AN INVESTIGATION OF FLUORIDE REMOVAL FROM SEMICONDUCTOR WASTEWATER USING WATER SOFTENING SLUDGE

John L. McDonough, Corporate Facilities Engineer
Millipore Corporation
Bedford, Massachusetts 01730
James C. O'Shaughnessy, Associate Professor
Department of Civil Engineering
Northeastern University
Boston, Massachusetts 02115

INTRODUCTION

Historically, the removal of fluoride from acidic industrial wastewater has been performed with the use of commercial lime. The importance of lime is to supply the divalent calcium ion, Ca^{2+}, necessary to precipitate calcium fluoride, CaF_2. In the semiconductor industry, acidic fluoride-bearing wastewater is formed by a chemical etching process based on hydrofluoric acid.

Similarly, the removal of hardness from municipal and industrial water supplies is also accomplished using lime. The resulting water softening process generates precipitated calcium carbonate ($CaCO_3$) sludge which is usually thickened and disposed of offsite. One of the least practiced methods of water softening sludge disposal is codisposal [1].

The codisposal process is based on the following: (1) the softening sludge is of some value in the treatment/disposal of another waste; or (2) the lime sludge is of no value and simply takes advantage of the economies of scale of joint disposal. The first condition is attractive because it uses a waste to treat a waste thereby eliminating the need to purchase quantities of chemical reagents. Using high pH liquid or semisolid alkaline waste, such as water softening sludge for neutralizing an acidic waste, has major opportunities for use in the industrial sector.

The objective of this investigation was to determine the feasibility of using water softening sludge to treat a fluoride bearing wastewater generated by a semiconductor manufacturer. The underlying objective of this project therefore was to investigate the potential for using a waste to treat a waste. This treatment method would apply to industries that process their own water supplies for hardness removal and who may also generate fluoride wastes or be proximate to other industries that do. Another potential application would be in a municipal/industrial waste exchange agreement. The net effect of using one waste to treat another would be a reduction in treatment costs.

A review of the literature indicated few documented codisposal methods.

REGULATORY REQUIREMENTS

The 1962 United States Public Health Service (USPHS) Drinking Water Standards established recommended optimum, as well as maximum fluoride concentrations. The 1975 EPA Interim Primary Drinking Water Regulations, established under the provisions of the Safe Drinking Water Act (PL 93-523), promulgated maximum contaminant levels (MCL) for 10 inorganic chemicals, including fluoride. The MCL for fluoride was the same as the maximum concentration previously established by the USPHS. Since water consumption, and thus fluoride intake, increases with increasing air temperature, the standards were established as a function of annual average maximum daily air temperature.

Recently, EPA proposed regulations under the Clean Water Act to limit effluent discharges to waters of the United States and the introduction of pollutants into publicly owned treatment (POTW's)

The semiconductor subcategory, as researched by EPA, consisted of 257 facilities; 77 were direct dischargers and 180 were indirect dischargers. The major pollutants found were toxic organics, fluorides and total suspended solids. For discharges resulting from the manufacture of semiconductors, EPA has proposed the following fluoride effluent limitations for any existing point source subject to best available technology (BAT) and any new source subject to new source performance standards (NSPS).

	Maximum for Any 1 Day	Average of Daily Values for 30 Consecutive Days
		MILLIGRAMS PER LITER (mg/l)
Fluoride Total	32.0	17.4

These limitations also apply to discharges generated by the manufacture of electronic crystals for an existing point source regulated by BPT or BAT as well as new sources subject to new source performance standards (NSPS) [2].

LITERATURE REVIEW

Effects of fluoride are both beneficial and detrimental to the environment; they have been extensively studied and are well-documented in the literature.

The literature contains several studies involving the removal of fluoride from industrial wastes using various methods. The majority of these studies were performed in the 1970's and involved bench scale testing of various industrial wastewaters. At one time it was thought that pH values of 11.0 or above were necessary to achieve good fluoride removal using lime. Later it was realized that the excess calcium contributed by the high dosages, rather than the high pH, was responsible for precipitation of CaF_2.

