

THE LEACHING OF SOME ELEMENTS OF
ENVIRONMENTAL IMPORTANCE IN
BLAST FURNACE AND STEEL MAKING SLAGS

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The objective of this exploratory study was to determine the potential availability of a number of environmentally important elements in slags used for fill and embankment applications. About 132,000 tons of blast furnace and basic oxygen furnace slag will be used in an extensive construction project at Port Dover Harbour. When possible, water samples from a fill site were obtained. However, the main part of the study was done in the laboratory where slag samples were subjected to a sequential extraction procedure which simulates a variety of environmental conditions to which the slag may be exposed. A useful feature of this approach is the ability to estimate not only short-term elemental releases but also what might become mobile in a time frame of months to years.

SAMPLE COLLECTION AND ANALYTICAL METHODS

a) Hamilton-Harbour Site - Application of Blast Furnace Slag

Surface water samples were collected on June 8, 1983 using a triangular grid pattern (Figure 1), returned to the laboratory and filtered through 0.5 um teflon membranes. The filtrates were

to ca. pH 2 with 1:1 HNO_3 and analyzed by D.C. Argon Plasma Atomic Emission Spectrometry (DCPAES) and by Flame and Graphite Furnace Atomic Absorption Spectrometry.

b) Port Dover Harbour Development - Proposed Use of Basic Oxygen Furnace, "Steel-making" Slag

The bulk sample consisted of some ~ 0.3-0.5 cm fragments but mostly fine-grained silty material. A tarry residue was noted which may be a contaminant from steel works rubbish.

Triplicate 1 g sub-samples of this slag were subjected to the procedure outlined in Figure 1. All extracts were separated by centrifugation, made up to a final volume of 25 ml and analyzed by DCPAES.

In order to determine easily soluble constituents which may be very readily available, triplicate 1 g sub-samples were leached with 10 ml of doubly-distilled water for 24-hour periods with gentle agitation. The supernatants were decanted after centrifugation and a further 10 ml of doubly-distilled water were added. The procedure was followed for 120 h of contact time. Extracts were analyzed by DCPAES.

RESULTS AND DISCUSSION

Hamilton Harbour Site

The water samples were obtained about two months after the filling and embankment project had started. Visible discoloration of the adjacent waters of the Harbour was evident as a result of elemental sulfur and other sulfides washed out of the slag bed. The sulfur likely formed from the reduction of CaSO_4 during stagnant conditions. As a laboratory exercise, a 3-5 cm piece of blast furnace slag from the site was placed in distilled water. Within three hours, elemental sulfur was formed and the pH of the extract had risen to 10.6.

The pH and specific conductance of the samples collected on June 8 are shown in Table 1. Station 1 was located in the area where discoloration of the water column was most pronounced. This station showed the lowest pH and highest specific conductance relative to the control station No. 11 and those are likely the result of sulfide oxidation and the production of H^+ together with leaching of particulate material. At the other five locations immediately adjacent to the slag bed, the effect of leached material is less evident.

The concentrations of major and minor elements (Table 2) in general show highest levels adjacent to the slag bed except for Zn which is present at higher levels at stations in the main body of the Harbour.

BOF Slag

The amounts of various elements which were detected by DCPAES in sequential distilled-water extracts of BOF slag are generally very low except for Ca which is a very mobile cation in this material (Table 3). Although a better data set could have been obtained by analysing the extracts by graphite furnace AAS, particularly for Cd and Pb, this was not done because of time limitations. Nevertheless Pb and P are present in low but detectable concentrations after the first 24 hours of leaching. Cd only begins to be detected after 5 days.

Total concentrations of Zn, Cd, Pb, Cu, Ni and Mo (Table 4) indicate that the BOF slag is not highly contaminated with these elements. The sequential extraction procedure shows that most of the elements are associated to a large extent with Fe and Mn oxides and sulfides. The latter values can be viewed as an estimate of the total amount of potentially leachable material resulting from the oxidation of sulfides over a period of months or years. The presence of Ca and Mg sulfides in this type of slag suggests that the rate of oxidation of part of the material would be quite rapid as these sulfides are geochemically unstable in water. The kinetics of oxidation of other heavy metal sulfides would be expected to be much slower. The concomitant release of acidity might be expected to cause desorption/

dissolution of trace metal ions adsorbed or occluded in Fe and Mn oxides. Some evidence to support this overall process is provided by the analyses of water at the Hamilton Harbour site.

