

The effect of particle size and interfering ions on fluoride removal by activated alumina

JJ Schoeman* and H MacLeod

National Institute for Water Research, Council for Scientific and Industrial Research, P O Box 395, Pretoria 0001, South Africa.

Abstract

The effect of particle size and interfering ions on fluoride removal by activated alumina was investigated to gain a better understanding of the process. The rate of fluoride adsorption on smaller particles was significantly greater than on larger sized particles. The optimum pH for fluoride removal was found to be about 6. However, it could be advantageous to remove fluoride at pH 4 to 5 where less competition from silicate was experienced. Silicate (as Si) and phosphate from 5 to 80 mg/l were found to have very little effect on fluoride removal efficiency. Sulphates in the concentration range from 100 to 1 600 mg/l were found also to have very little effect on fluoride removal efficiency. It appeared that the single most important factor affecting fluoride removal efficiency was the hydroxide and bicarbonate alkalinity of the water.

Introduction

Fluoride in excess of 1,5 to 2,0 mg/l is known to cause permanent mottling of tooth enamel and the long-term intake of 3 to 10 mg/l may result in abnormal bone growth both in humans and animals (Holden, 1970; Bishop and Sancoucy, 1978; Sorg, 1978). On the other hand, a fluoride level of about 1 mg/l has been shown to significantly reduce dental cavities in children (Holden, 1970; Bishop and Sancoucy, 1978) and this concentration level is widely recommended for the growth and maintenance of strong and healthy teeth.

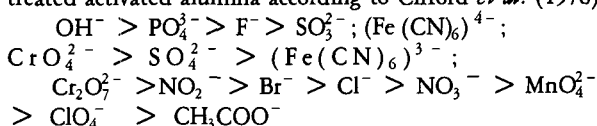
The removal of high concentrations of fluoride (2 to 8 mg/l) from underground waters by the activated alumina defluoridation process is practised only at a few places in the USA (Rubel and Woosley, 1978). Two full-scale activated alumina defluoridation plants (500 m³/d each) were recently installed in South Africa (Schoeman, 1985; Schoeman and Leach, 1986) to reduce the fluoride content of an underground mine water source from about 8 mg/l to less than the recommended limit of 1,5 mg/l, set by the South African Bureau of Standards for potable water. A reduction in the performance of the activated alumina for fluoride removal was experienced during pilot tests when design criteria were being developed for the full-scale plants (Schoeman and Botha, 1985). This reduction in performance took place when the pH of the feedwater was allowed to increase from about 5 to 8, when no feedwater pH control was applied. A reduction in the performance of the full-scale plants for fluoride removal was experienced as a result of metal hydroxide and silicate fouling of the activated alumina (Schoeman and Leach, 1986). Silicates are adsorbed by activated alumina and appeared to be more difficult to desorb by caustic soda than fluoride. Therefore, to eliminate or reduce fouling of activated alumina by silicates, it is necessary to know the condition (pH) under which silicates are adsorbed by activated alumina.

Activated alumina particle size (Bishop and Sancoucy, 1978), initial fluoride concentration (Mazounie and Mouchet, 1984) and the presence of alkalinity (Savinelli and Black, 1958), phosphate and sulphate (Clifford *et al.*, 1978) in a feedwater can affect the activated alumina process for fluoride removal to various degrees. Activated alumina has a relatively high selectivity for phosphate and sulphate (Clifford *et al.*, 1978). No mention is made of bicarbonate ions by Clifford *et al.* All these ions, when

present in a feedwater, can interfere with fluoride removal. However, the conditions under which interference takes place, are not completely documented. Therefore, the objectives of this study were to determine the effect of pH on silicate and fluoride removal, to study the effects of particle size, initial fluoride concentration and the effect of the concentration of interfering ions on fluoride removal, in an attempt to optimise and gain a better understanding of the activated alumina process for fluoride removal.

Mechanism of fluoride removal

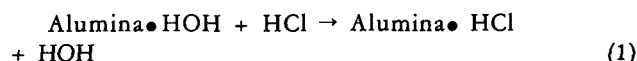
The common anions are preferred in the following order by acid-treated activated alumina according to Clifford *et al.* (1978).



