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TREATMENT OF WASTE WATER FROM S-40 ROCKET FACILITY

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I The use of liquid fluorine as a rocket oxidant results in exhaust products containing hydrogen fluoride. The hydrogen fluoride is absorbed in the water supply used to cool the exhaust products and is collected as a 0.78% HF solution in the waste receiver. The spray cooling design specifications and water requirements are presented in a report by P. M. Ordin and T. W. Reynolds. The HF solution cannot be disposed of in the storm or sanitary sewer because of the safety restrictions on the allowable limits of fluoride concentrations. Several methods of removal of the fluorine waste are presented below:

A. Treat exhaust waste with calcium hydroxide (or other chemicals) which precipitates the fluoride as insoluble $Ca\ F_2$. Allow the solids to settle in the receiver, pump the supernatant liquid into the sanitary sewer and collect the solids for disposal. The solid matter from the waste receiver can be treated as follows:

(a) Pump $Ca\ F_2$, $Ca(OH)_2$ slurry to a collection pit, allow it to settle for removal as dry cake which serves as an excellent fill material.

(b) Pump slurry through filter and collect dry cake for fill.

(c) Pump slurry into portable tank and dispose in safe area.

B. Treat the exhaust waste with NaOH which yields a 1.7% NaF solution. This waste to be removed as follows:

(a) Dispose through NACA sanitary sewer system after dilution to allowable fluoride concentration.

(b) Load into portable tank cars and dispose in safe area.

C. Collect 0.75% HF solution in receiver and dispose of as with the NaF solution.

II Methods of Removing Fluorides from Water

A. Calcium Phosphates

The use of bone for removing fluorides is probably based on the anion exchange properties of apatites. The carbonate radical in the apatite comprising bone, $nCa_3(PO_4)\ CaCO_3$ is replaced by the fluorides in the water, forming an insoluble fluorapatite. The material is regenerated with sodium hydroxide and the fluoride removed in the form of the soluble sodium fluoride. The estimated cost of using this method would be about $25,000 per m.g. fluoride. A similar process utilizes animal charcoal which is essentially tricalcium phosphate and carbon. A porous, granular type of tricalcium phosphate has been developed for use in contact filters. When the fluoride removal capacity of the bed is exhausted, the material can be regenerated with a 1% NaOH solution; one pound caustic soda is required per cu. ft. of tricalcium phosphate. The chemical costs for the fluoride removal process at this plant totaled about $130 per m.g.

B. <u>Adsorption with Aluminum Compounds</u>

Materials, including aluminum sulfate, sodium aluminate, zeolites, bauxite, silica gel, sodium silicate, and various adsorbent clays and earths, have been tested. With the exception of aluminum sulfate, all of the materials were found to be impracticable. Aluminum sulfate and other aluminum salts used in combination with insoluble compounds in contact beds or as a flocculant mass remove the fluoride by the formation of an aluminum fluoride complex or by adsorption on the floc. The material is removed by settling and filtration. Results indicate that concentrations of hydrous aluminum sulfate from 335 to 513 p.p.m. are required to remove 4 p.p.m. of fluoride con. In order to obtain maximum fluoride reductions, optimum hydrogen ion concentration is necessary. Dehydrated aluminum oxide or partially hydrated alumina have been suggested for use in contact beds. Calcined alumina has been tried in field tests and rated as fairly good with respect to fluoride removal efficiency. When the bed becomes exhausted, the fluorides are removed by washing with a dilute caustic solution. Cost for these methods is about $275 per m.g.

C. Ion Exchange Process

Organic resinous anion exchange material made from various diaminobenzenes or phenols and formaldehyde are somewhat selective for fluorides yielding insoluble hydroxides. The material is first conditioned with a 4% soda ash solution, neutralized with a dilute acid and soaked with a 4% solution of aluminum sulfate. The exchange capacity is based on 1,240 grains of fluoride per cu. ft. Chemical costs amount to about $90 per m.g.

The above methods have been considered for water treatment plants where the task involved is to reduce the fluoride concentration from about 8.5 p.p.m. to 1.5 p.p.m. A concentration of 1 to 1.5 p.p.m. is considered to be safe for drinking water. The reported effects of fluorides in drinking water for humans is give in Table I. The recommended procedure for removing large concentrations of fluoride ion is the lime treatment in which the fluoride is removed as the insoluble calcium fluoride. In many instances, further treatment is necessary to reduce the fluoride concentration to the accepted 1 p.p.m.

