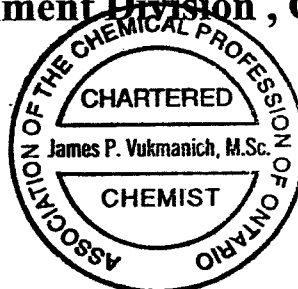


**THE EFFECTS OF FLUORIDATING AGENTS ON THE
CHEMISTRY OF THUNDER BAY DRINKING WATER**

Submitted by:

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Executive Summary

The water chemistry of Thunder Bay treated water poses unique problems for additional treatments and especially corrosion control.

This report describes the effects of three fluoridating agents on the chemistry of Thunder Bay drinking water and in particular their effect on lead-pipe corrosion. Static corrosion tests were performed with hydrofluorosilicic acid (H_2SiF_6), sodium silicofluoride (Na_2SiF_6), and sodium fluoride (NaF), each at concentration levels of 0.5, 0.7, 1.5 parts per million as fluoride ion. One additional experiment was conducted using a pH (pH=8.5) adjusted solution of hydrofluorosilicic acid at each of the three levels. The static corrosion tests used lead coupons that were fabricated from common lead water supply pipe. The experiments measured the amount of lead leached into solution from the coupons immersed in the solution of the fluoridating agent. Fixed samplings at 6, 24, 96, 168, and 360 hours were analysed.

The fluoridating agent that caused the greatest amount of lead leaching was the solution of un-buffered hydrofluorosilicic at a concentration of 0.7 ppm. The rate was about 2.6 times the control. When the same hydrofluorosilicic acid is used in a pH adjusted solution (pH=8.5) the relative corrosion rate was about 8 times lower, than the un-buffered acid.

Sodium silicofluoride was found to have a relative corrosion rate of about 1.4 times lower than free hydrofluorosilicic acid.

The solution of sodium fluoride at 0.7 ppm as fluoride had the lowest corrosion rate.

The findings show that all the fluoridating agents chosen increase the corrosion of lead pipe to some extent in Thunder Bay tap water. The pH adjusted hydrofluorosilicic acid appears to be the best compromise since it had the next lowest corrosion rate. This choice would require an additional neutralizing agent, sodium hydroxide for pH adjustment.

Introduction

The drinking water produced at the Bare Point Water Treatment Plant is taken from Lake Superior. It can be described as a high quality, low alkalinity soft water. It is low in dissolved major ions and metals. The silica level is low and the natural fluoride content is at trace levels (1).

As a consequence of these characteristics Thunder Bay drinking water has little buffering capacity and is corrosive to common plumbing materials. Furthermore, under certain circumstances the most widely used fluoridating agents can also increase the corrosivity of the water (2) (3). Currently the City is considering a proposal to fluoridate the drinking water. Therefore this “jar study” has been undertaken.

This report describes the effects of three fluoridating agents on the chemistry of Thunder Bay drinking water and in particular their effects on lead pipe corrosion. Static corrosion tests were performed using lead coupons fabricated from common lead water supply pipe. The agents used were; hydrofluorosilicic acid (H_2SiF_6), sodium silicofluoride (Na_2SiF_6), and sodium fluoride (NaF).

Hydrofluorosilicic acid is a clear to straw-yellow, fuming liquid compound normally sold as a 25% w/w aqueous solution with a fluorine content of 19% by weight. Sodium silicofluoride is a dry, white coloured free flowing crystalline solid with a purity of 98% and fluorine content of 61% by weight. Sodium fluoride is a dry, white coloured free flowing powder with a minimum purity of 98% and a fluorine content of 45% by weight.

Experimental

Materials

All fluoridating agents and the sodium hydroxide used for the tests, were NSF (National Sanitation Foundation) approved for use in drinking water treatment. The product specifications are listed in Appendix A. Water used for this study was taken directly at the treatment plant and analyzed for pH, alkalinity, fluoride and residual chlorine. Stock solutions using the liquid hydrofluorosilicic acid were prepared directly by adding an approximate volume of the acid to ten litres of water. The exact concentrations of fluoride ion were achieved by analysis of the solution for fluoride and subsequent serial dilution to the appropriate concentration with additional tap water. Stock solutions of the solids; sodium silicofluoride and sodium fluoride were prepared by weighing out dried portions of sodium silicofluoride (1.64959 grams) and sodium fluoride (2.21003 grams) placed in separate one litre volumetric flasks and made up to the mark with tap water. The resulting solutions (1000 mg/L as F^-) were stirred overnight

to ensure complete dissolution. The required concentrations for the jar tests were prepared by serial dilution of the stock solutions.

