United States
Environmental Protection
Agency

Research and Development

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/S2-83-085 Jan. 1984

Project Summary

Polishing Industrial Waste Stream Effluents Using Fly Ash-Natural Clay Sorbent Combination

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Described herein is a laboratory evaluation of the use of new, fly ash-natural clay sorbent combinations and, of the use of activated alumina for the polishing of industrial effluent containing fluorides and heavy metals. The work was conducted at the New Jersey Institute of Technology in Newark, New Jersey.

The new sorbent materials studied were acidic and basic fly ashes and natural clays such as bentonite, bauxite, illite, kaolinite, zeolite, and vermiculite.

Industrial waste effluents (3.8 x 10^6 liters per day) generated by the feldspar mining and processing industry contained significant concentrations of fluoride, iron, lead, chromium, and cadmium.

In the laboratory evaluation, activated alumina treatment was included for comparison with the effectiveness and cost of treatment using the new sorbent combinations.

The most effective new sorbent combination for the feldspar waste stream was a mixture of illite, basic fly ash, and lime. Lime was used to maintain a pH of 6.3.

Fluoride and iron in the wastewater were reduced from concentrations of 17.5 mg/l and 4.5 mg/l to 1 mg/l and 0.020 mg/l, respectively. Lead, chromium, and cadmium concentrations were reduced from 0.12 mg/l, 0.05 mg/l, and 0.15 mg/l to 0.013 mg/l, 0.015 mg/l, and 0.010 mg/l, respectively.

While the treatment process was designed for maximum removal of fluoride, it also provided effective removal of the heavy metals. Maximum removal of fluoride was achieved at a pH of 6.3 with a minimum contact time of six hours between the sorbent and waste stream.

Regeneration of the spent sorbent can be accomplished with 1% H_2SO_4. A 20% loss in sorbent capacity was observed after the first regeneration. Subsequent regenerations resulted in no further loss of sorbent capacity.

Estimated materials costs for the illite/basic fly ash/lime sorbent combinations with spent sorbent regeneration are 13.3 cents per 3.8 x 10^3 liters (1000 gallons) of wastewater. The use of activated alumina with regeneration costs twice as much.

Estimated materials costs for the illite/basic fly ash/lime sorbent combination used once (without regeneration) are 45 cents per 3.8 x 10^3 liters (1000 gallons) of wastewater.

Activated alumina without regeneration costs $4.95 per 3.8 x 10^3 liters (1000 gallons) of wastewater.

Disposal of the spent illite/basic fly ash/lime sorbent combination, when no regeneration is done, should pose no problem. Repeated washing showed no significant loss of sorbed cations and anions.

This report was submitted in fulfillment of Grant No. R-805666 by the New Jersey Institute of Technology under the sponsorship of the U.S. Environmental Protection Agency. This report

covers the period October 1, 1977 to October 31, 1978, and work was completed as of December 31, 1978.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of this laboratory investigation was to establish the feasibility, both technically and economically of using inexpensive combinations of fly ash and clays as new sorbents for a polishing treatment of industrial wastewaters.

The new sorbents have been found effective for removal of heavy metals, toxic anions, and organics from leachate that is generated from industrial sludges deposited in landfills (EPA-600/2-80-052, June 1980).

The present study explores the use of fly ash/clay sorbent combinations for a polishing treatment of an industrial effluent for the removal of fluorides and heavy metals.

The wastewater used for this investigation came from a feldspar mining and processing operation generating wastewater at a rate of 3.8×10^6 liters per day.

The study was undertaken to investigate the removal of fluorides, heavy metals, and organics that may be present in significant concentrations in this waste stream.

Materials and Methods

Materials

The sorbent materials selected for this investigation were fly ashes, zeolite, vermiculite, illite, kaolinite, bauxite, bentonite, and activated alumina, the latter for comparison purposes. The selection of these materials was based on economic considerations, availability, and potential for pollutant removal. Origin and preparation of sorbent materials is described in the final report.

