

Davy**BENCH SCALE DEMONSTRATION:****IN-PULP TREATMENT OF HAMILTON HARBOUR SEDIMENT**

A report of laboratory testwork carried out between 16 January and 31 March 1994 by Davy International Environmental Division for the Wastewater Technology Centre under WTC Contract 3-6015. This contract forms part of the COSTTeP RFP-006. Funding for the project was provided by Environment Canada's Great Lakes Clean-Up Fund.

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**BENCH SCALE DEMONSTRATION: IN-PULP TREATMENT OF HAMILTON
HARBOUR SEDIMENT**

This programme of testwork was carried out by Davy International Environmental Division under contract to Wastewater Technology Centre. The conclusions are based upon the test results and relate solely to the sample of sediment provided by WTC and the scope of work performed. The scope of work was carried out under WTC contract 3-6015 (DI-ED contract C48525) and the ownership and confidentiality of the information contained in this report are defined in the contract.

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BENCH SCALE DEMONSTRATION: IN-PULP TREATMENT OF HAMILTON HARBOUR SEDIMENT

EXECUTIVE SUMMARY

1. BACKGROUND

The Canadian Federal Government established the Great Lakes Clean-Up Fund to support a long term programme to facilitate the rehabilitation of Areas of Concern (AOC) in the Great Lakes where the lake sediment has been found to be severely polluted. Part of this programme is the Contaminated Sediment Treatment Technology Programme (COSTTEP) to identify, demonstrate and disseminate information on technologies suitable for cleaning up contaminated sediment. The Wastewater Technology Centre (WTC) manage the COSTTEP programme and selected the in-pulp process being developed by Davy International Environmental Division (DI-ED) for assessment under contract 3-6015.

DI-ED is an International, Process Engineering/Contracting Organisation with a strong operation in Canada and has been developing an innovative in-pulp process. In pulp adsorption is operated commercially for recovery of gold from ores and is now being adapted to sediment and soil remediation. The key unit operation is a unique counter current contactor in which a leached pulp flows counter current to an adsorbant such as ion exchange resin or activated carbon to remove the contaminants from the leach solution.

A programme of laboratory testwork and a Quality Assurance (QA) programme were agreed between DI-ED and WTC, with the objectives of demonstrating the technology, obtaining data necessary for pilot plant design, and to show that the Ontario guidelines for sediment could be achieved. This report describes the testwork.

2. SAMPLE CHARACTERISATION

The sample used was taken from Hamilton Harbour and was a viscous grey slurry with a strong organic smell. The slurry was continually mixed to enable representative samples to be taken for testwork. The pulp was characterised for pulp density, size analysis, loss on ignition, acetone soluble organic material as well as metal contamination. Metals were determined by US EPA digestion methods and atomic adsorption spectrophotometry with x-ray fluorescence (XRF) analysis being used to confirm the absence of other metal contaminants.

The sample was 90% finer than 90 microns making it amenable to in-pulp treatment. However, 2% was coarser than 350 microns and will require pretreatment. The sample contained a magnetic fraction that was assumed to be an iron alloy although its low solubility in acid leaches suggested that it was not plain carbon steel fragments or dust. The iron content of the harbour slurry was 19% and a magnetic separation pretreatment step is a possibility.

The loss on ignition (LOI) at 900°C was 22% with about 8% being lost at 450°C. Only approximately 2% of the sample was soluble in acetone leaving 20% as insoluble organic material which probably includes coal or coke breeze. The organic fraction will also require a processing step.

XRF analysis did not detect any metallic elements of concern beyond those already identified by WTC. The in-pulp process is particularly appropriate to metals contaminants and determination of metal contaminants was an important part of the programme and was subject to a varied QA programme that gave a high level of confidence in the results. Zinc, lead, iron and manganese levels in the sediment sample exceeded the Ontario "severe effect" guidelines while copper, chromium and nickel contaminant levels were between the "severe effect" and "limited effect" levels.

3. LEACH TESTWORK

Initially a series of leach screening tests were carried out to determine the most appropriate leaching reagent. It was found that in order to achieve low absolute levels of metal contamination it was necessary to leach with strong mineral acid. Based on this information, four agitation leaches were carried out to determine the rate of dissolution of contaminants. Effervescence occurred, probably due to the presence of carbonates, and required careful addition of the acid. Dissolution of contaminants was substantially complete in 90 minutes. However calcium and some iron dissolved and these metals will compete with contaminants in the adsorption stage. It was therefore considered beneficial to try a two-stage leach: a mild leach to dissolve calcium and iron followed by a strong leach to remove contaminants. To achieve this a sequential leach screening test was conducted in which increasing quantities of acid were added, and this was followed by two-stage leaches. Although some separation of contaminants from iron and calcium could be achieved both leach solutions contained dissolved contaminants and will require further processing to recover the contaminants. In all tests the Quality Assurance programme gave good results, giving confidence in the data.

4. ADSORPTION TESTWORK

As with the leach testwork, a series of screening tests were carried out using a number of adsorbants on the two filtrates from the two-stage leach. On the basis of these results a chelating resin was selected for the kinetic test programme in which the leach liquor was contacted with different concentrations of resin. A series of four tests were carried out on the second filtrate at different resin/liquor ratios and the rate of adsorption was monitored. The high level of iron present in solution inhibited the adsorption of contaminants and a pretreatment to remove iron (eg magnetic treatment) is desirable. The magnetic pretreatment stage discussed earlier may be beneficial in this regard.

5. PRECIPITATION TESTWORK

During the adsorption screening tests, precipitation had been observed to remove the contaminants and precipitation tests were carried out on both filtrates to examine the effect of varying pH on metals removal. Although precipitation removed contaminants, some metals remained in solution and would require further processing.

6. FLOWSHEET DEVELOPMENT

The complexity of the Hamilton Harbour sediment means that a multiple stage treatment is necessary and within the time and scope limitation of the programme agreed with WTC, it was not possible to carry out testwork on all these unit operations. However, it has been assumed that iron and organic contamination can be successfully achieved and three flowsheet options were proposed, all with common pretreatment and post-treatment stages. The first flowsheet was based on precipitation for over 95% removal of most contaminants and will require polishing to remove the remainder of the contaminants. The second flowsheet assumed that iron can be removed magnetically and a resin can be found that is selective for contaminants over calcium (as observed in some screening tests). The third flowsheet employs magnetic pretreatment and a two-stage leach to remove calcium. Further testwork will be necessary to identify which is the preferred flowsheet option.

7. CONCLUSIONS

- a) The test programme proposed by Davy International was successfully carried out and showed that all contaminants apart from iron could be leached to below the Ontario severe guidelines. The iron was shown to be magnetic and it may be possible to remove this by magnetic separation.
- b) The high concentration of calcium and iron ions in solution inhibited

adsorption and further work will be required to develop the adsorption stage. Two flowsheets to overcome this problem have been proposed based on the results obtained and require further investigation. An alternative flowsheet based on precipitation has also been proposed.

BENCH SCALE DEMONSTRATION: IN-PULP TREATMENT OF HAMILTON HARBOUR SEDIMENT

1. INTRODUCTION

The Great Lakes have been a major location for industrial activity in both the United States of America and Canada. Historically various inorganic and organic pollutants were discharged accidentally or deliberately into the Great Lakes. As these pollutants built up in the Lakes their effect became apparent and in 1972 the USA and Canada signed an Agreement to clean up the Great Lakes. During the past twenty years effort has concentrated on controlling point source discharges and a major improvement in water quality has been achieved. This programme has been so successful that water quality is such that pollutants are able to migrate back into the water from the lake sediment thus mitigating the upstream achievements. It is therefore now necessary to consider remediating the sediments to avoid a gradual discharge of precipitated pollutants back into the water-courses.

Simultaneously, during the past twenty years the Lakes have been surveyed to identify Areas of Concern (AOC) where pollution is considered to be very high. Seventeen AOC's have been identified within the Canadian side of the Lakes. Surveys have identified that these contaminants are inhibiting the growth of organisms that live in or on the sediment and a reduced diversity of species has been noted. Since these organisms are part of the food chain there is also an accumulation of toxins throughout the chain, including humans.

There is therefore a need to clean up the sediments in these AOC's and to prevent further discharge from contaminated land sites. The Canadian Federal Government have therefore set up the Great Lakes Clean-Up Fund to support a long term programme to rehabilitate these areas. The Clean-Up Fund initiated three separate programmes, each focussing on one aspect of the rehabilitation of contaminated sediment: assessment, removal and treatment. Part of this programme is the Contaminated Sediment Treatment Technology

Programme (COSTTEP). COSTTEP intends to encourage the development of new technologies for remediating contaminated sediment by providing funding for bench, pilot and demonstration scale projects. Under this programme the Wastewater Technology Centre (WTC) have been selecting appropriate innovative technologies for funding support to demonstrate their applicability to treating Great Lakes sediments. The testwork performed by Davy was conducted with sediments collected from Randle's Reef, in Hamilton Harbour. Hamilton Harbour is among Canada's 17 Areas of Concern (AOC). Due to years of industrial steel making activity in the area, Hamilton Harbour sediments have become severely contaminated with heavy metals and polycyclic aromatic hydrocarbons.

Davy is an international contract engineer with a strong operation in Canada. Davy has been developing flowsheets for remediation of metal contaminated soils and sediments based on innovative in-pulp technology. This key process step was originally developed for commercially recovering metals such as gold and uranium which are present in very low concentrations in their natural ores. The technology is based on the use of an ion exchange resin or granular carbon adsorbent which is mixed in counter current flow with a leach slurry directly derived from the leach section of the process. Solid/liquid separation is therefore avoided, making the technique particularly attractive for fine material such as sediments which are difficult to separate from solution. Davy has been developing the process for treating soil from a wood treatment site that is contaminated with copper, chromium, arsenic, zinc and lead. The project is one of a very limited number of projects addressing metal contamination and the development project has been accepted into the European Community Eureka/Euroenviron scheme, the USEPA SITE Emerging Technology Programme and the NATO CCMS Pilot Study on Soil Remediation. The technology is particularly appropriate to Great Lakes sediments and an expression of interest was submitted to WTC in August 1993.

WTC reviewed Davy's expression of interest and considered that the technology could be appropriate for treatment of soil and sediment from the Great Lakes.

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WTC therefore requested a proposal which was submitted by Davy in October 1993. This was reviewed by WTC and WTC requested that Davy should reduce the scope of work in order to meet WTC's requirements. This was done in December 1993 and a contract was placed with Davy in January 1994 by WTC under WTC's standard terms and conditions for the reduced scope of work to be executed (Contract 3-6015). This report is the final report describing the testwork carried out under this contract between January and March 1994.

2. PROJECT DESCRIPTION

2.1 Project Objectives

The objectives of the programme were:

- a) To demonstrate the application of proprietary Davy technology for metals contaminant removal from the selected sediment.
- b) To determine the specific process parameters for,
 - i) leaching of contaminants from the sediment (ie preferred reagent, concentration, and pulp density),
 - ii) in-pulp extraction of metals contaminants (ie preferred adsorbent and the preferred adsorbent/pulp ratio),
 - iii) recovery of the contaminants from the adsorbent in a concentrated form for subsequent disposal or re-use.
- c) To obtain data necessary for the design of an on-site pilot plant to verify the efficacy of the process.
- d) To achieve the contaminant removal efficiency required to meet the appropriate Province of Ontario guidelines.

2.2 Description of the Technology

The process being developed by Davy is based on in-pulp adsorption of leached contaminants thus avoiding solid/liquid separation and recovering the contaminants in a concentrated form. The technique can be used on soil samples but is particularly appropriate for sediments. A detailed description for the technology is given in Appendix 1 but the pertinent points are discussed in this section.

No two soils or sediments are the same and process conditions need to

be optimised for each material. The initial stage of the development programme is therefore to characterise the feed material. This is done by measuring particle size, material type, contaminant concentration and substrate analysis. These analyses are essential to identify flowsheet requirements such as pretreatment, or potential interferences due to other leachable elements.

If appropriate, a pretreatment stage may be incorporated. This makes the technology complimentary to soil washing processes which recover contaminants in a fines fraction leaving a relatively clean coarse fraction. However, some soils are not amenable to soil washing and in this case the whole soil may be treated. Screening removes tramp material and, if appropriate, coarse material may be crushed for leaching. Sediments may need dewatering. Pretreatment required for wood treatment sites may be the removal of wood chips. Davy have investigated such soils and found that wood treated with copper-chromium-arsenic (CCA) is not amenable to leaching and it is preferable to remove the wood by size separation or flotation at an early stage in the process.

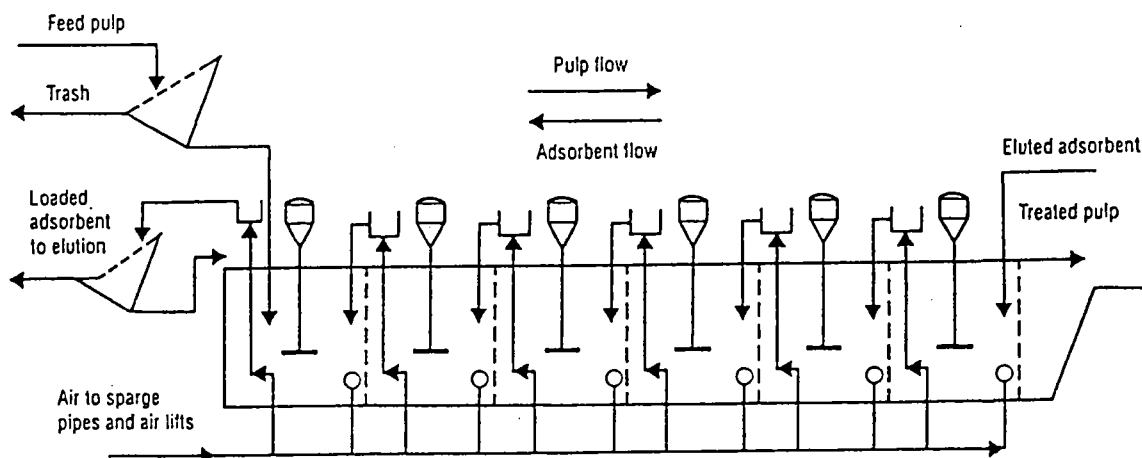
After the appropriate degree of pretreatment the soil or sediment is leached with appropriate reagents. These are selected on the basis of experience, and typically include the common mineral acids and alkalies with or without oxidising agents. More specific reagents can be investigated if metal removals fail to meet the required level. Reagent strength, pulp density and time are important variables to monitor and the leaching characteristics of various size fractions of the feed material are monitored if a large size range exists or specific materials, such as wood chips, are present.

If the sample is a soil then coarse material can be separated by hydrocyclone and washed with water with the liquors returning to the fines pulp. For a sediment this step is unlikely to be required.

The key stage in the process flowsheet is in-pulp adsorption using ion exchange resins for metal contaminants. Activated carbon or other adsorbents may also be used. Operating an in-pulp extraction stage avoids solid/liquid separation, washing of the fine materials and treatment of dilute solutions. The innovative feature is the counter current in-pulp contactor developed by Davy for recovery of metals such as gold and uranium from ores.

A series of stirred contactors are used with screens separating the stages, as shown in Figure 1. Leach pulp flows through the screens and therefore from one end of the contactor to the other by gravity. The adsorbent has a larger particle size than the leach pulp particles and is retained within each agitated stage. Transfer of the adsorbent from one stage to the next, counter-current to the pulp flow, is achieved by air lifts. The barren pulp leaving the contactor meets the fresh adsorbent entering the contactor thus achieving the lowest possible contaminant level in the pulp. Conversely, the fresh pulp entering the contactor meets the partially loaded adsorbent leaving the contactor, so ensuring effective use of the adsorbents capacity.

Figure 1 Davy Improved CIP Adsorption Plant Design



After leaving the contactor, the decontaminated pulp undergoes final treatment, such as pH adjustment and dewatering, prior to final disposal.

The loaded adsorbent leaving the opposite end of the contactor is regenerated. Acid is typically used for most metal extractions. Resin elution generates a concentrated solution containing the contaminants. If the contaminant is a single metal it may be recovered by precipitation, reduction, or electrowinning techniques. Mixed metals precipitation is usually most appropriate with contaminants going to a secure disposal site or for further treatment, although this is usually uneconomic.

The technique is highly applicable to metal contamination although it may also be possible to adapt the technique to organic contamination. In this case activated carbon would be used as an additional adsorbent.

2.3

Benefits of the Technology

The benefits of the leach-RIP/CIP (carbon-in-pulp/resin-in-pulp) technology discussed above as applied to the treatment of the Great Lakes sediments are summarised as:

- a) The process has potential for removing both metal and organic contaminants from the sediments.
- b) Extensive dewatering of the sediments is not required as the process operates directly on slurries containing up to 50 wt% solids.
- c) Solid/liquid separation and solids washing of fine materials such as lake and harbour sediments would normally require large and expensive equipment. In the proposed treatment process, contaminants are removed directly from the leach slurry and solid-liquid separation and solid washing is thus avoided.

- d) Metal contaminants are produced in a concentrated form which can readily be disposed of by conventional means, eg encapsulation and secure storage. Alternatively contaminants could be recovered by conventional processes. Recovery is not however expected to be economically attractive in this case.
- e) Similar process steps and equipment to that used to treat one sediment can be used in readily adapted plant to treat other Great Lakes sediments.
- f) The technology is readily scaleable and a plant capable of treating 50,000 tpy can be made transportable.

2.4 Outline of the Development Programme

The following programme was proposed and carried out.

- a) Preliminary activities.

Preparation of health and safety documentation. A quality assurance programme and analytical procedures were agreed with WTC.

- b) Soil quantification.

Screen analysis of the sediment. Chemical analysis of sediment fraction for Cu, Cr, Ni, Zn, Pb, Mn, Ca, Fe, Al.

- c) Preliminary flowsheet evaluation.

Based on the chemical analysis and Davy's know-how, a preliminary flowsheet evaluation was made to identify appropriate reagents, concentrations, recycles etc.

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d) Leach screening tests.

A series of shake tests were carried out on 100 g samples following Davy's standard leach procedure.

e) Agitation leaches.

A series of agitation leaches were carried out on the sediment samples using the preferred reagents identified from (d) above.

f) Adsorbent screening.

Resins were conditioned, leach solution was prepared and shake tests were carried out to screen for suitable adsorbents.

g) In-pulp adsorption isotherms.

The preferred resin from (f) was contacted with leach liquor at several resin/pulp ratios to obtain adsorption isotherms.

h) Flowsheet review.

The flowsheet was reviewed based on the data obtained.

This programme schedule was prepared to obtain the maximum information within the time constraint set by WTC.

2.5 Analytical Procedures

Davy employed US EPA procedures and these are tabulated in Appendix 2.

The main variation from WTC's recommended procedures is the use of

HCl/HNO₃ in US EPA protocols since the use of HF within UK laboratories is restricted.

Duplicate samples were taken and were provided to WTC as requested.

2.6**Quality Assurance**

Davy operates to BS 5750 (ISO 9001) for its research activities and is familiar with US EPA Quality Assurance Project Plan requirements. However, following discussions with WTC personnel it was agreed that a full QAPP was inappropriate for the current laboratory testwork. However, it is still necessary to obtain quality data to have confidence in the pilot plant design. The following actions were therefore carried out for quality control:

- a) Analyses were performed in duplicate by Davy.
- b) Additional duplicate samples were retained for check analysis by WTC as requested.
- c) Each test included at least one blank and one lake sediment quantified by Canmet or one spiked sample. This procedure did not rigorously meet WTC's 10% rule but approximated to 10% of samples over the whole programme.
- d) Elemental mass balances were carried out for each test. It should be noted that these mass balances include the samples withdrawn for analysis.
- e) Spreadsheet calculations were reviewed and a number of calculations were manually checked.

- f) An audit was carried out by WTC on 7 February 1994, see Appendix 3.

2.7 Environmental Assessment

A preliminary environmental assessment of Davy's technology was carried out by Davy prior to the test programme.

- a) Sediment and soil disturbance.

Being an ex-situ process there are both negative and positive impacts. A negative impact is the disturbance of the sediment and possible migration on excavation. Similarly, returning the cleaned sediment will disturb the environment but it is expected that recovery will take place. The main concern would be migration of pollutants.

For a soil site, excavation can have an effect through dust emission and interference with water flows on the site. This disturbance can be controlled and may be turned to advantage by landscaping of the site.

A positive benefit of ex-situ treatment is that migration of reagents or contaminants cannot take place during the processing operation.

- b) Atmospheric emissions.

Atmospheric emissions should be small due to low temperature and wet operation. However, there is a possibility of gaseous emission in the leach stage if anaerobic activity has produced sulphides, arsenides etc. Such emissions were noted in the test programme and gas scrubbing may be required in any

commercial plant.

c) Aqueous emissions.

Decanted water from excavated sediment may be contaminated and may require treatment. By recycling aqueous streams it should be possible to meet statutory requirements for discharges and this would be part of the design of any commercial plant.

d) Solid emissions.

Returning the cleaned solids (sediment or soil) to the site may introduce other anions and the impact will need to be considered. This is dependent on whether an insoluble salt forms, for example the formation of calcium sulphate. This may be turned to advantage in providing nutrients to re-establish bio activity (eg nitrate).

The precipitated residue containing contaminants will be of small volume but will probably still require further processing (eg fixation) before disposal.

3. SAMPLE CHARACTERISATION - PROCEDURES

3.1 Sample Description

One plastic container of gross weight 32.5 kg and approximate volume of 23 litres was received from WTC. The sample was given the reference D8/94 and Davy's normal administrative procedures were followed. A typical analysis was provided by WTC and is given in Table 3.1.

**Table 3.1 Typical Hamilton Harbour Sediment Analysis
(Supplied by WTC)**

	Typical Analysis (dry weight basis) mg/kg	Ontario Sediment Guidelines	
		Severe Effect mg/kg	Lowest Effect mg/kg
Pb	458	250	31
Cr	88.6	110	26
Cu	64.5	110	16
Ni	49.6	75	16
Zn	2380	820	120
Mn	1830	1100	460
Fe	9.5%	4%	2%
Co	27.6	-	-
Mg	10,000	-	-
B	238	-	-
Sb	356	-	-
Tl	425	-	-

The sample was a thick grey mixture of water and solids with a strong smell of organic material. The sample was tipped into a 40 litre container. The sample container was washed and the washings added to the sample and a total of 3 litres of water were added to the pulp. The pulp was mixed both manually and with an impeller to maintain a

well mixed slurry for sampling. The additional water was required to reduce the viscosity of the pulp. The pulp continued to be stirred throughout the programme in order to minimise problems of segregation.

During the mixing a strong organic smell was present and precautions were taken to protect operators from the fumes. These consisted mainly of containment, use of fume hoods, and ventilation of the laboratory. The laboratory air was tested by Foxborough Miran Air Analyser and recorded a level of 10 ppm total hydrocarbons 10 cm above the surface of the pulp.

3.2

Sampling Procedure

Two duplicate samples of the pulp of approximately 200 mls volume were extracted from the stirred slurry by beaker, then weighed and oven dried at 105°C before reweighing. From these samples an estimate was made of the solids density for use in calculating the required sample volumes for future tests. A slight error will occur due to any volatile organic material that is present with a high vapour pressure below 100°C, but this is believed to be small.

These two samples were chemically analysed in duplicate as grab samples. A further eight samples of 10 mls each were taken by pipette to produce statistical confidence in the bulk analysis. Davy's QA document for contaminated soil describes the theory behind this number of samples and is based on the statistical deviation found in previous samples of fine soils.

Finally, a sample of 1 litre was taken for size analysis.

3.3 Size Analysis

A series of stainless steel screens of British Standard screen size were used to screen the sediment. Screens ranged from 350 microns to 45 microns with the 212 micron screen being absent.

The sample of sediment was wet screened with water washing and light brushing through the series of screens with the final pulp being vacuum filtered on 542 filter paper (2.7 micron pore size). Although the pulp appeared viscous it screened reasonably well. The screens were oven dried at 105°C but drying was slow, possibly due to organic contamination.

The screens were therefore washed with acetone to remove organic material and assist drying and the washings were collected and filtered. The dried solids were rescreened as before to provide a total dry screen analysis. The acetone washings were discoloured and were collected. The minus 45 micron material was slurried with acetone, filtered and the acetone added to the other washings for analysis.

A variety of techniques are available for size analysis below 45 microns but are often dependent on other properties in addition to particle size (for example, particle density is important in sedimentation techniques). This means that size analysis by two different techniques may give different results. In view of this, and the fact that size distribution below 45 microns does not affect the process, the sub 45 micron material was not analysed further.

3.4 Loss on Ignition

In order to determine the approximate organic content of the sediment a number of loss-on-ignition analyses were carried out on oven dried samples. Weighed samples were heated to 900°C, left for 8 hours,

removed and cooled in a desiccator before reweighing.

Analysis of the sediment for organic material was excluded from the proposal. However it was considered useful to know the approximate organic content. Complete analysis for organic material is complex and usually requires an organic extraction such as the Soxhlet or Likens-Nickerson method. However, two measurements can be used as guidelines. Firstly, total carbon content can be measured by controlled oxidation of a sample, collecting the off-gas and determining the CO₂ content by adsorption (Strohlein analysis). Carbon content is calculated back from this figure. A second approach is to use loss on ignition as a guideline. The loss-on-ignition (LOI) is a much simpler technique although it is more susceptible to error (eg incomplete loss due to charring of organic material, loss of inorganic components from hydroxides or carbonates, gain due to oxidation of inorganic components). Despite this it can provide an initial approximation and LOI to carbon ratios for organic materials are generally found to be in the range of 1 to 3 depending on whether the source is chemical or biological.

Davy therefore used loss on ignition measurement as a crude guide to organic content.

3.5

Acetone Soluble Organic

As noted above, some organic material dissolved in acetone. Both acetone and hexane are commonly used for organic analysis and a mixed solvent is proposed by both the US EPA and WTC. WTC also propose freon, dichloromethane and methylene chloride for particular organic fractions. Although organic analysis had been excluded from the test programme, acetone was selected for a determination of the soluble organics. This is a non-critical measurement and acetone is therefore acceptable.

In addition to the screen sample, samples of feed material were extracted in a Soxhlet apparatus using acetone. The acetone was subsequently distilled off and the non-volatile organic material was determined gravimetrically.

3.6 Chemical Analysis

As previously noted, Davy employs US EPA methods for sample preparation prior to analysis by atomic adsorption techniques. Dried samples of the solids were crushed in a pestle and mortar and weighed. The solids were digested by method 3050 using concentrated nitric acid followed by addition of hydrogen peroxide to oxidise metals to their highest valency state. Some organic contamination will also be oxidised. The solids were digested and dilute hydrochloric acid was added to dissolve the digested solids for analysis by atomic adsorption spectrophotometry.

Aqueous samples were also digested with nitric acid followed by dissolution in hydrochloric acid according to method 3010.

Blank samples were prepared in a similar manner. For reference a sample of Canadian Lake Sediment of certified composition (source - Canmet) was analysed by the same method. Spiking was carried out by standard addition to the solid prior to digestion.

The digested solutions were made up to standard volumes and aspirated into an atomic adsorption spectrophotometer. The instrument was calibrated using three standards and drift was checked by re-analysing one standard at the end of the test. Each sample was analysed in triplicate by the machine and the average was used since the standard deviation of the three readings was small.

3.7 X-ray Fluorescence Analysis

One grab sample of the feed material was submitted for XRF analysis to identify whether other metal contaminants may be present. The presence of strontium and zirconium was noted but these elements are not normally of concern and no further analysis was carried out for these elements.

3.8 Magnetic Behaviour

The high iron analysis together with the metallic appearance of the dried screened fractions suggested that metallic iron may be present. The dried screened fractions were therefore tested with a magnet. Significant magnetic fractions were present. A magnetic pre-treatment may therefore be possible but would require additional testwork on the slurry to determine to what extent the organic fraction would inhibit a clean cut. Davy has experience in magnetic separation and recovery (eg in the Sirofloc process) but this pre-treatment was not pursued at this stage. Instead, a mild acid leach was included to remove metallic iron and simulate a pre-treatment.

4. SAMPLE CHARACTERISATION - RESULTS

4.1 Pulp Density

Pulp density measurements are shown in Table 4.1. The pulp density is dependent on settlement in storage and water addition to produce a pulp that could be stirred. Pulp density is only used for determining sample size for analysis and testwork and does not affect plant design. It is thus a non-critical measurement.

