**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# The Adsorbing Colloid Flotation of Fluoride Ion by Aluminum Hydroxide in Aqueous Media

Ann N. Clarke[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

**To cite this Article** Clarke, Ann N. and Wilson, David J.(1975) 'The Adsorbing Colloid Flotation of Fluoride Ion by Aluminum Hydroxide in Aqueous Media', Separation Science and Technology, 10: 4, 417 — 424

**To link to this Article: DOI:** 10.1080/00372367508058030

**URL:** http://dx.doi.org/10.1080/00372367508058030

SEPARATION SCIENCE, 10(4), pp. 417–424, 1975

# The Adsorbing Colloid Flotation of Fluoride Ion by Aluminum Hydroxide in Aqueous Media

ANN N. CLARKE and DAVID J. WILSON

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

## Abstract

Up to 15.7 ppm fluoride can be removed from solution, pH 7.3 to 7.8, by adsorption onto colloidal aluminum hydroxide at a concentration of 40 ppm Al. This adsorbing colloid–adsorbed ion combination is then removed by foaming with 40 ppm sodium lauryl sulfate. After 30 min the concentration of fluoride is 0.0 ppm. The concentration of aluminum is also 0 ppm. Efficiency of removal slowly decreases with increasing ionic strength. Chloride ion interference is minimal.

## INTRODUCTION

The removal of trace metals and other contaminants from aqueous systems is readily achieved using foam separation methods. The extensive literature in this field is reviewed by Lemlich (*1*, *2*), Somasundaran (*3*), and others. However, there is relatively little in the literature concerning the removal of inorganic anions. Grieves et al. (*4*) discussed the removal of $I^-$ from water by foam separation using the cationic surfactant ethylhexadecycldimethylammonium bromide (EHDA) as the collector-frother. Primiani et al. (*5*) used EHDA to remove phosphate from aqueous media by continuous foam fractionation. Chaine and Zeitlin (*6*) used adsorption colloid flotation to separate arsenate and phosphate from seawater. The collector was $Fe(OH)_3$ and the anionic surfactant was sodium dodecyl sulfate (NLS).

Fluoride ion, $F^-$, is toxic to humans. Concentrations as low as 1 ppm $F^-$ have been seen to cause mottling of teeth and dental defects (*7*). Soluble fluorides are readily and completely absorbed from the gastrointestinal tract. The main site of fluoride storage is in the bones (*8*) where the $F^-$ ions substitute for the $OH^-$ ions in the hydroxyapatite of bones and teeth. This substitution can lead to sclerosis of the bones, calcification of ligaments, and general wasting (*9*). The fluoride ion has been implicated with varying degrees of substantiation in allergies, kidney and heart disease, and mongoloidism (*10*, *11*). It has recently been demonstrated (*12*) that fluoroaluminum complexes as well as free $F^-$ are utilized significantly by the body. Aluminum is used in treating drinking water.

The concentration of $F^-$ in the worlds' lakes and rivers is usually less than 1 ppm. Seawater has a concentration of 1.3 ppm (*13*). The mining of cryolite ($3NaF \cdot AlF_3$) and its use as a solvent in the production of aluminum and the use of fluorapatite ($CaF_2 \cdot 3Ca_3(PO_4)_2$) as a fertilizer can increase localized concentrations to a dangerous level. Table 1 lists acceptable fluoride concentrations under various conditions.

For the aluminum industry the cost of reducing the discharge of pollutants from primary smelting plants is directly proportional to the cost of removing fluoride (*14*). The best available technology (BAT), a dry scrubber system, requires high capital outlays in plant conversions and the highest cost per ton of aluminum in new plants. Wet scrubbers, while less expensive, are less efficient. They are, however, considered by EPA the "best practicable control technology available" (BPT).

More recently developed techniques for the removal of fluorides from waste waters appear to leave too high a concentration in the water (*15*) to meet requirements or involve electrical energy consumption, heating, reduced pressure, or chemicals (e.g., HF) which would require special handling (*16*, *17*).