The wastewater used in this study resulted from mining and processing of feldspar ore. The wastewater was collected in five 5-gallon, lined drums and transported to the laboratory. Three shipments of the wastewater, three drums each time, were made during the one-year study. The results of the analysis of three separate shipments of wastewater are listed in Table 1.

Table 1. *Analysis of Feldspar Wastewater*

Contaminants	*Concentration mg/l*		
	Sample 1	*Sample 2*	*Sample 3*
F	*4.0*	*17.5*	*5.8*
Cel	*27*	*32*	*39*
CN	*0.0*	*0.009*	*0.008*
SO_4	*64*	*82*	*57*
Ca	*5.2*	*6.7*	*11.3*
Cd	*0.009*	*0.007*	*0.015*
Cr	*0.007*	*0.008*	*0.05*
Cu	*0.035*	*0.047*	*0.02*
Fe	*1.8*	*4.5*	*0.3*
Mg	*1.7*	*3.7*	*1.9*
Ni	*0.054*	*0.044*	*0.15*
Pb	*0.019*	*0.013*	*0.12*
Zn	*0.054*	*0.076*	*0.18*
COD	*14*	*20*	*18*
pH	*5.5*	*4.9*	*6.3*

Methods

The investigation was performed in three different phases: (1) static studies, (2) dynamic studies, and (3) spent sorbent regeneration.

1. *Static studies:* The static studies evaluated the effectiveness of sorbents for removal of major contaminants from feldspar wastewater, the effect of pH on sorbent capacity, the relation between sorbent capacity and the desired effluent concentration, and the length of contact time between sorbent and wastewater. Sorbent materials were contacted with wastewater in an Erlenmeyer flask.

2. *Dynamic studies:* Lysimeter studies provided dynamic conditions to evaluate the removal capacity of the most effective sorbent mixture, illite/basic fly ash/lime, (determined as a result of static studies), for fluorides and iron present in the feldspar wastewater. Two different hydraulic systems were studied; gravitational flow and expanded-bed flow. Lysimeters were constructed of Plexiglass* tubing, supported in a vertical position.

In the gravitational flow operation, wastewater was fed to the top of the column. A constant hydraulic head was maintained in the lysimeters at all times, and the volume of wastewater through the packed sorbent material was continuously monitored.

In the upflow expanded-bed operation, the wastewater was fed through the bottom of the bed at a velocity sufficient to expand the bed without loss of the sorbent in the overflow.

3. *Sorbent regeneration:* The spent regeneration studies were carried out under batch conditions. A 1% solution of sulfuric acid was used as the reagent.

*Mention of tradenames or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

Results and Discussion

Results of Static Studies

The sorbent materials were examined for their effectiveness to remove fluoride and iron from wastewater because these two contaminants were present at highest concentrations in the feldspar wastewater (see Table 1). Both illite and kaolinite showed comparable removals in reducing the fluoride concentrations to below 1.5 mg/l (Figure 1).

Basic fly ash was found most effective in reducing iron from 1.8 mg/l to 0.02 mg/l (Figure 2).

The illite sorbent capacity for removal of fluoride shows dependence upon pH, with optimum pH for fluoride removal at pH of 6.3. The *Kaolinite sorbent capacity* for fluoride removal shows no dependence on pH (Figure 3).

The sorbent capacity of a sorbent and for a given pollutant decreases as the initial concentration of the pollutant decreases in the waste stream. Understanding the relationship between sorbent capacity and desired effluent concentration is important in estimating the amount of sorbent required to achieve the desired effluent concentration.

A minimum contact time of six hours between the sorbents and feldspar wastewater is required to insure maximum removals of fluoride.