D. Lime Treatment

Remove the fluoride by forming the insoluble calcium fluoride:

$$2HF + Ca(OH)_2 \longrightarrow CaF_2 + 2H_2O$$

The theoretical quantity of $Ca(OH)_2$ required is 2 lbs. per 1 lb. fluorine. Using the theoretical quantities should result in a concentration of CaF_2 in solution of 0.0017 gr/100 gr H_2O (solubility) which gives a fluoride concentration of 8 p.p.m. To make the water safe for drinking purposes, the fluoride concentration would have to be further reduced to about 1 p.p.m. Experimental work involving the precipitation of CaF_2 from an HF solution with $Ca(OH)_2$ indicates that the reaction does not follow the theoretical quantities. The effective removal of fluorine as CaF_2 seems to depend upon a certain alkalinity due to excess $Ca(OH)_2$. Experiments carried out at General Electric Co. and at the Pennsylvania Salt Manufacturing Co. indicate that the maximum removal of fluoride is obtained when 2.5 to 3 times the theoretical quantity of $Ca(OH)_2$ is used. Experiments at the General Electric Co. indicate that when the calculated excess of $Ca(OH)_2$ drops below about 3000 p.p.m. as $Ca(OH)_2$, they do not get the maximum removal of fluoride.

Results of some General Electric experiments are presented in Table II. For initial fluoride concentrations from 1000 to 5000 p.p.m., the quantities of $Ca(OH)_2$ equivalent to about twice the theoretical, resulted in fluoride concentrations in the filtrate of about 11 to 15 p.p.m. Using six times the theoretical amount of $Ca(OH)_2$, reduced the fluoride concentration in the filtrate to the theoretical value of 7.6 p.p.m. Experiments carried out at the NACA indicated that using about 1.5 times the theoretical amount of $Ca(OH)_2$ reduced the fluoride concentration in the filtrate to about 50 p.p.m. A plot of the fluoride concentration in the filtrate against the quantity of $Ca(OH)_2$ used for both the G.E. and NACA experiments is given in Figure 1.

III Sodium Hydroxide Treatment

A method of treating the HF waste solution is to add NaOH and form NaF, a salt which will be completely soluble in the quantity of water involved. This method of treatment does not remove the fluoride ion and can only be used if the fluoride concentration is reduced to safe limits. The purpose of obtaining the fluoride as sodium fluoride rather than keeping the waste as an HF solution is for safety. The NaOH treatment results in a neutral solution while the HF solution is acid and harmful.

IV Details of Treatment System for 20,000 Lb. Thrust $H_2 + F_2$ Unit

Propellants -	$H_2 + F_2$
Thrust -	20,000 lbs.
Flow fluorine -	61 lbs/sec

Maximum capacity of fluorine tank - - 9600 lbs.

Maximum running time (Fluorine tank capacity) -- 157 sec.

Water flow - - - - 50,000 g.p.m.

Total water used in run

start	-	15 seconds
run	-	157 seconds
end	-	15 seconds
Total time - -		187 seconds

Maximum water - - (187)(6900) = 1,290,000 lbs. = 156,000 gal.

Concentration of HF in waste water

- assume all HF absorbed in water - $\frac{10,120}{1,290,000}$ = 0.78% HF

lbs. HF in water = 10,120 lbs. (506 mols)

Concentration of fluoride ion in water - 7460 p.p.m.

The safe concentration of fluoride ion that could be released from the NACA site through the sewer system is about 5 p.p.m. Since the waste water in the collection tank contains a fluoride concentration of 7460 p.p.m., a dilution rate of 1500 - 1 would be required. The quantity of waste water in the receiver for various engines running times is given below:

Run time, seconds	Waste water, gallons
157	156,000
120	142,000
90	113,000
60	75,000
30	50,000

The necessary dilution of 1500 gallons per 1 gallon of waste solution can be obtained by a combination of using the water that normally flows through the sanitary sewer system and making up the difference, to the required amount, by the addition of fresh water. Records of the flow through the sanitary sewer system at the NACA have indicated a minimum flow of 170 g.p.m. with an average daily flow for the seven day week of about 350 - 450 g.p.m. The NACA sanitary sewer system provides for a pumping station on the NACA site which then leads into the City system at the Hillside-Grayton pumping station. A by-pass system is also provided in both the NACA and City sanitary sewer system which permits an overflow into the storm sewer when the flow exceeds about 600 g.p.m. in the NACA system and over 800 g.p.m. in the City system.

Using a value of 170 g.p.m. as the water available for dilution from the sewer system, the removal of the HF solution by dilution would require an input of 1330 g.p.m. for 1 gallon of waste solution.

The addition of 1330 g.p.m. for 1 gallon of the waste solution would result in a fluoride concentration at the NACA pumping station of 5 p.p.m., a safe concentration.