Corrosion Coupons

The lead corrosion coupons were made in-house from standard half-inch lead water supply pipe obtained from Sewer and Water South. Pieces were fabricated by taking five centimeter sections of pipe, slitting it down one side and pressing it into flat medallions about one millimeter thick. The medallions were scraped clean using a hardened steel tool, to create a clean fresh surface. The medallion was then sheared into small rectangles of dimension 2 cm long, 1 cm wide, and 1 mm thick. A small one millimeter in diameter hole was drilled in the coupon. The clean coupons were then conditioned by placing them in a beaker of city tap water for 3 days.

Static Corrosion Test Method

The static tests were conducted in 500 mL polyethylene terephthalate (PET) jars with polyethylene lids. The lead coupons (4) were suspended in the test solutions using a nylon fishing line through the hole in the coupon and the jar lid. Three jar sets consisting of 500 mL solutions of 0.5, 0.7, and 1.5 ppm as fluoride ion for hydrofluorosilicic acid, sodium fluorosilicate, and sodium fluoride respectively plus one control solution of Thunder Bay tap water were prepared. A fourth set using 0.5, 0.7, and 1.5 ppm as fluoride ion hydrofluorosilicic acid solutions at pH=8.5 were also set up. The control was tap water. In total 16 static test jars were set up, of these 4 served as controls. A 20 mL aliquot of the test solutions were withdrawn at time intervals of 6, 24, 96, 168, and 360 hours. The aliquots were preserved with nitric acid. An external accredited laboratory (ALS laboratory Group, Thunder Bay Lab) analyzed all solutions for lead using inductively coupled plasma optical emission spectrometry (ICP-OES).

Data Computation

The lead data from the static tests were compiled using an Excel spreadsheet. The data is presented graphically in the form of lead leach concentration vs. time (Graphs 1 to 4). For quality control purposes the data sets were evaluated using a statistical two way ANOVA analysis. Relative rates of corrosion were calculated using the average slopes of the plotted data (see example 1.0). Using this method a comparison of test solutions to controls could be made.

Example 1.0

$$\text{RATE} = \frac{\text{Final lead conc. ug}^*/\text{L} - \text{Initial lead conc. ug/L}}{\text{Final time hours} - \text{Initial time hours}}$$

$$\text{RATE (units)} = \text{ug/L/hour.}$$

* ug = micrograms

Results

Parameter	Bare Pt. treated	0.5 mg/L as F ⁻ HFS*	0.7 mg/L as F ⁻ HFS*	1.5 mg/L as F ⁻ HFS*
pH	7.54	7.36	7.27	7.01
Total Alkalinity	44.3	42.7	42.1	38.1
Fluoride mg/L	<0.03	0.7	0.967	2.45
Chlorine mg/L	1.41			

TABLE1: Water Chemistry of Bare Pt. Treated and Various Additions of Hydrofluorosilicic Acid (HFS) *.

Time hr.	6	24	96	168	360	RelativeRate ug/L/hr
Conc. as F ⁻ mg/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	
0.5	219	301	632	713	1020	2.263
0.7	445	412	678	665	1630	3.347
1.5	899	746	838	1200	1650	2.121
Control	272	321	553	615	718	1.259

TABLE 2: Lead Results and Relative Corrosion Rates for Hydrofluorosilicic Acid

Time hr.	6	24	96	168	360	RelativeRate ug/L/hr
Conc. as F ⁻ mg/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	
0.5	78	155	525	516	724	1.825
0.7	27	195	546	789	869	2.378
1.5	36	178	590	758	829	2.240
Control	29	93	310	522	593	1.593

TABLE 3: Lead Results and Relative Corrosion Rates for Sodium Silicofluoride

Time hr.	6	24	96	168	360	RelativeRate ug/L/hr
Conc. as F ⁻ mg/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	
0.5	1080	3900	1500	458	692	-1.096
0.7	1800	1820	546	1920	1900	0.2825
1.5	1950	2400	2370	2350	2400	1.271
Control	25	65	243	393	462	1.234

TABLE 4: Lead Results and Relative Corrosion Rates Sodium Fluoride.

