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ENGINEERING AND ANALYTICAL PROGRAM FOR SITE CLEAN UP

TAYLOR INSTRUMENT CO.
DIVISION OF SYBRON CORPORATION
ROCHESTER, NEW YORK 14601

MARCH 1982

LOZIER
ARCHITECTS/ENGINEERS

TABLE OF CONTENTS

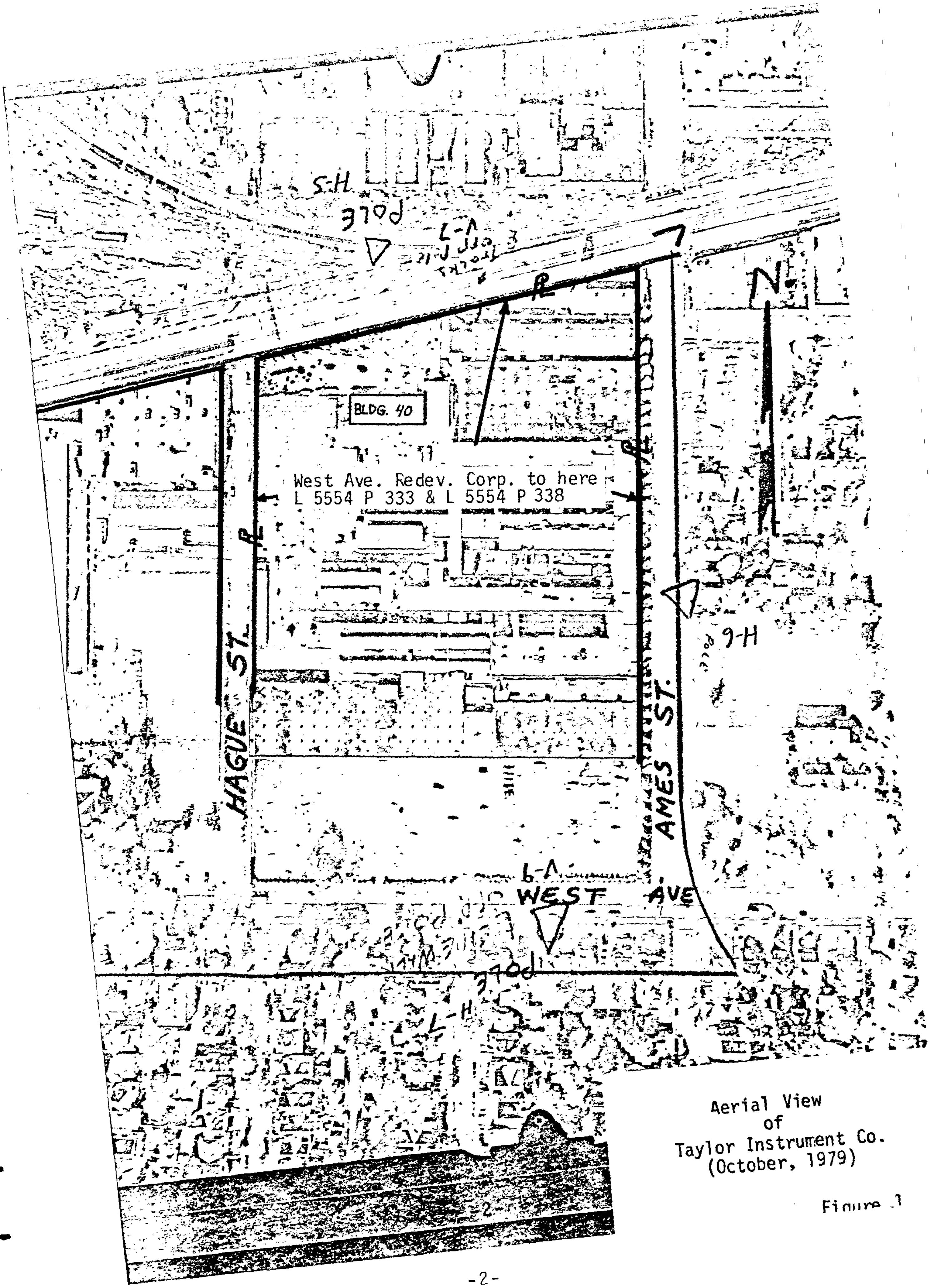
LIST OF FIGURES

APPENDICES

BACKGROUND

Taylor Instrument Company ("Taylor"), a division of Sybron Corporation, has a manufacturing facility which is located at 95 Ames Street in Rochester, New York. At this facility Taylor manufactures various instrumentation items and systems. During 1981 Taylor discovered that a portion of the grounds at the Ames Street facility had been contaminated with elemental (or metallic) mercury. The contaminated area is shaded in yellow on Figure 1. This area was apparently contaminated as a result of a mercury reclamation operation which was used by Taylor at the Ames Street site until approximately 1965. The exact circumstances by which the mercury was placed in the soil have not been established. Although some of the site surface area has traces of broken thermometer glass and miscellaneous instrumentation hardware, three (3) areas of the site exhibit heavy accumulations of broken thermometer glass ("hot spots"). Lozier, Inc. and its subsidiary, Lozier/Camo Laboratories ("Lozier") were subsequently hired by Taylor to investigate the nature and extent of the soil contamination. On January 11, 1982, an Engineering and Analytical Report on Mercury Contamination ("January 1982 Report") at the Taylor site was submitted to United States Environmental Protection Agency ("E.P.A.") and to the New York State Department of Environmental Conservation ("N.Y.S.D.E.C."). Section III of the January 1982 Report summarized the data which had been collected and included the following statements:

2. Generally speaking, mercury concentrations in the soil are higher toward Building 40 and within the first three feet of



Aerial View
of
Taylor Instrument Co.
(October, 1979)

Figure 1

overburden. Based on an analysis of the driller's log the majority of the area appears to have been filled with an ash/cinder mixture to varying depths. The present data also indicates higher mercury concentrations in those portions of the site where [heavy accumulations of] glass shard deposits were noted.

3. There is a general decrease in mercury concentrations laterally outward from the presently presumed center (0-0°) of the contamination and vertically downward within the soil profile, except as noted in number 4 below.
4. Field operations within the project area have revealed other areas of broken glassware on the ground and thus possibly high mercury concentrations. This relationship is based on the findings to date at [two sampled positions] where areas of high [surface] glass concentration have also been high in elemental mercury [concentration in the soil].
5. The breadth and depth of the mercury contamination problem at the Taylor Instrument site has not yet been analytically defined. However, information to date indicates that:
   a. There is mercury contamination in both the soil and water, and
   b. The EP Toxicity test results indicate that at least some of the in place soil and mercury material can be considered a hazardous waste, if it is ever removed from the site.
6. Tests for pH were run at the Lozier/Camo Laboratory on four (4) separate soil samples. These test results indicated a

pH ranging from 6.8 to 7.2.

7. Analytical data does not indicate mercury in the groundwater in excess of the State groundwater limits any great distance from the two presently known high mercury concentration positions, i.e., water samples withdrawn from positions C-135° and D-0° were not in excess of the State standard.

