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NEUTRALIZATION METHOD FOR A HYDROFLUORIC ACID RELEASE

By

Dennis L. Williams and Lewis E. Deacon
Process Technology Department
Technical Division

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ABSTRACT

A laboratory investigation of methods for neutralizing a release at the hydrofluoric acid tank farm at the Portsmouth Gaseous Diffusion Plant has revealed that the best neutralization method incorporates the use of a lime/water slurry. In this method, settling of suspended solids in the liquid is enhanced by the application of sodium dodecyl sulfate, which causes immediate flocculation and settling. Dilution and expulsion of the supernatant liquid above the flocculated solids result in an effluent which meets the one part per million fluoride limit established by the U.S. Environmental Protection Agency. A fluoride specific ion electrode is used to determine fluoride concentration. This method presently is being adapted for use in the hydrofluoric acid tank farm and is being considered for use at the plant's fluorine generation facility. It could be adapted for use in any facility that contains fluoride in aqueous solution.

INTRODUCTION

The neutralization pit at the hydrofluoric (HF) acid tank farm at the Portsmouth Gaseous Diffusion Plant until recently was filled with limestone ($CaCO_3$) rocks that were intended to react with and neutralize any liquid HF spill that might occur. A recent study to evaluate the ability of limestone to cope with an HF spill demonstrated that the initial reaction between limestone and HF produces a water insoluble coating of calcium fluoride (CaF_2) on the surface of the rocks that prevents further reaction.[1] Thus, the limestone at the acid tank farm would not neutralize a spill at that facility even though more than the theoretical amount of limestone needed were available.

The unsuitability of the existing system prompted a laboratory investigation of alternate methods for dealing with a release of HF at the acid tank farm. The work was undertaken on two premises: (1) that a water spray would be used to knock down and solubilize released HF and that the resulting solution would be directed to the neutralization pit; and (2) that the method developed would be employed only for releases in which the entire volume of the HF/water solution resulting from the contained release would not exceed the capacity of the neutralization pit.

Of extreme importance in this work was the requirement that the effluent from the neutralization pit after neutralization be as environmentally acceptable as possible, especially relative to fluoride concentration. This necessitated developing a method that would produce a water insoluble fluoride salt that could be contained within the neutralization pit. The fluoride content of the supernatant liquid, in order to meet environmental standards, would have to be either at or below the EPA limit (1 ppm) or low enough to allow minor dilution with water to achieve the limit.

EXPERIMENTAL PROCEDURE

A fluoride specific ion electrode was used in conjunction with a compatible electrometer to detect fluoride concentration rather than use the standard titrimetric method. This detection method was chosen because it enables the detection of real-time changes at very low HF concentrations with high sensitivity and because it does not involve time-consuming titrations.

Since the specific ion electrode measures ionic activity (a_m) in millivolts and mean ionic activity coefficients (γ_m) are available in the literature, actual concentrations (C_m) can easily be calculated using the equation $a_m = \gamma_m C_m$. In practice, standard solutions of the ion to be measured are prepared and calibration curves are constructed by plotting ionic activity versus ion concentration. In this study, an extra step was added due to difficulties encountered in preparing standard solutions of HF. Potassium fluoride (KF) was substituted for HF as the standard source of fluoride ions. A calibration curve was prepared to compare fluoride ion activity for KF as a function of electrode potential

in millivolts; this curve is shown in Figure 1. A second calibration curve, shown in Figure 2, was constructed by plotting the activity of fluoride ions in aqueous HF (derived from literature values for the mean ionic activity coefficient) versus actual concentration of HF. These curves were then used to determine the fluoride concentration in the test solutions by converting the measured electrode potential in millivolts to fluoride ion activity using Figure 1, and then converting fluoride ion activity to fluoride ion concentration using Figure 2. A standard calomel electrode was used as a reference with the fluoride electrode.

Aqueous HF test solutions were prepared by dilution of stock 48-51 percent hydrofluoric acid. The HF concentration in these solutions was approximately 0.1 molar; however, initial concentrations were always determined as parts per million. Since the assumption was made that a water deluge device intended for use at the HF tank farm would expel copious amounts of water in relation to the amount of HF expected in a typical release, 0.1 molar concentrations were selected as being representative of the solutions expected in a release situation.

BEAKER TESTS

Initial evaluations were performed in one-liter polyethylene beakers to eliminate any possible reaction between HF and glass. This precautionary measure was later found to be unnecessary when contact time between HF and glass was held to a minimum.

Lime (CaO) and alumina (Al_2O_3) were tested for suitability since both are commonly used on plantsite and, hence, are easily obtainable. Sludge from the new lagoon at the plant's water treatment facility was also selected for testing because it contains nearly pure calcium carbonate ($CaCO_3$), which could react favorably.

Experimental conditions and results of the individual test runs are given in Table I. HF solutions were prepared by adding approximately 1 ml of stock HF to 300 ml tap water. Fluctuations in the initial solution concentrations were caused by imprecise measurement of the stock HF aliquots and the tendency of the concentration of the stock HF to change with time due to evaporation. The fluoride electrode was positioned in the upper one inch of the solution. Reactants were weighed immediately prior to each run and were added to the test solutions in powder form.

A second series of tests was initiated to study the effects of slurrying lime in water before the lime was added to the test solutions. The results of these tests are illustrated in Figure 3. The slurries were prepared by adding the properly weighed amount of lime to about 200 ml tap water followed by vigorous stirring for approximately one minute. Each slurry was rapidly added to the 300-ml test solution resulting in a total volume of about 500 ml. Dilution effects were ignored although they were certainly present. All test solutions were stirred throughout the reaction period.

