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### Leaching Studies of Inorganic and Organic Compounds from Fly Ash

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## LEACHING STUDIES OF INORGANIC AND ORGANIC COMPOUNDS FROM FLY ASH

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Fly ash is produced in massive quantities by fossil fuel based power plants and waste incinerators, and contains high levels of potentially toxic chemicals. Various leaching tests exist to determine the available fractions, but the outcome is strongly dependent on the experimental conditions, and these have not yet been harmonised at the international level. In order to test existing protocols for heavy metals, several intercomparisons were organised within the framework of an EU-INCO project "ANALEACH", in which seven institutes from five countries participated. Two existing reference materials were made available for the project and test batches of two new fly ash reference materials were produced. Availability tests, leaching tests and pH-stat tests were studied and critical steps in the procedures were identified. Fly ashes can also contain large amounts of inorganic sulphur and nitrogen compounds, and the determination and leaching behaviour of these compounds were also studied. In one intercomparison for metals, inorganic S and N-compounds were also included. A five-step leaching test was optimised for fly ash in order to link metal fractions to different types of binding. Column leaching experiments were carried out to investigate leaching from fly ash into soil, mimicking the effects of (acid) rain on fly ash deposited on topsoil after atmospheric transport. The major fraction of the leached metal ions was retained by the soil. Also large numbers of organic compounds (including many toxic ones) were identified in fly ash extracts, especially in city waste incinerator ash. Leaching procedures based on ultrasonic extraction were developed for organic compounds and an intercomparison exercise was organised. In a field study at the river Nitra (Slovakia) numerous organic pollutants were found at elevated levels downstream from a major fly ash dump site.

**Keywords:** Fly ash; Trace metals; Organic compounds; Leaching experiments; Ultrasonic extraction

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## INTRODUCTION

Fly ash is the fine particulate waste material remaining after incomplete combustion. It is produced in massive quantities annually, mainly by fossil fuel based power plants. The problem is particularly serious in Central Europe, where brown coal is a major energy carrier. Waste incinerators are another major source. Fly ash contains large amounts of toxic substances, which can be strongly or loosely bound to the matrix. Often fly ash is disposed of in landfills, and it can be expected that leachates from such disposal sites contain some of these toxic compounds [1], thus posing an environmental threat. For risk assessment the potentially hazardous fraction, i.e. the fraction that can leach from the matrix under typical environmental conditions, needs to be determined [2]. Another reason for studying leaching properties from fly ash is to evaluate its potential for re-use in construction materials [3].

Depending on the aim of the measurement, leaching tests can be subdivided into relatively quick compliance tests (e.g., European leaching test [4]) and more extensive material characterisations (e.g., pH-stat tests at a range of pH values [5] or sequential leaching tests [6,7]). The outcome of such measurements often depends rather critically on the experimental conditions and over the years several measurement protocols have been developed by standardisation agencies in various countries. Unfortunately, the results of leaching tests carried out in different countries cannot be compared as long as the test methods have not been harmonised at the international level [8].

In light of these problems, the EU-INCO project "ANALEACH" was initiated. A major aim was to compare existing protocols, in particular protocols that are being developed by international committees such as CEN Technical Committee 292 [5]. Availability tests, leaching tests and pH stat tests were studied in order to identify critical steps in the procedures. Fifteen intercomparisons (both total metal determinations and leaching tests for metals) were organised, using fly ash reference materials as test samples.

Inorganic sulphur and nitrogen compounds are important constituents of fly ash, and the analysis and leaching behaviour of these compounds were also included. For the interpretation of leaching test results it is necessary to understand the leaching processes in terms of the physico-chemical properties of the element species and the matrix. A five-step leaching test [6] similar in concept to sequential leaching schemes for elements in soil [7] was optimised for fly ash. The results can be used to link metal leaching behaviour to different types of binding.

Submicrometer fly ash particles may be emitted from power plant smoke stacks in spite of electrostatic filters, and thus enter the environment. Therefore a column leaching study was carried out to investigate leaching from fly ash to soil, mimicking the effects of (acid) rain on fly ash deposited on topsoil after atmospheric transport.

