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**A process for treatment of APC residues  
from municipal solid waste incinerators: Preliminary results**

**Ole Hjelmar and Henrik Birch**

**VKI**

**Agern Allé 11**

**DK-2970 Hørsholm**

**Denmark**

## **INTRODUCTION**

The problem of environmentally safe management of the residues from air pollution control (APC) systems at municipal solid waste (MSW) incinerators, particularly the residues from the semidry/dry acid gas cleaning processes (dry scrubber residues), has not yet been solved in a satisfactory and sustainable manner. These residues are in many cases simply stored indefinitely in big bags or they are landfilled under conditions that in the long term may not be able to prevent potentially harmful constituents from leaching and leaking into the environment. The APC residues, including fly ash, are in many countries classified as hazardous or special waste due to their high contents of soluble salts (particularly calcium chloride) and trace elements/heavy metals. The semidry/dry APC residues are strongly alkaline due to a content of excess lime, and the high pH favours the leaching of several contaminants, particularly lead.

This paper presents preliminary results of a study of a process for treatment of semidry/dry APC residues and fly ash from MSW incinerators. In the process the contaminants are partly removed, partly immobilized thus improving the above mentioned situation and allowing for subsequent safe management (i.e. utilization or landfilling) of the treated residues.

## **DESCRIPTION OF THE PROCESS**

The primary objective of the study was to establish a treatment process which would render dry scrubber residue and fly ash from MSW incinerators acceptable for landfilling under sustainable conditions, i.e. without requiring total encapsulation or extended operation, management and aftercare. Another requirement was that any wastewater produced by the process should be treated in such a manner that it can be accepted for discharge into the sewer system or directly into a surface water body.

Numerous studies<sup>1,2,3,4</sup> have demonstrated that it is virtually impossible to achieve the above mentioned objectives at a reasonable cost through direct solidification/stabilization or thermal treatment of raw scrubber residue. One of the major reasons for this is that the dry scrubber residues typically contain 25 to 50 percent of readily soluble salts (mainly calcium chloride) which will leach relatively fast from the solid matrix resulting from many solidification/stabilization processes. Cement-based solidification/stabilization techniques generally create highly alkaline porewater which tends to mobilize amphoteric components such as lead and zinc that are present in significant amounts in raw scrubber residues. In many thermal treatment processes partial (re)evaporation of both the chlorides and some of the trace elements will cause problems. It has also been demonstrated that chemical stabilization of raw dry scrubber residue alone or as a component of combined ash may immobilize lead, cadmium and certain other constituents of the scrubber residues rather effectively<sup>5,6,7</sup>. One such example is the phosphate based WES-PHix ash stabilization process developed by Wheelabrator Environmental Systems Inc.<sup>8</sup> Since these processes focus only on immobilization of the trace elements/heavy metals, the salts are relatively unaffected by the treatment and will leach unhindered from the stabilized products after landfilling. The process described in this paper is also, in part, based on phosphate fixation of some of the trace elements, but it differs significantly from those mentioned above because the additives are applied to an aqueous suspension of a washed product from which most of the soluble salts have been removed.

From an environmental perspective, a well buffered residue with a neutral to slightly alkaline pH in contact with water and a low content of soluble salts and leachable trace elements will often be preferable. The study described in this paper has been aimed at establishing a treatment process which is able to produce treated APC residues with such properties.

Since the presence of large amounts of readily soluble material in the dry scrubber residue is a major obstacle to the achievement of an acceptable result, the basic principle of the process developed in this study is removal of most of the soluble salts in an initial aqueous extraction of the residue followed by chemical stabilization of the extracted residue. The extraction and stabilization may be carried out simultaneously or in two (or more) separate stages. The latter is preferable since it ensures the most effective removal of salts from the product. Various extraction and treatment schemes have been investigated in laboratory and pilot scale. A pilot scale extraction unit was installed at an incinerator plant (KARA in Roskilde, Denmark) and used to test and partially optimize extraction and dewatering conditions (e.g. L/S, contact time, number of extraction steps, pH control vs. no control, addition of carbon dioxide). Trace elements were successfully removed from the extract by conventional methods (pH adjustment and TMT polishing). The salt containing treated extract may be discharged into a marine recipient or the salts (mainly calcium chloride) may be recovered. The solid remnant from the extraction was treated with various additives designed to immobilize specific trace elements, especially under conditions similar to those the treated residues may be expected to be subjected to in the future. The stabilization efficiency was tested and optimized using pH-static leaching procedures supported by hydrogeochemical modelling. The best performing stabilized residues were subjected to a more comprehensive test programme.