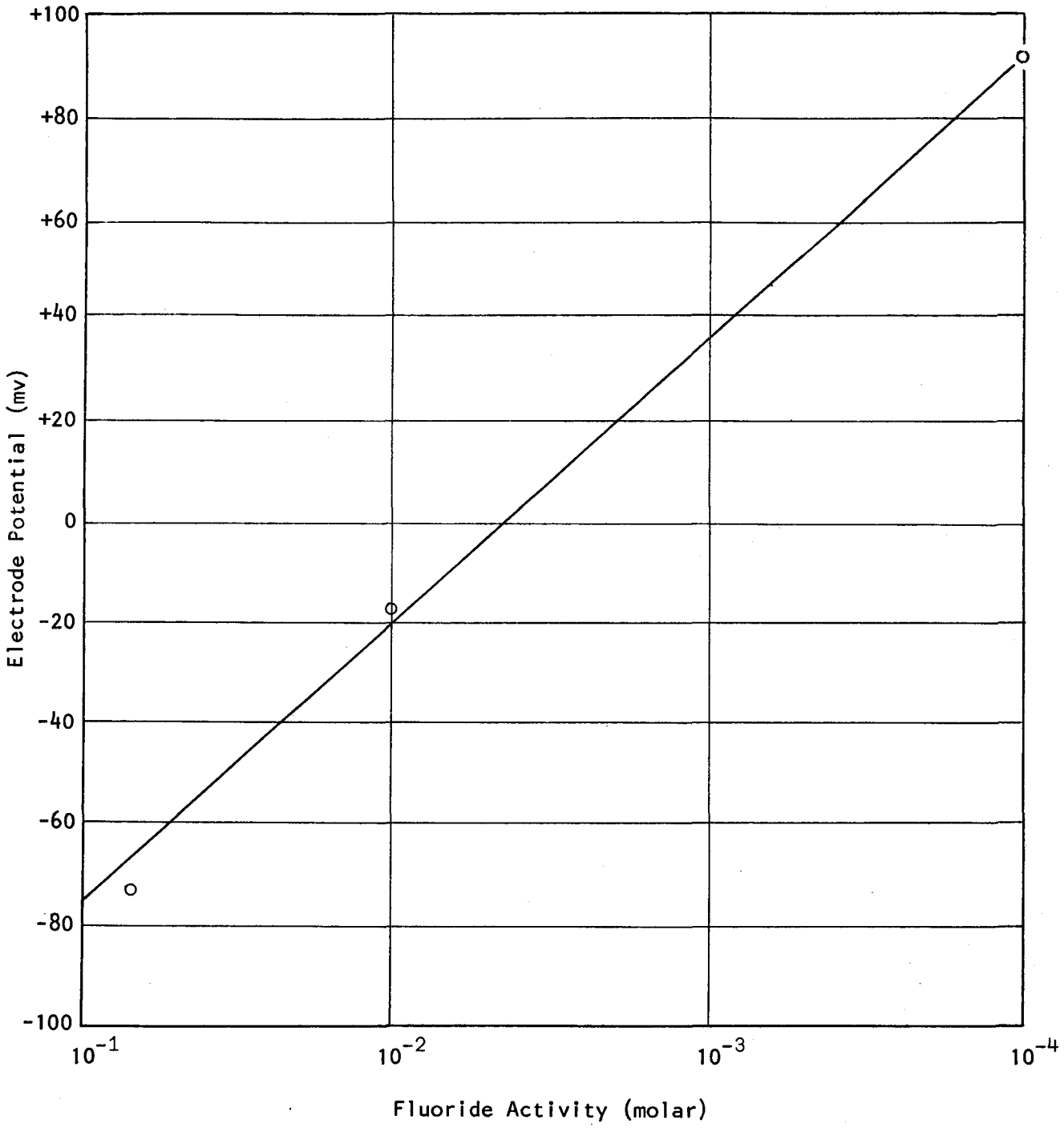

FIGURE 1 ELECTRODE POTENTIAL VS FLUORIDE ION ACTIVITY IN AQUEOUS POTASSIUM FLUORIDE AT 24°C

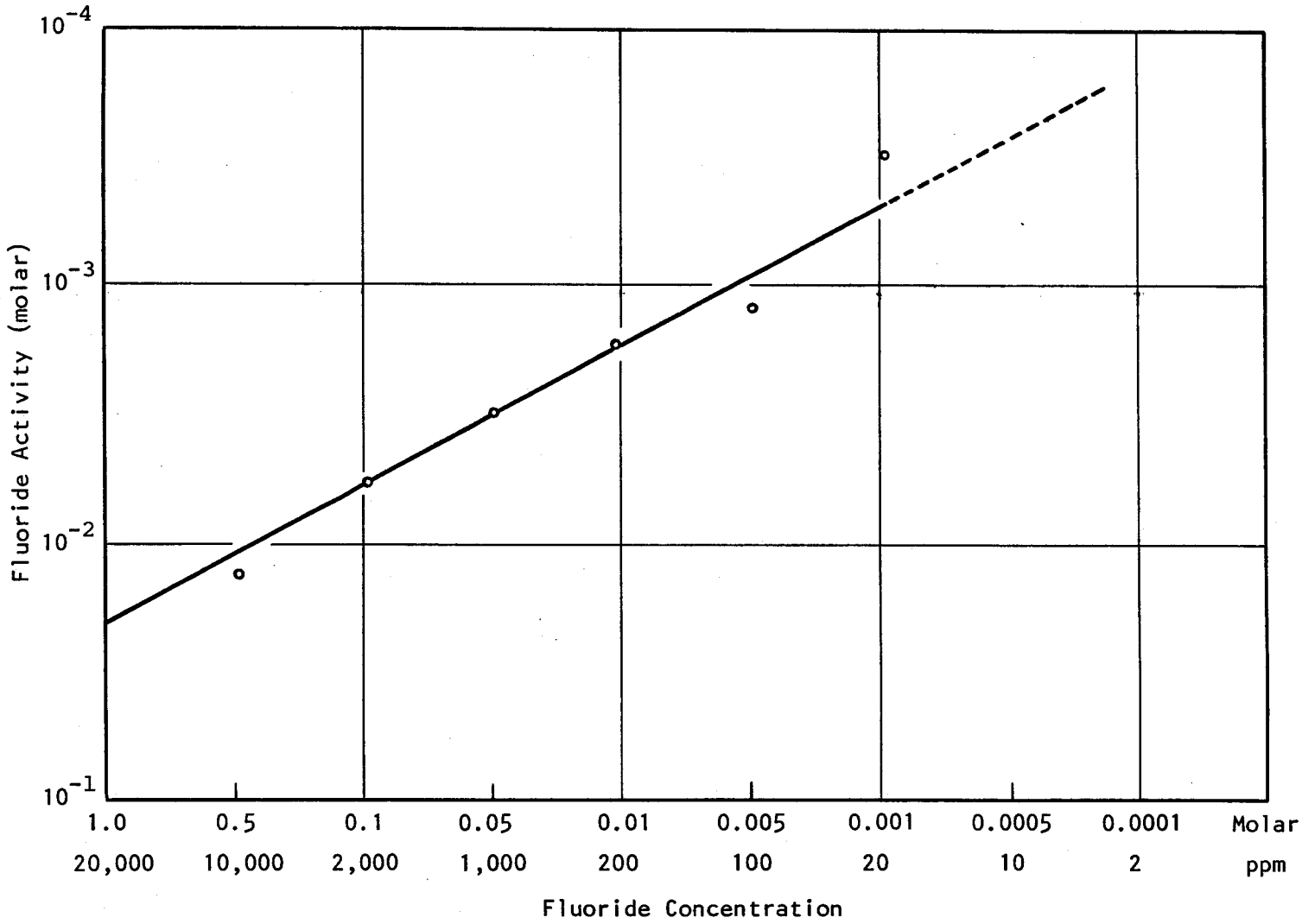

FIGURE 2 FLUORIDE ION ACTIVITY VS FLUORIDE CONCENTRATION IN AQUEOUS HYDROFLUORIC ACID AT 25° C

TABLE I RESULTS OF BEAKER TESTS

Reactant	Molar Ratio To HF	Unstirred	Stirred	HF Concentration in ppm					Final Conc./ Time (Min.)
				Initial	1 Min.	5 Min.	10 Min.	30 Min.	
Lime (CaO)	1:1	X		3,000	3,000	3,000	2,400	1,900	1,800/45
Lime (CaO)	1:1		X	3,000	1,750	1,150	1,050	900	900/30
Lime (CaO)	2:1		X	1,900	840	280	175	135	8/90
Lime (CaO)	5:1		X	1,750	19	8	6	~ 6	--
Alumina (Al_2O_3)	1:1	X		1,450	1,450	1,600	1,650	--	--
Sludge ($CaCO_3$)	1:1		X	1,800	7,200	3,600	2,000	--	--