Williams [3] investigated the effect of carbonate in an acidic fluoride waste and its relation to previous work performed by Parker and Fong [4]. His experiments compared the efficiency of fluoride removal in wastes that were carbonated by aeration and in wastes that were stripped of carbonates by nitrogen gas. His results indicated that during formation of precipitates, competition for available calcium between the carbonate and fluoride ions reduces the precipitation of calcium fluoride.

Friedman et al [5] investigated the effects of dolomitic lime addition for fluoride removal on a 40% NH_4-F solution and a 49% HF solution. The dolomitic lime used contained about 30% MgO.

Mooney et al [6] evaluated the addition of pulverized calcium carbonate and lime for treatment of high-acidity cooling wastes from production of phosphoric acid. The studies indicated that the rate of fluoride precipitation is dependent on the calcium concentration, but more importantly on the rate of dissociation of $CaCO_3$ to calcium ions. Further, this rate of dissociation was reported to depend on the kinetics involved in acid neutralization. Prewetting of the calcium carbonate and use of a particle size sufficiently small to offer as much surface area as possible improved reactivity.

Investigations by Link and Rabosky [7] utilized two distinct chemical additions for fluoride removal. First, lime provided the calcium and hydroxide necessary for fluoride precipitation and downstream neutralization of acid wastewaters, respectively. Second, ferrous sulfate was added for coagulation.

Studies by Parker and Fong [4] using lime ($Ca(OH)_2$) on both synthetic hydrogen fluoride wastewater and actual process wastewater (feldspar mining solutions) showed that residual fluoride concentrations passed through an initial minimum at pH range of 7.5 to 8.5. Addition of more lime increased the fluoride concentration and pH to approximately 11, after which more lime addition decreased fluoride ion concentration to a second minimum slightly lower than the first.

Zabban and Helwick [8] studies various defluoridation procedures including calcium precipitation followed by chemical addition of either alum or a mixture of alum-sodium hexametaphosphate.

Work performed by Rohrer [9] showed that a combination of lime-calcium chloride in approximately a 1:1–2:1 weight ratio consistently reduced fluoride in plant wastewaters from 725 mg/l to 15–20 mg/l. Rabosky and Miller [10], using lime precipitation and coagulation with alum and polyelectrolyte, reported super-natant fluoride concentrations of 1-2 mg/l with an initial concentration of 90-135 mg/l fluoride in distilled water.

Investigations by Miller [11] addressed the problem of fluoride precipitation in lime treated effluent having a relatively low fluoride concentration of about 40 mg/l at a pH between 2 and 3. A considerable portion of the work involved and developed of a fluoride compound which was much less soluble than calcium fluoride.

Rohrer's first investigations [12] of lead and fluoride wastes, over a ten-year period, indicated that low residual fluoride levels could be achieved if the following conditions were applied. Lowder [13] reported that for a metal finishing wastewater containing 60 to 100 ppm of fluoride, about 7 lb. of hydrated lime per 1,000 gallons of waste (1.2 g/l) would precipitate calcium fluoride.

Zabban and Jewett [14] indicated that fluoride concentrations in a glass plant effluent could be maintained below a fluoride concentration of 20 mg/l (as F).

Culp and Stoltenburg [15] reported fluoride reductions from 3-4 mg/l to 0.8-1.12 mg/l in direct proportion to the amount of magnesium hardness removed during potable water treatment and attributed the removal to sorption of fluoride onto the magnesium hydroxide floc.

TREATMENT THEORY

Calcium is one of the primary components found in most water softening sludges (see Table I). Hence, the reaction of fluoride by treatment using water softening sludge can be generalized as:

$$CaCO_3 + 2HF \rightarrow CaF_2 \downarrow + CO_2 \uparrow + H_2O$$

The overall process of treatment of acidic fluoride wastewater with $CaCO_3$ can be described by differential equations which relate the concentrations of hydrogen ions and carbonic species in the water. The solubility curve of a wastewater containing fluoride and carbonate can be developed by the simultaneous solution of all pertinent equilibrium and solubility equations. The principal chemical relationships for fluoride removal using water softening sludge include: fluoride ion chemistry, water softening chemistry, carbonate chemistry, calcium fluoride precipitation chemistry, and the neutralization of acidity.