Results of Lysimeters Studies

Based on the results of static studies, a mixture of 50% illite and 50% basic fly ash was selected for lysimeter studies to

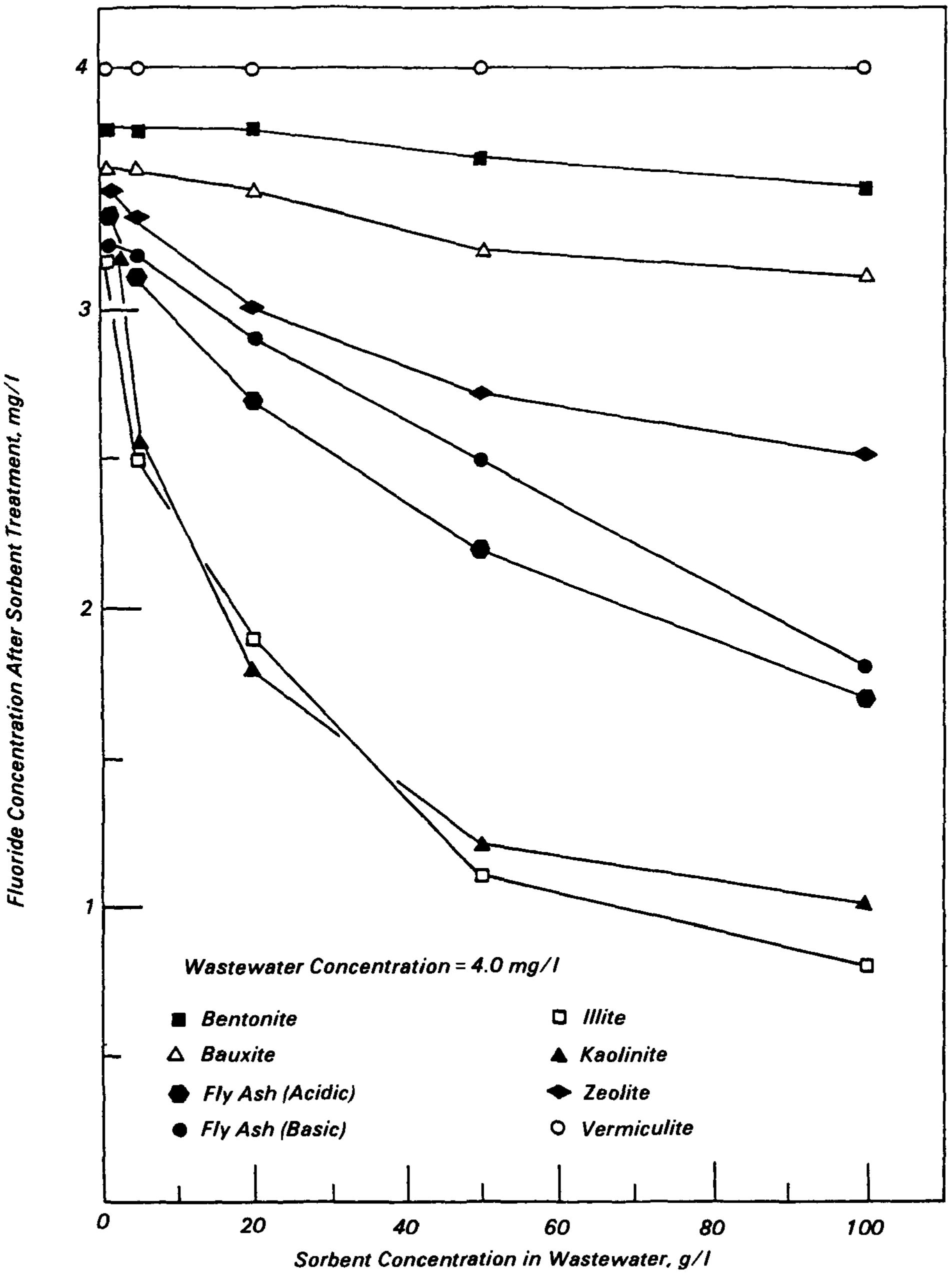

Figure 1. Fluoride treatment (batch conditions).

determine that mixture's effectiveness in reducing both fluoride and iron to acceptable levels under dynamic (flowing) conditions.

Gravitational Flows

Experiments performed under gravitational flow operation showed that the sorbent particle size range influenced the reduction of fluoride (best removals at small particle size ranges) but did not effect the removal of iron (Figure 4).