One of the most promising process configurations was a two-stage process in which the residue from a semidry APC process without precollection of fly ash was first extracted with water at a liquid to solid ratio (L/S) of approximately 3 l/kg in a continuously stirred tank. The slurry was then

passed through a filter press and the remnant collected on the filter was subsequently washed with an amount of water corresponding to  $L/S = 4.6$  l/kg. The remnant was resuspended in an amount of water corresponding to  $L/S = 3.1$  l/kg in a stirred tank, and an amount of phosphoric acid corresponding to approximately 35 kg  $H_3PO_4$ /ton of raw scrubber residue (dry weight basis) was added. Carbon dioxide was then added to the stirred suspension by means of a diffusor placed at the bottom of the tank and used to maintain a pH of 9.0 in the suspension for 2 hours. The suspension was then transferred to the filter press, washed with an amount of water corresponding to  $L/S = 3.2$  l/kg and subsequently dewatered by compression in the filterpress. On a dry weight basis, the amount of washed residue from the first stage of the process corresponds to approximately 720 kg/ton of raw scrubber residue and the amount of final product corresponds to 746 kg/ton of raw scrubber residue. The initial raw scrubber residue, the washed filter cake from the first extraction and the final product were subjected to leaching tests in order to assess and compare their quality.

The primary purpose of adding carbon dioxide to the suspension is to lower the pH of the suspension and the final product without losing alkalinity. The carbon dioxide reacts with the excess lime in the residue (relatively high in this particular scrubber residue = 15 percent, calculated as hydrated lime) to form calcium carbonate. The lower pH will lower the solubility of the amphoteric trace elements. Some of the trace elements may also form carbonates with low solubility. The addition of carbon dioxide alone (without phosphoric acid) produces a remnant with low leachability of many trace elements. If a full scale scrubber residue treatment facility is located at an incinerator plant, the carbon dioxide could be supplied by dispersing a sidestream of the flue gas through the suspended residue.

Although some test runs with recycling of washwater were performed, the water consumption has not been optimized. The total water consumption which corresponds to approximately 13.9 l/kg is too high and could probably be reduced to less than half that amount without significant changing the product quality. This is particularly important if there is a desire to recover the calcium chloride from the wastewater. The wastewater treatment process is comparable to the treatment processes normally used at wet scrubber systems. The sludge produced by the treatment of the wastewater from the process has relatively favourable landfilling properties.

## PRELIMINARY RESULTS

The quality of the untreated scrubber residue, the washed residue and the treated scrubber residues was evaluated and compared in terms of leachability by subjecting each of the products to pH-static leaching tests at  $L/S =$  approximately 5 l/kg and 100 l/kg, respectively. Some of the residues were also subjected to a two-step serial batch leaching test at  $L/S = 0-2$  l/kg and 2-10 l/kg, respectively.

The pH-static leaching tests were carried out by contacting the residues with the appropriate amounts of demineralized water in covered (but not sealed) vessels for 24 hours. A constant pH of 5, 6, 7, 8, 9, 10 and 11, respectively, was maintained automatically in 7 parallel tests at each  $L/S$  value by feedback control and addition of the necessary amounts of  $HNO_3$  and  $NaOH$ . The material was kept in suspension by continuous stirring with a paddle. At the end of the contact period the suspensions were filtered through 0.45  $\mu m$  filters and subjected to chemical analysis (most elements

were determined by ICP-MS or ICP-AES). The tests carried out at L/S = 5 l/kg provide information about the leaching as a function of pH under conditions where several saturation phenomena are likely to occur, whereas the tests carried out at L/S = 100 l/kg represent the behaviour of the system when the conditions approach an availability controlled situation for many components.

The serial batch leaching test was carried out in accordance with the proposed European Standard compliance batch leaching test for leaching of granular waste materials and sludges, Procedure C (Draft European Standard prEN 12457<sup>9</sup>). The materials were leached with demineralized water in a closed bottle for 6 hours by end over end rotation at 10 rpm at L/S = 2 l/kg, the eluate was separated off by filtration through a 0.45 µm filter, new water was added to L/S = 8 l/kg and the leaching procedure was repeated for a period of 18 hours after which the second eluate was filtered. Both eluates were subsequently analyzed for the same parameters as the extracts from the pH-static tests. It is a requirement that the granular material to be tested must be < 10 mm and 90 % (w/w) must be < 4 mm. This requirement is of no concern in this case since all the residues consist of very fine particles (65 to 85 percent < 0.125 mm). This test in which the pH is controlled by the solid phase represents a more "natural" situation than the pH-static leaching tests. The results may with some caution be interpreted as two points on a curve describing the leaching from a landfill containing the tested material in terms of leachate composition or accumulated leached amounts of various components as a function of L/S (or, for a specific physical scenario, as a function of time).

Four residues were subjected to the pH-static leaching tests: The untreated scrubber residue (marked 57a), the washed residue (marked 51), a residue from a two-stage process in which the washed residue has been stabilized with carbon dioxide, but not with phosphoric acid (marked 69), and a residue from the previously described two-stage process in which the washed residue has been treated both with carbon dioxide and phosphoric acid (marked 70).

The results of the pH-static leaching at L/S = 5 l/kg are shown in figures 1a, 1b and 1c. The results of the pH-static leaching at L/S = 100 (data for the washed residue missing) are shown in tables 2a, 2b and 2c. The results of the serial batch leaching test are shown in table 3a and 3b for the untreated residue, the washed residue and the stabilized washed residue (CO<sub>2</sub> + H<sub>3</sub>PO<sub>4</sub>).