However, on the basis of this exploratory field and laboratory investigation, it is not possible to unequivocally state that the above scenario would occur at the Port Dover site to the detriment of surface water quality of the adjacent harbour waters. Consideration should be given to minimizing the effect of any release of acidity by amending the slags with dolomite and/or lime. The required quantities of the latter would have to be determined by laboratory experiments to ascertain how much dolomite and/or lime to mix in to achieve a pH Ca 5.5. A rough guide would be provided by summing the concentrations of Co, Zn, Cd, Cu, Ni, Cr, P, Be, and V in the sulfide-bound fraction and assuming a 1:1 neutralizing stoichiometry for their ions with the amending substance.

The analyses of water at the Hamilton Harbour site clearly show an impact on water quality some two months after the start of that project. Further field sampling, before, during and for a year after projects such as these is required in order to provide a proper scientific basis on which to assess the environmental risks posed by the use of slags as fill and embankment material in Harbours.

TABLE 1

pH AND SPECIFIC CONDUCTANCE ($\mu S\ cm^{-1}$ at $25^{\circ}C$) OF SURFACE WATER
SAMPLES ON JUNE 8, 1983

Station	pH	Specific Conductance
1	7.81	640
2	8.20	632
3	8.25	630
4	8.32	619
5	8.30	619
6	8.35	619
7	8.40	625
8	8.35	617
9	8.35	625
10	8.50	628
11	8.51	619

TABLE 2
DISSOLVED ELEMENTAL CONCENTRATIONS AT THE HAMILTON HARBOUR SITE
($\mu\text{g.l}^{-1}$ UNLESS OTHERWISE INDICATED)

	Zn	Cd	Fe	Mn	Pb	Cu	mg.l^{-1}		Si
							Ca	Ba	
Stn. 1	9.3	0.28	50	620	0.9	3.7	78	0.044	0.42
Stn. 2	7.5	0.33	41	650	0.8	2.5	74	-	0.40
Stn. 3	7.2	0.28	53	610	1.4	3.0	74	0.044	0.34
Stn. 4	5.9	0.22	70	390	1.2	2.4	65	-	0.19
Stn. 5	5.5	0.16	42	410	1.0	3.0	71	0.042	0.13
Stn. 6	6.2	0.17	43	430	1.2	3.0	64-	-	0.16
Stn. 7	8.5	0.12	416	340	13.4	3.9	70	-	0.14
Stn. 8	6.7	0.22	50	380	1.1	2.8	71	-	0.29
Stn. 9	14.4	0.18	42	390	1.8	3.5	75	-	0.15
Stn. 10	11.8	0.12	110	440	1.1	3.3	53	-	0.20
Stn. 11	6.0	0.12	67	400	1.9	3.3	57	-	0.19

Levels of Ba at two stations in the open waters of the Harbour were
0.027 and 0.029 mg.l^{-1}

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TABLE 3

LEACHABILITY OF BOF SLAG WITH SEQUENTIAL DISTILLED WATER EXTRACTION.
CONCENTRATIONS IN $\mu\text{g}\cdot\text{g}^{-1}$

Time	Fe	Mn	Pb	Ca	P	Si	Ba
24 H	n.d.	n.d.	0.4	10800	2.7	n.d.	0.4
48 H	n.d.	n.d.	0.7	10370	n.d.	6.4	0.5
72 H	9.1	4	n.d.	9600	n.d.	7.1	0.4
96 H	8.6	n.d.	n.d.	8170	n.d.	n.d.	0.3
120 H	1.2	n.d.	n.d.	8250	n.d.	n.d.	0.3

n.d. - none detected

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TABLE 4

CHEMICAL FORMS OF SELECTED ELEMENTS AND TOTAL CONCENTRATIONS IN BOF
STEEL SLAG. CONCENTRATIONS IN $\mu\text{g}\cdot\text{g}^{-1}$

	Co	Zn	Cd	Pb	Cu	Ni	Cr	P	Be	Ba	V	Mo
Exchangeable Forms	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carbonate/Surface Oxide bound forms	n.d.	n.d.	n.d.	3	n.d.	n.d.	n.d.	24	n.d.	14	n.d.	n.d.
Bound to Fe-Mn Oxides	20	72	0.09	21	8.4	5.7	370	650	0.3	85	355	n.d.
Bound to Sulfides	1.7	15	0.02	n.d.	4.6	1.0	4.8	50	0.08	8	40	n.d.
Total Concentration	67	160	0.11	38.6	26.4	13	870	910	0.38	170	395	7.1

n.d. - None detected. Note that detection limits for the
LiCl/CsCl/MeOH matrix are higher than those for distilled water.