In comparison to leaching studies of heavy metals, the presence and leaching behaviour of organic compounds in fly ash has received only limited attention [9,10]. Sometimes specific classes of target compounds were analysed, such as PAHs [11,12] or PCDDs and PCDFs [13–15]. However, as will be shown below, fly ash samples contain a broad range of organic compounds, such as aliphatic hydrocarbons, phthalates, fatty acids, sulphur containing compounds, chlorinated benzenes and alkylbenzenes. To the best of our knowledge no leaching tests for organic compounds from fly ash have been published so far. Therefore an important aim of this project was to identify and

quantitate organic compounds in fly ash samples, study their leaching behaviour and assess their potential impact on the environment.

## MATERIALS AND METHODS

### Preparation of Fly Ash Reference Materials

For the intercomparisons large batches of thoroughly homogenised fly ash were needed. Two fly ash reference materials had been prepared before at the EU-Joint Research Centre in Ispra (Italy). CW3 originates from incinerated chemical waste amended sewage sludge collected at Ludwigshafen, Germany. CW6 originates from a city garbage incinerator in Milano, Italy and consists of the finest particles collected prior to the outlet of the plant. Two new fly ash materials were collected from brown-coal-fuelled power plants. Fly ash material CW10 was supplied by Slovenské elektrárne, a.s. (Slovak Republic); the material is representative for the Chalmová dumpsite. CW11 originates from a brown coal based power plant in Hungary. The materials were dried at ambient temperature and passed through a jaw crusher. Bigger lumps were sieved off; the fraction  $< 2$  mm was dried at  $105^{\circ}\text{C}$  and passed through a tungsten carbide hammer mill. The ground material was sieved over a  $90\ \mu\text{m}$  sieve and homogenised for two weeks. Ten subsamples were taken from the homogenising drum and the homogeneity was tested by XRF spectrometry for Si, Al, Ti, Ca, Mg, K, S, P, Fe, Mn, Cr, Ni, Zn, Cu, and Pb. All elements tested showed variabilities  $< 2\%$ . Fly ash extracts (digests) were prepared from all four fly ash reference materials by placing 36 g of sample in a 2 L beaker in aqua regia with a liquid-to-solid ratio (L/S) = 10, for a week at room temperature. Excess acid was removed by slow boiling until the formation of a dense sludge, and 2 M  $\text{HNO}_3$ , was added. The mixture was heated to boiling, cooled and filtered. After several days of equilibration a white residue had formed at the bottom of the containers, which was then filtered off. The filtrate was diluted with Nanopure water (Millipore), mixed and left to equilibrate for 24 h. Aliquots of the digest solutions were then sealed in glass ampoules.

Finally, two multi-element standard solutions containing the most relevant elements at known but undisclosed concentrations were prepared by diluting standard solutions of As, Cd, Cr, Cu, Ni, Pb, Se, V, and Zn in 0.1 M  $\text{HNO}_3$ .

### Digestion and Leaching Protocols

For intercomparison exercises on total element determination a protocol was chosen based on the findings of Mester *et al.* [16]. Microwave destruction of 200 mg fly ash was carried out in a teflon bomb after addition of  $\text{HNO}_3$ , HF and  $\text{HClO}_4$ . A second microwave program was run after cooling down and addition of  $\text{H}_3\text{BO}_3$ . Participants were free to use their own detection and calibration methods.

Leaching test schemes for trace metals from different countries were collected and a selection was made of protocols to be tested, taking into account recent developments at CEN and in the EU-SMT thematic network on leaching tests [8]. It was decided to focus on three leaching test types: an availability test (at  $\text{pH} = 7$  and  $\text{pH} = 4$ ) based on the Scandinavian Nordtest protocol NT ENVIR 003 [17], the European leaching test pr EN 12457 Part C (without pH control) [4] and the material characterisation approach suggested by CEN 292 WG6 (pH stat test at a range of controlled pH conditions) [5].

TABLE I Main experimental parameters of the leaching protocols for metals as used in this study

<i>Test</i>	<i>No of steps</i>	<i>Leachant</i>	<i>L/S ratio</i>	<i>pH</i>	<i>Stirring mode</i>	<i>Test duration</i>	<i>Sample intake</i>	<i>Ref.</i>
Availability test	2	De-ionised water (with addition of HNO <sub>3</sub> )	1st step: 100 2nd step: 100	Under control 1st step: 7 2nd step: 4	Magnetic stirring	1st step: 3 h 2nd step: 18 h	1 g	[17]
European leaching test	2	De-ionised water	1st step: 2 2nd step: 8	Not under control	End-over-end tumbling	1st step: 6 h 2nd step: 18 h	10 g	[4]
pH stat test	1	De-ionised water (with addition of HNO <sub>3</sub> )	10	Under control; various pH values	Magnetic stirring	24 h	5 g	[5]

For the intercomparisons the specified sample intakes were decreased because of the limited availability of the fly ash reference materials. This was considered acceptable given the small particle size and homogeneity of the samples. Solvent volumes and labware sizes were adjusted accordingly. Characteristics of these tests are listed in Table I. For detailed protocols see Ariese *et al.* [18].

