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Waste Materials in Construction: Putting Theory into Practice

ICP-MS, Hydride Generation-ICP-MS, and CZE for the Study (Analysis and Speciation) of Solidification/Stabilisation of Industrial Waste containing Arsenic.

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ABSTRACT

Different analytical methods were applied to analyse the leachates obtained from leach tests on S/S industrial waste containing arsenic and the treated percolate water from a landfill. ICP-MS was used to determine total As and other elements, hydride generation-ICP-MS for the determination of As (III) and capillary zone electrophoresis (CZE) for As (III) and As (V).

Interferences and matrix effects were studied in detail and corrected for. For the leachates, no corrections were required, for treated percolate water with lower As concentrations, in the case of ICP-MS important corrections were necessary.

Results for different types of leach tests (extraction, static and semi-dynamic) and for treated percolate waters are presented.

1. INTRODUCTION

In this laboratory a detailed study is made of solidification/stabilisation of industrial waste containing arsenic (1) (2) (3).
This includes :

- optimisation of the solidification/stabilisation method using extraction tests;
- study of the leaching of contaminants from monolithic samples using static and semi-dynamic leach tests;
- characterisation and treatment of percolate waters from a landfill where such solidified waste is landfilled.

For such a study analytical methods are required to determine accurately the total As concentration of the leachates and simultaneously the concentration of important elements such as Ca, Sb and Pb. ICP-MS (inductively coupled plasma-mass spectrometry) was used for this purpose. As in the case of As, interferences may occur due to formation of polyatomic ArCl-ions, this interference was studied in detail. Moreover, matrix effects that may be an important source of systematic errors in ICP-MS were considered. Since the leaching behaviour and the toxity of As depend strongly on the oxidation state of the As, speciation of As in solution is required. Hydride-generation ICP-MS was used for the speciation of As, as it allows, under well chosen conditions, to determine only As (III) and no As (V). A more rapid method for speciation of As (III) and As (V) was found in CZE (capillary zone electrophoresis).

In this paper the analytical methods and the interferences will be described and results obtained will be intercompared and discussed.

2. EXPERIMENTAL

Waste material and percolate water

The waste material originates from a metallurgical process and was subjected to solidification/stabilisation according to different recipes.

The percolate water originates from a landfill where the solidified/stabilised waste is landfilled together with other waste material. This percolate water is treated in a sewage treatment plant with $FeCl_3$ and $Ca(OH)_2$ and filtered to lower the metal concentration. The filtrate was also analysed.

ICP-MS

The ICP-MS used is a PLASMAQUAD PQ-2 Plus from VG-Elemental. It is used in standard operating conditions with a Meinhard nebuliser for sample introduction.

Hydride generation-ICP-MS

A continuous flow hydride generator was used with a membrane gas/liquid separator to separate AsH_3. The set-up is shown schematically in Fig. 1. Arsine diffuses through the silicone rubber membrane and is carried with the argon flow to the plasma. Sample uptake rate is 6 ml/min; uptake rate of the $NaBH_4/NaOH$ (15 g/l^{-1}/0.1 M) solution is 3 ml/min. The sample solution is buffered with acetic acid/sodium acetate (0.1 M) to pH=5.
Under these conditions no As (V) is reduced to As (III).

CZE

A Waters Quanta 4000 capillary ion analyser with on-line UV-detection at 185 nm was used for this work. A 60 cm long by 75 µm i.d. fused silica capillary coated with a polyimide layer on the outside was used. Before each use the capillary was conditioned for 30 min with buffer solution which containes 2 ml/100 ml of OFM (osmotic flow modifier solution) to reverse the electro-osmotic flow. The instrument was used with a negative potential applied to the injector side of the capillary, so that the anions migrate towards the anode because of their own mobility. Moreover the coating of the capillary with OFM reverses the electro-osmotic flow and thus increases the overall migration speed of the anions towards the anode. Table 1 summarises the experimental parameters. For sample injection both hydrostatic injection and electromigration were used (4).