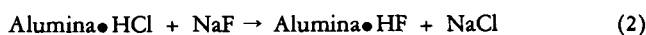
In a treatment process, the more preferred ions can be used to displace lesser preferred ions. Thus activated alumina is seen to be an inorganic ion exchanger with an anion selectivity sequence different from that of a typical weak-base synthetic organic ion-exchange resin. Fluoride which is the least preferred ion by organic resins, is one of the most-preferred ions by activated alumina. This unusually high fluoride preference is why activated alumina is the adsorbent of choice (Macair, 1953) for single-contaminant fluoride removal in water where many lesser preferred ions are present to compete for adsorption (ion-exchange) sites. With respect to regeneration, alumina is similar to weak-acid or weak-base resins in that both acids and bases must be used for the adsorption-regeneration cycle.

A simplified adsorption-regeneration cycle for the removal of fluoride, phosphate or silicate can be visualised as follows (Clifford *et al.*, 1978).

When neutral (water-washed) alumina is treated with acid, e.g. HCl, acidic alumina is formed in accordance with Reaction (1).

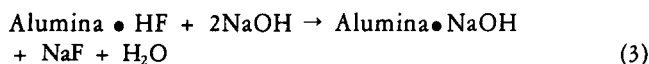


If this acidic form is contacted with fluoride, phosphate, silicate or sulphate ions, they displace the chloride ions, providing hydroxide ions are absent (i.e., slightly acidic feed solution) as in Reaction (2).

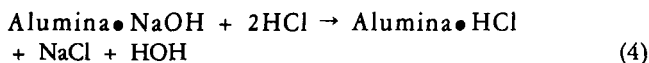


*To whom all correspondence should be addressed.
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To regenerate the fluoride-containing adsorbent, a dilute solution of the most preferred ion, hydroxide, is used. The regeneration occurs in accordance with Reaction (3).



Since alumina is both a cation and an anion exchanger, sodium ions are exchanged for hydrogen when Na^+ is in excess in the regenerating solution and H^+ is absent (high pH). To restore the fluoride removal capacity, the basic alumina is contacted with an excess of dilute HCl (Reaction 4).



The acidic alumina, alumina•HCl, is now ready for another fluoride (phosphate, silicate or organic anion) adsorption cycle.

The above mechanism for fluoride removal on activated alumina is based on the experimentally supported hypothesis of Umland (1956) that the adsorption of dissociated salts on activated alumina can formally be interpreted as a 'simultaneously' occurring exchange reaction of H^+ against metal cations and OH^- against acid radicals. For economic reasons, sulphuric acid rather than hydrochloric acid is used for acidification in large-scale processes.

Nature of silicates in water supplies

All the silicon (Si) present in the lithosphere is combined with oxygen as silicates (metasilicates - SiO_3^{2-} , or orthosilicates - SiO_4^{4-} , or as an inert form of sand, e.g. quartz - SiO_2). Silica (SiO_2) dissolves in water as either H_4SiO_4 or H_2SiO_3 . These substances are very weak acids and are present in water as non-ionised or slightly ionised species (Kunin, 1980). Whether the silica, which dissolves in water, is present as slightly ionised or non-ionised orthosilicic- or metasilicic acid, is unclear.

The major factors which affect the solubility of silica in water are temperature, pH, nature of the solid phase and pressure (Kunin, 1980). The solubility of silica in water increases above pH 7 and below pH 3. The solubility between pH 3 and pH 7 is approximately 180 mg/l as SiO_2 . Silica becomes more ionised at higher pH values ($\text{pH} > 7$), and therefore strong base anion exchangers are usually used for silica removal.

Experimental

Materials

Chemically pure grades of the following reagents were used: NaF, $\text{Na}_2\text{SiO}_3 \bullet 5\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \bullet 10\text{H}_2\text{O}$; NaH_2PO_4 ; NaHCO_3 ; H_2SO_4 and NaOH. 'Compalox' activated alumina, manufactured by Martinswerk, West Germany, which is being used in the full-scale defluoridation plants, was used for the studies. 'Compalox' activated alumina is produced from aluminium hydroxide derived from the Bayer process.