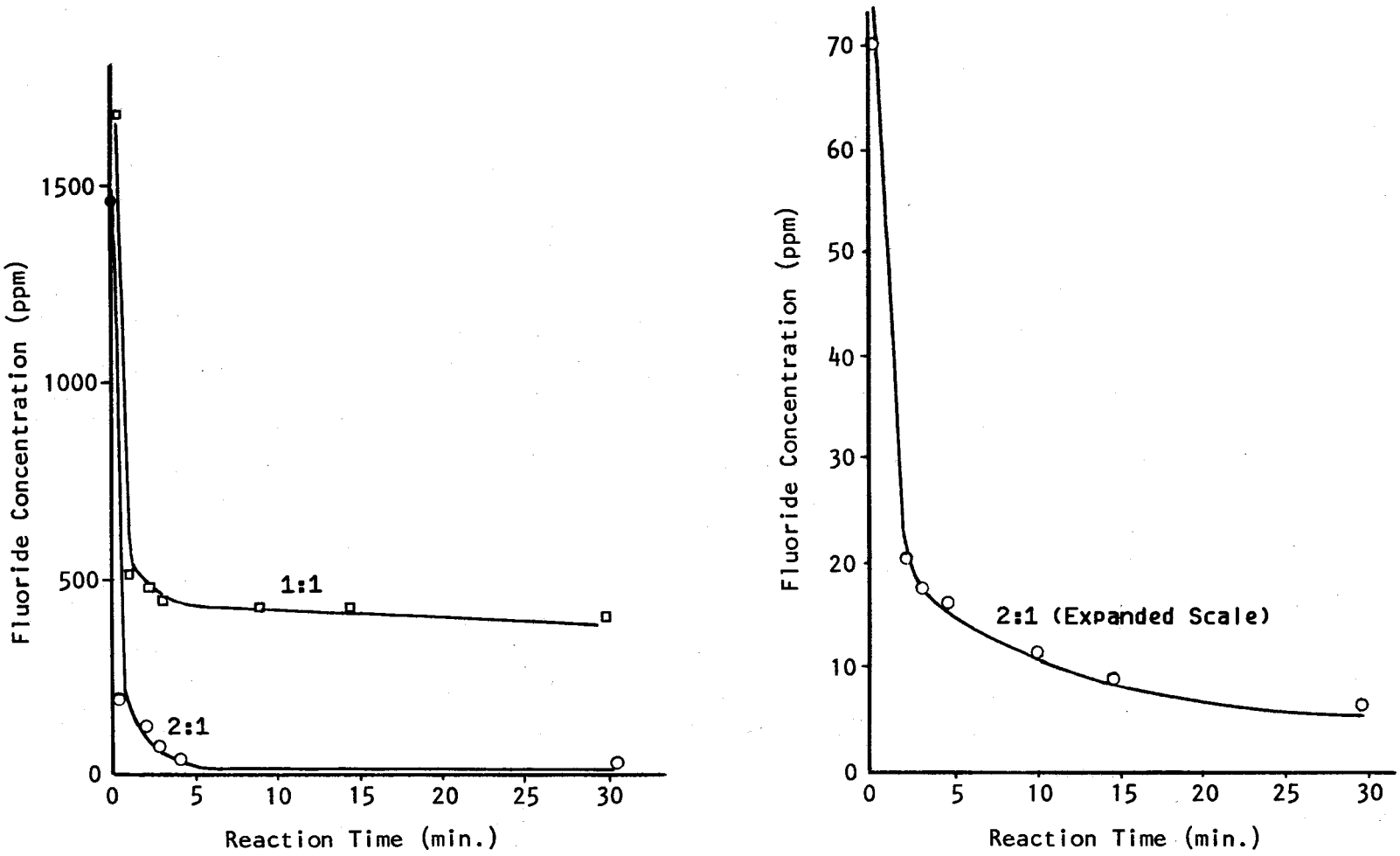

FIGURE 3 LIME SLURRY TEST RESULTS

NEUTRALIZATION PIT SIMULATION TESTS

In order to more closely simulate conditions in the neutralization pit at the HF acid tank farm, a Plexiglass container was constructed for conducting the neutralization tests. The general configuration of the container and the associated test equipment are shown in Figure 4. The container was designed with the solution entry point at a higher elevation than the exit. This permitted the formation of a cascade effect by cutting appropriately sized vees in the two mixing baffles. An 8-liter polyethylene jug was used as a reservoir to contain the HF solution and a Veristaltic pump was used with Tygon tubing to transport the HF solution to the Plexiglas container. The fluoride electrode was placed in the upper one inch of solution in the lowest tank section. Standard laboratory stirrers adjusted to moderate stirring speeds were used.

Tests were normally carried out by preparing the 0.1 molar HF solution in the polyethylene jug and pumping it at slow-to-medium speed into the container. When the first section of the container was slightly more than half-filled, the lime, either as a powder or slurry, was added and stirring was initiated. The HF solution was continuously pumped into the container until the entire 8 liters were in the first two container sections; stirring was started in the second section as the mixture started flowing over the first baffle. After the pumping was stopped, both sections were stirred for several minutes to allow sufficient reaction time. Stirring was then stopped to allow suspended solids to settle. Following the settling period, tap water was pumped into the container so that the third section was filled and a section-to-section flush was established. The solution that passed into the third section was tested for fluoride content with the fluoride electrode.

FLOCCULATION STUDIES

Flocculation tests were performed to find a suitable agent for enhancing settling rates. These tests were carried out in substantially the same manner as the neutralization pit simulation tests. Following the reaction period, stirring was continued while a predetermined amount of the agent to be tested was added to the reaction mixture. Stirring was continued for approximately 5 minutes and then stopped. Visual observations were then made to determine floc size and settling times.

RESULTS AND DISCUSSION

BEAKER TESTS

The results presented in Table I are shown graphically in Figures 5 and 6. Sludge from the water treatment facility is not included in the graphs due to its observed, but unexplained, unsuitability. As was expected, alumina was not satisfactory due to the relative

