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Defluoridation of Waters using Combination of Aluminium Chloride and Aluminium Sulphate

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In Nalgonda Technique using aluminium sulphate for defluoridation, the sulphates are increased considerably in the treated water. The allowable concentration of sulphate without affecting the potability of water is 400 mg/l (maximum). Indian groundwaters are often characterized by high basicity and fluorides requiring aluminium sulphate doses greater than 1 000 mg/l resulting in sulphates in excess of 400 mg/l in treated water. To overcome this difficulty aluminium chloride is recommended to supplement or supplant aluminium sulphate in treating difficult waters. Aluminium chloride is found to be as efficient as aluminium sulphate in removing fluorides. The quantity of the two chemicals required to be applied, alone or in combination, to achieve different fluoride levels in the treated water have been studied and the results are reported in this paper.

INTRODUCTION

Techniques for the defluoridation of water and their limitation were studied by Bulusu, *et al*[1]. The materials studied include clays, ion exchange resins, activated carbons, sulphonated coals, magnesium compounds, serpentine minerals, iron, sodium aluminate and aluminium sulphate. The Nalgonda Technique of defluoridation was developed and its cost was compared with the cost of pumping water and with other techniques[1]. The technique which involves the addition of sodium aluminate or lime and aluminium sulphate in sequence followed by flocculation, sedimentation, filtration and disinfection has been demonstrated in several villages and a 2 270 m^3/day demonstration plant was installed at Kadiri in the Anantapur District of Andhra Pradesh to treat 4.1 to 4.8 mg F/l water to obtain 0.4 to 1.5 mg F/l in treated water corresponding to an alum dose requirement of 494 mg/l.

In India, fluoride waters are often characterized by very high alkalinity with fluorides exceeding 10 mg F/l. Earlier work[1–3] revealed that to achieve permissive limit (1 mg F/l) and excessive limit (2 mg F/l), large alum doses are required which increased the sulphate concentration in the treated water beyond maximum allowable limits[4]. It has, therefore, become necessary to find ways to treat such waters with high alkalinity and fluorides so that the treated water conforms to standards for sulphates and other parameters.

During continued R & D efforts on defluoridation, it was observed that aluminium chloride removed fluorides as efficiently as aluminium sulphate. Therefore, further work on fluoride removal using aluminium sulphate, aluminium chloride and combination of the two was undertaken through jar tests with samples containing 4 to 24 meq/l basicity and 2 to 21 mg F/l. This paper discusses the results.

MATERIALS AND METHODS

Ferric Chloride

Ferric chloride hastened settlement of floc in the jar test and the optimum dose ranged from 1% to 2% of the aluminium salts applied in the jar test. Experiments with ferric chloride confirmed its inability to remove fluorides even at 1 000 mg/l dose and hence it did not contribute to the fluorides removal in the study. For the sake of uniformity, the ferric chloride dose was maintained at 2% of aluminium salts dose all through.

Test Water

Tap water with pH 7.2-8.4 ; alkalinity 0.8-4.5 meq/l ; calcium 1.5-2.2 meq/l ; sulphates 5-15 mg SO_4/l ; and chlorides 8-24 mg Cl/l was used in the laboratory studies. The test water was prepared by adjusting the composition of the tap water with distilled water, sodium bicarbonate and sodium flouride, to achieve 4 to 24 meq/l basicity and 2 to 21 mg F/l for studies.

Jar Tests

Jar tests were performed on a multiple stirring device fitted with 77×25×2 mm strip on each of the six vertical shafts. Five hundred aliquots of test sample was taken in each 600 ml beaker. Mixing started at 80-100 rpm and continued for one minute after the addition of reagents. Mixing then continued at 35-45 rpm so that the total stirring time was maintained at ten minutes at both stirring speeds. After the mixing, the test beakers were removed and allowed to settle quiescently for one hour,

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except for the disturbance while taking pH reading after five minutes. The supernatant after one hour sedimentation in the beaker was clear (with turbidity below 2 NTU) except where otherwise recorded.

Analytical

Fluoride was tested on the settled filtered sample using selective ion electrode and high ionic strength adjustment buffer to swamp variations in the ionic stength and containing a chelate to complex aluminium preferentially. The addition of the buffer will complex concentrations upto 5 mg Al/l and release the fluoride as free ion.