Composition of Pretoria tap water

Pretoria tap water spiked with approximately 40 mg/l of fluoride with the following composition (Table 1) was used in the batch adsorption experiments.

TABLE 1
COMPOSITION OF PRETORIA TAP WATER SPIKED WITH APPROXIMATELY 40 mg/l OF FLUORIDE

Constituent	Concentration (mg/l)
Na^+	45
K^+	6
Ca^{2+}	54
Mg^{2+}	9
Si^{4+}	5,3
SO_4^{2-}	117
P (total phosphate)	0,3
P (orthophosphate)	0,2
Cl^-	54
Alkalinity (CaCO_3)	68
F^-	40

Varying amounts of sodium meta-silicate (expressed as Si), sodium hydroxide, sodium bicarbonate, sodium sulphate and sodium dihydrogen phosphate were added to the tap water to make solutions of varying composition for the batch adsorption experiments. The pH of the water samples was adjusted with caustic soda and sulphuric acid as appropriate.

Preparation of activated alumina before use

The unused activated alumina (Al_2O_3) as supplied was regenerated before use as follows: a convenient amount of activated alumina (approximately 50 g) was backwashed at 50% bed expansion with tap water to remove fines. The material was then regenerated with 10 bed volumes (BV) 1% sodium hydroxide solution at a flow rate of approximately 4 BV/h. Excess caustic soda was removed by backwashing with tap water for 30 min. The activated alumina was then neutralised with 15 BV 0,025 M sulphuric acid and excess acid removed by a water rinse. The regenerated activated alumina was dried overnight at 105 °C and stored in a desiccator before use in the adsorption experiments.

Batch experiments

Activated alumina at a dosage of 12,5 g/l was used in all the batch adsorption experiments. The pH of the water samples (400 ml each) to which different dosages of fluoride, silicate, sulphate, phosphate, etc., were added, was adjusted with either 0,25 or 0,5M sulphuric acid or caustic soda to pre-determined values. Five gram of activated alumina was then added to the water samples (400 ml each) in plastic bottles and the batch adsorption experiments were conducted at 22-25 °C by shaking on a wrist-action shaker. The pH of the samples was corrected every 30 to 60 min depending on the pH changes observed. Samples (15 ml each) were taken at regular intervals during the batch adsorption experiments for fluoride, silicate, alkalinity, phosphate and sulphate analyses. Fluoride was determined with the fluoride specific ion electrode and all the other ions were determined according to standard methods (Standard Methods, 1975).

Fluoride adsorbed and removal efficiency

The fluoride, sulphate, silicate and phosphate adsorbed in a given period of contact time and the removal efficiency were calculated as follows:

Amount of fluoride adsorbed or removed $qt = C_0 - C_t$ and percentage removal efficiency = $100 (C_0 - C_t) / C_0$

where:

- t = contact time in hours;
- qt = the amount of adsorbate adsorbed within the given period of contact time in mg/l;
- C₀ = the initial concentration of the adsorbate in solution in mg/l at t = 0;
- C_t = the final concentration of the adsorbate in solution in mg/l after the contact time of t hours.

Results and discussion

Effect of alumina particle size on the rate of fluoride adsorption

The effect of two different activated alumina particle sizes on the rate of fluoride adsorption is shown in Figure 1.

The rate of fluoride adsorption by the smaller sized particles (0,5 to 1,0 mm) is significantly greater than that of the larger sized (1,0 to 3,0 mm) particles. The BET surface area of the smaller sized particles was 300 m²/g and that of the larger sized particles 306 m²/g. This shows that no additional intra-particle surface area has been made available by breaking up the particles into a smaller sized fraction. Therefore, the higher fluoride adsorption rate of the smaller sized particles cannot be ascribed to a larger intra-particle surface area.

The smaller particles are approximately half the size of the larger particles. Therefore, the external surface area of the smaller sized particles would be approximately 2,5 times that of the larger particles. This external surface area, however, is negligible in comparison with the total surface area. However, this extra external surface area of the smaller sized particles is responsible for the faster rate of adsorption by giving the fluoride ions better access to the internal adsorption sites.