The results demonstrate the effect of the treatment on most contaminants, most notably lead, cadmium, chloride, sodium and potassium. Good results were obtained both with carbon dioxide alone and carbon dioxide and phosphoric acid. The phosphate is needed to minimize the leaching of lead at lower pH values. Only a few contaminants, particularly chromium, are mobilized by the treatment with phosphoric acid.

## CONCLUSION

A process for treatment of dry scrubber residues from MSW incinerators have been developed and tested in pilot scale. The process involves an initial aqueous extraction followed by a resuspension and treatment of the filtercake with phosphoric acid and carbon dioxide to reach a stabilized product with highly improved leaching properties. The wastewater from the process may be discharged after treatment (pH adjustment and TMT polishing). Preliminary results of leaching tests performed on

untreated and treated residues are presented to demonstrate the effectiveness of the treatment process. Good results were obtained both with carbon dioxide alone and carbon dioxide and phosphoric acid. The phosphoric acid is needed to minimize the leaching of lead at lower pH values.

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## ACKNOWLEDGEMENT

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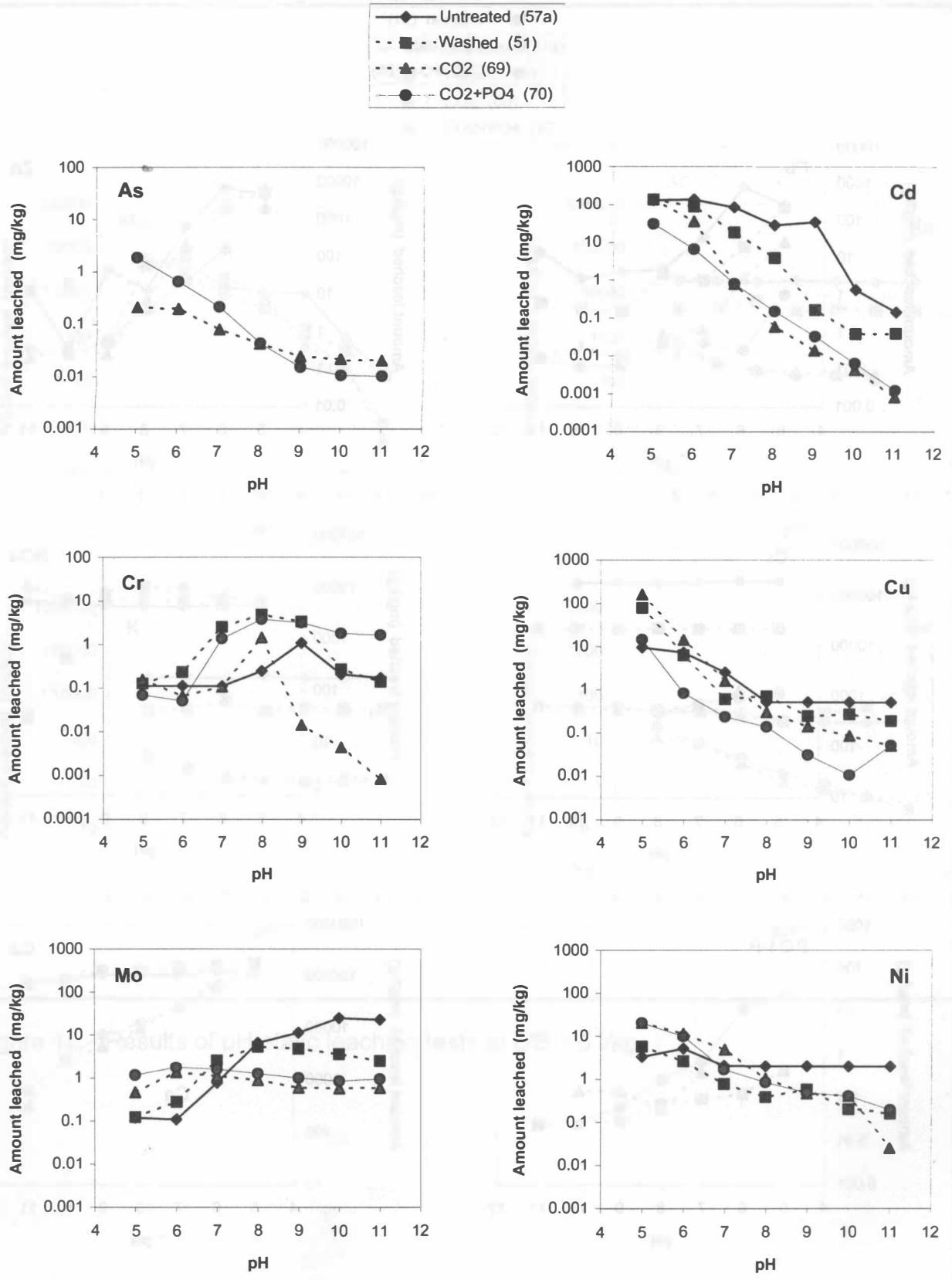