If calcium and fluoride are present in quantities greater than minimum solubility values, then fluoride can be precipitated from solution as calcium fluoride according to the solubility product expression:

$$(CA^{+2})\ F^{-2}) = K_{SP} = \text{Constant}$$
$$K_{SP} = 3.4 \times 10^{-11} \text{ at } 18°C$$

Which means that given an excess of calcium fluoride in pure water at room temperature, there will be 16 mg/l of soluble CaF_2, or 7.8 mg/l of soluble fluoride. Since the solubility product is a constant, the concentration of the fluoride anion must decrease as the concentration of the calcium cation increases.

In many industrial applications, fluorides are found in complexed forms of acids such as hydrofluoric or fluorosilic acids. Treatment of fluoride bearing, acidic wastewaters requires some form of acid neutralization in order to increase pH thereby decomplexing the HF ion. At pH values above approximately 6.0 calcium fluoride solubility is virtually independent of pH since all of the fluoride exists as free uncomplexed fluoride ion.

Table I. Chemical Composition of Dry Solids From Water Softening[1]

	Percent by Weight		
Constituent	Boulder City, Nevada	Miami, Florida	Cincinnati, Ohio
Silica, Iron, and Aluminum Oxides	2.6	1.5	4.4
Calcium Oxide	48.8	52.1	49.5
Magnesium Oxide	7.0	2.8	2.3
$CaCO_3$ Equivalent	87.2	93.0	88.1

LABORATORY STUDIES

Laboratory studies were conducted to meet the following two objectives: first, characterize fluoride wastewater and water softening sludge with respect to parameters affecting their chemical interaction; second, evaluate the potential for utilizing water softening sludge in lieu of lime, ($Ca(OH)_2$), for the treatment of fluoride wastewater.

A sample of water softening sludge was obtained from an Indiana pharmaceutical manufacturer that treated its own groundwater supply for hardness reduction. The sludge was drawn directly from the manufacturer's clariflocculator unit.

A sample of fluoride bearing wastewater was obtained from a Massachusetts computer manufacturer that makes its own integrated circuits. Hydrofluoric acid is used to etch-out a circuit pattern on the chips. After etching is complete, a series of acid cleaning and deionized water rinsing steps occur thus forming the fluoride bearing wastewater. The wastewater is collected and treated in a batch operation by conventional physical/chemical treatment methods using lime.

Samples of the fluoride wastewater and lime softening sludge were analyzed for those parameters that would likely affect the acid-base and precipitation chemistry of their interaction. These parameters included pH, total fluoride, acidity, carbonate, and calcium. Titration curves were developed to determine the buffering capacity of the fluoride wastewater (acidity) and of the water softening sludge (alkalinity). The interpretation of both the total acidity and alkalinity results was conservative, recognizing that both values represent only gross characteristics of the sample.

Bench scale tests (jar tests) were conducted to investigate the treatability of the semiconductor fluoride wastewater by the water softening sludge. Experiments were carried out on both synthetic fluoride wastewater solutions as well as the actual plant wastewater [16]. Reagents used in the tests included lime ($Ca(OH)_2$), thickened softening sludge (15% total solids), and dewatered softening sludge (29% total solids).

Reagent grade lime ($CA(OH)_2$) was added in weighed (to 0.1 g) amounts. Water softening sludge was added volumetrically (to 1 ml) amounts using sludge pipets. An important aspect of adding the softening sludge to the jars was to maintain a reasonably constant solids concentration.

Fluoride measurements were performed using an Orion Model No. 94–09 fluoride electrode [17]. The samples were not filtered prior to the residual fluoride determination.

RESULTS AND DISCUSSION

Waste Characteristics

Results of the analyses performed on the semiconductor fluoride wastewater are shown on Table II. Total fluoride concentration was 340 mg/l using either Total Ionic Strength Adjustment Buffer (TISAB) or sodium acetate buffers in the determination. Total acidity, as measured to pH 8.3, was 10,000 mg/l as $CaCO_3$.