Bishop and Sancoucy (1978) and Mazounie and Mouchet (1984) have shown that the fluoride removal capacity of activated alumina increases when the particle size decreases. Bishop and Sancoucy used particle sizes of approximately 0,6 to 1,2 mm; 0,6 to 0,85 mm and 0,3 to 0,6 mm. They demonstrated that the difference in capacity was a result of the increased surface area per unit volume of the smaller sized particles. However, we found that the surface area per unit volume for particle sizes of 0,5 to 1,0 mm and 1,0 to 3,0 mm was virtually the same.

The adsorption isotherms (Figure 1) started to level off after about 5 h of adsorption. The fluoride and other ions adsorbed were determined after 10 h of adsorption in all further adsorption experiments. These values are not true equilibrium values but are considered to be close enough to equilibrium for this study.

Effect of initial fluoride concentration on fluoride adsorbed

The effect of the initial fluoride concentration on the amount of fluoride adsorbed after 10 h is shown in Figure 2.

The fluoride adsorbed increases almost linearly over the initial concentration range of 20 to 80 mg/l of fluoride. The fluoride adsorbed after 10 h of adsorption at initial fluoride concentrations of 20, 40 and 80 mg/l, was 19,0; 38,5 and 73,5 mg/l respectively. This proves that activated alumina can reduce high fluoride concentrations (20 to 40 mg/l) to about 1,5 mg/l and less after a 10 h contact period. The residual fluoride concentration after 10 h adsorption at the initial fluoride concentration of 80 mg/l was 6,5 mg/l. However, adsorption equilibrium had not

been attained after 10 h of adsorption at this high fluoride concentration so that more fluoride could have been adsorbed.

Bishop and Sancoucy (1978) and Mazounie and Mouchet (1984) showed that fluoride removal capacity of activated alumina increased linearly over the initial fluoride concentration ranges of 4 to 12,0 mg/l and 2,5 to 15,0 mg/l. Therefore, it appears that fluoride adsorption on activated alumina increases almost linearly over the concentration range of 2,5 to 80 mg/l.

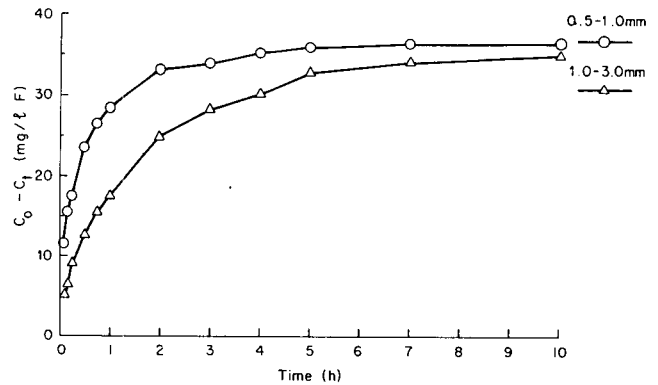


Figure 1
Effect of alumina particle size (0,5-1,0 mm and 1,0-3,0 mm) on the rate of fluoride adsorption at pH 5.
C₀ = 37,5 mg/l F.

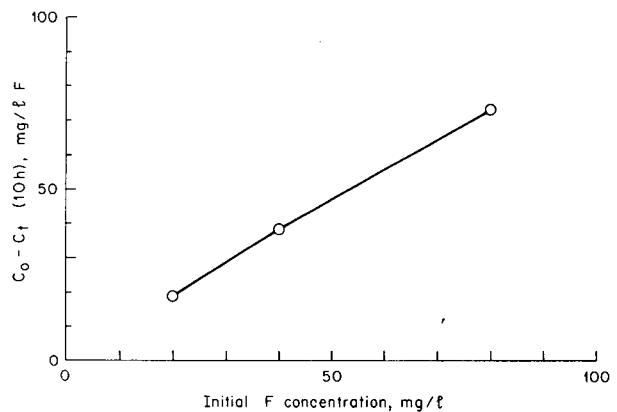


Figure 2
Effect of initial fluoride concentration on the amount of fluoride adsorbed at pH 5 after 10 hours adsorption.
C₀ = 20; 40; 80 mg/l F.

Effect of hydroxide alkalinity on fluoride removal

The effect of hydroxide alkalinity expressed as phenolphthalein alkalinity (P-alkalinity) on the fluoride removal efficiency is shown in Figure 3.