## RESULTS AND DISCUSSION

In order to evaluate the performances of the participating laboratories in metal leaching tests and to identify critical steps in the protocols, a series of intercomparisons was organised following the classical “step-by-step” approach of the European Community Bureau of Reference/BCR [19]. Specifically, intercomparisons were organised on metal standard solutions (to check the instrumental performance and calibration), fly ash extracts (to check the instrumental performance in case of real samples), and four fly ash matrix materials (to check the overall performance of digestion/leaching and determination procedures). In total, fifteen different intercomparisons involving 6 laboratories were organised on metals.

### Total Metal Determinations

As a first step, in order to verify the calibration of the various analytical methods in the participants' laboratories, an intercomparison was organised on the determination of total element contents. Five samples posing an increasing level of analytical difficulty were used: a multi-element standard solution, two fly ash digests and two untreated fly ash samples, CW3 and CW6. A high degree of comparability was obtained for most of the nine elements (As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn) in all samples, including the undigested fly ashes. The highest level of agreement with relative standard deviations (RSD) < 10% for all analyses in all samples was obtained for Cu and Zn [20]. It was concluded that the final analytical methods were under control in all participating laboratories, and that possible differences observed in future leaching experiments could be attributed to differences in leaching conditions. In the second year this exercise was repeated with the two new fly ash materials CW10 and CW11. Also this time the

results for the standard multi-element solution and the two digests were very good, but larger between-laboratory variations were obtained for the untreated fly ash samples [18]. Most probably this was due to the lower metal contents and stronger binding to the matrix in comparison to fly ashes CW3 and CW6, rendering the digestion conditions much more critical (in particular for Cr).

### Availability and Leaching Tests for Metals

Intercomparisons were organised based on the availability test, the European leaching test and the pH-stat test as listed in Table I. In general, when leaching tests were applied, the analytical uncertainty between the partners was higher than that achieved in a total metal content determination, both due to the lower levels of the elements and the inherent difficulty of applying multi-step procedures in a reproducible way. As expected, also in the intercomparisons on leaching tests the higher the concentrations, the lower the intra- and intervariability. As an example, this is illustrated for Zn in Fig. 1, which shows the results of the individual laboratories and that of the whole group.

With regard to the total metal content intercomparisons, the intravariability of the laboratories for Zn ranged from 0.4 to 10%, while the intervariability between laboratories was less than 10% (Figs. 1a,b). On the contrary, the intercomparisons on pH-stat leaching tests showed a higher variability. For instance, the relative standard deviation obtained for Zn in the pH-stat test at pH3 was ca. 20% in case of material CW6 (Fig. 1c) and higher than 50% in case of material CW3 (Fig. 1d), which has a much lower total Zn content than CW6.