8. It appears that the worst concentrations of mercury in the soil are above the groundwater table. However, conclusive information on the seasonal fluctuations in the groundwater table is not available, and this could have an impact on any mercury migration.

9. Groundwater data is still insufficient to conclusively determine the flow direction, depth and condition of the groundwater. In addition, there is no firm data indicating whether or not the groundwater is part of a moving aquifer or is perched groundwater.

10. It is probable, in the opinion of the testing laboratory, that the mercury present on the site consists of three forms:

    a. metallic mercury
    b. inorganic divalent mercury
    c. methyl or phenyl mercury

(January 1982 Report at pages 9-11.)

On January 22, 1982 Frank Shattuck, P.E. (Regional Solid Waste Engineer) of N.Y.S.D.E.C. requested (by telephone) that Taylor provide N.Y.S.D.E.C. with a proposal for an engineering solution dealing with the mercury at the Taylor site. Lozier has researched feasible procedures for dealing with mercury contamination of both the soil and aqueous media. Because the contamination in the groundwater is merely a symptom of the high concentration of mercury in the surrounding soil matrix, methods for dealing with mercury contamination of the soil were pursued. This proposal, for treatment of the hot spots through chemical fixation and installation of a leachate collection system, is submitted to N.Y.S.D.E.C. in response to Mr. Shattuck's request.

ALTERNATIVE ENGINEERING SOLUTIONS

Three (3) different remedial approaches were initially identified as possibly being feasible at the Taylor site. Those three (3) methods are as follows:

A. On-Site Chemical Fixation of the Mercury

B. On-Site Encapsulation of the Mercury

C. Excavation and Disposal of the Contaminated Soil Material in a Secure Landfill.

<u>Option 1: On-Site Chemical Fixation of the Mercury</u>

Because of the complex chemistry which is often involved and because of the scarcity of empirical data from past treatment efforts with contaminated soils, this alternative has generally been approached with caution. Site specific bench-scale tests would have to be performed before any on-site treatment measures were attempted. If, however, a chemical fixation method could be identified which would permanently fix in-place the contaminating material, then the potential environmental hazard would be eliminated. Because of the relatively untried nature of this alternative, collection, analysis and possible treatment of any leachate might be required. Based upon the above considerations, it was decided to investigate whether a potential treatment technology existed.

The basis for Lozier's research into this option is based on the article presented in Appendix "A". The basic chemical principles employed by this treatment option are outlined in Appendix "B", and a detailed description of the methodology is contained in

Appendix "C".

Option 2: On-Site Encapsulation of the Mercury

A detailed discussion of this method is presented in Appendix "D". The logistics of on-site encapsulation present many drawbacks. First of all, the physical characteristics of the site and the anticipated required depths for the work suggest the need to protect the adjacent structures. Second, with the railroad to the north, usable access to the site is possible from only two directions. Third, due to the existing surface elevations and the established perimeter characteristics of the area to make room for the containment layers, i.e., clay and liner, a substantial amount of contaminated material would still have to be excavated and disposed of at a secure landfill. If this excess material were not removed from the site, additional work would be required in order to avoid surface drainage problems. Additionally, any on-site encapsulation operation would render this site unusable for any future development other than perhaps as a parking lot.

This option is essentially a long term storage approach rather than a treatment alternative, and hence the risk continues of environmental contravention in the future. While Taylor would probably be able to retain long term control over the storage area, placement, monitoring, and maintenance of the impervious material which would surround the contaminated material would be difficult. Furthermore, there is no guarantee that Taylor or a fiscally responsible successor in interest will exist for as long as maintenance will be required. Experience with the encapsulation method employed at other hazardous material/waste areas is of limited duration and therefore of limited value in selecting a permanent solution.

Option 3: Excavation and Disposal

A detailed discussion of this method is presented in Appendix "E". While complete (or partial) excavation and removal of the contaminated material should eliminate from the site the risk of future environmental damage, the success of this alternative is dependent on the hazardous material/waste transporters used and on the owners and operators of the storage facility (assumed to be a secure landfill) which ultimately receives the excavated material. The risk of environmental damage is not eliminated but rather it is transferred to another site. The perpetual monitoring and maintenance of the buried contaminated material, however, should be performed by experienced hazardous material/waste handling personnel. Since nothing is done to treat the contaminated material, this solution must be viewed as a placing of the material into storage where it would be controlled for as long a time as the landfill remains secure (albeit a "final" storage situation is generally assumed). There also are no guarantees that the present regulatory standards and enforcement measures will remain as stringent in the future.

CHEMICAL FIXATION AND METHODOLOGY

As indicated in the January 1982 Report, while the breadth and depth to which mercury has migrated through the soil at the Taylor site has not been analytically defined, the highest soil mercury concentrations were found in the first three feet of overburden and at the locations where heavy accumulations of broken thermometer shards were found on the ground surface.

After reviewing the data contained in the January 1982 Report, and upon making the presumption that leachate collection would probably be required for some period of time after treatment by chemical fixation had been accomplished, it was theorized that if the bulk of the mercury within the soil could be chemically locked in place, then there would be little or no subsequent mercury migration from the areas of high mercury concentration. This would be achieved since there would be no "new" mercury available for solubilization and/or migration from the areas of high mercury concentration. Any of the mercury which is not fixed and which might go into solution with the groundwater could be collected in a leachate collection system and treated if necessary before disposal.

Based on the above analysis, we propose that chemical fixation be attempted only in those areas with heavy surface accumulations of broken thermometer (and other instrumentation) shards.

The chemical fixation approach consists of three phases. The initial step of Phase I would be to positively identify all hot spots by means of a detailed surface inspection of the subject site with a representative of N.Y.S.D.E.C. Site inspections and surface work to date have located three (3) hot spots which are identified on the surface by heavy accumulations of broken glass. Upon careful inspection, the glass shards can be identified as broken fragments of thermometers and other instrumentation glass. While three (3) hot spots have been identified to date, there may be others on the site presently hidden by light brush which covers some of the site. Concurrently with the site inspection, a detailed topographic map of the area should be made and all significant elevations established. The second step in this phase would be the performance of extensive hydrogeological field tests and associated lab analyses. These tests are required to establish the characteristics of the in-place soil and groundwater. The scope of such field work would include the following elements:

A. Ten (10) 3" wells. These wells would be of standard PVC construction and installed for the purpose of establishing the groundwater quality of the area. It is anticipated that these wells would be installed to an average depth of approximately 20', however, if rock were encountered, they would be terminated above the rock. A valuable byproduct of the installation of these wells is the information on soil horizons which will become evident during the drilling operations. Six (6) wells would probably be installed on site, one (1) well installed north of the railroad tracks, one (1) east of Ames Street, one (1) west of Hague Street, and one in the parking lot just south of the subject site.

B. Two (2) lysimeter clusters of three (3) each would be installed within the subject site. Each cluster would be installed within a radius of 5'. Each lysimeter would be installed at a different depth, but all would be installed within the vadose zone. The entire region overlying the water table, including the topsoil zone is defined as the vadose zone. The installation of this instrumentation would provide information regarding infiltration from the surface through the vadose zone, and the migration of the groundwater through the vadose zone, down into the saturated zone.