Table II. Fluoride Wastewater Characteristics

pH	1.1-1.5
Fluoride	340 mg/l
Total Acidity	10,000 mg/l $CaCO_3$ (@ pH = 8.3)
Total Calcium	5.6 mg/l
Antimony	<0.05 mg/l
Arsenic	<0.025
Beryllium	<0.1
Cadmium	<0.05
Chromium	<0.10
Copper	<0.10
Lead	<0.010
Mercury	<0.001
Nickel	<0.05
Selenium	<0.05
Silver	<0.05
Thallium	<0.050
Zinc	0.034

Table III. Water Softening Sludge Characteristics

Parameter	Raw Sludge	Thickened Sludge	Dewatered Sludge
pH	10.5-10.8	10.8	-
Total Alkalinity mg/l as $CaCO_3$	135,000	208,500	-
Total Solids, Percent	9.7	15.0	29.0
Total Fixed Solids, Percent	9.3	14.4	27.8
Total Volatile Solids, Percent	0.4	0.6	1.2
Total Calcium, mg/l as Ca	34,500	-	-
Total Magnesium, mg/l as Mg	3,200	-	-
Total Fluoride, mg/l as F	ND[a]	-	-

[a] ND = Not Detected.

Results of the analyses on the water softening sludge are shown on Table III. Where appropriate, values are shown for both the raw sludge and for the thickened sludge. As noted, pH values ranged from 10.5 to 10.8. Total calcium and magnesium, as determined by atomic absorption spectrophotometry, were 34,500 mg/l as Ca and 3,200 mg/l as Mg, respectively. No fluorides were detected in the sludge. Total alkalinities for the raw and thickened sludges were 135,000 mg/l and 208,500 mg/l $CaCO_3$, respectively.

Jar Tests

Jar tests were performed to study the effects of using water softening sludge in the treatment of fluoride wastewater. Based partially on the results of solids analyses, it was decided that thickened sludge would be used in the jar tests because it best represents the type of material that would provide:

- sufficient amounts of chemical solids at a pumpable consistency without unnecessary water,
- sufficient calcium to react with the precipitate fluoride,
- acid neutralization capability,
- small enough particle size offering as much surface area as possible to improve reactivity [6].

Since previous researchers had used lime in the treatment of various fluoride wastewaters, it was decided to confirm the effectiveness of lime in treating the semiconductor waste. The results indicate that lime is very effective in the removal of fluoride from this wastewater. Figure 1 shows the effect of lime dosage on residual fluoride while Figure 2 shows the effect of pH on residual fluoride. A lime dosage of 7.2 mg/l ($Ca(OH)_2$ resulted in a total residual fluoride concentration of 4 mg/l at pH 9.5 which is below the theoretical solubility of fluoride (7.8 mg/l) discussed previously. Increasing the lime dosage resulted in an increase in fluoride concentration until a second fluoride minima (20 mg/l) was reached at a dosage of 14.0 g/l and pH of 12.0. This double minima effect was noted in the literature by several researchers including Parker and Fong [4], Rohrer [9], and Williams [3]. Figure 3 shows a substantial reduction in fluoride concentration at a pH of 4.0 with minimal additional fluoride removal at increasing pH levels. Therefore, contrary to several articles in the literature, significant fluoride removal was obtained at low pH values. For example, a residual fluoride concentration of 7 mg/l was achieved at pH of 4.1 without the benefit of filtration. Further, fluoride removal was not affected by pH variations between a range of 3.0 to 10.0. This corresponds to the wastewater's pH range of minimal buffering capacity with regard to acidity. At pH levels greater than 10.0, the residual fluoride concentration began to increase.

To summarize, the results of jar tests performed on the fluoride wastewater using lime supported conclusions previously reached by others and demonstrated the effects of the lime treatment of semiconductor fluoride wastewater. These include the following:

- Lime is effective in the treatment of fluoride in semiconductor wastewaters.
- The amount of fluoride removed is dependent on the lime dosage. A resulting plot of residual fluoride versus lime dosage shows two minimum values of fluoride residual.
- A significant fluoride reduction was achieved at low pH values although pH was a secondary factor to lime dosage in terms of fluoride removal.
- Treating a wastewater of low acidic buffering capacity with lime could result in excessively high effluent pH levels. Therefore, additional treatment (pH reduction) may be required prior to final discharge.

Figure 4 shows jar test results using dewatered softening sludge which contained in excess of 27% fixed solids. Two residual fluoride minimas were noted similar to the results found using lime. The first minima, 10 mg/l, was achieved with 10 mls sludge or an equivalent dosage of 24.3 g/l $CaCO_3$.