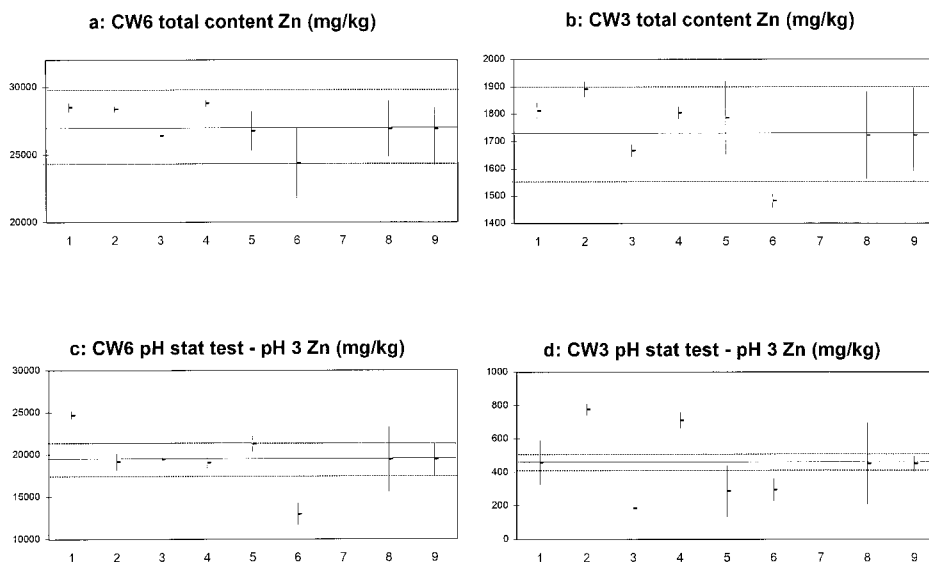


FIGURE 1 Illustration of intercomparison results on total determination and pH-stat leaching test for Zn. Concentrations are in mg/kg fly ash; error bars indicate single standard deviations. Frames 1a and 1b show the results obtained on total Zn determination for fly ash materials CW6 and CW3 respectively. Frames 1c and 1d show the Zn results obtained during pH-stat intercomparisons performed at pH=3 for the same materials. In the bar graphs the participating laboratories are identified by numbers from 1 to 6, number 8 represents the mean of all data with the associated standard deviation and number 9 represents the mean of all data plus or minus an arbitrary 10%.

The results of the European leaching test and the availability test have been described [18]. Deviations were discussed at technical workshops, and often these could be traced back to critical steps in the protocols. This resulted in the following recommendations:

- For the 2-step European leaching test the samples should be agitated in a closed system to avoid the influx of CO<sub>2</sub>. In the case of the availability test (and also the pH-stat test) the beaker should be covered with parafilm or similar.
- The stirring rate is critical: use a slow rotational shaker for the 2-step leaching test and a mechanical or magnetic stirrer (slow, no bubbles) for the availability test.
- Do *not* add water to make up for losses over the filter.
- Do *not* rinse the filters with acid, as remaining traces of acid could influence the pH and thus the leaching behaviour of material on the filter.
- If several replicate tests are performed in parallel, the samples should always be treated in the same order, taking into account the time for the slowest step.
- In the 2-step European leaching test the pH and conductivity should be measured right before filtration (after settling of the heavier particles) and after filtration.

It should be stressed that leaching studies carried out with different protocols in terms of pH can lead to totally incomparable results. For instance, the European leaching test [4] is performed by adding deionised water, whereas the Italian leaching test [21] specifies the addition of acetic acid. A comparison between these two tests was performed with fly ash CW6 and as expected very large differences were found [21]. Due to the alkaline nature of the fly ash, the final solution pH during the European leaching test was ca. 10–11, while in case of the Italian leaching test the final pH was close to 7. In general, more leaching was observed with the Italian test; for instance the Pb and Zn results were three orders of magnitude higher, and the Cd levels even five orders of magnitude higher than with the European leaching test!

### **pH-stat Tests for Metals**

In the course of the project also four pH-stat [5] intercomparisons were organised, using fly ashes CW6, CW10, CW11 and CW3. The test was carried out at pH = 3, 5, 11, and without pH control, that is, at the materials' natural pH after mixing with deionised water (typically 10–12). The degree of comparability that could be obtained was strongly dependent on the matrix, the analyte levels and the leaching pH. In general, the leached amounts were highest at low pH, while practically no leaching occurred at neutral or alkaline pH (exceptions: Cr and S). This meant that for most metals the detection sensitivity became problematic in high-pH experiments, and a poor intercomparability was no longer automatically an indication of variations in the leaching procedures. Later intercomparisons were carried out at pH = 3 and 5 only. During the intercomparisons several observations were made:

(a) In the pH-stat intercomparisons performed on materials CW6, CW10 and CW11, laboratories using manual pH control would regularly adjust the pH during the first hours of leaching, but noted a pH increase when the fly ash suspensions were left unattended overnight. Nevertheless, no significant differences were observed between the results obtained with automatic titrators and those using manual pH control. This indicated that the leaching is almost complete during the first hours of extraction. To verify this hypothesis, a comparison between two pH-stat procedures on CW3 material, with

TABLE II Effect of extraction time on pH-stat test results for six elements, obtained for CW3 fly ash. Results in mg/kg fly ash  $\pm$  std dev