Hydroxide dosages of 10, 20, 40, 80, 160 and 320 mg/l were added to the tap water containing about 40 mg/l of fluoride. A

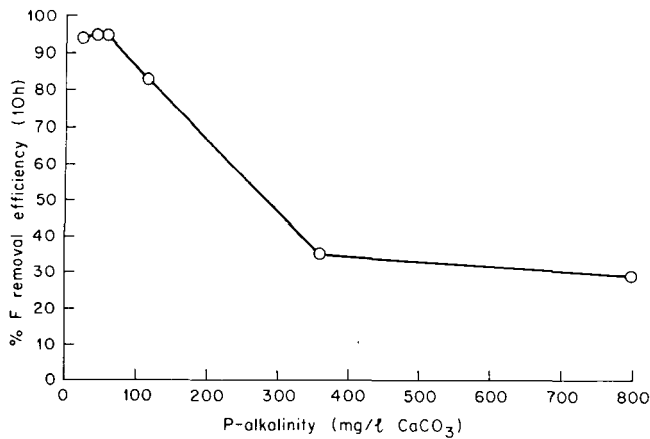


Figure 3
Effect of P-alkalinity on fluoride removal efficiency.
 $C_0(F) = 39,5 \text{ mg/l}$

whitish precipitate formed after the addition of the hydroxide ions showing that some water hardness was removed from the water. The water samples were filtered and the P-alkalinity determined before and after 10 h of adsorption.

P-alkalinity in excess of about 60 mg/l (as CaCO₃) has a dramatic effect on fluoride removal efficiency. The fluoride removal efficiency was reduced from about 95% at a P-alkalinity of 60 mg/l (as CaCO₃) to 35% at a P-alkalinity of 360 mg/l (as CaCO₃). A further increase in P-alkalinity did not appear to have a further significant reduction in fluoride removal efficiency.

The initial and final pH values of the samples to which the different dosages of hydroxide ions were added, are shown in Table 2.

The pH of the water is significantly reduced after 10 h of adsorption as a result of hydroxide ion adsorption. Savinelli and Black (1958) showed that as the alkalinity of the water increases, the capacity to remove fluoride decreases. Thus, it is apparent that the hydroxide alkalinity in the water is competing with the fluoride ions in the exchange process.

P-alkalinity	Initial pH	pH after 10 h
26	9,47	7,77
46	9,82	7,56
60	10,62	7,53
148	11,22	7,75
360	11,63	8,83
800	11,89	10,71

Effect of bicarbonate alkalinity on fluoride removal

The effect of bicarbonate alkalinity expressed as total alkalinity (T-alkalinity) on fluoride removal efficiency is shown in Figure 4.

Bicarbonate dosages of 40, 80, 160, 320 and 640 mg/l were added to tap water containing about 40 mg/l of fluoride and the T-alkalinity measured. In the one case the pH was adjusted to 7 before adsorption was started and in the other case the pH was adjusted to 5 before adsorption and kept at 5 during adsorption.

The results indicate that the fluoride removal efficiency is significantly affected by an increasing amount of T-alkalinity at

pH 7. The fluoride removal efficiency was reduced from 95% at an initial T-alkalinity of 74 mg/l (as CaCO₃) to 79% at an initial T-alkalinity of 556 mg/l (as CaCO₃). It appears that the fluoride removal efficiency starts to decrease more rapidly at initial T-alkalinity levels of 170 mg/l (as CaCO₃) and higher.

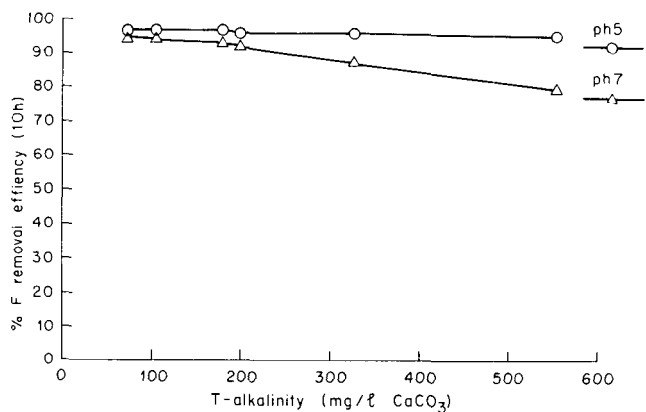


Figure 4
Effect of T-alkalinity on fluoride removal efficiency at pH 7 and 5.
 $C_0(F) = 39,5 \text{ mg/l}$