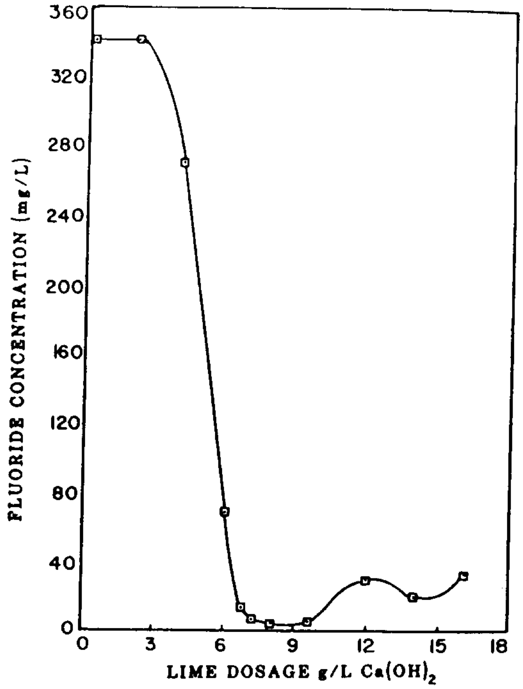

Figure 1. Effect of lime dosage on residual fluoride.

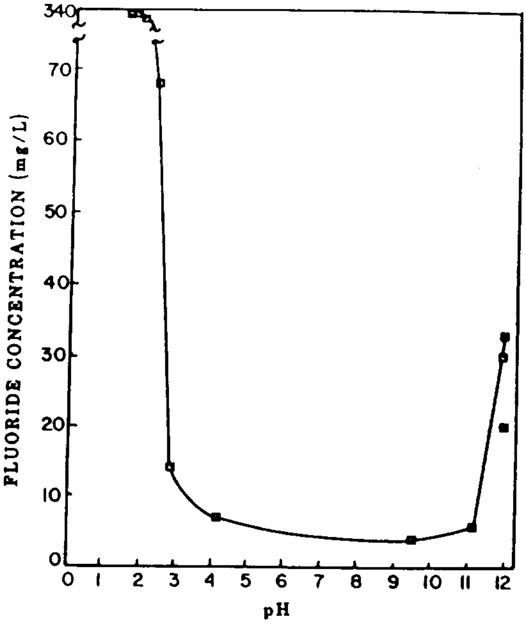

Figure 2. Effect of pH on residual fluoride using lime.

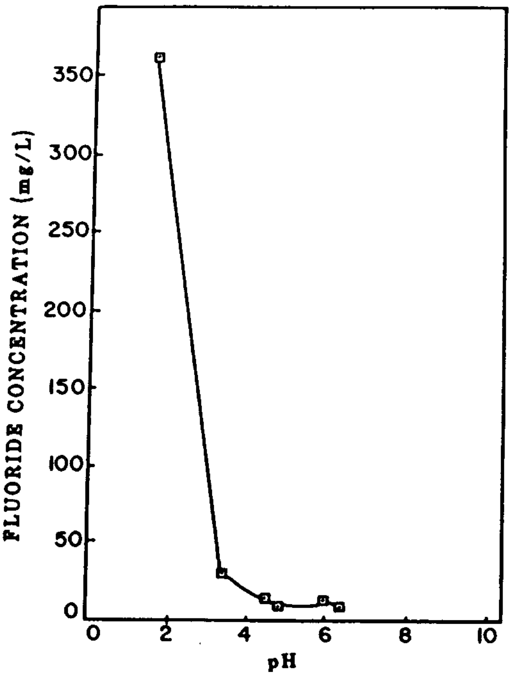

Figure 3. Effect of pH on total residual fluoride using dewatered sludge.