Table 4.1 Pulp Density Measurements for Hamilton Harbour Sediment

Sample	Volume	Wet Weight	Pulp Wet Density	Dry Weight	Dry Pulp Density
	mls	g	g/cc	g	g/cc
Grab	250	334.14	1.336	116.49	0.466
Size Analysis Sample	250	-	-	126.98	0.508
Leach Test Sample	250	-	-	136.44	0.546
	250	-	-	135.40	0.542
	250	-	-	134.98	0.540
	250	-	-	135.80	0.543
	250	-	-	134.00	0.536
	250	-	-	135.69	0.543
	250	-	-	136.59	0.546
	250	-	-	134.00	0.536
	250	-	-	135.34	0.541
Average (leach samples)	-	-	-	135.26	0.541
Standard Deviation	-	-	-	0.817	0.004

4.2

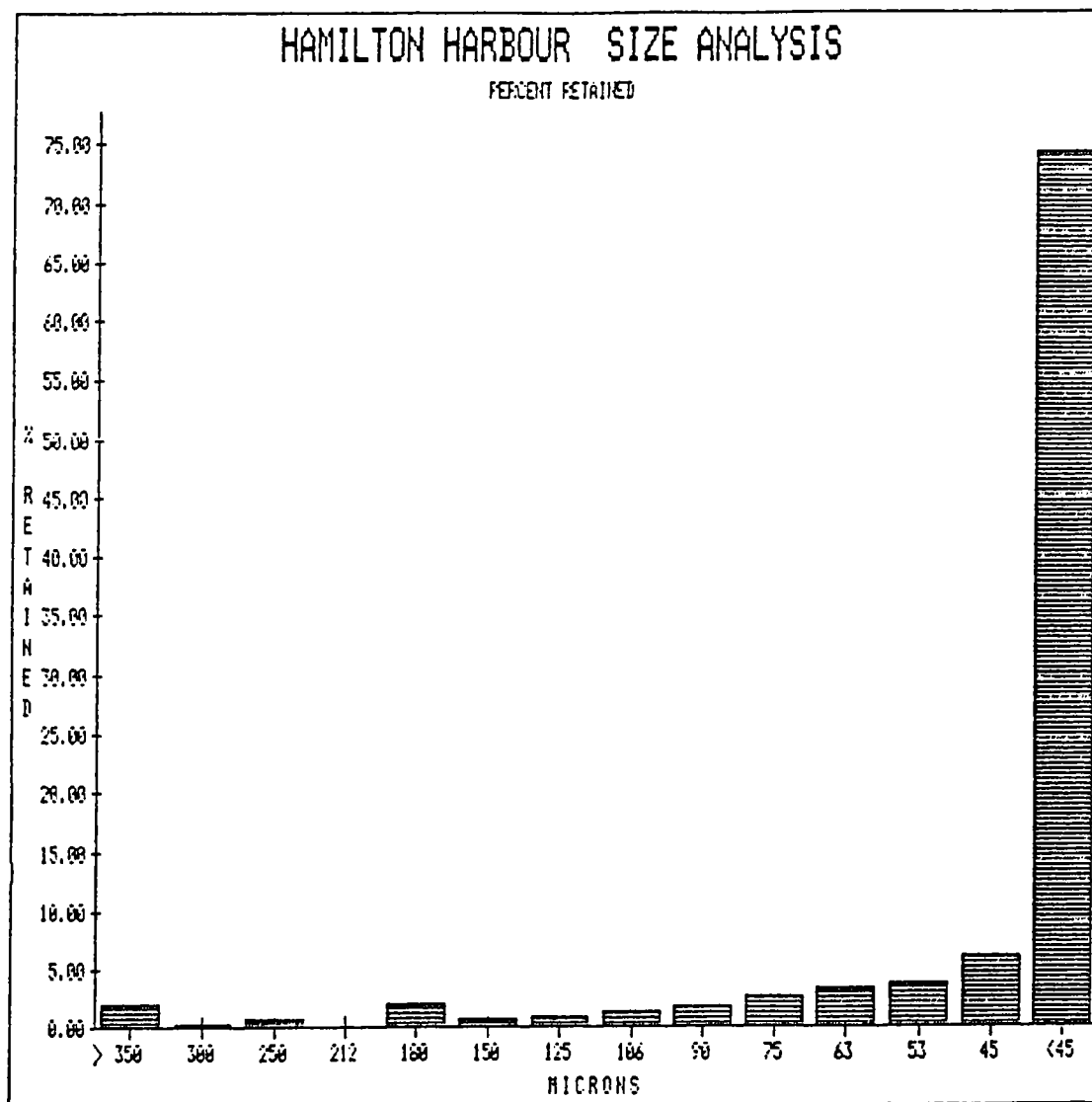
Size Analysis

The size analysis is presented in Table 4.2 and Figure 4.1. A small amount of material (2%) was coarser than 350 microns. This should not however present any processing difficulties. Results were also examined on a log-log plot and no anomalies are observed apart from a slight aberration at 180 microns owing to the absence of the 212 micron screen. The bulk of the material (75%) is less than 45 microns and 90% is finer than 90 microns. The size distribution suggests that the sediment is homogeneous material rather than a mixture of material from multiple sources (for example, from the steel plant and from natural sediment).

Table 4.2 Size Analysis of Hamilton Harbour Sediment

Screen	Weight	Wt %	Cum wt %	Log Size	Log Cum wt %
350	2.64	2.08	2.08	2.544	0.318
300	0.42	0.33	2.41	2.477	0.382
250	1.00	0.79	3.20	2.398	0.505
212				2.326	
180	2.54	2.00	5.20	2.255	0.716
150	0.90	0.71	5.91	2.176	0.771
125	1.30	1.02	6.93	2.097	0.841
106	1.66	1.31	8.24	2.025	0.916
90	2.40	1.89	10.13	1.954	1.006
75	3.22	2.54	12.66	1.875	1.103
63	4.26	3.35	16.02	1.799	1.205
53	4.60	3.62	19.64	1.724	1.293
45	7.74	6.10	25.74	1.653	1.411
<45	94.30	74.26	100.00	-	2.000
Total	126.98	100.00			

Figure 4.1 Size Analysis of Hamilton Harbour Sediment
Percent Retained On Screen



The particle size distribution indicates that the sediment should be amenable to in-pulp processing.

4.3 Organic Content (Acetone Soluble and Loss On Ignition)

Two grab feed samples (DB1 and DB2) were dried and analysed for loss on ignition at 450 and 900°C. There is a slight difference between the two samples at 450°C (Table 4.3) which may be due to sample inhomogeneity, but in general the metal analyses and the total LOI from the 450°C sample showed good consistency. Acetone extraction also showed good consistency between both grab samples and the cumulative filtrate from the screening testwork.

Table 4.3 Organic Analysis of Hamilton Harbour Sediment

Sample	% Acetone Soluble	LOI 450°C	LOI 900°C
Screen Sample	2.0	-	-
Grab Sample (DB1)	2.03	8.7	22.4
Grab Sample (DB2)	2.02	5.4*	20.7*

* Acetone washed.

The acetone soluble material represents 2% of the feed and from a comparison of DB1 and DB2 it is possible that this reports as LOI at 450°C. The LOI at 450°C is significant (5.4 - 8.7%) and the total LOI is high at 22%. Discussions with WTC suggested that the sediment may contain coke or coal breeze from a steel works. This could account for the high LOI that is not acetone soluble. A known by-product of steel works is oily millscale and the sediment probably contains some of this material. However, it is not known with any precision in what form the organic material is present.

Since remediation will also be required for organic matter it is proposed that this is carried out prior to metals treatment to avoid interference by competitive adsorption. Various pre-treatments could be considered such as bio-remediation, solvent washing or flotation. However, for the present programme no pre-treatment was included and a further programme of testwork on pre-treatment of organics is recommended. It was anticipated that pre-treatment will improve on the metals removal although one leach test suggested that this may not necessarily be the case.

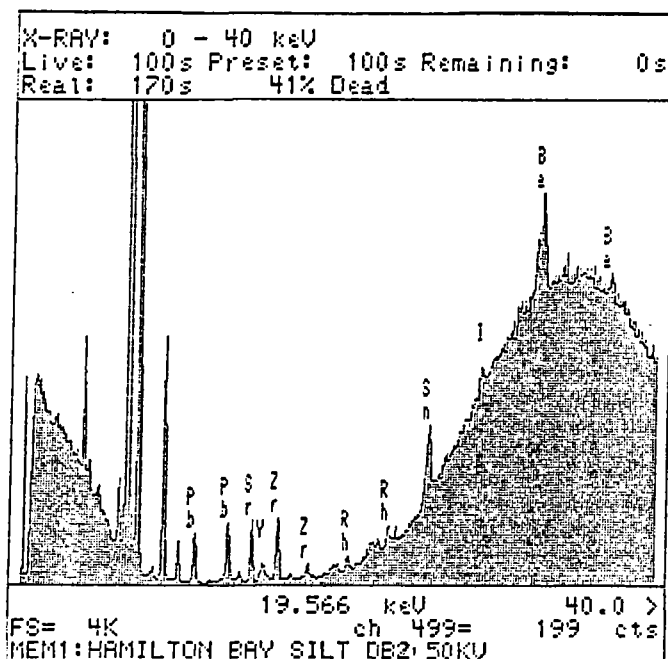
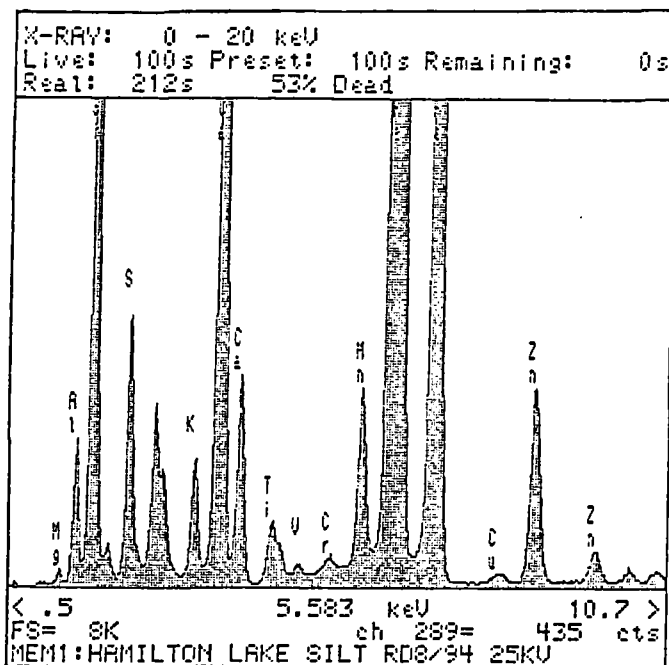
4.4

X-Ray Fluorescence Analysis

Figure 4.2 presents two XRF analyses showing different parts of the elemental spectrum. The elements identified by WTC are present together with expected gangue materials (Ca, Al, Fe). Other elements noted include Sr, Zr, Sn and Ba. These elements are not normally considered as contaminants (apart from Sn in Denmark and Holland) and are not recorded in the Ontario guidelines. Consequently, no further analysis was carried out for these metals.

Sulphur was recorded, in the XRF spectrum and was also noted by the slight smell of H_2S in the leach tests. This would probably be present as sulphide due to anaerobic conditions in the sediments but could be present in other forms. No further analysis was performed in this programme.

Figure 4.2 X-Ray Fluorescence Analysis of Hamilton Harbour Sediment



4.5 Feed Analysis**4.5.1 Quality Assurance**

Table 4.4 shows the analysis of 8 replicate samples together with duplicates of the grab sample taken for pulp density measurement (DB1) and the grab sample taken by WTC (DB2). Sample DB1 was also taken for analysis by WTC. Also presented are a blank and the lake sediment standard together with the standard analysis provided by Canmet.

The blank sample was acceptably low in all metals with the possible exception of aluminium (0.3) and nickel. A level of 0.12 mg/l Ni was recorded for the blank compared with 0.40 - 0.55 mg/l for the digest solutions. There is therefore some uncertainty in the nickel analyses, although the aluminium analyses are believed to be acceptable (aluminium is a non-critical measurement).

The standard lake sediment sample used instead of a spike sample was in acceptable agreement with the Canmet analysis except for chromium and manganese, but these are in good agreement for the Canmet analysis of these elements by HNO_3/HCl digest, which is similar to the technique used by Davy.

The duplicate analyses on DB1 grab sample have standard deviations of less than 2.5% of the average except for aluminium at 5.5%. Sample DB2 has 5 elements with standard deviations within 2.5% of the average and all within 5% of the average. The average of DB1 is within one standard deviation of the average of the 8 replicates for all elements except Cu, Ni, Mn where they are within 2 standard deviations. There is therefore a statistical confidence of the analyses being the same.

present as carbonate due to marine shells (none were visible in the screen sample) then high acid consumption will occur. The effervescence noted in the leach screening tests suggests that carbonate is present.

These major elements together with the LOI account for half the sediment and will result in 3 major streams requiring disposal (iron/iron oxide at approximately 20 - 25%, coke/coal/organic at approximately 20 - 25% and gangue at approximately 50%). In addition there could be an organic stream from acetone washing and a metal contaminant stream for disposal. Flowsheet design therefore needs to take these factors into consideration.

Contaminants are present in high concentrations for zinc, lead, iron and manganese. Copper, chromium and nickel are present at below 100 mg/kg and are between the Ontario "lowest effect level" and "severe effect level". Leach testwork therefore concentrated on the zinc, lead and manganese with the other three contaminants having a lower priority.

Table 4.4 Feed Analysis of Hamilton Bay Sediment

HAMILTON BAY SILT - DR8/94

Sample	Zn	Cu	Pb	Fe	mg/kg Cr	Ni	Al	Ca	Mn
1	4827	93.7	793.9	195000	67.82	41.89	11130	44879	3637
2	4783	91.5	802.4	181200	65.63	50.71	10043	42359	3604
3	4821	91.6	797.8	191100	68.73	52.79	10169	45219	3588
4	4863	90.3	793.0	194300	68.48	45.65	10212	45058	3575
5	4727	89.5	793.9	188200	73.19	56.93	10694	43814	3587
6	5003	90.2	787.7	194500	69.35	46.57	10800	45675	3529
7	4794	90.7	790.4	189500	68.77	43.86	11233	44852	3517
8	4866	92.5	789.3	188900	70.38	53.29	11301	44842	3547
DB1	4799	95.6	778.8	188200	69.42	40.25	11470	45377	3480
DB1	4776	92.3	804.7	188900	68.23	40.14	10616	44551	3537
DB2	4786	93.7	760.8	200200	79.77	48.86	11776	49656	3649
DB2	4820	91.6	814.6	189600	84.64	47.80	12229	49592	3585
BLANK	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.1	0.1
LKSD1	319.3	41.1	83.3	20400	10.77	17.63	5084	55245	487
CANMET LKSD	331.0	44.0	82.0	28000	31.00	16.00			700
CANMET HNO3/HCl	337.0	44.0	84.0	18000	12.00	11.00			460
AVG 1-8	4835.6	91.2	793.5	190338	69.04	48.96	10698	44587	3573
STD 1-8	81.5	1.4	4.8	4570	2.16	5.25	506	1041	40
% STD 1-8	1.7	1.5	0.6	2.4	3.1	10.7	4.7	2.3	1.1
AVG DB1	4787.8	93.9	791.7	188550	68.83	40.19	11043	44964	3509
STD DB1	16.3	2.3	18.4	495	0.84	0.08	604	584	40
% STD DB1	0.3	2.5	2.3	0.3	1.2	0.2	5.5	1.3	1.1
AVG DB2	4802.9	92.7	787.7	194900	82.2	48.3	12002	49624	3617
STD DB2	23.8	1.5	38.0	7495	3.4	0.7	320	45	46
% STD DB2	0.5	1.6	4.8	3.8	4.2	1.5	2.7	0.1	1.3
WTC TYPICAL	2380.0	64.5	458.0	95000	88.6	49.6			1830.0

Table 4.5 Comparative Analysis of Canmet Lake Sediment

	Provisional Values for Total Elements as Supplied by CANMET After Analysis by 35 Laboratories	Provisional Values for Partial Extraction by HNO ₃ /HCl	Provisional Values for Partial Extraction by Dilute HNO ₃ /HCl	Previous DRD Results Using EPA Method 3050	
Element	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Zn	331	337	335	307.6	302.3
Cr	31	12	-	10.5	10.7
Cu	44	44	44	38.3	39.0
Mn	700	460	410	440.8	446.2
Ni	16	11	12	18.2	20.5
As	40	30	-	25.9	26.3
Pb	82	84	83	86.2	84.5
	%	%	%	%	%
Fe	2.8	1.8	1.8	2.12	1.93
Al	4.12	-	-	0.47	0.48
Ca	7.71	-	0	6.56	6.62
SiO ₂	40.1	-	-	-	-

5. SCOPE OF WORK**5.1 Leach Screening Procedure**

Nine 250 mls samples of the stirred bulk slurry were extracted and dried to provide known weights for the leach screening tests. 10 gram samples of the dried solids were taken for chemical analysis. The remaining 100 gram samples formed a cake and were each lightly crushed to break the cake. Each sample was placed in a 1 litre bottle together with 600 mls of the desired reagent. A pulp density of 15% was used to ensure adequate leach reagent was present. The sample pH was noted together with any observation of effervescence. The flasks were then agitated in an orbital incubator at ambient temperature at 200 cycles per minute. The solutions were monitored for pH at hourly intervals for 5 hours, and after 24 hours the samples were removed from the incubator and vacuum filtered on a 525 Whatman filter paper. The solids were washed, dried and reweighed. The filtrate volumes were noted, the washings were added and the solutions were evaporated down to 200 mls to concentrate the contaminants.

Solids were digested by method 3050 and liquids by method 1030 prior to analysis by AAS. Again, a blank and a sample of certified Lake Sediment were also analysed.

Leach reagents are given in Table 5.1. Three mineral acids were selected at the same normality (calculated to be in excess to react with all the iron and calcium present in the sample) together with sulphuric acid at two other concentrations, a mixed acid, citric acid and water plus surfactant. The low, pH 3, sulphuric acid test was chosen to try and dissolve the metallic iron and simulate magnetic pre-treatment.

Table 5.1 Selected Leach Reagents

Reagent	Logic Behind Selection
Water + 1% Lauryl Sulphate	Extra lauryl sulphate added to be above the concentration for micelle formation (0.2%).
Sulphuric Acid - 4N - 2N - pH 3	Stronger acid than Thunder Bay. Base case equivalent to iron and calcium content. Leach of metallic iron only.
Hydrochloric Acid - 2N	Chloride attack of stainless steel chips and slightly soluble lead salt.
Nitric Acid - 2N	Soluble lead salt.
Citric Acid - 2N	Natural organic acid and probably more acceptable to the public. Chelating properties. May react with organics present?
1:1 Sulphuric/Nitric Acid - 2N	Sulphuric acid more readily ionised but nitrate ion beneficial for lead.
Sulphuric Acid - 2N (acetone wash)	Investigate the influence of organics such as oil on leaching.

On addition of any of the acids some effervescence was observed together with a slight smell of hydrogen sulphide. Samples were shaken until effervescence ceased and the flasks were sealed and agitated but gas evolution continued overnight and three flasks ruptured. Six of the nine tests were successfully completed.

5.2

Agitation Leach Tests

A set of four agitation leaches were performed. The procedure in the Davy leach manual was followed. For each leach test 750 mls of pulp were taken and dried to determine the solids weight. The dried cake was lightly crushed by hand and 10 grams were taken for feed analysis. 700 mls of the required reagent were added to a one litre polystyrene square container (mixer box) and the 75 mm diameter, single flat blade impeller was inserted. The impeller was then rotated at 300 rpm. The 100 g of weighed feed material was added over a 90 minute period to avoid excessive effervescence. At given time intervals after the 90

minute period the pulp pH was monitored and a 50 ml sample of pulp was extracted by pipette. This was vacuum filtered on a Whatman 524 filter paper and the filtrate retained for analysis whilst the solids were returned to the leach.

At the end of 24 hours the test was terminated and the pulp was vacuum filtered. The solids were dried and the filtrate volume and residue mass were recorded. Samples were taken for analysis using the procedures described in Section 3.6.

The four tests (LT 10 - 13) were carried out using 2N HNO₃, 4N HNO₃, 2N HCl and 2N HNO₃/H₂SO₄ (equimolar).

5.3

Sequential Leach

The results of the above leach tests showed that calcium was also being solubilised. It was therefore planned to leach the soil at different acid concentrations to determine whether calcium and contaminants were solubilised simultaneously. For leach test 14, 300 grams of dried sediment were mixed with 700 mls deionised water in a one litre square box.

A solution of 35% nitric acid by volume was prepared and 20 ml aliquots (equivalent to 10 mls conc [70%] acid) were added. Once the pH of the pulp had stabilised at a steady value, this was recorded and a 30 ml aliquot of pulp was removed and vacuum filtered with the solids being returned to the slurry. A further 20 mls of 35% nitric acid were added and the procedure repeated. Initially effervescence limited the rate of addition although addition of anti-frother resulted in the froth being controllable.

After addition of 100 mls conc acid (equivalent approximately to 2N addition in the test LT10) the acid addition continued in 40 ml aliquots

(20 mls concentrated acid) until a total of 200 mls concentrated acid had been added (equivalent approximately to 4N addition in LT11). This procedure was adopted to minimise dilution effects.

The final slurry was agitated over an 19 hour period before being filtered and the solids washed with a solution of water and nitric acid at pH 2.

The filtrates were digested and analysed by the agreed procedures as were the feed and final residue.

5.4 Two Stage Leach

From LT 14 it appeared that although zinc was solubilised under all acid additions, it may be possible to preferentially solubilise calcium to achieve a filtrate with a low free acid content for final treatment. The solid from this leach would then be contacted with fresh acid to remove the contaminants and this acid solution could then be recycled to the first stage leach. In order to simulate this, a two stage leach was performed although fresh acid rather than recycled acid was used for the first leach stage. The leach was also used to produce filtrates for the ion exchange tests. The test was carried out at four times the original scale of leach test.

3000 mls of pulp were dried, crushed and weighed. 1200 g of solids were made up to a 30% solids pulp with 2800 mls of 1.5N HNO₃ (98.2 gpl HNO₃) with the solids being added gradually over 30 minutes to avoid excessive effervescence. A 5 litre perspex cubic mixer box was used, stirred at 200 rpm with a 100 cm, four 45° inclined blade impeller. Samples of filtrate were taken and filtered after 30, 60 and 120 minutes. After 120 minutes the leach was stopped and the slurry was vacuum filtered. The residue was washed with 1.5 litres of pH 2 nitric acid and sampled and the filtrate, washings and residue samples were retained for analysis. The wet residue was not weighed but was re-pulped with

the same volume of 2800 mls of 4.3N nitric acid (270 g/l). The second leach continued for two hours with one intermediate sample being obtained after one hour. Residues, filtrates and washings were retained and sampled by the procedures already described.

A second two-stage leach was also carried out to prepare filtrates for the kinetic resin-in-pulp tests. 3600 grams of dried sediment were slurried with 8.0 litres of deionised water in a 10 litre cubic mixer box. 532 mls concentrated nitric acid (70% concentration) were slowly added over a two hour period to the pulp to avoid excessive frothing. This corresponds to 63 gpl nitric acid and approximates to 1N acid. The pulp was stirred at 250 rpm with a 125 mm, four inclined blade impeller for two hours before being vacuum filtered and washed with two litres of pH 2 nitric acid. In this test the filtrate and washings were combined to avoid the possibility of solids crystallising from solution. The residue was sampled and was returned to the mixer box and retreated by being stirred with 7.0 litres water and 1596 mls concentrated nitric acid corresponding to 189 gpl nitric acid addition over a 4.5 hour period. This was followed by 2 hours agitation before vacuum filtration and washing with pH 2 nitric acid. Again, washings and filtrate were combined.

5.5 Resin Screening Tests

The filtrates from the first and second stage leach of LT 15 were taken and the pH of the second stage filtrate was adjusted by the addition of NH_4OH to bring the pH to 2 without causing precipitation. Samples of these solutions (100 ml aliquots) were shaken with 50 mls of adsorbent which had previously been prepared in the hydrogen form by agitation with 5% H_2SO_4 followed by washing with deionised water until the recovered washings had a pH greater than 3.0. The adsorbants used are given in Table 5.2.

Table 5.2 Adsorbent used in Screening Tests

	Reagent	Type	Reactive Group
1	Amberlite 200	Strong Acid	Sulphonic
2	Amberlite C467	Chelating	Aminophosphonic
3	Purolite S940	Chelating	Aminophosphonic
4	Amberlite IR120	Strong Acid	Sulphonic
5	Lewatit TP207	Chelating	Iminodiacetic
6	Amberlite	Strong Acid	Sulphonic
7	Amberlite IRC718	Chelating	Iminodiacetic
8	Chelamine (Metafix)	Chelating	Aminophosphonic
9	Lewatit OC1060 MD	Chelating	Aminophosphonic
10	IRC76	Weak Acidic	Carboxylic
11	Carbon	Norit RF23	Impregnated with $\text{Fe}(\text{OH})_3$ (as received sample - no washing).
12	Magnetite		Regenerated with NaOH and water washed to pH 6.
13	Precipitation		NH_4OH to pH 7

The samples were shaken for 3 hours and then left gently shaking in an orbital incubator overnight.

The resins were filtered and washed free of solution using deionised water. The filtrate and washing were bulked and digested according to EPA method 3050 and analysed.

5.6 Precipitation Test

In order to examine the effect of precipitation at various pH's, 500 mls of filtrate from the first and second leach of LT 15 (two-stage leach) were taken. 100 mls of each liquor was taken for analysis

and the remaining 400 mls of each filtrate was neutralised with 1N NaOH to pH 3. Once the pH had stabilised, 100 mls of the stirred liquors were removed and filtered and washed. The precipitate was weighed and the filtrate retained.

The remaining 300 mls (plus the volume of caustic addition) was further neutralised to pH 5 and the procedure repeated. This procedure was further repeated at pH 7 and pH 9.

Filtrates and washings were combined and digested using EPA method 3050 and analysed by AAS.

5.7

Kinetic Resin Loading Tests

In order to obtain kinetic data on resin loading a series of resin leach stir tests was carried out on leach test LT 16 filtrate 2 using conditioned Lewatit TP 207 resin.

4 x 1 litre aliquots of LT 16 filtrate 2 were placed in separate 2 litre baffled beakers and conditioned resin TP 207 (H^+ ion form) was added at liquid:resin ratios of 2, 4, 6 and 8.

Sample aliquots of the contents were taken after 2, 15, 30, 60 and 120 minutes stirring. The resin in the aliquot was quickly separated from the solution and 50 ml aliquots of solution were retained. At the end of the two hour mixing period, the resin and solutions were filtered and retained. The filtrate from the first of these tests was recontacted with fresh conditioned resin at a 2:1 ratio using the same procedure. The sample solutions were digested and all solutions analysed for contaminants using AAS methods.

6. RESULTS AND DISCUSSION

6.1 Leach Screening Tests

6.1.1 Reagent Selection

Previous extensive testwork by Davy on soil samples has shown that strong mineral acids are required to achieve low absolute levels of contamination. Milder reagents such as organic acids and chelating reagents may be effective at removing readily soluble material, and have a particular niche where single metal contamination is present, but they cannot achieve low total contamination levels. This observation has a sound scientific basis since the contaminants are often associated with iron oxide/hydroxide compounds and examination of EH-pH diagrams shows that a pH below 2 is required to dissolve these species.

It should be noted, however, that strong acids will affect the structure of the sediment and the resultant residue may not be readily disposed of. A risk assessment will therefore be required to determine whether to accept a milder leach and achieve a product with a structure that allows it to be re-used even though it may have a higher contaminant level. For this programme it was decided to try and achieve low absolute levels since the leach (and downstream processing) can be made less aggressive if required, but it is more difficult to proceed in the opposite direction. The Ontario "severe effect level" guidelines were selected as an initial target with the "lowest effect level" as an ultimate target. These values are similar to European limits with the Ontario guideline for chromium being a lower level than European limits and zinc being a higher level. A zinc level lower than the Ontario guidelines is desirable.

Davy's initial size analysis of the Hamilton Harbour sediment indicated a coarser metallic-looking fraction that proved to be magnetic. The subsequent analysis revealed over 19% iron and loss on ignition analysis gave over 20% at 900°C suggesting a high organic content. Discussions with WTC revealed that the sediment may contain a high proportion of steel plant waste (chips, grindings, etc) and coal/coke breeze. The low chromium and nickel analysis suggests that the steel is either carbon or low alloy steel and may thus be amenable to magnetic separation. Davy has experience of magnetic separation of fine (less than 10 microns) magnetite in the Sirofloc process and this could be applied to a pre-treatment stage. Solvent washing could be used to remove organics. Flotation could also be applied to remove much of the coal and associated organics and these pre-treatment steps may be expected to improve the leaching stage by reducing the metal loading (primarily iron, but also zinc from galvanising and lead from free machining steels) and removing the adsorptive capacity of the coal. However, these two steps will require a development programme of their own and this was beyond the scope of the present programme. For this initial assessment it was decided to proceed with the treatment of the whole sample since leaching ought to be improved following a pre-treatment.

6.1.2 Leach Test - Quality Assurance

The Quality Assurance results are given in Table 6.1. The liquid blanks are low with nickel being highest at 0.04 mg/l compared with a reading of 0.13 for the surfactant filtrate. For the solid blank the readings are low with only Mn, Ca and Al being above 0.1 mg/l and all below 1.0 mg/l. Ca and Al are non-critical measurements and the blank values for all three elements are small compared with digestion readings.