Increases in sorbent particle size ranges allow larger flows, but at the same time it significantly decreases the effectiveness of the sorbent bed for removal of fluoride.

Experiments with gravitational flow showed that very large flows cannot be handled by sorbent beds under gravitational feed. Thus, passing of the feldspar wastewater in the amount of 3.8 x 10^6 liters per day would be impractical.

On the other hand, experiments with the upflow expanded-bed treatment showed that large volumes of wastewater can be easily treated in this way, and adequate contact time for the sorbent to interact with the wastewater can be maintained. Operation of the upflow expanded-bed in the illite/basic fly ash/lime sorbent mixture in the lysimeters resulted in reduction of fluoride levels from 5.8 mg/l to 1.5 mg/l in the feldspar wastewater (Figure 5).

Another practical way of contacting sorbents with industrial wastewaters is by adding the illite/basic fly ash/lime mixture directly to the waste stream. The sorbents added to the waste can be removed in sedimentation basins, provided that adequate settling rates are encountered. Settling tests carried out on the illite/basic fly ash/lime mixture showed that this particular mixture has compatible settling rates.

The use of the new sorbent mixture without regeneration of the spent sorbent is economically and technically feasible.

Conclusions

1. On the basis of laboratory tests, the illite/basic fly ash/lime sorbent combination appears to be effective for treating waste streams generated by the feldspar mining and processing industry. The sorbent combination can be added directly to the waste stream and the spent sorbent removed by sedimentation at a loading rate of 1.77 x 10^4 l/m²/day (432 gal/ft²/day). Also, the waste stream can be treated in a sorbent bed operated in an upflow expanded-bed mode. A six-foot-deep sorbent bed can treat the above flows at a loading rate of 7400 l/m² (180 gal/ft²). This sorbent combination reduced the iron, lead, chromium, cadmium, and fluoride concentration to levels that are generally acceptable for potable water supplies.
2. Reliance upon gravitational flow through the sorbent bed is impractical for treatment of a feldspar waste stream. The permeability of sorbents limits the treatment to loadings as low as 575 l/m²/day/ (14 gal/ft²/day). A sorbent bed with surface area of 6.7 x 10^3 M² (7.2 x 10^4 ft²) would be required to avoid ponding at a 3.8 x 10^6 l/day / (1 MGD) flow rate.
3. Increasing the gravitational flow through a sorbent bed by increasing the particle size in the bed is not practical for treating large volumes of wastewater. An increase in the particle size results in a decrease in the volume of wastewater that can be treated with a given weight of sorbents. Ap-