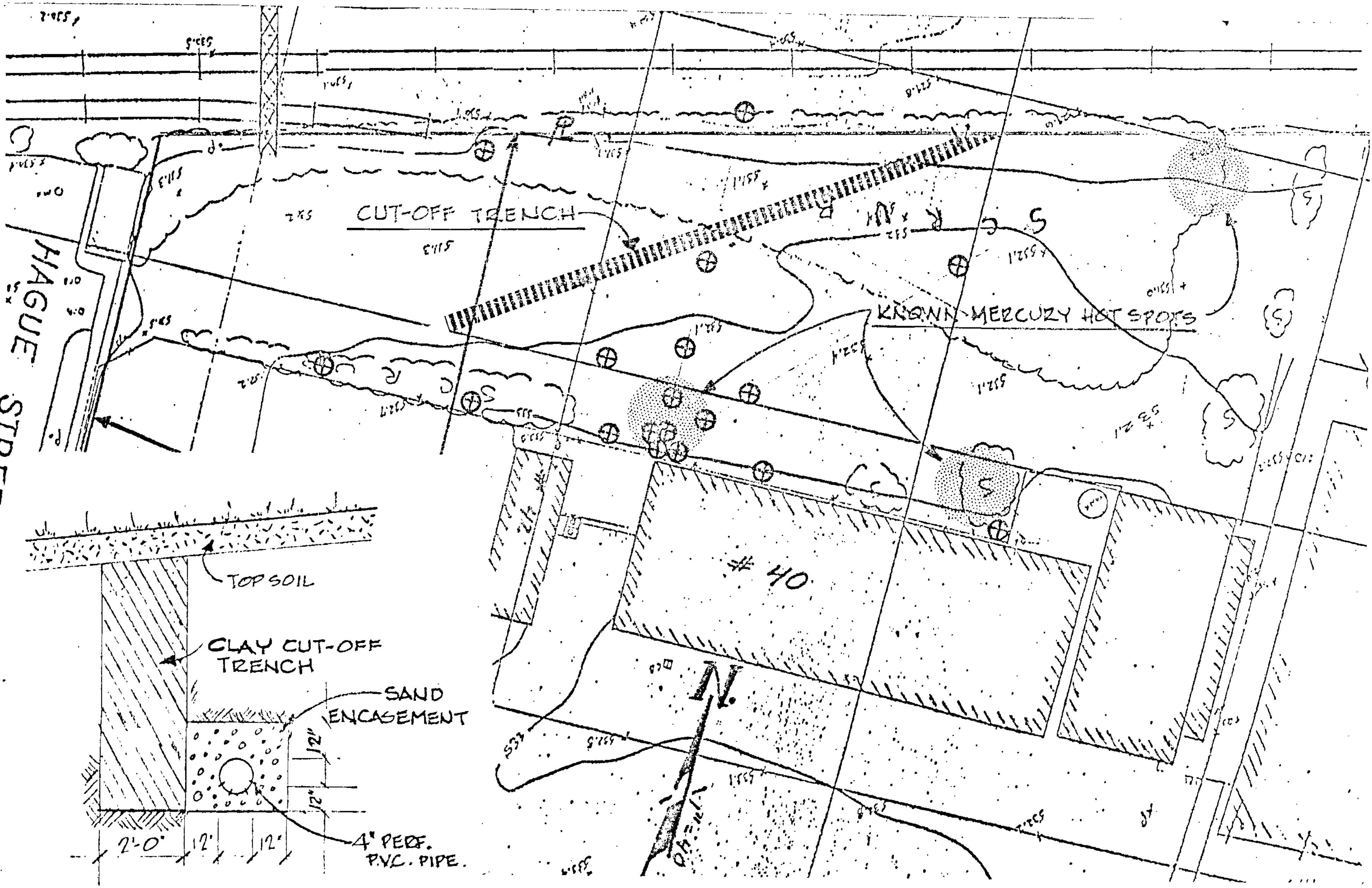
C. Three (3) piezometers would be placed on site. One (1) piezometer would be installed within a 6" casing into rock. The casing would be left in place and grouted to the surface. It is anticipated that two (2) to three (3) packer tests would be run within the rock before the piezometer was installed. A packer test is a sealed and pressurized water test which can be performed within a rock zone in order to determine the rock permeability. The implementation of packer tests within the rock would yield information on the overall integrity of the rock as a possible barrier against water migration. The remaining two (2) piezometers would be installed within augered holes which terminate above the rock. The piezometers which are approximately 1' long would be placed in sand at different elevations within the saturated zone. Piezometers are used in determining the groundwater level in the saturated zone. Information would also be obtained on the permeability of and the vertical gradients within the soil overburden.

D. In three (3) of the six (6) on-site wells selected under item A, slug tests would be performed using the soil withdrawn from the well installations. Slug tests help to determine the permeability of the overburden and the direction of groundwater movement through the soil.

Bench testing of representative soil samples from the subject site will constitute the third step in Phase I. These soil samples would be composite samples from the located hot spots. The soil samples would first be split into two (2) equal portions with Total Mercury, EP Toxicity, and Neutral Leaching Medium tests being performed on one (1) portion to establish a base datum point. Using iron pyrite concentrations of between 1% and 3% (in 1/2% increments) by weight, iron pyrite would be mixed with the soil samples. After the various concentrations of iron pyrite are mixed with the second half of the soil samples the Total Mercury, EP Toxicity and Neutral Leaching Medium tests would be performed, again. Control samples will also be run for all tests. Also during Phase I, discussion should be undertaken with the Monroe County Department of Wastewater Management to advise them regarding any contemplated discharge.

Should the results of Phase I meet the standards agreed upon by N.Y.S.D.E.C., then the data established in Phase I would be used to refine the methodology proposed under Phase II. The field work from Phase I will establish the principal soil and groundwater parameters needed to plan and possibly alter Phase II of the program. It is presently thought that the hot spot excavations will consist of areas 30' in diameter at the surface, and 10' - 15' at the base of the excavation, with an overall depth of excavation of approximately 12'. The presently known three (3) hot spots would require an excavation of approximately 1000 cu. yds. The iron pyrite to be used in the chemical fixation of the mercury is available in Pennsylvania, and comes in 100# bags. The contaminated material and the iron pyrite would be mixed using equipment which will insure a uniform product mixture. The product can then be returned to the excavations and compacted in place.

The last step of this phase would be the installation of the clay cut-off trench and leachate collection system. The width of the trench would be about 2', but the location, depth and length of the trench would have to be established after inspecting the data from Phase I. (see Figure 3). The leachate collection system would consist of perforated PVC pipe laid in an acceptable filtering medium and piped to a central location where it can be treated if necessary. It is proposed that this leachate be discharged to the local sewer system of the City of Rochester. However, if this leachate violates the applicable requirements of the Monroe County Department of Wastewater Management, it would have to be treated on site by Taylor before it could be



SECTION THRU TRENCH
N.T.S.

PARTIAL PLAN
TAYLOR INSTRUMENT CO.
LOCATIONS of MERCURY "HOT SPOTS": SECTION of CUT-OFF TRENCH

Figure 3

discharged.