Extraction tests

The DIN 38414 S4 test was used, to examine the effectiveness of the immobilization of As and other elements in S/S samples. 1 l of distilled water is added to 100 g of dried substance (<10 mm), so that the liquid-to-solid ratio, L/S, is 10 and shaken for 24 h in a closed vessel.

Static and semi-dynamic tests

Static (non-agitated) leach tests were carried out on monolithic solidified waste samples. The samples (ca. 35 g) were suspended in the centre of a vessel containing 350 ml of distilled water (L/S = 10). During the time of leaching, sample aliquots are periodicially taken from the homogenised solution and analysed.
Semi-dynamic leach tests, whereby the leachant is periodically replaced after intervals of static leaching, were also carried out. The samples (ca. 35 g) are suspended in 600 ml of leachant (distilled water) in a closed vessel , so that the liquid-to-surface area ratio (L/SA) is 10.

3. RESULTS AND DISCUSSION

Initial characterisation of the waste material

The waste material was analysed by ICP-MS after dissolution in a boiling mixture of conc. HNO_3 and HCl, filtration and dilution. Different batches were obtained and the concentrations ranged from 23 to 47 % (wt) for As, from 16 to 35 % for Sb and from 8 to 23 % for Pb.

A leachate of the raw waste material contained ca. 95 % of As (III), as shown by titration with iodine and with bromate.

X-ray diffraction of the waste material also indicated that most of the As occured as As (III) (As_2O_3).

ICP-MS

Table 2 gives experimental results for the apparent As concentration found in HCl solutions as a function of the chloride-concentration. As soon as the Cl-interference becomes significant, it must be corrected for. As the leachates contain only low concentrations of chloride, no correction is necessary. The situation is, however, different for treated percolate from the landfill, that contains much higher chloride concentrations (ca. 16 g/l giving an apparent As concentration around 800 µg/l), so that correction (see below) is necessary.
Fig. 2 shows the signal as a function of the Na_2SO_4 concentration for As, along with that for In. Important signal suppression starts to occur above about 200 mg/l of Na_2SO_4. For the leachates the total salt concentration was below 2 g/l. Therefore the samples were diluted by a factor of 10.
For the percolate and filtrate samples (salt concentration 30-40 g/l) higher dilution factors were required.
In all these cases using In as an internal standard after appropriate dilution was sufficient to correct for matrix effects and instrumental drift.

Hydride generation ICP-MS

Fig. 3 gives the % of As (III) found by HG-ICP-MS as described in solutions containing a total As concentration of 100 µg/l, but with varying amounts of As (III) and As (V) as a function of the % As (V). The agreement between % As (III) added and found is excellent, proving that only As (III) and no As (V) is measured.
Fig. 4 shows that in the presence of NaCl an important signal enhancement occurs for As (III). As verified from the mass spectrum this was not due to mass spectral interference. The reason for this enhancement is not yet clear. For a similar experiment with Na_2SO_4, no enhancement or suppression was noticed below 1 g l^{-1} of Na_2SO_4. To correct for the NaCl matrix effect, especially for the treated percolate, standard addition was used.

CZE

The effect of NaCl, KNO_3 and $NaNO_3$ on the As (III) and As (V) were studied and it was shown that for concentrations below 1 g/l no significant interference effects occured.

Leaching tests on S/S samples

For the leaching test all As concentrations were higher than 5 mg/l, so the interference of Cl was negligible. Moreover, as the salt concentrations were low, 10 - fold dilution combined with the use of In as an internal standard was sufficient to correct for matrix effects.

Extraction tests

Fig. 5 gives the As concentration in the leachate obtained for extraction tests on solidified samples prepared using addition of cement (1.1 weight unit per unit of waste), water and varying amounts of lime to the waste sample. Addition of lime lowered the As concentration in the leachate to around 5 mg/l.

