4.84	5.44
10	0.97	0.86	0.74	0.61	5.78	5.76	6.20	6.25
11	0.73	0.72	0.94	0.86	5.81	5.70	5.94	6.24
12	0.67	0.81	0.78	0.94	5.78	6.12	6.21	6.30
13	0.83	0.66	0.61	0.54	5.82	6.23	6.31	6.38
14	0.86	0.72	0.64	0.53	5.76	6.12	6.12	6.41
15	0.79	0.76	0.78	0.64	5.86	6.23	6.13	6.51
16	0.92	0.97	0.84	0.93	5.91	6.12	6.24	6.53
17	1.00	0.93	0.86	0.74	5.91	6.23	6.12	6.34
18	0.98	0.89	0.65	0.73	5.81	6.19	6.14	6.19
19	1.02	1.01	0.76	0.67	5.96	5.89	6.03	6.42
20	0.85	0.96	0.82	0.93	5.91	6.21	6.07	6.22
21	0.72	0.85	0.81	0.55	5.83	6.23	6.04	5.75
22	0.94	0.94	0.87	0.78	5.84	6.31	6.11	6.29
23	0.79	0.92	0.78	0.67	5.76	5.96	6.08	6.12
24	0.87	1.02	0.95	0.76	5.74	5.79	6.10	6.22
25	0.91	0.95	0.87	0.75	5.86	5.82	6.05	6.25
26	0.84	0.80	0.78	0.88	5.78	6.02	6.07	6.31
27	1.03	0.93	0.82	0.92	5.75	6.01	6.04	6.05
28	0.88	0.89	0.84	0.95	5.77	6.10	6.31	6.14
29	0.83	0.96	0.92	0.87	5.83	6.00	6.11	6.23
30	0.79	0.98	0.87	0.71	5.84	6.12	6.12	6.49
31	0.89	0.94	0.93	0.87	5.87	6.15	5.95	6.45
32	0.91	0.93	0.85	0.87	5.76	6.12	6.04	6.17
33	0.87	1.01	1.12	0.83	5.75	5.77	5.89	6.34
34	0.91	1.04	0.96	0.95	5.77	6.11	6.07	6.10
35	0.88	1.11	1.05	0.86	5.67	5.77	5.87	6.32
36	0.85	1.05	0.95	0.96	5.86	6.19	6.11	6.05
37	0.66	1.12	0.94	0.90	5.75	6.13	6.01	5.86
38	0.92	1.08	0.95	0.87	5.78	6.11	6.04	5.95
39	0.99	1.17	0.96	0.85	5.96	6.05	6.12	6.42
40	1.21	1.20	0.95	0.82	5.65	6.17	6.03	6.52
41	0.94	0.94	0.72	0.94	6.11	6.20	6.02	6.43

42	1.04	0.98	0.93	0.78	6.04	6.24	6.05	6.27
43	1.07	1.18	1.23	0.89	6.02	6.03	6.18	6.43
44	1.12	1.12	0.95	1.10	6.20	6.11	6.08	6.19
45	1.07	1.05	0.99	1.12	6.14	6.06	6.22	6.09
46	1.05	1.02	0.93	0.93	5.93	6.07	6.12	6.00
47	1.31	1.15	1.20	0.94	5.98	6.31	6.15	6.38
48	1.22	1.07	0.95	0.95	5.94	6.15	6.01	6.12
49	1.43	1.12	0.89	1.01	5.76	6.12	6.34	5.79
50	1.24	1.16	1.21	0.96	5.86	6.12	6.23	5.93
51	1.14	1.21	1.21	1.05	5.67	5.78	6.04	6.36
52	1.21	1.11	1.02	1.02	5.78	6.14	6.14	5.82
53	1.12	1.05	1.03	0.94	5.57	6.05	5.94	6.35
54	1.24	1.07	1.04	0.95	5.77	6.06	6.13	5.65
55	1.07	0.96	1.01	0.97	5.75	5.56	6.11	5.71
56	1.03	0.93	1.02	0.89	5.74	6.14	6.06	5.56
57	0.98	0.94	0.91	0.92	5.72	6.12	6.07	5.70
58	1.05	1.02	0.96	0.94	5.82	6.15	6.12	5.6
59	1.13	1.05	0.91	0.87	5.88	5.65	6.12	5.79
60	1.14	1.03	1.03	0.97	5.78	6.23	6.11	5.69
61	1.12	1.06	0.97	0.86	5.73	6.12	6.21	6.31
62	1.26	1.21	1.04	0.98	5.74	6.07	6.12	6.03
63	1.21	1.02	0.95	0.85	5.77	6.08	6.14	5.86
64	0.98	0.92	0.87	0.96	5.73	6.14	6.17	6.37
65	1.12	0.98	0.87	0.87	5.74	6.21	6.14	6.36
66	1.52	1.35	1.21	1.12	5.86	6.06	6.23	5.79
67	1.71	1.55	1.32	1.33	5.63	5.56	6.04	5.69
68	1.82	1.76	1.42	1.41	5.45	6.14	6.14	6.34
69	1.71	1.66	1.51	1.32	5.96	6.12	5.94	6.03
70	2.13	1.84	1.63	1.42	5.65	6.15	6.13	5.86
71	2.05	1.75	1.51	1.32	6.11	5.65	6.11	5.81
72	2.27	1.85	1.62	1.41	6.04	6.23	6.06	6.35
73	2.30	2.15	1.81	1.63	6.02	6.12	6.18	5.65
74	2.26	1.91	1.72	1.52	6.20	6.11	6.08	5.71
75	2.50	2.28	1.81	1.61	6.14	6.06	6.2	5.73
76	2.71	2.37	1.93	1.72	5.98	6.07	6.12	5.71
77	3.01	2.58	2.62	2.11	5.94	6.31	6.14	6.36

PA, nearly cent percent fluoride removal has been observed with 6, 9 and 12 h residence time for n = 2 to 6. There seems to be a breakthrough around n = 70 when the fluoride removal decreases rapidly to less than 80 %. An advantage of using 0.01 M of PA concentration the higher final pH compared to that observed with higher concentrations of the acid.

The above results show that in comparison to the performance of AA, CA and OA PA is more effective in removing fluoride in the AELD method.

Effect of varying initial concentration of fluoride

The effect of varying initial concentration of F^- on the performance of this treatment process has been investigated by using different initial concentration of fluoride, *viz.*, 5, 10 and 20 mg/L and the results of these experiments have been presented in Fig. 3.19 (A,B,C) and Table 3.13 up to n = 50. The pH values of the treated water starting with 0.01 M PA, is similar in all experiments with different initial F^- concentration. Similarly, the pH values of the water after treatment with 0.05 and 0.1 M PA are also alike for all the experiments with different initial F^- concentration. Therefore, in the plot pH values of the experiment with only initial $[F^-]$ = 5 mg/L have been presented. In case of 0.1 M PA and 5 mg/L initial F^- concentration the removal capacity of the limestone is very much satisfactory up to n = 380 (Fig. 3.19A). Similar type of result has been shown by the 0.05 M PA concentration where a good removal has been achieved up to n = 325 and 315 for initial 5 mg/L and 10 mg/L fluoride concentration respectively.

It has been observed that with initial $[F^-]$ = 5 mg/L and PA = 0.01 M the same lot of limestone can be used to more than 190 times which is an interesting observation of this experiment. This 0.01 M acid concentration can therefore be used for the practical field where the F^- concentration of groundwater is around 5 mg/L. However, with 10 or 20 mg/L initial concentration the removal seems to be relatively poorer with 0.01 M PA. In this case, the same limestone bed can be used for n= 60 or 70. The removal improves with higher acid concentrations, viz., 0.05 and 0.1 M. From this experiment it has been observed that with lower initial concentration of fluoride the repeated usability of the limestone column and hence the fluoride removal capacity of the limestone improves.

Estimation of the defluoridation capacity of limestone with PA

The capacity of the limestone for defluoridation of water using 0.01, 0.05 and 0.1 M PA has been estimated by taking the different experimental parameters into consideration. The results of this estimation have been presented in the Table 3.14 which show high capacity and hence efficiency of the treatment process.

The amount of limestone taken for each experiment was 0.6 kg. The total quantity of the water that can be treated by this quantity of the limestone has been found to vary with the initial concentration of fluoride and the initial concentration of PA. As usual, with higher acid concentration and lower initial concentration of fluoride, the treatment process gives better results i.e., purifies larger quantities of water. The capacity of limestone or the efficiency of the AELD process with PA has been found to be much better than that with AA, CA or OA. By increasing the size of the limestone column the volume of treated water can be increased. It has been found that the F^- removal is good also with 1 h residence time (Fig. 3.17) and therefore by reducing the treatment time to 1 h more water may be treated in a day. To increase the capacity of the limestone when the initial concentration is high, say 20 mg/L, arrangement of more than one column in series can be done. This should also bring the final pH to near neutral.

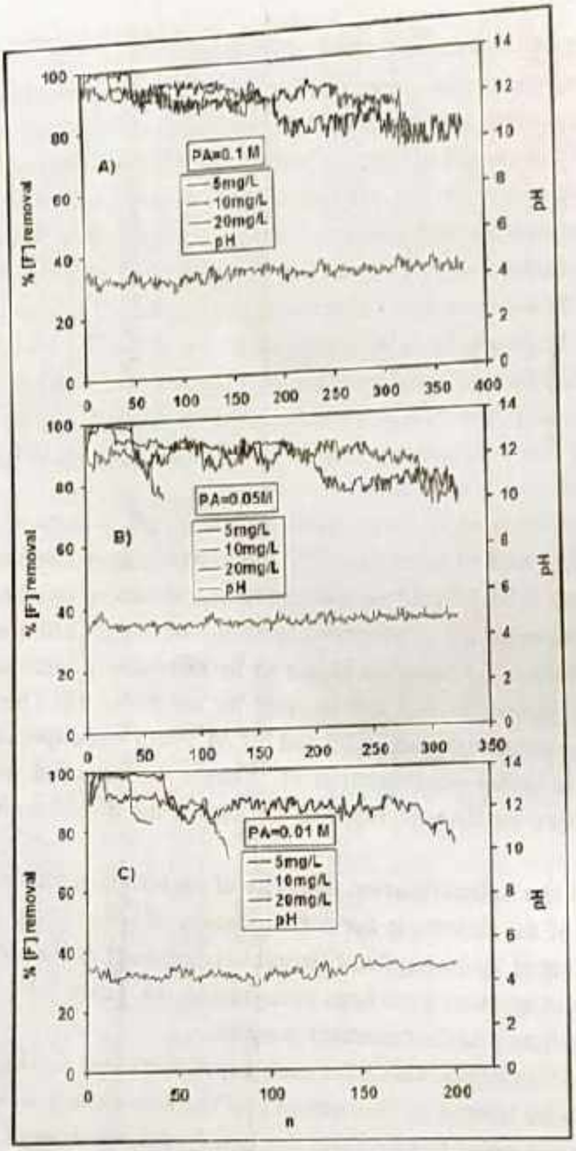

Figure 3.19. The percent F$^-$ removal and pH of the water *vs.* number of repeated use of the same limestone (n), after treatment for 3 h, when the acid concentration (A) 0.1 M, (B) 0.05 M and (C) 0.01 M PA was added to the fluoride containing water before filtration.

Table 3.13. The amount of remaining F$^-$ in the treated water starting with initial 5, 10 and 20 mg/L initial F$^-$ concentration containing 0.01, 0.05 0.1 M PA before filtration through limestone column after 3 h treatment for n=50.

n	0.01 M			0.05 M			0.1 M		
	5 mg/L	10 mg/L	20 mg/L	5mg/L	10 mg/L	20 mg/L	5 mg/L	10 mg/L	20 mg/L
1	0.45	1.00	2.00	0.35	0.52	1.80	0.25	0.73	0.71
2	0.52	0.26	2.10	0.42	0.03	1.72	0.32	0.71	0.78

3	0.41	0.21	0.08	0.31	0.02	2.40	0.21	0.74	0.85
4	0.21	0.01	0.07	0.11	0.08	2.51	0.01	0.24	0.77
5	0.24	0.01	0.30	0.14	0.02	2.55	0.04	0.18	1.20
6	0.15	0.01	0.32	0.05	0.27	2.61	0.01	0.19	0.88
7	0.01	0	0.35	0.01	0.18	3.21	0.01	0.19	1.30
8	0.02	0.05	0.42	0.02	0.21	2.82	0.01	0.23	0.94
9	0.02	0.36	0.22	0.01	0.24	1.71	0.01	0.24	1.81
10	0.02	0.97	0.32	0.01	0.27	1.82	0.01	0.02	0.97
11	0.04	0.73	0.29	0.04	0.20	2.12	0.03	0.05	1.05
12	0.01	0.67	0.26	0.01	0.02	1.92	0.01	0.02	1.02
13	0.02	0.83	0.22	0.02	0.03	1.95	0.01	0.02	1.06
14	0.02	0.86	0.21	0.02	0.06	2.51	0.01	0.03	0.80
15	0.01	0.79	0.31	0.01	0.01	2.12	0.01	0.02	1.21
16	0.02	0.92	0.26	0.02	0.07	2.31	0.01	0.16	1.27
17	0.02	1.00	0.12	0.02	0.03	2.43	0.01	0.17	1.31
18	0.05	0.98	0.35	0.05	0.05	2.61	0.04	0.09	1.32
19	0.04	1.02	0.47	0.04	0.05	2.32	0.03	0.07	1.25
20	0.05	0.85	0.32	0.05	0.03	2.41	0.04	0.06	1.72
21	0.04	0.72	0.25	0.04	0.06	2.42	0.03	0.06	1.65
22	0.05	0.94	0.34	0.05	0.05	1.82	0.04	0.05	1.45
23	0.04	0.79	0.56	0.04	0.06	1.41	0.03	0.06	1.55
24	0.03	0.87	2.80	0.03	0.03	1.72	0.02	0.03	1.72
25	0.03	0.91	2.71	0.03	0.24	2.11	0.02	0.02	1.82
26	0.02	0.84	2.90	0.02	0.34	1.72	0.01	0.03	1.60
27	0.05	1.03	3.32	0.05	0.66	1.81	0.04	0.06	1.51
28	0.06	0.88	3.11	0.06	0.54	1.92	0.05	0.07	1.40
29	0.06	0.83	3.42	0.05	0.58	1.81	0.05	0.06	1.20
30	0.04	0.79	3.21	0.04	0.56	2.10	0.03	0.46	1.22
31	0.07	0.89	3.40	0.07	0.58	2.12	0.06	0.77	1.31
32	0.05	0.91	3.33	0.05	0.65	1.91	0.04	0.78	1.21
33	0.08	0.87	3.51	0.07	0.62	1.81	0.07	0.84	1.22
34	0.07	0.91	3.42	0.07	0.67	1.72	0.06	0.86	1.11
35	0.06	0.88	3.51	0.06	0.66	1.62	0.05	0.95	1.12
36	0.06	0.85	3.62	0.06	0.63	1.81	0.05	1.11	1.21
37	0.06	0.66	3.41	0.06	0.53	2.12	0.05	0.94	0.91
38	0.09	0.92	3.52	0.09	0.55	2.11	0.08	0.89	1.12
39	0.08	0.99	3.70	0.08	0.54	2.22	0.07	0.84	0.98
40	0.15	1.21	3.83	0.14	0.58	2.12	0.14	1.20	1.12
41	0.04	0.94	4.52	0.04	0.60	2.32	0.03	0.97	1.21
42	0.24	1.04	3.92	0.23	0.56	2.51	0.02	0.90	1.33
43	0.35	1.07	4.11	0.34	0.62	2.31	0.02	0.80	1.41
44	0.51	1.12	4.32	0.50	0.61	2.21	0.02	0.74	1.62
45	0.61	1.07	4.21	0.60	0.67	2.34	0.01	0.60	1.51
46	0.42	1.05	4.12	0.41	0.69	2.32	0.04	0.52	1.33
47	0.46	1.31	4.41	0.45	0.73	2.74	0.05	0.56	1.42
48	0.57	1.22	4.51	0.56	0.72	2.61	0.05	0.67	1.22

49	0.75	1.43	4.61	0.74	0.76	2.42	0.03	0.87	1.41
50	0.74	1.24	4.82	0.73	0.73	2.71	0.06	0.84	1.20

Table 3.14. The maximum value of 'n' up to which the remaining fluoride concentration is 2 mg/L and the quantity of water defluoridated till then (capacity) per kg of limestone for different initial concentrations of fluoride with different PA concentrations for a treatment time of 3 h.