Alkalinity (basicity) was measured titrimetrically using methyl orange indicator and chloride using argentometric method. Sulphate was determined turbidimetrically using spectrophotometer and 420 nm wavelength with suitable dilutions. pH was measured by digital pH meter.

Experiments

Experiments were carried out with aluminium sulphate, aluminium chloride and combination of these two in equal proportion by weight, on test waters having fluoride range 2-21 mg F/l, alkalinity range 4-21 meq/l to achieve fluoride levels of 0.5, 1.0, 1.5 and 2 mg F/l in the treated water.

In all the samples ferric chloride was added corresponding to 2% of the chemical used. The settleability was poor in samples where the alkalinity was insufficient and the dose applied was high. The sample remained turbid and did not settle properly even after two hours sedimentation. Additional alkalinity was required to be added in such cases to supplement the initial alkalinity. The transition of excellent settling to poor settling was sharp. Such samples are identified in the Tables with asterisk (*) to stress that it is not possible to achieve the desired level of fluoride in the treated water and hence such doses are not to be applied to water without alkalinity correction.

TABLE 1 ALUMINIUM SULPHATE REQUIRED TO ACHIEVE DIFFERENT FLOURIDE LEVELS IN TREATED WATER FROM RAW WATERS WITH VARIOUS INITIAL FLUORIDES AND BASICITY LEVELS

Flouride Level In Treated Water, mg f/l	Test Water Fluoride, mg f/l	Aluminium sulphate dose (mg/l) Required Corresponding to Basicity (meq/l) of					
		4	8	12	16	20	24
0.5	2.0	310	500	670	750	1030	—
	3.0	385	585	735	920	1130	—
	4.0	430*	670	820	1020	1200	—
	5.0	520*	690	920	1085	1250	—
	6.0	640*	740	950	1150	1280	—
	7.0	—	770*	1100	1230	1300	—
	8.0	680*	800*	—	1260	1350	1400
	9.0	—	830*	1200*	1300	1370	—
	11.0	—	—	—	—	1470	—
	12.0	800*	910*	1250*	1380*	1520	1580
	16.0	1010*	1030*	—	1500*	1640	—
	17.0	—	—	1300*	—	1670*	—
	21.0	1180*	1260*	1390*	1600*	1920*	—
1.0	2.0	150	290	320	360	640	—
	3.0	250	410	480	570	810	—
	4.0	350	510	580	770	890	—
	5.0	390	570	710	—	1000	—
	6.0	570*	—	—	870	1060	—
	7.0	—	640	950	1150	1190	—
	8.0	630*	680	—	—	1220	1300
	9.0	—	740	1080	1260	1280	—
	11.0	—	800*	—	—	1350	—
	12.0	740*	850*	1160	1350	1390	1500
	16.0	970*	—	—	1480*	—	—
	17.0	—	—	1230*	—	1570	—
	21.0	1240*	—	1310*	1540*	1850*	—
1.5	2.0	45	80	120	150	180	—
	3.0	135	190	250	320	450	—
	4.0	190	370	—	460	—	—
	5.0	280	420	500	530	760	—
	6.0	400*	—	—	630	—	—
	7.0	—	450	800	950	1080	—
	8.0	580*	500	—	—	—	1200
	9.0	—	670	970	1020	1160	—
	11.0	—	700		—	1250	—
	12.0	690*	790	1080	1250	1300	1420
	16.0	930*	910*	—	1400	—	—
	17.0	—	—	1170	—	1500	—
	21.0	1200*	990*	1250*	1480*	1780*	—
2.0	2.0	0	0	0	0	0	—
	3.0	180	220	280	370	390	—
	4.0	240	280	350	440	580	—
	5.0	310	350	420	530	680	—
	6.0	370	430	500	600	780	—
	7.0	420*	450	560	770	970	—
	8.0	530*	500	640	—	—	1100
	9.0	—	600	760	980	1080	—
	11.0	—	640	—	—	1190	—
	12.0	640*	740	1000	1160	1220	1350
	16.0	890*	850	—	1300	—	—
	17.0	—	900	1120	—	1440	—
	21.0	1150*	960*	1190	1400	1730	—