With pH control at pH 5, on the other hand, where a great part of the initially added bicarbonates were destroyed, little inhibition of fluoride removal took place. The fluoride removal efficiency was only reduced from 97 to 95%. It therefore appears that bicarbonates can enter into competition with fluoride for adsorption sites on the activated alumina.

Effect of pH on fluoride and silicate adsorbed

The effect of pH on fluoride and silicate (as Si) exchange is shown in Figure 5.

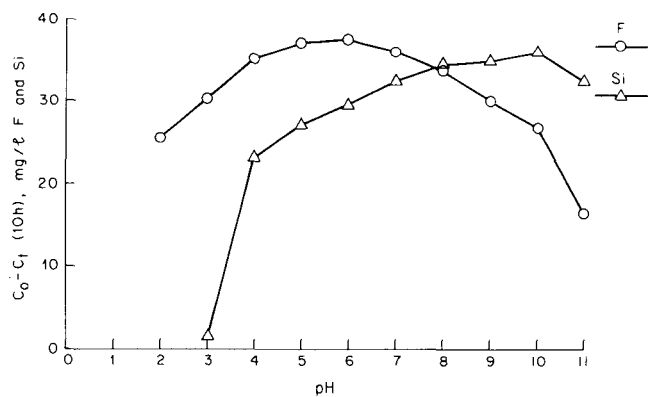


Figure 5
Effect of pH on fluoride and silicon adsorbed.
 $C_0(F) = 38,5 \text{ mg/l}$; $C_0(Si) = 37,5 \text{ mg/l}$.

There exists an optimum pH for both fluoride and silicate removal by activated alumina. The optimum pH for fluoride removal was shown to be about 6. This result is more or less in agreement with data obtained by Choi and Chen, (1979); Wu, (1978); and Mazounie and Mouchet, (1984). Fluoride removal starts to decrease above pH 6 as a result of more competition from silicate and bicarbonate ions. At pH above 10, fluoride removal

decreases sharply as a result of stronger competition from hydroxide ions. Fluoride removal also starts to decrease sharply below pH 4 as a result of the formation of weakly ionised hydrofluoric acid. The sharp decrease in fluoride removal below pH 4 may also be the result of the formation of positively charged alumina complexes (AlF^{2+} and AlF_2^+) (Choi and Chen, 1979) which are repelled from the positively charged alumina ($\text{alumina} \bullet \text{H}^+$).

The optimum pH for silicate removal appears to be about 10. Clifford *et al.* (1978) reported an optimum pH for monomeric silica ($\text{Si}(\text{OH})_4$) removal between pH 8 and 8,5. Our results show that there is a steady increase in silicate removal from pH 4 onwards until the optimum amount is removed at pH 10. Above pH 10 there is a reduction in silicate removal as a result of stronger competition with hydroxide ions. Very little silicate is removed at pH 3 and less. The reason why more silicate is removed with increasing pH is most probably due to silicate becoming more ionised with increasing pH.

From the adsorption data (Figure 5) it would appear that it might be more advantageous to remove fluoride at about pH 4 to try to reduce silicate adsorption as far as possible because silicate can affect fluoride removal more at higher pH ($\text{pH} > 4$). Silicates, however, should be effectively removed from activated alumina by acid and caustic soda treatment (Behrman and Gustafson, 1940; Schoeman, 1985).

The adsorption isotherms showed that the fluoride to silicate (as Si) removal ratio was 7,5 after 1 h of adsorption; 2,13 after 5 h and 1,5 after 10 h of adsorption (Figure 1). This shows that silicate removal starts to increase with increasing contact time which suggests that it could be advantageous to use shorter retention times in columns to inhibit silicate removal.