Initial [F⁻]	[PA]	n	Capacity in L/ kg
5	0.01	180	60
	0.05	325	108
	0.10	380	126.6
10	0.01	70	23
	0.05	315	105
	0.10	330	110
20	0.01	30	10
	0.05	85	28.3
	0.10	190	63.3

Comparative Evaluation of the performance of the four acids w.r.t. Fluoride removal performance

In this defluoridation study, four acids *viz.*, AA, CA, OA and PA have been used to increase the calcium ion activity in the limestone column by adding the acid to the fluoride water before filtration through the column. The acids have shown good performance with respect to their capacity to dissolute the limestone in the column for precipitation of fluoride as calcium fluoride. The acids liberate Ca^{2+} from the limestone and forms their respective salts namely, calcium acetate, calcium citrate, calcium oxalate and calcium phosphate. Among these salts calcium phosphate has an advantage over the others, which has already been used in defluoridation process. In presence of water molecules in the column calcium phosphate transforms into calcium phosphate hydroxide i.e. HAP. There are number of works has been done with HAP for defluoridation and it has been found to be a good fluoride scavenger. It can precipitate and adsorb fluoride forming calcium fluoride and calcium FAP respectively. Thus the formation of HAP in the limestone column gives an extra advantage to the treatment process. In comparison to HAP, the other salts of the acids does not show fluoride removal ability as has been investigated by taking the laboratory chemicals of those three salts for defluoridation, rather they hinders the limestone defluoridation process by blocking the limestone surface. This may be the reason of the low capacity of fluoride removal by the limestone chips in this defluoridation process where AA, CA and OA have been used. Adsorption of F^- is also possible on the new surfaces of limestone created after dissolution and on the surfaces of HAP.

In addition to this the neutralization of all the acids except PA has been found to be very fast and neutralization completes within 3-4 minutes. But neutralization of PA in the limestone column has been found to be very slow and takes up to 24 h (Fig 3.17). A shortcoming of this slow neutralization is that the treatment process by PA requires pH correction of the effluent water, which is not needed by the other three acids. However, despite this limitation, PA is far better than the other acids in terms of the fluoride removal capacity of the limestone. Considering the benefits and shortcoming of the acids used in this treatment process, the order of the acids in terms of increasing the capacity of the limestone for acid enhanced limestone defluoridation process is as follows: PA>>OA> CA> AA.

A Comparative Cost-benefit analysis

A low cost fluoride removal process is always desirable. The acids used in the present process are of low cost. Limestone being very low-cost has a little effect on the total cost. The total costs per liter of water have been estimated to be

Table 3.21. Cost-benefit analysis of the AELD process. The cost of the acids and limestone used in the estimation are the retail prices.

Acid	Strength of acid	Cost in Rs/L
AA	0.03	0.259
	0.06	0.277
	0.1	0.251
CA	0.01	0.372
	0.05	1.053
	0.1	2.187
OA	0.01	*
	0.05	0.273
	0.1	0.341
PA	0.01	0.054
	0.05	0.206
	0.1	0.398

*cannot bring F^- to below 2 mg/L

The cost of removing F^- per liter of water from 10 mg/L to below 2 mg/L has been presented in Table 3.21. It can be observed from the table that, AA, OA are more cost effective in comparison to CA having higher price. The capacity of the limestone has been increased to a significant amount when PA was used. The use of PA leads to higher capacity of the limestone and the amount of treated water is also increased. From the consideration of the cost of the per liter of the water, the amount of acid and limestone needed for the treatment process and the time required for the treatment, the use of PA is the best for this technique. Use of higher concentration of the acids increases the cost but also increases the capacity of limestone, which is also desirable. As a whole the method is quite cost-effective with all four acids.

Overall Development Objective 2:

- *Optimization of chip size of crushed limestone, column size, etc. w.r.t. quantity of groundwater and concentration of fluoride:*

Limestone particle size selection.

Crude limestone and powdered limestone of particles size <170 μm were obtained from Bokajan Cement Factory, Bokajan, Assam, India. The crude limestone was crushed into different particle sizes *viz.*, 1-2 mm, 2-3 mm and 3-4 mm sizes to use in the experiments. The composition of limestone based on chemical analysis is given in Table 1.

Table 1. Chemical composition of limestone sample.

Sl. No.	Composition	% Weight of dried material
1	Calcium carbonate $CaCO_3$	85.0-90.0
2	Magnesium carbonate $MgCO_3$	0.8-1.6
3	Calcium oxide CaO	40.0-45.0
4	Magnesium oxide MgO	0.8-1.2
5	Silica SiO_2	10.0-14.0
6	Aluminium oxide Al_2O_3	4.0-5.0
7	Iron oxide Fe_2O_3	2.5-3.5
8	Loss on ignition	33.5-37.5

The selection of the appropriate particle size for limestone defluoridation processes was done after performing some preliminary experiments. All the particle sizes have been used in the batch tests and in the column tests using different acid concentrations. The powder of size <170 μm created problem in the filtration process, since limestone powder possesses some cementing properties. The same type of problem was faced during the use of 1-2 mm sized particles. The batch studies were performed using these two sizes. However, in column experiment the smaller particles blocked the filtration process. The 2-3 and 3-4 sizes were better in terms of solid-liquid ratio, since larger gaps between the particles provided spaces for more water than the <170 μm and 1-2 mm sized particles. In comparison to the 3-4 mm size, the 2-3 mm size particles showed greater fluoride removal capacity which may be due to the increase in surface area in the smaller one. For batch experiments 3-4 mm size particles were also used. The 2-3 mm size particle has been selected for all the column experiments which were the major experiments of the present study.

Some batch studies have been done as preliminary study for evaluation of the amount of AA and CA to be added to the fluoride water for defluoridation. In the first batch tests with crushed limestone, a set of half liter size plastic bottles were filled with 3-4 mm size limestone particles and 10 mg/L F^- solutions having varying concentrations of 0.016 to 0.20 M of AA were added to fill up to the top level of limestone. The experiments were repeated with CA of varying concentrations from 0.01 to 0.10 M and crushed limestone chips of 3-4 mm.

The column experiments were carried out in plexiglass column reactors with fixed bed of crushed limestone chips of 2-3 mm size. The water holding capacity of a 600 cm^2 inner volume reactor filled with 2–3 mm size crushed limestone chips was about 200 mL.

The effect of initial concentration of fluoride in the water is an important factor in the AELD process. It is difficult to remove fluoride from water containing low initial F^- concentration as it is difficult to achieve supersaturation of F^- and Ca^{2+} at low initial concentration of F^-. To lower the fluoride level from a concentration like 50 mg/L directly through precipitation, needs addition of a sufficiently high amount of calcium ion. Therefore, to investigate the influence of initial concentration of fluoride on fluoride removal by the AELD the experiments were carried out with different initial fluoride concentrations, *viz*. 5, 10, 15 and 20 mg/L using all acids.

Overall Developmental Objectives 3:

- *Optimization of retention time:*

Effect of contact time in Batch Test with AA

The dependence of the removal of F^- on contact time (t) with crushed limestone in the batch was examined by measuring the remaining F^- concentration in water samples withdrawn from the containers after t = 3, 6 and 12 h and the results are presented in Fig. 3.2. The removal of F^- was found to increase with increasing the contact time. The removal continued to improve even beyond 12 h up to the acid concentration of 0.10 M. The remaining F^- concentration decreased almost linearly with the contact time up to 12 h. The slope slightly decreased with increasing the concentration of the acid. This indicates that at higher concentration of the acid the F^- removal is not only better but also quicker. It can be seen from Fig. 3.2 that the equilibration times for F^- removal in the presence of 0.1 M AA is about 6 and 12 h, respectively and the equilibration time increases with decrease in the concentration of the acid. So, the 12 h time can be taken as the total treatment time, since it mimics an overnight treatment along with good fluoride removal.

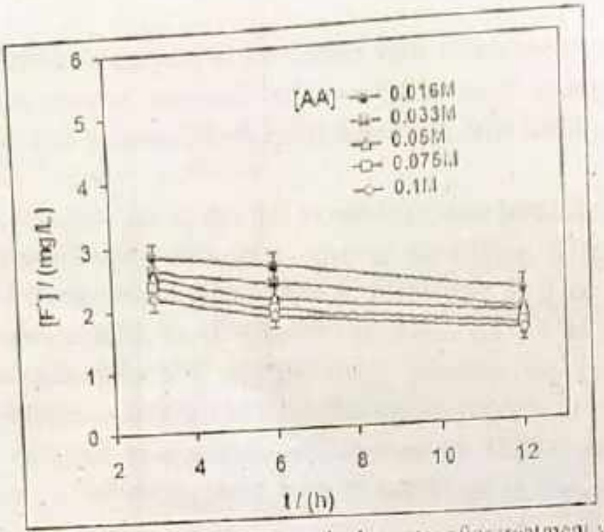

Figure 3.2. Remaining [F^-] present in the water after treatment with crushed limestone of size 3-4 mm for varying contact time, (t) in h in the presence of AA for n = 1 of the batch test.

Effect of residence time in column test with AA

The Fig. 3.4 shows that there is an increase in F^- removal capacity of the limestone with increase in residence time. A less residence time is always desirable in any water treatment process. Here in 6 h of residence time F^- removal is satisfactory only upto 4-5 times repeated use of the same limestone. On increasing the treatment time to 12 h, 80 % removal can be obtained upto n = 10-12. A 12 h residence time can be compared to an overnight exposure of the F^- water to the limestone particles which is very

Table 3.2. Remaining [F^-] and pH of the water after treatment of 0.03, 0.06 and 0.1 M AA containing 10 mg/L fluoride in distilled water, using 2-3 mm size limestone chips column for (A) 6 h, (B) 12 h and (C) 24 h residence time.

(A) 6 h	0.03 M		0.06 M		0.1 M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	1.88	7.28	1.46	7.24	1.26	7.55
2	1.91	7.77	1.47	7.32	1.34	6.82
3	1.97	7.45	1.35	7.22	1.46	7.22
4	2.03	7.55	1.54	6.92	1.48	6.92
5	2.50	6.82	1.77	6.88	1.53	6.88
6	2.71	7.22	2.46	6.54	1.64	6.54
7	3.42	6.68	2.66	6.65	1.67	6.65
8	3.67	6.92	2.72	6.42	1.75	7.22
9	3.67	6.85	2.92	6.41	1.84	6.68
10	4.10	6.44	3.08	6.09	2.03	6.92
11	4.24	6.92	3.17	6.82	2.18	6.85
12	4.53	6.88	3.26	7.22	2.52	7.28

(B)12 h	0.03 M		0.06 M		0.1 M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	1.40	6.90	1.21	7.31	0.97	6.25
2	1.60	6.75	1.31	7.27	1.21	6.34
3	1.73	6.67	1.30	7.28	1.18	6.54
4	1.81	6.71	1.24	7.18	1.54	6.37
5	2.13	6.54	1.46	7.05	1.38	6.28
6	2.55	6.66	2.13	6.63	1.39	6.26
7	2.88	6.73	2.25	6.76	1.36	5.96
8	3.20	6.63	2.55	6.54	1.48	6.04
9	3.45	6.58	2.41	6.46	1.55	6.14
10	3.67	6.65	2.52	6.13	1.85	5.96
11	3.72	6.53	2.64	6.37	1.92	6.27
12	3.97	6.49	2.76	6.28	2.14	6.42

(C) 24 h	0.03 M		0.06 M		0.1 M	
n	F(mg/L)	pH	F(mg/L)	pH	F(mg/L)	pH
1	1.17	7.21	1.15	7.35	1.02	7.65
2	1.38	7.78	1.15	7.46	1.09	7.18
3	1.52	7.54	1.16	7.37	1.12	6.73
4	1.59	7.65	1.17	7.26	1.16	6.63
5	1.80	7.18	1.40	7.17	1.20	7.18
6	2.16	7.50	1.96	6.68	1.26	7.05
7	2.66	7.09	2.09	6.87	1.31	6.63
8	3.13	7.28	2.49	6.69	1.44	6.76
9	3.24	7.13	2.28	6.50	1.58	6.54
10	3.30	6.52	2.47	6.11	1.65	7.26
11	3.42	6.63	2.53	6.54	1.84	7.17
12	3.56	6.58	2.67	6.37	1.79	6.68

common in household water purification processes. It can be mentioned here that even if the fluoride removal further improves slightly with 24 h of residence time, a residence time of 6 or 12 h may be more suitable for practical purposes.

Effect of contact time in Batch Test with CA

The dependence of the removal of F^- on contact time, t with crushed limestone in the batch was examined by measuring remaining F^- concentration in water samples withdrawn from the containers after t = 3, 6 and 12 h and the results are presented in Fig. 3.9. The removal of F^- was found to increase with increasing contact time. From the plot it can be seen that the slope rapidly decreased to almost zero at 0.10 M of CA. This means, the fluoride removal attains equilibrium rapidly on the first time use of the crushed limestone and the equilibration time increases with n.

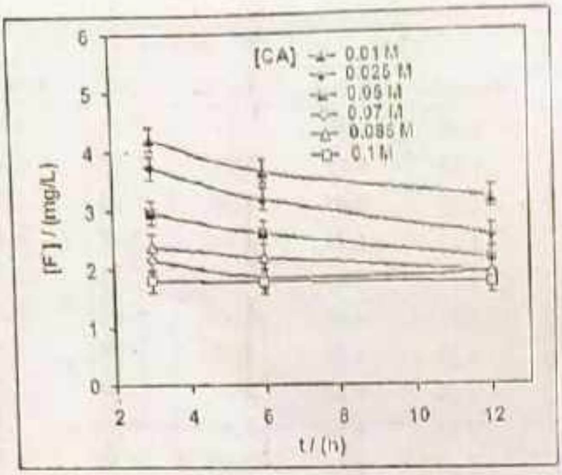

Figure 3.9. Remaining [F^-] present in the water after treatment with crushed limestone of size 3-4 mm for varying contact time, (t) in hour in the presence of CA for n = 1 of the batch test.

It can be seen from Fig 3.9 that the equilibration times for F^- removal in the presence of 0.1 M CA is about 6 h and the equilibration time increases with decrease in the concentration of the acids in both cases.

Effect of residence time in Column Test with CA

The effect of residence time on fluoride removal in this experiment can be observed clearly from Fig. 3.10 and Table 3.5. There was a little improvement in the fluoride removal beyond a residence time of 6 h which is evident from the data available on the table. A minimum residence time of 6 h will be needed for the treatment process and 12 h can be selected as the maximum treatment time for effective F^- removal. It can be mentioned here that even if the fluoride removal further improves slightly with 24 h of residence time, a residence time of 6 or 12 h may be suitable for practical purposes, needing at the most an overnight exposure of acidified fluoride water in the crushed limestone fixed bed reactors.

Effect of residence time in Column Test with OA

In case of OA experiment a residence time of 6 h shows a better F^- removal performance in comparison to AA and CA. It can be seen from the table that there is a very smal difference between the remaining fluoride concentration after 6 h and 12 h with 0.05 an also with 0.1 M OA concentration. Thus it appears that a 6 h residence time is sufficient fo AELD using OA. A further decrease of residence time may be possible if the solid liqu ratio is increased.

Effect of residence time on defluoridation and pH with PA

Fig. 3.17 (A& B) shows the results of the preliminary investigation of this PA enhance limestone defluoridation, where 0.1 M PA, 10 mg/L initial fluoride concentration and 2- mm size limestone particles have been used. Fluoride removal performance of th experiment was observed starting from 1 min to 24 h of residence time. In Fig. 3.17 (A) the plots of concentration of remaining fluoride and pH in the water after limestone treatment against residence time starting from 1 to 1440 min (i.e. 24 h) have been shown. In the inset of Fig. 3.17 (B) the results of fluoride removal during the treatment time of 1 to 30 min have been shown in expanded form and the data can be seen in Table 3.9. It can be observed from the Fig. 3.17 (B) that within 1 min of residence time the fluoride concentration decreases to 1.4 mg/L from initial concentration of 10 mg/L and the removal increases with increase in the residence time.

The concentration of fluoride in the treated water was found to be 1 mg/L within 30 min of residence time. The removal performance of the limestone column further increased with the residence time above 1 h and gradually, but with very slight increase, continues up to 12 h Fig. 3.17 (A).

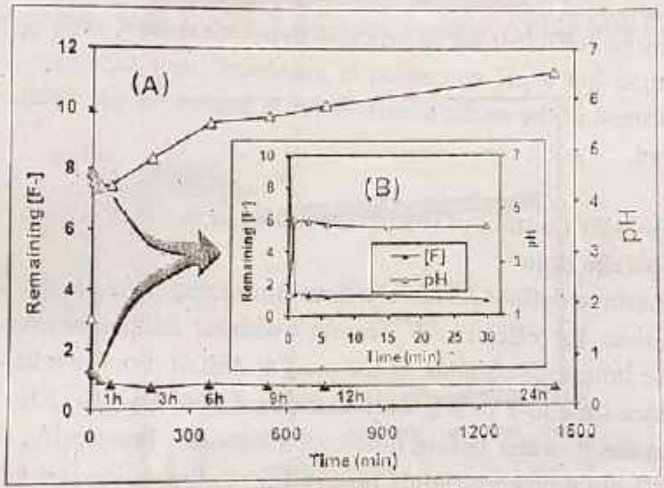

Figure 3.17. Concentration of remaining fluoride and pH of the water *vs.* residence time (A) 0-24 h after treated with 2-3 mm size limestone when initial $[F^-]$=10 mg/L. (B) inset the variations are shown in expanded form for 0-30 min. Concentration of PA = 0.1 M.