The quantities of water involved, however, would result in an overflow into the storm sewer since the flows would be over 600 g.p.m. The overflow would be safe with respect to the fluoride concentration but would be dangerous because of its acid nature. The HF solution (.73%) stored in the reservoir is toxic and would be difficult to handle; the diluted waste containing 5 p.p.m. of fluoride is still somewhat dangerous since the solution has a Ph of 4. The limits established by the City of Cleveland with respect to waste concentrations are presented in Table III and indicate acceptable Ph limits between 5.5 and 9.

Treating the HF solution in the waste receiver with sodium hydroxide results in the formation of the sodium fluoride salt which would be completely soluble in the amount of water present. This solution is neutral or slightly basic. The problem of reducing the fluoride concentration with this solution is the same as with the HF solution. A dilution rate of 1500 gallons per 1 gallon of waste solution would have to be used to obtain 5 p.p.m. of fluoride ion. Using the 170 g.p.m. existing in the sewer as part of the necessary dilution and adding the additional 1330 g.p.m. of water, the time required to empty the waste water receiver, at a pumping rate of 1 g.p.m., is given below:

Engine running time	Total time
157 sec.	10.9 days
120	9.9
90	7.8
60	5.2
30	3.5

The quantities of dilution water required vary from 66,000,000 to 208,000,000 gallons and the emptying times at a rate of 1 g.p.m. vary from 3.5 to 11 days. These quantities and times are excessive and appear to make this method of removal undesirable.

VI A second technique of removing the waste is to dispose of either the HF or NaF solution off the NACA site. The solution can be pumped into truck tank cars and driven to a safe area for dumping. The largest truck tank car available has a capacity of 6000 gallons necessitating from 10 to 26 trips to empty the waste receiver. The disposal off the NACA site remains a problem since the material will continue to be capable of creating a public nuisance

VII Reaction with $Ca(OH)_2$

$$2\ HF + Ca(OH)_2 \longrightarrow CaF_2 + 2\ H_2O$$

The reaction with $Ca(OH)_2$ forms an insoluble precipitate of CaF_2 and removes most of the fluorides from the solution. As previously stated, the efficiency of removal of the fluoride ion as CaF_2 is dependant upon the amount of $Ca(OH)_2$ used. From Figure 1, using 1.5 times the theoretical amount of $Ca(OH)_2$ would yield a fluoride concentration of about 45 p.p.m.; 1.75 times the theoretical, a fluoride concentration of about 38 p.p.m. and twice the theoretical, a concentration of 30 p.p.m.

The amounts of $Ca(OH)_2$ required, CaF_2 collected and density of the solid mixture for the different running times are given in Table IV. Using 1.75 times the theoretical quantity of $Ca(OH)_2$ would require a reduction in fluoride concentration from 38 p.p.m. to 5 p.p.m., a dilution rate of 7.5 to 1. Since the minimum flow in the sanitary sewer system is 170 g.p.m., a flow of the supernatant liquid of 22 g.p.m. would be sufficiently diluted to provide 5 p.p.m. at the NACA pumping station. In addition, since this total flow of 192 g.p.m. is far from the overflow rate of 600 g.p.m., the solution will be further diluted to about 2 p.p.m. at the Hillside-Grayton pumping station. Should the flow in the NACA sanitary sewer reach the overflow rate of 600 g.p.m. and the waste solution pumping rate maintained constant at 22 g.p.m., the fluoride concentration in the overflow would be only 1.7 p.p.m.; a completely safe concentration.

It is suggested that the $Ca(OH)_2$ treatment be employed using 1.75 times the theoretical quantity. The solid CaF_2 - $Ca(OH)_2$ mixture would be allowed to settle and the supernatant liquid pumped into the sanitary sewer at a rate of about 30 g.p.m. The supernatant liquid would conform to the sewer waste specifications with a Ph of about 8. The Ph of the supernatant waste in the collection vessel is around 9 and is reduced to about 8 when diluted. A plot of Ph of the supernatant liquid against the amount of $Ca(OH)_2$ is given in Figure 2. With a pump rate of 30 g.p.m. for the waste solution, the total time for emptying the tank is as follows:

Running time, sec.	Total time, days
157	3.6
120	3.3
90	2.6
60	1.7
30	1.2

VIII Removing the fluoride as the insoluble CaF_2 introduces the problem of settling and removing the solids. Results of experimental studies of the settling rate of CaF_2 - $Ca(OH)_2$ slurries are presented in Figure 3 . The results of the small scale experiments indicate that with a 1% HF solution and 1.75 times the theoretical quantity of $Ca(OH)_2$, the solids would settle to about 5% of the total volume within 2-3 hours. The nature of the precipitate is loose and flocculant, making it possible to be pumped with a slurry pump. The precipitate has remained in the loose flocculant condition for over 60 hours.