Extraction conditions	Cd	Cr	Cu	Ni	Pb	Zn
pH = 3; 24 h	2.61 $\pm$ 0.10	147 $\pm$ 38	721.7 $\pm$ 8.3	39 $\pm$ 3	33.0 $\pm$ 5.2	912 $\pm$ 89
pH = 3; 7 h	2.64 $\pm$ 0.10	125 $\pm$ 24	685 $\pm$ 45	27 $\pm$ 2	28.8 $\pm$ 1.1	776 $\pm$ 34
pH = 5; 24 h	1.09 $\pm$ 0.01	207 $\pm$ 25	26.6 $\pm$ 5.2	16.9 $\pm$ 0.4	12.7 $\pm$ 2.1	77 $\pm$ 5
pH = 5; 7 h	1.08 $\pm$ 0.14	198 $\pm$ 8	17.7 $\pm$ 10.4	16.1 $\pm$ 2.1	18.3 $\pm$ 1.1	235 $\pm$ 21

duration times of 24 and 7 h, respectively, was carried out in a single laboratory. The results (Table II) show no significant differences between the two datasets, with the only exception of Zn at pH5. In this case a much lower Zn concentration was found after 24 h than after 7 h. This could be imputable to some re-adsorption phenomena, as reported for soil samples subjected to the “3-step” BCR sequential extraction procedure [22]. In that case re-adsorption phenomena were observed for Zn and Pb only at the first step. However, the occurrence of an experimental artefact can not be excluded.

(b) Unrealistically high procedural blank values were found by the participants in the pH-stat intercomparisons performed on materials CW6, CW10 and CW11. According to the original draft protocol of CEN TC 292 WG6 [5] the blank was to be determined by performing an extraction without the sample, adding the same amount of 5 M nitric acid as in the case of the pH = 3 experiment (worst-case approach). However, without the buffering of the fly ash, the resulting solution reaches a pH much lower than 3, leading to a stronger solubilisation of contaminants from the apparatus (labware, stirrer, etc.) than during the actual pH-stat test at pH = 3. In other words, this type of procedural blank leads to an overestimation of the real blank value.

(c) In the pH-stat protocol a temperature range of  $20 \pm 5^\circ\text{C}$  is specified. However, in some cases an increase in temperature of  $5^\circ\text{C}$  led to a marked increase in the leached amounts [23]. Since temperature is likely to be important whenever the leaching process is governed by slow diffusion, tighter temperature tolerances are recommended.

Finally, the results, statistical analysis and technical discussions led to the following recommendations regarding the pH-stat test:

- Leaching tests at neutral or alkaline pH are often less precise (many concentrations close to their LOD). Such measurements are less suitable for leaching intercomparisons, since the datasets would suffer from random analytical errors. For material characterisation purposes, on the other hand, measurements at high pH provide information on the leaching under natural, basic conditions, and are therefore important for environmental risk assessment.
- For fly ash materials (in this study  $< 90 \mu\text{m}$ ) most metals and sulphur leach during the first few hours of the experiment. Meaningful pH-stat tests could therefore be carried out with 7 h extraction times instead of 24 h. Manual titration appears to be an acceptable alternative to the use of automatic titrators.
- Temperature conditions during leaching should be specified more precisely.
- When only small amounts of material are available (e.g., in the case of expensive reference materials) the specified sample intake and correspondingly all solvent volumes, beaker sizes, etc., can be decreased. This is of course only acceptable for thoroughly homogenised materials with small particle sizes.



- Two separate blank experiments should be carried out: a procedural blank without sample at the pH of the regular experiments (and NOT using the same amount of acid as in the regular experiments) and a reagent blank to check the element levels in the acid. If a significant blank value is found in the acid a correction should be made in proportion with the volume of acid used in the actual leaching test.
- Prior to the pH-stat test, a preliminary titration is recommended, to check both the natural pH and the buffering capacity of the material. With this information the volume of acid needed to reach a certain pH is known beforehand and the volume of water to be added to reach the specified L/S ratio can be adjusted accordingly.

### **Inorganic Sulphur- and Nitrogen Compounds; Total Contents**

Since sulphur compounds are often present at high levels in fly ashes, it is important to determine their leachability under various conditions, not only from an environmental point of view, but also to study their potential for re-use, e.g. in the construction industry. An X-ray fluorescence method was developed for the rapid determination of total sulphur in fly ash samples. Various sample preparation methods were tested; the results were compared with those obtained with inductively coupled plasma-optical emission spectroscopy (ICP-OES) after total digestion [24].