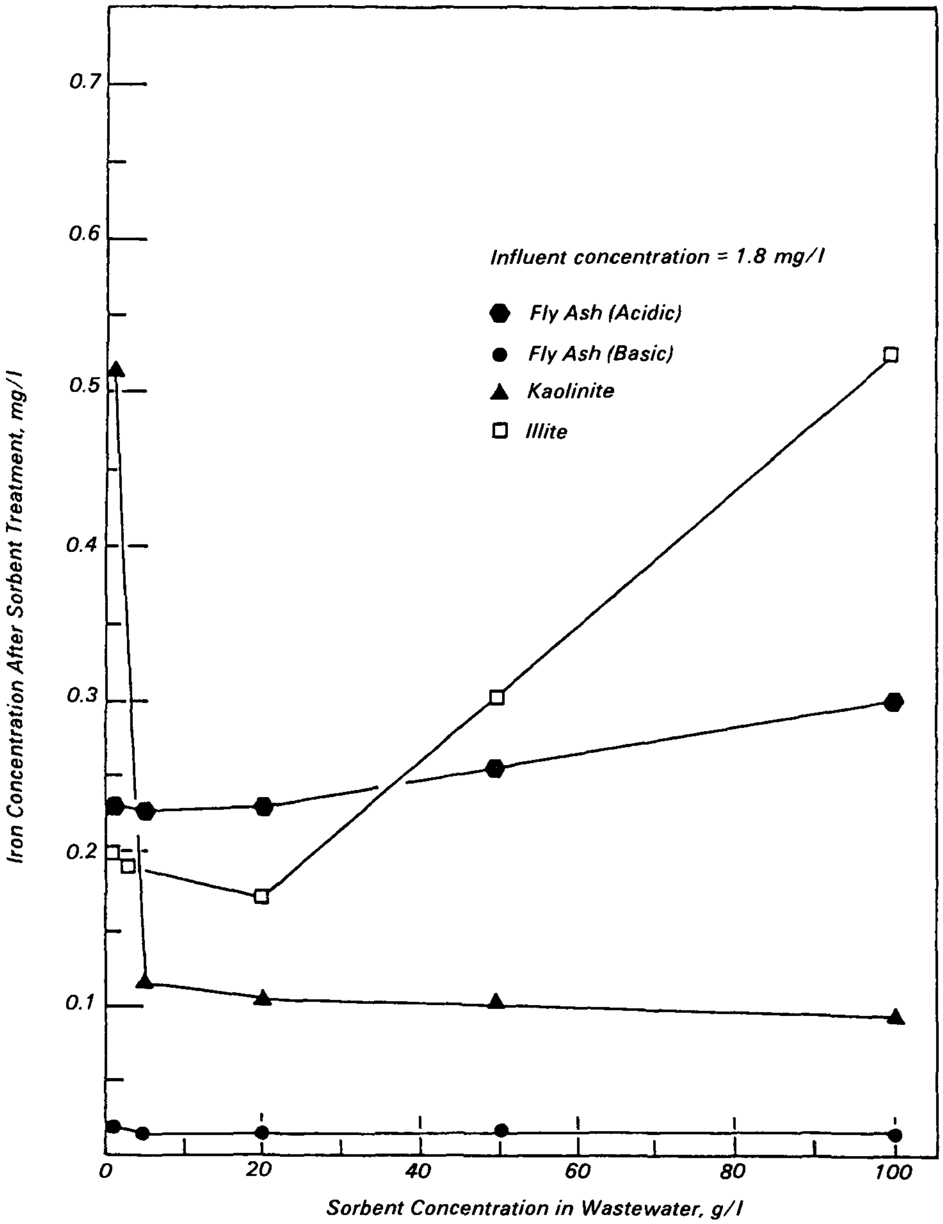

Figure 2. *Iron treatment (batch conditions).*

parently, the advantage of the increased pore volume of the bed by increasing the particle size is offset by a reduction in the sorbent capacity due to the decrease in particle surface area encountered with the larger particles.

4. The conditions required for maximum removal of the fluoride also provide effective treatment of iron, lead, chromium, and cadmium present in the feldspar waste stream. The maximum sorbent capacity for the removal of fluoride occurs at a pH of 6.3, with a contact time of six hours between the sorbents and wastewater.
5. The material costs associated with the use of the illite/basic fly ash/lime sorbent for treating 3.8×10^3 l (1000 gallons) of feldspar waste stream with regeneration is estimated on the basis of laboratory scale testing to be one third that associated with the use of activated alumina. These costs amount to 13 cents per 3.8×10^3 and 45 cents per 3.8×10^3 l for the sorbent combination and activated alumina, respectively. The difference is primarily associated with the use of NaOH in the regeneration of activated alumina.
6. It appears that the spent sorbent combination may be disposed of easily. The sorbent contaminants do not seem to pose any threat to ground or surface waters. Repeated washing of different amounts of sorbents did not indicate any fluoride concentration above 1.1 mg/l in the rinse water. This eliminates the problem associated with the disposal of a metal hydroxide as CaF_2 sludge from the regeneration process. However, replenishing the spent sorbents with unused sorbents raises the treatment costs to 45 cents per 3.8×10^3 liters. Disposal of spent activated alumina without regeneration would amount to $4.95 per 3.8×10^3 liters.