Table 6.1 Quality Assurance Results for Leach Screening Test

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	0.02	0.05	0.03	0.04	0.07	0.2	<0.01	0.11	-
Blank	<0.01	0.03	<0.01	0.02	0.04	<0.01	0.01	0.01	0.01
Blank	<0.01	0.02	<0.01	0.02	0.04	<0.01	0.01	0.01	0.01
Lake Sediment	335	100	46	45	31	509	28000	49900	6357
Canmet Sediment Analysis	331	82	44	31	16	700	28000	77100	41200
Canmet Acid Extraction	337	84	44	12	11	460	18000	-	-
Spike	29800	5882	4895	4895	5625	28400	211600	48200	12400
Average Feed Analysis	4794	777	83	79	49	3553	188900	48300	12400
Spike Addition	25000	5000	5000	5000	5000	25000	-	-	-
% Elemental Mass Balance									
LT1	105.4	109.5	104.2	65.6	98.5	102.9	93.8	100.3	101.0
LT2	104.2	109.4	110.1	76.3	102.6	106.4	93.7	115.5	59.3
LT3	104.1	109.5	109.6	82.1	95.7	104.2	91.3	113.5	101.3
LT4	97.9	98.2	111.5	71.4	87.2	104.7	91.3	98.0	100.5
LT5	106.8	101.5	113.9	116.4	100.3	103.1	97.1	97.0	95.6
LT6	106.2	103.4	110.2	66.8	122.3	101.4	93.8	102.5	103.3
Duplicate Analyses: Standard Deviation as Percentage of Mean									
DB2 Feed	0.5	4.8	1.6	4.2	1.5	1.3	3.8	0.1	2.7
DB3 Feed	2.0	2.7	0.1	3.3	1.4	0.7	0.9	0.2	2.4
DB5 Feed	2.9	3.6	5.8	0.9	3.8	0.9	0.1	0.5	1.0
DB6 Feed	1.6	3.9	1.9	1.0	0.1	0.5	0.3	1.3	1.5
DB7 Feed	0.0	2.3	1.8	1.7	4.3	1.0	0.3	0.6	3.4
DB9 Feed	1.4	1.7	2.5	3.5	0.1	0.9	0.2	0.6	2.2
DB10 Feed	0.2	2.4	2.2	4.4	0.4	0.1	1.7	0.2	2.4
DB11 Feed	3.0	4.4	0.2	10.6	2.3	0.7	1.7	1.3	0.6
DB5 Res	2.5	0.0	3.7	2.2	4.5	4.2	5.0	1.0	6.0
DB6 Res	0.5	1.9	0.1	1.4	12.0	1.1	0.1	13.5	4.3
DB7 Res	1.3	0.0	13.2	2.9	2.1	0.6	1.8	4.4	4.2
DB9 Res	4.1	8.9	0.3	5.0	3.9	1.4	2.7	9.7	7.4
DB10 Res	2.8	3.0	1.1	1.3	0.3	0.9	2.8	0.3	5.5
DB11 Res	1.4	3.6	0.5	3.4	4.0	5.2	4.5	1.8	0.8
DB5 Filt	0.7	0.5	0.6	3.5	0.2	1.8	2.3	0.0	3.3
DB6 Filt	0.4	0.8	0.4	1.3	1.4	0.0	0.1	0.6	4.9
DB7 Filt	0.6	0.8	0.4	1.2	0.3	0.0	0.5	1.3	0.0
DB9 Filt	10.5	8.2	6.1	5.6	0.3	1.1	0.3	0.7	6.1
DB10 Filt	17.8	24.1	9.4	12.9	0.0	14.4	0.0	2.3	2.1
DB11 Filt	0.5	0.4	0.3	1.5	0.2	1.7	2.6	0.8	3.0

0.0 indicates less than 0.05%

The analysis of the Lake Sediment standard was acceptable although showing slightly more variation than previously. The spiked sample of DB2 also gave good agreement for Zn, Mn (25 mg added to 1 gram sample) and Pb, Cu and Cr (5 mg added) but was slightly high on Ni.

Statistical analysis of the duplicates (Table 6.1) shows that most duplicates have a standard deviation much less than 5% of the average value with only 2 feed analyses, 8 residue analyses, 10 filtrate analyses exceeding the 5% level. The majority of these analyses were on the samples where poorest leaching occurred (citric acid, and water plus surfactant). Consequently the actual readings are low and any variation due to instrumentation sensitivity will therefore be proportionally greater.

The average of the duplicates of all eight feed samples (16 samples in total) had deviations between 1 and 6.5% of the average of the eight samples taken for the original feed analysis, a range of figures well within acceptable limits. The average is in good agreement with earlier analyses (Table 4.4) although it is slightly lower for Cu (83 cf 91) and slightly higher for Cr (79 cf 69) and Al (12400 cf 10700).

The elemental mass balances are generally very good. Cu, Ni exceeded 10% variation on 6 occasions but this is not unreasonable since they are also present in low levels (less than 100 mg/kg). Ca and Al show 3 excursions beyond 10%: Ca is acceptable being within 15% whilst the Al excursion is poor at 59.3% and is unaccounted for. Cr showed very poor elemental mass balances. Duplicate analyses on sediment, leachate and residue show good consistency and the cause of this poor balance is unaccounted for although it was noted that the average feed analysis was 79 mg/kg compared with 69 previously. Chromium

is present below the Ontario "severe effect level" guidelines and this discrepancy is therefore not critical.

From a quality assurance aspect the results (apart from Cr) are very good and can be used with confidence for comparing the leach reagents.

6.1.3 Leach Test Results

Three tests failed due to equipment failure. These were: sulphuric acid at pH 3; 4N sulphuric acid; and mixed sulphuric/nitric acid. These failures are not critical and were taken into consideration in the agitation leach tests. Results from the 6 successful tests are summarised in Table 6.2 and Tables 6.3 - 6.8 show the spreadsheets for each leach test. From Table 6.2 it can be seen that the tests with surfactant (LT5), gave poor leach results. The solution pH rose slightly from 7 to about 9. The removal was negligible with the residue analysis having no statistical difference from the feed analysis.

Citric acid (LT4) had a more moderate pH than the mineral acids (pH 1.5 rising to 2.4) as shown in Table 6.6. Percentage removals were comparable with mineral acids for most elements but were lower for Zn, Pb, Cu and resulted in a higher residual level of these contaminants. Higher concentrations may be more effective (1 molar was used compared with 2 molar monobasic acids) but this results in a high concentration due to its large molecular weight and solubility difficulties may be encountered at higher strengths. Furthermore, there is a major cost difference and citric acid was therefore discounted as it had not shown any major benefits.

Sulphuric acid showed little difference between acetone washed and unwashed sediment (LT1 and LT6). The difference may or

may not be statistically significant but is sufficiently small to indicate that a pretreatment to remove acetone soluble material may not be necessary and leaching can be carried out effectively on as-received material (it is assumed that drying has had little effect on solubility).

The three mineral acids (H_2SO_4 , HNO_3 , HCl) all had the same concentration (2N) and can be directly compared. Results from all three acids are similar. Percentage removal is typically 70 - 90% with lower removal (40 - 60%) of the contaminants present in small concentrations (less than 100 mg/kg). Sulphuric acid did not attack lead and may be discounted as leachant on its own. However, it did not leach calcium which remains as calcium sulphate and this will be beneficial for downstream processing since it will reduce the concentration of ions present for adsorption. The solubility of iron was low in all 3 leaches and a magnetic fraction was observed in the residue. The process implication is that magnetic separation could be applied as a post treatment rather than a pretreatment. This too was unexpected and a pretreatment had been expected to be required.

On the basis of these results nitric acid was selected as preferred reagent: it will dissolve lead and it dissolved less iron. Hydrochloric acid was discounted as chloride ions can present difficulties with materials of construction and its leaching effectiveness was similar to nitric acid.

Table 6.2 Contaminant Removal for Hamilton Harbour Sediment

Reagent	% Removal								
	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
2N H ₂ SO ₄	84	-5	40	64	45	79	40	5	51
2N HNO ₃	88	93	71	55	45	74	28	97	93
2N HCl	88	94	63	57	53	80	40	98	52
1M Citric	63	61	-9	53	48	76	42	95	4
Surfactant	-6	-1	-14	-16	1	-3	3	-4	5
Acetone/H ₂ SO ₄	87	1	35	62	26	82	41	3	50

Reagent	mg/kg in Residue								
	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
2N H ₂ SO ₄	841	875	56	32	31	823	125500	51100	6800
2N HNO ₃	753	72	32	48	35	1246	180900	2090	1250
2N HCl	806	71	42	49	33	999	163600	1620	8580
1M Citric	2660	456	125	52	39	1226	156900	3500	10700
Surfactant	4917	812	87	82	49	3542	179800	45100	11500
Acetone/H ₂ SO ₄	724	903	59	36	41	745	128400	52900	7150

Table 6.3 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 1 - 2N H₂SO₄

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 1 (DE5) 17-FEB-1994 10:00:17 AM

EXPERIMENTAL CONDITIONS

INPUTS

LEACH SOLUTION	2N H ₂ SO ₄	ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION	14.3 wt%										
WEIGHT SOIL SAMPLE	100.0 g	SOIL ANALYSIS (mg/kg)	4822.5	743.4	83.4	78.4	49.6	3538.0	185730	48230	12464
VOLUME LEACH SOLUTION USED	600.0 ml	RESIDUE ANALYSIS (mg/kg)	640.8	874.8	55.7	32.0	30.6	822.6	125547	51077	6622
VOLUME SLURRY	ml	FINAL LEACH FILTRATE CONC (mg/l)	574.0	4.4	4.9	3.0	2.9	385.0	8222	364	860
		1st WASHINGS CONC (mg/l)									

EXPERIMENTAL MEASUREMENTS

CALCULATED RESULTS

			Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
RESIDUE WEIGHT	89.3 g										
FINAL FILTRATE & WASHINGS	755.0 ml	WEIGHT METAL IN SOIL SAMPLE (mg)	482	74	8	8	5	354	18573	4823	1246
1st WASHINGS VOL	0.0 ml	WEIGHT METAL IN FINAL RESIDUE (mg)	75	78	5	3	3	73	11211	4561	609
		LEACH - WEIGHT EXTRACTED (mg)	433	3	4	2	2	291	6208	275	649
		LEACH - WEIGHT IN SAMPLES (mg)									
		1st WASH - WEIGHT EXTRACTED (mg)									

ACID CONSUMPTION

CONC ACID	%	MASS BALANCE - (out/in) %	105.4	109.5	104.2	65.6	98.5	102.9	93.8	100.3	101.0
DENSITY OF ACID	g/ml	% EXTRACTABLE LEACH	89.9	4.4	44.5	29.2	43.4	82.2	33.4	5.7	52.1
VOL ACID USED	ml	% EXTRACTABLE 1st WASH									
ACID CONSUMPTION	g/kg soil	% EXTRACTABLE TOTAL	89.9	4.4	44.5	29.2	43.4	82.2	33.4	5.7	52.1
		% REMOVED	84.4	-5.1	40.4	63.6	44.9	79.2	39.6	5.4	51.1

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME	SAMPLE VOL	pH	ACID IN SLURRY FILT	SAMPLE TIME	FILTRATE CONCENTRATION (mg/l)								
(mins)	(ml)		g/l	(mins)	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		0.8		0									
60		0.8		60									
150		0.8		150									
210		0.8		210									
270		0.9		270									
330		0.9		330									
1440		0.9		1440	574.0	4.4	4.9	3.0	2.9	385.0	8222.0	364.0	860.0

Mass Balance

Mass Loss	10.7 g
Mass in Solution	-7.9 g as metal ions
Mass as Anions	-7.1 g as anions (CO ₃)
	10.9 g as anions (SO ₄)
Total Loss	6.7 g

Table 6.4 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 2 - 2N HNO₃

SOIL SAMPLE		HAMILTON HARBOUR		LEACH TEST NUMBER 2		17-FEB-1994		10:58:44 AM						
EXPERIMENTAL CONDITIONS						INFUUS								
LEACH SOLUTION		2N HNO3		ELEMENT		Zn	Pb	Cu	Cr	Ki	Mn	Fe	Ca	Al
PULP CONCENTRATION		14.3 wt/%												
WEIGHT SOIL SAMPLE		100.0 g		SOIL ANALYSIS (mg/kg)		4656.0	772.5	80.5	79.0	46.7	3510.0	186159	47260	12301
VOLUME LEACH SOLUTION USED		600.0 ml		RESIDUE ANALYSIS (mg/kg)		752.5	71.8	51.9	48.4	34.9	1246.0	180854	2093	1246
VOLUME SLURRY		ml		FINAL LEACH FILTRATE CONC (mg/l)		493.0	90.0	7.4	2.8	2.5	320.0	4663	6028	725
				1st WASHINGS CONC (mg/l)										
EXPERIMENTAL MEASUREMENTS						CALCULATED RESULTS								
RESIDUE WEIGHT		73.7 g				Zn	Pb	Cu	Cr	Ki	Mn	Fe	Ca	Al
FINAL FILTRATE & WASHINGS		660.0 ml		WEIGHT METAL IN SOIL SAMPLE (mg)		470	77	8	8	5	351	18616	4726	1230
1st WASHINGS VOL		0.0 ml		WEIGHT METAL IN FINAL RESIDUE (mg)		55	5	2	4	3	92	13352	154	92
				LEACH - WEIGHT EXTRACTED (mg)		434	79	7	2	2	262	4103	5305	638
				LEACH - WEIGHT IN SAMPLES (mg)										
ACID CONSUMPTION				1st WASH - WEIGHT EXTRACTED (mg)										
CONC ACID		%		MASS BALANCE - (out/in) %		104.2	109.4	110.1	76.3	102.6	106.4	93.7	115.5	59.3
DENSITY OF ACID		g/ml		% EXTRACTABLE LEACH		92.4	102.5	80.9	31.2	47.5	80.2	22.0	112.2	51.9
VOL ACID USED		ml		% EXTRACTABLE 1st WASH										
ACID CONSUMPTION		g/kg soil		% EXTRACTABLE TOTAL		92.4	102.5	80.9	31.2	47.5	80.2	22.0	112.2	51.9
				% REMOVED		88.2	93.1	70.8	54.8	44.9	73.8	28.4	96.7	52.5
EXPERIMENTAL LEACH TEST RESULTS														
SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN SLURRY g/l	FILT	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)								
						Zn	Pb	Cu	Cr	Ki	Mn	Fe	Ca	Al
0		0.8			0									
60		0.8			60									
150		0.8			150									
210		0.8			210									
270		0.9			270									
330		0.9			330									
1440		0.9			1440	493.0	90.0	7.4	2.8	2.5	320.0	4663.0	6028.0	725.0
Mass Balance														
Mass Loss		26.3 g												
Mass in Solution		-10.9 g as metal ions												
Mass as Anions		-7.1 g as anions (CO3)												
		0.2 g as anions (K2CO3)												
Total Loss		8.7 g												

**Table 6.5 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 3 - 2N HCl**

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 3 (D57) 17-FEB-1994 02:11:07 PM

EXPERIMENTAL CONDITIONS

LEACH SOLUTION 2N HCl
PULP CONCENTRATION 14.3 wt/%
WEIGHT SOIL SAMPLE 100.0 g
VOLUME LEACH SOLUTION USED 600.0 ml
VOLUME SLURRY ml

INPUTS

ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
SOIL ANALYSIS (ng/kg)	4690.7	777.0	80.9	80.9	49.4	3548.0	189521	47105	12555
RESIDUE ANALYSIS (ng/kg)	806.2	70.9	42.3	49.2	33.0	998.5	163560	1623	8384
FINAL LEACH FILTRATE CONC (ng/l)	462.5	89.5	6.6	3.6	2.7	335.0	6535	5848	750
1st WASHINGS CONC (ng/l)									

EXPERIMENTAL MEASUREMENTS

RESIDUE WEIGHT 70.0 g
FINAL FILTRATE & WASHINGS 895.0 ml
1st WASHINGS VOL 0.0 ml

CALCULATED RESULTS

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
WEIGHT METAL IN SOIL SAMPLE (ng)	469	78	8	8	5	355	18952	4711	1256
WEIGHT METAL IN FINAL RESIDUE (ng)	56	5	3	3	2	70	11449	114	601
LEACH - WEIGHT EXTRACTED (ng)	432	80	6	3	2	300	5849	5234	671
LEACH - WEIGHT IN SAMPLES (ng)									
1st WASH - WEIGHT EXTRACTED (ng)									

ACID CONSUMPTION

CONC ACID %
DENSITY OF ACID g/ml
VOL ACID USED ml
ACID CONSUMPTION g/kg soil

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
MASS BALANCE - (out/in) %	104.1	109.5	109.6	82.1	95.7	104.2	91.3	113.5	101.3
% EXTRACTABLE LEACH	92.1	103.1	73.0	39.5	48.9	84.5	30.9	111.1	53.5
% EXTRACTABLE 1st WASH									
% EXTRACTABLE TOTAL	92.1	103.1	73.0	39.5	48.9	84.5	30.9	111.1	53.5
% REMOVED	88.0	93.6	63.4	57.4	53.2	80.3	39.6	97.6	52.1

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE SAMPLE pH ACID IN
TIME VOL SLURRY FILT
(mins) (ml) g/l

SAMPLE
TIME
(mins)

FILTRATE CONCENTRATION (ng/l)

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0									
60									
150									
210									
270									
330									
1440	462.5	89.5	6.6	3.6	2.7	335.0	6535.0	5848.0	750.0

Mass Balance

Mass Loss 30.0 g
Mass in Solution -12.6 g as metal ions
Mass as Anions -7.1 g as anions (CO₃)
0.2 g as anions (NO₃)
Total Loss 10.5 g

**Table 6.6 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 4 - 1 M Citric Acid**

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 4 (REF) 17-FEB-1994 02:26:37 PM

EXPERIMENTAL CONDITIONS			INPUTS										
LEACH SOLUTION	1M Citric		ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al	
PULP CONCENTRATION	14.3 wt/%												
WEIGHT SOIL SAMPLE	100.0 g		SOIL ANALYSIS (mg/kg)	4960.0	811.2	80.3	76.8	51.9	3564.7	187705	48808	12698	
VOLUME LEACH SOLUTION USED	600.0 ml		RESIDUE ANALYSIS (mg/kg)	2861.4	456.2	125.6	52.2	38.5	1226.0	156916	3457	10707	
VOLUME SLURRY	ml		FINAL LEACH FILTRATE CONC (mg/l)	325.8	52.0	0.2	2.0	2.0	312.5	6713	4935	575	
			1st WASHINGS CONC (mg/l)										
EXPERIMENTAL MEASUREMENTS			CALCULATED RESULTS										
RESIDUE WEIGHT	69.8 g			Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al	
FINAL FILTRATE & WASHINGS	520.0 ml		WEIGHT METAL IN SOIL SAMPLE (mg)	496	81	8	8	5	356	18771	4881	1270	
1st WASHINGS VOL	0.0 ml		WEIGHT METAL IN FINAL RESIDUE (mg)	186	32	9	4	3	86	10953	244	747	
			LEACH - WEIGHT EXTRACTED (mg)	360	48	0	2	2	268	6176	4540	529	
			LEACH - WEIGHT IN SAMPLES (mg)										
ACID CONSUMPTION			1st WASH - WEIGHT EXTRACTED (mg)										
ACID CONSUMPTION													
CONC ACID	%		MASS BALANCE - (out/in) %	97.9	98.2	111.5	71.4	87.2	104.7	91.3	98.0	100.5	
DENSITY OF ACID	g/ml		% EXTRACTABLE LEACH	60.4	59.0	2.3	24.0	35.5	80.7	32.9	93.0	41.7	
VOL ACID USED	ml		% EXTRACTABLE 1st WASH										
ACID CONSUMPTION	g/kg soil		% EXTRACTABLE TOTAL	60.4	59.0	2.3	24.0	35.5	80.7	32.9	93.0	41.7	
			% REMOVED	62.5	60.7	-9.2	52.6	48.2	76.0	41.6	95.0	41.1	
EXPERIMENTAL LEACH TEST RESULTS													
SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN SLURRY FILT g/l	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)								
					Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		1.5		0									
60		2.2		60									
150		2.3		150									
210		2.3		210									
270		2.3		270									
330		2.4		330									
1440		2.4		1440	325.8	52.0	0.2	2.0	2.0	312.5	6712.5	4935.0	575.0

Mass Balance

Mass Loss 30.2 g
 Mass in Solution -11.9 g as metal ions
 Mass as Anions -7.3 g as anions (CO₃)
 0.4 g as anions (HCO₃)
 Total Loss 11.4 g

**Table 6.7 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 5 - 1% Lauryl Sulphate**

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 5 (DE10) 17-FEB-1994 02:40:19 PM

EXPERIMENTAL CONDITIONS		INPUTS									
LEACH SOLUTION	1% Surfactant	ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION	14.3 wt%										
WEIGHT SOIL SAMPLE	100.0 g	SOIL ANALYSIS (ng/kg)	4782.3	830.8	78.6	73.1	50.7	3569.3	191730	48518	12487
VOLUME LEACH SOLUTION USED	600.0 ml	RESIDUE ANALYSIS (ng/kg)	4916.5	812.2	86.6	82.3	48.5	3542.0	179751	45112	11924
VOLUME SLURRY	ml	FINAL LEACH FILTRATE CONC (ng/l)	3.2	0.5	0.0	0.0	0.1	2.5	53	58	3
		1st WASHINGS CONC (ng/l)									
EXPERIMENTAL MEASUREMENTS		CALCULATED RESULTS									
RESIDUE WEIGHT	103.4 g		Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
FINAL FILTRATE & WASHINGS	700.0 ml	WEIGHT METAL IN SOIL SAMPLE (ng)	478	83	8	7	5	357	19173	4852	1249
1st WASHINGS VOL	0.0 ml	WEIGHT METAL IN FINAL RESIDUE (ng)	508	84	9	9	5	366	18586	4685	1192
		LEACH - WEIGHT EXTRACTED (ng)	2	0	0	0	0	2	37	40	2
		LEACH - WEIGHT IN SAMPLES (ng)									
ACID CONSUMPTION		1st WASH - WEIGHT EXTRACTED (ng)									
CONC ACID	%	MASS BALANCE - (out/in) %	106.8	101.5	113.9	116.4	100.3	103.1	97.1	97.0	95.6
DENSITY OF ACID	g/ml	% EXTRACTABLE LEACH	0.5	0.4	0.0	0.0	1.4	0.5	0.2	0.8	0.2
VOL ACID USED	ml	% EXTRACTABLE 1st WASH									
ACID CONSUMPTION	g/kg soil	% EXTRACTABLE TOTAL	0.5	0.4	0.0	0.0	1.4	0.5	0.2	0.8	0.2
		% REMOVED	-6.3	-1.1	-13.9	-16.4	1.1	-2.6	3.1	3.9	4.6

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME	SAMPLE VOL	pH	ACID IN SLURRY FILT	SAMPLE TIME	FILTRATE CONCENTRATION (ng/l)								
(mins)	(ml)		g/l	(mins)	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		7.0		0									
60		9.2		60									
150		8.5		150									
210		8.6		210									
270		8.7		270									
330		8.7		330									
1440		8.7		1440	3.2	0.5	0.0	0.0	0.1	2.5	52.9	57.7	3.3

Mass Balance

Mass Loss	-3.4 g
Mass in Solution	-0.1 g as metal ions
Mass as Anions	-7.3 g as anions (CO ₃)
	7.2 g as anions (NO ₃)
Total Loss	-3.5 g

Table 6.8 Leach Screening Test on Hamilton Harbour Sediment
Leach Test 6 - 2N H₂SO₄ on Acetone Washed Sediment

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 6 (DE11) 17-FEB-1994 02:50:15 PM

EXPERIMENTAL CONDITIONS

INPUTS

LEACH SOLUTION	2N H ₂ SO ₄	ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION	14.3 wt%										
WEIGHT SOIL SAMPLE	100.0 g	SOIL ANALYSIS (ng/kg)	4777.4	790.3	78.4	80.4	47.4	3564.8	186934	47337	12509
VOLUME LEACH SOLUTION USED	600.0 ml	RESIDUE ANALYSIS (ng/kg)	724.0	903.1	59.2	35.6	40.5	745.3	128363	52962	7150
VOLUME SLURRY	ml	FINAL LEACH FILTRATE CONC (ng/l)	622.0	4.8	4.9	3.2	3.2	415.0	8562	370	540
		1st WASHINGS CONC (ng/l)									

EXPERIMENTAL MEASUREMENTS

CALCULATED RESULTS

			Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
RESIDUE WEIGHT	86.7 g										
FINAL FILTRATE & WASHINGS	715.0 ml	WEIGHT METAL IN SOIL SAMPLE (ng)	478	79	8	8	5	356	18653	4734	1251
1st WASHINGS VOL	0.0 ml	WEIGHT METAL IN FINAL RESIDUE (ng)	63	78	5	3	4	65	11129	4567	620
		LEACH - WEIGHT EXTRACTED (ng)	445	3	4	2	2	297	6408	265	672
		LEACH - WEIGHT IN SAMPLES (ng)									
		1st WASH - WEIGHT EXTRACTED (ng)									
ACID CONSUMPTION											
CONC ACID	%	MASS BALANCE - (out/in) %	106.2	103.4	110.2	66.8	122.3	101.4	93.8	102.5	103.3
DENSITY OF ACID	g/ml	% EXTRACTABLE LEACH	93.1	4.3	44.7	28.5	48.3	83.2	34.3	5.6	53.7
VOL ACID USED	ml	% EXTRACTABLE 1st WASH									
ACID CONSUMPTION	g/kg soil	% EXTRACTABLE TOTAL	93.1	4.3	44.7	28.5	48.3	83.2	34.3	5.6	53.7
		% REMOVED	66.9	0.9	34.5	61.6	25.9	81.9	40.5	3.1	50.4

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME	SAMPLE VOL	pH	ACID IN SLURRY FILT		SAMPLE TIME	FILTRATE CONCENTRATION (mg/l)								
(mins)	(ml)		g/l		(mins)	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		0.6			0									
60		0.6			60									
150		1.1			150									
210		0.8			210									
270		0.9			270									
330		1.0			330									
1440		1.0			1440	622.0	4.8	4.9	3.2	3.2	415.0	8562.0	370.0	540.0

Mass Balance

Mass Loss	13.3 g
Mass in Solution	-8.1 g as metal ions
Mass as Acids	-7.1 g as anions (CO ₃)
	7.1 g as anions (K ₂ O)
Total loss	5.2 g

6.1.4

Overall Mass Balance

Whilst elemental mass balances are good, overall mass balances are only 90 - 95%. To calculate the mass balance the loss due to metal ions in solution has been calculated for each leach. In addition it has been assumed that calcium is present as carbonate (eg marine shells) and the CO_3 ion is lost on dissolution. The calcium remaining in the residue is assumed to be a salt (sulphate for H_2SO_4 , unknown for other acids but taken as the acid anion for calculation purposes).

The surfactant showed a mass gain and the cause is unknown unless some surfactant is retained by the soil. Other losses range from 5.2 to 11.4 g. Leach tests LT1 and LT6 show figures differing by 1.5 g which may correspond with the acetone soluble material (2%). In order to check whether any organic material had been lost, LOI determinations were carried out (Table 6.9). This showed that there was little loss in LOI on leaching and the cause of the poor total mass balance is therefore unidentified although a possible explanation may be some dissolution of silica.

Table 6.9 Loss on Ignition on Hamilton Harbour Residues

Leach Test Number	Sample	% LOI at 900°C
1	DB5 Res	21.4
2	DB6 Res	21.2
3	DB7 Res	22.9
4	DB9 Res	22.1
5	DB10 Res	22.9
6	DB11 Res	20.1
	DB1	22.4
	DB2 Acetone Washed	20.7

6.1.5 Conclusions

- a) Strong mineral acid is the preferred leachant and nitric acid was selected for further evaluation.
- b) Pretreatment with acetone is not required for metals removal.
- c) A pre or post treatment for magnetic removal of iron is an option.

6.2 Agitation Leach Tests**6.2.1 Introduction**

The results of the four standard agitation leach tests are shown in Tables 6.10 - 6.14. The feed analyses were averaged from duplicate samples.

6.2.2 Agitation Leach - Quality Assurance

Table 6.10 presents the Quality Assurance results from these tests.

Table 6.10

Quality Assurance Results for Leach Tests LT10 - LT13

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	0.02	0.05	0.02	<0.01	0.02	0.16	0.01	0.15	0.4
Blank	0.01	<0.01	0.03	<0.01	0.02	0.03	0.01	0.01	0.02
Blank	0.01	<0.01	0.03	<0.01	0.01	0.04	0.01	0.01	0.02
Lake Sediment	323	94	43	13	22	452	22090	67930	5890
% Mass Bal LT10	97.6	102.3	99.2	99.1	100.5	88.1	99.7	110.1	96.8
% Mass Bal LT11	98.4	104.9	89.2	75.3	89.7	107.0	96.5	105.7	91.9
% Mass Bal LT12	97.6	101.3	97.3	100.0	95.3	105.1	97.5	111.5	91.2
% Mass Bal LT13	99.6	100.1	101.5	121.1	102.5	104.3	100.6	97.7	90.0

Quality Assurance Results for LT 14

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	<0.01	0.06	0.1	0.01	0.02	0.1	0.02	0.01	<0.01
Blank	0.01	0.02	<0.01	<0.01	<0.01	0.01	0.01	0.03	0.2
Blank	0.01	0.02	<0.01	<0.01	<0.01	0.01	0.01	0.02	0.2
Lake Sediment	306	104	49	10	21	464	20740	65190	5067
Lake Sediment	317	102	50	9	21	466	21300	65890	5103
% Mass Bal	98.6	109.1	104.2	103.5	99.8	106.3	90.3	117.4	111.9

Table 6.10 (continued)

Quality Assurance Results for LT 15

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	0.3	<0.01	<0.01	<0.01	<0.01	0.1	0.02	0.02	0.2
Blank	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.1
Blank	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.1
Lake Sediment	329	80	40	20	20	449	22430	63800	4985
Lake Sediment	330	80	40	20	20	459	22470	63920	4984
% Mass Bal LT10	97.0	101.5	97.0	96.9	105.5	104.9	103.3	110.1	100.7

Quality Assurance Results for LT 16

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	0.1	0.1	<0.01	<0.01	<0.01	<0.01	0.03	0.4	<0.01
Lake Sediment	328	109.3	39.8	9.9	19.9	447	21370	55660	5039
Lake Sediment	330	109.9	40.0	10.0	20.0	460	22430	55940	5005
% Mass Bal	106.8	115.4	92.4	90.4	108.6	112.2	114.0	162.6	101.4
Canmet Analysis	331	82	44	31	16	700	28000	77100	41200
Lake Sediment Analysis									
Canmet HNO ₃ /HCl extract	337	84	44	12	11	460	18000	-	-
DRD Analysis EPA3050	305	85	39	11	19	440	20000	66000	4800

The blanks are acceptable although the first blank is slightly high in Mn, Ca and Al. The lake sediment standard is close to the Canmet figures using HNO_3/HCl extraction. Lead is slightly high and calcium and aluminium are low but are consistent with DRD analyses using method EPA 3050. Elemental mass balances are good and there is confidence in the results.