Phase III of this program would be a post-monitoring program to gauge the gradual reduction in mercury availability within the site. Once the major mercury sources have been tied up, the leachate collected should gradually exhibit an overall reduction in mercury. To monitor this occurrence, it would be proposed to monitor the leachate from the site on a monthly basis and the groundwater wells within the site on a quarterly basis. Should the leachate exhibit a gradual mercury reduction or remain at levels below the State groundwater standards for mercury for at least six (6) months, then at the end of the first year the monitoring program could be reduced to testing the leachate quarterly and the groundwater wells semi-annually. Should the leachate remain at levels below the applicable groundwater standards during the second year, at the end of the second year it would be proposed to discontinue the monitoring program. If, however, during the second year, mercury concentration levels are above groundwater standards, the same testing program would be extended into the third year and beyond as necessary. At any point after the first two years, should the analyzed mercury levels be below groundwater standards for twelve (12) consecutive months, then the monitoring (leachate and groundwater collection) program would be discontinued.

It is anticipated that, prior to the commencement of each phase, a brief report will be submitted to N.Y.S.D.E.C. detailing

1) the actions to be taken during that phase,

2) data to be collected during that phase, and

3) proposed criteria to be used to decide whether or not the phase can be deemed a success.

Once N.Y.S.D.E.C. has reviewed and approved the proposal, including the data to be collected and the judgement criteria, Taylor will begin work on that phase of the remedial work. Following the completion of a phase, a brief report analyzing the results of the work done during the phase and a detailed proposal on the items to be included in the next phase will be submitted to N.Y.S.D.E.C. The above cycle would then be repeated.

The success of such a phased approach will be dependent upon cooperation between all parties involved in the process, especially in the area of reaching mutual agreement, <u>at the proposal stage</u>, on necessary data to be collected and on establishing judgment criteria. While some amount of flexibility will probably have to be left until the data analysis stage, all parties must be aware of the basic framework within which decisions will be made.

If the work done during any phase indicates either that chemical fixation will not (or did not) work or that further remedial measures are necessary, the subsequent phases can be either modified or the entire approach can be abandoned. If this occurs then N.Y.S.D.E.C. and Taylor will have to reanalyze the situation and develop a new approach.

After review and conceptual approval of the overall project is given by N.Y.S.D.E.C., Taylor will submit a detailed outline of its proposed bench testing. Subject to any modifications prompted by N.Y.S.D.E.C. review, Taylor will then request a formal approval before implementing Phase I. It is anticipated that Phase I can be begun within three (3) weeks after N.Y.S.D.E.C. approval is received.

Section IV of this proposal contains a tentative schedule for the entire Chemical Fixation program.

PROGRAM IMPLEMENTATION AND SCHEDULING

The implementation of the proposed program presented in the preceeding section would develop under the following time frame.

1. Submission of the proposed engineering/analytical program to N.Y.S.D.E.C. for conceptual approval — Mar. 12, 1982
2. Receipt of N.Y.S.D.E.C. conceptual approval of the proposed program — Date A.
3. Submission of a detailed report covering the proposed bench scale testing and hydrogeological field work and lab testing. — Date A. + one (1) week.
4. Receipt of N.Y.S.D.E.C. approval of the testing and field work programs. — Date B.
5. Once NYSDEC gives approval to proceed with Phase I mobilization to start the field work associated with Phase I would take approximately three (3) weeks. Present estimates place the amount of time required to do the actual field work associated with Phase I at five (5) weeks. The turnaround time on the lab testing for the field work associated with Phase I would take approximately four (4) weeks. A compilation of all the test data into a report for Phase I including all aspects of the hydrogeological work and the iron pyrite

	testing would take approximately three (3) additional weeks. This report would then be submitted to N.Y.S.D.E.C. for approval.	Date B + fifteen (15) weeks.
6.	Receipt of N.Y.S.D.E.C. approval to commence with Phase II.	Date C.
7.	Preparation of plans and specifications; approval of this work by N.Y.S.D.E.C. and the hiring of a contractor.	Date C + ten (10) weeks.
8.	Mobilization to implement Phase II would take approximately three (3) weeks after receipt of N.Y.S.D.E.C. approval. Actual time required to perform Phase II is anticipated to be approximately three (3) weeks, (15 working days).	Date C + six (6) weeks
9.	Commencement of monitoring the leachate and groundwater at the site.	Date D.
10.	Submit Phase II report including record drawings to N.Y.S.D.E.C. for approval	Date C + nine (9) weeks.
11.	Submission of the Phase III monitoring reports to N.Y.S.D.E.C. (and possibly the	

	Monroe County Department of Wastewater Management) as they are ready after each agreed upon testing period, including an approximate three to four (3-4) weeks testing turnaround time.	Date D + four (4) weeks and periodically thereafter.
12.	Submission of a request on behalf of Taylor to N.Y.S.D.E.C. for a declaration that the site clean-up project at Taylor is deemed complete and that on-site monitoring (leachate and groundwater collection) can be discontinued.	Date E.

APPENDIX "A"

Mercury Removal from Water by Iron Sulfide Minerals. An Electron Spectroscopy for Chemical Analysis (ESCA) Study

James R. Brown*, G. Michael Bancroft, and William S. Fyfe

Departments of Chemistry and Geology, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Ronald A. N. McLean

Domtar Ltd., Senneville, Quebec, Canada

■ Using ESCA (electron spectroscopy for chemical analysis) and atomic absorption spectroscopy as analytical techniques, we show that naturally occurring sulfides are excellent adsorbers for aqueous solutions of Hg^{2+} and Hg^0. The Hg concentration in chlor-alkali effluent can be decreased dramatically to less than 100 ppt.

Mercury pollution of natural waters by man's activities (*1–3*) has created severe problems in many countries of the world. It has been estimated that the land-derived flux of mercury to the oceans is four times the preman level (*4*). In addition, an increased use of coal and geothermal steam for electrical generation will, without further abatement measures, increase mercury (and other heavy metal) contamination of the atmosphere and hydrosphere. Of particular recent ecological concern has been the mercury pollution from industrial plants and their associated dump sites (*2*).

Although mercury losses from these plants have been reduced greatly in the last decade (*5,6*), economical and efficient methods must be devised to decrease further losses to the environment. Because the solid-solution adsorption reaction is known to control many heavy ion concentrations in the environment, we looked for a common economical mineral to adsorb Hg from such industrial waste. Pyrrhotite (FeS) and pyrite (FeS_2) ores seemed ideal candidates for a number of reasons. Mercuric ions have a large affinity for sulfide, as evidenced by the solubility product for HgS and a preliminary adsorption study on heated pyrite (*7*). Iron sulfides are common and economical minerals to mine throughout the world and are usually quite accessible in localities where mercury contamination is dominant. For example, most massive sulfide mining operations (Pb, Zn, Cu) separate and discard huge amounts (thousands of tons) of iron sulfides yearly. Iron sulfide and its oxidation products should pose little pollution threat if dumped into contaminated waterways. If mercury exchanges for surface lattices sites, the displaced iron and/or sulfur is precipitated by natural processes.