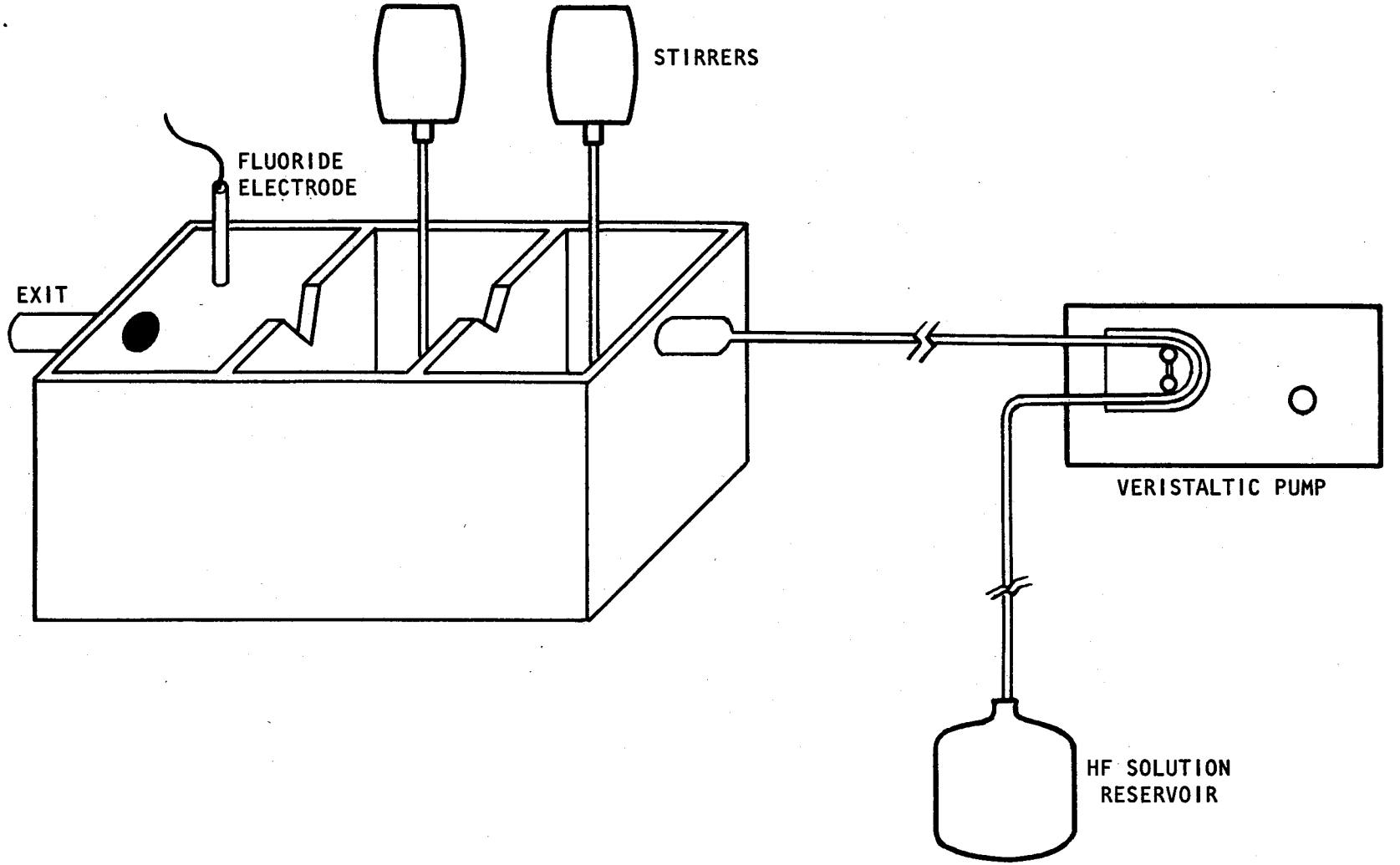

FIGURE 4 LABORATORY-SCALE SIMULATION OF HF NEUTRALIZATION PIT

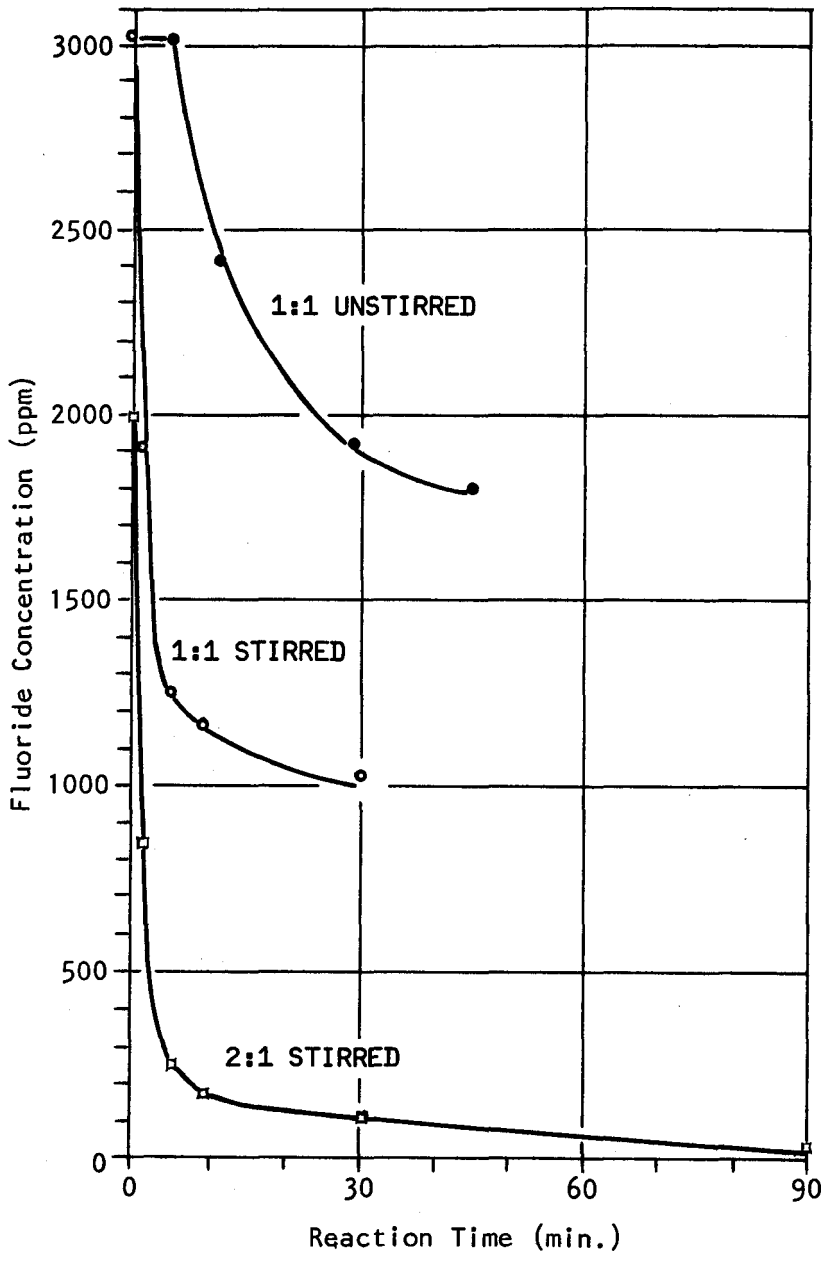

FIGURE 5 LIME POWDER NEUTRALIZATION TESTS

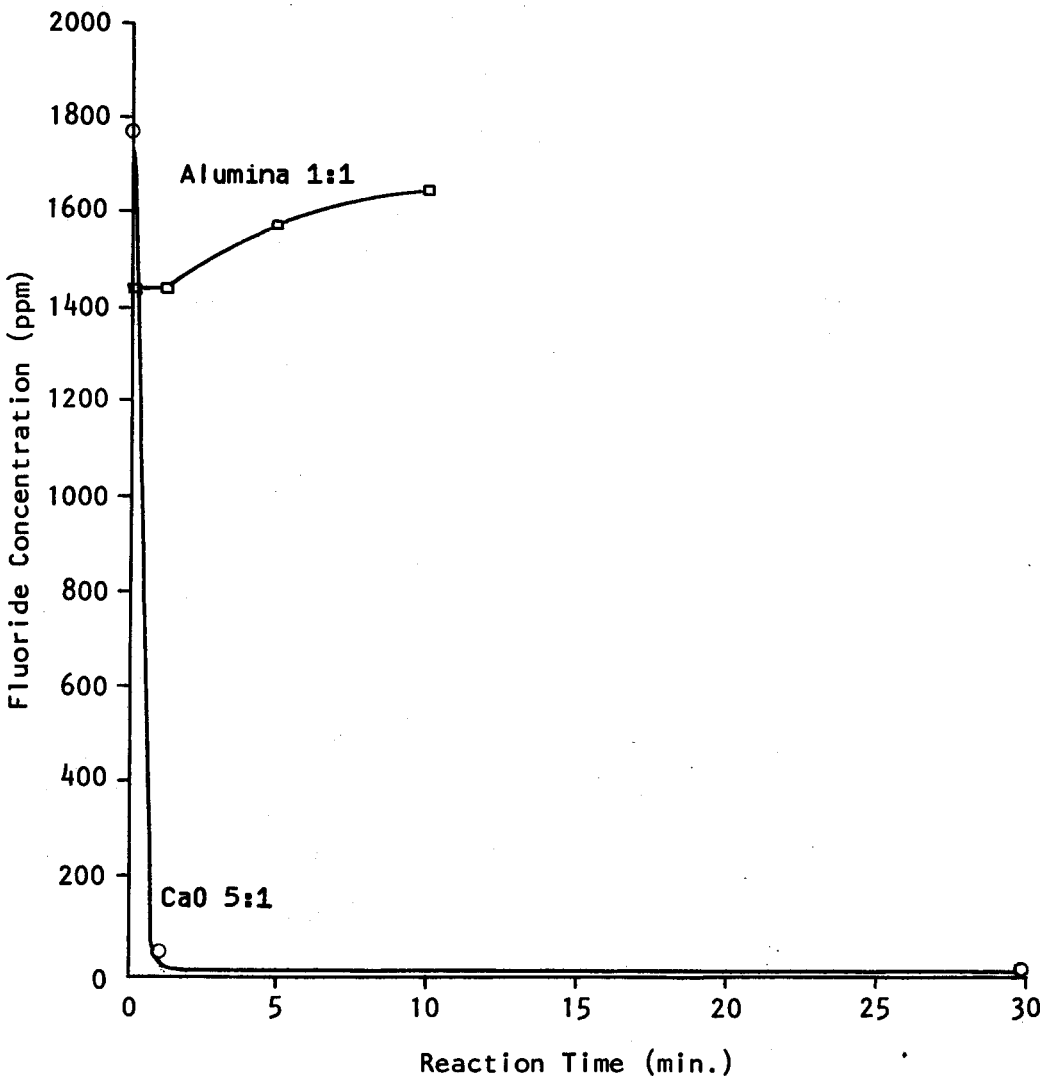

FIGURE 6 LIME AND ALUMINA POWDER NEUTRALIZATION TESTS

high solubility of AlF_3 in water (5.59 grams per liter water at 25°C, as compared to 0.016 grams per liter water at 18°C for CaF_2).[2] The expected behavior of alumina is shown by the increase in fluoride activity as the reaction proceeds. The reaction that takes place can be expressed as:

$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \quad (1)$$

It is unfortunate that AlF_3 is so soluble since one mole of alumina can neutralize six moles of HF.

Two general conclusions can be drawn from the reactions with lime: (1) increasing the lime concentration decreases both the final fluoride concentration and the time needed to achieve that concentration; and (2) stirring is essential for complete reaction within a reasonable time period. These conclusions are based on the 1:1, 2:1, and 5:1 ratio tests. The 5:1 ratio reached acceptable fluoride levels within 5 minutes; the 2:1 ratio took 90 minutes to achieve the same level; and the 1:1 ratio (stirred) will never reach that level if the shape of the curve continues unchanged. The two 1:1 ratio tests showed that stirring is necessary for efficient reaction.