Figure 1a: Results of pH-static leaching tests at L/S = 5 l/kg

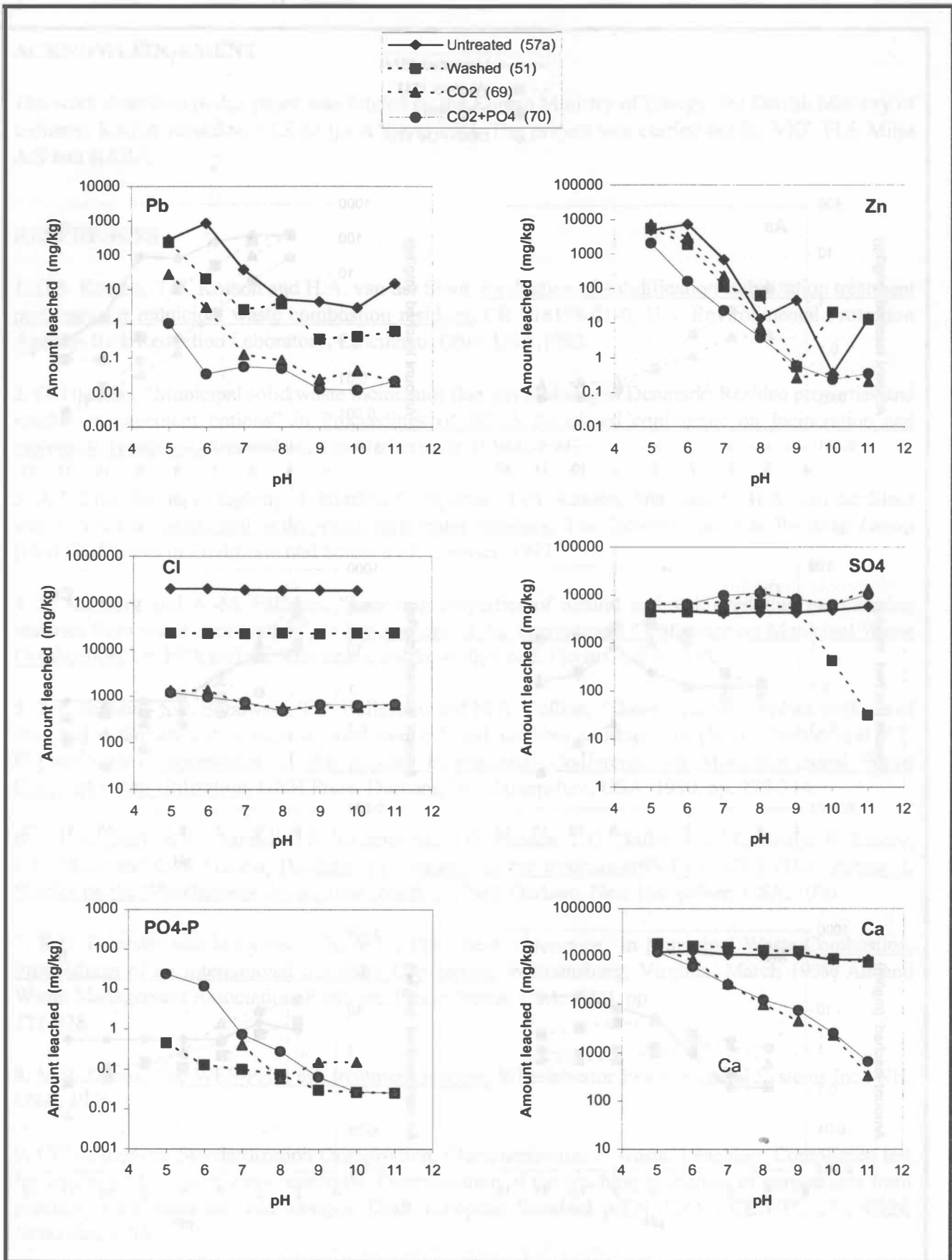


Figure 1b: Results of pH-static leaching tests at L/S = 5 l/kg.