However, there are very little differences in the fluoride removal in between 3 to 24 h of residence time. The pH of the water after addition of 0.1 M PA was 1.78 which was found to exhibit an irregular behavior with residence time. The neutralization of PA by limestone has been found to be a slow process requiring about 24 h for completion. Fig. 3.17 shows that the pH of the water suddenly increases to 4.59 from 1.78 within 1 min, then there is a decreasing trend up to 15 min and the again starts to increase [Fig. 3.17 (B)].

Table 3.9. Remaining $[F^-]$ and pH of the treated water after 0-24 h of residence time. PA = 0.1 M, Initial $[F^-]$ = 10 mg/L.

Time (min)	F (mg/L)	pH
0	10.00	1.78
1	1.40	4.59
3	1.30	4.54
6	1.20	4.41

15	1.20	4.28
30	1.00	4.34
60 (1h)	0.87	4.34
180 (3h)	0.73	4.85
360 (6h)	0.83	5.55
540 (9h)	0.75	5.67
720 (12h)	0.71	5.89
1440 (24h)	0.67	6.54

The reason for the observed irregular behavior of the pH with increase in the residence time could not be ascertained at this stage. The above results indicate that due to the slow neutralization of PA the water remains acidic up to about 12 h. Since limestone dissolution continues by the acidic water, the fluoride removal also continues for long time and the F$^-$ removal capacity of the limestone increases. The results also indicate that a residence time of 1-3 h may be sufficient for an efficient fluoride removal performance by using PA in the AELD method but a pH correction is necessary after treatment which may be done by further treatment of the acidic treated water in another crushed limestone column or by any other method.

Comparative Evaluation of the performance of the four acids w.r.t. Residence time

Simple limestone defluoridation is a time consuming process and it requires almost 20 h of residence time for effective F$^-$ removal without adding any chemical or passing CO$_2$ through the limestone column. In the present AELD process it has been possible to reduce the residence time to 1 to 3 h with addition of PA and 6 to12 h with addition of AA, CA and OA to the F$^-$ water before limestone treatment. Practically, the residence time of any water purification process should be small for reducing the cost of the treatment process. A 12 h residence time can be practical for an overnight treatment process of household water purification unit. A reduction of residence time is possible in case of the PA where 95 % of fluoride removal was possible within 1-3 h of treatment time with all experimental concentrations of the acid *viz.*, 0.01, 0.05 and 0.1 M. Thus, from the consideration of treatment time PA is useful acid for this acid enhanced limestone defluoridation process.

A Small Pilot Scale AELD Experiment with PA

Since PA is has shown the best AELD, we have started a small pilot scale AELD experiment with PA. The arrangement of the experimental set up is shown in Fig. 3.20.

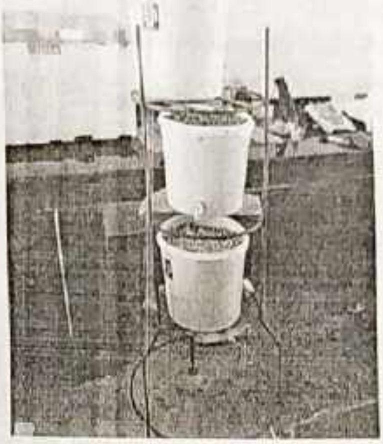

Fig. 3.20. Pilot scale experimental set up of AELD with PA.

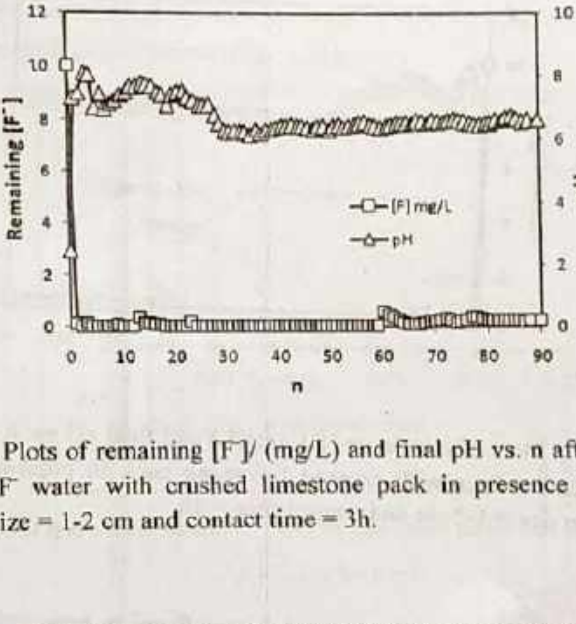

Fig.3.21. Plots of remaining [F⁻]/ (mg/L) and final pH vs. n after treatment of 10mg/L F⁻ water with crushed limestone pack in presence of 0.01M PA. Particle size = 1-2 cm and contact time = 3h.

The results of the pilot test show much better fluoride removal than the laboratory study. Over 50 litre of water has been defluoridated so far per kg of limestone from 10mg to less than 0.2 mg without any noticeable change in the fluoride removal ability of the limestone. The final pH is also near neutral. Thus the present small scale pilot test shows that the AELD with 0.01M PA can be tested in a large scale pilot scheme.

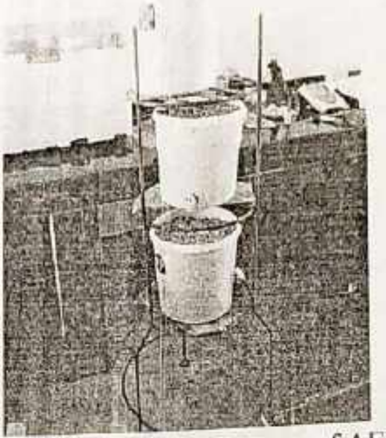

Fig. 3.20. Pilot scale experimental set up of AELD with PA.

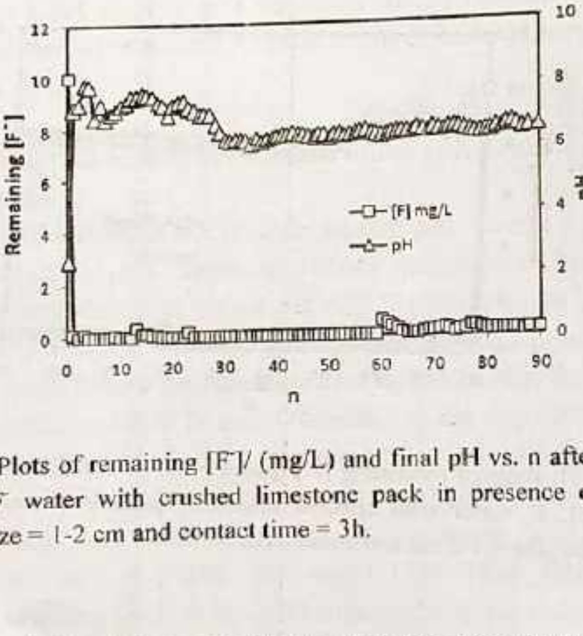

Fig.3.21. Plots of remaining $[F^-]$/ (mg/L) and final pH vs. n after treatment of 10mg/L F^- water with crushed limestone pack in presence of 0.01M PA. Particle size = 1-2 cm and contact time = 3h.

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produced during the course of the reaction. Scanning Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Optical Microscopy has also been used earlier in order to examine the morphological effects of different reactants and circumstances on lime material. Therefore, for further verification of the precipitation and adsorption mechanism of this AELD process, XRD, FTIR, TGA-DSC, SEM-EDX, XPS have been applied to analyze limestone samples before use and after use in the treatment process. These analyses also helped in determining the formations of any hazardous substances in this process and the quality of the limestone with respect to reuse after the treatment process.

Saturation Index (SI) calculation

SI of batch experiment of limestone defluoridation

A positive saturation index of fluorite, SI_f in the water after treatment of the acidified water with crushed limestone indicates precipitation to control the F^- removal. The SI values for AA have been found within the range of 0.98 to 1.35 and for CA the range was 0.7 to 1.27 in the batch experiments (Fig. 3.21).

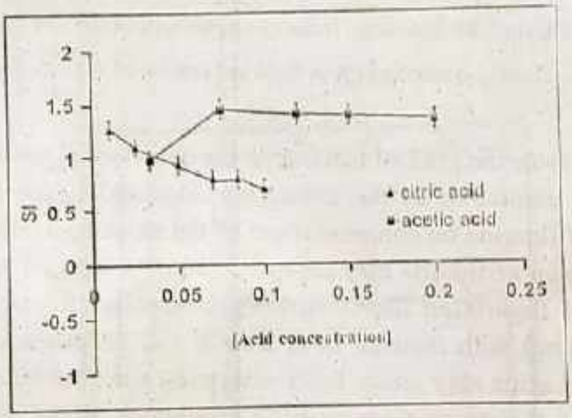

Figure 3.21. Saturation Index of batch tests performed using AA and CA for n = 1.

All the values are positive, which indicates precipitation to control the F^- removal. However, adsorption of fluoride from water over calcite may also take place along with precipitation in the present case.

SI of column experiments of limestone defluoridation

The SI values of the column experiments of 0.1 M AA, CA, OA and PA enhanced limestone defluoridation where fluoride has been removed from 10 mg/L initial concentration using 2-3 mm size limestone is shown in Fig. 3.22. The SI values were plotted against the no. of repeated use of the same limestone chips, n. It can be observed from the figure that, the SI values started with negative value for each acid, gradually increases and become positive after 2-6 times use of the same limestone chips. The positive value of SI indicates precipitation of fluorite to be the major mechanism of fluoride removal. Since neutralization of the acids does not practically depend on n as indicated by the constancy of pH with n (Fig. 3.4), the precipitation of fluorite is expected to take place equally with all n. Thus the observed negative SI with lower n may be due to significant removal of fluoride by adsorption on calcite in addition to the precipitation of fluorite.

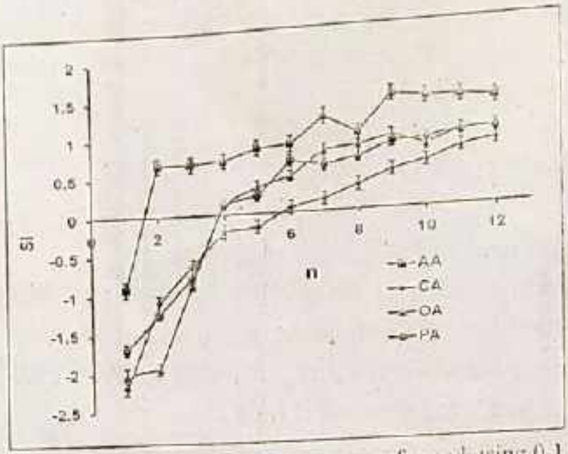

Figure 3.22. Saturation Index of column tests performed using 0.1 M acetic, citric, oxalic and PA in fixed bed column of 2-3 mm size limestone.

This also explains the gradual increase in the observed SI with n, which can be attributed to a gradual saturation of the adsorption sites and hence a gradual decrease in the adsorption of fluoride on continuous use of the same limestone chips. Therefore, even if the precipitation of fluorite may take place equally with all n, a gradual decrease in the adsorption of fluorite on limestone is the reason for the observed overall decrease in fluoride removal with increase in n. Here it can be mentioned that, the dissolution of calcite by the acids may create fresh adsorption sites on the calcite surface allowing the adsorption process to continue even on continuous use of the limestone chips although the adsorption gradually decreases with n. The excess free Ca^{2+} ions generated by the dissolution of limestone by the acids combine with the F^- present in water and get precipitated. The BIS guideline value of Ca^{2+} in drinking water is 75 mg/L (desirable limit) to 200 mg/L (permissible limit). The Ca^{2+} concentration in the treated water was found to be within the range of 8 mg/L initially which increased to 109 mg/L on repeated use of the same limestone sample for AA, CA, OA and PA. Thus the values of Ca^{2+} concentration remain within soft or moderately soft range of total hardness of water. The moderate hardness can be removed by simple methods using water softeners. However, the slight higher Ca^{2+} concentration above the desirable limit may also work as a potential calcium supplement for patients of fluorosis and osteosporosis.

XRD study

X-ray of crude limestone and limestone after use

The XRD patterns of crude limestone and limestone after reaction with different acid containing fluoridated water have been shown in Fig. 3.23. It can be seen from Fig. 3.23(A) that the intensity and the distance between crystal planes of diffraction peaks are in good agreement with the standard spectrum of the crystalline calcite polymorph of calcium carbonate.

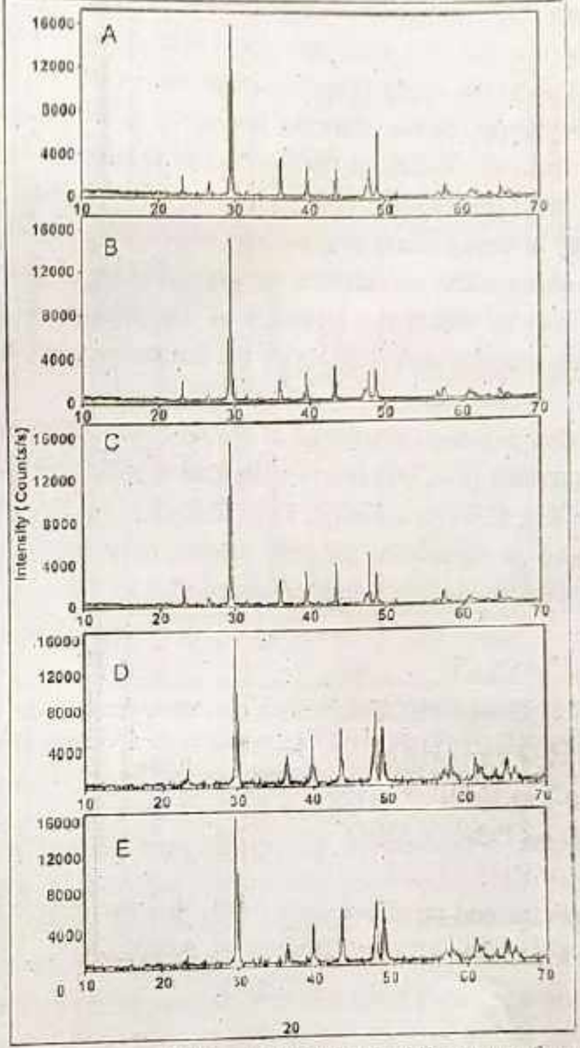

Figure 3.23. The XRD spectra of (A) crude limestone and limestone after use in the column experiment with (B) AA, (C) CA, (D) OA and (E) PA.

The 20 values of the XRD spectrum which are 23°, 29.5° (strong), 36.12°, 39.5°, 43.5°, 47.5° and 48.5°; correspond to the calcite polymorph of calcium carbonate [*d* spacings (Å): 3.86 (102), 3.02 (104), 2.48 (110), 2.27 (113), 2.07 (202), 1.91 (108) and 1.87 (116), respectively]. The XRD pattern of the limestone after use in the reaction shows some similar type of differences with that recorded before use [Fig. 3.23 (B,C,D,E)]. The relative intensities of the peaks at 36.12°, 39.5°, 43.5° reversed after use of the limestone indicating relative damage to the respective planes decreasing in the order (110) > (113) > (202). On the other hand, the relative intensities of the peaks at 47.5°, and 48.5° also reversed after use of the limestone whereas the peak at 47.5° corresponding to plane (108) is expected to be diminished more than that of the peak at 48.5° which corresponds to the plane (116). The increase in the relative peak intensity at 47.5° can be attributed to diffraction from the plane (202) of fluorite (CaF_2) which gives rise to a strong intensity. This indicates formation of fluorite on the limestone surface due to the reaction of free Ca^{2+} produced by dissolution of limestone in presence of acid, adsorption of fluoride on limestone or due to penetration by fluoride slightly into the limestone. The above variations in the XRD pattern however do not indicate very significant changes in the limestone after use for the defluoridation. The extent of the changes in the relative intensities is more in the case of the limestone used with AA than that used with CA with equal exposure to the acidic fluoride solutions. This indicates greater morphological effect of AA than that of CA on the limestone. In case of OA and PA increment of the peak at 47.5° corresponding to (202) plane of fluoride has been observed with a little higher intensity in comparison to the peaks observed when limestone was used with AA and CA. This observation reveals that the precipitation of fluorite may be more in case of OA and PA, due to which the intensity of the peak at 47.5° became higher. Thus, it indicates higher morphological effect on the limestone when treated with OA and PA.

XRD of the other products produced in the reaction of limestone with F^- water

In general limestone ($CaCO_3$) reacts with acid to give free Ca^{2+} and CO_2. In presence of AA (CH_3COOH), CA ($H_3C_6H_5O_7$), OA ($H_2C_2O_4$) and PA (H_3PO_4) limestone gives free Ca^{2+} and there is formation of the respective calcium salts of the acids, due to dissociation of the acids following the equations:

$$CaCO_3 \rightarrow Ca^{2+} + CO_2\uparrow \tag{3.7}$$

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^{-} + H_3O^{+} \tag{3.8}$$

$$H_3C_6H_5O_7 + H_2O \leftrightarrow C_6H_5O_7^{(3-)} + 3H_3O^{+} \tag{3.9}$$

$$H_2C_2O_4 + H_2O \leftrightarrow C_2O_4^{2-} + 2H_3O^{+} \tag{3.10}$$

$$H_3PO_4 + H_2O \leftrightarrow PO_4^{3-} + 3H_3O^{+} \tag{3.11}$$

The XRD spectra and structure of the salts and the respective peak positions have been presented in Fig. 3.24, 3.25 and Table 3.15, respectively.