RESULTS

To arrive at the optimum dose requirements under varying test conditions, a total of 318 jar tests were performed and 1908 samples examined that formed 144 tables detailing pH (5 min and 24 hours after settling), alkalinity, chloride, sulphate, fluoride and conductivity. Tables 1-3 which form a part of this data show the doses of aluminium sulphate, aluminium chloride and a combination of the two in equal proportions to be added for waters containing 4 to 24 meq/l alkalinity and 2 to 21 mg F/l to achieve 0.5, 1.0, 1.5 or 2.0 mg F/l in the treated water. The residual alkalinity and the pH of the samples treated was satisfactory, except where marked with asterisk (*). The extensive information on pH, fluoride, alkalinity, chloride, sulphate and conductivity of individual samples is deliberately left out of this communication due to the brevity of the space.

Sulphate and Chloride—Limitations

According to Cox[4], the maximum allowable concentrations of sulphate ($SO_4^{=}$) and chloride (Cl^-) affecting potability of drinking water are 400 mg/l and 600 mg/l, respectively. These correspond to 1 000 mg/l aluminium sulphate and 750 mg/l aluminium chloride (anhydrous), respectively according to the experimental data.

The implication is that it is not desirable to exceed 1 000 mg/l aluminium sulphate and 700 mg/l aluminium chloride while defluoridating water. When a combination of these chemicals has to be used due to unfavourable raw water alkalinity and fluorides, it is preferable not to exceed a dose combination of 700 mg/l aluminium sulphate and 700 mg/l aluminium chloride,

TABLE 2 ALUMINIUM CHLORIDE REQUIRED TO ACHIEVE DIFFERENT FLOURIDE LEVELS IN THE TREATED WATER FOR RAW WATERS WITH VARIOUS INITIAL FLUORIDE AND BASICITY LEVELS

Flouride Level in Treated Water, mg f/l	Test Water Fluorides, mg f/l	Aluminium chloride (mg/l) Required Corresponding to Basicity of (meq/l)					
		4	8	12	16	20	24
0.5	2.0	145	210	250	310	360	420
	3.0	172	240	320	365	480	590
	4.0	195	260	350	420	500	610
	5.0	218*	277	430	440	530	640
	6.0	240*	290	440	455	550	-00
	7.0	—	—	460	490	560	—
	8.0	290*	320	—	—	—	870
	9.0	—	330	470	520	580	—
	11.0	—	—	—	—	610	—
	12.0	350*	360*	490	550	620	930
	16.0	380*	390*	—	590	—	—
	17.0	—	—	500	—	660	960
	21.0	400*	430*	540	660	830	1110
1.0	2.0	85	110	145	185	240	335
	3.0	122	160	220	265	340	475
	4.0	155	200	250	355	375	510
	5.0	170	210	335	380	420	570
	6.0	185	250	—	—	—	640
	7.0	215*	—	390	445	500	—
	8.0	270*	270	—	—	—	800
	9.0	—	300	420	470	540	—
	11.0	—	—	—	—	570	—
	12.0	325*	335	455	515	585	870
	16.0	360*	370*	—	560	—	—
	17.0	—	—	480	—	640	940
	21.0	380*	410*	515	636	800	1070
1.5	2.0	35	40	60	75	125	190
	3.0	75	85	120	160	220	360
	4.0	125	145	160	290	305	400
	5.0	140	175	260	320	400	505
	6.0	165	215	—	—	—	570
	7.0	—	—	325	395	450	—
	8.0	250*	—	—	—	—	730
	9.0	—	270	375	425	500	—
	11.0	—	—	—	—	530	—
	12.0	300*	315	425	480	550	810
	16.0	340*	350	—	535	—	—
	17.0	—	—	455	—	620	900
	21.0	365*	395*	485	610	765	1030
2.0	2.0	0	0	0	0	0	0
	3.0	70	95	120	175	—	240
	4.0	90	100	155	230	270	350
	5.0	125	140	185	270	330	440
	6.0	145	180	235	300	—	510
	7.0	170	200	270	350	400	—
	8.0	230*	—	—	—	—	660
	9.0	—	240	330	380	460	—
	11.0	—	—	—	—	490	—
	12.0	280*	290	390	440	520	750
	16.0	320*	330	—	500	—	—
	17.0	—	—	430	—	590	870
	21.0	350*	380*	460	580	730	980