It was found that the digestion procedures employed for heavy metals could also be used for the determination of the total sulphur content in fly ashes. Various analytical techniques were tested to determine the sulphur content in the digests, namely ICP-OES, gravimetry and ion chromatography (IC). All methods gave comparable results. No generally applicable method was found for total nitrogen in fly ash digests, since typical digestion procedures are performed with large amounts of nitric acid, which would hamper the nitrogen determination.

### **Leaching of Inorganic Sulphur Compounds**

The leaching of sulphur compounds could be carried out together with that of heavy metals without any adaptations. For the determination of sulphur ions in leachates an IC method was developed employing a conventional HPLC apparatus, a low-capacity anion-exchange column and indirect photometric detection [25]. In general, because the sulphur contents in leachates were usually rather high (in the mg/l range for CW6), the determination did not cause problems and very good repeatabilities (RSD typically below 4%) were achieved. A conventional photometric method with dimethyl-*p*-phenylenediamine (ISO 10530; LOD = 0.05 mg/l) was used for the determination of traces levels of sulphides in leachates. A photometric method with fuchsine was used for the determination of sulphites, but these were not found (LOD = 0.2 mg/L). For the determination of the total sulphur content in leachates, an OES-ICP method operating at 180.669 nm was developed and validated. The IC and OES-ICP methods gave comparable results. The sulphate content could be considered equal to the total sulphur content in the leachate [25].

A pH-stat test was also used to characterise the leachability of inorganic sulphur compounds from the fly ash samples [26]. The tests were performed at regular pH values in the range of 3–11. The constant pH values were maintained by adding diluted nitric acid or sodium hydroxide solutions. The results are shown in Fig. 2. The leached

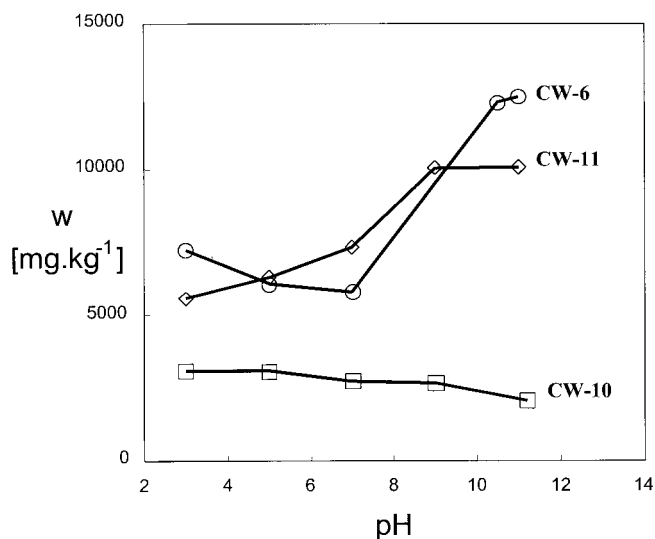


FIGURE 2 pH dependence of leached amounts of sulphur (in mg/kg fly ash) in a pH-stat experiment for different fly ash materials.

amounts increased at high pH (>8) in the case of CW6 and CW11, while almost no pH dependence was observed in the case of fly ash CW10. The only S-containing inorganic compound identified in the leachates was sulphate. The pH-stat test showed an excellent precision for S: repeatability RSDs (4 replicates) were in the range of 4–9% and reproducibility RSDs (8 laboratories) were in the range of 4–11%.

### Leaching of Inorganic Nitrogen Compounds

As mentioned above, with most existing tests procedures one cannot study the leachability of nitrogen compounds because nitric acid is specified to obtain the desired pH value. However, tests employing pure (demineralised) water as leachant can be applied, such as EN 12457, DIN 38414-S4 and a new Czech procedure (decree No. 339/1997 Sb [27]). Nitrogen can be present in leachates in the form of nitrate, nitrite and/or ammonia. Common water analysis methods are usually recommended for the determination of these compounds in leachates, e.g. ISO 5664 for ammonia, ISO 7890 for nitrates and EN 26 777 for nitrites.

A specific IC method for the simultaneous determination of nitrates and nitrites in leachates was developed and validated. The separation was carried out on a low-capacity anion-exchange column. Separated ions were detected by direct photometry at short wavelengths near 200 nm.