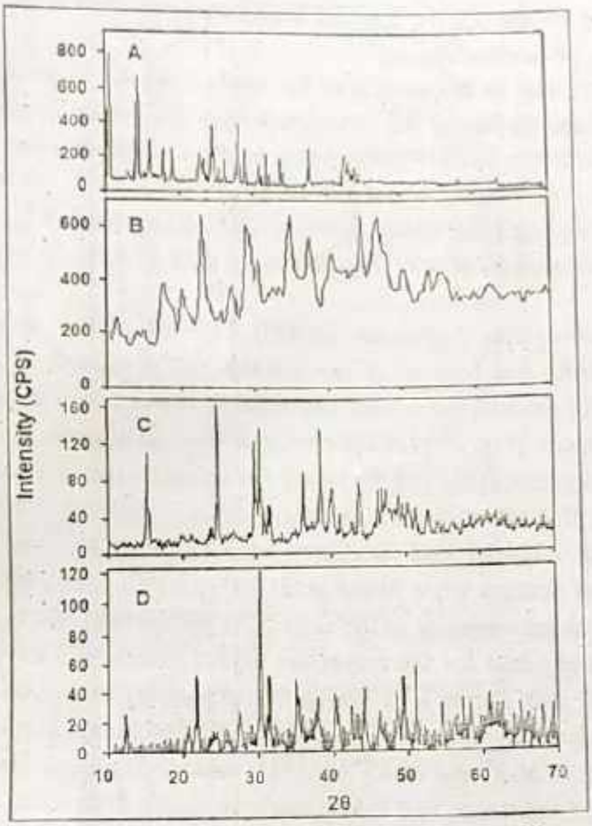

Figure 3.24. XRD spectra of the salts produced after the reaction of limestone with acid added fluoride water (A) calcium acetate, (B) calcium citrate, (C) calcium oxalate and (D) calcium phosphate hydrate (HAP).

Calcium acetate: When the experiment was performed in presence of AA, no white coloured precipitates of calcium acetate was observed in the column because calcium acetate is soluble in water. However, during the filtration of the effluent water from the column, some white coloured crystals were observed in the side of the filter paper in case of AA. These crystals were separated from the filter paper and analyzed with XRD. The main peaks were found at 10.72°, 14.51°, 23.45°, and 25.95° of 2θ value. The spectra are shown in Fig. 3.24 (A) which resembles with ICDD data number JCPDF-190199 and with literature for the XRD of calcium acetate.

Calcium citrate: In the experiments with CA and OA, some white powdery precipitates were found in the column. Those white precipitates were separated from the surface of the limestone particles and analyzed in XRD. The XRD patterns of the powdery substance obtained during defluoridation in the presence of CA is as shown in spectra B in Fig. 3.24, which is similar to the XRD spectra of laboratory grade calcium citrate. This indicates the powdered compound produced on the surface of the limestone to be calcium citrate. The observed formation of the precipitate of calcium citrate on the limestone surface may block further reaction of CA or F^- with limestone. Thus, the lesser morphological change of the limestone when used with CA than that when used with AA, as indicated by the XRDs, may be attributed to inhibition of limestone degradation by precipitates of calcium citrate.

Calcium oxalate: In the same way the white coloured powders were separated from the used limestone surface of the OA experiment. The white powder produced in the column should be calcium oxalate formed as a result of neutralization of OA by limestone. The major peak positions were found at 14.83°, 24.42°, 29.92°, 29.94°, 36.9° and 38.2° for the respective plans (100), (040), (200), (122), (223) and (061). The XRD of the powder shows good agreement with the diffraction data of calcium oxalate JCPDF-771160 [Fig. 3.24 (C)].

Calcium phosphate hydroxide (HAP): The solid after treatment with PA has been collected from the bottom of the column and analyzed in XRD. In this experiment, formation of calcium phosphate and HAP is expected. The spectra of the solid obtained after treatment [Fig. 3.24 (D)] shows a clear evidence of the formation of calcium phosphate hydrate (HAP) in the limestone column after reaction of the limestone with PA containing fluoride solutions. In this spectrum, presence of limestone residue at 29.5° with strong intensity and formation of FAP has also been detected. The main peak positions of spectra were found at 21.55°, 31.95°, 35.6°, 40.1° and 50.75° diffraction angles which corresponds to the respective plans (111), (211), (301), (221) and (321) for HAP and the peaks for the respective crystal planes of FAP have been presented in the Table 3.15 and Table 3.16 which are according to ICDD database number JCPDF-861199. A prominent peak of limestone was also found at 29.95° for (104) plan with two other peaks at 56.9° and 57.85° for (211) and (122) plan respectively. This observation of the peaks of limestone and HAP clearly indicates the reason behind the high removal of fluoride in comparison to the other acids, since, both limestone and HAP together contribute to precipitate fluoride as CaF_2 and FAP respectively.

Earlier it was reported that though fluoride is absorbed by limestone, HAP has the highest capacity of adsorption of fluoride. Precipitation and adsorption by both limestone and HAP is taking place in this treatment process. However, the calcium fluoride peaks are not found in this process which may be suppressed due to the presence of large amount of HAP. To analyze the presence of CaF_2 in the calcium salts, CaF_2 was separated following a standard procedure and then taken for XRD analysis.

XRD of calcium fluoride

In the XRD spectra of limestone after use [Fig. 3.23 (B,C,D,E)] it has been found that at diffraction angle of 47.5° the peak intensity was increased which can be attributed to

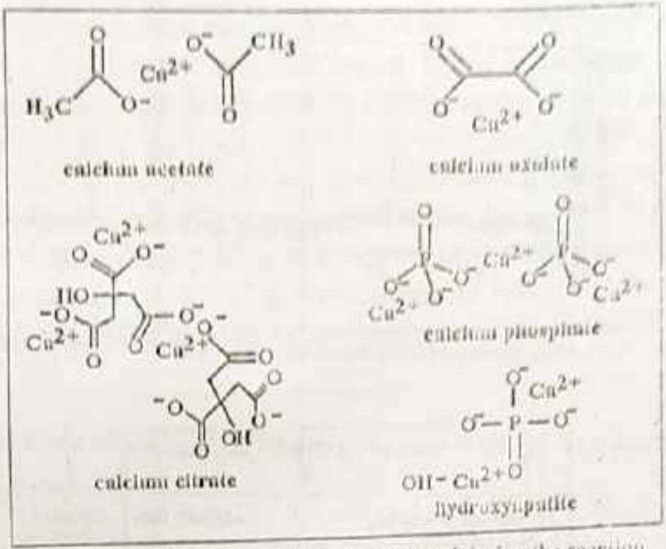

Figure 3.25. Structures of the salts produced during the reaction between limestone and AA, CA, OA and PA.

Table 3.15. The main XRD peak positions of the salts produced in the limestone column after used in the AELD process.

AA	CA	OA	PA
10.72°	17.5°	14.83°	21.55°
14.51°	23°	24.42°	31.95°
23.45°	29.5°	29.92°	35.6°
25.95°	35°	29.94°	40.1°
	40.5°	36.9°	50.75°
	47°	38.2°	

diffraction from the plane (202) of fluorite (CaF_2). However, in the XRD spectra of the calcium salts the evidence of precipitation of CaF_2 is not apparent, probably due to masking of the signals of small amount of fluorite by those of large excess of the calcium salts of respective acids. An attempt was made to separate the fluorite expected to be present with the calcium oxalate precipitates using a standard method. The white powder separated from the limestone surfaces was dissolved in 0.5 M HCl and then diluted with distilled water. The solution was heated in boiling water bath and allowed to settle for overnight. The supernatant solution was collected and its F^- concentration was measured which showed 0.3 mg fluoride in 40 gm of the used crushed limestone chips. The supernatant solution was evaporated to dryness and the solid residue was washed with distilled water and its XRD was recorded. The XRD pattern of the residue [Fig. 3.26] clearly resembles with the standard XRD spectrum of calcium fluoride available in the literature.

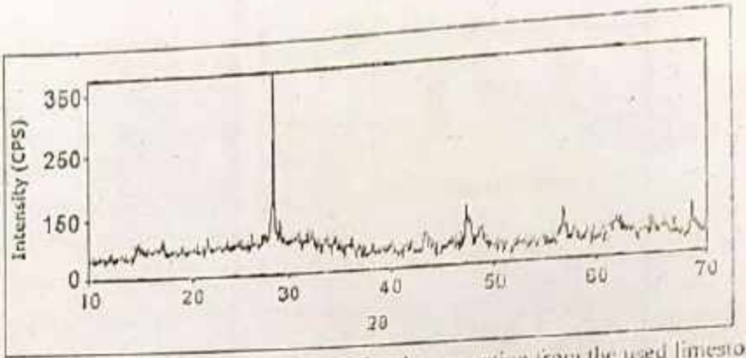

Figure 3.26. XRD spectra of CaF_2 found after the separation from the used limestone.

Table 3.16. The XRD peaks of CaF_2 and $Ca_5(PO_4)_3F$ for the respective planes.

Calcium Fluoride		Calcium fluoroapatite	
28.27°	(111)	27.35°	(021)
47.02°	(220)	31.25°	(112)
55.77°	(311)	37.7°	(222)
68.68°	(400)	42.7°	(131)
		45.9°	(231)

Thus, it is evident that in presence of large quantities of calcium salts calcium fluoride peak intensities were too low to detect but when separated the peaks were found with reasonable intensity. The formation of FAP in the limestone column during the experiment with PA has been observed from the XRD spectra of the HAP. In the spectra of HAP [Fig. 3.24(D)] some peaks have been found which matches with FAP and the 2θ values with respective plans have been given in the Table 3.16. From the XRD study it is clear that limestone dissolves in presence of AA, CA, OA and PA generating Ca^{2+} ions which subsequently precipitates as calcium acetate, calcium citrate, calcium oxalate, calcium phosphate hydrate (HAP), calcium fluoride and FAP.

FTIR study

FTIR spectra of limestone before and after use

The IR spectrum of carbonate minerals show three prominent absorption bands in the regions $v_3 = 1450\text{-}1420$, $v_2 = 890\text{-}870$ and $v_4 = 720\text{-}700$ cm^{-1}. The IR spectra of different limestone samples before and after treatment of the acidified fluoride containing water has been shown in the Fig. 3.27. The main peak positions of the present crude limestone sample [Fig 3.27 (A)] have been estimated at 1429, 875 and 711 cm^{-1}, respectively; which are consistent with that of reference $CaCO_3$[303]. An observed broadening of the v_3 peak may be due to the crystal field effects[304]. A comparison of the IR spectrum of the crude limestone with the calcite standard infrared spectrum indicates the crystal structure of the limestone sample to be high purity calcite. The IR spectra of the used limestone samples after separation from the precipitate formed on the surface are almost identical with that of the limestone before use. This indicates absence of a significant adsorption or penetration by any ions into the limestone crystal. It can be observed from the IR data that O-H stretching frequency is apparent in all the spectra of used limestone ranging from 3350-3450 cm^{-1} [Fig. 3.27 (B,C,D,E); Table 3.17]. For used limestone, water may penetrate to the core of the particles and even after drying some portion of moisture remained in the used limestone. In the IR spectra of the precipitates of the calcium salts, the presence of O-H stretching frequency may be due to hygroscopic nature of the substances. The band near 1430 cm^{-1} in parent limestone remains at the same position in the used limestone which is characteristic position of carbonate minerals.

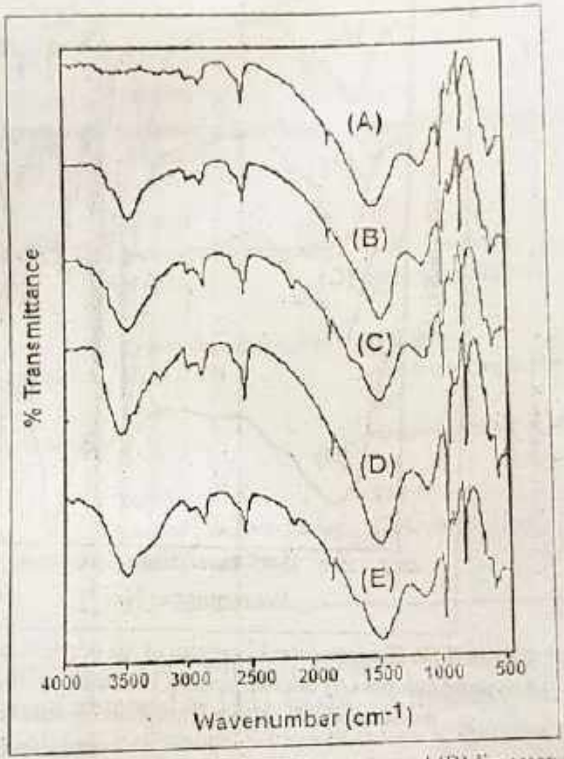

Figure 3.27. Characteristic IR spectra of the (A) crude limestone and (B) limestone after use with AA, (C) CA, (D) OA and (E) PA.

The IR spectra of the products produced during this process

In these treatment processes of limestone defluoriation the formation of calcium salts of the acids were also evident from the IR data obtained from the samples of limestone. As described in the XRD analysis the limestone salt samples were collected and their IR spectra are shown in Fig. 3.28. Presence of O-H group in all the spectra is evident and two small bands near 3000 cm^{-1} can be seen in the spectra of calcium acetate, calcium citrate and calcium oxalate which is due to C-H stretching. However this band is not observed in the spectra of HAP formed after the reaction of limestone with PA containing fluoride. After reaction with AA, CA and OA containing fluoride water, limestone forms corresponding salts of carboxylic acids, which is indicated by the bands at 1609.89, 1615.50 and 1619 cm^{-1} for the antisymmetric stretching of O-C-O bonds and the bands at

1446.89, 1434.90 and 1378.12 cm^{-1} for the symmetric stretching of the carboxylate groups of calcium acetate, calcium citrate and calcium oxalate respectively[305-306]. The higher observed frequencies compared to that of the free COO^- indicate the ionic character of metal –COO^- coordinate bond which is also theoretically proved earlier[306]. In the spectra of carboxylate salts the carbonyl stretching frequency is lowered from the value found for the parent carboxylic acid because the O-C-O bond possesses more single-bond character due to resonance[307].

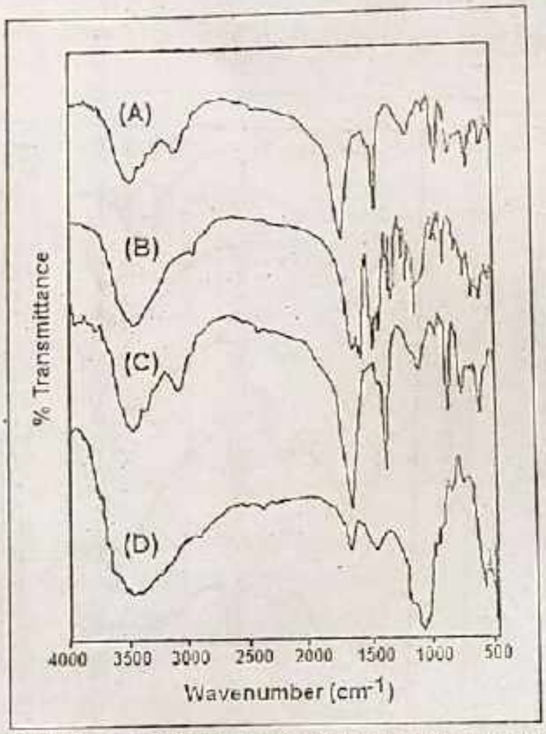

Figure 3.28. Characteristic IR spectra of the precipitates formed in the limestone column (A) calcium acetate, (B) calcium citrate, (C) calcium oxalate and (D) calcium phosphate hydrate (HAP).

Ca-O interaction was observed in the IR of calcium oxalate showing band in the finger print region at 517.75 cm^{-1}. The IR frequencies of the precipitate obtained with AA, CA and OA have been found to be similar to the reported IR of calcium acetate, IR of laboratory grade calcium citrate and calcium oxalate indicating the precipitates to be calcium citrate, calcium acetate and calcium oxalate respectively. The infrared spectrum of the product after the reaction of limestone with PA containing fluoride water has been shown in Fig. 3.28 (D). This spectrum is somewhat different from the IR spectra of other Ca-salts.

The fundamental frequencies of the PO_4^{3-} group have been observed at 960.16 and 1034.98 cm^{-1}. The vibration of the P-OH group has been assigned to a low intensity band observed at 957.21 cm^{-1}. The overlapping of the stretching vibrations of structural OH^- and physically adsorbed water leads to a broad band at 3481.96 cm^{-1} which is supported by

Table 3.17. Characteristic IR data (wavenumber, cm^{-1}) of the precipitates formed in the limestone column.