Since the waste receiver will be closed and an integral part of the duct configuration, it would be advantageous to precipitate the fluoride in a separate, open container. The HF solution exiting from the duct into the receiver may be collected as the HF solution or as a NaF solution by adding NaOH. At the completion of the run, the solution can be pumped to a separate open reservoir where the $Ca(OH)_2$ is added and the fluoride precipitated. Schematic diagrams and quantities involved for the processes are given in Figure 4 .

TABLE I

REPORTED EFFECTS OF FLUORIDES IN DRINKING WATER FOR HUMANS

Concentration of fluorides, in ppm.	Reported Effect
0.2	Mottled teeth in 1% of children
0.6	No effects at this concentration, or lower
0.8	No effects at this concentration, or lower
0.6 to .09	Mild mottling of teeth
0.8 to 1.5	Threshold for mottling of teeth
0.9	Mild mottling of teeth
0.9	Mottling occurred as a result of high water use
0.9	Critical concentration for mottling
1.0	Threshold for mottling of teeth
1.0	10% of children had mottled teeth
1.0	90% of children had mottled teeth
1.0 to 2.0	Mild to moderate mottling
1.2	No effect at this concentration
1.4	No skeletal sclerosis found
1.5	Limiting concentration for drinking water
1.7 to 1.8	50% of children had mottled teeth
2.0	Gave mottling and weakening of tooth structure
2.0 to 3.0	Retained in system
2.0 to 3.0	Moderate to severe mottling
2.5	75 to 80% children had mottled teeth
3 to 4	Not likely to cause endemic cumulative toxic fluorosis in adults
3 to 6	Gave Severe mottling
4.0	90% of children had mottled teeth
4.4 to 12	Caused chronic fluorosis and affected skeletal system
5.0	This concentration had no effect on height, weight, of bone structure in adults
6.0	Threshold for appreciable effect on bones
6.0	100% of children had mottled teeth
6.0	Gave pitting and chipping of tooth enamel
11.8	Gave chronic fluorine intoxication to adults.
12	Affects deciduous teeth
13.7	100% of children had mottled teeth
115	Sub-lethal in drinking water
180	Toxic to man in drinking water
2000	Lethal dose in drinking water

(Taken from "Water Quality Criteria" by State Water Pollution Control Board, Sacramento, Calif., SWPCB Publication No. 3, pp. 256, 1952)

TABLE II

REMOVAL OF FLUORIDE FROM WASTE BY TREATMENT WITH $Ca(OH)_2$

General Electric Company results - obtained
by Paul Ordin from Mr. R. W. Goodman -
Glass Technology Laboratory

Sample Weight in grams	Fluoride P.P.M.	Theoretical $Ca(OH)_2$ Required	Grams $Ca(OH)_2$ at Neutral Point	% of Theoretical at Neutral Point	Total $Ca(OH)_2$ Added in grams	$Ca(OH)_2$ Used Theoretical	Fluoride Concentration in Filtrate P.P.M.	Excess $Ca(OH)_2$ in effluent P.P.M.
3200	5124	32.8	22.0	70%	62.0	1.9	12.6	6000
3826	5300	40.0	28.0	70%	84.0	2.1	15.2	11,600
3685	3220	23.8	16.5	70%	49.5	2.1	11.4	7000
3884	1070	8.3	6.3	70%	18.9	2.3	12.4	2700
3798	475	3.7	2.9	80%	9.5	2.6	30.4	1500
3742	494	3.6			22.0	6.0	7.6	1500
3900	323	2.5			15.5	6.2	7.6	3333
3855	334	2.6			10.3	4.0	10.0	2000

TABLE III

SPECIFICATIONS FOR WASTE DISPOSAL

City of Cleveland
Department of Public Utilities
Division of Sewage Disposal

The following is a list of trade wastes that should not be discharged into the city sewers:

a. Any liquid or vapor having a temperature of higher than 150 degrees F.

b. Any water or waste which may contain more than 100 parts per million by weight of fat, oil or grease.

c. Any gasoline, benzene, naptha, fuel oil or other flammable or explosive liquid, solid or gas.

d. Any garbage which has not been properly shredded.

e. Any ashes, cinders, sand, mud, straw, shavings, metal, glass, rags, feathers, tar, plastics, wood and paunch manure.

f. Any water or wastes having a pH lower than 5.5 or higher than 9.0, or having any other corrosive property capable of causing damage or hazard to structures, equipment and personnel of the sewage works.

g. Any water or wastes containing a toxic or poisonous substance such as iron, chromium, zinc, copper and cyanide in sufficient quantity to injure or interfere with any sewage treatment processes.

h. Any water or wastes containing suspended solids of such character and quantity that unusual attention or expense is required to handle such material at the sewage treatment plant.