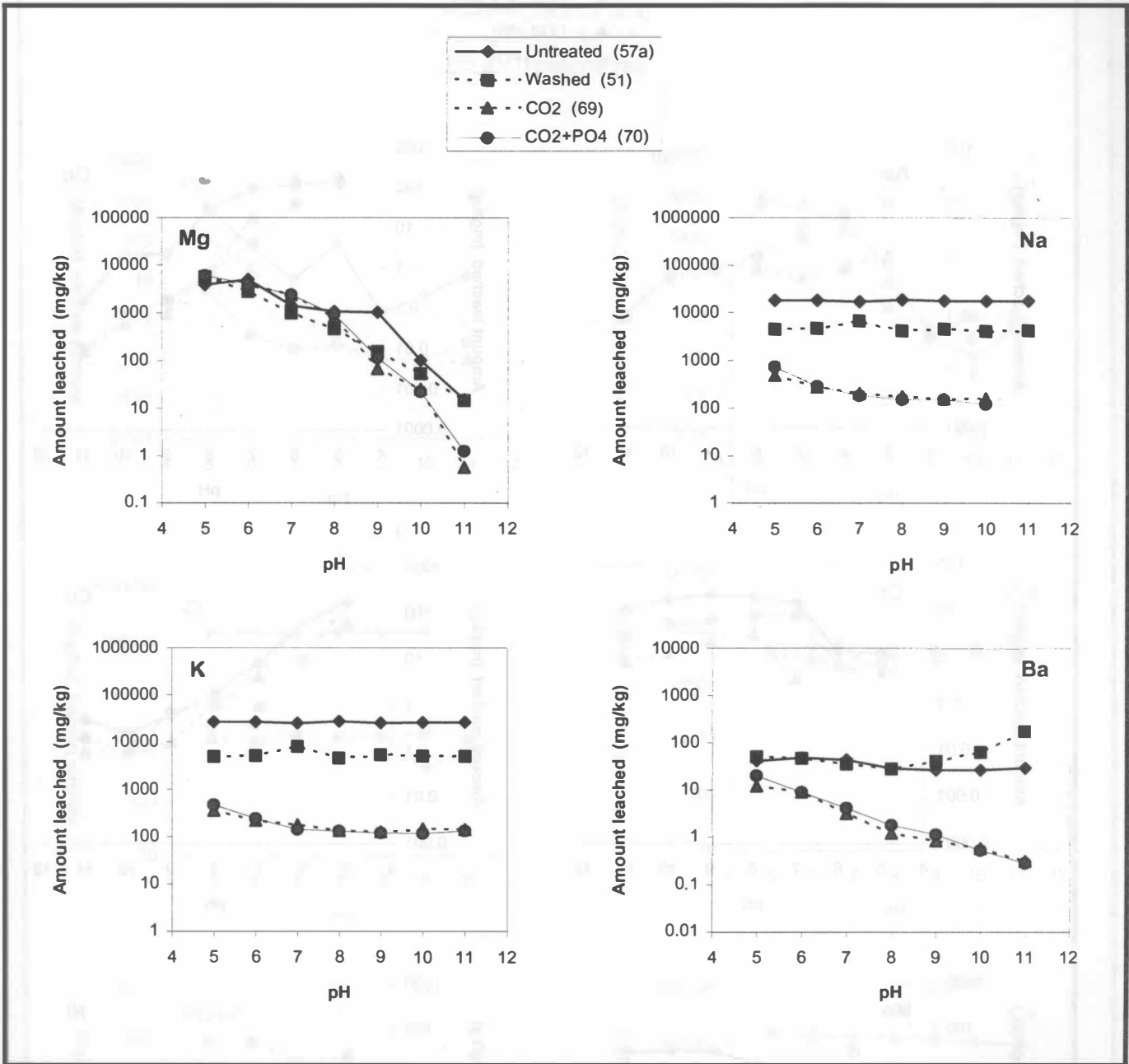


Figure 1c: Results of pH-static leaching tests at L/S = 5 l/kg.