Crude Limestone	Precipitate formed with AA	Precipitate formed with CA	Precipitate formed with OA	Precipitate formed with PA
	3378.27 (O-H stretching)	3447.30 (O-H stretching)	3437.28 (O-H stretching)	3481.17 (O-H stretching)
1429.23 (asymmetric stretching of O-C-O)	1609.89 (asymmetric stretching of O-C-O)	1615.50 (asymmetric stretching of O-C-O)	1619.41 (asymmetric stretching of O-C-O)	1648.52 cm^{-1} bending vibrations of water
1032.65 (symmetric stretching of O-C-O)	1446.89 (symmetric stretching of O-C-O)	1434.90 (symmetric stretching of O-C-O)	1378.12 (symmetric stretching of O-C-O)	1122.58 HPO_4 stretching
	949.69 (stretching of C-C)	1078.59 (out of plane stretching of C-H)	1031.74 (out of plane stretching of C-H)	1034.98 PO_4^{3-} stretching
857.44 (asymmetric CO_3 deformation)	671.09 (symmetric twisting and rocking of the O-C-O)	839.74 (bending out of plane C-H)	662.96 (symmetric twisting and rocking of the O-C-O)	957.21 P-(OH) stretching
711.94 (symmetric CO_3 deformation)	620.50 (out-of-plane stretching vibrations of the O–C–O)	605.56 (out-of-plane stretching vibrations of the O–C–O)	517.75 cm^{-1} Ca-O interaction	567 cm^{-1} PO_4^{3-} bending

a low intensity band at 1648.52 cm^{-1} which is assigned to bending vibrations of strongly adsorbed water. The band observed at 1433.35 cm^{-1} is probably due to the presence of a very small amount of calcium carbonate. To lower frequencies, two bands assigned to the PO_4^{3-} ion can be found: the intense band at 1032 cm^{-1} (ν3) and the low intensity band at 567 cm^{-1} (ν4). Thus, the IR spectrum in Fig. 3.28 (D) indicates the formation of calcium phosphate hydrate (HAP).

TGA analysis

TGA analysis of the limestone before and after use with AA, CA, OA and PA and of the precipitates obtained after reaction of limestone with fluoride water containing AA, CA, OA and PA has been carried out in the temperature range of 0-700°C and the mass loss *vs.* temp curves have been presented in the Fig. 3.29, Fig. 3.30 and Table 3.18.

Crude Limestone: Calcium carbonate normally starts to decompose above 800°C. When a material is near to 100% pure it melts sharply. Presence of impurity lowers the final melting temperature and the melting usually occurs over a wider range. The TGA curve of the present crude limestone before use [Fig. 3.29 (A)] shows a slow decomposition of the material from 472 °C onwards, which may be due to the presence of some impurities.

From 600-700 °C there is a relatively sharper mass loss, which indicates the starting of degradation of $CaCO_3$.

Used Limestone: The TGA obtained for limestone after use with AA, CA, OA and PA [Fig. 3.29 (B,C,D,E)] are almost identical with that obtained before use, except a small mass loss in the range of 471-474°C range. This may be due to the decomposition of some of the calcium salt remained with the limestone after treatment.

Calcium acetate: In the TGA curve of the precipitate obtained after limestone treatment using AA [Fig. 3.30 (A)], three significant mass losses have been observed at 120°, 402° and 596 °C. The mass loss at 120 °C can be attributed to evaporation of water molecule followed by loss of carbon dioxide at 402 °C and finally loss of CO_2 to form stable calcium oxide at 596 °C[309]. Thus the curve corresponds to calcium acetate formed by combination of acetate ion and calcium ions dissolved from limestone.

Calcium citrate: In the TGA curve of the precipitate obtained after limestone treatment using CA [Fig. 3.30 (B)] two significant mass losses have been observed at 128 and 450 °C. The endothermic peak at 128 °C is due to the removal of water molecule present within the calcium citrate powder. The sharp mass loss at 450 °C may be due to the decomposition of calcium citrate. The decomposition pattern also resembles with the TGA curve of pure calcium citrate indicating the precipitate to be of calcium citrate.

Calcium oxalate: The curve of the calcium oxalate gives three reaction steps with increase in temperature as shown in Fig. 3.30 (C).

$$CaC_2O_4.H_2O\ (s) \rightarrow CaC_2O_4\ (s) + H_2O\ (g) \qquad (3.12)$$

$$CaC_2O_4\ (s) \rightarrow CaCO_3\ (s) + CO\ (g) \qquad (3.13)$$

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \qquad (3.14)$$

The three steps of weight loss can be seen in the curve at 172 °C, 476 °C and 660 °C which can be attributed to the release of water molecule, carbon monoxide and carbon dioxide, respectively, as shown in Eq. 3.12-3.14. The weight loss at 474 °C from the used limestone can also be attributed to loss of carbon monoxide.

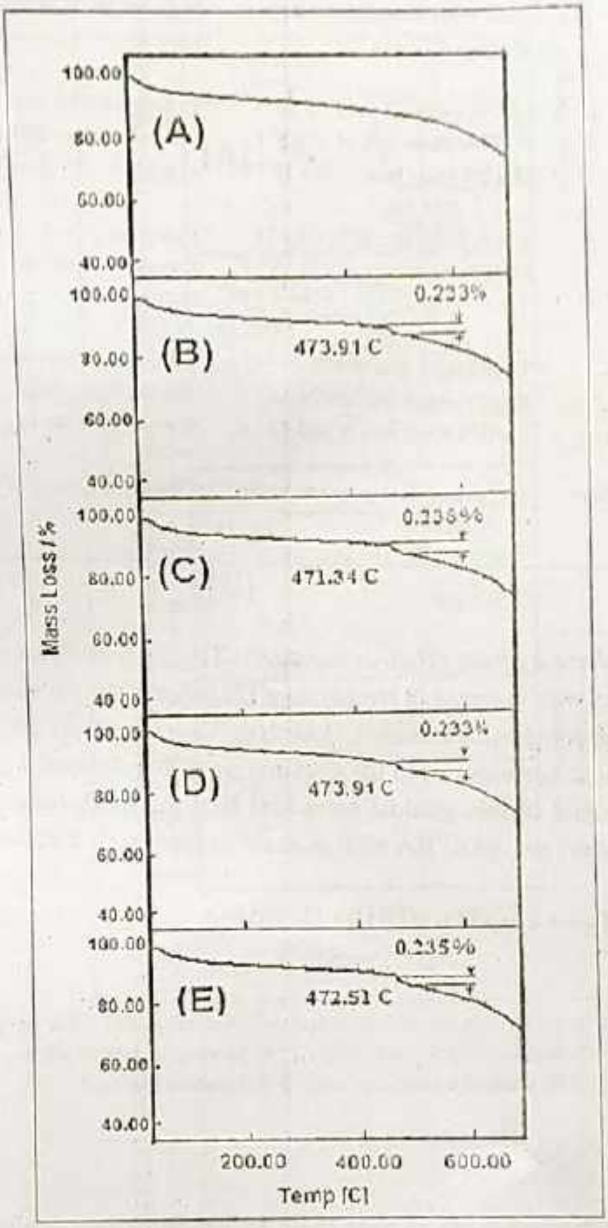

Figure 3.29. Characteristic TGA curves of the (A) crude limestone and limestone after use with (B) AA, (C) CA, (D) OA and (E) FA.

Table 3.18. Decomposition temperatures of the crude limestone and limestone after use and the salts produced in the limestone column.

Name	Mass loss temperature	Assignment
Limestone (before use)	Slow decomposition 472 °C onwards	Because of some impurity in the limestone

Limestone (after use)	Small mass loss about 0.23% in the range 471-474 °C	May be decomposition of calcium salt impurity
Calcium acetate	7.56 % mass loss at 120.16 ° C 30.39% mass loss at 402.5° C 25.23% mass loss at 596.16 ° C	Evaporation of water molecule Loss of carbon dioxide Final loss of CO_2 to form CaO
Calcium citrate	6.24% mass loss at 128.64 ° C 21.73% mass loss at 450.15 ° C	Removal of water molecule Decomposition of calcium citrate
Calcium oxalate	7.61% mass loss at 172.17 ° C 12.66% mass loss at 476.38 ° C 25.42% mass loss at 660.13 ° C	Release of water molecule Carbon monoxide Carbon dioxide
Calcium phosphate hydrate (HAP)	15.78% mass loss at 250.62 ° C	Dehydroxylation of the HAP

***Calcium phosphate hydrate (Hydroxyapatite)*:** The TGA analysis of HAP demonstrates a slow mass loss with increase in temperature [Fig. 3.30(D)]. An endothermic peak at 250 °C has been observed which started from 100 °C and ends at 290 °C. This peak with 15.78 % mass loss corresponds to the dehydration of hyroxyapatite and loss of physically adsorbed water and further gradual mass loss after this peak may be due to the gradual release of hydroxyl groups of HA with increase in temperature according to the Eq. 3.15:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x + xH_2O \qquad (3.15)$$

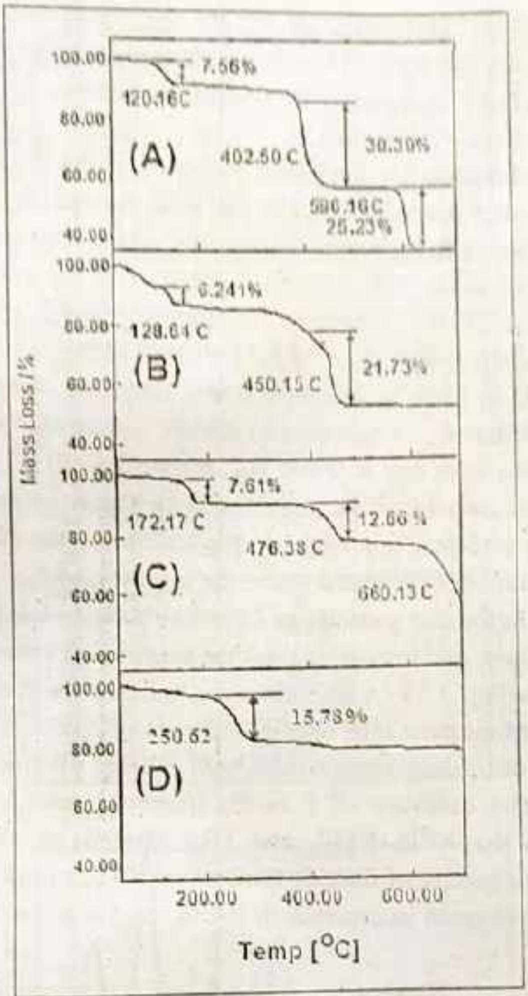

Figure 3.30. TGA curves of the respective calcium salts of the acids produced in the limestone column (A) Calcium acetate (B) Calcium citrate (C) Calcium oxalate (D) Calcium phosphate hydrate (HAP).

XPS Study

Precipitation of calcium fluoride and other salts in this experiment has been confirmed from saturation index calculation and from XRD, FTIR and TGA analysis of the limestone before and after use. To examine the adsorption of fluoride in the limestone surface, XPS study has been carried out with limestone samples before and after use. In addition to fluoride, adsorption of carbon and phosphorous on the limestone surface is also possible during this experiment, since, the AA, CA and OA contain C and PA contains P as primary element. Therefore, XPS study was also carried out for these two elements. The results of these analyses have been presented in Fig. 3.31, 3.32, 3.33.

Fluorine. XPS of limestone chip surfaces before use [Fig 3.31 (A)], did not show the presence of any F^-, whereas those of the limestone chips recorded after use for defluoridation with all the acids showed significant intensities at binding energy values of 685.6 and 684.2 eV, respectively, corresponding to F-1s [Fig. 3.31 (B,C,D,E)]. This suggests significant adsorption of F^- on the limestone chip surfaces during the defluoridation with the acids. Thus, the XPS confirms that although precipitation is the main mechanism of F^- removal in the present case, adsorption of F^- on the calcite surfaces also contribute to the F^- removal.

Carbon. The intensities for the peaks for C-1s in the XPS of limestone chip surface before use and after use with AA, CA and OA, showed significant variations indicating presence of carbon with the environment other than that of carbonate on the chip surfaces after use with all acids [Fig. 3.32 (A,B,C,D)]. The observed relative areas (%) of the peaks for C-1s of the limestone surfaces at 284.6, 286.4 and 289.3 eV were 68.4:12.0:19.6 (before use), 52.7:18.8:28.5 (after use with AA), 41.2:27.1:31.7 (after use with CA) and 45.9: 19.3: 34.8 (after use with OA). The observed variation in the relative areas can be attributed to adsorption of acetate, citrate and oxalate on the limestone chip surfaces after use with AA, CA and OA, respectively. The adsorption of acetate, citrate and oxalate ions may block the sites for the reaction between F^- and limestone on the limestone chip surfaces; this may be responsible for the observed decrease in fluoride removal with number of repeated use of the same limestone.

Phosphorous. In the fine particles of limestone produced during the reaction between PA containing F^- water and limestone chips the presence of P has been detected in XPS study which is in the Fig. 3.33 (A,B). In the crude limestone the presence of P has not been detected. In the limestone after use the existence of 2p electron of P was detected at 134.0 and 135.7 eV of binding energy value with relative percentage of area of 88.3 and 11.7 respectively. The existence of P in the limestone after use supports the information obtained from the XRD, FTIR, and TGA analysis about the formation HAP. HAP possesses high capacity of fluoride removal which has been reflected in the results of the experiments performed in presence of PA in comparison with experiments with AA, CA and OA.

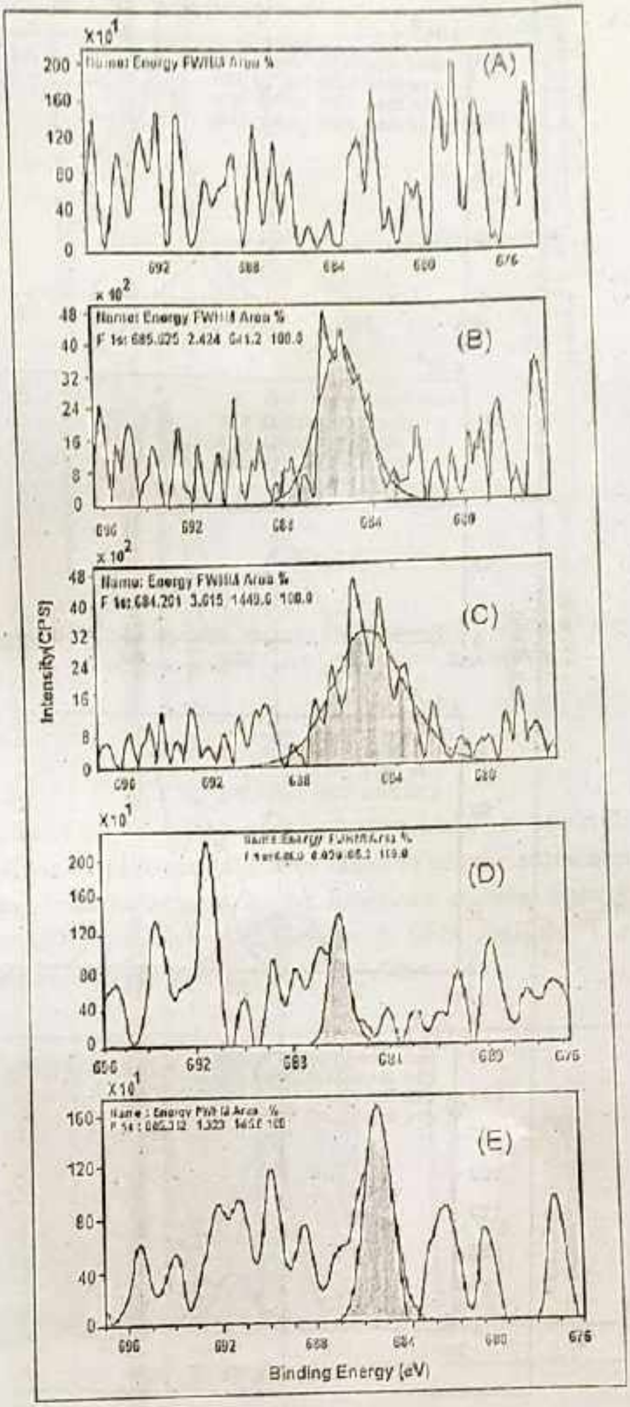

Figure 3.31. XPS spectra (A) crude limestone and the limestone after used in the experiment with (B) AA, (C) CA, (D) OA and (E) PA for F-1s electron.