Static tests

Fig. 6 shows the results for a static test carried out on a sample solidified according to the same recipe, but with 1.0 weight unit of lime per unit of waste. The concentrations of As and Ca in the leachate are shown as a function of the leach time, along with the pH-values of the leachate. The plot for As shows an initial increase of the concentration followed by a decrease to approximately 5 mg/l. The results can be explained by the formation of a slightly soluble $CaHAsO_3$ precipitate.

At the end of the static leach test, a sample was taken from the leachate and analysed for As (III) by HG-ICP-MS (100-fold dilution) and for total As by ICP-MS. Ca. 87 % of the As was in the As (III) state.

Semi-dynamic leach tests

Fig. 7 shows the results for Ca and As for a semi-dynamic leach test, for a sample solidified according to the same recipe. The results are presented as the cumulative fractions released (CFR) over the total leach period as a function of the square root of the leach time. After an initial leaching period of ca. 12 h, the CFR plots can be fitted by a straight line, indicating that diffusion is the release mechanism.

Percolate water

The percolate water after water treatment (addition of $FeCl_3$ and $Ca(OH)_2$ and filtration was analysed. Because of the low As-concentration, the interference of Cl in ICP-MS can no longer be neglected. The correction for $Ar^{35}Cl$ on As was based on the ratios $Ar^{35}Cl$ /$Ar^{37}Cl$, $Ar^{35}Cl/^{35}ClO$ and $Ar^{35}Cl/^{37}ClO$. The latter two ratios were determined experimentally by adding chloride to the sample matrix, the former was deduced from the $^{35}Cl/^{37}Cl$ ratio. Moreover standard addition was applied to correct for matrix effects. The results are shown in Table 3, indicating that correction for the Cl-interference is necessary and that the 3 correction methods give results that are in good agreement. Results for As (III) obtained by HG-ICP-MS are also given in Table 3. Calibration with aqueous standards gave somewhat higher results than standard addition, probably because of the previously described signal enhancement due to NaCl. Ca. 10 % of the total As is present in the As (III) form.

A study of the treatment of the percolate water was also carried out. Increasing amounts of CaO were added to precipitate As. The percolate was diluted (20 ml in 50 ml) and 0, 0.15, 0.2 and 0.3 g of CaO were added. After filtration the samples were analysed using CZE, HG-ICP-MS and ICP-MS. Table 4 summarises the results. The results for As(V) obtained by CZE are in good agreement with those for total As obtained by ICP-MS. The As (III) concentrations were below the detection limit of CZE, but could be detected by HG-ICP-MS. For an amount of CaO of 0.3 g/50 ml almost all As precipitates.

Table 1 : Experimental parameters for CZE.

pH of buffer solution	10
concentration of sodium phosphate buffer	2.5 mM
voltage applied	10 kV
injection time for hydrostatic injection	90 s
electromigration	
injection time	60 s
applied voltage	20 kV

Table 2 : Apparent As concentrations as a function of increasing Cl concentration.

Cl concentration (g l^{-1})	Apparent As concentration (μg l^{-1})
0.0035	0.29
0.007	0.33
0.0175	0.995
0.035	2.61
0.07	5.66
0.175	13.9
0.35	26.1
0.7	53.9
1.75	122
3.5	231
7.0	386
17.5	836

Table 3 : Results for As in the treated percolate water.

ICP-MS (100-fold diluted samples) * Correction method	As-concentration (µg/l)
No correction	1050 ± 315
Standard addition	828
$^{40}Ar^{37}Cl$ + std. addition	213 ± 10
$^{35}Cl^{16}O$ + std. addition	214 ± 10
$^{37}Cl^{16}O$ + std. addition	224 ± 10

HG-ICP-MS (10 fold diluted samples)	As (III) concentration (µg/l)
No correction **	24.1 ± 3.1
Standard addition ***	20.9

* n = 6, the results are the mean and standard deviation for 6 independent measurements (6 samples each with 3 repeats).

** n = 3, the results are the mean and standard deviation for 3 independent measurements.

*** Deduced from 4 samples with additions of 0, 5, 10 and 20 µg/l As (III), each measured three times.

Table 4 : Results for As (III), As (V) and total As in percolate waters treated by adding CaO. Results in mg/l.