TABLE 3 ALUMINIUM CHLORIDE AND ALUMINIUM SULPHATE REQUIRED TO ACHIEVE DIFFERENT FLUORIDE LEVELS IN TREATED WATER FOR RAW WATERS WITH VARIOUS INITIAL FLUORIDES AND BASICITY LEVELS

Fluoride Level in Treated Water, mg F/l	Test Water Fluorides, mg F/l	Al_2SO_4 $16H_2O$ and $AlCl_3$ Dose (each) in mg/l Required Corresponding to Basicity of (meq/l)					
		4	8	12	16	20	24
0.5	2.0	90	160	190	250	330	380
	3.0	105	180	210	290	375	415
	4.0	125	200	230	330	385	430
	5.0	—	—	240	—	400	450
	6.0	130	215	260	350	—	510
	7.0	—	230	280	370	425	530
	8.0	140	240	290	—	—	550
	9.0	150	250	315	380	440	570
	11.0	165*	270*	320	—	460	—
	12.0	170*	280*	330	400	480	600
	16.0	190*	300*	—	450*	—	—
	17.0	195*	315*	355*	—	570	660
	21.0	215*	325*	390*	510*	650*	780*
1.0	2.0	59	105	115	130	180	210
	3.0	75	130	150	190	295	330
	4.0	100	155	175	260	300	340
	5.0	105	170	200	—	350	390
	6.0	115	180	210	270	—	455
	7.0	—	195	245	335	380	—
	8.0	130	—	—	—	—	—
	9.0	140	230	285	345	405	495
	11.0	—	—	—	—	425	—
	12.0	160*	265*	305	380	445	560
	16.0	175*	285*	—	415	—	—
	17.0	—	—	335	—	545	635
	21.0	200*	315*	365*	480	620*	735*
1.5	2.0	21	29	37	43	63	125
	3.0	45	64	77	100	220	245
	4.0	77	115	130	175	—	270
	5.0	—	—	165	—	295	330
	6.0	105	155	—	—	—	400
	7.0	—	—	210	285	335	—
	8.0	125	—	—	—	—	—
	9.0	—	205	260	310	370	—
	11.0	135*	—	—	—	390	—
	12.0	145*	250	280	350	410	525
	16.0	165*	265*	—	395	—	—
	17.0	—	—	315	—	515	605
	21.0	190*	305*	340	450	590	690
2.0	2.0	0	0	0	0	0	0
	3.0	38	57	85	115	140	160
	4.0	56	75	120	140	190	245
	5.0	73	100	130	175	245	270
	6.0	90	125	160	200	—	330
	7.0	—	—	175	235	290	—
	8.0	110	150	—	—	—	360
	9.0	—	185	230	280	330	—
	11.0	—	—	—	—	355	—
	12.0	130	235	255	330	380	490
	16.0	150*	250	—	370	—	—
	17.0	—	—	285	—	490	580
	21.0	175*	290*	315	420	560	650

to prevent adverse effects on the potability of treated water. The results in Table 3 show that at this limit of 700 mg/l for combination treatment, it is possible to achieve 0.5 mg F/l in treated water for the waters studied, whereas, there are limitations to achieve 0.5 mg F/l with aluminium sulphate or aluminium chloride alone as can be seen from Table 1 and 2.

Experimental investigations reveal that it is possible to defluoridate all naturally occuring fluoride waters in India through suitably choosing aluminium sulphate or aluminium chloride or combination treatment to achieve 0.5, 1.0, 1.5 or 2.0 mg F/l in the treated water and without adversely affecting potability of water.