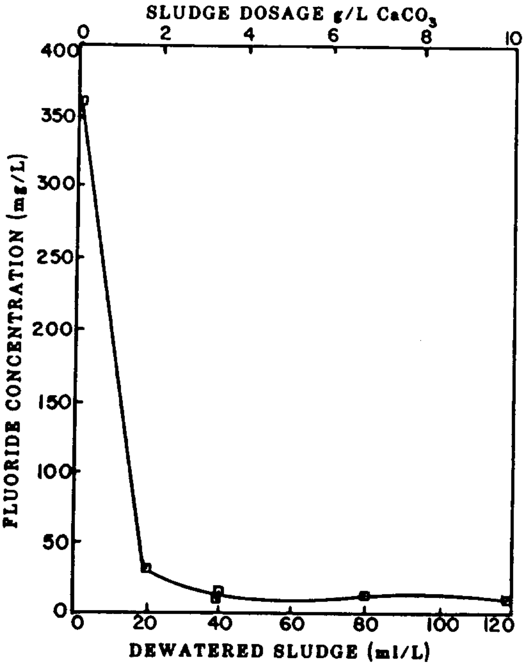

Figure 4. Effect of dewatered sludge dosage on total residual fluoride.

The second minima was achieved with 30 mls sludge or an equivalent dosage of 72.9 g/l $CaCO_3$. Final pH values for both minimas occurred at 4.9 and 6.3 respectively, as shown on Figure 3. Note that excessively high pH values were not required to achieve significant fluoride reduction. In fact, given the chemistry of calcium carbonate, a pH of 8.3 would be the maximum level that could be achieved.

During the above testing a question arose regarding the determination of fluoride in acidic wastewater and the appropriate buffers to be used. A side-by-side comparison was performed using sodium acetate buffer and Total Ionic Strength Adjustment Buffer (TISAB).

This comparison was performed in conjunction with jar tests using thickened softening sludge containing approximately 14% solids. Figure 5 shows that the use of sodium acetate versus TISAB did affect fluoride values initially with sodium acetate yielding more conservative results. However, the minimum values reached were essentially the same. The sodium acetate buffer appears to be more effective in decomplexing the HF ion.

Figure 6 shows that the lowest residual fluoride levels were achieved using thickened water softening sludge at a dosage of 10 to 12 g/l $CaCO_3$. Minimum fluoride levels were found at pH 5 to 6. The effect of TISAB versus sodium acetate is more evident on Figure 7; however, the minimum levels achieved were again essentially the same at pH 5.0 to 5.5. The sodium acetate fluoride analyses were more conservative at pH values from 2.0 to 5.0. At pH 3.5 the residual fluoride using TISAB was 70 mg/l while using sodium acetate the residual fluoride was 125 mg/l.

Considering that no polymers or other coagulants were used, the CaF_2 product settled well following mixing resulting in a clear supernatant generally within 30 to 60 minutes. Some of the jars contained some trapped gas (probably CO_2) in the settled precipitate. Gentle stirring helped release the gas. The precipitated material formed using softening sludge appeared to settle more rapidly and compact better than those formed using lime. The amount of sludge formed by the softening sludge reaction was about equal to the amount added to the wastewater.

Finally, Figure 8 is a plot of residual fluoride versus meq/l dosage for both lime and thickened softening sludge. The figure indicates that the thickened sludge is initially more effective than lime in removing fluoride residual of 4 mg/l versus 14 mg/l. The double minima residual fluoride effect is clearly evident using lime while not so evident using the softening sludge. The position of the thickened softening sludge curve with respect to the lime is a function of the solids content of the sludge and the amount of available calcium. More dilute sludge would shift the position of the curve to the right of the lime curve.

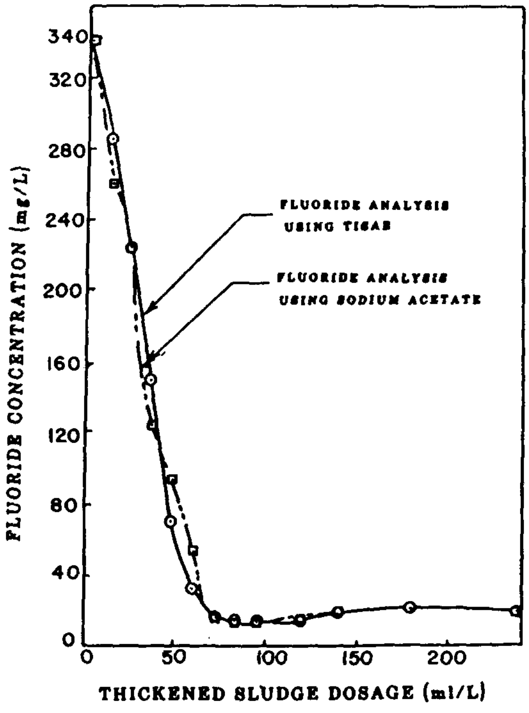

Figure 5. Effect of thickened sludge on residual fluoride.