CaO added (g/50 ml)	CZE* hydrostatic		CZE* electromigration		ICP-MS**	Hg-ICP-MS***
	As (V)	As (III)	As (V)	As (III)	As total	As (III)
0	55.5 ± 1.8	<5	59.6	<0.5	55.9 ± 0.7	0.440 ± 0.067
0.15	44.3 ± 0.4	<5	42.4	<0.5	42.1 ± 0.1	0.249 ± 0.025
0.2	40.7 ± 3.5	<5	37.8	<0.5	38.9 ± 0.5	0.285 ± 0.003
0.3	<7.5	<5	<0.75	<0.5	0.65 ± 0.27	0.0096 ± 0.0012

* on 20-fold diluted samples

** on 200-fold diluted samples

*** on 100-fold diluted samples

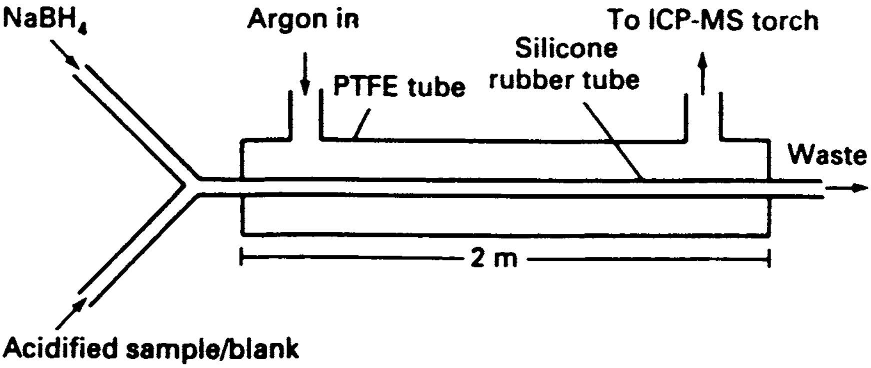

Fig. 1 Set-up for hydride generation.

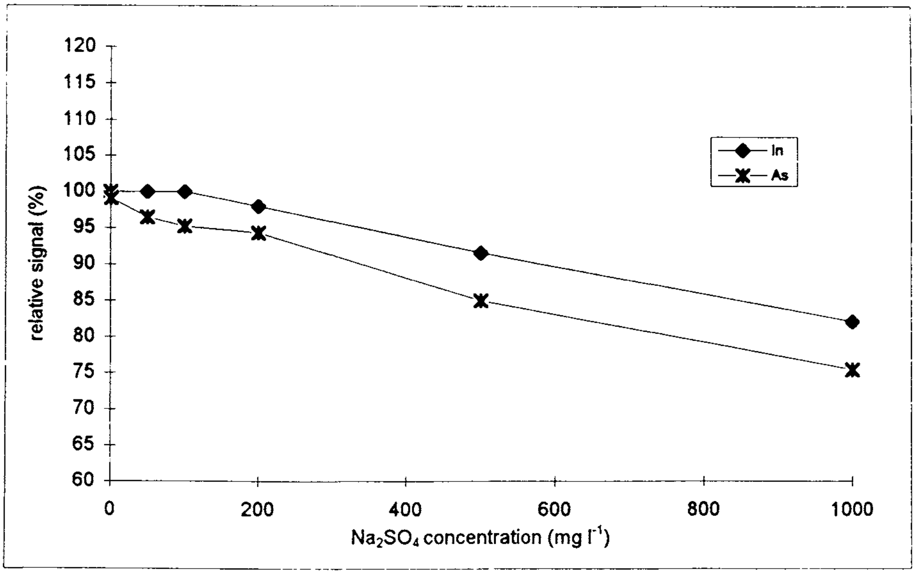

Fig. 2 Signal suppression in ICP-MS for As and In as a function of the Na$_2$SO$_4$ concentration.