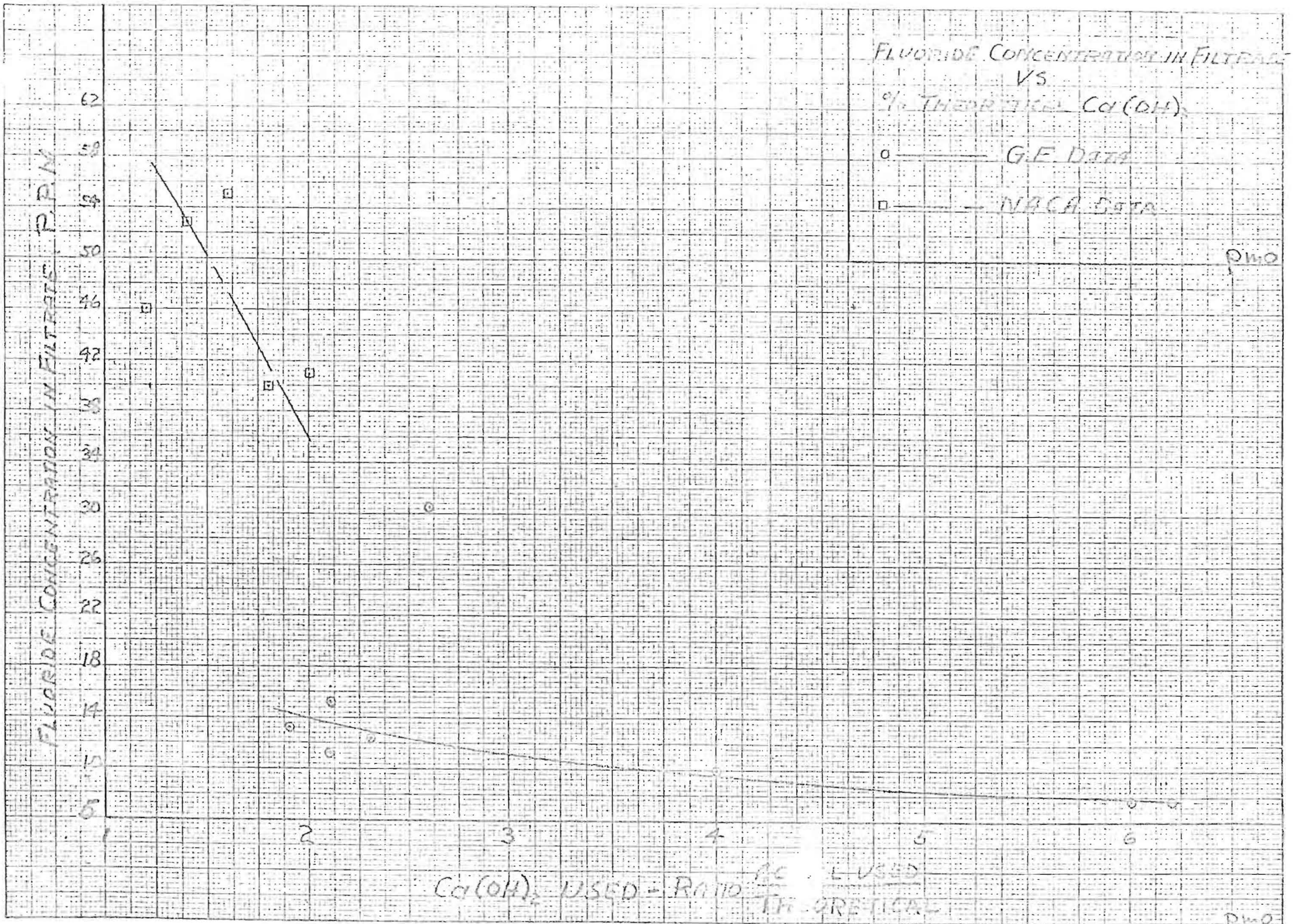
i. Any noxious or malodorous gas or substance capable of creating a public nuisance.

TABLE IV

TOTAL SOLIDS COLLECTED

Run Time Seconds	$Ca(OH)_2$ Required, lbs. (a) ratio $\frac{\text{actual}}{\text{theoretical}}$ 1.5	1.75	2.0	CaF_2 lbs.
157	28,800	33,000	38,400	19,700
120	22,000	25,700	29,400	15,100
90	16,500	19,250	22,000	11,330
60	11,000	12,800	14,650	7,520
30	5,500	6,420	7,320	3,760
Specific Gravity of Solids	(CaF_2 - $Ca(OH)_2$) Mixture			
	2.91	2.84	2.76	

(a) The total amount of $Ca(OH)_2$ required is also the total amount of solids collected since the molecular weights of $Ca(OH)_2$ and CaF_2 are just about the same.