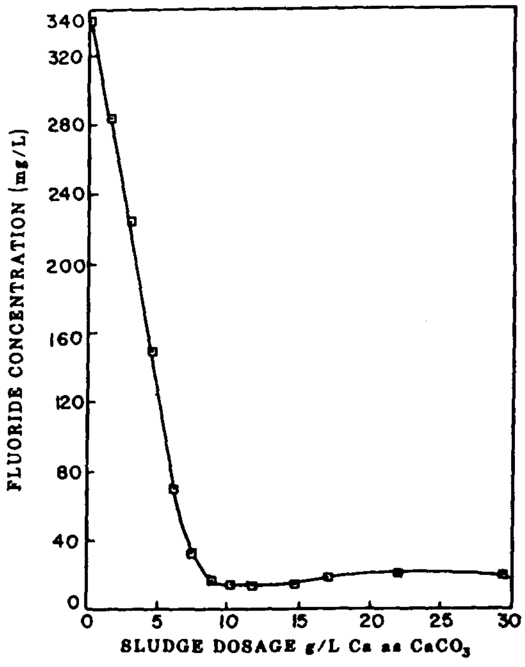

Figure 6. Effect of thickened sludge on residual fluoride.

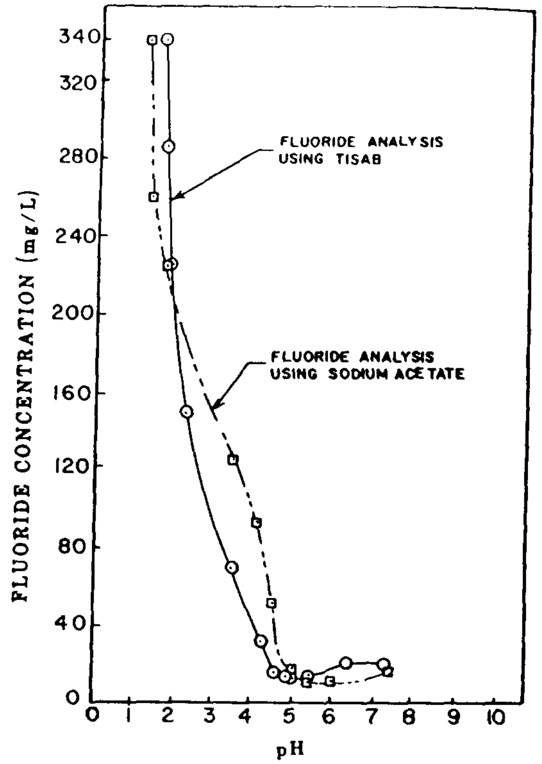

Figure 7. Effect of pH on residual fluoride with thickened sludge addition.

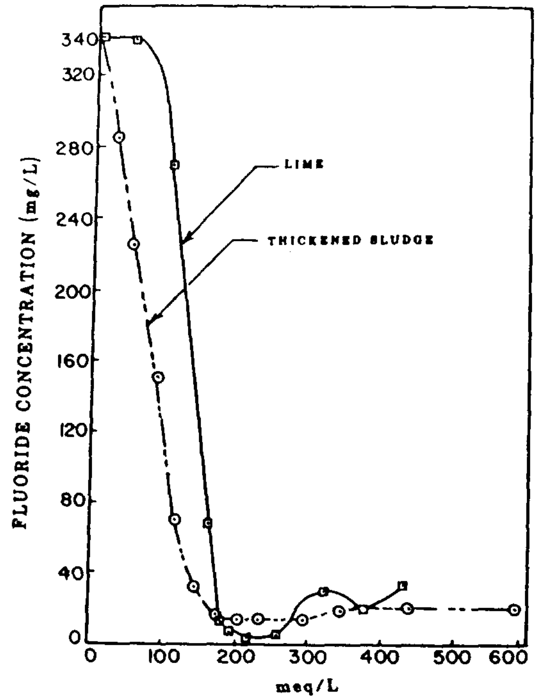

Figure 8. Residual fluoride versus equivalent chemical additions for lime and sludge.