The ability of the mineral fluorite, $CaF_2$, to adsorb oleic acid has been known for a long time. In a recent paper by Sorensen (*18*), various minerals with and without fluoride present and their adsorption of various anionic collectors were investigated. The results indicate that adsorption of anionic collectors onto simple salt minerals is only in part determined by the cations of the lattice. Obvious similarities between various fluoride minerals necessitate a theory assigning a specific role to the fluorine.

We here report on a study which was undertaken to effect the removal of fluoride from aqueous systems at industrial waste concentrations down to legal values by adsorbing colloid flotation. Three colloids at various pH's were investigated: $Fe(OH)_3$, $CaCO_3$, and $Al(OH)_3$. Since the nature of

TABLE 1

Permissible Fluoride Concentrations

| System | Description | Agency | $F^-$ (ppm) | Ref. |
|---|---|---|---|---|
| Drinking water | Daily air temp | | | |
| | 50–54 °F | PHS[a] | 1.2 | *21* |
| | 64–71 °F | PHS[a] | 0.9 | *21* |
| | 79–90 °F | PHS[a] | 0.7 | *21* |
| Industrial process water | | Petroleum industry | 1.2 | *4* |
| Effluent-primary aluminum smelting | BPT, daily max | EPA | 2000[b] | *14* |
| | BPT, daily max (monthly av) | EPA | 1000[b] | *14* |
| | Existing plant | | | |
| | BAT, daily max | EPA | 100[b] | *14* |
| | BAT, daily max (monthly av) | EPA | 50[b] | *14* |
| | New plant | | | |
| | BAT, daily max | EPA | 50[b] | *14* |
| | BAT, daily max (monthly av) | EPA | 25[b] | *14* |

[a] Public Health Service.

[b] This figure reflects fluoride concentrations as, for example, lb $F^-$ per 1000 lb finished product. For conversion to aqueous concentration the plant's flow and total weight of product must be used.

the adsorbing colloid-adsorbed ion combination was not known, each was foamed with both NLS, an anionic surfactant, and hexadecyltrimethylammonium bromide (HTA), a catonic surfactant.

## EXPERIMENTAL

The experiments were carried out using a glass column 90 cm in length with an inside diameter of 3.5 cm. There was a side arm near the bottom to accommodate a microcombination pH electrode. The rubber stopper plug in the bottom of the column held the gas inlet tubing to the fritted glass sparger and a septum and a stopcock for small and large sample capabilities, respectively. A lipped side-arm near the top of the column served as a foam outlet.

House air was employed. Its flow was controlled by a pressure regulator followed by a microvalve with vernier control. The air was then passed through concentrated sulfuric acid and indicating silica gel to remove oils, moisture, etc; ascarite to remove acid; deionized water for controlled rehumidification; and glass wool to remove any remaining particulates. Flow rates were taken with a soap film flow meter connected into the system directly after the column. The flow rate averaged 35 ml/min.

Stock solutions of $Al^{3+}$, $Fe^{3+}$, and $Ca^{2+}$ were prepared and kept at an acid pH with $HNO_3$ in polyethylene containers. Stock solutions of $CO_3{}^{2-}$ and of 100 ppm $F^-$ were also prepared and stored in polyethylene containers. The appropriate amount of the cation of the collector (and anion in the case of $CaCO_3$) was added to a 250 ml flask. The appropriate amount of $F^-$ was also added. The solution was brought to volume. The pH was then adjusted to the desired level with 1 *N* NaOH. The solution was then poured in from the top of the column. The sides were rinsed with a minimum of deionized water, less than 3 ml. The appropriate surfactant was injected with a syringe through the septum in the rubber stopper plug. Samples were removed by syringe through the same septum at timed intervals.

To keep volume changes minimal, highly concentrated surfactant solutions were prepared. To facilitate the preparation of HTA at high concentrations, the cationic surfactant was first dissolved in 1 or 2 ml of ethanol (for a final volume of 1 liter). The NLS dissolved readily in water; it was first washed with ether in a Soxhlet apparatus for 8 hr at a rate of a cycle per 6 min to remove possible lauryl alcohol contamination.