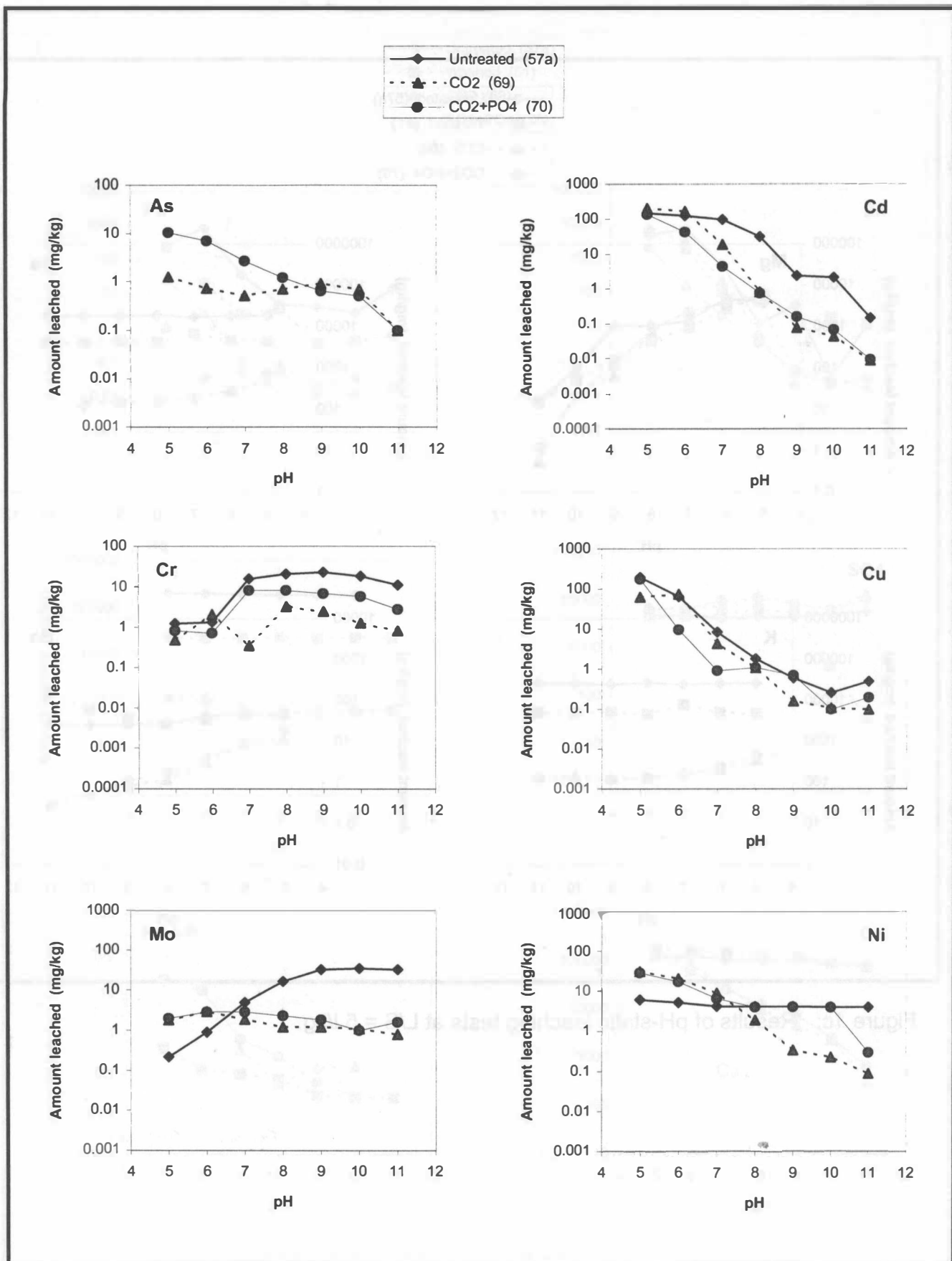


Figure 2a: Results of pH-static leaching tests at L/S = 100 l/kg.

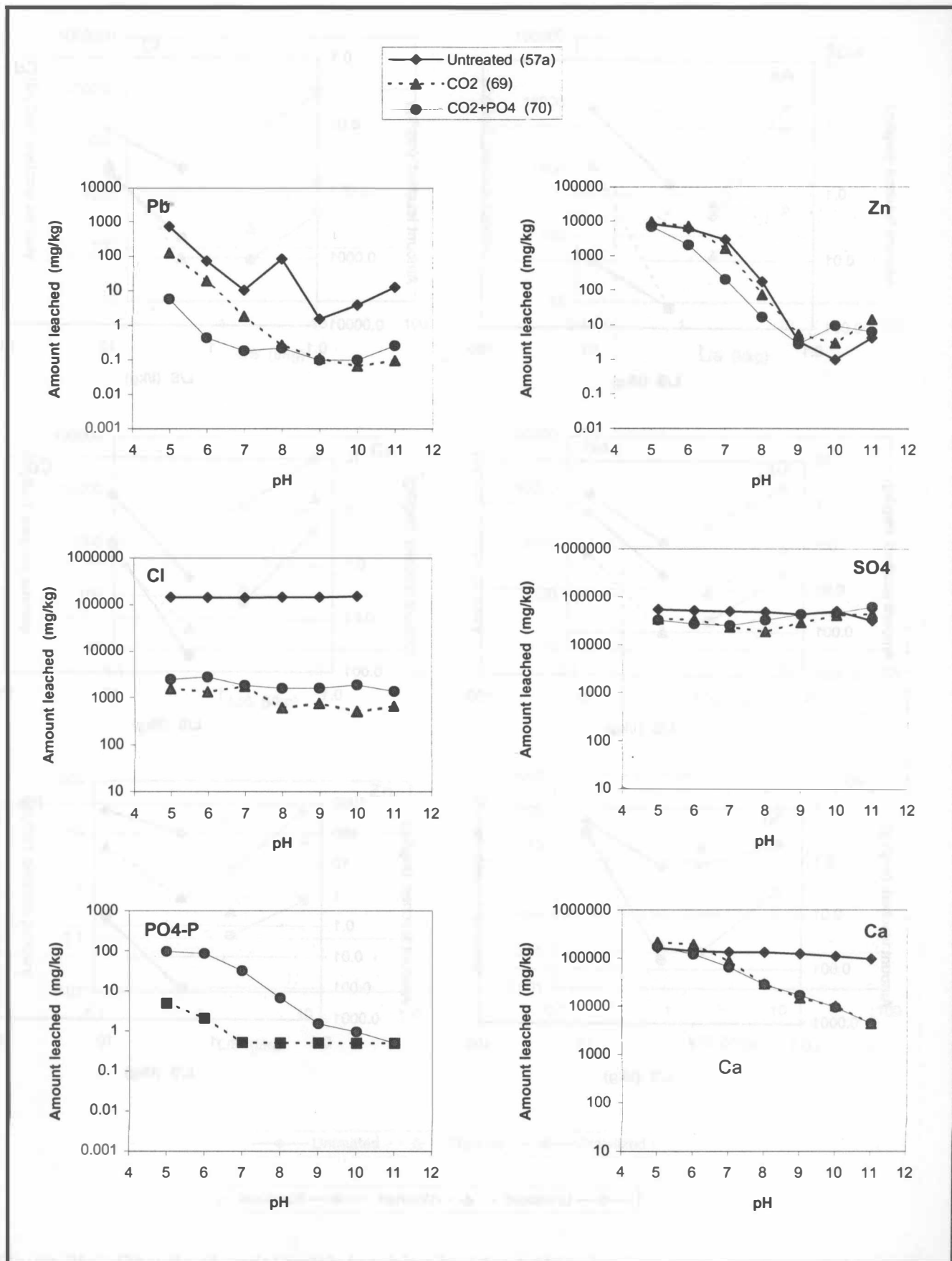


Figure 2b: Results of pH-static leaching tests at L/S = 100 l/kg.