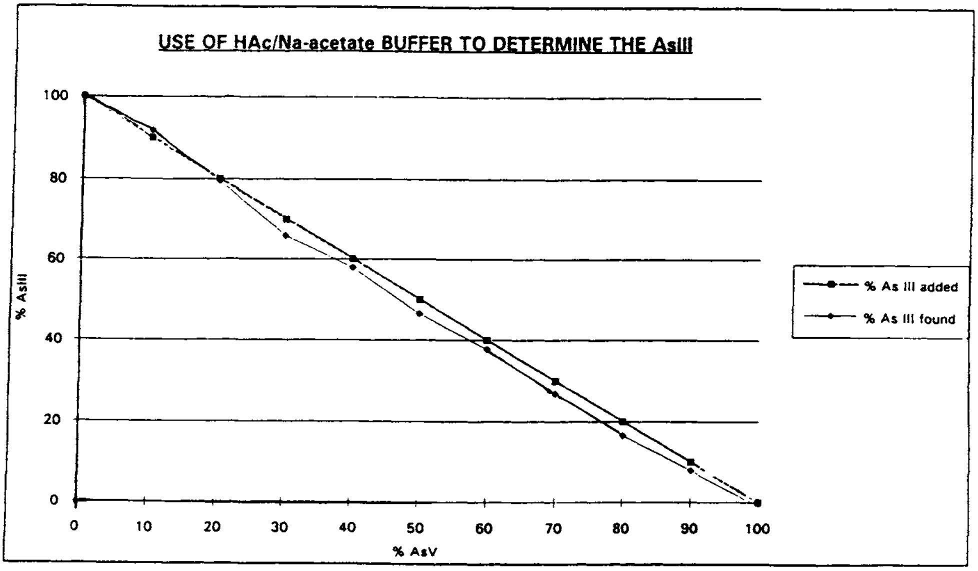

Fig. 3 Percentage As (III) found by HG-ICP-MS in solutions containing 100 µg/l As, as a function of the percentage As (V), compared to the percentage As (III) added.

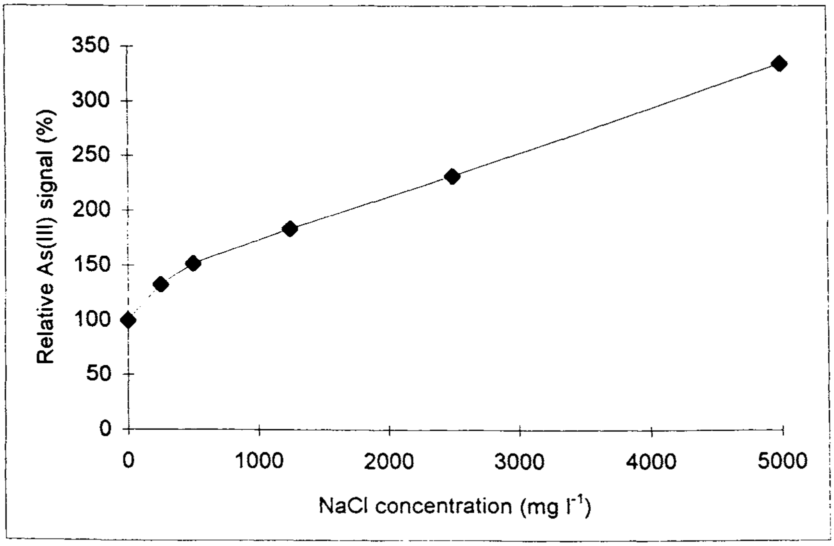

Fig. 4 As (III) signal (relative units) in a solution containing varying concentrations of NaCl.

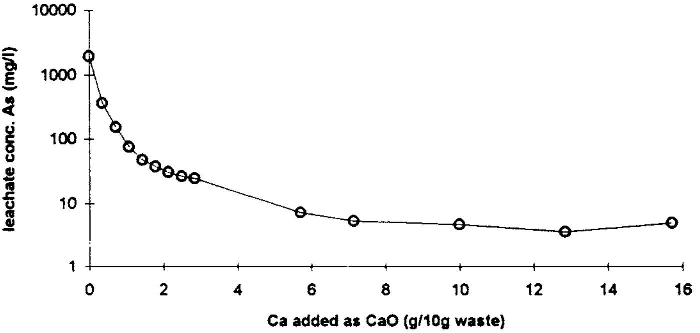

Fig. 5 As concentration in the leachate for extraction tests on S/S samples prepared with addition of different amounts of CaO.