The column was scrubbed *in situ* with a long handled brush after each run. It was then rinsed thoroughly with deionized water and drained.

The analyses for fluoride were performed by the SPADNS method (*19*). The quantitative analysis of the residual aluminum concentration was performed by an adaptation of the Aluminon test (*20*). To the sample, 1 ml of 3 *M* ammonium acetate was added, followed by 1 ml of 1% aluminon reagent. The solution was mixed thoroughly and heated on an electric hot plate. The solution was then cooled to room temperature and 1 ml of 3 *M* ammonium carbonate was added. The volume was adjusted to 25 ml. The solution was read on a spectrophotometer at a wavelength of 715 mμ. The absorbance curve was essentially linear between 0 and 1 ppm Al. New standards must be prepared for each set of analyses. The accuracy achievable with this procedure was ±10% or better.

## RESULTS

Neither $Fe(OH)_3$ or $CaCO_3$ proved successful in removing $F^-$ from water when foamed with either HTA or NLS. Each system was run at various pH's ranging from approximately 3 to 10. The NLS was quite efficient, however, at removing the $Fe(OH)_3$ colloid, as evidenced by the color change of the solution.

The $Al^{3+}$ [or $Al(OH)_3$] formed a complex (*7*, *22*) with the $F^-$, making the anion unavailable for analysis by the SPADNS method. Foaming with HTA would not remove the complex at either acidic or basic pH's. NLS, however, did effect removal, performing best in the approximately neutral pH range of 7.3 to 7.8.

At pH's below 7 a hydro-alumino-fluoride complex is formed as evidenced by the low free $F^-$ analysis before any surfactant is added. In acid pH's, however, there is no aluminum removal after 30 min as evidenced by the aluminum test described earlier. At pH's above 8 the complex appears to decompose, returning free $F^-$ to the solution. An actual example of this follows: A solution of 10 ppm $F^-$ and 40 ppm $Al^{3+}$ was prepared. At a pH of 2.0 the free $F^-$ was found to be 1.5 ppm. The pH was then adjusted to 8.1 in the column. After 60 sec of foaming, the free $F^-$ concentration was 1.9 ppm. After 20 min at a pH of 8.6, the $F^-$ concentration in the solution had increased to 8.2 ppm.

The removal of the colloidal complex is effected over approximately a 0.5 pH unit for two reasons: (a) The $CO_2$-free air is mixing with the $CO_2$-containing water. Subsequently the $CO_2$–$H_2CO_3$ equilibrium is established, reducing the aqueous $CO_2$ concentration and increasing the pH. This effect was observed by not adding the surfactant and noting the pH increase as the air was bubbled through the Al-F solution in the column. (b) The second, and probably dominant effect, is the ion flotation of $H^+$ by $LS^-$ (*1*). A larger pH range, 7.1 to 7.9, can be successfully employed as long as the majority of the foaming occurs within the 7.3 to 7.8 range.

Parameters of the experimental runs other than pH were: 10 ppm $F^-$, 40 ppm $Al^{3+}$, 40 ppm NLS in a total volume of 250 ml, and ambient room temperature, 24 to 25°C. These conditions and the above pH range will be implied by the subsequent use of the term "optimum system." Both the fluoride and aluminum concentrations of this system were reduced to zero within a 30 min period, as indicated by their respective quantitative tests. A typical removal curve is shown in Fig. 1.