Three separate sets of adsorption experiments have been carried out. In the first two experiments, 0.1 to 1.0 g of powdered (<200 mesh) pure Sudbury pyrrhotite or pyrite was stirred in deionized distilled water in polypropylene or borosilicate beakers for approximately 2 h to obtain equilibrium. The pH was adjusted to between 4 and 9. Solutions of $HgCl_2$ were added to the stirred FeS to give initial Hg concentrations between 1 and 200 ppm in a first study and 20 and 100 ppb in a second study. In the second study, large concentrations of Cl^- were added to simulate chlor-alkali waste. At selected times, 10-mL aliquots were removed and centrifuged to remove any iron sulfide powder. The samples were then analyzed for mercury by cold vapor chemical (*8*) or graphite furnace flameless atomic absorption methods (*9*).

To show the great utility of the ESCA technique for studying metal sorption on solids directly, and to study further the effect of chloride ion concentration, a third set of experiments was performed. High grade pyrrhotite and pyrite ores were cut into small pieces with a 1-cm^2 surface and then ground and polished. Each sulfide plate was washed thoroughly in acetone and deionized distilled water and air-dried prior to ESCA (XPS) analysis for surface trace impurities of silica (SiO_2), mercury, chlorine, etc. A review of this ESCA technique has been previously published (*10–12*). The theory of ESCA and its recent applications in surface analysis have been critically reviewed by Hercules (*13–15*). These plates were then placed in 500 mL of various concentrations of mercuric chloride or elemental mercury (Hg^0) at pH 4–7. After a specific time in solution, each plate was carefully removed from its reaction solution and dipped five times in fresh deionized water to remove unadsorbed, adhering Hg ions (*10, 16*). Each plate was then air-dried and analyzed using the ESCA technique for the following elements: Hg, Cl, S, Fe, C, and O.

The data for the mercuric ion uptake in the first experiment are summarized in Figure 1. The data indicate an adsorption process, as the mercury loss from solution is proportional to the weight of powdered FeS and the initial mercury ion concentration. The Langmuir adsorption expression (*17*) was used to determine the maximum adsorption capacity (X_m, 3.55×10^{-2} mol of Hg/mol of FeS) and the adsorption constant (b, 6.05×10^4) for the FeS powder. The equilibrium results fit well to the Langmuir adsorption equation and adsorption isotherm. The good linear fit to the Langmuir equation indicates a sorption process proportional to sorbent surface area and sorbate concentration at constant pH.

Table I summarizes the Hg uptake at much lower Hg contents for both Hg^{2+} and Hg^0 with FeS and FeS_2. These results are notable for two reasons. Firstly, with the exception of Hg^0 on FeS, over 95% of the Hg is removed from solution in all cases. Secondly, the adsorption is not decreased by the chloride ion concentration. This result contrasts with previous studies involving the removal of mercury from solution by other materials where increasingly greater Cl^- content reduced the mercury adsorption from solution (*18*).

The ESCA results using both pyrrhotite and pyrite plates, at a solution pH of ~4 ($HgCl_2{}^0$ species dominant) and variable sodium chloride content (0, 100, 1000 ppm), are shown in Tables II and III. These results show that for each initial mercuric ion concentration and constant time of reaction, the sorption rate of mercury *increased* with increasing chloride concentration, especially at low initial Hg concentrations. Mercury sorption rates on iron sulfide minerals thus do not follow a simple cation hydrolysis relationship as previously suggested for oxides (*19*). The highest Hg intensities correspond to near monolayer coverage. In the ESCA studies, little chloride and no sodium ions were detectable, although the initial solution concentration of NaCl was as large as 1000 ppm. This indicates that the mercury sorption is highly specific.

A sulfide plate studied at pH ~7 (Table II) produced a much lower sorption rate with respect to the results at pH ~4. This again indicates the pH influence upon sorption rates (see also Table I). It was also found that pyrrhotite sorbed much larger weights of mercury ions than pyrite, assuming equivalent initial mercury, sodium, and chloride ion concentrations. Thus, surface lattice sites and solubility differences are important sorption reaction parameters.

0013-936X/79/0913-1142$01.00/0

Table I. Results of Hg^{2+} and Hg^0 Adsorption by 1-g Iron Sulfide Minerals

Hg species and mineral type[a]	pH	[Hg] initial, ppb	[Cl] initial, ppm	[Hg] final, ppb	% Hg reduction in solution
A. Hg^{2+}–FeS	4.4	20	0	0.14	99.3
	6.5	20	0	0.35	98.3
	9.8	20	0	1.00	95.0
	4.6	20	100	0.12	99.4
	7.0	20	100	0.40	98.0
	9.7	20	100	0.45	97.8
	4.4	100	0	0.57	99.4
	6.5	100	0	1.5	98.5
	9.5	100	0	4.30	95.7
	4.6	100	100	0.60	99.4
	6.7	100	100	1.3	98.4
B. Hg^0–FeS	4.5	30	0	5.1	83.0
–FeS_2	4.5	30	0	0.10	99.7
C. chlor-alkali plant waste–FeS					
CA 1[b]	5.5	2000	>1000	60	97.0
	4.4[c]	2000	>1000	40	98.0
CA 2[d]	6.2	5	<100	0.10	98.0
	4.4[c]	5	<100	0.05	99.0

[a] 100 mL of solution shaken for 1 h, and then allowed to settle 1 h before analysis of the supernatant. [b] Nontreated chlor-alkali processing water. [c] pH adjusted by dropwise addition of 1 M HCl. [d] Treated chlor-alkali processing water.

Table II. ESCA Study of Mercury Adsorption on Iron Sulfides; Variation with Chloride Concentration

init Hg concn, ppm[a]	mineral type[b]	solution pH	react. time, min[c]	Hg 4f peak area intensity (× 10^4)[d] at init chloride concn, ppm		
				0	100	1000
A. Hg^{2+} reactions						
0.02	FeS	4	1440	3.6	29.4	38.7
0.10	FeS	4	5		0.42	0.47
	FeS	4	60	0.82	2.12	7.30
	FeS	4	1440	30.6	56.9	69.5
	FeS	7	1440	2.3	6.0	2.3
1.0	FeS	4	60	53.0	43.8	38.2
	FeS	4	1440	40.6	40.6	52.4
0.02	FeS_2	4	1440	1.0	7.4	9.4
0.10	FeS_2	4	1440		14.00	10.0
B. Hg^0–H_2O equilibrium reactions						
0.03	FeS	5.7	2880	2.54		
	FeS_2	5.7	5760	18.6		
	FeS_2	5.7	5760	16.0		
C. Hg^0	FeS		2880	31.3		
	FeS_2		5760	32.8		

[a] 500 mL of Hg solution used. [b] Cut pyrrhotite or pyrite ore. [c] Mineral plates dipped five times in fresh water to remove Hg solution. [d] Peak area intensity for 50 scans of Hg 4f.

Several pyrrhotite and pyrite plates reacted in elemental mercury (Hg^0) and in elemental mercury in water (Table II) were also studied by ESCA for sorption rates; pyrite appears to be a superior adsorber for Hg^0. An earlier study of Hg^0 solubility in water at 22 °C indicated an equilibrium mercury content of ~25 ppb (*20*). It is apparent that iron sulfide minerals concentrate mercury ions and atoms from extremely dilute mercury solutions, efficiently and specifically.