OBSERVATIONS

Chemical precipitation of fluoride by use of multivalent metal ions was investigated by many researchers since 1933. In addition to the studies on alum coagulation by Boruff[5,6] this approach has also been investigated by Kempf, *et al*[7], and Scott, *et al*[8]. Culp and Stotlenberg[9] showed that fluoride ion content in a water supply can be reduced from 3.6 mg/l to 0.25 mg/l by using 225 mg/l alum at pH 6.5 to 7.5. In 1973, Rabosky and Miller[10] indicated that fluoride removal by chemical method of lime precipitation was most difficult when fluoride concentration was below 20 mg/l, *ie*, removal by lime is ineffective in dilute solutions of fluoride. Cox[4] concluded that there is no economical means of removing fluorides by the usual treatment procedures, except when softening of waters containing megnesium is practized. When magnesium is not present in waters, dolomitic lime should be used in the softening process to furnish the magnesium needed to precipitate the fluoride. Bulusu, *et al*[1], studied the use of magnesia in detail and were convinced that large doses are necessary. Moreover the pH of the treated water was beyond 10 and its correction by acidification of carbonation is unavoidable.

Results among the various researchers on alum coagulation[5–10] varied considerably, probably because of variation in analytical procedures of fluoride, raw water, mixing and settling. Because the alum doses required for fluoride removal are much higher than those commonly used for turbidity and colour removal, the fluoride removal using aluminium sulphate has not been considered a very practical solution by these researchers and was not followed-up.

However, Nawlakhe, *et al*[2,3] and Bulusu, *et al*[1] concluded that aluminium sulphate treatment, called 'Nalgonda Technique', could effectively remove fluoride; the efficiency of the technique was elaboratorly confirmed in the laboratory[2] and later demonstrated in several fluoride affected villages[3]. The satisfactory performance of the 2 270 m^3/day plant at Kadiri in treating 4.1-4.8 mg F/l water at Rs 1.15 per m^3 established the method. Bulusu, *et al* proved that Nalgonda Technique for the removal of fluorides was the cheapest and easily adaptable treatment both for individual and community level.

However, problem of aluminium sulphate contributing to the sulphate in the treated water and its effect on the potability remained. Further R & D showed that aluminium chloride removed fluorides as efficiently as aluminium sulphate leading to detailed investigations with aluminium chloride as supplement and supplant to aluminium sulphate. The application of aluminium chloride is useful for maintaining sulphate and chloride within levels that would not adversely affect the potability of the treated water. The combination treatment is of potential value where the raw water has such fluoride and basicity requiring aluminium sulphate doses in excess of 1 000 mg/l. In the combination treatment, 700 mg/l each of the two chemicals provides treated water with a fluoride 0.5, 1.0, 1.5 or 2.0 mg F/l.

CONCLUSIONS

The usefulness of aluminium chloride as a defluoridating chemical applied to the water either alone or in combination with aluminium sulphate is established. The data presented in the Tables deals with the doses of aluminium chloride, aluminium sulphate or combination necessary to achieve 0.5, 1.0, 1.5 and 2.0 mg F/l in the treated water. The waters studied contained 2 to 21 mg F/l and 200 to 1 200 mg/l alkalinity expressed as $CaCO_3$. The values are useful as a ready reckoner for practical application to waters where fluorides and alkalinity are known and high. Depending upon the nature of the flouride waters, the treatment can be chosen and the doses selected to achieve the desirable flouride level in the treated water.

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DISCUSSION

Prof R C Singh

(i) How do you compare removal of flourides by aluminium chloride and aluminium sulphate with that of the rice husk method developed by NEERI ? Is the former superior to lime and aluminium sulphate ?

(ii) Once flourosis occurs, can it be reversed ? If so, how ?

(iii) The 0.5 Mgd plant appears to be a pilot plant ? Was deflouridation tried on a larger scale ?

(iv) Excess aluminium can damage the kidneys. Permissible levels of aluminium are 0.2-0.5 mg/l. Was aluminium level measured ?

Author

(i) Deflouridation using aluminium chloride and/or aluminium sulphate is much more efficient and cheaper than with paddy husk carbon.

(ii) To the author's knowledge fluorosis is not reversible particularly mottled enamel and skeletal flourosis.

(iii) The 2 270 m^3/d (0.5 Mgd) plant is a full scale deflouridation plant and the largest based on this principle.

(iv) The doses of aluminium salts are dependent on the basicity of the water. With treated water having 2-3 meq/l basicity the occurrence of soluble aluminium is not possible.