Results from the tests in which lime was slurried prior to reaction with HF solutions indicate a substantial decrease in the time required for complete reaction. Typical 2:1 ratio lime powder and slurry test results are compared in Figure 7. Slurried lime reduces fluoride concentration to acceptable levels in approximately one-third the time it takes for powdered lime to do the same. The increased particle surface area and pre-wetting that results from slurrying, in addition to slaking, are undoubtedly major contributors to this effect.

NEUTRALIZATION PIT SIMULATION TESTS

Results of tests conducted in the simulated neutralization pit essentially paralleled those obtained in the beaker studies. Ratios of 2:1/CaO:HF resulted in much lower fluoride concentrations than did 1:1 ratios. CaO slurries again reached acceptable fluoride levels in approximately one-third the time for powdered lime. All flocculating agents tested left turbid liquid in the tank sections with the exception of sodium dodecyl sulfate, which enhanced coagulation and settling of virtually all suspended solids when it was used in concentrations of 250–500 ppm.

One potential problem which was noticed during these tests was the tendency of the sludges produced by flocculating agents to be disturbed by solution flowing through the vees cut in the mixing baffles. This caused slight remixing and carry-over into the next tank section. However, the sludge produced by sodium dodecyl sulfate was so dense that no disturbance was noted when liquid flowed through the vees.