Effect of silicate on fluoride removal efficiency at different pH values

The effect of increasing silicate dosage (expressed as Si) on fluoride removal efficiency at different pH values is shown in Figure 6.

The percentage fluoride and silicate removal at initial fluoride-silicate (as Si) concentrations of 40 mg/l each, at different pH values after 10 h of adsorption, is shown in Table 3.

It appears that an increasing silicate (as Si) dosage from 5 to 80 mg/l has little effect on fluoride removal efficiency at pH values of 4 to 7. At pH 5 the fluoride removal efficiency was reduced from 98 to 96% and at pH 4 from 95 to 94%. However, fluoride removal efficiency was more significantly reduced at pH

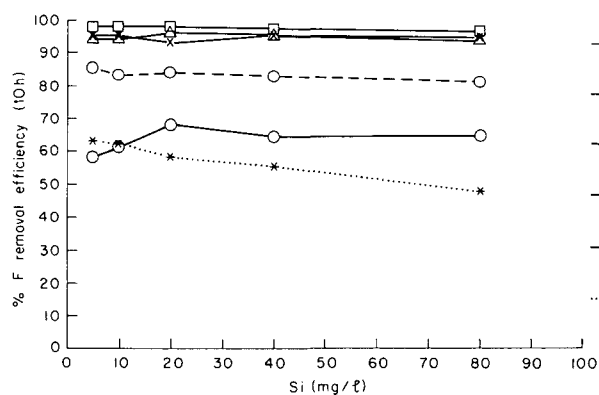


Figure 6
Effect of silicon dosage on fluoride removal efficiency at different pH values.
 $C_0(\text{F}) = 40 \text{ mg/l}$.

TABLE 3
PERCENTAGE FLUORIDE AND SILICATE REMOVAL AT INITIAL FLUORIDE-SILICATE (AS Si) CONCENTRATION OF 40 mg/l EACH AT DIFFERENT pH VALUES AFTER 10 H OF ADSORPTION

pH	% F removal	% Si removal
3	64	12
4	95	65
5	97	78
7	95	79
9	82,6	92
10	55	97
11	26	93

values from 9 to 11 where more silicate is removed (Table 3). At pH 10, the fluoride removal efficiency was decreased from 63 to 47%. The fluoride removal efficiency also decreased from pH 9 to 11 as a result of hydroxide ion adsorption.

The data in Table 3 show that there is an optimum pH for fluoride removal at a pH of about 5. The residual fluoride concentration at this pH after 10 h of adsorption was 1,2 mg/l. Significantly less silicate is removed at pH 4 and 3.

Effect of phosphate on fluoride removal efficiency at different pH values

The effect of increasing phosphate dosage on fluoride removal efficiency at different pH values is shown in Figure 7.

An increasing phosphate dosage from 5 to 80 mg/l appears to have little effect on fluoride removal efficiency at pH values of 4 to 7. At pH 5 the fluoride removal efficiency remained constant at 97%, while it was slightly reduced from 95 to 93% at pH 7. At pH 9, the fluoride removal efficiency was more significantly reduced from 93 to 87%.

Phosphate removals of nearly 100% were achieved at pH 5. This indicates that activated alumina can also successfully be used for phosphate removal. This is in agreement with phosphate removal studies on activated alumina by Narkis and Meiri (1981).

Effect of sulphate on fluoride removal efficiency

The effect of sulphate dosage on fluoride removal efficiency at different pH values is shown in Figure 8.

Increasing the sulphate dosage from 100 to 1 600 mg/l has very little effect on fluoride removal in the pH range from 5 to 7. At pH 5, the fluoride removal efficiency was only reduced from 98 to 97%. A more significant reduction in fluoride removal efficiency was experienced at pH 9 and 10. At pH 10, the fluoride removal efficiency was reduced from 83 to 72%.

No sulphates were removed at pH 5. In fact, the sulphate content of the solution increased after fluoride adsorption showing that sulphates were displaced by fluoride ions from the activated alumina. This indicates that fluoride removal by activated alumina is an ion-exchange process.

Conclusions

The rate of fluoride adsorption on smaller sized particles (0,5 to 1,0 mm) is significantly greater than on larger sized particles (1 to 3 mm). The faster rate of fluoride adsorption on the smaller particles can be ascribed to the larger surface area of the smaller particles. Significantly longer service runs should result from the use of the smaller sized particles in column runs.