Process water samples (CA1 and CA2) were collected at a large chlor-alkali plant in Canada, and Hg adsorption was studied using both iron sulfide powder and plates. The adsorption results (Tables IC and III) are consistent with those using our prepared mercury solutions. The ESCA results (Table III) indicate that a significant amount of mercury in the 500-mL 5-ppb solution is removed, and the powder results (Table IC) show that this Hg content is reduced to $\leq$0.1 ppb. The ESCA results again indicate that the sorption rate increases with decreasing pH.

Some recent studies on mercury in fish in Quebec indicate that the natural existence of sulfide minerals, such as pyrite and pyrrhotite, may be a factor in reducing the availability of mercury to biota in otherwise sensitive areas. In contrast to

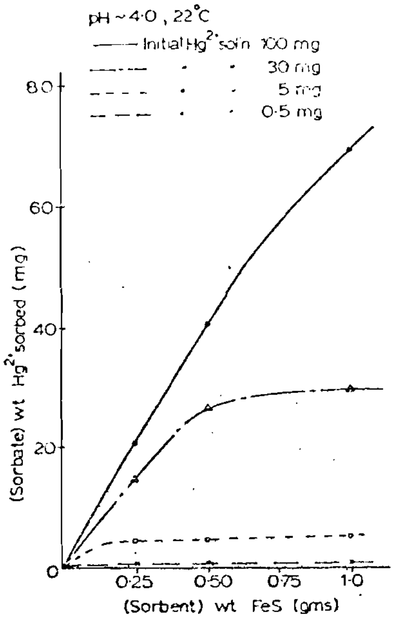


Figure 1. Mercuric ion adsorption on powdered FeS in 500 mL of solution. The time of reaction in each case is 30 min

Table III. ESCA Study of Mercury Sorption by Iron Sulfides from Chlor-Alkali Processing Waters

chlor-alkali processing solution type [a]	iron sulfide ore [b]	reaction time, h [c]	peak area intensity Hg 4f ($\times 10^4$) [d]
1. CA 1 (pH ~5.5)	FeS	1.0	1.1
		24.0	3.0
		48.0	6.9
CA 1[e] (pH ~4.0)	FeS	4.0	nil
		24.0	4.5
		48.0	27.5
	FeS_2	24.0	7.0
2. CA 2 (pH ~6.2)	FeS	6.0	0.83
		24.0	2.10
CA 2[e] (pH ~4.0)	FeS	4.0	27.3
		24.0	7.1
		48.0	19.3
	FeS_2	24.0	2.7

[a] As per Table II. [b] As per Table II. [c] As per Table II. [d] As per Table II. [e] pH adjusted by dropwise addition of 1 M HCl.

accepted theory, the mercury concentration in fish (*21*) was lowest in regions unaffected by point sources with the highest sediment mercury concentrations. This supposed anomaly can be explained by the presence of relatively high concentrations of sulfide minerals in the regions with the highest sediment mercury concentrations.

Our results of mercury adsorption on iron sulfides indicate the potential use in eliminating both mercuric ions and elemental mercury atoms from polluted natural waters, industrial waste, and process waters. The observed residual solution values compare to levels in ocean water (~5 ppt) and rain (~1 ppt) (*22*). A more detailed investigation involving the most efficient design of a pilot plant and related chemical parameters to best use iron sulfide ore is in progress.

Literature Cited

(1) Fimreite, N., Ph.D. Thesis, University of Western Ontario, Ontario, 1970.
(2) Lindberg, S. E., Turner, R. R., *Nature (London)*, 268, 133–6 (1977).
(3) Habashi, F., *Environ. Sci. Technol.*, 12, 1372–6 (1978).
(4) Wood, J. M., Goldberg, E. D., in "Global Chemical Cycles and Their Alterations by Man", Stumm, W., Ed., Berlin Dahlam Konferenzen, 1977, pp 137–53.
(5) Perry R., "Mercury Recovery from Contaminated Waste Water and Sludges", Environmental Protection Technology Series, Report EPA 660/2-74-086, Dec 1974.
(6) Krenkel, P. A., *Crit. Rev. Environ. Control*, 5, 314–8 (1974).
(7) Feick, G., Johanson, E. E., Yeaple, D. S., Environmental Protection Technology Series Report, EPA-R2-72-077, Oct 1972.
(8) Manning, D. C., *At. Absorpt. Newsl.*, 9, 97–9 (1970).
(9) Alder, J. F., Hickmann, D. A., *Anal. Chem.*, 49, 336–9 (1977).
(10) Bancroft, G. M., Brown, J. R., Fyfe, W. S., *Chem. Geol.*, 19, 131–44 (1977).
(11) Bancroft, G. M., Brown, J. R., Fyfe, W. S., *Anal. Chem.*, 49, 1044–7 (1977).
(12) Bancroft, G. M., Brown, J. R., Fyfe, W. S., *Chem. Geol.*, 25, 227–43 (1979).
(13) Hercules, D. M., *Anal. Chem.*, 42, 20A–40A (1970).
(14) Hercules, D. M., in "Characterization of Metal and Polymer Surfaces", Lee, L. H., Ed., Vol. 1, Academic Press, New York, 1977, p 399.
(15) Hercules, D. M., *Anal. Chem.*, 50, 734A–44A (1978).
(16) Brown, J. R., Ph.D. Thesis, University of Western Ontario, Ontario, 1978.
(17) Anderson, B. J., Jenne, E. A., Chao, T. T., *Geochim. Cosmochim. Acta*, 37, 611–22 (1973).
(18) Reimers, R. S., Krenkel, P. A., *J. Water Pollut. Control Fed.*, 46, 352–65 (1974).
(19) MacNaughton, M. G., James, R. O., *J. Colloid Interface Sci.*, 47, 431–40 (1974).
(20) Stock, A., Cucuel, F., Gerstner, F., Köhle, H., Lux, H., *Z. Anorg. Chem.*, 217, 241–4 (1937); from works of Linke, W. F., "Solubilities of Inorganic Chemicals", Vol. 1, American Chemical Society, Washington, D.C., 1958, p 1179.
(21) Penn, A., "The Distribution of Mercury, Selenium and Certain Heavy Metals in Major Fish Species from Northern Quebec", Environment Canada Report, unpublished data.
(22) Mukherji, P., Kester, D. R., *Science*, 204, 64–6 (1979).

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APPENDIX "B"

All inorganic compounds will to some extent dissolve and dissociate in water into their component ions. This ionization is a reversible (or equilibrium) reaction and can be expressed as such. Assume that a salt with the chemical formula AB is added to water.

$$AB \rightleftharpoons A^+ + B^- \qquad (1)$$

Either "A" or "B" ions can be taken out of solution by creating conditions, physically or chemically, under which they will combine with other chemical entities so as to form a compound less soluble than AB. This fundamental chemical concept can be used to remove polluting ions, such as mercury, from water.