Maintaining the optimum aluminum and NLS concentrations and the pH, the fluoride concentration was increased to 19.7 ppm. The fluoride remaining in solution after 30 min was 4.0 ppm for a removal of 15.7 ppm. The aluminum concentration was zero. Under analogous conditions with a concentration of 27.6 ppm $F^-$, the remaining $F^-$ after 30 min was 11.8 ppm, for a removal of 15.8. This corresponds to an Al/F removal ratio

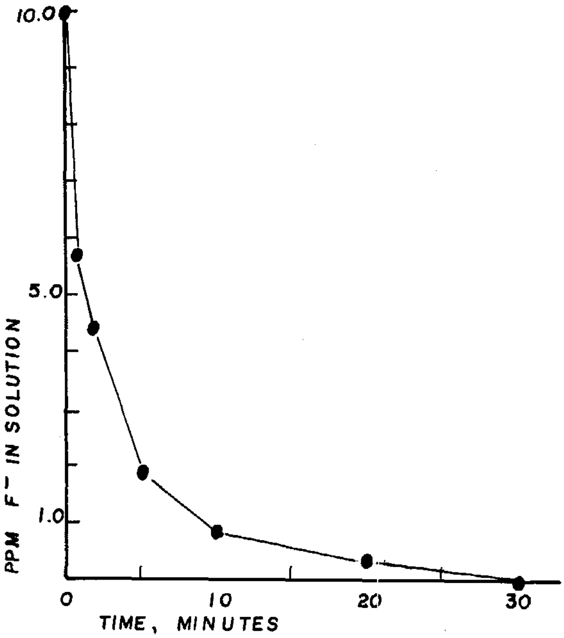

FIG. 1. Typical fluoride removal curve. Optimum system (see text).

(ppm Al added/ppm F removed) of 2.54. Increased NLS concentration (72 ppm) did not improve the $F^-$ removal. A system containing 120 ppm $Al^{3+}$, 26 ppm $F^-$, and 43 ppm NLS yielded complete (<0.1 ppm) $F^-$ removal within 30 min. The residual aluminum in solution was 53 ppm, for a removal ratio of 2.57.

$NaNO_3$ was used to vary the ionic strength of an optimum system. An optimum system with no added $NaNO_3$ has an ionic strength of 0.01. The results are seen in Fig. 2. The system's removal efficiency decreases very slowly with increasing ionic strength compared to other studies (*23*). At concentrations of $NaNO_3$ above 2.5 *M*, the foams were very poor and there was essentially no aluminum removal.

Because of its ubiquitous nature and similarity to $F^-$, chloride ion was studied as a possible interference to the system. An optimum system with 0.5 *M* NaCl added decreased the fluoride removal by at most 8.3% over the 0.5 *M* $NaNO_3$ system. An optimum system containing 1.0 *M* NaCl decreased the fluoride removal by 8.2% over the 1 *M* $NaNO_3$ system. An

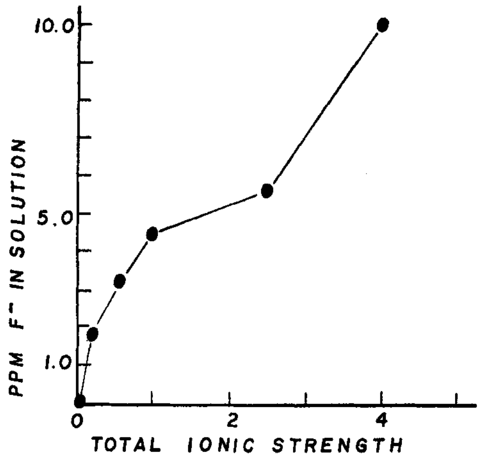

FIG. 2. Residual fluoride as a function of ionic strength. Optimum system (see text). $NaNO_3$ was the added inert salt.

optimum system including 8.9 ppm $Cl^-$ showed zero ppm $F^-$ in solution at 30 min.

When the Al-F-NLS solution was stored for more than a week in laboratory quality glassware, leaching of Al occurred. Borosilicate glass (Pyrex, Kimax, etc.) is 2% by weight $Al_2O_3$ (*24*) or 10,6000 ppm Al. Concentrations as high as 25 ppm Al were analyzed after an 8-day delay when solutions initially containing 0 ppm Al were stored at a pH of about 8. Analyses within 1 day of sampling posed no problem.