SUMMARY AND CONCLUSIONS

The results of this investigation show that the codisposal of water softening sludge by use in the reatment of acidic fluoride wastewater is both feasible and effective.

To deliver adequate calcium in the treatment of fluoride wastewater, the use of thickened water oftening sludge is recommended. Thickened softening sludge also provides sufficient chemical solids t a pumpable consistency without unnecessary water. In addition the thickened sludge provides a reater degree of acid neutralizing capacity.

The use of water softening sludge in the treatment of the wastewater did not result in excessively igh effluent pH levels which would require reacidification prior to discharge. Conversely, treatment f the wastewater with lime did result in high final pH levels due in part to the wastewater's lack of uffering capacity. High pH levels were not required to achieve significant fluoride reductions.

On an equivalent basis, lime was only slightly more effective in the removal of fluoride than the hickened softening sludge.

The precipitated material formed using the water softening sludge settled better than the precip-tated material formed using lime. It appears that the particle size and wetted nature of the water oftening sludge is better suited for dissociation to calcium ion than limestone or pulverized calcium arbonate.

REFERENCES

1. American Water Works Association (AWWA) Committee Report, "Lime Softening Sludge Treatment and Disposal", *Journal AWWA* (November 1981).
2. Environmental Protection Agency, 40 CFR Part 269, "Electrical and Electronic Components Point Source Category; Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards", *Proposed Regulation* (Tuesday, August 24, 1982).
3. Williams, Donald H., "pH Control in Fluoride Removal", *Thesis*, Graduate School, University of Texas at Austin (May 1982).
4. Parker, Dr. C. Leon and Fong, C. C., "Fluoride Removal: Technology and Cost Estimates", *Industrial Wastes* (November/December 1975).

5. Friedman, Ronald B. Arnesen, Richard, and Friedman, A. A., "Multisolution Approach to an Electronic Firm's Complex Wastewater Discharge Problems", *Proceedings of the 35th Purdue Industrial Wastes Conference* (May 1980).
6. Mooney, Gregory A., Thompson, Cliff G., and Nogueira, Alfred T., "Removal of Fluoride and Phosphorous from Phosphoric Acid Wastes with Two-State Lime Treatment", *Proceedings of the 33rd Purdue Industrial Wastes Conference,* (May 1978).
7. Link, William E. and Rabosky, Joseph G., "Fluoride Ion Removal from Wastewater Employing Calcium Precipitation and Iron Salt Coagulation", *Proceedings of the 31st Purdue Industrial Wastes Conference* (May 1976).
8. Zabban, Walter and Helwick, Robert, "Defluoridation of Wastewater", *Proceedings of the 30th Purdue Industrial Wastes Conference* (May 1975).
9. Rohrer, Kenneth L., "Lime, $CaCl_2$; Beat Fluoride Wastewater", *Water and Wastes Engineering* (November 1974).
10. Rabosky, Joseph G. and Miller, James P., Jr., "Fluoride Removal by Lime Precipitation and Alum and Polyelectrolyte Coagulation", *Proceedings of the 29th Purdue Industrial Waste Conference* (May 1974).
11. Miller, D. G., "Fluoride Precipitation in Metal Finishing Waste Effluent", *AIChE Symposium Series, Water* (1974).
12. Rohrer, Kenneth L., "An Integrated Facility for the Treatment of Lead and Fluoride Wastes", *Industrial Wastes,* 118:36-39 (September/October 1971).
13. Lowder, L. R., "Fluoride Waste Puzzle Solved", *Water and Wastes Engineering,* 8(3):B6-B9(March 1971).
14. Zabban, Walter and Jewett, H. W., "The Treatment of Fluoride Wastes", *Proceedings of the 23rd Purdue Industrial Waste Conference* (May 1967).
15. Culp, Russell L. and Stoltenberg, Howard A., "Fluoride Reduction at LaCrosse, Kansas", *Journal of The American Water Works Association* (March 1958).
16. McDonough, John L., "An Investigation of Fluoride Removal from Semiconductor Wastewater Using Water Softening Sludge", *Masters Report,* Department of Civil Engineering, Northeastern University, Boston, MA (February 1984).
17. Orion, *Instruction Manual for Fluoride Electrodes Model 94-09 and Model 96-09,* Orion Research Incorporated (1982).