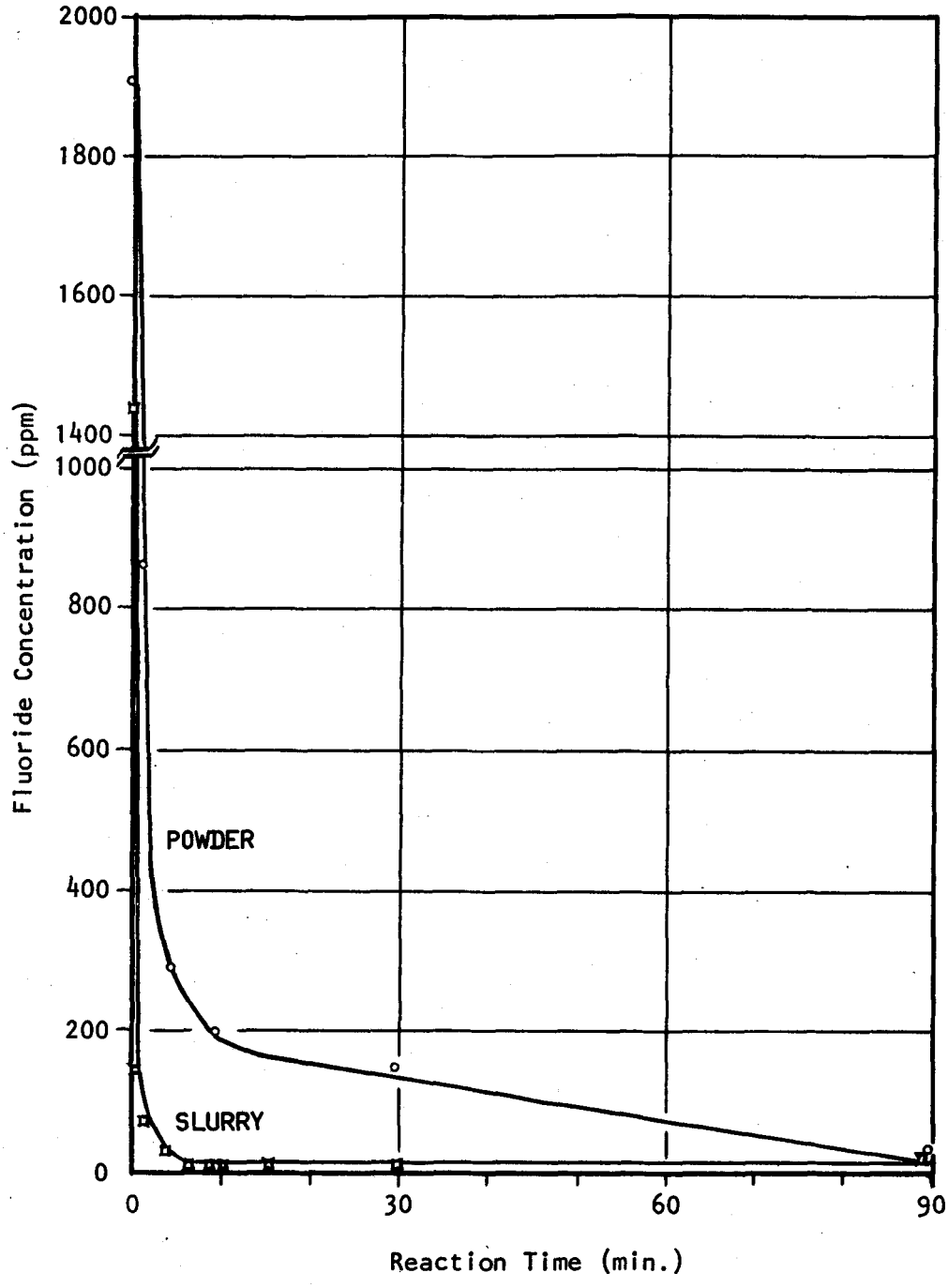

FIGURE 7 COMPARISON OF 2:1 RATIO LIME POWDER AND SLURRY TESTS

The lowest fluoride concentration obtainable by the use of lime was about 6-8 ppm (the solubility limit for CaF_2 in water), which is above the EPA limit of 1 ppm for water-borne fluoride. As a result, the supernatant liquid in the container sections must be diluted to achieve the EPA limit. This is the reason that tap water is pumped into the container following sludge settling. The same procedure will be necessary at the HF neutralization pit.

FLOCCULATION STUDIES

Neutralization of released HF turned out to be only half of the problem encountered in this study. Slurried lime not only reduces fluoride concentration efficiently, but also produces a very fine dispersion of CaF_2 that does not settle out even after a period of several days. The overall reaction is expressed as:

$$CaO + 2HF \rightarrow CaF_2 \downarrow + H_2O \qquad (2)$$

Any unreacted lime settled out quickly, but the CaF_2 remained as a suspension. This suspension could not be discharged from the neutralization pit since the solubility of CaF_2 in water is above the EPA allowed level. Thus, a means had to be found for removing CaF_2 from the supernatant liquid.

Several methods exist for enhancing the precipitation and settling of suspended solids. Flocculating polymers, heavy metal ions, and adsorbed organic salts are some of the more commonly used materials. They all generally increase coagulation by charge neutralization. Suspended solids normally carry a static charge that causes the individual particles to repel one another and, thus, hinder coagulation and subsequent settling. Flocculating agents neutralize these charges and act as coagulation centers.

The flocculating agents that were tested for efficacy are listed in Table II. Flocculating polymers were being investigated for other purposes when the problem of CaF_2 suspensions occurred. Thus, the two polymers tested were those known to work well with suspensions of lime in water. The results, however, obviously showed that what works well with lime does not necessarily work well with CaF_2. In all tests, the supernatant liquid was turbid and remained so for more than 24 hours. The best results were obtained with ferric ion and sodium dodecyl sulfate. Sodium dodecyl sulfate was judged superior because of the lack of turbidity in the supernatant liquid when it was used in concentrations of 250-500 ppm. Also, the disposition of the iron-containing sludges produced when ferric ions are used is more difficult. Results obtained using combinations of the three best flocculants proved to be disappointing. As shown in Table II, the combination of TFL-352 and sodium dodecyl sulfate produced a sludge of such voluminous nature that it would fill the HF neutralization pit. The combination of TFL-352 and ferric ion was totally ineffective; the two flocculants appeared to counteract each other, leaving the suspension virtually untouched.

TABLE II TESTS OF FLOCCULATING AGENTS*

Agent	Concentration (ppm)	Observations and Remarks
Flocculating Polymers		
Tretolite TFL-352	1* *	Stirred for 15 minutes. Some good floc formed, settled out fairly quickly. Supernatant liquid very turbid. Did not clear after 24 hours.
Tretolite TFL-352	100	Stirred for 5 minutes. Very good floc, but supernatant liquid still turbid.
Dow XRF-4111L	1* *	Stirred for 15 minutes. Small floc which settled slowly. Supernatant liquid very turbid. Did not clear after 24 hours.
Inorganic Salts		
Sodium Silicate (50% aqueous solution)	1000	Stirred for 5 minutes. Very small floc with extreme turbidity in supernatant liquid.
Fe^{+3} (as $FeCl_3$)	1000	Stirred for 5 minutes. Good floc, fast settling, low turbidity.
Organic Salts		
Sodium Dodecyl Sulfate	1000	Stirred for 5 minutes. Very good floc, fast settling, some turbidity.
Sodium Dodecyl Sulfate	500	Stirred for 5 minutes. Very good floc, settling within 10 minutes, no noticeable turbidity.
Sodium Dodecyl Sulfate	250	Same as 500 ppm.
Sodium Dodecyl Sulfate	100, 50	No floc.
Combinations		
1. TFL-352	2	Stirred for 5 minutes. Gives immediate voluminous floc. On settling, floc occupies approximately 2/3 of total volume. Supernatant liquid clear.
Sodium Dodecyl Sulfate	1000	
2. TFL-352	2	No apparent effect. Appears to counteract each other.
Fe^{+3} (as $FeCl_3$)	1000	

* All flocculating tests were performed on 0.1 molar HF solutions that had been neutralized with lime slurry used in a 2:1 ratio. Reaction times were always at least one-half hour.