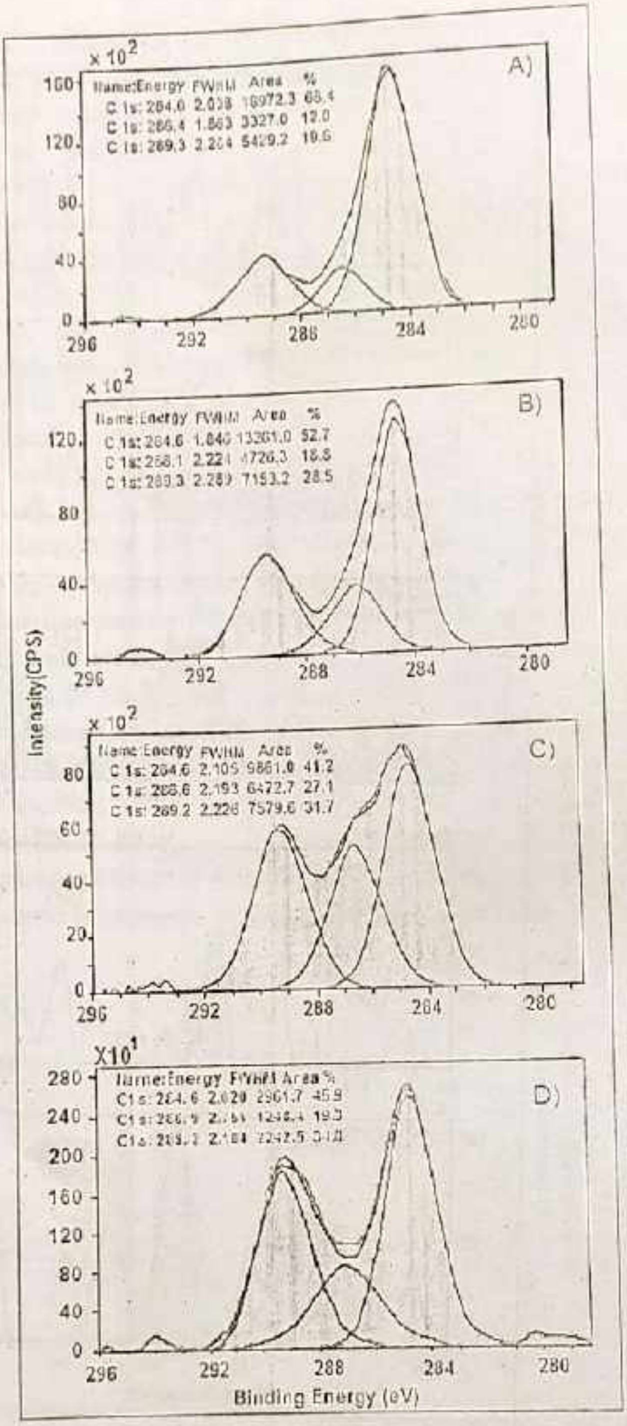

Figure 3.32. XPS spectra (A) crude limestone and the limestone after used in the experiment with (B) AA, (C) CA and (D) OA for C-1s electron.

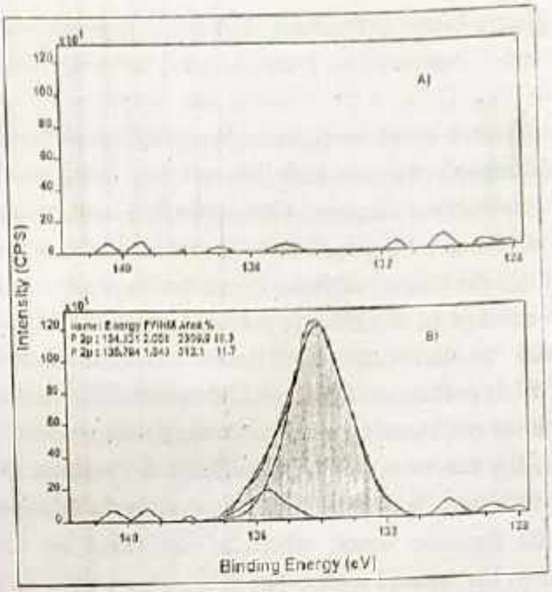

Figure 3.33. XPS spectra (A) crude limestone and the limestone after used in the experiment with (B) PA for P-2p electron.

SEM-EDX study

SEM micrographs of the limestone samples before and after use with AA, CA, OA and PA containing fluoridated water have been taken to see the surface morphology change. To quantify the elements present in the limestone surface Energy Dispersive X-ray Spectroscopy or EDX has been used along with SEM analysis. The SEM-EDX of the crude limestone has been presented in the Fig. 3.34.

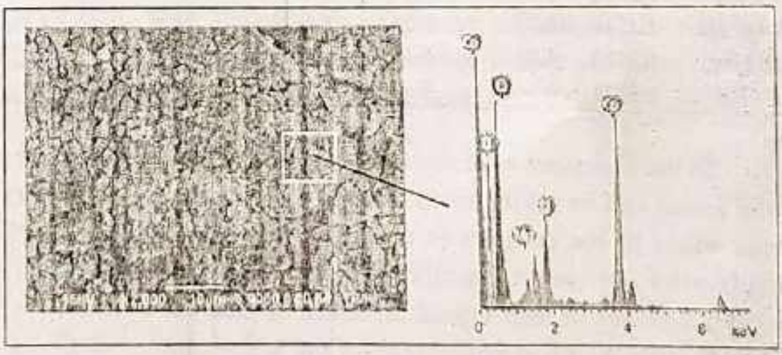

Figure 3.34. SEM-EDX spectra of crude limestone.

Limestone particle size of 2-3 mm has been selected for all the column experiments performed and along with these particles lots of limestone powders of different sizes also present which can be observed from the SEM micrograph. Although 2-3 mm size particles are better for precipitation of F⁻, for adsorption smaller size particles give large surface area giving better efficiency. The EDX spectrum of the crude limestone shows different elemental composition present in the natural crystalline limestone which have been given in the Table 3.19. During the reaction between AA, CA, OA and PA containing fluoridated water with limestone, different salts of the acids has been produced within the limestone column which has been analysed in XRD, FTIR, TGA and they were detected as calcium acetate, citrate, oxalate and phosphate hydroxide. The SEM-EDX spectra of these salts (Fig. 3.35) clearly show the degradation of limestone surface forming salts on limestone surface. From the figure it can be seen that in each salt a minimum percentage of fluoride is present which may be due to the presence of little amount fluoride in that very point where EDX was taken. This suggests significant adsorption of F$^-$ or presence of precipitated calcium fluoride.

In order to examine the elemental composition of the salts EDX was taken and the atomic percentage has been given in the Table 3.19. From these values one can note that the amount of Ca has decreased which is due to dissolution of limestone after reaction with the acidic fluoride water, which is confirmed by corresponding increase in the amount of Ca in the treated water. The table shows that the percentage weight of carbon has increased in case of the use of AA, CA and OA because of the precipitation of the acids as their respective calcium salts.

Table. 3.19. Elemental percentage obtained from EDX of crude limestone and different calcium salts produced from the reaction between the limestone and acidic fluoride solution.

Element/ Shell	X-ray Energy (KeV)	Atomic% (before)	Atomic% (calcium acetate)	Atomic% (calcium citrate)	Atomic% (calcium oxalate)	Atomic% (hydroxy- -apatite)	Atomic% (CaF$_2$)
Ca / Kα	3.6905	14.66	5.10	7.68	6.57	2.63	31.58
C / Kα	0.2774	19.84	20.65	33.36	31.25	28.59	0
O / Kα	0.5249	63.53	56.63	56.67	57.21	55.48	0
F / Kα	0.6768	0	9.81	1.06	2.37	4.62	63.17
Mg / Kα	1.2536	0.75	1.29	0.27	0.34	0.92	0
Si / Kα	1.7398	1.23	6.52	0.96	1.41	5.87	5.24
P / Kα	2.0134	0	0	0	0	1.84	0

In the limestone after use with AA [Fig. 3.35 (A)], the observed appearance of the white grains can be attributed to formation of fluorite. The appearance of white colours at the edges of the particles in the SEM micrographs [Fig. 3.35 (B)] of the limestone sample after use may be attributed to the calcium citrate crystals formed during the process. The needle like crystal structure of calcium oxalate [Fig. 3.35 (C)] has been obtained from the SEM micrograph of the white powder produced in the column where OA was used for the experiment. Presence of P was observed in the limestone residue obtained in the column after the experiment carried out with PA [Fig. 3.35 (D)]. The amount of oxygen remains almost same probably due to the presence of this element in the crude limestone as well as in the acid. Although Mg and Si were found in small quantities in the unused limestone, in case of limestone used with AA and PA, the atomic percent of these two elements are quite high. This may be due to dissolution of calcium carbonate of the surface leaving Si and Mg to increase. Another possibility is that in the particular position where EDX has been taken, the percentage of these two elements may be high.

In the limestone used with CA the percentage of these two elements are lower than that in the crude limestone. This can be attributed to adsorption of the calcium citrate salt on the surface of the limestone particles suppressing the percentage of Si and Mg on the surface. Thus the SEM and EDX data obtained from the experiments reveal that fluoride has been precipitated as well as adsorbed on the surface of the limestone.

The SEM and EDX were recorded also for the same sample, extracted from the precipitate produced in the column with all the acids, which has been used to take XRD spectrum for detection of CaF_2 (Section 3.5.2.3.) The SEM and the EDX of this extract has been shown in Fig. 3.36, which shows different size of the particles stacked together. The EDX indicates the presence of fluoride in the extracted sample. However, the amount of fluoride formed is too small compared to the quantity of used limestone.

Summary of the mechanism of defluoridation with the four acids in the AELD

- The mechanism of this fluoride removal technique with limestone in presence of AA, CA, OA and PA containing fluoride water has been evaluated from the calculation of saturation index (SI) of fluorite and from the analysis of the limestone particles by XRD, FTIR, TGA, XPS & SEM-EDX before and after use.
- SI calculation indicates that initially the fluoride removal was dominated by adsorption of fluoride on the surface of the fresh limestone and after the use of the limestone for 2-4 times the adsorption sites were saturated and precipitation of CaF_2 became the principal mechanism of the process.
- XRD study point outs the high purity of the fresh limestone. In presence of the acids limestone precipitates as the respective salts of the acid and fluoride removal occurs via precipitation of CaF_2. The XRD spectra of calcium salts and CaF_2 were in accordance with the literature. XRD analysis of the limestone before and after use also indicates that there is a little morphological effect of the acids on the

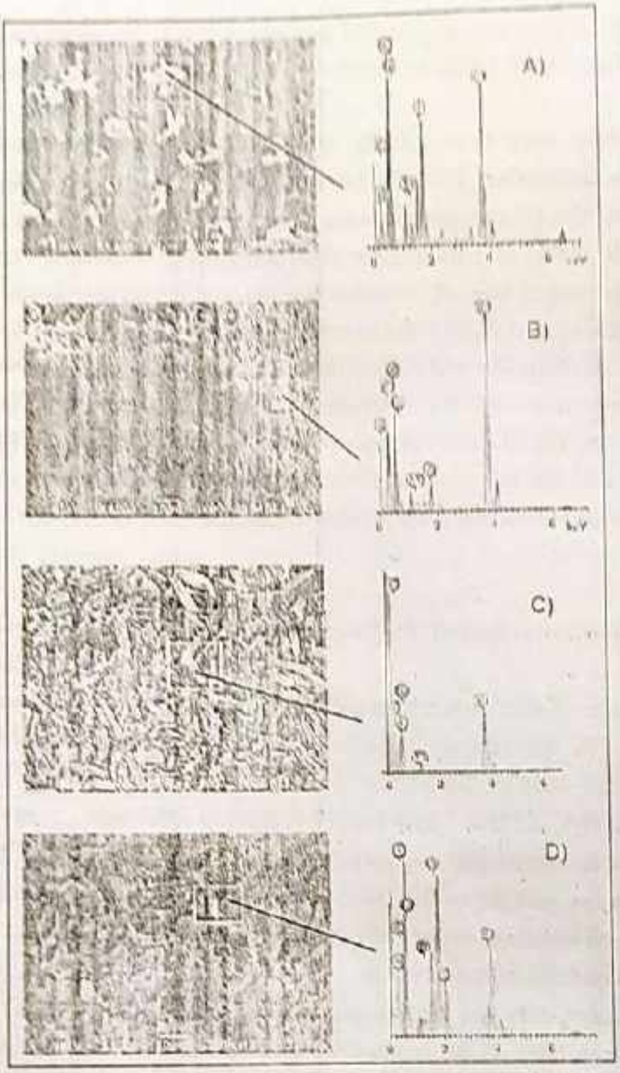

Figure 3.35. SEM-EDX spectra of calcium salts produced in the limestone column (A) calcium acetate, (B) calcium citrate, (C) calcium oxalate and (D) HAP.

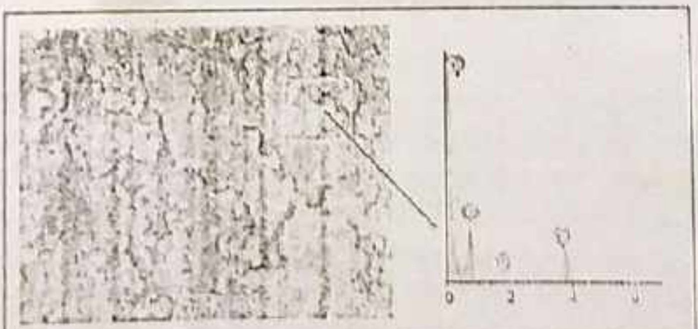

Figure 3.36. SEM-EDX spectra of calcium fluoride obtained from the limestone powder produced in the column after treatment.

limestone and only the surface part of the limestone was degraded, the inner part remains intact and limestone is reusable after the experiment.

- FTIR spectra of the fresh and used limestone reveal the limestone forms respective salts of the acids and the limestone retains its original quality and reuse of the limestone is possible.
- TGA analysis of the limestone before and after use also supports the information obtained from XRD and FTIR analysis.
- XPS study gives the information on the adsorption of fluoride on the surface of the limestone particles obtained after treatment. Adsorption of carbon was also found on the surface of the used limestone which indicates the formation of the carboxylic acid salts of the respective acid *viz.*, AA, CA and OA and gradual decrease of the fluoride removal capacity of the limestone in this cases may be due to the adsorption of the these acids salts. In case of the limestone used with PA adsorption of phosphorous was found and since calcium phosphate hydroxide (HAP) itself is a better fluoride scavenger than limestone the removal capacity of the limestone increases to high extent in this case.
- From SEM-EDX analysis it was found that the surface part limestone has degraded for precipitation of fluoride and salts of respective acids. The EDX of the limestone and the salts of the acids formed in the limestone column indicate the atomic percentage of the elements present.
- All these analysis point outs that, while both precipitation and adsorption contribute to the fluoride removal, a rapid precipitation is the major mechanism of the removal.
- Fluoride removal capacity of limestone has been increased to a high level by the use of PA in comparison to AA, CA and OA.
- Residence time of the water in the limestone column is lowest in case of PA. It needs 1-3 h of treatment time while the other acids need 6-12 h for effective fluoride removal.
- Reuse of the limestone is possible as it has been observed that the quality of the *limestone remains intact after the treatment process from the XRD, FTIR, TGA, XPS* and SEM-EDX study.
- There are no heavy metals present in the treated water, only Fe and Mn has been increased slightly which can be removed by using simple plant ash treatment.
- The overall treatment cost of the water is also very low due to the low price of the chemicals and limestone, which makes the ABLD process with the four acids suitable for rural applications.

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- There are no heavy metals present in the treated water, only Fe and Mn has been increased slightly which can be removed by using simple plant ash treatment.
- The overall treatment cost of the water is also very low due to the low price of the chemicals and limestone, which makes the AELD process with the four acids suitable for rural applications.

Intermediate objective 2:

- *Treatment of Used Limestone for Reuse:*

Analysis of the limestone sample before and after use

To evaluate the exact mechanism of the limestone defluoridation process in presence of different acid the limestone samples before use and after use in the treatment process have been analysed using different analytical tools. The effect of these acids on the quality of the limestone during the AELD process has been studied to evaluate the reusability of the limestone. The reaction products that formed during the AELD process have also been analyzed. The analytical techniques that have been used for detail study of the morphology of the limestone before and after use are XRD, FTIR, TGA, SEM-EDX and XPS

Study of the precipitation of fluoride

To find out the presence of fluoride the precipitate formed in the limestone column reactor, the powder produced in the limestone surface has been separated and dissolved in 0.5 M HCl. After dilution of that solution by distilled water they were heated in boiling water bath and allowed to settle for overnight. The supernatant liquid was collected and F^- concentration was measured with fluoride ion selective electrode using an ion meter.

Comparative Evaluation of the performance of the four acids w.r.t. Reuse of limestone

The limestone used in these experiments have been analyzed by applying different analytical tools and it was observed that the limestone retains its original quality, only the surface part of the limestone degraded. During the F^- removal process the surface of the particles is dissolved forming respective calcium salts except for PA. The salts produced in the limestone column can be separated. To reuse the limestone for defluoridation again the surface of the used limestone has been washed thoroughly and again applied for defluoridation purpose using the same technique. It has been found that the limestone still has the capacity of removing fluoride from the water; however, the removal capacity has been decreased than the fresh limestone to some extent.

Intermediate Objective 3.