Time hr.	6	72	144	312	RelativeRate ug/L/hr
Conc. as F ⁻ mg/L	Lead ug/L	Lead ug/L	Lead ug/L	Lead ug/L	
0.5	34	53	87	135	0.3300
0.7	49	69	107	174	0.4085
1.5	23	74	123	147	0.4052
Control	25	96	127	185	0.5228

TABLE 5: Lead Results and Relative Corrosion Rates Hydrofluorosilicic Acid, pH=8.5.

Discussion

There are very few studies in the recent literature (5) that addresses the problem of lead pipe leaching of drinking water with added fluoridating agents. In this study three common agents were tested at three different concentration levels expressed as fluoride ion in order to gain any insights to changes in water chemistry and specifically lead leaching. Three levels were chosen; 0.5 mg/L this is normally given as the lowest level in water that would still retain a beneficial dental effect, 0.7 mg/L considered as the optimal fluoride concentration and 1.5 mg/L as the maximum acceptable concentration (MAC) as stated in *Ontario Drinking Water Objectives, Rev. 1994*.

The basic water chemistry for Bare Pt. treated water is well documented(1). However, TABLE 1 shows some of the important characteristics of the water and the influence of three concentrations of the most common fluoridating agent, hydrofluorosilicic acid. Addition of increasing amounts of the hydrofluorosilicic to

treated water show a decreasing trend in pH. At the optimum fluoride level of 0.7 mg/L the pH of the water is depressed 3.5% with a corresponding alkalinity decrease of 5%. This result is typical for an unbuffered soft water.

The static corrosion tests are more revealing when it comes to potential corrosive effects. GRAPH 1 to GRAPH 4 are plots of lead leaching over time with the three agents at three different concentration levels. In all cases some quantifiable increase in lead leaching does occur and is clearly related to compound and concentration of the added materials.

GRAPH 1 shows that the calculated relative rate of corrosion for hydrofluorosilicic acid (0.7 mg/L as F⁻) is, 3.347 ug/L/hr. This is about 2.6 times the rate of the control (see TABLE 2).