Flocculating polymers were added as 1 ppm aqueous solutions. $FeCl_3$ was added as either solid crystals or concentrated aqueous solutions. Sodium dodecyl sulfate was added as either powder or concentrated aqueous solution.

* * Concentration normally recommended by manufacturer.

PROPOSED PLANT NEUTRALIZATION SYSTEM

Figure 8 is a schematic of a proposed plant neutralization system. In an actual release of HF, the following sequence of events is envisaged. Upon the detection of an HF leak, an automatic sprinkler deluge system would activate and flood the enclosure with water spray. Most of the released HF would presumably be dissolved in the water spray and led, via piping, to a neutralization pit. The fluoride content of the containment water would be monitored with fluoride electrode #1. Output from the electrode could be used to control a lime slaker or a slaker could be controlled manually using the output from the electrode to determine the amount of lime needed for neutralization. As Section 1 begins to fill, the stirrer would be started to keep the mixture in constant motion. Section 1 would fill until the level of the first baffle is reached, at which point the mixture would cascade over the baffle and begin to fill Section 2. The Section 2 stirrer would be started at this point to insure thorough mixing and to prevent settling. If, at this point, the leak at the HF tank farm has been repaired, the water spray would be stopped and Sections 1 and 2 would be stirred until fluoride electrode #2 indicates that reaction is complete. Stirring would be continued as the required amount of sodium dodecyl sulfate (250-500 ppm in the final solution) is added to both sections. Stirring would be stopped approximately 5 minutes after addition of the sodium dodecyl sulfate, and the sludge allowed to settle for at least 15 minutes. Water could then be introduced to Section 1 to flush and dilute the supernatant liquid until Sections 3 and 4 are filled. The fluoride concentration of the effluent would be measured and monitored with fluoride electrode #3.

Should the leak not be stopped by the time Section 2 is one-half to three-quarters filled, sodium dodecyl sulfate should be added to Sections 1 and 2 with continued stirring. Excess mixture would flow into Section 3 where the sludge would settle out. Once the leak is stopped, stirring could be halted in Sections 1 and 2 and the sequence above could then be resumed.

In the event that the leak could not be stopped by the time Section 4 begins to fill, stirring in Sections 1 and 2 should be continued and additional sodium dodecyl sulfate added as needed in the hope that sufficient settling would occur in Section 3 and, to a limited extent, in Section 4 and that the fluoride content of the effluent would not increase drastically. The fluoride content would certainly be much lower than if there were no treatment at all.

As soon as the situation is under control and it is certain that the effluent meets environmental standards, the neutralization pit sections could be pumped free of liquid. The sludge could then be pumped out for disposal or allowed to dry before removal.

Determination of the amount of lime to be used in a release situation would have to be made at the time of the release since both the concentration and flow rate of the HF solution to be neutralized must be known. However, preliminary calculations could be made to lay a foundation for later use. Continuing with the assumption that a typical HF

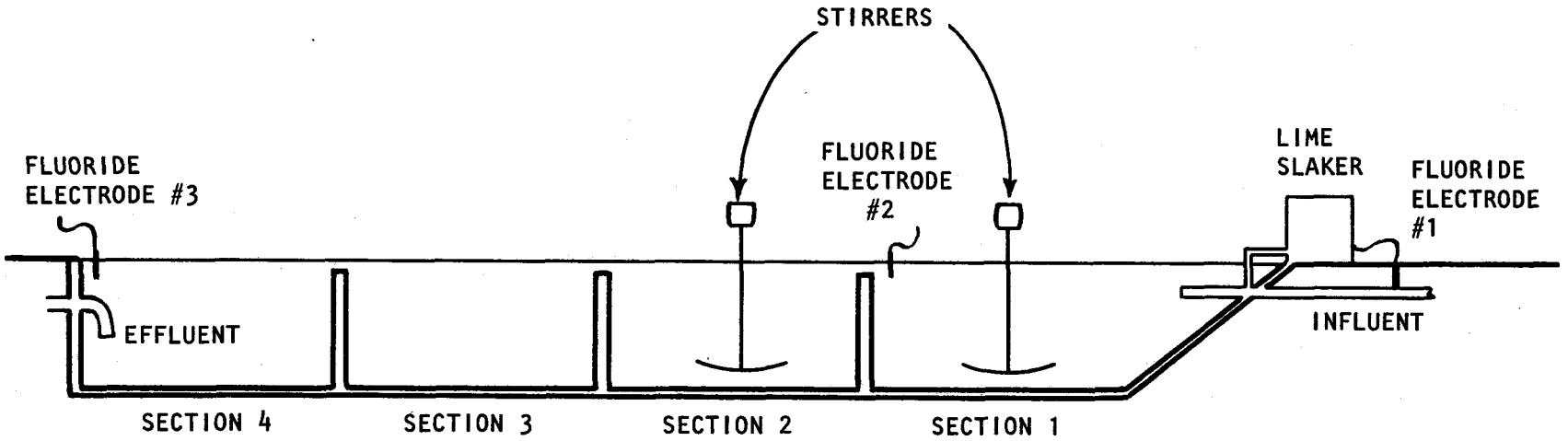

FIGURE 8 SCHEMATIC OF PROPOSED SYSTEM

solution will be 0.1 molar, 93.8 pounds of lime would be needed to neutralize 1000 gallons of the solution. This figure was calculated on the basis of using a 2:1 molar ratio of lime to HF.

The amount of sodium dodecyl sulfate that would be needed is easier to estimate since it is dependent only on the total volume of solution and not on HF concentration. Thus, 2.09 pounds of sodium dodecyl sulfate added to 1000 gallons of liquid would produce a solution that contains 250 ppm of the salt.

CONCLUSIONS

Laboratory test results have shown that a lime/water slurry method could be successfully used at the HF tank farm to neutralize an HF release providing certain minor modifications are made to the existing HF neutralization pit. This method could be adapted for use in any facility that contains fluoride in aqueous solution.

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