6.2.3**LT 10 - 2N Nitric Acid (Table 6.11)**

The leach with 2.35 N nitric acid shows very good elemental mass balances with all apart from Mn and Ca being within 10% of full accountability. The total mass balance shows a 24 gram loss after accounting for cations taken into solution and allowing for calcium all being present as carbonate and any insoluble calcium assumed to be present as sulphate. This is a simplification but is reasonable for the purpose of the calculations. This loss may partly be anions associated with the cations (although anion masses as oxide or hydroxide are generally less than cation masses); partly it may be sample loss on the filter papers during intermediate sampling; but in part it could be dissolution of other materials (organic or siliceous) and corresponds to 8% of the feed. The leached sediment appeared sandy (crystalline) in nature. However, the presence of silica was sometimes detected in the leach solutions during analysis.

The filtrate analyses show that dissolution is complete within 90 minutes and most elements show a decline in concentration in solution thereafter. This may be precipitation due to a change in pH from 1.2 to 1.6, or it may be a solubility effect.

Acid usage was high with only 0.6 gpl free acid in the final filtrate compared with 148.4 gpl in the feed.

The removal efficiencies (based on solid analyses) are over 80% for Zn, Pb and Mn but are lower for the elements present at lower levels (Cu, Cr, Ni). Only 12% iron dissolved but resulted in a filtrate containing 7 gpl iron and 19 gpl calcium. Filtrate analyses suggest that contaminant removal efficiencies may have been higher had the test terminated after 90 minutes. However, despite the high removals, zinc was still above the Ontario "severe effect level" guidelines although lead and manganese are within the guidelines. Iron is above guideline levels but may be reduced magnetically.

Table 6.11 Standard Leach Test LT10 - 2N HNO₃

SOIL SAMPLE		HAMILTON HARBOUR		LEACH TEST NUMBER 10 (DB13) 24-FEB-1994 09:00:1024-FEB-1994										
EXPERIMENTAL CONDITIONS				INPUTS										
LEACH SOLUTION		2N HNO3		ELEMENT		Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION		30.0 wt %		SOIL ANALYSIS (mg/kg)		4854.0	756.0	91.0	44.0	45.0	3466.0	174824	48543	13235
WEIGHT SOIL SAMPLE		300.0 g		RESIDUE ANALYSIS (mg/kg)		1143.0	198.0	65.0	33.0	39.0	674.5	201098	1525	11025
VOLUME LEACH SOLUTION USED		700.0 ml		FINAL LEACH FILTRATE CONC (mg/l)		1420.0	253.0	14.1	6.6	5.4	666.0	7168	19312	1628
VOLUME SLURRY		830.0 ml		1st WASHINGS CONC (mg/l)		162.5	26.0	2.3	0.8	0.8	114.2	1105.0	2155.0	190.6
EXPERIMENTAL MEASUREMENTS				CALCULATED RESULTS										
RESIDUE WEIGHT		229.5 g		WEIGHT METAL IN SOIL SAMPLE (mg)		1456	227	27	13	14	1040	52447	14563	3971
FINAL FILTRATE & WASHINGS		560.0 ml		WEIGHT METAL IN FINAL RESIDUE (mg)		262	45	15	8	9	201	46152	350	2550
1st WASHINGS VOL		1060.0 ml		LEACH - WEIGHT EXTRACTED (mg)		795	130	8	4	3	485	4014	10615	912
				LEACH - WEIGHT IN SAMPLES (mg)		170	28	2	1	1	109	973	2582	158
ACID CONSUMPTION				1st WASH - WEIGHT EXTRACTED (mg)		163	28	2	1	1	121	1171	2284	202
CONC ACID		%		MASS BALANCE - (out/in) %		97.6	102.3	99.2	99.1	100.5	88.1	99.7	110.1	96.8
DENSITY OF ACID		g/ml		% EXTRACTABLE LEACH		66.3	70.1	35.7	35.3	28.0	57.1	9.5	92.0	27.9
VOL ACID USED		ml		% EXTRACTABLE 1st WASH		13.3	12.2	8.9	6.4	6.3	11.6	2.2	15.7	5.1
ACID CONSUMPTION		g/kg soil		% EXTRACTABLE TOTAL		79.6	82.2	44.6	41.7	34.2	68.8	11.7	107.7	33.0
				% REMOVED		82.0	80.0	45.4	42.6	53.7	80.7	12.0	97.6	36.3
EXPERIMENTAL LEACH TEST RESULTS														
SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN SLURRY g/l	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)									
					Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al	
0		0.6	148.4	0										
90	30.0	1.2		90	1493	243	15	8	7	945	9018	23114	1718	
180	30.0	1.5		180	1387	238	15	8	6	900	7857	21883	1600	
240		1.5		240										
300	30.0	1.6		300	1590	245	15	8	6	895	7657	21450	1700	
360		1.6		360										
420		1.6		420										
480	30.0	1.6		480	1407	223	16	8	6	898	7900	19636	1573	
1440.0		1.5	0.6	1440	1420	253	14	7	5	866	7168	19312	1628	
Mass Balance														
Mass loss		70.5 g												
Mass in Solution		-25.2 g as metal ions												
Mass as Anions		-21.8 g as anions (Cl ⁻)												
		0.8 g as anions (SO ₄ ²⁻)												
Total loss		24.3 g												

6.2.4**LT11 - 4N Nitric Acid (Table 6.12)**

Leach test 11 was carried out with 4.3 N nitric acid and gave good elemental mass balances with all elements apart from chromium being within 11% of accountability. Total mass loss was 10% of the feed, slightly higher than with two normal nitric acid.

The pH remained lower at 0.3 and apart from an apparent reduction in contaminant concentration at 180 minutes, the filtrates show a slight increase in leaching with time (iron increased the most with a 55% increase from 90 minutes to 24 hours). Removal rates were high but 31% iron was also dissolved and this may present problems in downstream processing. The residue was within the Ontario "severe effect level" guidelines for all elements except iron, although it would be preferable to see lower zinc and manganese levels. Acid usage was higher (from initial concentration 270.7 gpl to final concentration of 49.9 gpl) and left a higher free acid in the final filtrate that will require treatment.

Table 6.12 Standard Leach Test LT11 - 4N HNO₃

SOIL SAMPLE HAMILTON HARBOR LEACH TEST NUMBER 11 (DE13) 24-FEB-1994 09:23:1624-FEB-1994

EXPERIMENTAL CONDITIONS

LEACH SOLUTION 4N HNO₃
 PULP CONCENTRATION 50.0 wt %
 WEIGHT SOIL SAMPLE 300.0 g
 VOLUME LEACH SOLUTION USED 700.0 ml
 VOLUME SLURRY 650.0 ml

INPUTS

ELEMENT Zn Pb Cu Cr Ni Mn Fe Co Al
 SOIL ANALYSIS (mg/kg) 4854.0 756.0 91.0 44.0 45.0 3466.0 174824 48543 13235
 RESIDUE ANALYSIS (mg/kg) 597.0 43.0 36.0 20.0 27.0 1017.0 167656 2058 8433
 FINAL LEACH FILTRATE CONC (mg/l) 1775.0 321.7 21.5 6.7 8.1 1208.0 20378 19960 2563
 1st WASHES CONC (mg/l) 167.1 21.0 2.6 0.9 1.0 114.0 1832.0 1675.0 211.8

EXPERIMENTAL MEASUREMENTS

RESIDUE WEIGHT 215.6 g
 FINAL FILTRATE & WASHES 520.0 ml
 1st WASHES VOL 1180.0 ml

CALCULATED RESULTS

Zn Pb Cu Cr Ni Mn Fe Co Al
 WEIGHT METAL IN SOIL SAMPLE (mg) 1456 227 27 13 14 1040 52447 14563 3971
 WEIGHT METAL IN FINAL RESIDUE (mg) 129 9 8 4 6 219 36147 444 1818
 LEACH - WEIGHT EXTRACTED (mg) 923 167 11 3 4 628 10597 10379 1333
 LEACH - WEIGHT IN SAMPLES (mg) 164 37 2 1 1 130 1706 2592 249
 1st WASH - WEIGHT EXTRACTED (mg) 197 25 3 1 1 135 2162 1977 250

ACID CONSUMPTION

CONC ACID %
 DENSITY OF ACID g/ml
 VOL ACID USED ml
 ACID CONSUMPTION g/kg soil

MASS BALANCE - (out/in) %
 % EXTRACTABLE LEACH 58.4 104.9 89.2 75.3 89.7 107.0 96.5 105.7 91.9
 % EXTRACTABLE 1st WASH 76.0 89.9 49.5 34.6 37.9 72.9 23.5 89.1 39.8
 % EXTRACTABLE TOTAL 13.5 10.9 11.2 8.0 8.7 12.9 4.1 13.6 6.3
 % REMOVED 89.6 100.8 60.8 42.6 46.6 85.9 27.6 102.6 46.1
 91.2 95.8 71.6 67.3 56.9 78.9 31.1 97.0 54.2

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME (mins) SAMPLE VOL (ml) pH ACID IN SLURRY g/l
 0 30.0 0.4 270.7
 90 30.0 0.4
 180 30.0 0.2
 240 0.3
 300 30.0 0.3
 360 0.3
 420 0.3
 480.0 50.0 0.3
 1440.0 0.2 49.9

SAMPLE TIME (mins) FILTRATE CONCENTRATION (mg/l)
 Zn Pb Cu Cr Ni Mn Fe Co Al
 0 50 1545 310 19 9 7 1055 13130 23000 2067
 90 180 1482 295 19 9 7 1035 13167 20867 1967
 240 300 1563 313 20 9 8 1122 15080 21967 2153
 360 560
 420
 480 1550 300 20 9 8 1120 15473 20567 2127
 1440 1775 322 22 7 8 1208 20378 19960 2563

Mass Balance

Mass loss 84.4 g
 Mass in Solution -33.7 g as metal ions
 Mass as Anions -21.8 g as anions (CO₃)
 1.1 g as anions (SO₄)
 Total loss 29.9 g

6.2.5**LT 12 - 2N Hydrochloric Acid (Table 6.13)**

Hydrochloric acid had appeared to be the second most attractive leachant in the screening tests and one kinetic test was performed with 1.93 N for comparison with nitric acid.

Elemental mass balances are excellent, all being within 5% apart from calcium (11.5% difference) and aluminium (8.8% difference). Total mass balance is also very close to the 2N nitric acid leach with 8% loss.

Elemental concentrations in solution decline slightly as in LT10, and again this may correspond with the rise in pH from 1.8 to 2.1.

Elemental removals are similar to nitric acid (apart from being lower on manganese), and for most elements there may not be a statistical difference despite a slightly lower normality (1.93 compared with 2.35). Residue analysis was also similar with zinc manganese and iron being above the Ontario "severe effect " guidelines. These results confirm earlier conclusions that hydrochloric acid is a suitable leachant although it is slightly poorer for manganese and may present more limitations with materials of construction.

As with 2N nitric acid, acid usage was virtually complete being reduced from 70.5 gpl to 0.2 gpl.

Table 6.13 Standard Leach Test LT12 - 2N HCl

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 12 (DE12) 24-FEB-1994 09:42:5924-FEB-1994

EXPERIMENTAL CONDITIONS

INPUTS

LEACH SOLUTION	2N HCl	ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION	30.0 wt %										
WEIGHT SOIL SAMPLE	300.0 g	SOIL ANALYSIS (mg/kg)	4854.0	756.0	91.0	44.0	45.0	3466.0	174824	48543	13235
VOLUME LEACH SOLUTION USED	700.0 ml	RESIDUE ANALYSIS (mg/kg)	1100.0	144.0	50.0	32.0	34.0	1616.0	193796	1670	10195
VOLUME SLURRY	630.0 ml	FINAL LEACH FILTRATE CONC (mg/l)	1328.0	222.5	15.7	6.7	5.5	812.0	7291	18020	1476
		1st WASHINGS CONC (mg/l)	183.0	29.8	3.2	0.8	0.9	114.8	1248.0	2133.0	182.0

EXPERIMENTAL MEASUREMENTS

CALCULATED RESULTS

			Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
RESIDUE WEIGHT	229.1 g	WEIGHT METAL IN SOIL SAMPLE (mg)	1456	227	27	13	14	1040	52447	14563	3971
FINAL FILTRATE & WASHINGS	620.0 ml	WEIGHT METAL IN FINAL RESIDUE (mg)	252	33	11	7	8	370	44399	383	2336
1st WASHINGS VOL	980.0 ml	LEACH - WEIGHT EXTRACTED (mg)	823	138	10	4	3	503	4520	11172	915
		LEACH - WEIGHT IN SAMPLES (mg)	166	30	2	1	1	107	970	2594	191
ACID CONSUMPTION		1st WASH - WEIGHT EXTRACTED (mg)	179	29	3	1	1	113	1223	2090	178
CONC ACID	%	MASS BALANCE - (out/in) %	97.6	101.3	97.3	100.0	95.3	105.1	97.5	111.5	91.2
DENSITY OF ACID	g/ml	% EXTRACTABLE LEACH	67.9	73.9	43.9	38.5	31.0	58.7	10.5	94.5	27.8
VOL ACID USED	ml	% EXTRACTABLE 1st WASH	12.3	12.9	11.5	5.9	6.5	10.8	2.3	14.4	4.5
ACID CONSUMPTION	g/kg soil	% EXTRACTABLE TOTAL	80.3	86.8	55.4	44.5	37.6	69.5	12.8	108.9	32.3
		% REMOVED	82.7	85.5	58.0	44.5	42.3	64.4	15.3	97.4	41.2

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH SLURRY	ACID IN FILT g/l	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)								
					Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		0.5	70.5	0									
90	30.0	1.8		90	1410	255	19	8	6	908	8700	22717	1660
180	30.0	2.0		180	1343	240	18	7	6	857	7937	20633	1533
240		2.2		240									
300	30.0	2.1		300	1420	255	19	8	7	912	8000	22433	1600
360		2.1		360									
420		2.1		420									
480.0	30.0	2.1		480	1362	238	19	8	7	860	7683	20760	1560
1440.0		2.1	0.2	1440	1328	223	16	7	6	812	7291	18020	1476

Mass Balance

Mass loss	70.9 g
Mass in Solution	-26.0 g as metal ions
Mass as Anions	-21.8 g as anions (CO ₃)
	0.9 g as anions (SO ₄)
Total loss	24.0 g

6.2.6**LT 13 - 2N HNO₃/H₂SO₄ (Table 6.14)**

The fourth leach test used equinormal amounts of nitric and sulphuric acid to give a nominal 2N solution. As with the other leaches the initial solution was sampled and titrated and found to be 2.25N. This test was carried out to see whether calcium solubility could be reduced by the presence of sulphate ion.

Elemental mass balances are again excellent with only chromium and aluminium not being within 5% of accountability. Total mass balance (allowing for calcium precipitation as sulphate) is a 6.9% loss, slightly lower than the other tests but comparable. Filtrate analyses show some declines and some rises with respect to time, but none are significant. Most of the leaching is complete within 90 minutes (the time taken to add all the sediment sample). The residue retains calcium and iron, but it also retains lead well in excess of the Ontario "severe effect" guidelines. Zinc and manganese are also above the guideline limits and mixed acid leach is therefore probably not attractive.

Acid usage was almost complete with the final filtrate titrating at 0.01 normal.

Table 6.14 Standard Leach Test LT13 - 2N HNO₃/H₂SO₄

SOIL SAMPLE HAMILTON HAREOUR LEACH TEST NUMBER 13 (DB13) 24-FEB-1994 09:13:4324-FEB-1994

EXPERIMENTAL CONDITIONS

LEACH SOLUTION 2N HNO₃/H₂SO₄
 PULP CONCENTRATION 30.0 wt %
 WEIGHT SOIL SAMPLE 300.0 g
 VOLUME LEACH SOLUTION USED 700.0 ml
 VOLUME SLURRY 830.0 ml

INPUTS

ELEMENT

SOIL ANALYSIS (mg/kg) Zn Pb Cu Cr Ni Mn Fe Ca Al
 RESIDUE ANALYSIS (mg/kg) 4854.0 756.0 51.0 44.0 45.0 3466.0 174824 48543 13225
 FINAL LEACH FILTRATE CONC (mg/l) 1051.0 603.5 55.0 36.0 35.5 1440.0 171533 37204 8676
 1st WASHINGS CONC (mg/l) 1357.0 75.0 13.5 6.6 4.9 793.0 7238 4060 1455
 1st WASHINGS CONC (mg/l) 250.3 14.2 3.5 1.6 1.0 155.0 1909.0 1470.0 274.0

EXPERIMENTAL MEASUREMENTS

RESIDUE WEIGHT 266.9 g
 FINAL FILTRATE & WASHINGS 560.0 ml
 1st WASHINGS VOL 1020.0 ml

CALCULATED RESULTS

WEIGHT METAL IN SOIL SAMPLE (mg) Zn Pb Cu Cr Ni Mn Fe Ca Al
 WEIGHT METAL IN FINAL RESIDUE (mg) 1456 227 27 13 14 1040 52447 14563 3571
 LEACH - WEIGHT EXTRACTED (mg) 281 161 15 10 9 384 45782 9930 2216
 LEACH - WEIGHT IN SAMPLES (mg) 760 42 8 4 3 444 4053 2274 804
 1st WASH - WEIGHT EXTRACTED (mg) 154 9 2 1 1 58 956 530 174
 1st WASH - WEIGHT EXTRACTED (mg) 255 14 4 2 1 158 1947 1499 279

ACID CONSUMPTION

CONC ACID %
 DENSITY OF ACID g/ml
 VOL ACID USED ml
 ACID CONSUMPTION g/kg soil

MASS BALANCE - (out/in) %
 % EXTRACTABLE LEACH
 % EXTRACTABLE 1st WASH
 % EXTRACTABLE TOTAL
 % REMOVED

Zn Pb Cu Cr Ni Mn Fe Ca Al
 99.6 100.1 101.5 121.1 102.5 104.3 100.6 97.7 90.0
 62.8 22.7 33.6 36.0 24.8 52.1 9.6 19.3 24.6
 17.5 6.4 13.1 12.4 7.6 15.2 3.7 10.3 7.0
 80.3 29.0 46.7 48.3 32.3 67.4 13.3 29.5 31.7
 80.7 29.0 45.3 27.2 29.8 63.0 12.7 31.8 41.7

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME (mins) SAMPLE VOL (ml) pH ACID IN SLURRY FILT g/l

0 0.6 2.25N
 90 30.0 1.7
 180 30.0 2.0
 240 2.0
 300 30.0 2.0
 360 2.0
 420 2.0
 480.0 30.0 2.0
 1440.0 2.0 0.01N

SAMPLE TIME (mins)

0
 90
 180
 240
 300
 360
 420
 480
 1440

FILTRATE CONCENTRATION (mg/l)

Zn Pb Cu Cr Ni Mn Fe Ca Al
 1263 72 13 7 5 825 8287 4550 1453
 1300 77 13 9 5 817 7987 4500 1473
 1248 72 13 8 5 803 7600 4300 1387
 1314 92 15 11 5 826 7964 4320 1480
 1357 75 14 7 5 793 7238 4060 1435

Mass Balance

Mass loss 33.1 g
 Mass in Solution -14.5 g as metal ions
 Mass as Anions -21.8 g as anions (CO₃)
 23.8 g as anions (SO₄)
 Total loss 20.6 g

6.3 Sequential Leach (Table 6.15)

6.3.1 Introduction

Following the observations from tests LT10 and LT11 it was decided to carry out a sequential leach or titration. The aim of this leach was to determine whether it would be possible to selectively leach calcium and leave the contaminants in the sediment for a subsequent leach. The results are shown in Table 6.15.

Table 6.15 Sequential Leach Test

SOIL SAMPLE HAMILTON HARBOUR		LEACH TEST NUMBER 14 (DB14) 02-MAR-1994 02:50:5302-MAR-1994											
EXPERIMENTAL CONDITIONS			INPUTS										
LEACH SOLUTION	HNO3		ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al	
PULP CONCENTRATION	30.0	Wt %											
WEIGHT SOIL SAMPLE	300.0	g	SOIL ANALYSIS (mg/kg)	5003	765.0	69.0	59.0	45.0	3527	171125	48044	10902	
VOLUME LEACH SOLUTION USED	700.0	ml	RESIDUE ANALYSIS (mg/kg)	808.5	56.0	50.0	44.0	30.0	1128	177632	1248	8231	
VOLUME SLURRY	830.0	ml	FINAL LEACH FILTRATE CONC (mg/l)	1174.0	230.0	15.7	9.0	6.5	800.0	6240.0	12010.0	1800.0	
			1st WASHINGS CONC (mg/l)	170.8	35.0	3.0	1.6	1.3	120.0	2680.0	2088.0	400.0	
EXPERIMENTAL MEASUREMENTS			CALCULATED RESULTS										
RESIDUE WEIGHT	211.0	g		Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al	
FINAL FILTRATE & WASHINGS	610.0	ml	WEIGHT METAL IN SOIL SAMPLE (mg)	1501	230	27	18	14	1058	51338	14413	3271	
1st WASHINGS VOL	1130.0	ml	WEIGHT METAL IN FINAL RESIDUE (mg)	171	12	11	9	6	238	37523	263	1737	
			LEACH - WEIGHT EXTRACTED (mg)	716	140	10	5	4	488	3806	7326	1058	
			LEACH - WEIGHT IN SAMPLES (mg)	400	59	4	2	2	263	1977	6967	374	
ACID CONSUMPTION			1st WASH - WEIGHT EXTRACTED (mg)	193	40	3	2	1	136	3028	2359	452	
CONC ACID		%	MASS BALANCE - (out/in) %	98.6	109.1	104.2	103.5	99.8	106.3	90.3	117.4	111.9	
DENSITY OF ACID		g/ml	% EXTRACTABLE LEACH	74.3	86.8	52.0	40.8	42.0	71.0	11.3	99.2	45.0	
VOL ACID USED		ml	% EXTRACTABLE 1st WASH	12.9	17.2	12.7	10.2	10.9	12.8	5.9	16.4	13.8	
ACID CONSUMPTION		g/kg soil	% EXTRACTABLE TOTAL	87.2	104.0	64.7	51.0	52.9	83.8	17.2	115.5	58.8	
			% REMOVED	88.6	94.9	60.5	47.5	53.1	77.5	26.9	98.2	46.9	
EXPERIMENTAL LEACH TEST RESULTS													
SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN CONC SLURRY FILT HNO3 ADDED g/l (ml)	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)								
					Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
0		8.0	0.0	0									
18	28.0	5.3	10.0	18	29	0.8	0.4	0.0	0.4	120	7	2971	2
53	30.0	5.2	20.0	53	53	1.3	0.3	0.0	1.0	200	7	7117	2
83	30.0	4.8	30.0	83	95	2.0	0.3	0.3	1.3	267	23	13333	3
105	30.0	3.5	40.0	105	203	3.0	0.3	0.3	1.7	333	120	14880	22
131	30.0	3.0	50.0	131	402	6.2	0.3	0.3	2.3	400	400	18027	82
150	30.0	1.5	60.0	150	1017	64.3	0.3	1.3	3.3	533	1467	20987	306
162.0	30.0	1.2	70.0	162	1353	143.3	10.0	2.7	4.0	533	2800	20413	461
172.0	29.0	0.8	80.0	172.0	1362	182.8	14.5	4.1	4.8	828	4414	20731	584
180.0	25.0	0.5	90.0	180.0	1500	216.0	17.6	5.6	5.6	960	6240	21864	745
185.0	30.0	0.3	100.00	185.0	1453	222.7	17.7	6.3	5.3	933	7333	20667	1867
192.0	30.0	0.1	120.0	192.0	1367	236.7	18.3	7.0	5.7	923	8800	19587	2600
200.0	30.0	0.0	140.0	200.0	1230	236.7	17.7	7.7	5.7	800	8400	15867	1733
210.0	30.0	0.0	160.0	210.0	1280	240.0	17.3	8.3	5.7	800	9200	14373	1753
218.0	30.0	0.0	180.0	218.0	1160	220.0	16.0	7.3	5.3	667	8400	12480	1467
250.0	50.0	0.0	200.0	230.0	1137	226.7	16.0	7.3	6.0	667	9467	13453	1600
1200.0		0.3		1200.0	1174	230.0	15.7	9.0	6.5	800	6240	12010	1800

6.3.2 Sequential Leach - Quality Assurance

The three blank analyses are all less than 0.05 (except lead at 0.06) and are acceptable. The two analyses of the lake sediment are also acceptable except for lead which is slightly high.

Elemental mass balances are again very good with only calcium and aluminium not being within 10% of full accountability. Lead is again slightly high.

Again there is cause for confidence in the results, although lead analyses may be slightly high due to the presence of a trace of lead in the acid used for digestion.

6.3.3 Discussion

This test may be compared with LT10 and LT11. The final contaminant removals are slightly less than LT11 and this may be due to a slight difference in acid concentration (3.9 compared with 4.3 N).

Element concentrations in solution have been plotted in Figures 6.1 and 6.2 (expanded scale). It is noticeable that once leaching is substantially complete (between pH 3 and 0.3) the concentration appears to decline until there is a slight increase for the 24 hour sample. This decline shows the effect of dilution as fresh acid is added and the final rise shows the effect of extended leaching times. The dilution effect is due to removal of 30 mls solution and addition of 20 or 40 mls acid and can be compensated for by expressing the results as total milligrams of contaminants leached, as in Figures 6.3 and 6.4, and these show that the total amount of contaminant removed is not declining, except in the case of calcium and iron which both show a decline between 4 hours and

20 hours. The important factor which can be clearly seen from these figures is that some leaching of all contaminants occurs at all acid additions, particularly manganese and zinc and hence it will not prove possible to selectively leach calcium and leave behind the contaminants.

It is also interesting to note that with the exception of lead and aluminium little further leaching occurred after the 180 minute sample (1.86N acid). This contrasts with LT10 and LT11 where slightly better leaching was obtained with 4N acid compared with 2N acid. The pH at this point was lower (0.5) compared with a final pH of 1.5 in LT10 confirming that less leaching has occurred.

Most of the contaminants were close to or below the Ontario "severe effect level" guidelines except for iron which analysed at 17% (virtually unchanged).