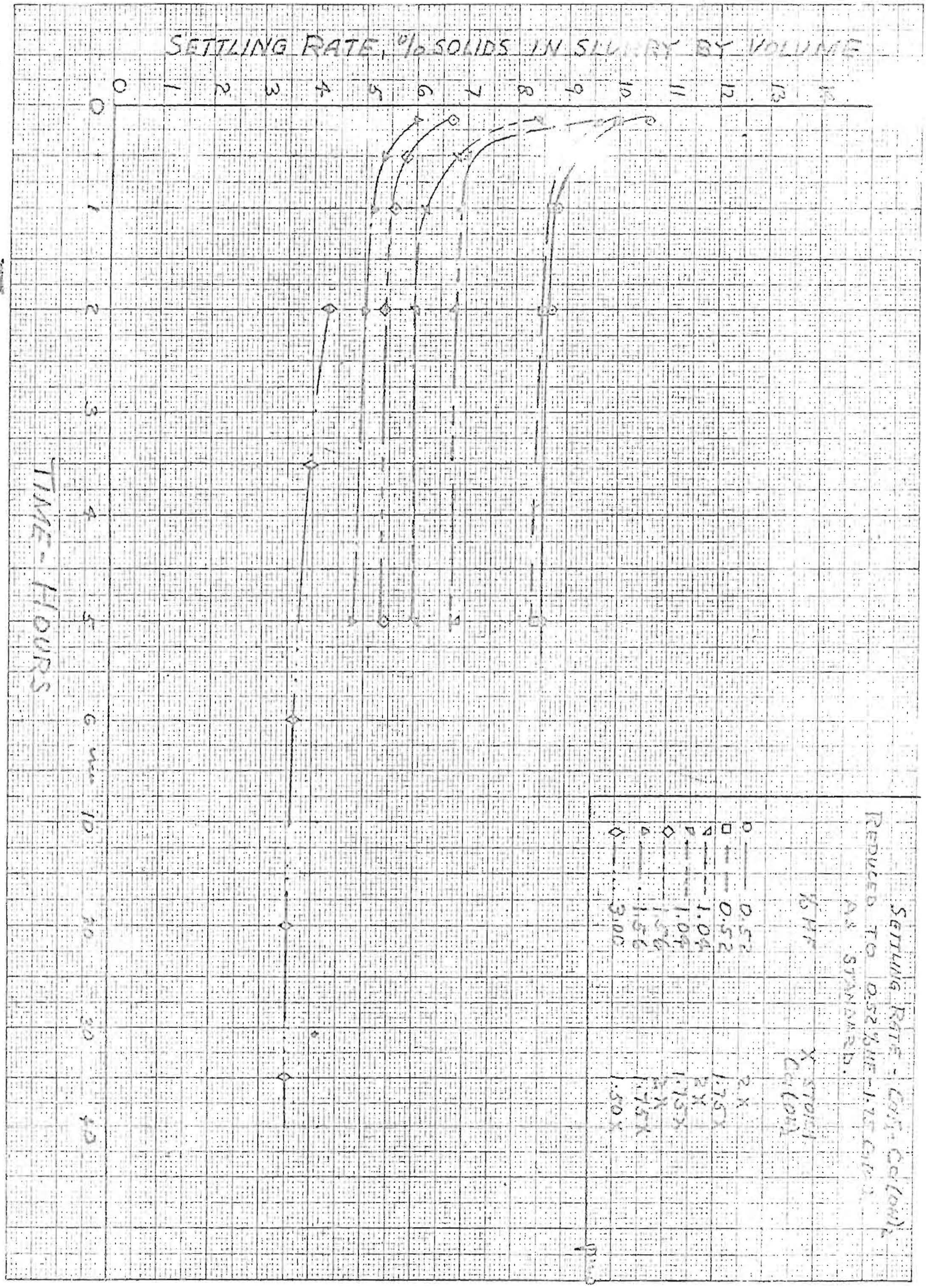


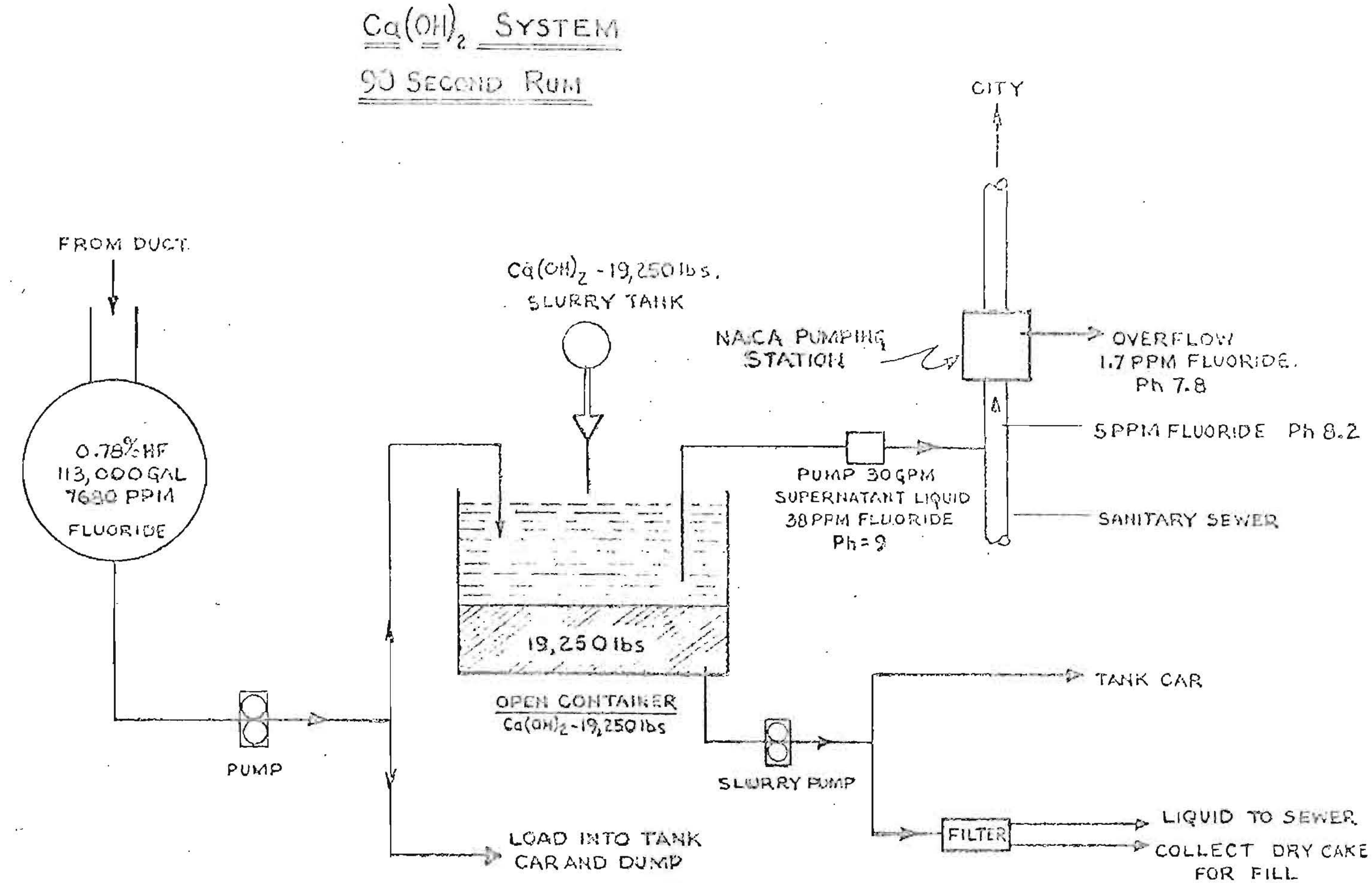
FLUORIDE CONCENTRATION IN FILTRATE
VS
% THEORETICAL Ca(OH)2
G.E. DATA
NACA DATA
FLUORIDE CONCENTRATION IN FILTRATE P.P.M.
62
58
54
50
46
42
38
34
30
26
22
18
14
10
6
1
2
3
4
5
6
Ca(OH)2 USED - RATIO
THEORETICAL
PWO
PWO

FIGURE 1


P.H. SUPERNATANT LIQUID
0
1
2
3
4
5
6
7
8
CLEAR SUPERNATANT LIQUID
CLOUDY
1
8
19
0 .1 .2 .3 .4 .5 .6 .7 .8 .9 .10 .11 .12 .13 .15 .16 .17 .21 .22
STOICHIOMETRIC AMOUNTS OF $Ca(OH)_2$

FIGURE 2


SETTLING RATE, % SOLIDS IN SLURRY BY VOLUME
TIME - HOURS
SETTLING RATE - CaF2 - Ca(OH)2
REDUCED TO 0.52% HF - 1.25 Ca(OH)2
AS STANDARD.
% HF X STOICH Ca(OH)2
0.52 2 X
0.52 1.75X
1.04 2 X
1.04 1.75X
1.56 2 X
1.56 1.75X
3.00 1.50 X