The amount of fluoride adsorbed by activated alumina increases almost linearly over the initial concentration range of 2,5 to 80 mg/l. Activated alumina can reduce high fluoride concentrations (20 to 40 mg/l) to less than 1,5 mg/l.

Fluoride removal efficiency by activated alumina is severely inhibited when the P-alkalinity (hydroxide alkalinity) exceeds 60 mg/l (as CaCO₃). Thus, it is apparent that the hydroxide alkalinity is competing with the fluoride ions in the exchange process.

Fluoride removal efficiency by activated alumina is also significantly affected by an increasing amount of T-alkalinity (bicarbonate alkalinity) at pH 7. The bicarbonates appear to compete with fluoride for adsorption sites on the activated alumina. However, acid treatment to pH 5 where most of the bicarbonates were destroyed, showed very little inhibition of fluoride removal at this pH.

Although the optimum pH for fluoride removal is about 6, it could be advantageous to remove fluoride at pH 4 to 5 where less competition from silicate is experienced. This would lessen the chance of fouling of the activated alumina by silicates which are best removed at pH 10 and increase capacity of activated alumina for fluoride removal.

The fluoride to silicate (as Si) removal ratio decreases with increasing adsorption time. This means that silicate removal in-

creases with increasing contact time. This suggests that it could be advantageous to use shorter retention times in columns to inhibit silicate removal.

It appears that an increasing silicate (as Si) dosage from 5 to 80 mg/l has little effect on fluoride removal efficiency at pH 4 to 7. However, this effect is more significant at pH 9 to 11 where more silicate is removed and where hydroxide ion adsorption is also stronger.

Phosphates in the concentration range of 5 to 80 mg/l appear to have very little effect on fluoride removal efficiency at pH 4 to 7. Phosphates can be effectively removed by activated alumina.

Sulphates in the concentration range of 100 to 1 600 mg/l appear to have very little effect on fluoride removal efficiency at pH 5 to 7.

It appears that the single most important factor affecting the fluoride removal efficiency of activated alumina is the alkalinity of the water.

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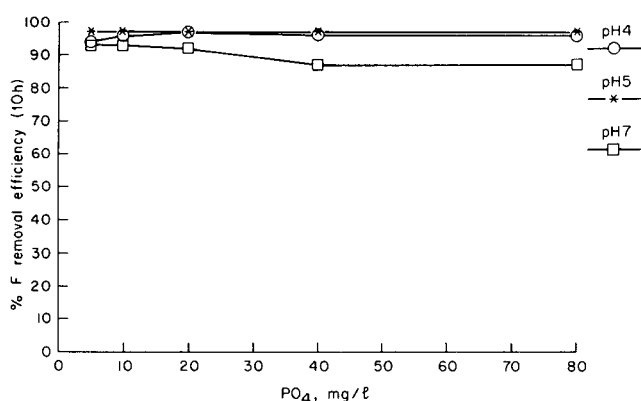


Figure 7
Effect of phosphate dosage on fluoride removal at different pH values.
Co (F) = 40 mg/l.

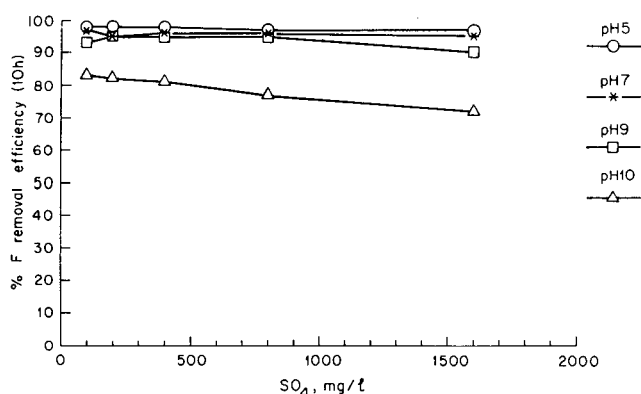


Figure 8
Effect of sulphate dosage on fluoride removal efficiency at different pH values.
Co (F) = 40 mg/l