Figure 6.1 Elemental Concentrations in Leach Liquor for Sequential Leach

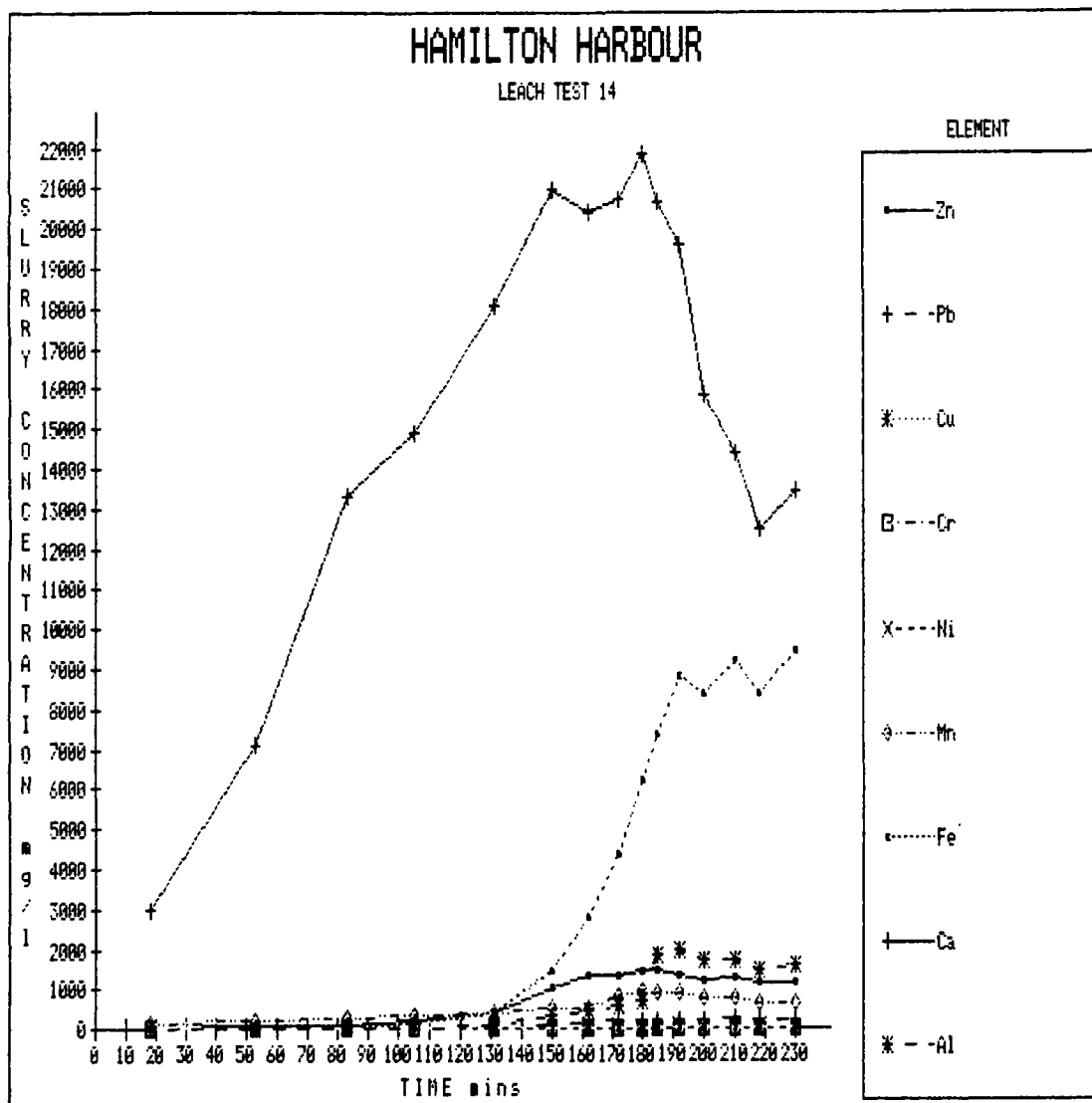


Figure 6.2 Contaminant Concentrations in Leach Liquor for Sequential Leach (Expanded Scale)

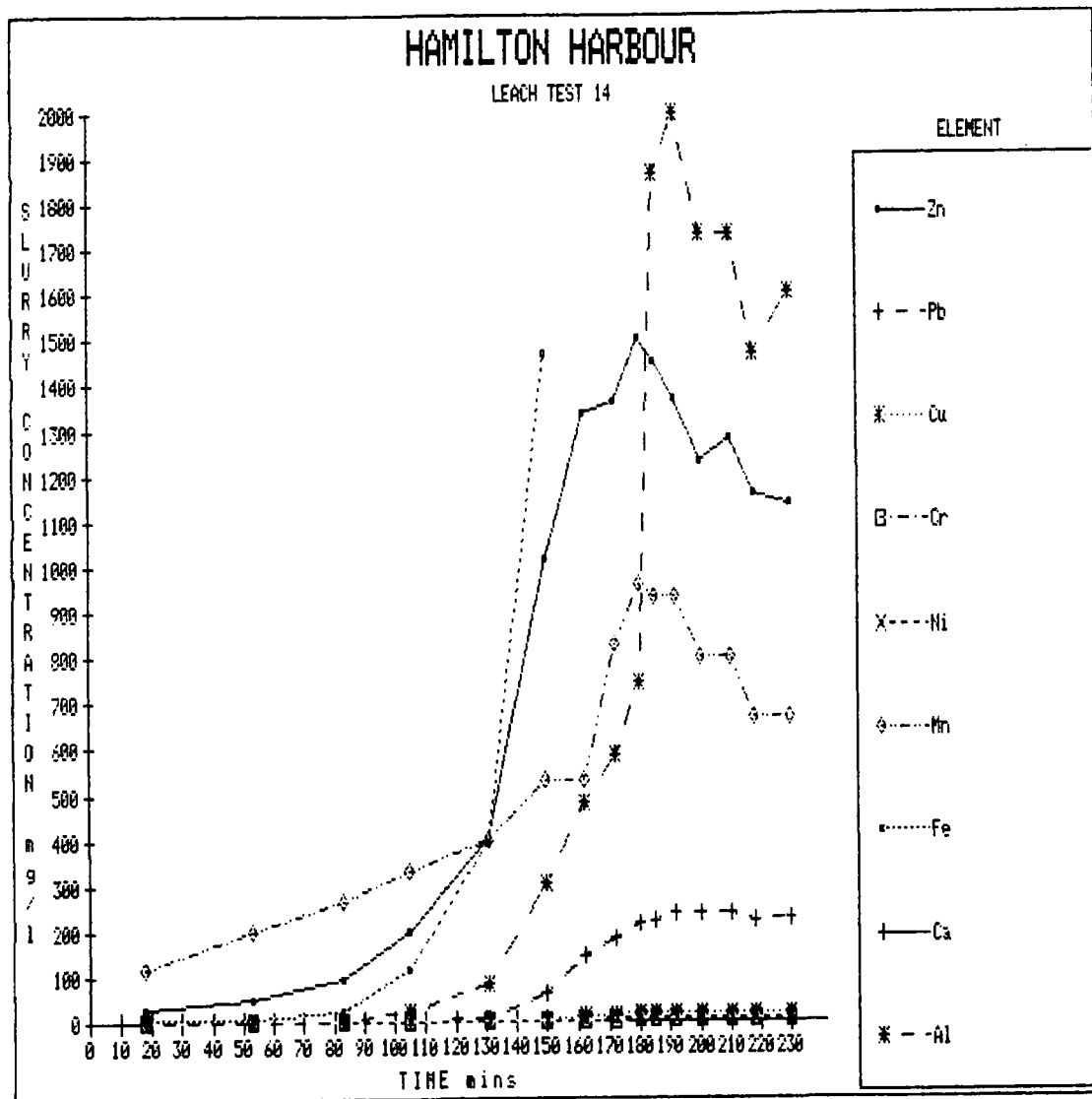


Figure 6.3 Milligrams of Elements Removed in Sequential Leach

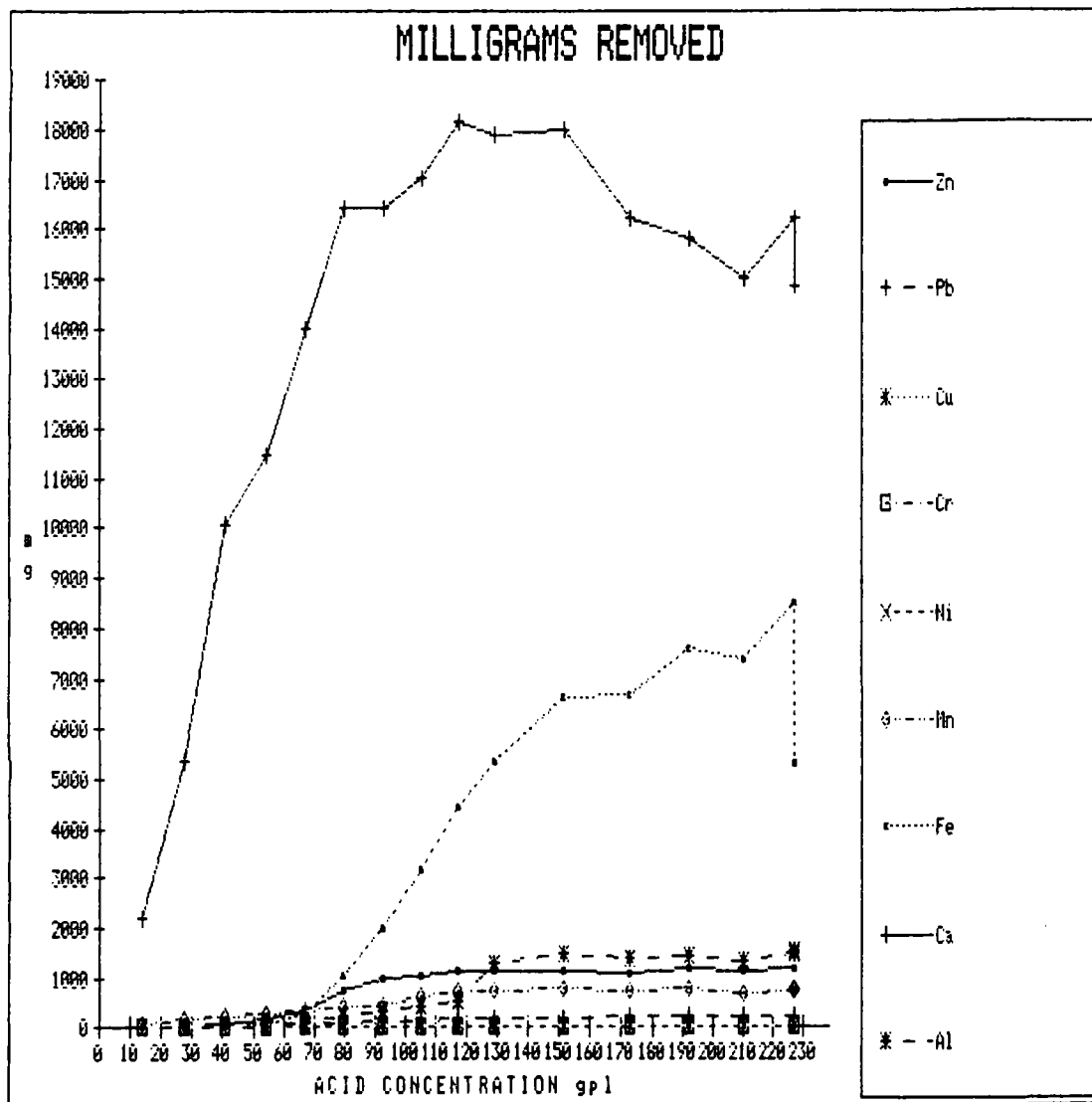
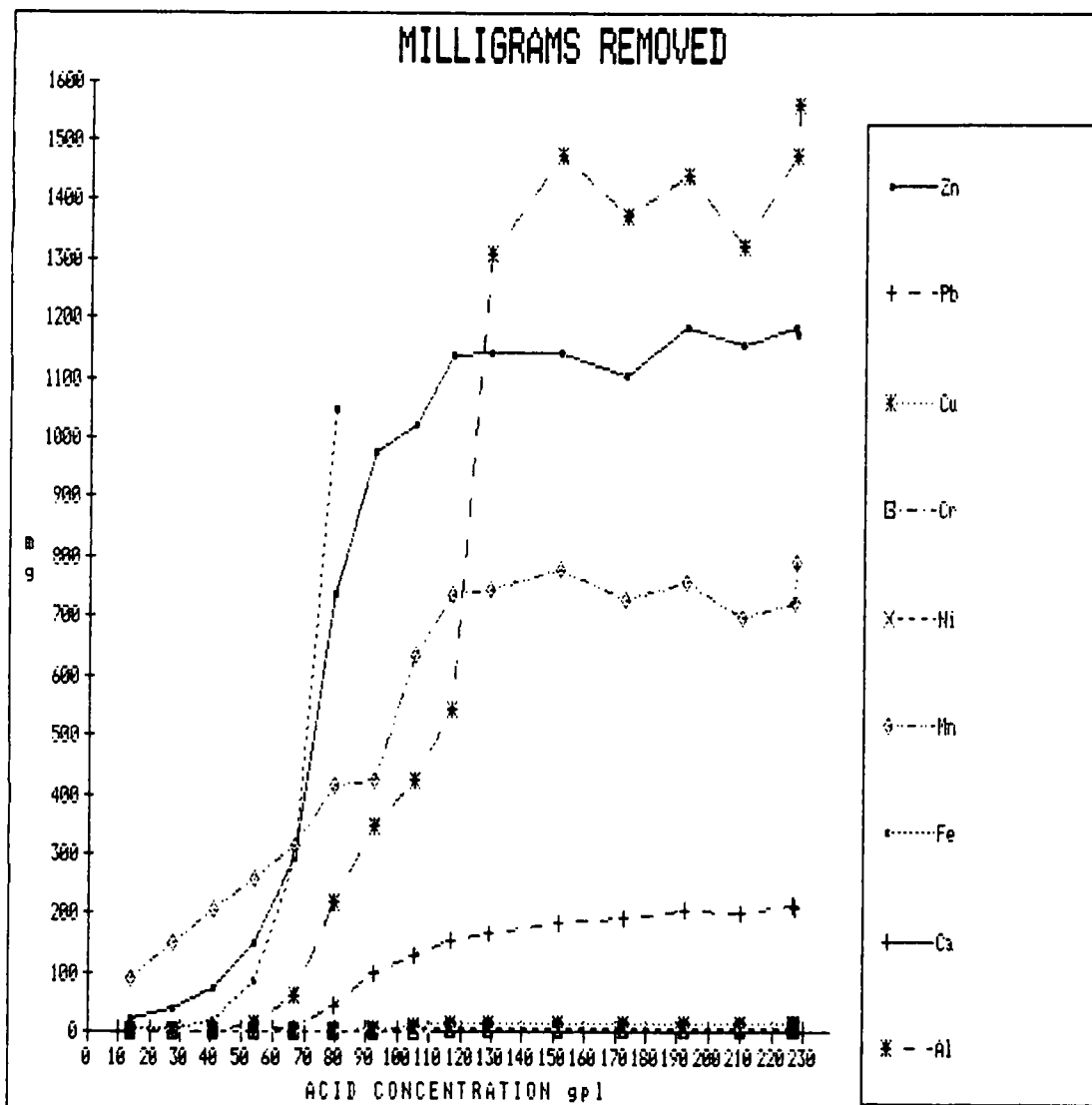


Figure 6.4 Milligrams of Contaminants Removed in Sequential Leach - Expanded Scale



6.4 Two Stage Leaches (Tables 6.16 - 6.17)**6.4.1 Introduction**

The two-stage leaches were carried out to determine whether lower contaminant levels may be achieved by contact with fresh acid, and to prepare filtrates for resin tests.

6.4.2 Quality Assurance for LT15

The blank analyses are all acceptable with the exception of one zinc analysis at 0.3. The lake sediment analyses are very close to the Canmet analysis which is based on 35 independent analyses. Elemental mass balances are all within acceptable limits and there is confidence in the results.

6.4.3 Discussion of LT15

The results of the first two stage leach (LT15) are presented in Table 6.16. Table 6.16 shows the overall mass balance for the two leaches combined and shows that overall elemental accountabilities are very good, all being within 10% of full accountability. The total mass balance shows a 10% loss, very close to that from the single stage leach with 4N nitric acid (LT11).

The two stages of the leach may be compared with both LT10 (2N nitric acid) and LT11 (4N nitric acid) and LT14 (sequential leach). With the first stage leach (1.5N acid) leaching is poorer than with the stronger acid concentrations. Leaching is substantially complete in 30 minutes and the contaminant concentration in solution appears to reduce, probably as the pH rises to 3.3. Acid consumption in this first stage was virtually complete. In the second stage with 4N nitric acid the bulk of the leaching was

complete within 1 hour but contaminants continued to leach over the next hour.

A large proportion the contaminants reported to the first leach. This acid concentration is comparable with the 162 minute sample in LT14 and contaminant levels in solution are similar though lower. The second leach contained higher levels of the minor contaminants but contained less zinc and manganese than the first leach since these had already been solubilised.

The first leach utilised virtually all the free acid although the second leach contains excess free acid (186 gpl) which could proceed to a first stage leach with fresh sediment.

The final residue was below the Ontario "severe effect" guidelines for all contaminants except manganese and iron.

Table 6.16 Two-Stage Leach Test LT15 - Combined Results

SOIL SAMPLE HAMILTON HARBOUR LEACH TEST NUMBER 15 (DP15) 07-MAR-1994 05:06:1507-MAR-1994

TWO STAGE LEACH

EXPERIMENTAL CONDITIONS

INPUTS

LEACH SOLUTION	HK03	ELEMENT	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Co	Al
PULP CONCENTRATION	30.0 Wt %										
WEIGHT SOIL SAMPLE	1200.0 g	SOIL ANALYSIS (mg/kg)	4578.0	777.0	90.0	80.0	40.0	3565.0	174234	49264	8214
VOLUME LEACH SOLUTION USED	2800.0 ml	RESIDUE ANALYSIS (mg/kg)	1st LEAC 2453.0	783.0	100.0	100.0	40.0	2274.0	206412	4986	8925
VOLUME SLURRY	3320.0 ml	FINAL LEACH FILTRATE CONC (mg/l)	1185.0	33.0	1.1	1.1	3.7	700.0	1835	19250	202
		1st WASHINGS CONC (mg/l)	595.0	16.3	0.5	0.7	2.4	375.0	992	9650	135.0
		RESIDUE ANALYSIS (mg/kg)	2nd LEAC 806.0	59.0	30.0	59.0	30.0	1321.0	195429	1979	7386.0
		FINAL LEACH FILTRATE CONC (mg/l)	460.0	22.0	20.4	9.8	3.3	320.0	10850	1450	781.0
		1st WASHINGS CONC (mg/l)	120.0	57.0	6.1	3.4	1.0	51.0	3045	280	203.0

EXPERIMENTAL MEASUREMENTS

FIRST LEACH		
RESIDUE WEIGHT	44.8 g	
FINAL FILTRATE & WASHINGS	2260.0 ml	
1st WASHINGS VOL	1440.0 ml	
SECOND LEACH		
RESIDUE WEIGHT	836.1 g	
FINAL FILTRATE	2820.0 ml	
WASHINGS	2240.0 ml	

CALCULATED RESULTS

	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Co	Al
WEIGHT METAL IN SOIL SAMPLE (mg)	5974	932	108	96	48	4278	209081	59141	9857
WEIGHT METAL IN 1st LEACH RESIDUE (mg)	112	35	4.5	4.5	1.8	102	9237	223	399
WEIGHT METAL IN FINAL RESIDUE (mg)	674	49	25	49	25	1104	163388	1655	6175
LEACH - WEIGHT EXTRACTED (mg) 1st LEAC	2497	75	2	2	8	1582	4147	43505	457
2nd LEAC	1297	626	57.5	27.6	9.3	502	30597	4089	2202
LEACH - WEIGHT IN SAMPLES (mg)	87	10	1	0	0	54	413	1143	42
1st WASH - WEIGHT EXTRACTED (mg) 1st	857	23	1	1	3	540	1428	13896	194
2nd	269	128	13.7	7.6	2.2	204	6821	627	455
MASS BALANCE - (out/in) %	97.0	101.5	97.0	96.9	105.5	104.9	103.3	110.1	100.7
% EXTRACTABLE LEACH	65.0	76.2	56.3	31.9	37.6	59.3	16.8	82.4	27.4
% EXTRACTABLE 1st WASH	18.8	16.2	13.3	9.0	11.9	17.4	3.9	24.6	6.6
% EXTRACTABLE TOTAL	83.8	92.4	69.6	40.9	49.5	76.7	20.8	107.0	34.0
% REMOVED	86.9	91.0	72.6	44.0	44.0	71.8	17.4	96.8	33.3

ACID CONSUMPTION

CONC ACID	%
DENSITY OF ACID	g/ml
VOL ACID USED	ml
ACID CONSUMPTION	g/kg soil

EXPERIMENTAL LEACH TEST RESULTS

SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN SLURRY g/l	ACID IN FILT g/l	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Co	Al
0		0.3	94.2		0										
15		2.3			15										
30	30.0	2.8			30		1267.0	80.0	4.7	3.3	4.7	733.0	2633	18000	425.0
60	30.0	3.2			60		1200.0	53.3	2.7	2.3	4.7	750.0	1967	18333	372.0
120		3.3	1.2		120		1105.0	33.0	1.1	1.1	3.7	700.0	1835	19250	202.0
SECOND LEACH						2nd LEACH									
0.0		0.0	270.3		0										
30.0		0.0			30										
60.0	30.0	0.0			60.0		443.0	200.0	19.7	11.0	3.3	310.0	9167	1767	663.0
120.0		0.0	186.5		120.0		460.0	222.0	20.4	9.8	3.3	320.0	10850	1450	781.0

Mass Balance

Mass loss	319.2 g
Mass in Solution	-119.3 g as metal ions
Mass as Anions	-68.7 g as anions (CO3)
	4.0 g as anions (SO4)
Total loss	115.2 g

6.4.4 Quality Assurance for LT16

The blank analysis is acceptable although zinc and calcium are slightly high. Calcium is a non-critical measurement and hence is acceptable. The lake sediment analyses are good except for a high figure for lead. This compares with the LT 14 Quality Assurance analysis.

Overall elemental accountabilities are good with lead, manganese and iron being between 10% and 15% variation from 100% accountability. All other elements are within 10% apart from calcium at 163%. This is a major discrepancy and the analyses were therefore rechecked. Results were confirmed and the cause of this discrepancy is unexplained.

With the exception of the calcium mass balance there is confidence in the results.

6.4.5 Discussion of LT 16

The results of LT16 are presented in Table 6.17. The acid concentration in the first stage leach had been reduced to 1N nitric acid to reduce the metal contaminant in solution (131 minute sample compared with 162 minute sample in LT14) whilst the second stage used 3N acid to give a total acid consumption of 4N similar to LT11 and LT14. No kinetic data was determined in this test since previous tests had shown that leaching is rapid.

Calculated elemental mass balances for the two leaches are affected by the assumption of the mass of residue left after the first leach. A figure of 3500 grams was selected to give reasonable balances in both leaches with the first leach slightly below 100% and the second leach slightly above 100%. The figure of 3500

grams is high if 159 grams of calcium have been extracted into solution, but a lower figure will give poorer balances between the two leach stages.

The resultant sediment analyses are presented in Table 6.18 where it can be seen that the residue analysis contains less contamination as higher acid strengths are used. A two-stage leach using the same total acid (LT16) does not appear to give better leaching than a single leach (LT11). Increasing contaminant removal was observed in the residue from the two stages of LT15 and LT16 whereas LT 14 suggested that contaminant removal did not increase beyond 1.86N acid addition. Leach test 15 appeared to give poorer results than LT 16 despite using 50% more acid overall and the cause of this difference is unknown.

These variations in results show that flexibility must be taken into account in flowsheet design in order to meet specific contaminant target levels. The bulk of contaminant leaching requires the addition of 2N acid at this sediment/liquor ratio. A two-stage leach is possible but does not effect separation of contaminants from major elements (calcium and iron) and may not improve overall contaminant removal.

Table 6.17 Two-Stage Leach Test LT 16 - Combined Results

SOIL SAMPLE		HAMILTON HARBOUR		LEACH TEST NUMBER 16 (DE16)										
				TWO STAGE LEACH										
EXPERIMENTAL CONDITIONS				INPUTS										
LEACH SOLUTION		HNO3		ELEMENT		Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
PULP CONCENTRATION		30.0	wt %	SOIL ANALYSIS (mg/kg)		4758.0	735.0	50.0	80.0	40.0	3509.0	186953	49000	11667
WEIGHT SOIL SAMPLE		3600.0	g	RESIDUE ANALYSIS (mg/kg)		4287.0	673.0	84.8	69.8	39.9	2946.0	166450	25923	9821
VOLUME LEACH SOLUTION USED		8532.0	ml	1st LEACH		145.0	2.4	0.2	0.2	1.1	274.0	3	19850	1
VOLUME SLURRY		9960.0	ml	FINAL LEACH FILTRATE CONC (mg/l)										
				1st WASHINGS CONC (mg/l)										
				RESIDUE ANALYSIS (mg/kg)		2nd LEACH	89.6	19.9	39.8	29.9	1159.0	191850	214	7476.0
				FINAL LEACH FILTRATE CONC (mg/l)		1070.0	195.0	16.7	9.7	4.0	540.0	13050	9000	1250.0
				1st WASHINGS CONC (mg/l)										
EXPERIMENTAL MEASUREMENTS				CALCULATED RESULTS										
FIRST LEACH														
RESIDUE WEIGHT		52.4	g	WEIGHT METAL IN SOIL SAMPLE (mg)		17273	2646	324	288	144	12632	673031	176400	59841
FINAL FILTRATE & WASHINGS		8000.0	ml	WEIGHT METAL IN 1st LEACH RESIDUE (mg)		225	35	4.4	3.7	2.1	154	9770	1358	515
				WEIGHT METAL IN FINAL RESIDUE (mg)		2088	268	60	119	90	3471	574711	641	22391
1st WASHINGS VOL			ml	LEACH - WEIGHT EXTRACTED (mg) 1st LEACH		1160	19	2	2	9	2992	27	158800	7
SECOND LEACH				2nd LEACH		14980	2730	233.8	135.8	56.0	7560	182700	126000	17500
RESIDUE WEIGHT		2995.0	g	LEACH - WEIGHT IN SAMPLES (mg)		0	0	0	0	0	0	0	0	0
FINAL FILTRATE		14000.0	ml	1st WASH - WEIGHT EXTRACTED (mg) 1st		0	0	0	0	0	0	0	0	0
WASHINGS			ml	1st WASH - WEIGHT EXTRACTED (mg) 2nd		0	0	0	0	0	0	0	0	0
				MASS BALANCE - (out/in) %		106.8	115.4	92.4	90.4	108.6	112.2	114.0	162.6	101.4
				% EXTRACTABLE LEACH		93.4	103.9	72.7	47.7	45.0	83.5	27.1	161.5	43.9
				% EXTRACTABLE 1st WASH		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				% EXTRACTABLE TOTAL		53.4	103.9	72.7	47.7	45.0	83.5	27.1	161.5	43.9
				% REMOVED		86.6	88.5	60.2	57.3	36.4	71.3	13.2	98.9	42.5
ACID CONSUMPTION														
CONC ACID		%												
DENSITY OF ACID		g/ml												
VOL ACID USED		ml												
ACID CONSUMPTION		g/kg soil												
EXPERIMENTAL LEACH TEST RESULTS														
SAMPLE TIME (mins)	SAMPLE VOL (ml)	pH	ACID IN SLURRY	FILT g/l	SAMPLE TIME (mins)	FILTRATE CONCENTRATION (mg/l)								
0		1.6	63.3		0	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
15		1.6			15									
30		1.6			30									
60		1.6			60									
120		2.0			120									
SECOND LEACH					2nd LEACH									
0.0		0.0	189.9		0									
30.0		0.0			30									
60.0		0.0			60.0									
120.0		0.0			120.0									
Mass Balance														
Mass loss		605.0 g												
Mass in Solution		-514.9 g as metal ions												
Mass as Anions		-264.6 g as anions (CO3)												
		1.5 g as anions (SO4)												
Total loss		-173.0 g												

Table 6.18 Comparison of Residues from Leach Tests

	Acid gpl	Zn mg/kg	Pb mg/kg	Cu mg/kg	Cr mg/kg	Ni mg/kg	Mn mg/kg	Fe mg/kg	Ca mg/kg	Al mg/kg
LT10	148.4	1143	198	65	33	39	875	201000	1525	11025
LT11	270.7	597	43	36	20	27	1017	168000	2058	8433
LT14	227.0	808	56	50	44	30	1128	178000	1248	8231
LT15A	94.2	2493	783	100	100	40	2274	206000	4986	8925
LT15B	270.3	806	59	30	59	30	1321	195000	1979	7386
LT16A	63.3	4287	673	85	70	40	2946	186000	25900	9821
LT16B	189.9	697	90	20	40	30	1159	192000	214	7476

6.5 Adsorbent Screening Tests

6.5.1 Introduction

Adsorbent screening tests were carried out using the adsorbents described in Section 5.5. Two series of tests were carried out on the filtrates from the two-stage leach, LT15.

6.5.2 Quality Assurance for Adsorbent Screening Tests

The quality assurance results are shown in Table 6.19. The blanks showed no detectable levels of contaminants apart from lead recorded at the 0.1 mg/l level.

Table 6.19 Quality Assurance Data for Resin Screening Tests

	Resin Screening Tests								
	Zn	Pb	Cu	Cr	Ni	Mn	Fe	Ca	Al
Blank	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Blank	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Precipitation Test									
Blank	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	0.3	0.01	0.1
Spike on Sample 10	5.0	5.1	5.0	2.0	5.0	10.0	10.3	10.0	10.1
	5	5	5	2	5	10	10	10	10
Kinetic Resin Test									
Blank	<0.01	0.03	0.01	0.02	<0.01	0.01	0.01	0.01	0.02
Spike on Sample 28	5.01	5.03	5.05	5.05	4.98	5.05	10.1	10.1	20.1
	5	5	5	5	5	5	10	10	20

6.5.3

Results with First Leach Filtrate

Results of resin screening tests using the filtrate from the first leach are given in Table 6.20. Four of these samples showed evidence of precipitation even though in three cases the pH of the solution declined (Purolite S940, a chelating resin, IRC 718, a weak cationic resin and Chelamine DB 15F1, a chelating resin). The cause of precipitation is unknown although it may be a solubility effect due to the concentration of ions in solution rather than precipitation of a hydroxide due to a pH change. Precipitation may, however, have affected the contaminant removal due to adsorption on the precipitate and results from these four tests are therefore suspect. In the case of activated carbon impregnated with iron hydroxide, the pH rose for both solutions and iron hydroxide precipitation will have occurred and may have adsorbed contaminants. The cause of this rise in pH is probably due to incomplete washing of the as-received carbon and entrained alkali being present.

The Amberlite 200 and 200C (strong cationic resins) both gave higher levels for contaminants (Ni, Cr, Cu, Zn) in the product than

the feed. A possible explanation is that these elements were already present on the resin from a previous use and despite conditioning of the resin they had not been removed by the resin preparation. These resins also gave higher final levels of these contaminants with the second leach filtrate.

The test with resin IRC 76 failed due to spillage and no results were obtained.

Magnetite gave higher Ni and Zn levels in the final filtrate and the cause of this is unknown. Apart from Cu and Pb other metal removal results were poor. Again, a rise in pH was noted although no precipitation was observed.

Four resins gave reliable results. Amberlite C467, an iminophosphonic chelating resin, gave moderate contaminant removals with some iron and aluminium removal but no calcium removal. Lewatit TP 207, another chelating resin with an iminodiacetic group, also gave moderate removals with little adsorption of the major cations. Lewatit OC 1060 a weakly acidic chelating resin, gave an increase in some contaminants with this filtrate although it did not do so with the second more acidic filtrate. Iron, aluminium and some calcium were adsorbed and this resin is neither selective nor highly efficient in contaminant removal with this filtrate. The final resin IR 120, a strong cationic resin gave moderate removals of contaminants although it also removed the major cations as well and would probably not be suitable for treating this filtrate.

The final test, precipitation at pH 7, produced 10.4 g precipitate/litre of solution, equivalent to 2.3% of the original sediment sample weight. High removals of all elements apart from calcium were obtained although the filtrate still contained contaminants that will

need to be removed.