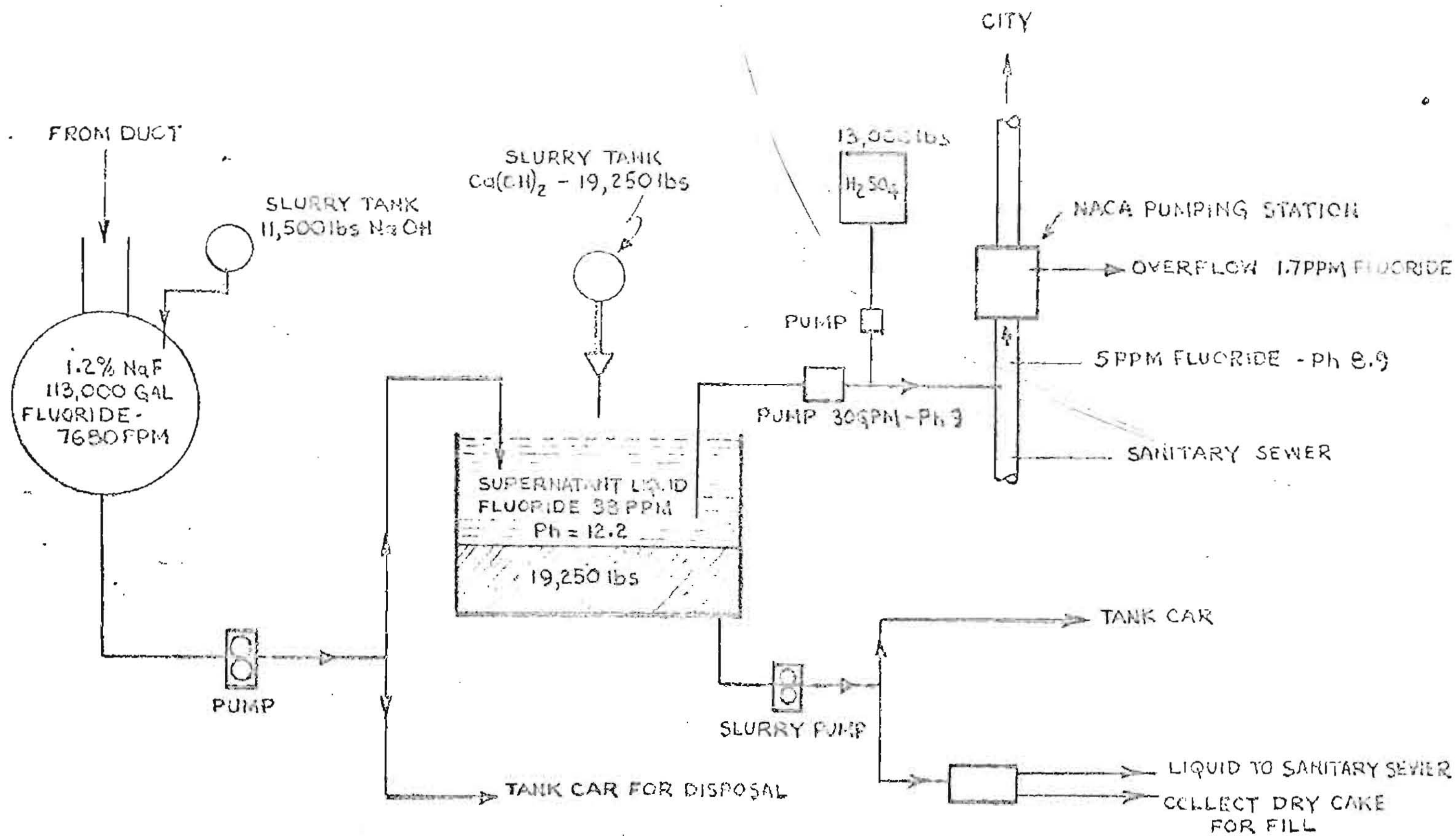


FLOW SYSTEM - FLUORIDE DISPOSAL
$Ca(OH)_2$ SYSTEM - 90 SECOND RUN

CAS-10337 3-3-55

FIGURE 4

BY .... DATE .... SUBJECT .... SHEET NO. .... OF ....
CHKD. BY .... DATE .... JOB NO. ....



FLOW SYSTEM - FLUORIDE DISPOSAL
NaOH - Ca(OH)$_2$ SYSTEM - 90 Sec. RUN

CAS-10338 3-3-55

FIGURE 5

BY .... DATE .... SUBJECT .... SHEET NO. .... OF ....
CHKD. BY .... DATE .... JOB NO. ....