The two oxidation states of mercury ions (Hg^{+2}) and (Hg_2^{+2}) can coexist in equilibrium, and this equilibrium is easily shifted. While mercury exists in a stable solution only as the mercurous ion (Hg_2^{+2}), the mercuric ion (Hg^{+2}) is easily (although temporarily) formed.

$$\underset{\substack{\text{elemental}\\ \text{(metallic)}\\ \text{mercury}}}{Hg^0} + \underset{\substack{\text{mercuric}\\ \text{ion}}}{Hg^{+2}} \rightleftharpoons \underset{\substack{\text{mercurous}\\ \text{ion}}}{Hg_2^{+2}} \qquad (2)$$

The mercuric ion can, under suitable conditions, react with organic material to form various organic mercury compounds. These type reactions can be represented by the following equilibria.

$$\begin{tikzcd}
\text{Organic material} + Hg^{+2} \arrow[r] \arrow[dr, shift left] & (CH_3)Hg \arrow[d, shift left] & (3) \\
 & CH_3Hg^+ \arrow[ul, shift left] \arrow[u, shift left] &
\end{tikzcd}$$

Thus it can be seen that, from the viewpoint of how readily mercury can leach into the groundwater and/or form the more toxic organic mercury compounds, that the mercury within the contaminated soil at the Taylor site, can be thought of as being available for transportation through the soil in the mercuric ion (Hg^{+2}) form.

If the mercury within the soil at the Taylor site were to remain buried in an insoluble form which could not migrate, then there is no chance that it would cause further environmental damage. However, if the mercury comes into contact with water (precipitation, groundwater or water from some other source) causing some of it to go into solution, then the potential for environmental damage is heightened. The data presented in the January 1982 Report indicates that, in the past, some of the mercury in the soil has, in fact, gone into solution.

One method that can be utilized to significantly reduce the amount of mercury which can go into solution is to find another ion which will react with and/or strongly adsorb mercury which is in solution, hence "locking" the mercury up and preventing its escape with the water. Ongoing Canadian studies (see Appendix A) indicate that the sulfide in iron pyrite (a common mineral with the chemical formula FeS_2) which is a by-product of mining iron ore can react with the mercury to effectively bind it in place.

$$Hg^{+2} + S^{-2} \rightleftharpoons \underset{\substack{\text{mercury sulfide} \\ \text{(solid)}}}{HgS} \qquad (4)$$

Mercury sulfide is extremely insoluble (see following table) and hence, once it is formed, the mercury ion will be prevented from further leaching or moving. Since mercury sulfide has a much lower solubility than ferric sulfide (iron pyrite) any mercury either in the elemental form or in any oxidation state, will be bound by the iron pyrite when they come into contact. Eventually the bulk of the mercuric ion should combine with the sulfide ion and form the highly insoluble mercury sulfide compound. Iron is a common element within groundwater and it is not generally thought to have negative environmental effects. The "locking up" of mercury in the sulfide complex with the concommitant release of iron into the water should have no detrimental effects. Mercury sulfide is considerably less toxic to soil microorganisms than mercury ions. Therefore, the formation of mercury sulfide at the Taylor site should also improve environmental conditions within the soil itself. This reaction, if it can be induced to occur at the Taylor site, should effectively remove the potential for further mercury contamination of the groundwater.

SOLUBILITY PRODUCTS*

$BaSO_4$	1.1 X 10^{-10}	Ag_2CrO_4	1.9 X 10^{-12}
BaF_2	1.7 X 10^{-6}	Ag_2S	1 X 10^{-51}
$BaCO_3$	1.6 X 10^{-9}	$Fe(OH)_2$	1.6 X 10^{-15}
$BaCrO_4$	8.5 X 10^{-11}	FeS	1 X 10^{-19}
$CaSO^4$	2.4 X 10^{-5}	$Zn(OH)_2$	4.5 X 10^{-17}
$Ca_3(PO_4)_2$	1.3 X 10^{-32}	ZnS	4.5 X 10^{-24}
CaF_2	1.7 X 10^{-10}	$ZnCO_3$	2 X 10^{-10}
$CaCrO_4$	7.1 X 10^{-4}	$Sn(OH)_2$	5 X 10^{-26}
$Mg(OH)_2$	1.8 x 10^{-11}	SnS	8 x 10^{-29}
PbS	7 x 10^{-29}	CuS	4 x 10^{-38}
$PbSO_4$	1.3 x 10^{-8}	$Cu(OH)_2$	1.6 x 10^{-19}
$PbCO_3$	1.5 x 10^{-13}	$Cu(IO_3)_2$	1.3 x 10^{-7}
$PbCrO_4$	2 x 10^{-16}	$Mn(OH)_2$	2 x 10^{-13}
$Pb(OH)_2$	2.8 x 10^{-16}	MnS	7 x 10^{-16}
$AgBrO_3$	5.2 x 10^{-5}	HgS	3 x 10^{-53}
$AgCl$	2.8 x 10^{-10}	CdS	1.4 x 10^{-28}
$AgBr$	5.2 x 10^{-13}	$Ni(OH)_2$	1.6 x 10^{-16}
Agl	8.5 x 10^{-17}		

* From W.M. Latimer, "Oxidation Potentials", 2nd ed., New York, Prentice Hall, Inc. 1952

REFERENCES

1. Ionic Equilibrium, A Mathematic Approach James N. Butler, Addison-Wesley Publishing Company, Inc. 1964

2. University Chemistry second edition, Bruce H. Maham, Addison-Wesley Publishing Company, Inc. 1969

3. Soil Microbiology second edition, Martin Alexander, John Wiley & Sons, 1977

APPENDIX "C"

OPTION 1: ON-SITE CHEMICAL FIXATION OF THE MERCURY

Chemical fixation of the mercury on site is an approach which would consist of three phases. In Phase I, additional hydrogeological field work, testing and lab analysis would be required to verify and expand upon the preliminary information obtained from the field work first performed on the site and presented in the January 1982 Report. Representative soil samples would be obtained in order that the chemical fixation theory may be bench tested in the laboratory. Bench scale testing is especially important at this site due to the heterogeneous nature of the soil in the upper layer. Soil samples representing the various concentrations of mercury in the soil and the various soil matrices within the site would be mixed with varying concentrations of iron pyrite (FeS_2). From the research that Lozier has done, it is most likely that the acceptable concentration of iron pyrite would probably be 2 or 2 1/2% by weight. However, iron pyrite concentrations ranging from 1% to 3% in 1/2% increments by weight would be tested to substantiate this research. With this information in hand, Phase II would then begin.

It is anticipated that the steps involved with Phase II would include the following:

1. The proximity of adjacent structures to the work area would require the removal of the existing perimeter fence.
2. Since the existing structures which border the periphery of the area are so close to the actual work area, and because

the contamination within the soil matrix extends to a depth below the existing footers, either sheeting or some other way of preserving the integrity of these structures might have to be employed.

3. Although our groundwater information is not extensive, well pointing or some other means of controlling the groundwater table might have to be employed in order to make this site stable for excavation work.

4. The work area would be excavated and that material stockpiled. This material would then be mixed with the iron pyrite at the percentage by weight established in the bench testing under Phase I. This chemically fixed material would then be returned to the excavation and compacted.

5. Then a leachate collection system of perforated PVC pipe in a filtering medium would be installed and piped to a central collection point.