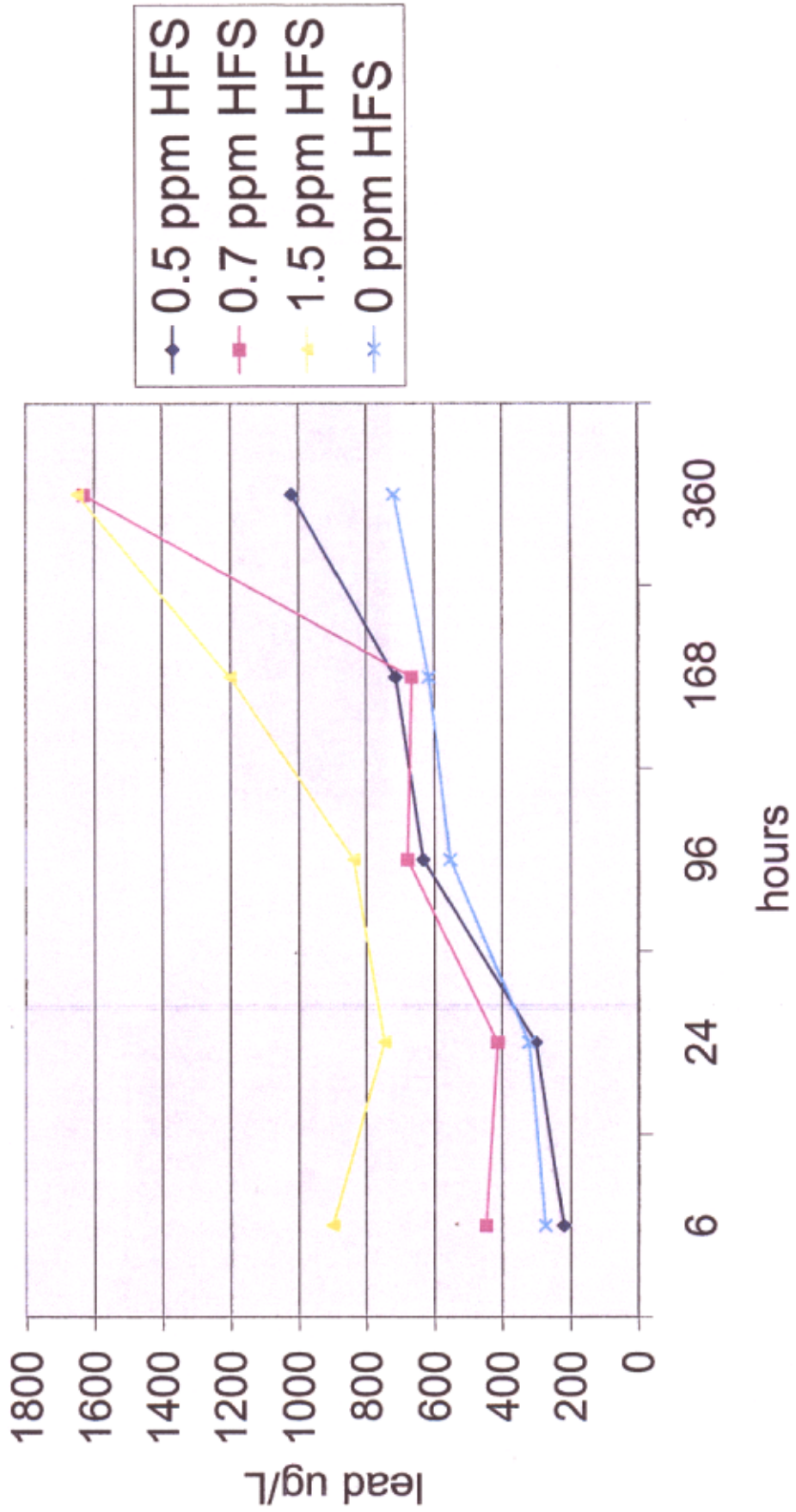
GRAPH 2 is a plot of the same experiment using a pH adjusted hydrofluorosilicic acid at pH = 8.5. The observed relative rate of corrosion for this solution at a concentration of 0.7 mg/L as fluoride ion was 0.4085 ug/L/hr, (see TABLE 5). Using a pH adjusted solution the lead leaching is about 8 times lower than hydrofluorosilicic acid alone. This observation is very encouraging since it may be possible to offset some of the corrosive effects of this fluoridating agent and for that matter the water itself, by simple addition of sodium hydroxide to the treated water.

GRAPH 3 is a plot of the lead leaching effects of sodium silicofluoride. The data is presented in TABLE 3. Overall the sodium silicofluoride had a lower effect on lead leaching than the unbuffered hydrofluorosilicic, with a relative rate of 2.378 ug/L/hr. This rate is about 1.4 times lower than the acid alone.