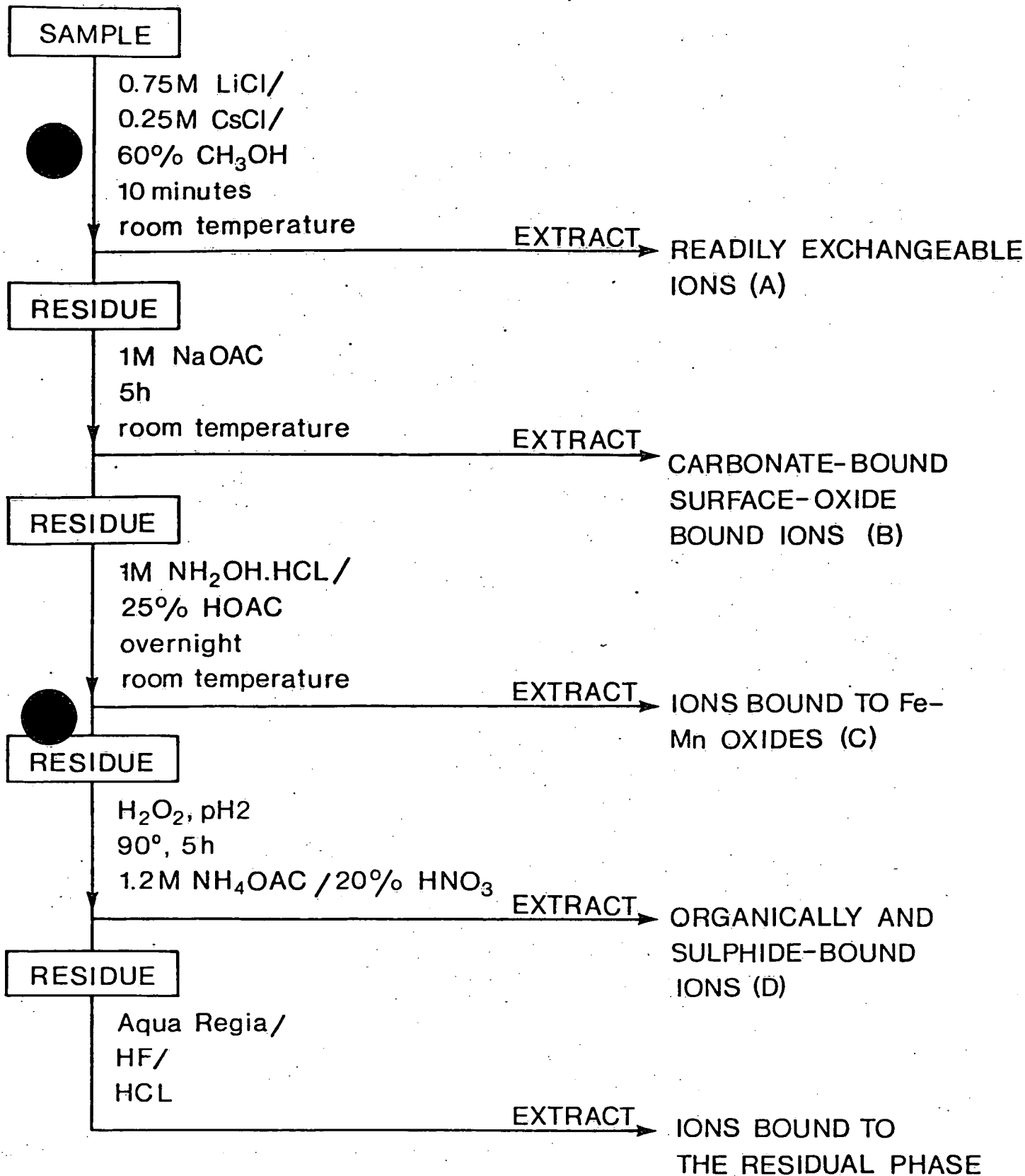
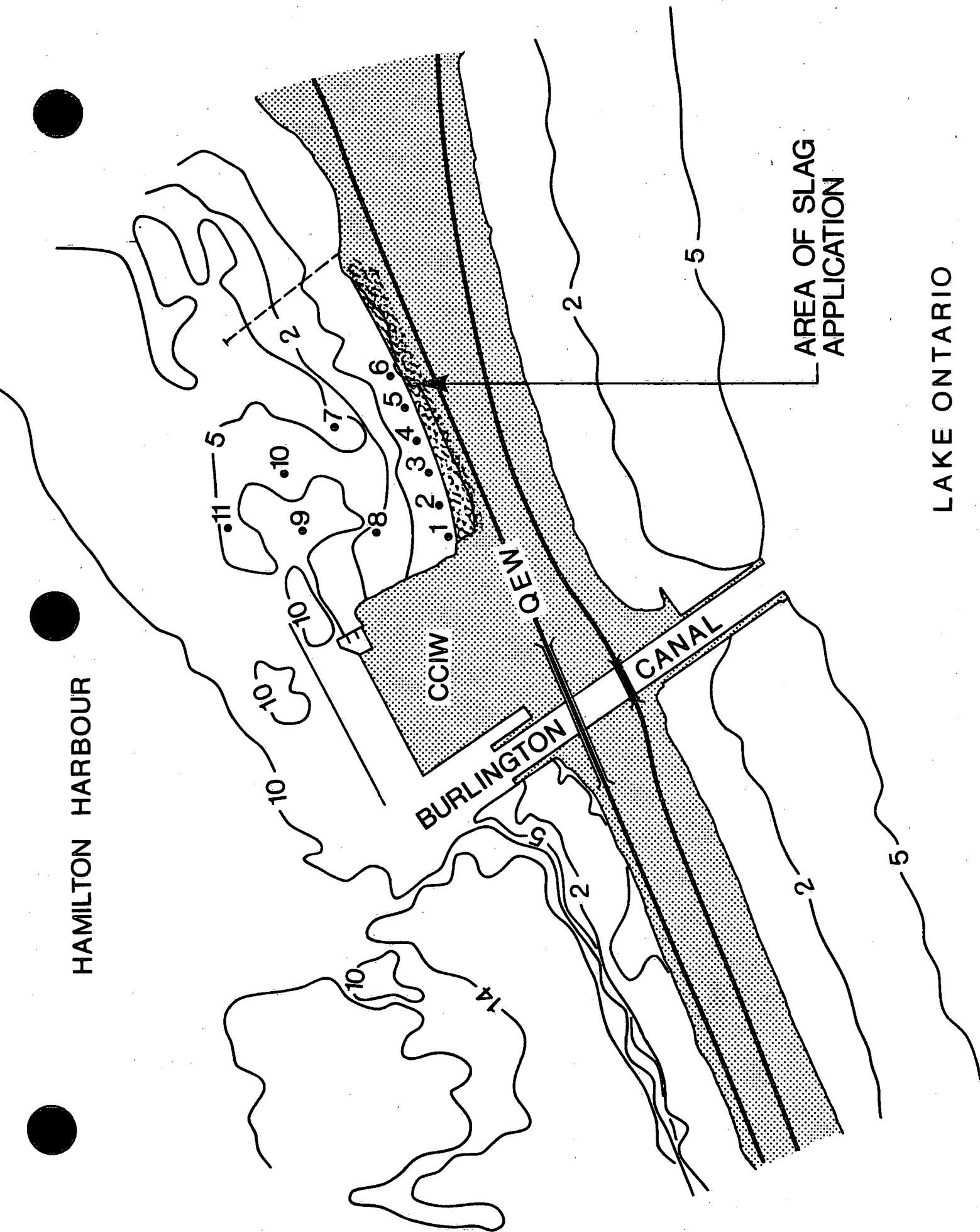


Fig1 Outline of the Sequential Chemical Extraction Procedure.

HAMILTON HARBOUR



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