Table 6.20 Resin Screening Test Results - First Filtrate

HAMILTON RESIN LEACH

SAMPLE	Ni	Cu	Cr	FIRST FILTRATE		Pb	Fe	Ca	Al	pH
				Zn	Mn					
AMB 200										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	50	57	29.7	940	455	4.7	1300	8500	460	0.98
% Removal	-1362	-5082	-2185	23	46	78	21	58	21	
AMB C467										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	2.73	0.8	0.9	1010	455	12.3	1055	22080	73.7	1.37
% Removal	20	27	31	18	46	42	36	-10	87	
PUR S940										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	3.5	1.1	0.9	1150	585	15.2	1510	15040	107	1.13ppt
% Removal	-2	0	31	6	30	28	9	25	82	
AMB IR120										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	1.71	7.7	0.4	290	295	13.9	920	8960	165.1	0.72
% Removal	50	-600	69	76	65	34	44	55	72	
LEW TP207										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	0.66	0.2	1.2	435	615	4	1475	20400	208	1.26
% Removal	81	82	8	65	27	81	11	-1	64	
AMB 200C										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	3.55	4.2	5.8	1005	445	50	1280	17360	342	0.78
% Removal	-4	-282	-346	18	47	-137	23	14	41	
IRC 718										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	1.43	0.2	0.6	905	670	4.6	1475	17920	179.5	1.88ppt
% Removal	58	82	54	26	20	78	11	11	69	
CHELAMINE										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	2.8	0.25	0.66	1041	746	20.7	1379	15400	371	2.26ppt
% Removal	18	77	49	15	11	2	17	23	36	
LEW OC1060										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	3.95	2.5	0.7	890	490	9.8	750	16400	7.2	0.89
% Removal	-15	-127	46	28	41	54	55	18	99	
IRC 76										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l										
% Removal										
CAR RF23										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	1.41	0.2	0.1	595	610	2.2	50	15400	80.3	4.03ppt
% Removal	59	82	92	52	27	90	97	23	86	
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	7.19	0.3	0.9	1185	830	4.2	1800	19400	460	3.85
% Removal	-110	73	31	4	1	80	-9	3	21	
Ppt @ pH 7										
Feed mg/l	3.42	1.1	1.3	1228	837.5	21.1	1653	20100	580	2.99
Filt. mg/l	1.14	0.2	0.6	21.7	230	2.8	160	19800	1.6	7
% Removal	67	82	54	98	73	87	90	1	100	

6.5.4 Results with Second Leach Filtrate

The first filtrate was high in calcium ions and calcium ions can be competitively adsorbed onto cation exchange resins and may crowd out the contaminant ions. An alternative approach may be to remove the contaminants in a second (strong acid) leach after the calcium has been dissolved in a first stage leach. This would increase acid usage but may have advantages for the flowsheet design. However, at low pH adsorption is low owing to the equilibrium between hydrogen ions on the resin and hydrogen ions in solution. To overcome this the pH of the second filtrate from leach test LT 15 was reduced to 2 using ammonium hydroxide prior to contact with the resin. Results are given in Table 6.21.

As with the first filtrate, Amberlite 200 and 200C both gave increases in contaminant concentrations.

Precipitation was not observed except with carbon and again this is believed to be due to incomplete washing and a rise in pH.

Magnetite gave no perceptible removal with this filtrate. Magnetite had been tested owing to its isoelectric properties and its ability to have a positive zeta potential in acid conditions and hence attract negative charged colloids which may then adsorb the contaminant cations. This does not appear to occur under the conditions tested.

Amberlite C467 again showed moderate removal with some limited removal of major cations. Purolite S940 did not cause precipitation with this filtrate. However, although the adsorption of major cations was limited, the removal of contaminants was not high. Amberlite IR 120 again gave moderate contaminant removal together with removal of the major cations. Lewatit TP 207 gave poorer results

than with the first filtrate and there appears to be inconsistencies with the calcium and iron removals between the two tests. A weak cationic resin IRC 718 removed the major cations in preference to the minor contaminants. Chelamine showed no removal apart from iron. It is noticeable that several resins appear to remove iron. Precipitation is unlikely to be the cause since pH declines. Lewatit OC 1060 showed some removal of contaminants but was not selective over the major elements. IRC 76 showed little removal under these conditions.

Precipitation at pH 7 resulted in 29.3 g/l of precipitate and removed the majority of the metals apart from calcium. Manganese removal by precipitation was poorer than with filtrate 1.

Table 6.21 Resin Screening Test Results - Second Filtrate

SAMPLE	Ni	Cu	SECOND FILTRATE			Pb	Fe	Ca	Al	pH
			Cr	Zn	Mn					
AMB 200										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	50	61	66.3	445	285	70	4800	1300	880	0.88
% Removal	-1892	-241	-333	4	13	53	36	15	15	
AMB C467										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	1.5	3.3	11	175	140	25.6	6900	1340	860	1.86
% Removal	40	82	28	62	57	83	9	12	17	
PUR S940										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.52	8.7	9.1	290	145	80	6900	1380	780	1.74
% Removal	0	51	41	38	56	46	9	10	25	
AMB IR120										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	1.69	20.5	7.1	260	145	125	3400	1080	260	0.78
% Removal	33	-15	54	44	56	15	55	29	75	
LEW TP207										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.48	1.4	14.4	415	250	130	625	2300	640	1.14
% Removal	1	92	6	11	24	12	92	-50	38	
AMB 200C										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.84	17.4	17.6	445	210	205	4400	6300	520	0.91
% Removal	-13	3	-15	4	36	-39	42	-312	50	
IRC 718										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.22	5.4	13.5	435	325	135	1750	1740	500	1.41
% Removal	12	70	12	6	1	8	77	-14	52	
CHELAMINE										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.66	19	14.2	454	350	141.7	2083	1400	667	1.25
% Removal	-6	-6	7	2	-7	4	72	8	36	
LEW OC1060										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.34	8.5	11.8	145	75	40	3300	1060	460	1.14
% Removal	7	53	23	69	77	73	56	31	56	
IRC 76										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.49	20.5	13	440	330	140	1655	6400	880	0.89
% Removal	1	-15	15	5	-1	5	78	-318	15	
CAR RF23										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	2.34	2.2	1.2	290	270	30.2	1640	1500	680	2.74ppt
% Removal	7	88	92	38	18	80	78	2	35	
MAGNETITE										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	4.41	17.5	15.3	465	355	185	8600	1700	960	1.8
% Removal	-76	2	0	0	-8	-25	-14	-11	8	
Ppt @ pH 7										
Feed mg/l	2.51	17.9	15.3	465	327.5	147.5	7550	1530	1040	2
Filt. mg/l	0.3	1.6	0	4.4	195	0.5	3	1480	0.5	7
% Removal	88	91	100	99	40	100	100	3	100	

6.5.5**Conclusions**

Under the conditions tested, none of the adsorbants gave acceptable performance for the process requirements. Both filtrates suffer from acidic conditions and a high concentration of other cations (primarily calcium but also iron and aluminium). Of the resins tested Lewatit TP 207 is most selective for contaminants over other major ions and was chosen for further evaluation in kinetic tests.

Precipitation was effective in removing the majority of contaminants but the filtrate still requires further processing. Precipitation was also selected for further evaluation.

6.6**Precipitation Test****6.6.1****Quality Assurance**

The blank gave acceptable figures with lead and iron being slightly high. The spiked sample (sample 10) gave increases close to the additions made, with lead and iron being slightly high.

6.6.2**Results of Precipitation on the First Filtrate**

This test examined the possibility of precipitating the contaminants from the filtrate of a two-stage leach. The results of the test precipitating contaminants from the first filtrate at various pH's are given in Table 6.22 and shown graphically in Figures 6.5 and 6.6.

Figure 6.5 shows that aluminium is substantially precipitated between pH 3 and pH 5 whereas iron requires a higher pH of 7 to 9. Calcium shows an increase in removal up to pH 5 and a decrease above pH 5. Calcium nitrate is very soluble (over 250 gpl calcium at ambient temperature) so crystallisation of calcium nitrate is unlikely to be the cause. A higher pH than 9 is required to precipitate lime (Ca(OH)_2) since saturated lime solution has a pH of 12.4 and the cause of this variation in calcium solubility is therefore unidentified.

Figure 6.6 shows that contaminant removal occurs between pH 3 and 7 except for manganese which requires a pH between 7 and 9. For some elements (lead and chromium) redissolution may be expected at higher pH due to their amphoteric nature with the formation of plumbates and chromates, and the results appear to confirm this. Zinc, a major contaminant, requires a pH of 7 to achieve over 90% removal but this still leaves the bulk of manganese in solution (73%) together with 30% of the iron and a pH of 9 is required to remove these contaminants.

The leach test had produced a filtrate close to neutral (1.2 gpl free acid or 25 meq/litre in Table 6.16). However, 133 meq/litre were required to achieve pH 7 and this apparent excess is the alkali required to react with metal cations such as iron to produce an hydroxide precipitate (in the free acid titration this is avoided by oxalate complexing). Precipitation at pH 9 would require 0.2 equivalents per litre of solution.

The precipitated filtrates still contain significant levels of contaminants and will require further processing.

Table 6.22 Results of Precipitation Test on First Filtrate

Solution pH	Stage Addition of 1N NaOH, mls	Milli equivalents /litre of NaOH in Soln	Test Volume mls	Sample Aliquot, mls	Sample No	Wt of ppt from 100 mls aliquot, grams
2.84	-	0	-	100	1	-
3.00	0.3	0.75	400	100	2	0.0994
5.00	18.9	61	319	100	3	0.4841
7.00	18.1	133	237	100	4	1.2778
9.00	11.2	199	148	100	5	2.1560

Filtrate Analyses, mg/l

	Cu	Ni	Cr	Zn	Pb	Mn	Fe	Ca	Al
Feed Solution	1	3.5	1	1090	30	680	1780	20000	590
pH 3	1	3.5	1	1090	29	650	1780	17750	555
% Removal	0.0	0.0	0.0	0.0	3.3	4.4	0.0	11.3	5.9
pH 5	0.2	3.5	0.3	951	18.4	585	1537	15700	23.3
% Removal	80.0	0.0	70.0	12.8	38.7	14.0	13.7	21.5	96.1
pH 7	0.2	1	0.2	81	2.1	498	520	16780	1.4
% Removal	80.0	71.4	80.0	92.6	93.0	26.8	70.8	16.1	99.8
pH 9	0.3	0.8	0.3	1.4	2.4	11.8	5.9	17840	1.9
% Removal	70.0	77.1	70.0	99.9	92.0	98.3	99.7	10.8	99.7

Figure 6.5 Removal of Major Cations from First Filtrate by Precipitation

PRECIPITATION TEST ON HAMILTON BAY
LEACH TEST 15 FILTRATE. (DB15F1 -
1st LEACH) USING 1N NaOH SOLUTION

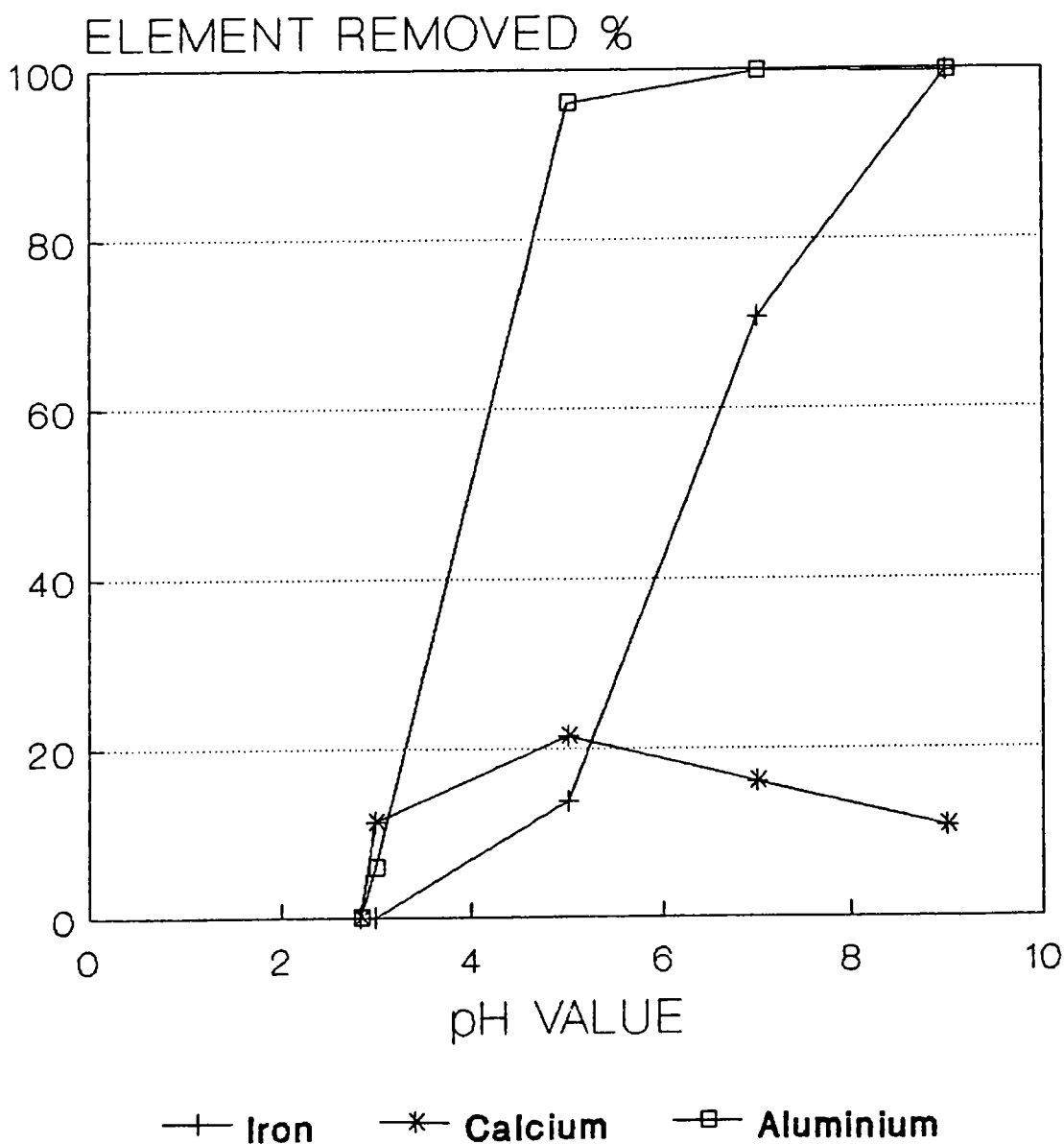
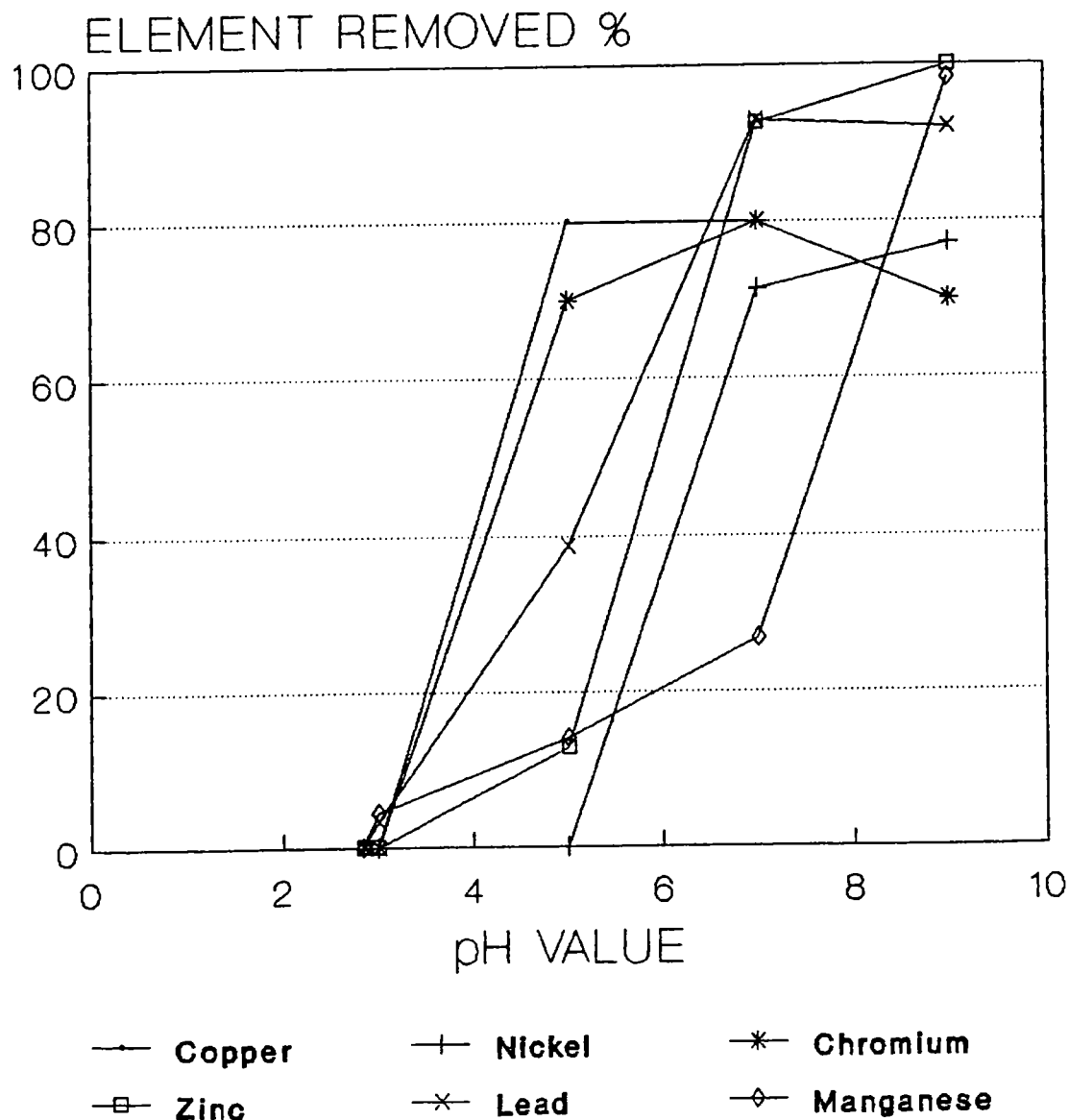


Figure 6.6 Removal of Contaminants from First Filtrate by Precipitation

PRECIPITATION TEST ON HAMILTON BAY
LEACH TEST 15 FILTRATE. (DB15F1 -
1st LEACH) USING 1N NaOH SOLUTION



6.6.3

Results of Precipitation with the Second Filtrate

The more acidic solution from a second stage leach could be recycled to the first leach or it could be treated directly to remove contaminants. The precipitation test was therefore repeated with the second filtrate and results are shown in Table 6.23 and Figures 6.7 to 6.8.

As with the first filtrate, aluminium is substantially removed between pH 3 and 5. Calcium results show some scatter with an initial apparent increase and an apparent high removal at pH 7, declining at pH 9. This shows the same trend as with the first filtrate but 90% calcium removal at pH 7 is surprisingly high and is unaccounted for. Iron precipitation occurs below pH 3 and this may be expected from EH pH diagrams. This being the case, it is surprising that with the first filtrate iron precipitation required a high pH (between 7 and 9). The contaminants were removed between pH 3 and 5, a lower pH range than with filtrate 1 and this is possibly due to the iron precipitation; firstly it may provide nuclei for precipitation and secondly iron hydroxide may adsorb contaminants. Manganese again requires a pH between 7 and 9 to achieve high precipitation.

Zinc, lead, copper and nickel appeared to show some redissolution and this may be expected for zinc and lead, although this is not expected for copper and nickel. A possible explanation could be an error in the analyses at pH 7 (with the low calcium figure) and the mass of precipitate figures may tend to confirm this; the precipitate mass decreases from pH 3 to pH 7 (despite a large reduction in the calcium concentration in solution), and increases between pH 7 and 9 (when calcium in solution increases). An increasing precipitate mass would be expected between 3 and 7 if calcium is precipitating at pH 7. These anomalies are

unexplained.

Metal contaminant precipitation was again optimum for most metals at pH 7 and required 0.33 eq/litre of alkali. Manganese requires a higher pH and needed 0.4 eq/litre. Precipitated filtrates still require further treatment before discharge.

Table 6.23 Results of Precipitation Test on Second Filtrate

Solution pH	Stage Addition of 1N NaOH, mls	Milli equivalents /litre of NaOH in Soln	Test Volume mls	Sample Aliquot, mls	Sample No	Wt of ppt from 100 mls aliquot, grams
1.57	-	0	-	100	6	-
3.00	125.5	239	525	100	7	2.5778
5.00	40.4	305	466	100	8	2.3280
7.00	17.1	336	383	100	9	2.0664
9.00	30.7	400	314	100	10	6.6893

Filtrate Analyses, mg/l

	Cu	Ni	Cr	Zn	Pb	Mn	Fe	Ca	Al
Feed Solution	17.9	2.5	12.5	390	190	275	9675	1500	1060
pH 3	16.9	2.4	1.3	328	145	236	41	1970	867
% Removal	5.6	4.0	89.6	15.9	23.7	14.2	99.6	-31.3	18.2
pH 5	2.5	1.9	0.0	263	20.3	192	3.5	1068	14.0
% Removal	86.0	24.0	99.7	32.6	89.3	30.2	100	28.8	98.7
pH 7	0.6	0.3	0.0	2.9	0.2	84.0	1.0	136	0.7
% Removal	96.6	88.0	99.8	99.3	99.9	69.5	100	90.9	99.9
pH 9	10.2	1.1	0.0	130	0.3	2.8	1.5	1297	2.3
% Removal	43.0	56.0	99.7	66.7	99.8	99.0	100	13.5	99.8

Figure 6.7 Removal of Major Elements from Second Filtrate by Precipitation

PRECIPITATION TEST ON HAMILTON BAY
LEACH TEST 15 FILTRATE. (DB15F2A -
2nd LEACH) USING 1N NaOH SOLUTION

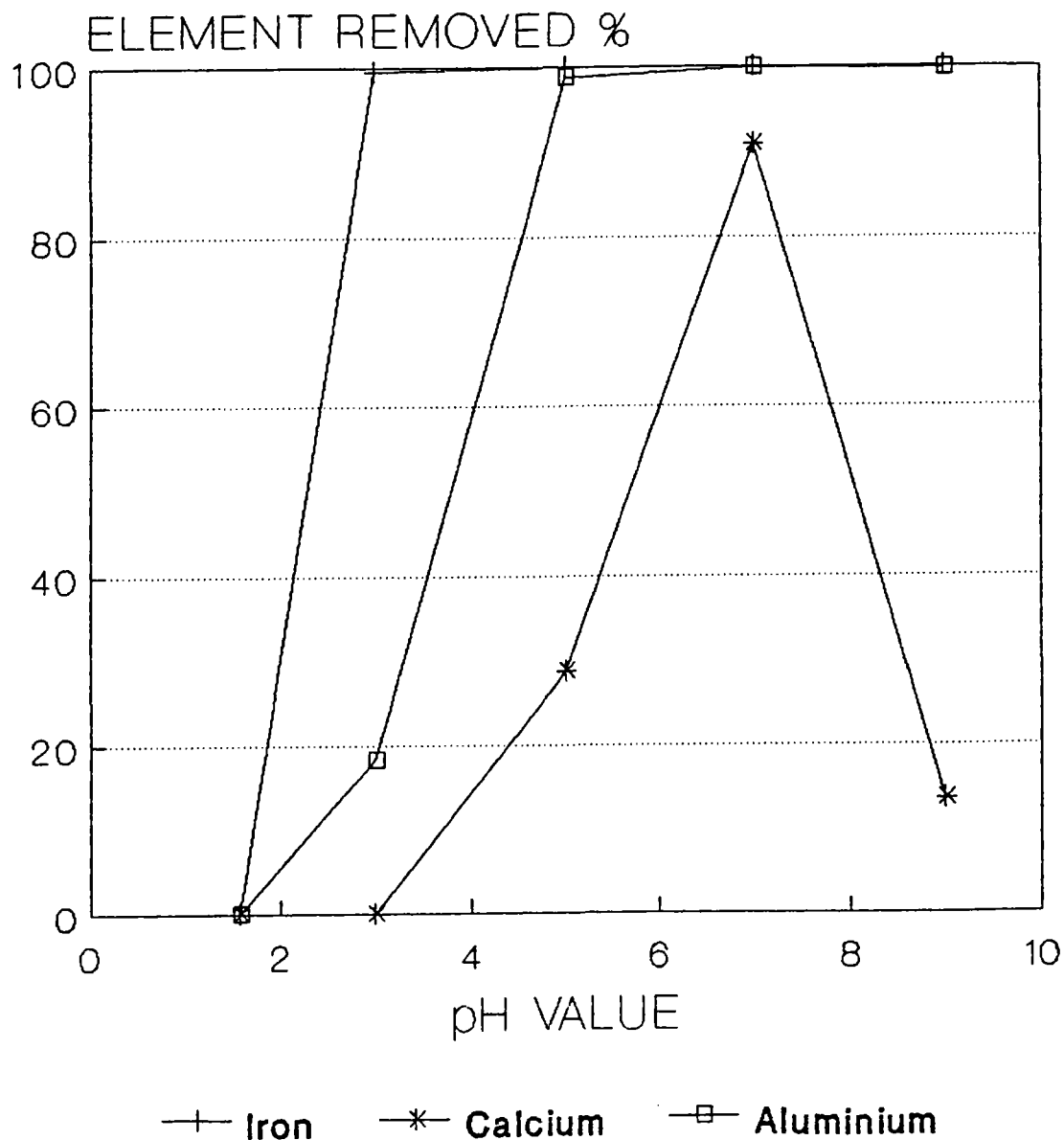
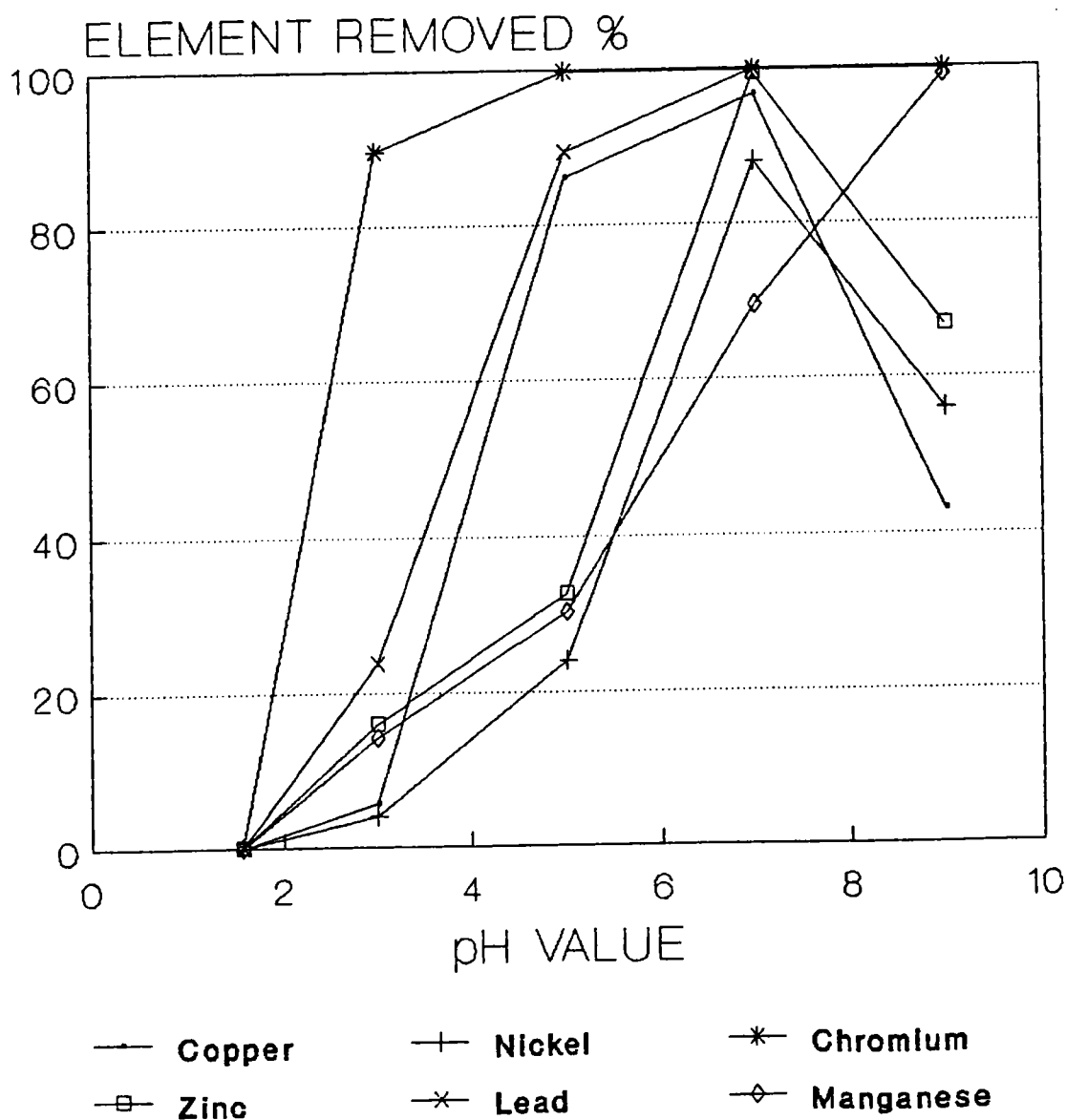


Figure 6.8 Removal of Contaminants from Second Filtrate by Precipitation

PRECIPITATION TEST ON HAMILTON BAY
LEACH TEST 15 FILTRATE. (DB15F2A -
2nd LEACH) USING 1N NaOH SOLUTION



6.6.4 Conclusions

Precipitation is an option for contaminant removal and at pH 7 precipitation removes most contaminants apart from manganese. However, the filtrate will still need further processing to remove remaining contaminant levels and the filtrate still contains calcium ions.

6.7 Kinetic Resin Loading Tests**6.7.1 Quality Assurance for Kinetic Resin Loading Tests**

Table 6.24 shows the Quality Assurance data, all of which are within acceptable limits. Lead is slightly high on the blank due its presence in the acid and the spiked sample (sample 28) gave increases in analysis close to the addition level.