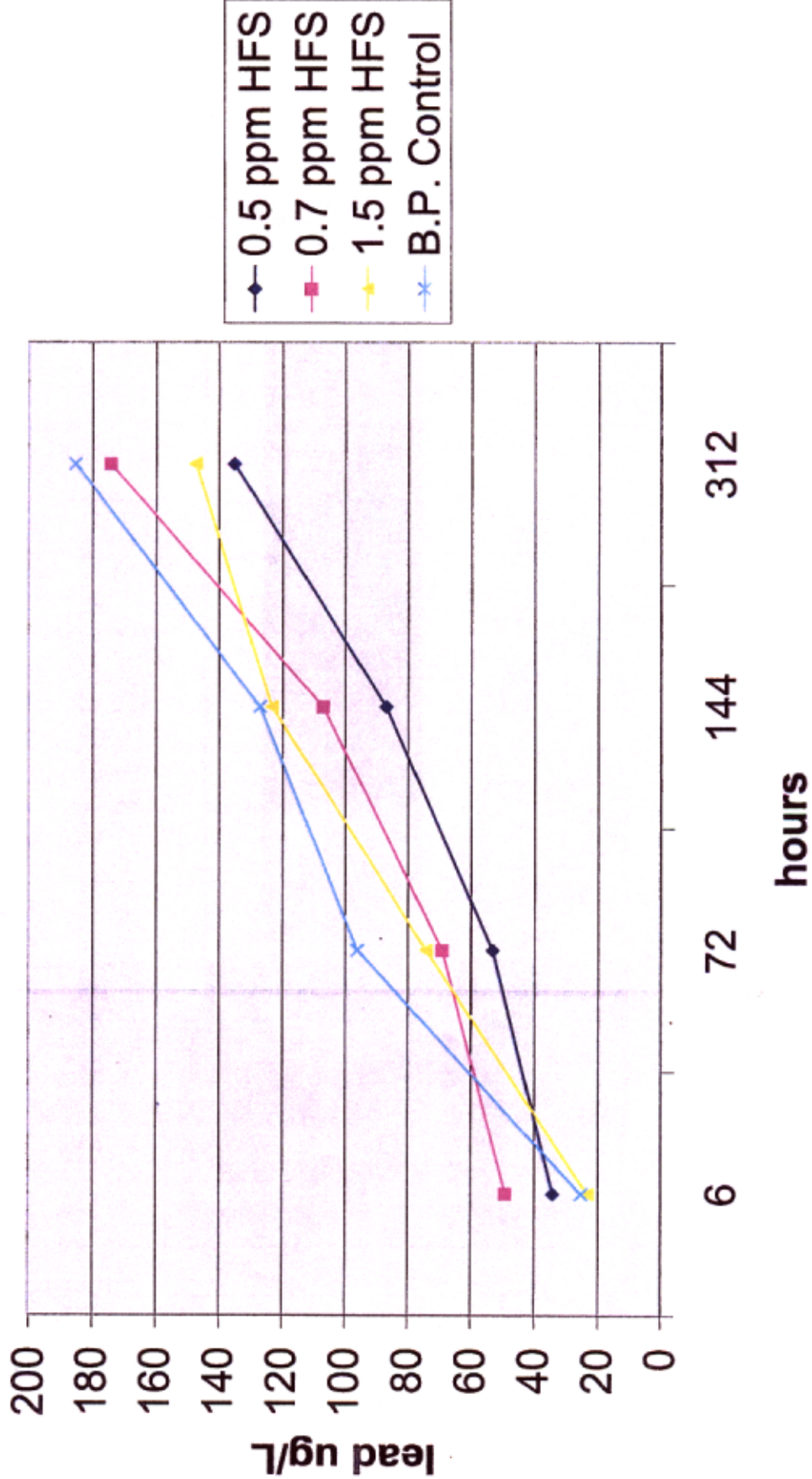
GRAPH 4 is a plot of the lead leaching effects of sodium fluoride at the test levels. The data is presented in TABLE 4. There were some data anomalies for this test compound especially at the lower concentration level. It appears that sodium fluoride had the lowest relative rate of corrosion with a rate of 0.2825 ug/L/hr. In light of some data quality no further comment can be made.

It should be noted that all control solutions yielded similar rates for each experiment. The average rate was 1.362 ug/L/hr with a standard deviation of 0.20 ug/L/hr. This indicated that the static corrosion test coupons were prepared in a consistent manner.