Recommendations

The results of this investigation show that, on a laboratory scale, the use of clay/fly ash sorbent combination for polishing the fluoride, iron, lead, chromium, and cadmium in waste stream flows from the feldspar mining and processing operation is both technically and economically feasible.

An industrial-scale project should be undertaken with the cooperation of Federal agencies to demonstrate the use of the fly ash/clay sorbent combination for polishing the heavy metal-# and fluoride-bearing waste streams on an industrial scale.

The development of inexpensive treatment technology would benefit industries that have treatment facilities but require additional polishing of their effluents for removal of heavy metals and fluoride to meet state and federal guidelines.

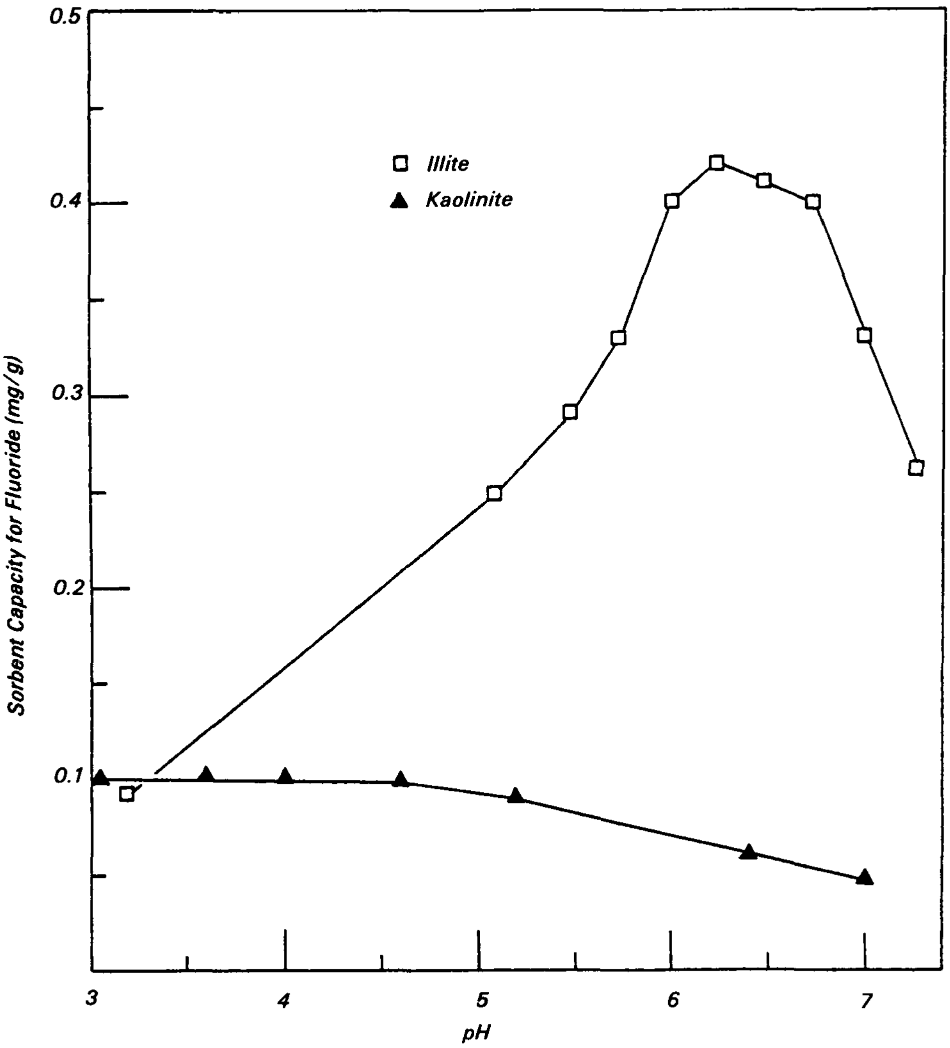

Figure 3. *pH effect on sorbent capacity for fluoride (batch conditions).*

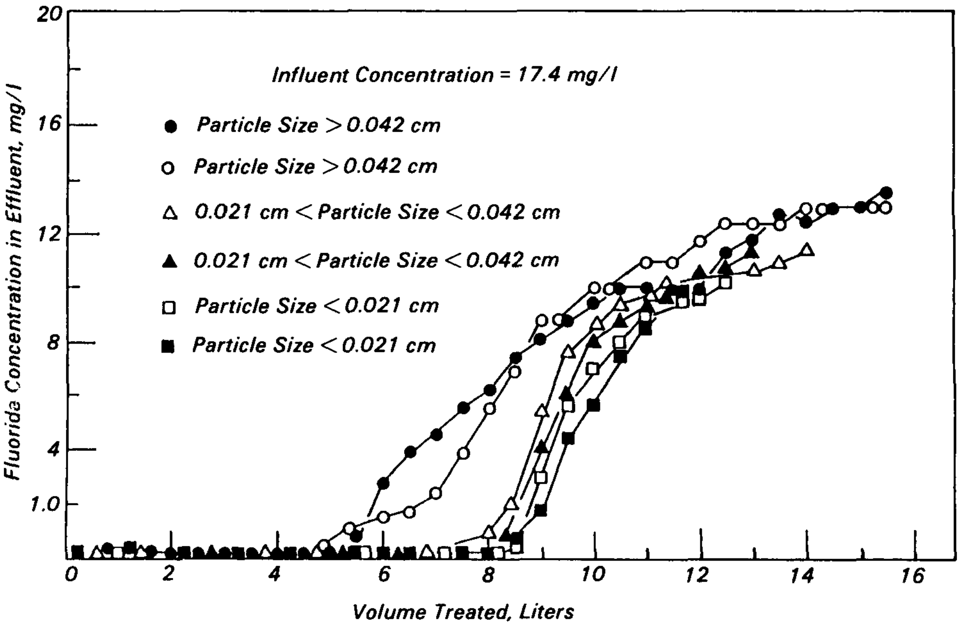

Figure 4. *Fluoride removal dependence on sorbent particle size (gravitational flow).*

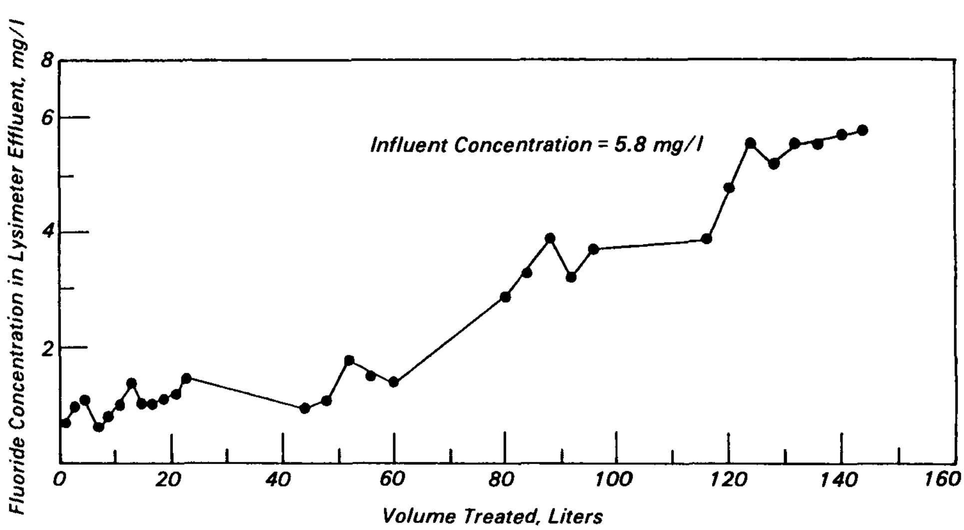

Figure 5. *Fluoride treatment (expanded bed flow).*

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***Mary K. Stinson** is the EPA Project Officer (see below).*
The complete report, entitled "Polishing Industrial Waste Stream Effluents Using Fly Ash-Natural Clay Sorbent Combination," (Order No. PB 83-259 663; Cost: $10.00, subject to change) will be available only from:
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