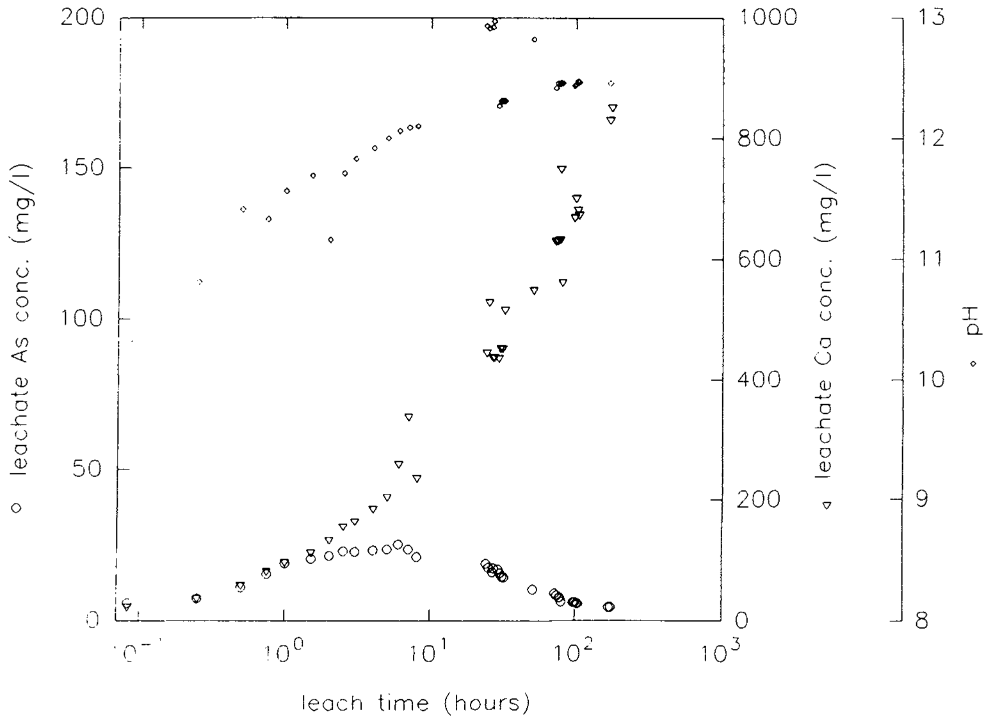

Fig. 6 Results of a static leach test on an S/S sample.

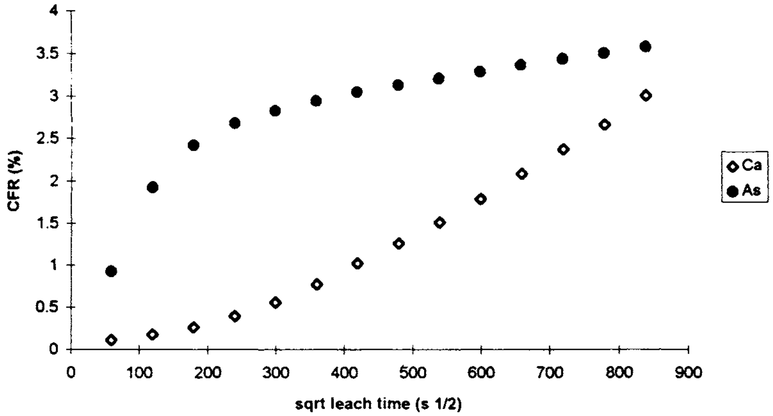

Fig. 7 Results of a semi-dynamic leach test on an S/S sample.

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