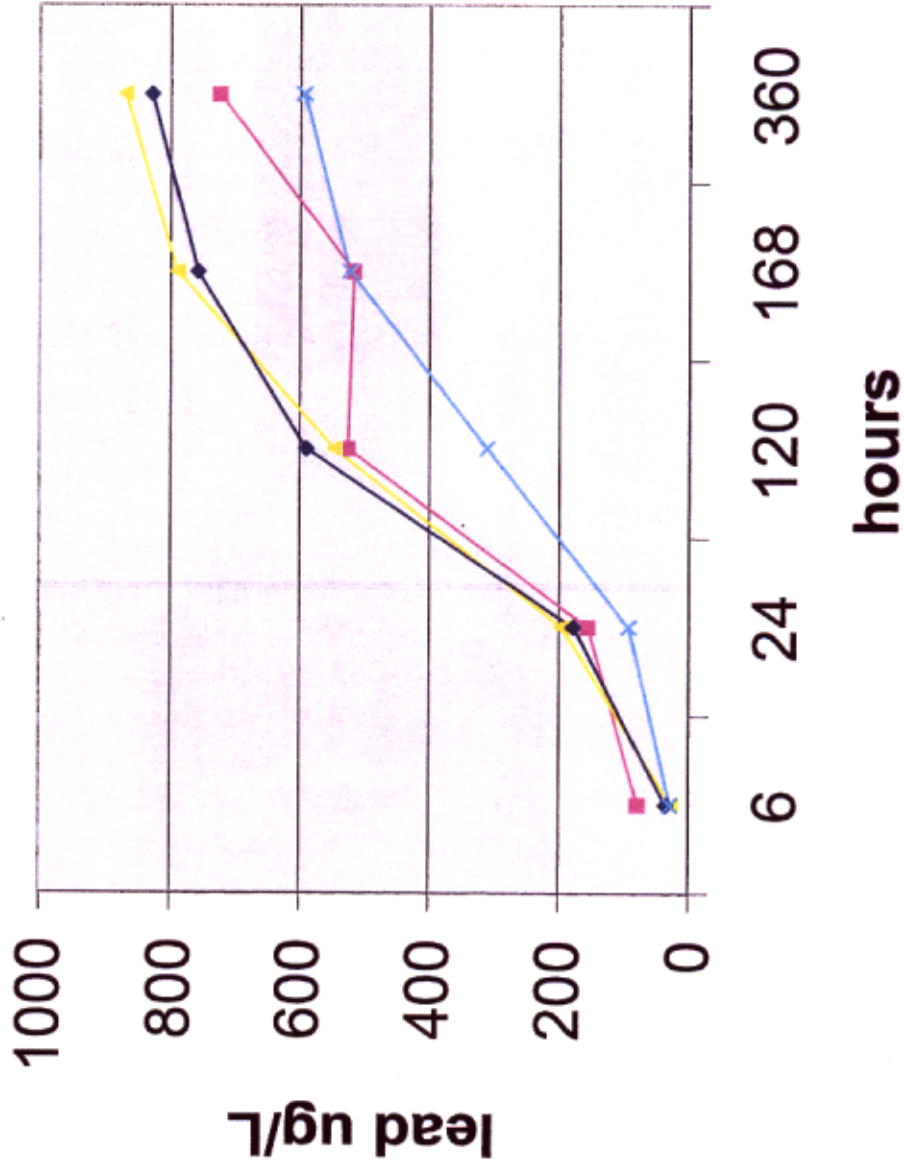
GRAPH 1: Lead leach vs time Hydrofluorosilicic Acid