- *Examination of Quality, e.g., pH and other contaminants of treated water w.r.t. its potability. Removal of Colour if appears in the treated water:*

Final pH in batch test with AA

The pH values of the treated water have been shown in Fig. 3.1 for n = 1, 3 and 5 and in Table 3.1 for n = 1-5. The pH of the influent fluoride solution comes to 2.75 at the highest amount of AA (0.2 M) added in this experiment. An interesting observation of this batch test is that the pH of the effluent water has been found in the neutral range. The final pH of the treated water was found to be in between 7.0 to 5.7 for water pre-acidified with AA, as shown in Fig. 3.1 and Table 3.1. The slightly lower values of pH can be brought to the acceptable range for drinking by passing the water through another limestone column after this treatment[3,128]. The final pH may also be maintained within the acceptable limit by optimization of the process parameters. Thus, the present method also has an advantage over use of MgO or CaO for defluoridation needing subsequent pH correction by adding more chemicals[284-285]. It can be mentioned here that no odor of vinegar was observed in the treated water which can be attributed to the neutralization of the AA by the limestone. Occurrence of precipitation of CaF_2 in the experiment can be proved by calculation of saturation index from the concentration of Ca^{2+} and F^- in the treated water which has been elaborated in the section 3.5.

Final pH in Column Test with AA

The initial pH values of the 0.03, 0.06 and 0.1 M AA containing fluoride water were 3.15, 3.00 and 2.89, respectively. After limestone treatment the variations in pH of the water with n are also shown in Fig. 3.4 and Table 3.2. The pH of the treated water was found to be in the range 6.0-7.5 with all three concentrations of the acid with limestone chip size of 2-3 mm indicating complete neutralization of the acids by limestone. Nevertheless, the lower limit of the acceptable range of pH of drinking water, can be easily adjusted as desired by simple techniques, such as treatment with plant ash or repeating limestone filtration without acid. The final pH range can be attributed to the remaining CO_2 or H_2CO_3 in the water produced in the neutralization reaction (3.1):

$$n\,CaCO_3 + 2BH_n \rightarrow n\,Ca^{2+} + 2B_n^- + H_2O + CO_2 \qquad (3.1)$$

where BH_n and B_n^- are the acid and its conjugate base. Evolution of CO_2 from the limestone in the reactors was observed on addition of the pre-acidified F^- solutions.

Final pH in Batch Test with CA

It has been observed from the batch tests with crushed limestone and added CA that the pH of the effluent water after the treatment comes to the near neutral range. The final pH of the treated water was found in between 7.0 to 6.2 as shown in Fig. 3.8 and Table 3.4. The slightly lower values of pH can be brought to the acceptable range for drinking i.e. within 6.5-8.0, by passing the water through another limestone column after this treatment. The final pH may also be maintained within the acceptable limit by optimization of the process parameters. Thus, the present method with CA also has an advantage over use of MgO or CaO for defluoridation needing subsequent pH correction by adding more chemicals.

Final pH in Column Test with CA

The initial pH of the 0.01, 0.05 and 0.1 M CA containing fluoride water was 2.61, 2.19 and 2.06 respectively. The pH of the effluent water from limestone filtration has been plotted in the Fig. 3.10 and given in the Table 3.5. During the reaction between limestone and acidic fluoride solution, the acid has been neutralized and the final pH of the treated water was found to be in the range 6.2-7.7 with all three concentrations of the acid (Eq. 3.2). Nevertheless, the lower limit of the acceptable range of pH of drinking water, can also be easily adjusted as desired by simple techniques, such as treatment with plant ash[286] or repeating limestone filtration without acid[3].The near neutral final of pH of the water after this treatment process is an advantage of the method.

$2C_6H_8O_7 + 3CaCO_3 = 3Ca^{2+} + 2C_6H_5O_7^{3-} + 3CO_2 + 3H_2O$ (3.2)

Final pH in AELD with OA

The initial pH of the 0.01, 0.05 and 0.1 M OA containing fluoride water was 2.10, 1.58 and 1.36 respectively. The final pH of the treated water in the present cases was found to be in the range 6.5 to 7.5 with all three concentrations of the acids (Fig. 3.15, 3.16 & Table 3.7, 3.8). This indicates complete neutralization of the OA by limestone as was observed previously with AA and CA (Section 3.1 and 3.2) which follows the neutralization reaction (3.3).

$CaCO_3 + C_2O_4H_2 \rightarrow Ca^{2+} + C_2O_4^{2-} + H_2O + CO_2\uparrow$ (3.3)

Evolution of CO_2 from the limestone in the reactors was observed on addition of the pre-acidified F^- solutions. It can be seen from Fig. 3.15 that though the increase in concentration of the acid increases the fluoride removal, the variation in the initial acid concentration has a little effect on the final pH of the treated water. Similarly, there was hardly any difference between the final pH of treated water collected after the residence time of 6, 12 and 24 h suggesting that the neutralization of the acid is rapid. The observed final pH range which is within the acceptable range for drinking water can be attributed to the remaining CO_2 or H_2CO_3 and Ca^{2+} in the treated water.

Neutralization of PA after AELD and pH correction

It can be observed from all the results of fluoride removal by AELD process with PA that although the fluoride removal performance of the limestone in presence of PA is impressive, the neutralization of PA requires longer time than that with the other acids. It may be due to the formation of HAP and FAP with low porosity because of which the diffusion of the acid in to limestone is slow. When acid concentrations were 0.01 M, 0.05 M and 0.1 M the pH of the water after treatment remained within the range of 5.4-6.6, 4.7-5.2 and 4.2-4.6. For better efficiency of this process a moderate acid concentration of 0.05 M may be suitable with adjustment of the pH after defluoridation. This neutralization may be done by adding a second crushed limestone column in series with this column and by filtering the water of the first column through the second column without adding acid[3]. The carbonate of the limestone will neutralize the water. The pH may be adjusted using other methods also.

Comparative Evaluation of the performance of the four acids
w.r.t. pH correction

The fluoride removal performance of the limestone in presence of PA is impressive, however, neutralization of PA requires more time than the residence time used in these experiments *viz.*, 3, 6, 9 or 12 h (Fig. 3.17, Fig. 3.18). The other three acids neutralize easily and the water after treatment does not need pH correction. It has been observed that in PA experiment with [PA] = 0.1 M, at 3 h pH is around 4.5. Even after 12 h of residence time the pH of the effluent water remains around 5, however, the remaining fluoride concentration is almost similar after 3 h and 12 h (Table 3.10). A moderate acid concentration of 0.05 M may be suitable with adjustment of the pH after defluoridation. This neutralization may be done by adding a second crushed limestone column in series with this column and by filtering the water of the first column through the second column wihout adding acid. The carbonate of the limestone will neutralize the water. The pH may also be adjusted using banana ash.

Effect of the presence of different anions in the water in Batch Test with AA

Groundwater and wastewater contain several different anions which may interfere in the adsorption or precipitation of fluoride during limestone defluoridation. To investigate the interference of co-existing ions, i.e., Br^-, Cl^-, PO_4^{3-}, SO_4^{2-}, and NO_3^- on fluoride removal, respective sodium salts have been added in a range of 100–500 mg/L to the fluoride solution before AELD treatment of the fluoridated water. The effects of the ions have also been evaluated by measuring the remaining fluoride after filtration. The determination of these ions was carried out by using standard methods.

Effect of other anions in Column Test with AA

The drinking water or wastewater contains many different ions which may influence the adsorption or precipitation of fluoride by limestone. Therefore, we have investigated the interference of the co-existing anions by adding sodium salts of the anions, viz. sodium salts of Br^-, Cl^-, PO_4^{3-}, SO_4^{2-}, and NO_3^- to the water along with the acids (Fig. 3.7).

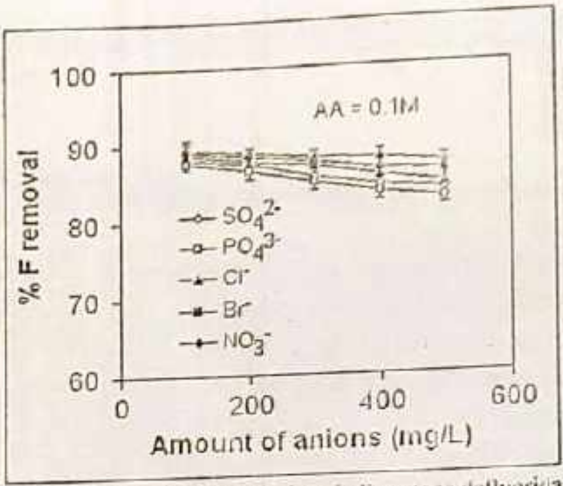

Figure 3.7. Effect of different anions in limestone defluoridation using AA. Initial concentration of fluoride is 10 mg/L.

The anions may be present in the water in different concentrations, so we have selected a range of concentration from 100 to 500 mg/L. The results of the experiment have been shown in Fig. 3.7. The lowering of the fluoride removal by the anions decreases in the order phosphate > sulfate > bromide > chloride > nitrate which agrees with the literature[118,234]. In the presence of the anions also the percent removal of fluoride remains within the range of 90-82 % in case of 0.1 M AA. Thus we can say that although the anions reduce the limestone defluoridation using the acids, the influence is quite small.

Effect of competing anions in Column Test with CA

The effect of the co-existing anions on this fluoride removal process has been investigated by adding sodium salts of the anions, viz. sodium salts of Br^-, Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^- to the water along with the acids before limestone treatment. The results of the experiment have been shown in Fig. 3.13. In the presence of the anions the percent removal of fluoride remains within the range of 90-95 %.

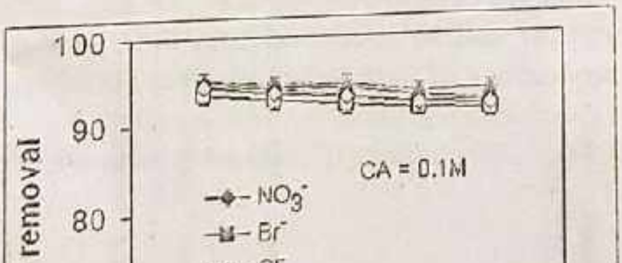

Figure 3.13. Effect of different anions in limestone defluoridation using CA. Initial concentration of fluoride is 10 mg/L.

There is a negligible difference in between the percent F⁻ removal in absence of the anions to the percent removal in presence of the anions. The influence of the anions on the fluoride removal process decreases in the order phosphate > sulfate > bromide > chloride > nitrate which agrees with literature[118,234]. Thus we can say that although the anions reduce the limestone defluoridation using the acids, the influence is quite small.

Effect of co-existing anions with OA

The interference by co-existing anions was investigated by adding sodium salts of the anions, *viz*., Br^-, Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^- to 10 mg/L fluoride solution in distilled water along with 0.1 M OA before the AELD process.

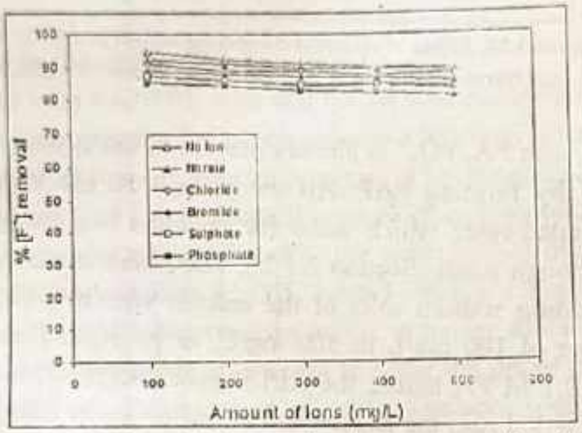

Figure 3.16. Effect of different anions in limestone defluoridation using OA. Initial concentration of fluoride is 10 mg/L.

A concentration range of 100 mg/L to 500 mg/L was chosen for anions. The results of the experiment have been shown in the Fig. 3.16, which indicates only a slight gradual decrease in the removal on increasing the concentration of the anions. However, the removal of fluoride remains within the range of 95-80 % even in the presence of the anions. The negative influence of the anions on the removal of fluoride, which can be attributed to competition of the ions with fluoride for the adsorption sites; was found to be in the order: phosphate > sulfate > bromide > chloride > nitrate which agrees with the literature[118,234]. It may however be noted that the influence of the co-existing ions is only a little.

Effect of co-existing anions in AELD with PA

The effects of some competing anions on the removal of fluoride by the AELD process with PA have been presented in Fig. 3.20. In case of the earlier experiments with AA, CA and OA, only a little influence of other ions was found where the highest interference was shown by PO_4^{3-}.

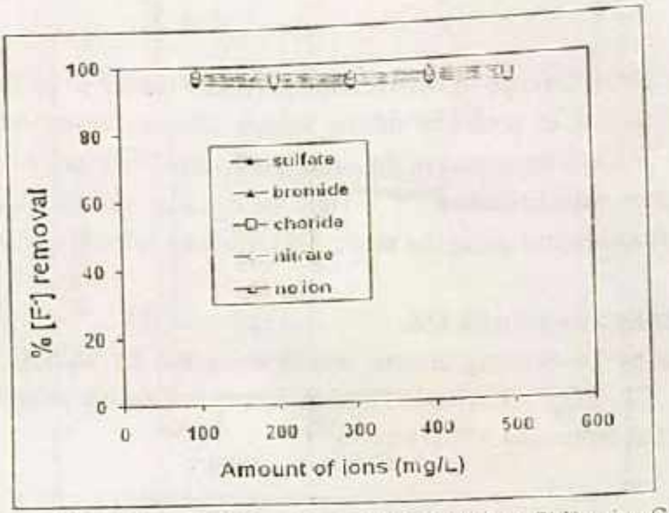

Figure 3.20. Effect of different competing anions in AELD using CA.
Initial concentration of PA and fluoride are 0.1M and 10 mg/L, respectively.

In this experiment with PA, PO_4^{3-} is already present in the system which directly helped in the removal of F^- by forming FAP. All the present AELD experiments with PA were carried out in groundwater which naturally contains the competing ions in different concentrations although small (Section 2.1.3.). The interference by co-existing anions was investigated by adding sodium salts of the anions, *viz.*, Br^-, Cl^-, SO_4^{2-} and NO_3^- in the concentration range of 100 mg/L to 500 mg/L, to 10 mg/L fluoride solution in distilled water along with 0.1 M PA before the AELD process. The result of this experiment has been plotted for n = 1. From the experiment on influence of competing ions it is clear that there is only a small interference by these competing ions on the fluoride removal by the AELD process with PA. The interference has been found to increase slightly with changing the competing ion in the order: $NO_3^- < Cl^- < Br^- < SO_4^{2-}$ but the fluoride removal still remains above 90%. The interference by the competing ions in the presence of PA has been found to be less than that observed in the presence of other acids. Therefore the AELD method with PA seems to be suitable for application for fluoride removal from groundwater having considerable concentration of these competing ions.

Residual oxalate in the treated water in AELD

The WHO does not prescribe any guideline value for oxalate in drinking water[75]. The present AELD process with OA precipitates calcium oxalate in the limestone column. Calcium oxalate dissolves freely in acid but is insoluble at a neutral or alkaline pH[288]. The pHs of the treated water in the present method have been found to be in the range of 6.5 to 7.7 (Fig 3.14, Fig. 3.15, Table 3.7). The concentration of oxalate in the treated water was determined by titrating against $KMnO_4$ solution by standard procedure and has been found to be 0.2(±0.02) mM[289]. Since high concentration of Ca^{2+} is already present in the treated water, the oxalate present in the treated water has been found to be precipitated by slightly increasing the pH of the solution above 7.0, which can be achieved by addition of about 0.1 g/L $NaHCO_3$[286,288].

It has been reported that calcium oxalate forms during human body metabolism and deposits in kidney[290]. Formation of kidney stone, of which about 80% is calcium oxalate, depends on the oxalate intake by human. The main sources of dietary oxalate are plant seeds and leaves. The oxalate content in some commonly used foods is 10 to 100 times higher in comparison to that present in the treated water. Oxalate from these seeds and leaves is absorbed by colon and small intestine of human body and the percentage of oxalate absorption is only 2-5%. It has also been reported that oxalate absorption by human depends on the individual's metabolism. Thus, from the considerations of the smallness of the quantity of remaining oxalate in the treated water and the percentage of oxalate absorption by human body, it appears that the possibility of the remaining oxalate causing renal stone is too little. Thus, the water should be potable after pH adjustment to about 8 and subsequent filtration.

Residual phosphate in the water after treatment

In the AELD process with PA, 0.01, 0.05 and 0.1 M acid concentration were added to the water before filtration through the limestone column. Certainly, after the treatment process the phosphate level of the water should increase. The phosphate concentration in the treated water was determined using standard method of estimation and the concentrations were found to depend on the amount added to the water before filtration. With 0.01, 0.05 and 0.1 M PA, phosphate was within 4.2-5.5, 5.4-6.3 and 6.8-8.0 mg/L range.