Table 6.24 Results of Resin Kinetic Loading Test

HAMILTON BAY		RESIN TEST ON LT16FILTRATE2						31-MAR-1994		
RATIO	TIME	Cu	Ni	Cr	Pb	Zn	Mn	Fe	Ca	Al
2:1	0mins	19.4	5.6	9.3	188.0	1126	580	12300	9000	750
	2mins	8.2	4.7	6.8	133.0	940	500	9050	8500	133
	15mins	4.2	4.6	7.8	126.6	938	510	7650	8300	130
	30mins	3.9	4.6	8.0	127.4	938	500	7100	8400	128
	60mins	3.3	4.7	7.4	132.6	945	500	7000	8300	127
	120mins	3.1	4.6	7.6	131.0	946	510	5800	8000	127
4:1	0mins	19.4	5.6	9.3	188.0	1126	580	12300	9000	750
	2mins	14.6	5.0	6.7	164.8	1045	530	10600	9000	138
	15mins	9.6	5.1	7.3	157.8	1030	520	9550	8900	135
	30mins	8.4	5.2	7.2	159.8	1030	530	9200	8900	136
	60mins	7.4	5.1	6.9	160.8	1021	530	8900	8900	135
	120mins	7.3	5.2	6.9	162.8	1060	550	8800	9100	142
6:1	0mins	19.4	5.6	9.3	188.0	1126	580	12300	9000	750
	2mins	15.4	5.2	7.1	171.4	1033	530	10700	8900	138
	15mins	12.3	5.3	7.1	166.0	1040	530	10200	8900	136
	30mins	10.9	5.2	6.6	166.4	1046	530	9900	9100	138
	60mins	10.2	5.2	6.6	167.2	1063	520	9750	9100	137
	120mins	9.7	5.3	6.6	167.8	1038	550	9450	9400	136
8:1	0mins	19.4	5.6	9.3	188.0	1126	580	12300	9000	750
	2mins	17.1	5.2	7.8	184.0	1103	550	11700	9500	147
	15mins	16.5	5.2	7.8	181.0	1045	550	11250	9500	166
	30mins	14.5	5.1	7.8	176.0	1032	540	10100	9400	162
	60mins	11.5	5.1	7.6	170.2	1026	540	9950	9000	136
	120mins	11.2	5.1	8.3	168.8	1026	550	9700	8900	134
Raff from 2:1 at 2:1	0mins	3.1	4.6	7.6	131.0	946	510	5800	8000	127
	2mins	1.1	3.7	9.0	95.8	938	520	4500	8600	128
	15mins	0.5	3.7	10.1	77.8	892	490	2900	8100	121
	30mins	0.3	3.8	8.7	65.0	723	400	1780	5900	98
	60mins	0.3	3.6	10.0	67.2	716	400	1320	5900	98
	120mins	0.2	3.8	10.7	71.8	748	400	910	6200	101
SPIKE	(Actual)	5.05	4.98	5.05	5.03	5.01	5.05	10.1	10.1	20.1
	(added)	5	5	5	5	5	5	10	10	20
Blanks		0.01	-0.02	0.02	0.03	-0.05	0.01	0.01	0.01	0.02

6.7.2

Discussion of Results

Table 6.24 also presents the results from the tests and these are shown graphically in Figures 6.9 to 6.11. These figures show that iron adsorption is taking place in the normal manner with respect to time. Calcium shows little adsorption except in the raffinate from Test 1 where some adsorption occurs once the iron has been substantially removed. Further calcium adsorption beyond the 30 minute sample may be inhibited by the loading already present on the resin. Figure 6.10 shows adsorption of the minor elements. Aluminium shows a high initial rapid removal. Copper shows a high initial removal and continuing removal thereafter. Other elements show some initial removal (2 minute sample) but little subsequent removal. In the case of the raffinate more removal occurs once the iron concentration has been reduced but adsorption was inhibited beyond 30 minutes.

The comparative adsorption isotherms for iron (the best adsorption curve) and zinc (a major contaminant) are plotted in Figures 6.11 shows the effect of resin concentration. Plotting these data against reciprocal time shows that from 15 minutes the results are linear (possibly diffusion control) whereas the initial adsorption is very rapid. This information can be used to derive kinetic data for the adsorption stage but no calculations have been performed in view of the poor overall adsorption of contaminants.

Figure 6.10 Results of Resin Kinetic Loading Tests - Contaminants

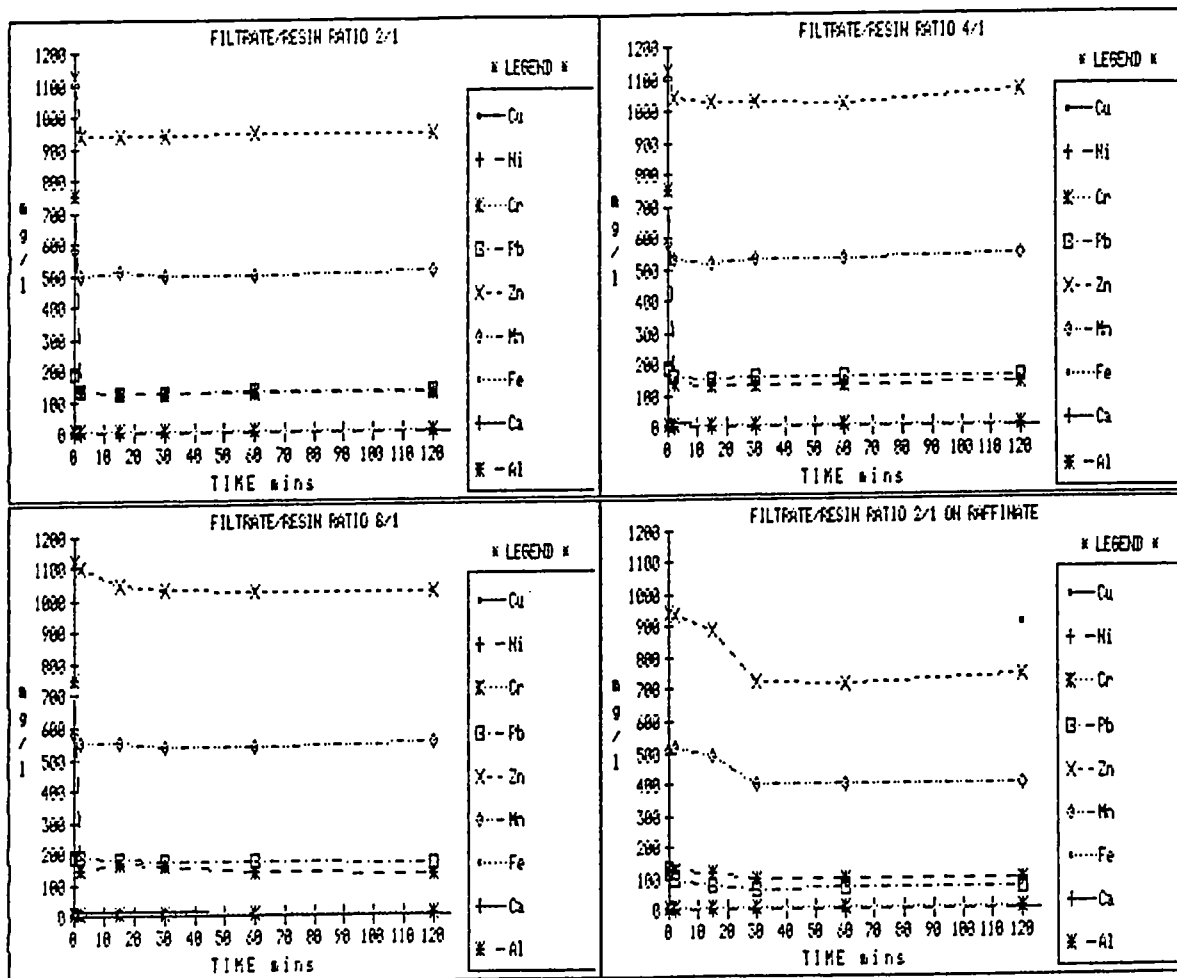


Figure 6.9 Results of Resin Kinetic Loading Test - Major Elements

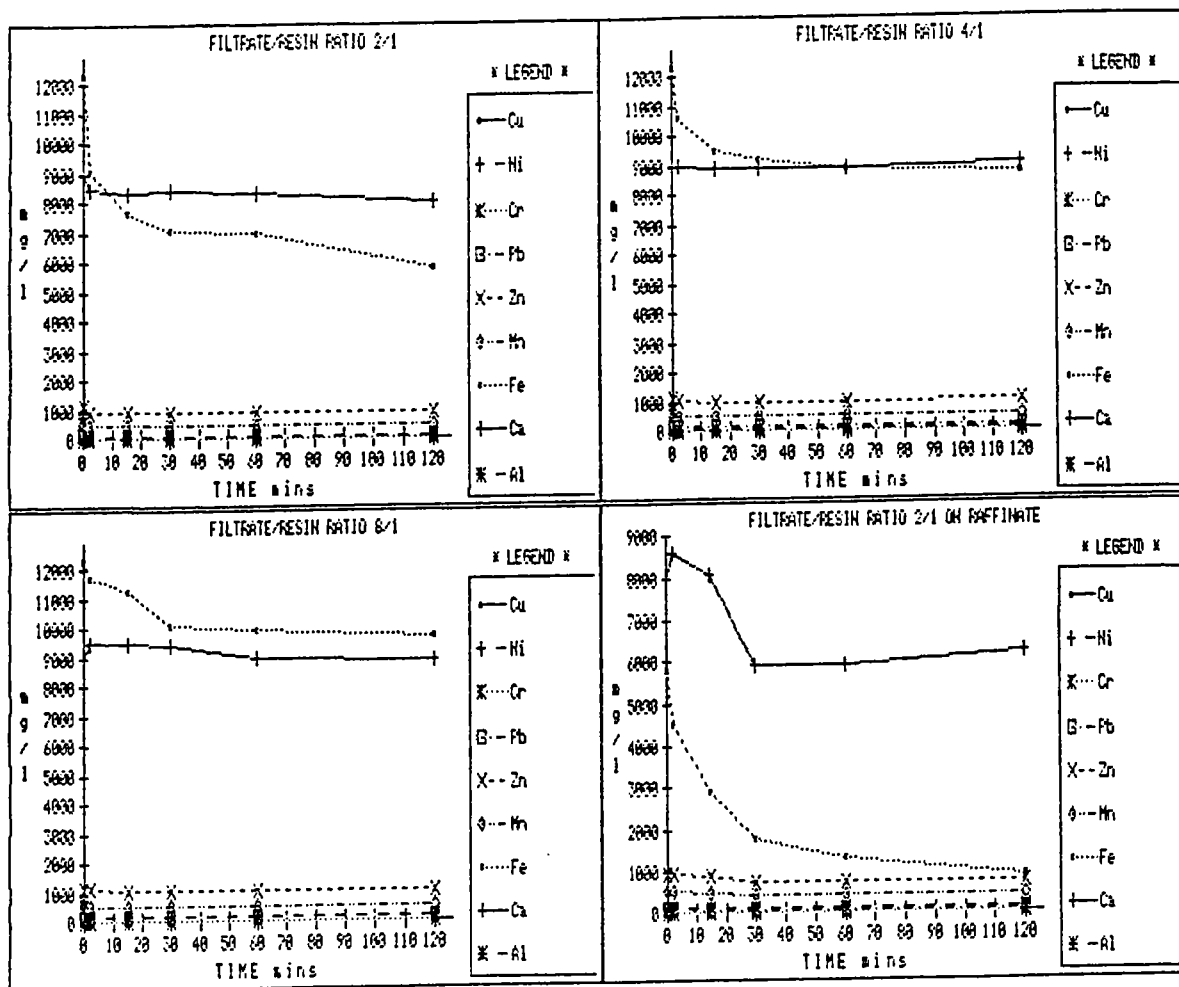
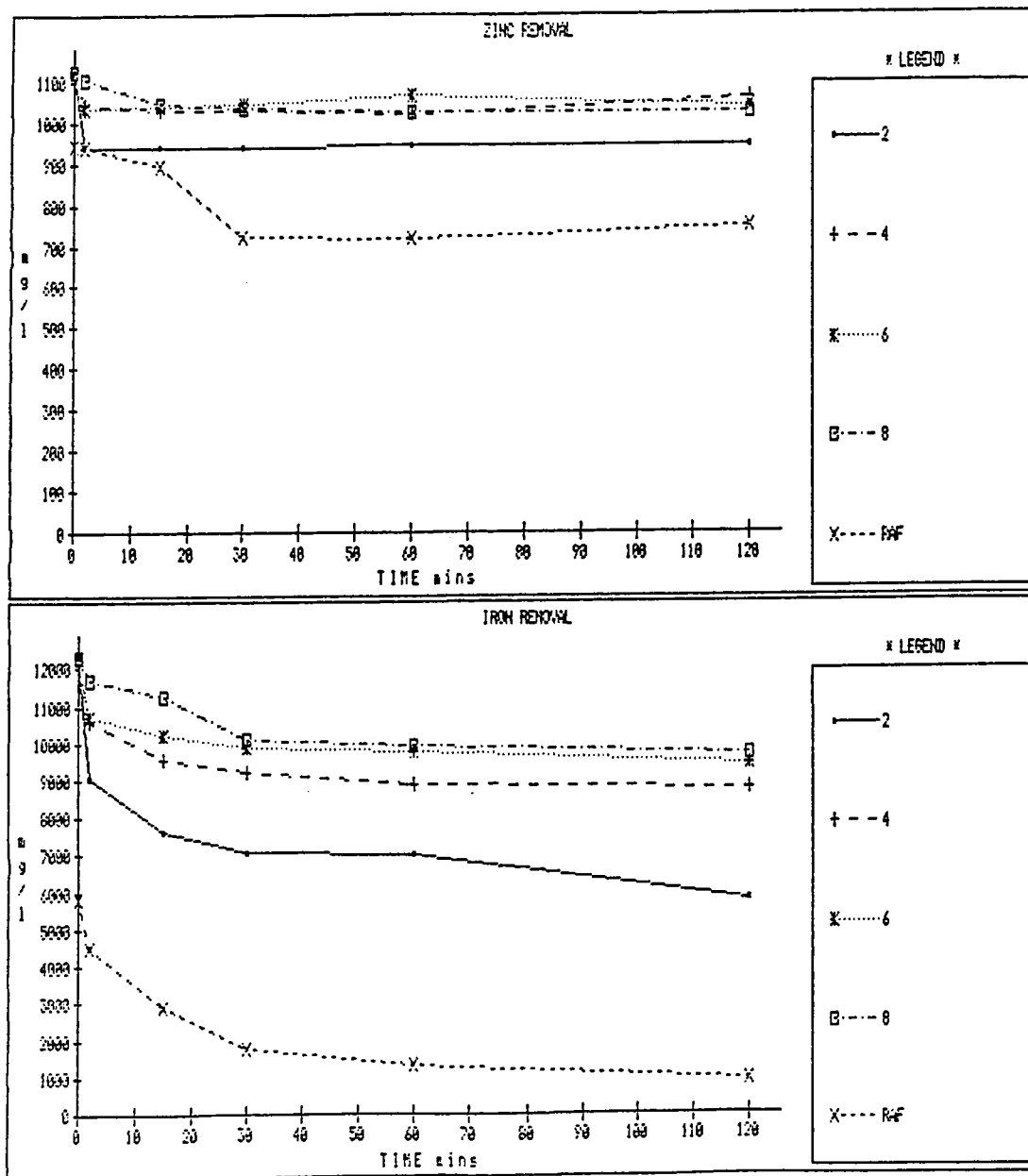


Figure 6.11 Rate of Iron and Zinc Removal at Different Filtrate/Resin Ratios



6.7.3**Conclusions**

Lewatit TP 207 was chosen from the resin screening tests to give selective adsorption over the major elements. However, the iron present in the second filtrate was adsorbed in preference to the contaminants. Further testwork would be necessary to see if adsorption using TP 207 was better with the first filtrate. Alternatively, a pre-treatment to magnetically remove iron may enhance performance of the adsorption stage.

7. PROCESS FLOWSHEET**7.1 Flowsheet Discussion**

On the basis of the testwork carried out by Davy International on the sample of sediment provided by WTC, treatment of the Hamilton Harbour sediment to meet Ontario guidelines is likely to require a number of individual unit operations and will generate several waste streams for disposal. Taking the sample provided with its analysis of 19% iron, 22% loss on ignition, 4800 ppm Zn, 800 ppm Pb, 3500 ppm Mn and 50 to 100 ppm of Cu, Cr, Ni, there is unlikely to be a clear separation into clean and contaminated fractions. Thus a ferrous fraction, an organic fraction, a heavy metal fraction and a clean sediment are likely to be produced. In addition there may be a fifth stream from the effluent treatment section due to other soluble salts such as calcium. This is both a problem encountered with the Davy process and will be a problem common to other treatment processes. Soil washing may concentrate contaminants but in view of the fine nature of the sediment (75% less than 45 microns) ready separation into a clean and unclean fraction is unlikely to occur.

The sediment contains a number of metals that exceed both the Ontario guidelines and other international criteria for soils and sediments as shown in Table 7.1. However it is necessary to consider the basis of these standards. In general these levels have been derived by risk assessment of the possible hazard to human health owing to entry into the human body through a variety of routes. For some elements the concern is phytotoxicity and standards are based on measurements of the effect of the presence of metals on the growth of various plants. In some cases the regulatory limits do not specify the analytical procedure and as noted with the Canmet analysis of the lake sediment, different

techniques may yield different results.

The USA have taken a different approach to many countries and have applied a leachability criterion, and the new Dutch A level's reflect an attempt to define availability of the contaminant. In the case of sediment the situation is more complex in that there are three factors:

- a) Dissolution back into the water.
- b) Disturbance of the benthic community through non-viability.
- c) Bioaccumulation in the food chain.

The basis of the Ontario guidelines is discussed in "Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario". Simpler treatment flowsheets will reduce contamination but will not achieve these guideline levels and in order to meet these guidelines it will have to be accepted that a complex train of unit operations will be required and a number of by-product streams will be generated.

The results of the Davy International test programme have been reviewed in the light of the above comments. The complexity of the sediment means that additional processing will be required and it has not been possible to investigate this within the time constraints of the present programme. Certain assumptions are therefore made in the following discussion.

Table 7.1 Comparison of Regulatory Levels

	Hamilton Harbour Analysis (8 samples) mg/kg	Ontario Guidelines For Sediment mg/kg		Danish (proposed) mg/kg	UK		US Leachability mg/l	Dutch		Superseded	
					Housing	Parks				Danish	Dutch
		Lowest Effect	Severe Effect		mg/kg	mg/kg				mg/kg	B mg/kg
Arsenic	NA	6	33	20	10	40	5	$15+0.4x(L+H)$	50	30	30
Lead	794	31	250	40	500	2000	5	$50+(L+H)$	600	100	150
Cadmium	NA	0.6	10	5	3	15	1	$0.4+0.007 \times (L+H)$	20	-	5
Chromium *	69	26	110	100	600	1000	5	$50+2x(L)$	800	160	250
Copper	91	16	110	200	130	130	-	$15+0.6x(L+H)$	500	100	100
Mercury	NA	0.2	2	(0.2)	1	20	0.2	$0.2+0.0017x(2L+H)$	10	2	2
Nickel	49	16	75	60	70	700	-	$10+(L)$	500	-	100
Tin	NA	-	-	50	-	-	-	20	300	-	50
Zinc	4835	120	820	200	300	300	-	$50+1.5x(2L+H)$	3000	-	500
Cobalt	NA	-	-	-	-	-	-	20	300	-	50
Molybdenum	NA	-	-	-	-	-	-	10	200	-	40
Barium	NA	-	-	-	-	-	-	200	2000	-	400
Iron	19%	2%	4%	-	-	-	-	-	-	-	-
Manganese	3573	460	1100	-	-	-	-	-	-	-	-

* Lower levels for Cr (vi). NA - not analysed. L - Clays. H - Humus

7.2 Flowsheet Options

7.2.1 Introduction

Three flowsheet options have been developed based on these test results and are shown in Figures 7.1 to 7.3. The core stages are discussed below and common process steps are discussed in the next section.

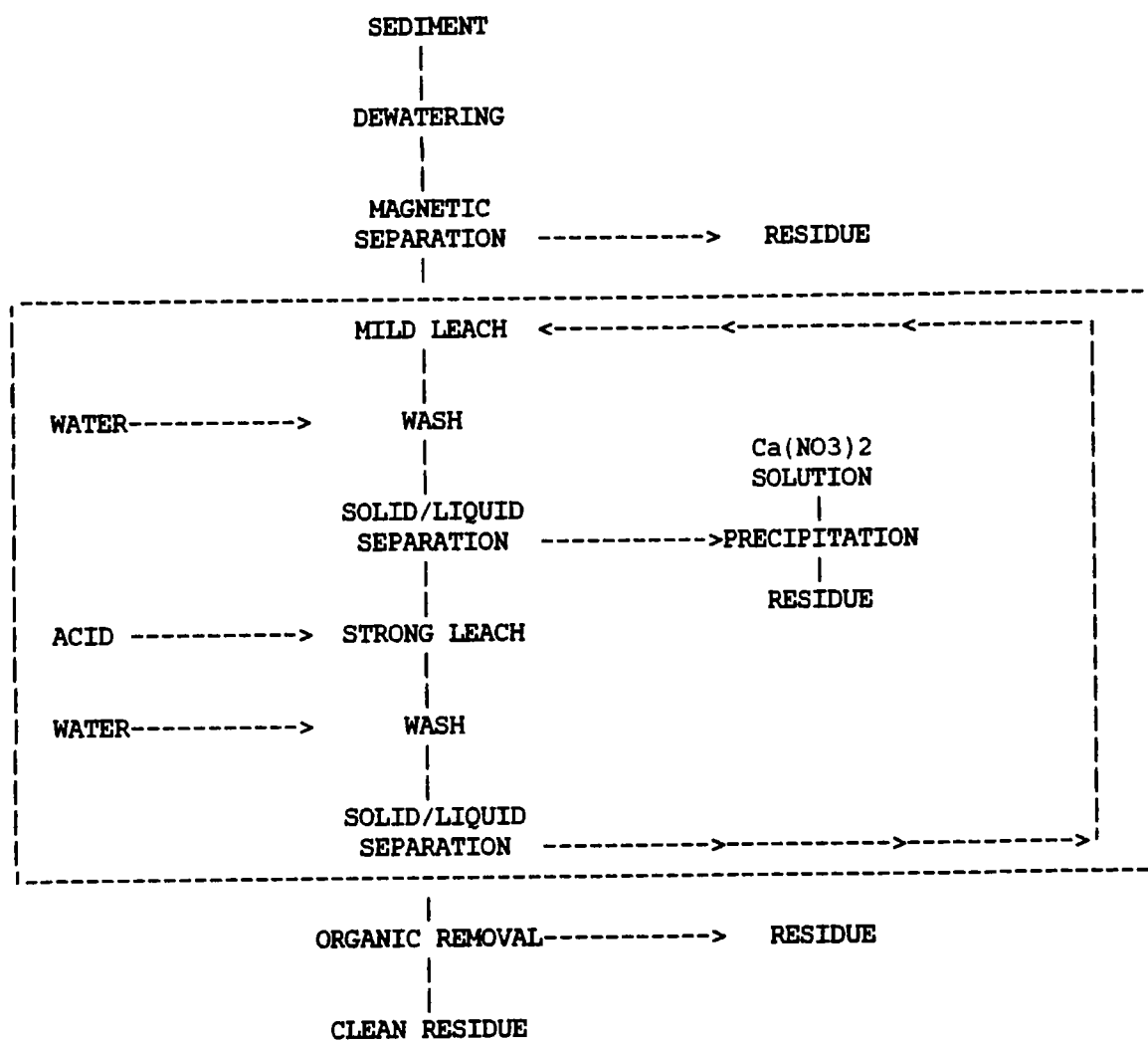
7.2.2 Simple Treatment Route

Figure 7.1 shows a simple treatment route. A mild acid leach would be followed by a strong acid leach. Since acid utilisation is incomplete in the second stage leach, the filtrate (containing contaminants) could be recycled to the first leach. Based on the results of LT 10 - 16 an acid concentration of 200 - 250 gpl nitric acid would be used in the second leach. The residual acid strength is unknown, but based on LT 11 and LT 15B it may be around 50 gpl and would be sufficient for the first leach (acid utilisation cannot be directly determined from the present tests since fresh acid was used for each leach). A water and acid balance will need to be carried out to ensure the filtrate from the first leach is still acidic (below pH 3) but has little free acid. Total acid usage will lie between that of LT 10 and LT 11. Based on LT 14 and assuming an acid balance can be maintained, the residue should have an analysis below the Ontario severe guidelines for metals. This sediment will then proceed for treatment of organic contamination.

The filtrate from the two-stage leach will contain calcium nitrate and contaminants and will need to be separated from the solids by a suitable process step. Washing is shown in Figure 7.1 although it may not be required if more dilute pulps are used. However a

displacement wash is probably required for a 30% pulp. The filtrate will have a greater contaminant level than the filtrate used in the present precipitation tests since a double leach has been used. However, assuming that comparable removals can be achieved by precipitation then the addition of milk of lime to achieve a pH of 7 will remove between 70 and 90% of contaminants. Separation of the precipitate will allow the pH to be raised to precipitate manganese without redissolving contaminants. The calcium nitrate solution will then require polishing to remove the final trace of contaminants, possibly by sulphide precipitation.

Figure 7.1 Simple Treatment Route using Conventional Unit Operations



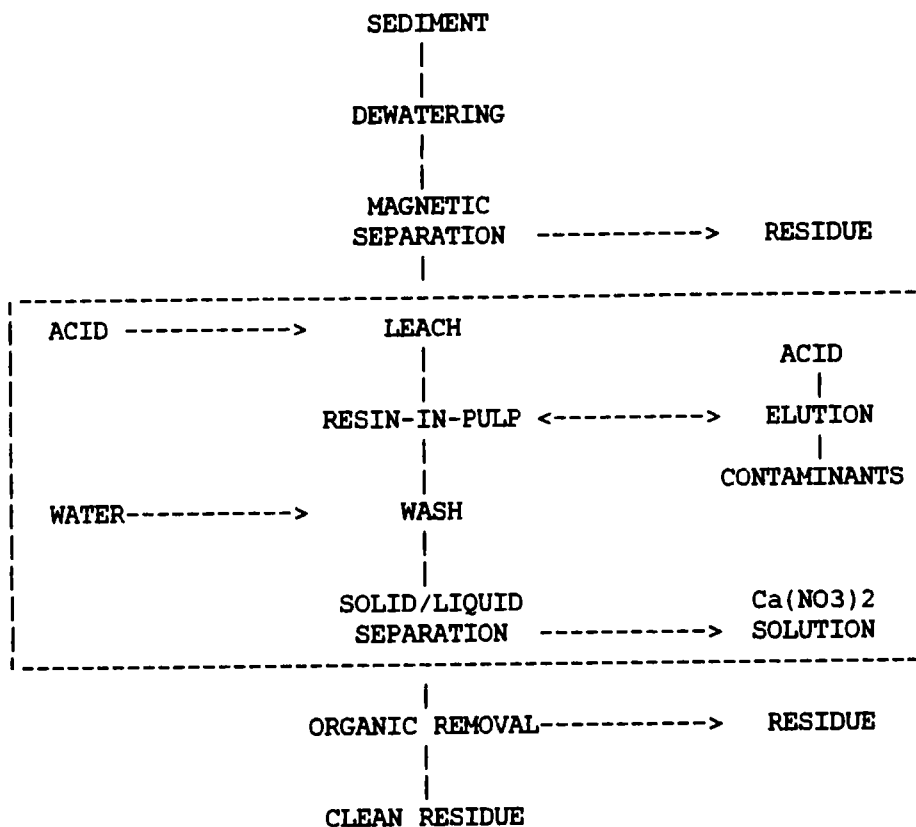
7.2.3**Single Stage Leach Plus Adsorption**

The leach screening test with Iowatit TP 207 iminophosphonic resin on the filtrate from the first and second leach showed no calcium adsorption. Resin IRC 718, another chelating resin with an iminophosphonic group, also showed low calcium removal although it also showed poorer contaminant removal. However, in both the screening and the kinetic tests with TP 207 on the second filtrate iron adsorption occurred and prevented adsorption of contaminants. It is therefore possible that a pretreatment to remove iron may result in a filtrate that can be treated by TP 207 (or equivalent) to remove contaminants from a calcium nitrate solution. Figure 7.2 is a flowsheet based on the assumption that this can be achieved.

A single stage leach will be performed. In this example 150 gpl acid is assumed based on LT 10 and LT 14, although this may be reduced if iron can be removed magnetically. The final filtrate is assumed to contain little free acid and the filtrate undergoes a chelating resin-in-pulp step.

The contaminants are extracted into the resin and recovered in the elution stage. The pulp proceeds to a solid/liquid separation with a displacement wash to recover calcium nitrate solution for further processing. The treated residue then proceeds for organic treatment.