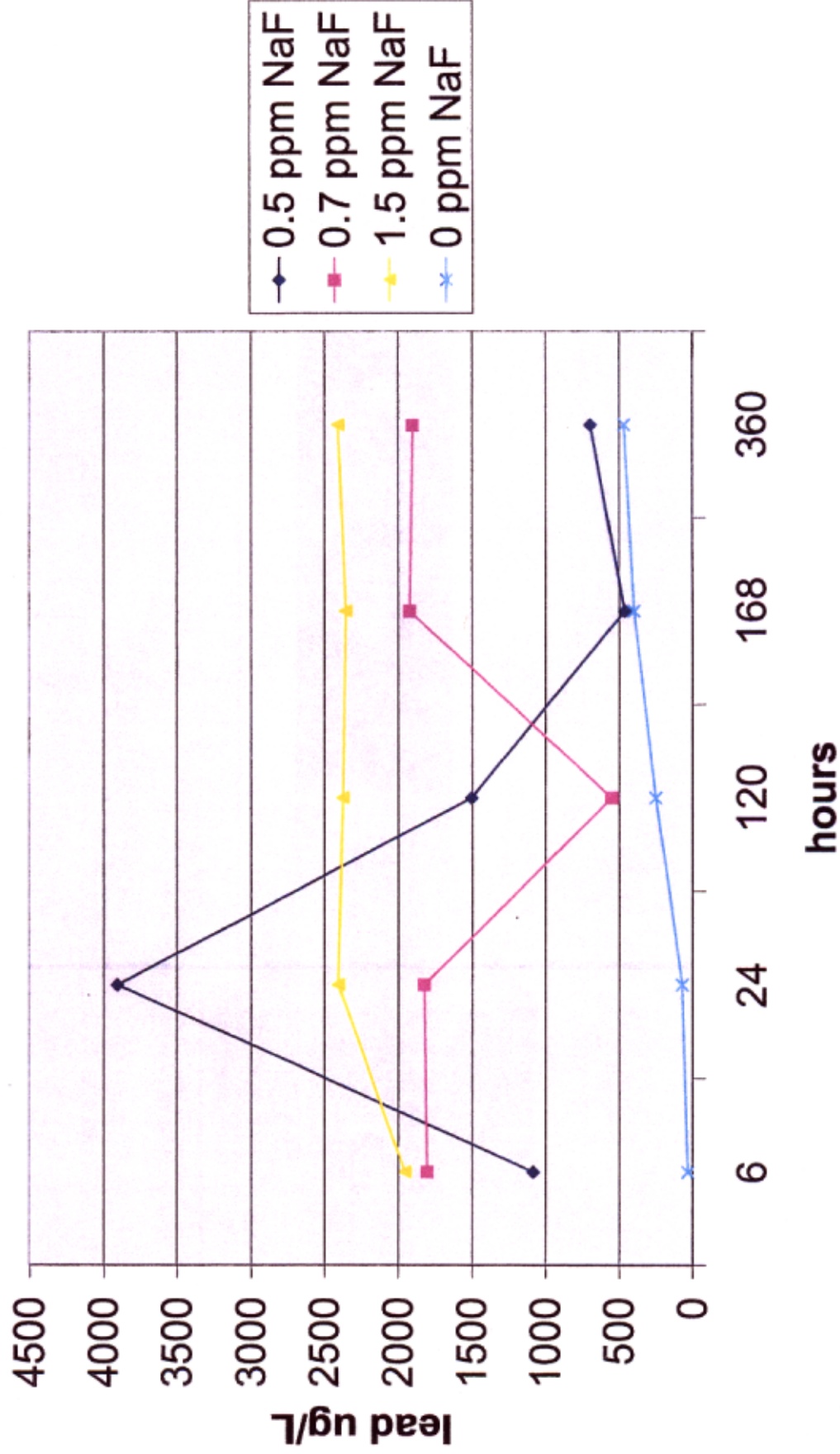
**GRAPH 2: Lead Leach vs Time Hydrofluorosilicic Acid
(pH= 8.5)**



GRAPH 3: Lead leach vs Time Sodium Silicofluoride



GRAPH 4: Lead leach vs Time Sodium Fluoride



Conclusion

The Thunder Bay drinking water is corrosive by nature. Addition of fluoridating agents to the water, especially hydrofluorosilicic acid would increase this tendency and hence increase lead levels at the consumer tap. The use of an anti-corrosion agent, such as sodium hydroxide as demonstrated in this experiment, would be needed to counteract this effect.

References

- (1) Drinking Water Quality 2008 Annual Report, City of Thunder Bay, February 2008
- (2) Fluoridation of Drinking Water and Corrosion of Lead Pipes in Distribution Systems, Center for Disease Control, <http://www.cd.gov> 07/07/2009.
- (3) Water Fluoridation and the Environment, H. F. Pollick, Int. J. Occup. Environ. Health 2004; 10;343-350
- (4) Corrosion Control in Drinking Water Distribution Systems, Health Canada, 2007
- (5) Effects of Fluoridation and Disinfection Agent Combinations on Lead Leaching from Leaded –Brass Parts, Maas, R.P. et al, NeuroToxicology 28 (2007) 1023-1031

Appendix A: Specifications Fluoridating Agents