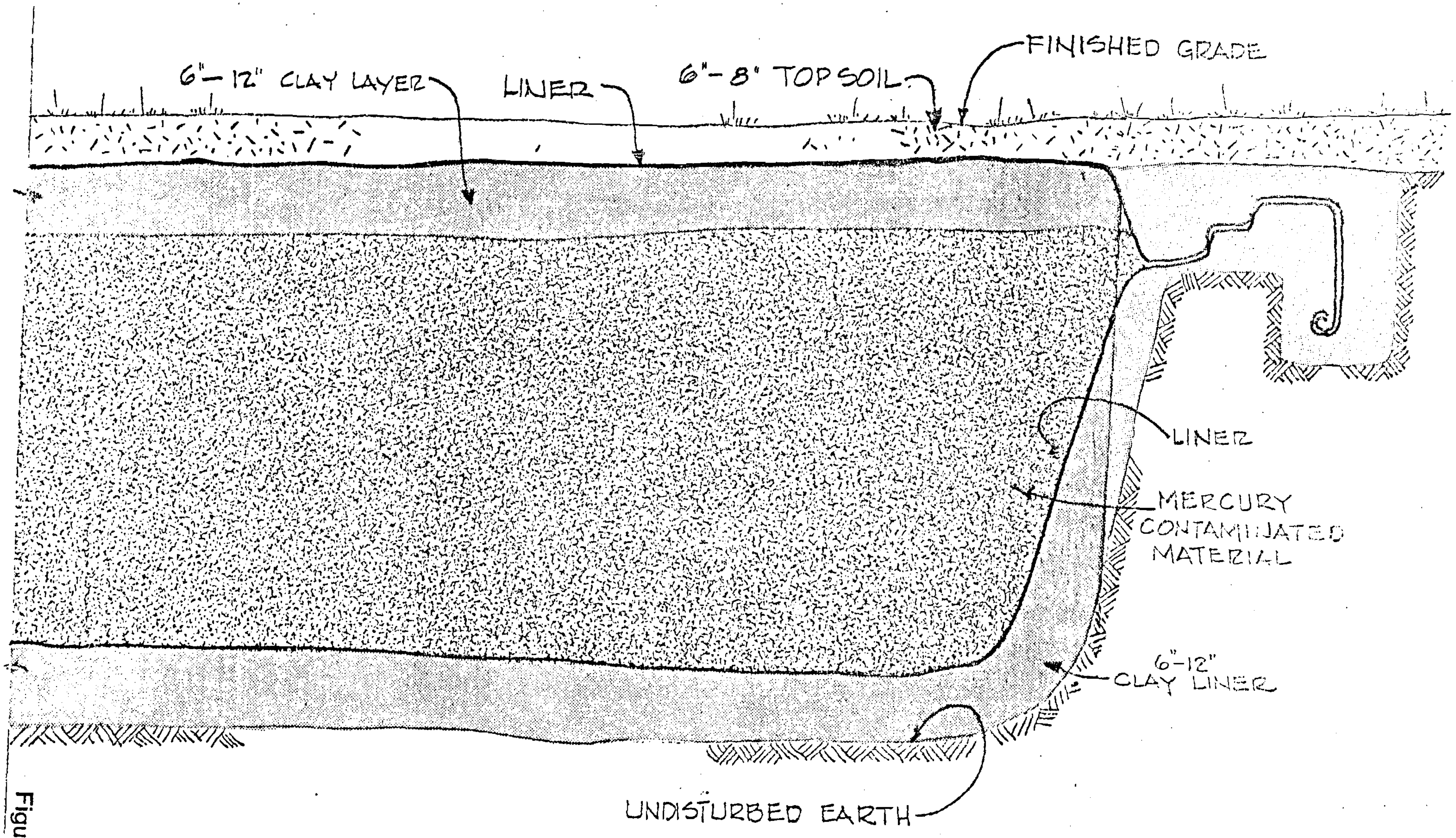
During Phase II of this option the leachate would be collected and monitored for the presence of mercury.

APPENDIX "D"

OPTION 2: ON-SITE ENCAPSULATION OF THE MERCURY

On-site encapsulation of a contaminated area is an approach which is well documented in the literature and one which has been employed in a number of areas throughout the country. The techniques and the materials are available that make this a viable system. Phase I of this option should consist of further field work and laboratory analysis to substantiate and broaden the present data on the soil and groundwater conditions at this site. The data obtained from this phase may also alter the procedures in Phase II. Due to the physical characteristics of the site, it is recommended that one-half of the site be worked on at a time. This approach is proposed in order to effectively install the encapsulation system and still maintain sufficient work area. Figure 2 depicts a typical cross section of this option. The following work sequence is proposed:

1. The proximity of adjacent structures to the area would require the removal of the existing perimeter fence.
2. Since the existing structures which border the area are so close to the actual work area, and since the contamination extends within the soil matrix to a depth below the existing footers, either sheeting or some other way of preserving the integrity of these structures might have to be employed.
3. Although current groundwater information is not extensive, well pointing or some other means of controlling the groundwater table might have to be employed in order to make this site stable for excavation.



TYPICAL ON-SITE ENCAPSULATION of THE MERCURY

Figure 2

4. Once the site was ready for excavation, one-half of the material in question would be excavated and stockpiled on the other half of the site.

5. After this excavation was performed, the first item to be placed in the excavated area would be an underdrain monitoring system consisting of perforated PVC placed in a proper filtering medium.

6. The next item to be placed would be a layer approximately 6" to 1' thick of bentonite clay.

7. On top of this clay layer would be placed an inner liner of an acceptable material, possibly Hytrel. Hytrel is a product manufactured by DuPont Co.

8. The contaminated material would then be replaced back into the area from which it came.

9. A 6" to 1' layer of bentonite clay would be placed on top of the replaced contaminated material.

10. A top liner would be placed on top of the upper clay layer and the upper and lower liners which, along with the clay are now forming an envelope around the contaminated material, would be wrapped together in a series of horizontal and vertical turns, and finally wrapped up underneath and buried in a peripheral bentonite clay trench. This trench would extend around the entire perimeter of the work area, and would constitute the outer seal for the envelope.

11. Once the first half of the site had been dealt with, as described above, the same sequence of events would be

repeated on the remaining work area. After the entire area had been sealed, the upper inert liner would be covered with approximately 6" to 8" of topsoil material to stabilize the top area and also to protect the liner. After the closure system is installed, the underdrain monitoring system should be monitored to insure system integrity.

APPENDIX "E"

OPTION 3: EXCAVATION AND DISPOSAL

Under this methodology it is proposed that two phases be employed. The first phase would once again involve more extensive hydrogeological testing to confirm the onsite soil and water conditions, and thereby establish the required area for excavation. Phase II would consist of physically excavating the contaminated material following all necessary safety and contamination/decontamination procedures. The contaminated material would be packaged as a hazardous waste and trucked to a secure landfill. The exact location for final disposal would be determined once N.Y.S.D.E.C. had made an exemption status determination. Backfill would be transported to the excavated site, and the site restored and regraded for possible future use. Lozier recommends that if this methodology were selected an organization such as CECOS International be used. Such organizations could offer a complete package of services and take full responsibility for the entire excavation and disposal operation.

It is unlikely that post-monitoring of this site would be required.