## CONCLUSION

The use of aluminum hydroxide as a collector colloid to float fluoride ion with NLS from water appears to present a simple and efficient method of removing this toxic contaminant. The chemicals used are common and inexpensive. The optimum pH range is essentially neutral. This, coupled with the system's relative insensitivity to ionic strength and chloride contamination, suggests that its use to remove fluoride from industrial waste waters is most feasible.

### Acknowledgment

We wish to acknowledge helpful discussions with Dr. Charles Lukehart.

## REFERENCES

1. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. R. Lemlich, in *Recent Development in Separation Science*, Vol. 1 (N. N. Li, ed.), CRC Press, Cleveland, Ohio, 1972.
3. P. Somasundaran, *Separ. Purif. Methods*, *1*, 1 (1972).
4. R. B. Grieves and D. Bhattacharyya, *Separ. Sci.*, *7*(2), 115–129 (1972).
5. S. Primiani, T. V. Nguyen, and C. R. Phillips, *Ibid.*, *9*(3), 211–226 (1974).
6. F. E. Chaine and H. Zeitlin, *Ibid.*, *9*(1), 1–12 (1974).
7. M. V. Stack and D. W. Fearnhead (eds.), *Tooth Enamel*, Wright, Bristol, England, 1965.
8. C. P. Stewart and A. Stolman (eds.), *Toxicology-Mechanisms and Analytical Methods*, Vol. 1, Academic, New York, 1960.
9. N. I. Sax (ed.), *Dangerous Properties of Industrial Materials*, 3rd ed., Reinhold, New York, 1968.
10. M. Prival, *Environment*, *16*(1), 12–18 (January/February 1974).
11. *Fluorides*, National Research Council, National Academy of Sciences, Washington, D.C., 1971.
12. J. A. Ruzicka and L. Mrklas, *Amer. Water Works Assoc.*, *66*, 53–55 (January 1974).
13. R. W. Fairbridge (ed.), *The Encyclopedia of Geochemical and Environmental Sciences*, Vol. IVA, Van Nostrand-Reinhold, New York, pp. 377–378.
14. *Federal Register*, "Nonferrous Metals Manufacturing Point Source Category," Part II, Vol. 38, No. 230, pp. 33170–33183, November 30, 1973.
15. T. Yamaguchi, H. Sato, M. Nakanishi, and T. Hara, Japanese Kokai 73 87,661 (Cl 91, 15 A9), (November 17, 1973); Appl. 72 17,689 (February 22, 1972); *Chem. Abstr.*, *80*, 87331g (1974).
16. M. Kanai, Japanese Kokai 73 55,193 (Cl 14, F4), (August 2, 1973); Appl. 71 90,447 (November 11, 1971); *Chem. Abstr.*, *80*, 63742r (1974).
17. K. E. Gunnarsson, Swedish Patent 360,122 (Cl. C. 23g), (September 17, 1973); Appl. 11967/70 (September 2, 1970); 4 page addition to Swedish Patent 340,933 (*Chem. Abstr.*, *78*, 7616Z); *Chem. Abstr.*, *80*, 74116r (1974).
18. E. Sorensen, *J. Colloid Interface Sci.*, *45*(3), 601–607 (1973).
19. *Standard Methods*, 13th ed., American Public Health Assoc., Washington, D.C., 1971, pp. 174–176.
20. F. J. Welcher and R. B. Hahn, *Semimicro Qualitative Analysis*, Van Nostrand, New York, 1963, p. 397.
21. J. W. Clark, N. Wiessman, and M. J. Hammer, *Water Supply and Pollution Control*, International Text Book Co., Scranton, Pennsylvania, 1971, pp. 241, 251.
22. N. A. Matwiyoff and W. E. Wagzman, *Inorg. Chem.*, *9*(5), 1031–1036 (1970).
23. B. B. Ferguson, C. Hinkle, and D. J. Wilson, *Separ. Sci.*, *9*(2), 125–145 (1974).
24. *Properties of Selected Commercial Glasses*, Pamphlet No. 83, Corning Glass Works, Corning, New York, 1963.

*Received by editor August 29, 1974*