Figure 7.2 Single Stage Leach Plus Adsorption with Selective Reagent to Avoid Calcium Adsorption



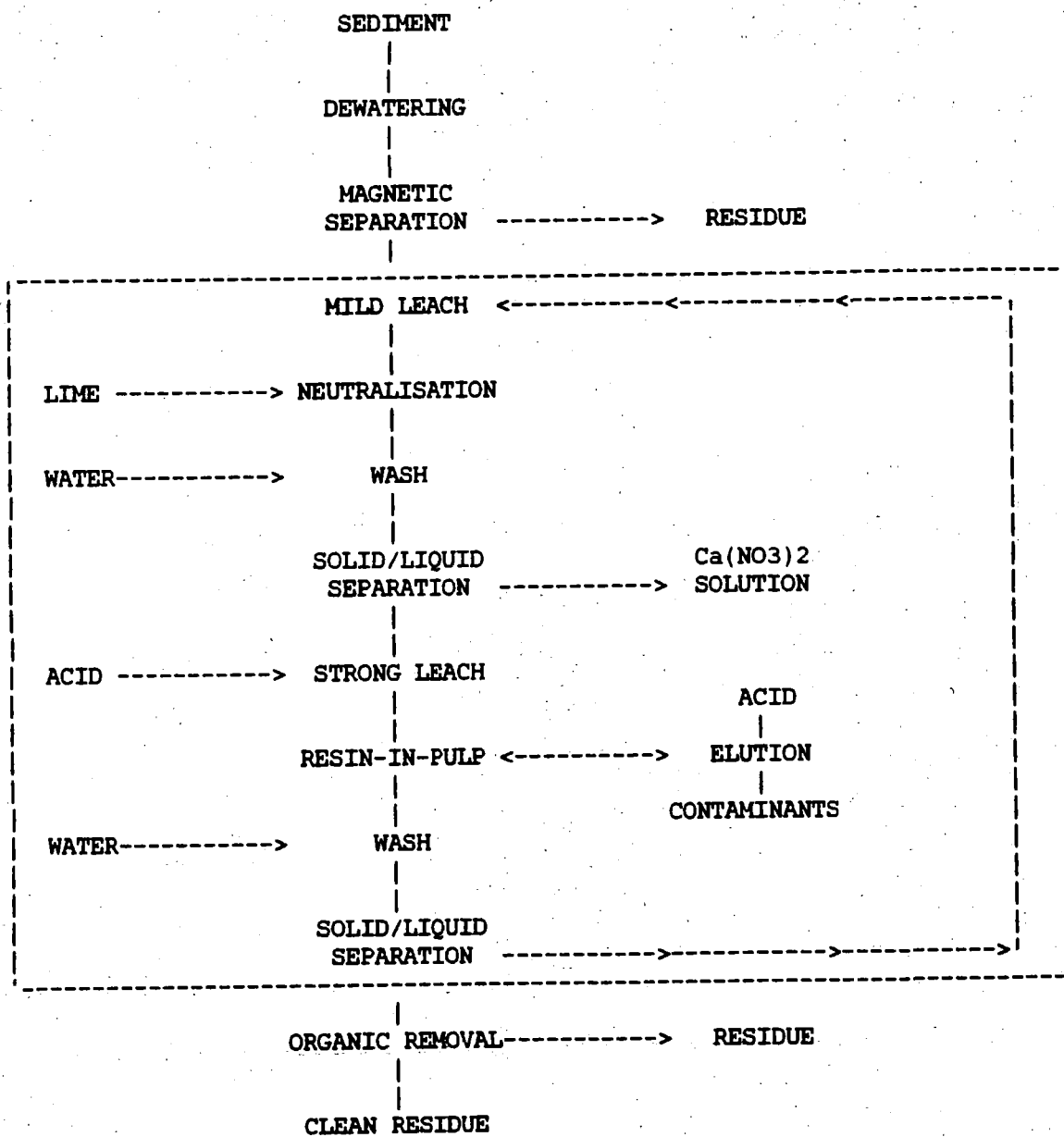
7.2.4**Two-Stage Leach Plus Adsorption**

Figure 7.3 is a flowsheet based on the assumption that a more selective resin or more selective conditions may be found for contaminant adsorption from an acid solution. A two-stage leach is employed to remove calcium prior to the contaminants and thus reduce the cation load on the adsorption stage. It has also been assumed that magnetic pretreatment, as discussed in the next section, will reduce the iron loading on the adsorption stage.

The sediment undergoes a mild leach with 60 to 90 gpl nitric acid similar to the LT 15 and LT 16 first stage leaches. As LT 14 shows, this will dissolve most of the calcium but will also dissolve some contaminants. Following the leach therefore the pH of the filtrate is raised to re-precipitate the contaminants. Preferably this will be done by milk of lime. Solid/liquid separation with a displacement wash will produce a calcium nitrate solution relatively free from contaminants and only requiring polishing treatment.

The sediment is now free of calcium and can be subjected to a strong acid leach similar to Stage 2 of LT 15 and LT 16, except that it will also contain the re-precipitated contaminants. Being low in calcium and iron it is anticipated that better adsorption of the contaminants will be achieved although adsorption from this acidic solution will need to be demonstrated. The adsorbant will go to an elution state for regeneration and recovery of contaminants whilst the solids undergo solid/liquid separation and a displacement wash to recover acid for recycle to the first leach. Any contaminants not adsorbed are therefore recycled for recovery and an equilibrium will be attained. The cleaned soil proceeds for further processing.

Figure 7.3 Two-Stage Leach Plus Adsorption



7.3 Common Process Steps - Sample Pretreatment**7.3.1 Introduction**

Four pretreatment steps may be considered: dewatering, size separation, magnetic separation and organic removal. These will be common to all flowsheets.

7.3.2 Dewatering

Depending on how the sediment is excavated a dewatering step may be required. The pulp received from WTC had settled over a period of time and 13% water was added to give a 34% w/w pulp that could be stirred. A pulp of 30% was used in the testwork and a similar pulp density is envisaged for a commercial plant since this pulp is not excessively viscous and yet minimises the volume of leachate. The plant probably will require a dewatering stage to achieve 30% solids and suitable storage to maintain a mixed system and avoid compaction of the solids. This needs to be designed in conjunction with the excavation system. For example, a dredger using clam buckets may deposit batches of sediment substantially dewatered whereas an extraction pump will produce a continuous feed and will require less storage but will require dewatering.

7.3.3 Size Separation

From the size analysis only 2% of the feed exceeded 350 microns in size. The in-pulp process can accept coarse material in a leach stage but will require more power to the impeller to maintain a suspension in the leach vessel, and coarse material will need separation before in-pulp adsorption. It is therefore anticipated that a single stage will be incorporated to remove tramp coarse material (eg shells, stones etc) and a cut size of 500 microns is proposed. Although the sediment

appeared viscous owing to the organic contamination it screened reasonably easily in the laboratory. However for a commercial plant and a fine cut size alternative hydraulic separation techniques need to be considered.

7.3.4 Magnetic Separation

No testwork was performed on magnetic separation although it was shown that a fraction of the material is magnetic. Magnetic separation may be hindered by the organic content of the as-received pulp and it would be preferable to conduct magnetic separation after removal of organics. However, a pretreatment stage to remove iron is preferred since it will reduce the iron content in the leach liquor and magnetic pretreatment is proposed. It has been assumed that this can be effectively achieved, although this will need to be verified for the successful operation of the three flowsheets discussed.

7.3.5 Organic Removal

Organic removal was beyond the scope of the present study. However, two important factors were observed. Firstly, only 2% of the sample is acetone soluble and a solvent wash will therefore still leave 20% LOI in the sediment. Secondly, two leaches with sulphuric acid on as-received and on acetone-washed sediment suggested there was little difference in leaching behaviour. A pretreatment for organic removal is therefore not essential.

In view of the high organic content and the lack of effectiveness of solvent washing, it is likely that the sediment will require thermal processing and it will be preferable to conduct this as a post treatment to avoid volatilisation of contaminants (lead, zinc) and to avoid drying and re-wetting. However, mineral processing alternatives such as froth flotation could also be considered.

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7.4 Common Process Steps - Post Treatment**7.4.1 Organic Treatment**

The removal of the organic material has already been discussed. Assuming this requires a thermal process this would be carried out as a post treatment.

7.4.2 Residue Conditioning

No conditioning of the residue is anticipated. Neutralisation may be required if washing is inadequate but this will result in soluble nitrate salts. It is assumed that this is undesirable although calcium nitrate has been proposed by the National Water Research Institute (NWRI) as a nutrient to encourage indigenous remediation by biodegradation.

7.4.3 Effluent Treatment

The main liquid effluent from these process flowsheets is calcium nitrate solution containing traces of contaminants. These contaminants may be further reduced by polishing techniques such as sulphide precipitation although the high nitrate ion concentration may affect solubility. This option needs further examination by modelling and testwork and Davy International has a licence for ESP, a simulation package that can be used to model effluent treatment problems such as this. This option would be examined in a subsequent phase of the test programme.

Disposal of calcium nitrate solution presents problems and this is a consequence of the calcium content of the sediment. The use of milder leaching reagents will reduce calcium dissolution but is unlikely to be effective for contaminant removal. Sulphuric acid produces calcium sulphate in the sediment but was ineffective for lead removal. Any

leaching process therefore has to address soluble calcium in the effluent. A preferred option would be regeneration of nitric acid from calcium nitrate by addition of sulphuric acid and precipitation of calcium sulphate. This could be examined but unless there is a high recovery it will result in calcium recycle and in the presence of sulphate ions which may inhibit lead dissolution (LT 13). Crystallisation may be required to remove the calcium nitrate but the solubility of calcium nitrate is very high and this process step will be energy intensive. Unless a use can be found for the effluent (such as NWRI's remediation process) crystallisation may be the only option for effluent treatment.

7.5**Ancillaries**

The ancillaries such as excavation of the sediment are beyond the scope of the present study. One ancillary process step is however noted and that is for suitable fume extraction on the leach stage for any acid fume or spray from effervescence, and for the slight evolution of H_2S noted in the leach tests.

8.**FUTURE WORK**

To develop a flowsheet further, the following laboratory testwork would be necessary.

- a) The magnetic extraction of iron should be examined to determine its effectiveness.
- b) Froth flotation and other mineral processing techniques should be examined for organic removal.
- c) Polishing of calcium nitrate solution requires investigation and demonstration.
- d) The effect of acid recycle from a second leach to a first leach should be examined. The dissolution of contaminants after precipitation in flowsheet 3 (Figure 7.3) needs confirming.
- e) Further testwork is required using TP 207 or other suitable resins on the calcium rich filtrate produced by flowsheet 2 (Figure 7.2).
- f) Further testwork is required on adsorption from the acid solution generated in flowsheet 3 (Figure 7.3).

9.

CONCLUSIONS

- a) The test programme proposed by Davy International was successfully carried out and showed that all contaminants apart from iron could be leached to below the Ontario "severe effect level" guidelines. The iron was shown to be magnetic and may be removed by magnetic separation.
- b) The high concentration of calcium and iron ions in solution inhibited adsorption and further work will be required to develop the adsorption stage. Two flowsheets have been proposed based on the results obtained and require further investigation. An alternative flowsheet based on precipitation has also been proposed.
- c) The sediment provided by WTC from Hamilton Harbour is complex and will be difficult to treat. Several product streams will be generated and require disposal. A risk assessment should be carried out and correlated with technologies that can be offered in order to determine the best option for the environment and the community.

APPENDIX 1 - IN-PULP TREATMENT OF SOILS AND SEDIMENTS**1. Description of the Process Technology****1.1 General Description**

The process under development by Davy is applicable to the remediation of metal and organic contaminated soils, dredgings, residues etc. As applied to metal and other inorganic contaminated sediments, the process comprises some or all of the following steps:

- a) Physical separation of the sediment fraction found in preliminary tests to have the highest concentration of contaminants, eg wood chips, wood fibre, etc. This step is optional and is probably unnecessary for a harbour sediment but may be required for a soil sample. Alternatively, this stage could be an alternative technique such as soil washing.
- b) Solubilisation of the contaminants by,
 - i) acid or alkaline leaching by the addition of leach reagents. The solubilisation is achieved by stirring an aqueous slurry of the sediment in conventional equipment, similar to those used in ore leaching, with addition of the required chemicals,
 - ii) the use of cation exchange resins in the hydrogen form to achieve simultaneous selective leaching and extraction of metals/inorganic contaminants under controlled conditions with minimum reagent addition.
- c) Adsorption of the solubilised contaminants directly from the leach slurry by appropriate solid particulate adsorbents or ion

exchange materials such as resins or active carbon in a well established process step called "resin-in-pulp" (RIP) or "carbon-in-pulp" (CIP). Solid liquid separation and solids washing are thus avoided. Following removal of the contaminant from the leach slurry by the particulate resin or carbon, which has a larger particle size than the contaminated solid material, it is separated from the cleaned sediment slurry by screening. This is the key step in the in-pulp treatment process.

- d) Elution or desorption of the contaminant from the resin or active carbon and resin or carbon recycle to the process for reuse.
- e) Recovery of acid for recycle from the resin eluate by eg,
 - i) acid retardation technology, using resins. This technology has been developed by a Canadian company, Ecotec, and employs a chromatographic effect.
 - ii) electrodialysis of the metal/inorganic content of the eluate.
- f) Concentrated metal and inorganic contaminants can now be precipitated, eg by lime addition, or recovered, eg by electrowinning in the case of metals. Precipitated contaminants can be disposed of in a concentrated form to secure landfill or marketed for an end use. Recovery of acid from the eluate minimises the material for disposal.

The resulting cleaned sediment can be recycled to the environment or used or disposed of in other ways, eg as non-toxic landfill.

The above general steps of leach and RIP/CIP can be combined in a variety of flowsheets depending on soil or slurry properties and contaminant type. One specific modification would be to combine leaching and RIP or CIP to operate as a resin-in-leach (RIL) or carbon-

in-leach (CIL) process and this can have distinct advantages when contaminants are strongly adsorbed on to active surfaces in the contaminated material.

A further innovation mentioned above and being developed by Davy for sodium removal from the red mud that results from bauxite leaching in the Bayer process, is to use cation exchange resins as acids in controlled leaching of specific materials. The addition of soluble acids is thereby avoided and acid leach products will not remain in the treated sediments.

1.2 Discussion of In-Pulp Technology

1.2.1 RIP/CIP Processes In Mineral Extraction

Conventional hydrometallurgical processes for the recovery of metals from ores usually involves crushing, grinding, leaching, solid/liquid separation and solids washing followed by metal recovery from solution. Solid-liquid separation and solids washing use large and expensive equipment occupying large land areas and it has long been recognized that there are major advantages in using ion exchange resins to recover metal values directly from leach slurries, often called pulps. These processes are called resin-in-pulp (RIP) and carbon-in-pulp (CIP). These advantages include:

- a) The elimination of solid-liquid separation and solids washing by RIP or CIP significantly reduces the size and cost of the post leach plant. To achieve efficient washing at least two tonnes of wash water are required per tonne of ore and large multistage counter current decantation (CCD) units are usually required.
- b) In-pulp recovery of metal values can be much more efficient than washing. When applied to contaminants removal, environmental

requirements can be much more easily achieved.

- c) The cost of the post leach flowsheet can be reduced by 40% by eliminating solid-liquid separation and solids washing.
- d) Solids washing becomes more difficult and more costly as the fines or clays content of the solids increases. The higher the fines content of the leach pulp, therefore the greater the attractiveness of RIP and CIP technology. Thus RIP and CIP are particularly attractive for treating sediments.

The RIP process is well established in the recovery of uranium, is practised in the recovery of gold and has been proposed for the recovery of base metals.

The uranium process utilises anion exchange resins to recover uranium which is present in the leach as the uranyl anion. Recoveries in excess of 99% from leach pulps containing 500-2000 ppm uranium are common using RIP processes.

The CIP process is commonly used in the recovery of gold and silver. Activated carbon is used to adsorb the gold and silver which are leached as cyanide complexes. In gold recovery, removal efficiencies exceeding 99% are achieved from leach pulps containing 2-10 ppm Au.

The most successful RIP/CIP contactors are stirred vessel contactors in which resin or carbon is stirred with the pulp. The process normally has multiple stages and operates continuously with the pulp and resin or carbon moving counter-currently. The larger resin or carbon particles are contained within the contact stages by vibrating, air swept or mechanically swept screens. As the pulp flows through the successive contactor stages it is depleted in metal content by adsorption onto the resin or carbon. The number of stages are

designed to achieve the required metal recovery. The resin or carbon is moved from stage to stage in a counter-current direction to the pulp flow by means of pumps or air lifts. The residence time of the resin or carbon in each stage of the contactor is thus much longer than the residence time for the pulp and high loading of metal values can therefore be achieved. When the loaded resin or carbon leaves the last contactor stage it is passed to an elution vessel where the metals are stripped for recovery before the resin or carbon is recycled to the RIP/CIP contactor. The high resin or carbon loadings result in high concentrations in the eluate from which the metal values are recovered.

1.2.2 The Davy RIP/CIP Contactor

Davy developed the first successful continuous counter current ion exchange modelling procedure in the 1970's. The development was successfully used in the design of commercial fluid bed ion exchange plants.

In the early to mid 1980's Davy made a significant engineering development which led to the fundamental re-design of the in-pulp contactor. The advantage of the Davy RIP/CIP contactor over other in-pulp contactors is the use of high concentrations of resin/carbon in the contactor which allows a reduction in the volume of the contactor stages and a significant reduction in plant size and cost. Metal recovery is maintained in the smaller contactor as metal extraction efficiency is dependent on the rate of resin/carbon loading which in turn is dependent only on the concentrations of metals on the resin/carbon and in solution.

High resin/carbon concentrations required the development of an appropriate hydraulic design for the contactor and a new interstage screen design. This development was carried out in a laboratory pilot plant followed by on site piloting at larger scale. Demonstration and

refinement of the multistage counter current modelling procedure for in-pulp process was also carried out.

The result was to produce the Davy CIP plant design which is shown diagrammatically in Figure 1 and further described in the references.

The plant consists of a series stirred box contactors in horizontal arrangement, each sharing a common wall, with no height difference between the stages. Pulp is introduced at one end of the plant and flows from the stage to stage through the air swept screens which retain the carbon (or resin) in each stage. Figure 1 shows the screen as part of the common wall, but an alternative arrangement involves side screens and side launders leading into the following pulp stage. Carbon or resin is moved in a counter-current flow either continuously or intermittently using air lifts or pumps. Interstage screens are required in CIP and RIP plants because the residence time of the carbon or resin must be much longer than that of the pulp in order to achieve a concentration effect on the adsorbent.

The reduced pulp residence time results in the Davy CIP plant size being up to 80% smaller than the size of conventional CIP plant. This size reduction results in a 44% reduction in capital cost for a CIP plant treating 100,000 t/month of mined ore. A plant containing two parallel streams, each handling 100,000 t/month, was commissioned in 1987 at the Ashanti gold mine in Ghana. Other plants are currently operating in Brazil and Ethiopia.

1.2.3

Application of Leach-RIP/CIP Technology to Treatment of Contaminated Soils, Sediments and Solid Residues.

a) Introduction.

RIP/CIP technology is suitable for the treatment of a wide range

of materials contaminated by both inorganic and organic wastes. The types of materials and contaminants which are suitable for treatment are described below.

b) Types of contaminated materials suitable for treatment.

To date leach-RIP/CIP technology has been used for the recovery of metals from ores. The ores are usually pretreated by crushing, and grinding to release and expose the mineral species for leaching. When the leached pulp is to be passed to an RIP or CIP process, separation of sands from clays is commonly carried out as sands are relatively easily washed. The sands wash solution is then added to the clays which are treated by CIP or RIP.

An additional driving force for removal of the contaminants from the clay will be present when the leach pulp comes into contact with the adsorbent in the RIP/CIP contactor. Particles in the leach pulp passing to the RIP/CIP stage must normally have a particle size of less than 150 μm to allow passage through the contactor screens.

A wide range of contaminated solids are suitable for treatment by leach- RIP/CIP technology,

- . soils,
- . sediments,
- . harbour and Bayou dredgings,
- . incinerator residues,
- . mine tailings,
- . industrial wastes.

Where these materials have a high fines content such as sediments and dredgings the in-pulp extraction option is more

attractive than alternatives, as discussed in Section 1.

The major variable in handling such a variety of wastes is the pretreatment steps required to produce a suitable leach pulp. In contrast to the treatment of ores, materials such as sediments and harbour dredgings will not need be submitted to crushing and grinding prior to leaching. When coarse materials are present and the contaminants are associated with the coarser fraction a crushing and/or grinding step can be incorporated. A simplified flow diagram of this scheme for metals/inorganic contaminants removal from dredgings is shown in Figure 2.

c) Inorganic contaminants suitable for treatment.

The key to the successful use of RIP/CIP technology for the treatment of contaminated materials is to match the leaching or extraction chemistry with the adsorption chemistry of the resins or carbon. It is important for the economics of the process that, as far as possible, the adsorption sites on the resin or carbon are used for removal of the target contaminants and not for any other competing species. This implies that some degree of selectivity is required either in the extraction step or the adsorption phase in order to optimise the process conditions.

Inorganic contaminants are usually solubilised with one or more of the following: acids, oxidising agents, chelating agents, alkalis or solvents. Mineral acids are considered to be the most widely applicable and cheapest extraction agents. However, acids not only release most of the contaminating toxic metals, but will also extract a significant amount of major cations (eg Na, Mg, Ca, Al and Fe). It, therefore, becomes important that the ion exchange resins used as an adsorbent show some selectivity towards the toxic metals. Commercially available resins include chelating

resins which exhibit selectivity for transition metals. Alternatively anion exchange resins can be used for contaminants which form anions. Another approach being considered is to extract the contaminants more selectively, using chelating agents or solvents, and to adsorb these complexes onto active carbons or resins.

A development programme carried out by Davy has identified the most suitable combination of extractants and adsorbents for a variety of metal contaminated soils. The whole range of toxic metals can be removed eg: As, Cu, Ni, Hg, Cr, Cd, Zn, Sn, Pb, Sb, Se. These metals commonly fall into groups characteristic of the source of the contamination. For example.

- . As, Cu, Cr - wood treatment sites,
- . Pb, Zn, As - pigments,
- . Pb, Cr, Sb - pigments,
- . Cr - galvanic,
- . Pb, Cu, Cd - galvanic,
- . Cd, Cr, Sn - galvanic,
- . Cu, Ni, Zn - mining/smelting/refining,
- . Hg - chlorine electrolysis,
- . Cu, As, Hg - pesticide formulation,
- . U etc - mining or refining facilities.

In addition to the treatment of toxic metals RIP/CIP processes will also find uses in the treatment of cyanide containing wastes.

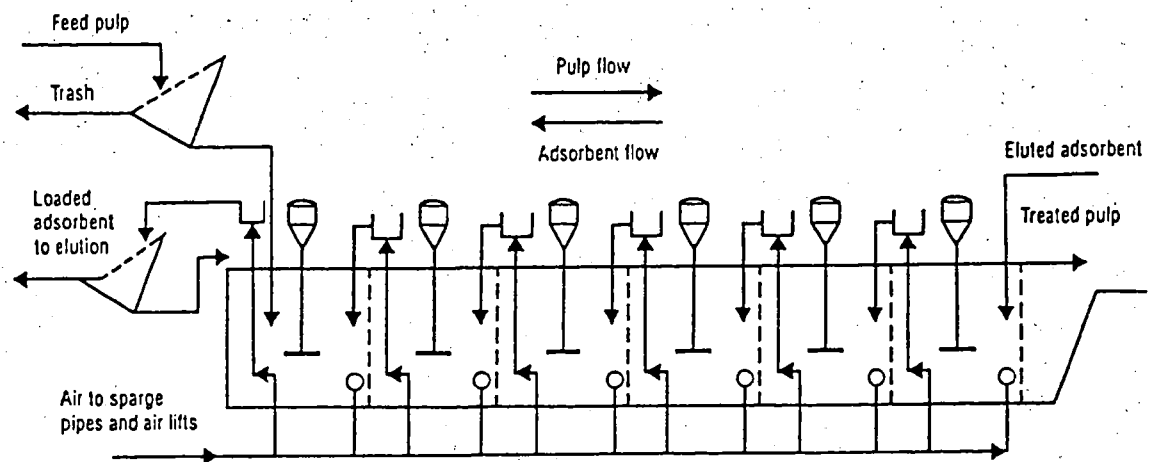
d) Organic contaminants suitable for treatment.

The technology may also be used to remove organic contaminants from sediments. In this case activated carbon would be used to adsorb released contaminants. Davy's development programme plans to include an investigation of the

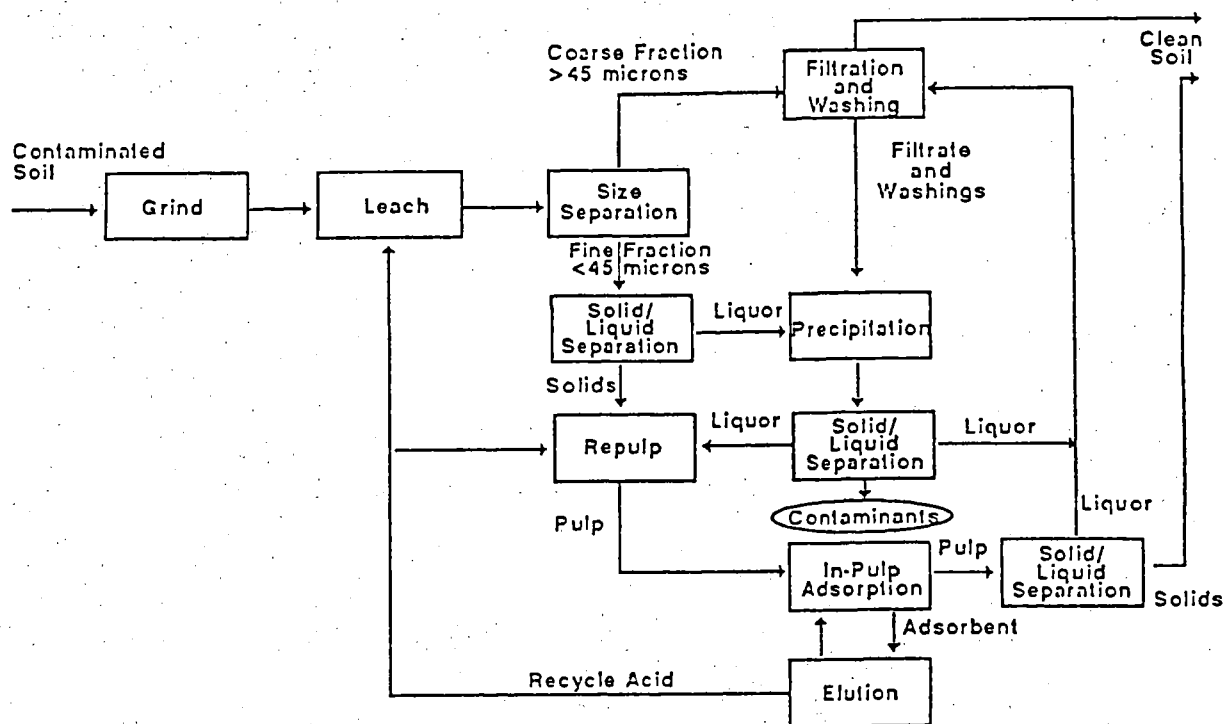
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use of surfactants, solvents and other reagents for the extraction of organic contaminants and to combine this with adsorption studies to investigate the capacity of activated carbons. This aspect was not, however, investigated in the present study.

Figure 1 Davy Improved CIP Adsorption Plant Design



**Figure 2 Schematic Diagram of the Leach-CIP/RIP
Treatment Process for Contaminated Soil**



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APPENDIX 2 US EPA DIGESTION METHODS

METHOD 3010

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for FLAA preparation for Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

- 4.1 Griffin beakers - 150-mL.
- 4.2 Watch glasses - Ribbed and plain.
- 4.3 Quantitative filter paper or centrifugation equipment.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If method blank is $< \text{MDL}$, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl . Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is $< \text{MDL}$, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3 .

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to 150-mL Griffin beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3 . Cover the

beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO₃. Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks (calibration and reagent) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.5 The method of standard addition shall be used for the analysis of all EP extracts (see Method 7000, Step 8.7).

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

<u>FLAA</u>		<u>GFAA</u>
Aluminum	Magnesium	Arsenic *
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Osmium	Cobalt
Chromium	Potassium	Iron
Cobalt	Silver	Lead
Copper	Sodium	Molybdenum
Iron	Thallium	Selenium
Lead	Vanadium	Thallium
	Zinc	Vanadium

NOTE: See Method 7760 for FLAA preparation for Silver.

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl, and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers - 250-mL.

4.2 Watch glasses.

4.3 Drying ovens - That can be maintained at 30°C.

4.4 Thermometer - That covers range of 0-200°C.

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrogen peroxide (30%), H_2O_2 . Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample.

7.2 Add 10 mL of 1:1 HNO_3 , mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2 . Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2 .

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to 100 mL with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with water.

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3 . The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with water.

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3 . For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each group of samples processed, preparation blanks (water and reagent) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.4 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals. American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

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APPENDIX 3 - WTC AUDIT REPORT

In-Pulp Treatment of Hamilton Harbour Sediment Bench-scale Demonstration and WTC Laboratory Audit

Wastewater Technology Centre (WTC) personnel visited the Davy laboratory in February 1994 to observe the bench-scale study conducted with Hamilton Harbour sediment. The bench study was conducted by Davy International, Environmental Division in Stockton-on-Tees, England, under contract to the WTC as part of the Contaminated Sediment Treatment Technology Program (Environment Canada's Great Lakes Cleanup Fund).

During the visit, a grab sample of untreated wet (DB1) sediment was collected by WTC staff. At the time of the audit, the vendor had not completed testing sufficient to conduct an optimized experimental run. Thus a treated sediment sample was not available for collection. However, an audit is conducted as a standard check on the quality of the analytical data generated in all CoSTTeP studies conducted under contract to WTC. The sample collected by WTC staff was subsequently analysed by WTC laboratories.

Table 1. compares the results of the chemical analyses for priority metals measured by the WTC to those recorded by Davy in Table 4.4 of their report. Both the WTC and Davy performed metals analysis using HNO_3/HCl digestion for dissolution of metals bound to the sediment matrix. The Davy laboratory subsequently analysed samples DB1 and DB2 by flame atomic adsorption spectrophotometry, while the WTC laboratory performed metals analysis on sample DB1 via inductively coupled argon spectroscopy (ICP).

The results of Table 1. confirm the severity of contamination in Hamilton Harbour sediment, for example, with zinc levels measured at more than 5-times the Ontario Severe Effect Level of 820 $\mu\text{g/g}$. Generally, there was good agreement between the WTC data and Davy data for the wet sediment. On average the Davy results were 16% higher than those measured by the WTC. Although, inherent differences (eg. calibration) in the types of instrumentation used to perform the analysis may explain the differences in results for the wet sediment. The relatively low variability in the Davy concentration data for both the wet and dried sediment samples supports the accuracy of the data values.

Table 1. Audit data summary for untreated Hamilton Harbour sediment

PARAMETER	AUDIT DATA COMPARISON* FOR UNTREATED WET SEDIMENT (DB1) AND UNTREATED DRYED SEDIMENT PULP (DB2)		
	WTC	DAVY	
	DB1	DB1	DB2
Zn	3960	4787	4803
Cu	63.5	94.0	92.3
Pb	529	792	787
Fe	21.8%	18.8%	19.5%
Cr	73.5	68.8	82.2
Ni	25.0	40.2	48.3
Mn	3100	3540	3620

* Unless otherwise indicated, all values in $\mu\text{g/g}$ dry weight basis