The pH of the treated water remains acidic in nature as can be observed from the Fig. 3.18 and Table 3.10. We made an attempt to bring the pH of the water to the potable range using bicarbonate salt. Precipitation of some substance was observed as the pH of the water was increased to about 7. The precipitate was separated and analysed. The XRD, showed peaks at 29.5°, 36.12°, 39.5°, 43.5° corresponding to calcium carbonate and at 21.55°, 31.95°, 35.6°, 40.1° corresponding to calcium phosphate suggesting the precipitate to be mixture of calcium carbonate and calcium phosphate. After that the phosphate level of the water was measured and it was found in the range of 1.5-2.3 mg/L. Phosphate is a non-toxic ion which does not figure in WHO's list of guideline values for drinking water. Therefore, the AELD method can be recommended even though there is a slightly elevated level of phosphate in the treated water.

Comparative Evaluation of the performance of the four acids w.r.t. residual heavy metals in the treated water

The limestone used in this fluoride removal experiments may contain heavy metals within it and the metals may leach out to the water during the treatment process. Therefore, the treated water has been tested for the presence of the heavy metals and the results are shown in the Table 3.20. Cadmium was not found in the water before as well as after the treatment. The concentrations of lead and copper were below the WHO guideline value before the treatment which further decreased after the treatment. The concentrations of nickel and chromium increased slightly after treatment but remained below the corresponding WHO guideline values. The concentration of cobalt, which does not figure in WHO's list, increased very insignificantly after the treatment. The concentrations of iron and manganese, which are nontoxic as such, have increased very slightly above the WHO guideline values. They are however below the maximum permissible values of 1.0 mg/L and 0.3 mg/L, respectively, in India.

Table 3.20. The concentrations of some heavy metals in the water before and after treatment by the AELD process along with the WHO guideline values.

Metals	Before Filtration (mg/L)	After Filtration (mg/L)				WHO guideline (mg/L)
		AA	CA	OA	PA	
Cadmium	0	0	0	0	0	0.005
Lead	0.002	0	0	0	0	0.05
Copper	0.120	0.054	0.061	0.087	0.076	1.0
Nickel	0.001	0.018	0.056	0.093	0.082	0.1
Chromium	0	0.004	0.001	0.002	0.004	0.05
Cobalt	0	0.001	0.003	0.002	0.001	-
Iron	0.131	0.382	0.402	0.445	0.391	0.30
Manganese	0	0.102	0.105	0.116	0.108	0.1

The excess iron and manganese can also be removed easily by conventional methods. Thus, the AELD process is safe as far as the heavy metals are concerned.

8(a). Milestones with Dates, Work Elements For Each & Responsible Organisation for Each Work Element

S. No.	Milestone	Target Date	Work Elements	Responsible Organisation
1	Study of mechanism of removal	Within 1st year	1. Study of precipitation of CaF_2 2. Study of adsorption of CaF_2 on limestone	DST DST
2	Optimization of processes	Within 1st half of 3rd year	1. W.r.t. quantity of acid 2. W.r.t. size of chip and column 3. Retention time	DST DST DST
3	Checking of quality of treated water	Within 3rd quarter of 3rd year	1. Potability test 2. Other decontaminations	DST DST

8(b) Milestones Achieved:

1. Study of mechanism of removal: The mechanism study was completed with AA and CA within the 1st year and the mechanism of defluoridation in AELD was found to be a combination of precipitation and adsorption. However we continued the study to gether support from more analytical techniques and with OA and PA.

2. Optimization of processes: The optimization work was completed within the set milestone of the 1st quarter of the 3rd year except that with PA which was completed within the 3rd quarter of the 3rd year.

3. Checking of quality of treated water: Completed within the 3rd quarter of the 3rd year as planned.

9. Deviations made from the original objectives: None.

10. Conclusions summarising the achievements and indications of scopes future work

Conclusions.

In the present work, in order to increase fluoride removal, to reduce the treatment time and to increase the capacity of the limestone, four different acids has been added to the F⁻ containing water before limestone treatment. These acids enhance the dissolution of limestone for efficient precipitation of F⁻ and also facilitate adsorption of fluoride. **The method named as Acid Enhanced Limestone Defluoridation (AELD) has been found to be a highly efficient, simple and cost effective defluoridation method having prospect of field application as evident from the findings of the present study narrated below.**

Formation of the calcium salts of the acids in the column was found. Calcium acetate is water a soluble salt whereas calcium citrate was found to be precipitated in the limestone column. The capacity of the limestone was not so much satisfactory which has been attributed to the low acid dissociation in the case of AA the blocking of the reaction sites by the calcium salt in the case of CA. OA is a stronger acid in comparison to acetic and CA and in was thought that it will liberate more amount of Ca^{2+} to precipitate F⁻ as CaF_2 in the crushed limestone column. The calcium salt of OA, viz., calcium oxalate, which is water insoluble, was formed in the limestone column in the presence of OA. The salt produced in the column hinders the reaction between the limestone and F⁻ ion causing a decrease in the fluoride removal, particularly after 12-15 times repeated use of the same limestone column. The calcium salt of PA, viz., calcium phosphate formed in the limestone column in the presence of PA is transformed into HAP which is a better hunter of F⁻. This salt does not block the reaction sites of the limestone, rather it itself reacts with F⁻ to form FAP which is again a strong adsorbent of F⁻. The experiments on defluoridation with PA have shown very interesting results.

The main findings drawn from the AELD experiments using different acids are as follows:

AELD with AA

- Addition of AA in 0.1 M concentration in the initial 10 mg/L fluoride containing distilled water as well as groundwater can enhance the removal capacity of the limestone up to 90 %.

- The fluoride removal which takes about 12 h for equilibration is slower than the neutralization of the acids.
- The final pH of the treated water after the AELD treatment with AA remains within the acceptable range for drinking water. The neutralization of this acid takes place within minutes after putting the acidic water into the limestone column.
- The same limestone column can be used repeatedly up to 10-12 times.
- The removal of fluoride gradually decreases with the number of repeated use of the same limestone column, n due to a gradual saturation of adsorption sites with fluoride.
- The effect of co-existing anions on the AELD with AA is quite small and decreases in the order: phosphate > sulfate > bromide > chloride > nitrate.
- The materials used are common and nontoxic and the method is simple which makes it easily acceptable to common people.

AELD with CA

- Addition of 0.1 M CA to the fluoride water before filtration through the limestone column can remove fluoride up to about 95 % from an initial concentration of 10 mg/L containing distilled water as well as groundwater. Fluoride removal to below 1 mg/L can be achieved by the method.
- CA is also neutralized quickly and the final pH of the treated water remains within the acceptable range for drinking water.
- The effect of co-existing anions on the fluoride removal by the present method is quite small and decreases in the order: phosphate > sulfate > bromide > chloride > nitrate.
- The fluoride removal takes about 6 or 12 h for equilibration.
- The same limestone can be used repeatedly up to 10-12 times.
- CA is non-toxic and used as common food additive which makes it easily acceptable for the users.
- The materials used are common and the method is simple which makes it easily acceptable to common people.

AELD with OA

- Addition of OA to contaminated groundwater before defluoridation by crushed limestone significantly improves the fluoride removal. About 95 % of fluoride can be removed from initial 10 mg/L fluoride concentration up to n = 13.
- This acid also neutralizes within minutes and the pH of the water after treatment remains in the neutral range.
- Up to 12-15 times of repeated use of the same limestone can give fluoride removal to below 1 mg/L from 10 mg/L.
- The method has been found to be effective even at low initial concentration of fluoride and is affected a little by competing ions.
- Precipitation of calcium oxalate salt has been found in the limestone column which blocks the further reaction of the acidic fluoride water with limestone.
- The effect of competing anions is negligible and follows the same order as AA and CA.

- The residual oxalate in the treated water should not be cause of concern.
- Simplicity of the method and the use of common and nontoxic materials make the method easily acceptable to the common people.

AELD with PA

- In this AELD process with PA, fluoride removal has been achieved to below 1 mg/L from an initial 10 mg/L within 1 h of treatment time with all three concentrations of PA, *viz.*, 0.01, 0.05 and 0.1 M.
- The removal capacity has been increased with increase in acid concentration and with treatment time. Most of the F^- was removed from the water within minutes and after that the removal takes place slowly. There is a very little increase in the fluoride removal after the treatment time of 3 h up to 24 h.
- The fluoride removal capacity of limestone is very high and increases with increase in the concentration of PA. The capacity of the 1 kg of limestone to remove fluoride from initial 10 mg/L to below 2 mg/L have been found to be 105 and 110 L using 0.05 M and 0.1 M PA.
- Fluoride removal from lower initial concentration gives better results in comparison to higher initial concentration. With 0.01 M PA and 5 mg/L initial F^- the amount of water can be treated is 126.6 L per kg of limestone.
- The effect of other ions in the AELD process with PA is negligible.
- The neutralization of PA by limestone is very slow. The acid is not neutralized even after 12 h of treatment time. This necessitates a pH correction of the water after the treatment. The pH correction can be done by filtering the treated water through another limestone column.
- The AELD process with PA is safe after complete neutralization of the acid.

The mechanism of fluoride removal in AELD

- It has been confirmed from the mechanism study of the AELD using the four acids that the fluoride removal in the process takes place through precipitation of calcium fluoride as well as through adsorption of fluoride by limestone. In the case of PA, however adsorption of fluoride by HAP also significantly contributes to the total fluoride removal.
- The observed high fluoride removal capacity of the limestone in presence of the acid is due to combined effects of precipitation of CaF_2 by high concentration of Ca^{2+} ion generated in situ in the reactor by dissolution of calcite by the acid and adsorption of fluoride on the limestone particles.
- In the analytical study of the limestone before and after use, formation of calcium salts of the acids has been found in the column. Calcium acetate salt is highly soluble and remains in the water whereas the calcium salts of CA, OA and PA, viz., calcium citrate, calcium oxalate and calcium phosphate are precipitated in the column. The calcium phosphate is converted into HAP in the presence of water.

- The residual oxalate in the treated water should not be cause of concern.
- Simplicity of the method and the use of common and nontoxic materials make the method easily acceptable to the common people.

AELD with PA

- In this AELD process with PA, fluoride removal has been achieved to below 1 mg/L from an initial 10 mg/L within 1 h of treatment time with all three concentrations of PA, *viz.*, 0.01, 0.05 and 0.1 M.
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- The fluoride removal gradually decreases with n in case of AA, CA and OA due to a gradual saturation of adsorption sites with fluoride and blocking of the reaction site by precipitated calcium salts of AA, CA and OA formed in the limestone column.
- In case of PA the corresponding salt, viz., HAP, is a good fluoride scavenger and therefore the removal capacity of the limestone is far better than the cases of the other acids. Limestone and hydroxyapatite, together worked for the F^- removal which occurs via precipitation as CaF_2 and adsorption of F^- on the surface of the limestone and hydroxyapatite.
- The precipitation of calcium fluoride is rapid in this treatment process whereas the adsorption is slow and continues beyond 6 hours.
- The limestone retains its original quality after the treatment process, only the surface part was degraded. It can be reused in further treatment process after washing the surface and may be used in the manufacturing of cement.

The comparative performances of the four acids

- The order of the efficiency of the acids in increasing the capacity of the limestone for defluoridation by AELD process is as follows: PA>>OA>CA>AA.
- While AA, CA and OA can bring the concentration of fluoride from initial 10 mg/L to less than 1 mg/L, PA can bring it down to less than 0.1 mg/L.
- PA is not only better in terms of increasing capacity of the limestone, it also reduces the treatment time. The concentration of PA required is also smaller than that of the other acids.
- The AELD process is safe as far as leaching of heavy metals from limestone to the treated water and the residual acids in the treated water are concerned.
- The AELD technique with AA, CA, OA and PA is a low-cost defluoridation process and the cost decreases on changing the acid in the order: OA<AA<CA<PA.
- From the consideration of the cost of the treatment per litre of the water, the quantity of acid and limestone needed and the time required for the treatment, PA seems to be the most suitable acid for AELD.

Finally, it can be stated that the AELD technique using the four acids in general and PA in particular is an economic and simple defluoridation technique having the potential for household and community level applications in countries like India where limestone is abundant.

Future scope

- Pilot scale study of the AELD technique using the four acids, specially, PA, can be carried out for scaling up and optimization of the different parameters, e.g., concentration of acid, residence time, etc., and adjustment of pH.
- The present study has used a static fixed bed column treatment in stop flow reactor. The performance of a continuous flow reactor can be evaluated.
- The reason behind the slow neutralization of PA by limestone can be investigated.

11. S&T benefits accrued:

(i) List of Research Publications with Details:

1. S.K. Nath, S. Bordoloi and R.K. Dutta, Effect of acid on morphology of calcite during acid enhanced defluoridation, ***J. Fluorine Chem.***, 2011.132, 19-26.
2. S.K. Nath and R.K. Dutta, Enhanced limestone defluoridation of water by acetic and citric acids in fixed bed reactor, ***Clean – Soil Air, Water***, 2010, 38, 614-622.
3. S.K. Nath and R.K. Dutta, Fluoride removal from water using crushed limestone, ***Indian J Chem. Tech.***, 2010, 17, 120-125.
4. S.K. Nath and R.K. Dutta, Enhanced limestone defluoridation in column reactor using oxalic acid, ***Process Safety Env. Protection***, 2011, XX, XXX-XXX.*(in press)* doi:10.1016/j.psep.2011.07.001
5. S.K. Nath, S. Bordoloi, S. Gogoi and R.K. Dutta, Acid enhanced limestone defluoridation of water using phosphoric acid: in situ generation of fluoride scavenger hydroxyapatite, (*Under communication*).
6. S.K. Nath, S. Gogoi and R.K. Dutta, A continuous flow study of acid enhanced limestone defluoridation of water using phosphoric acid. (*Under communication*).

(ii) Manpower trained on the project:

The JRF of the project will soon submit the PhD thesis.

(iii) Patents taken: (Filed)

1) "Enhanced limestone defluoridation of fluoride contaminated water in the presence of citric acid and acetic acid", R.K. Dutta and S. K. Nath, *Application No.: 1215/KOL/2008, dated 17/7/2008 13:20:01.*
2) "Enhanced fixed-bed limestone defluoridation of groundwater using a solid acid to get potable water", R.K. Dutta and S. K. Nath, *Application No.: 988/KOL/2010, dated 05/09/2010 11:33:45.*
3) "A highly efficient defluoridation method by in-situ generation of an efficient precipitant and strong adsorbents of fluoride in crushed limestone fixed-bed column and plug flow reactors", R.K. Dutta and S. K. Nath, *Application No.: 168/KOL/2011 dated 9/02/2011 12:58:39.*

(iv) Conferences attended:

1) International Seminar on **Frontier in Polymer Science and Technology** (POLY-2007) November 1-3, 2007, Guwahati, India. *Enhanced Iron-Loading on Phosphorylated Jute Fiber for Removal of Arsenic from Water.* Suresh K Nath, Suman Benerji, Ravi B. Srivastava and Robin K. Dutta.

2) The 2009 **Inorganic Contaminants Workshop** of **American Water Works Association**, February 28-March 2, 2010. Denver, CO, USA. *Enhanced limestone defluoridation by edible acids*, Robin K Dutta, Suresh K Nath.
3) International Conference on **Environmental Challenges: A Global Concern**, **ICEC 2010**, October 15-16, 2010, KMV Jalandhar, Punjab, India. *Limestone Defluoridation of Water in Presence of Edible Acids in Fixed Bed Reactor*, Suresh K Nath, Robin K Dutta.
4) Assam Science Society, **The 54th Annual Technical Session**, Feb 4, 2009, Tezpur University, India. *Enhanced Limestone Defluoridation by increased Ca^{2+} activity using acids*, Suresh K Nath, Shreemoyee Bordoloi and Robin K. Dutta.
5) National Seminar on **Emerging Trends in Polymer sciences and Technology, POLY 2009**. October 8-10, 2009. Dept. of Chemistry, Saurashtra University, Gujrat, India. *Synthesis of polyaniline/graphite composite and application in defluoridation of water*, Suresh K Nath, Surajit Konwer, Swapan K Dolui, Robin K Dutta.
6) National Seminar on **Crisis of Fresh Water, A Challenge to Humanity and Life Processes, What is the Solution?** August 17-18, 2010. Dept. of Chemistry, D.R. College, Golaghat, Assam, India. *Edible Acid enhanced Limestone Defluoridation of Water in Fixed Bed Reactor*, Suresh K Nath, Robin K Dutta.
7) DST Workshop on **Water Purification Possibility and Prospects**, Dept. of Chemistry, J.N.V. University, Jodhpur, India. *Acid enhanced limestone defluoridation by edible acid*, Robin K Dutta, Shreemoyee Bordoloi, Suresh K Nath.

(v) **Replication potential:**

We have developed a method, viz., Acid Enhanced Limestone Defluoridation (AELD) using limestone and a non-toxic acid. The AELD method using phosphoric acid has been found to be highly efficient and low cost. The method has the potential for practical application.

(vi) **Linkage developed:** None.

Name and signature with Date:

Dr. Robin Kumar Dutta
(Principal Investigator)

02/12/2011

(Dr. Tarun Kumar Maji)
(Co-Investigator)

Tarun Maji
02/12/2011