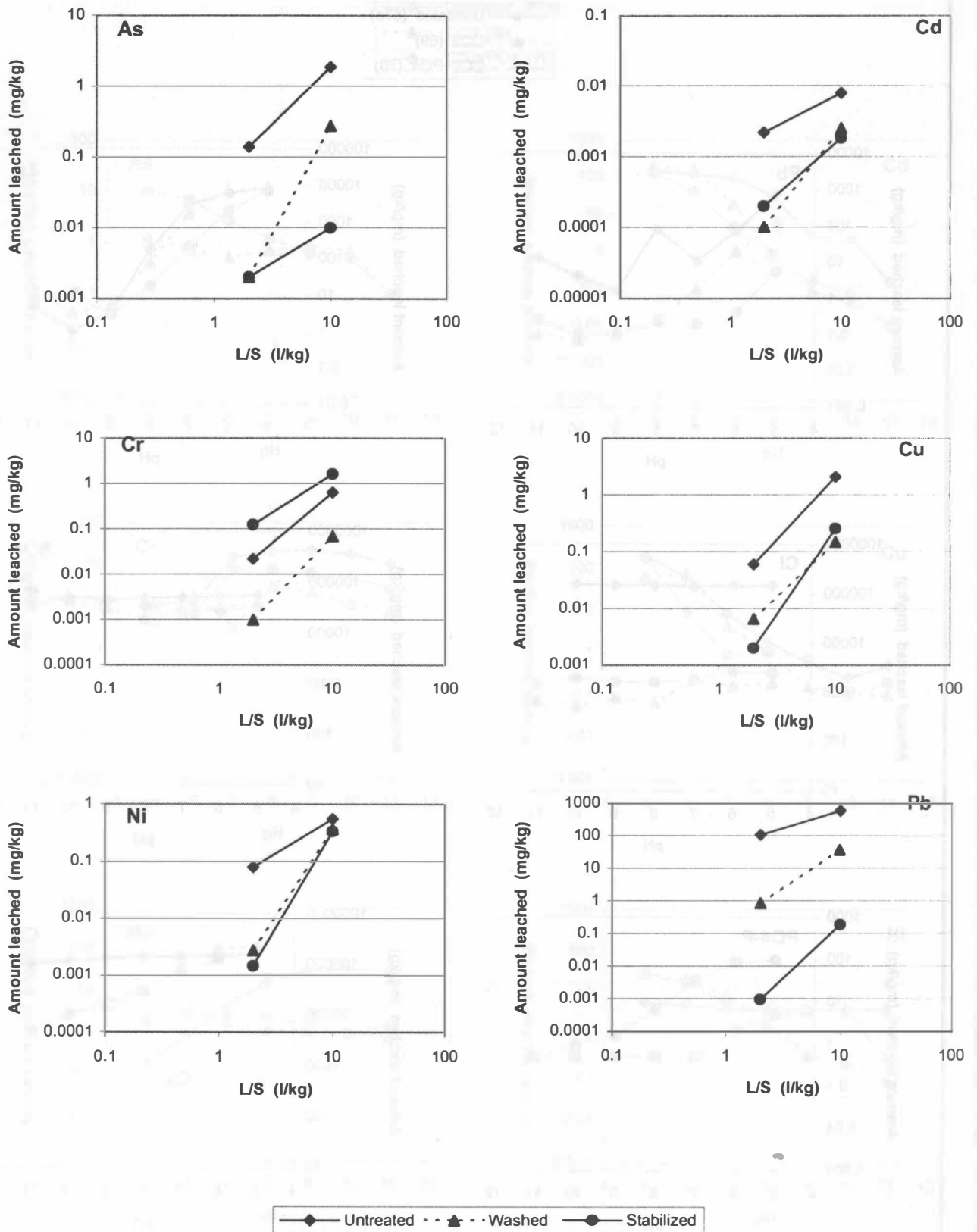
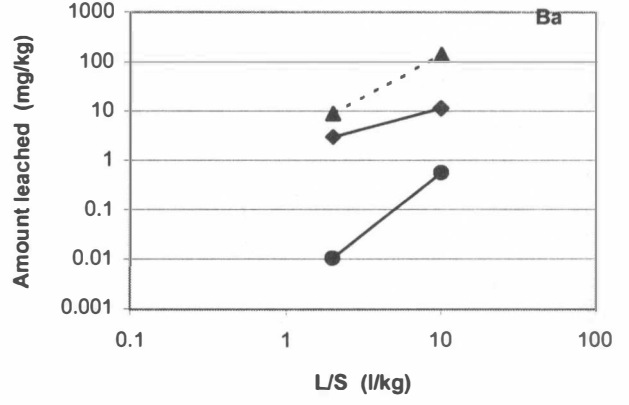
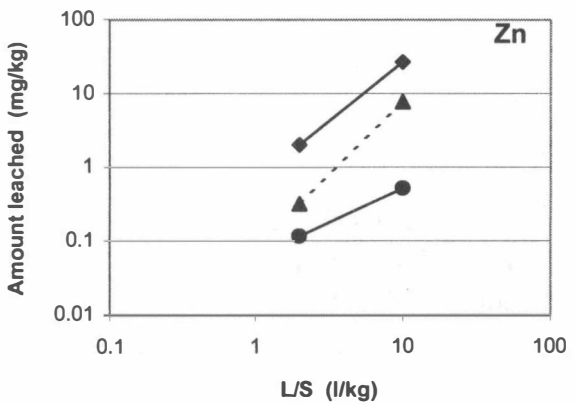
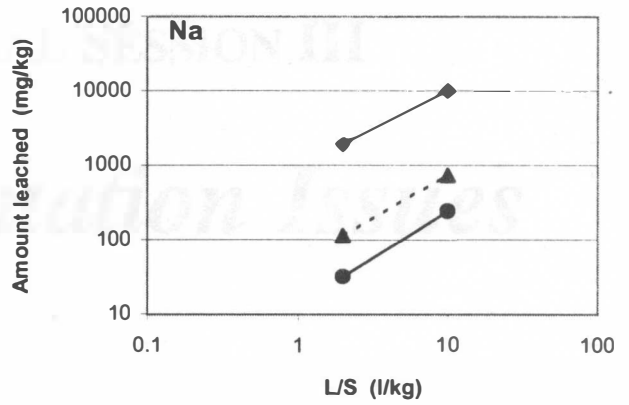
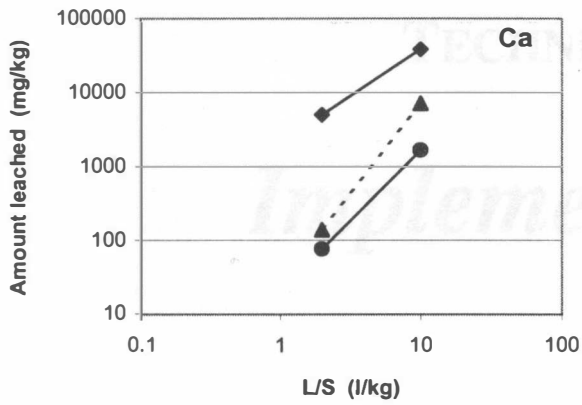
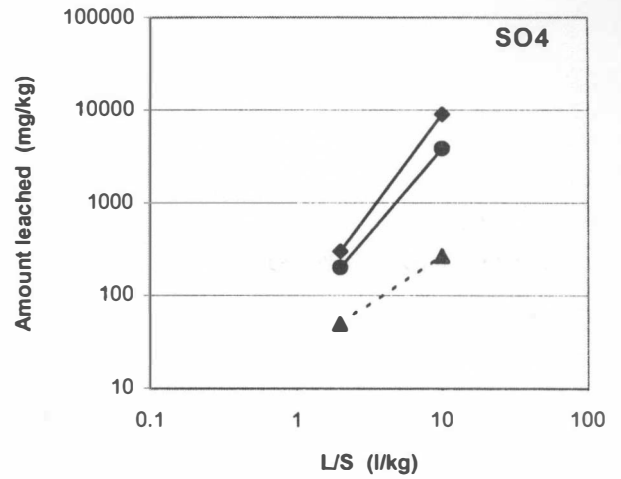
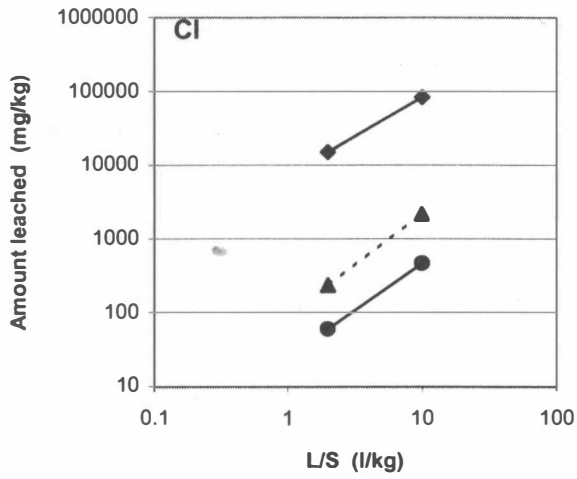


Figure 3a: Results of serial batch leaching test (two steps).



—◆— Untreated    - - ▲ - - Washed    —●— Stabilized

Figure 3b: Results of serial batch leaching test (two steps).