The concentrations of nitrogen compounds in fly ash leachates were usually rather low in comparison to the sulphate concentrations, but on the other hand some nitrogen species are considered rather toxic (e.g., nitrite). Trace amounts of nitrites (corresponding to less than 1 mg/kg fly ash) were leached from a Czech fly ash sample CZ1. Using the pH-stat protocol at natural pH (adding only demineralised water) nitrate levels corresponding to 42–50 mg/kg) were found in leachates from city waste incinerator fly ash CW6.

### Application of the National Czech Leaching Test to Fly Ash

In a separate study, the Czech national regulatory leaching test (decree No 339/1997 Sb [27]) was tested for selected inorganic contaminants, especially heavy metals but also S and N. The test is derived from DIN 38414-S4 and is comparable with the European draft standard prEN 12457-C. It specifies a L/S ratio of 10, demineralised water as leachant, 24 h contact time and slow, end-over-end rotational agitation. A fly ash test sample was collected from an electrostatic precipitator in a power station operated with North-Bohemian brown coal. The influence of the main parameters of the test, such as L/S ratio, time of leaching and the mode of agitation, was investigated [28]. Interestingly, the concentration of  $\text{Ba}^{2+}$  decreased with an increasing sample intake (not shown), which is related to increasing concentrations of sulphate as the  $\text{Ba}^{2+}$  concentration is governed by the solubility product of barium sulphate. The link of the  $\text{Ba}^{2+}$  concentration to the sulphate concentration was confirmed by comparing the experimental data with theoretical curves calculated from their solubility product.

When the contact time was varied between 2 and 24 h the leachability of most elements was only slightly influenced, with the exception of Ba, Cu, and especially Fe (Fig. 3). Probably, Fe ions participate in various secondary reactions (oxidation/reduction, precipitation of hydroxides) during the course of the leaching test. The intensity of agitation had no significant effect on the leachability of metals. Slow rotation (as specified in the protocol) was compared with intensive horizontal shaking but no differences were observed for any of the elements tested (Fig. 4).

The main performance characteristics of the test (repeatability and reproducibility) were determined with the aid of a collaborative study [29], using a procedure described in standard ISO 5725-2. Ten laboratories from the Czech Republic participated in the study. The results are summarised in Table III and show that for some elements a very good level of agreement was achieved. For sulphate the average repeatability was 4.4% and the interlaboratory reproducibility was 8.4%. In other cases larger interlaboratory differences were observed (e.g., for K, As, Zn,  $\text{NH}_4$ ). As an example, for ammonia a repeatability of 4.7% and a reproducibility of 43% were achieved. It is evident that in some laboratories systematic errors occur during the measurement of ammonia in leachates. A step-wise approach may be useful to identify the cause of these interlaboratory differences.

### Selective Leaching of Heavy Metals

As shown above, leaching is strongly dependent on the experimental conditions. Also, the leachable fraction of a particular element was found to be strongly dependent on the origin of the fly ash [31]. In order to understand the physico-chemical causes of these differences the binding of the various species to the matrix was studied in more detail. A five-stage sequential leaching procedure [6] was optimised and applied to different fly ash samples. The metals were partitioned into the following fractions: (1) exchangeable, (2) bound to carbonate, (3) bound to Fe/Mn oxides, (4) bound to sulphide compounds, and (5) bound to silicates (residual fraction).

### Optimisation of Step 1: Exchangeable Metals

For the first leaching step with ammonium acetate (exchangeable metals) several parameters were optimised: pH, buffer capacity, leaching time and liquid/solid ratio.

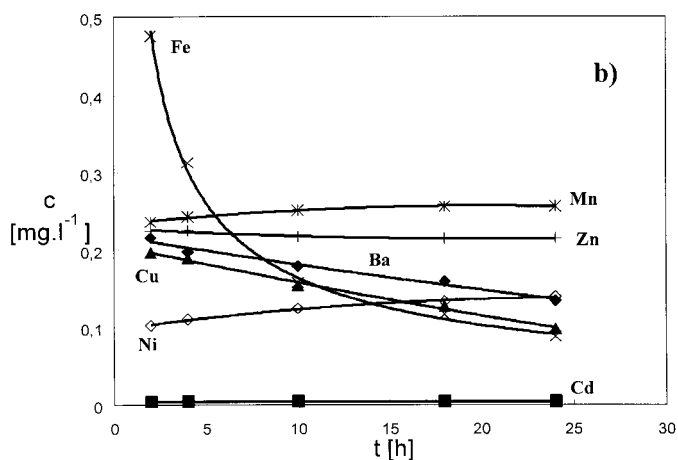
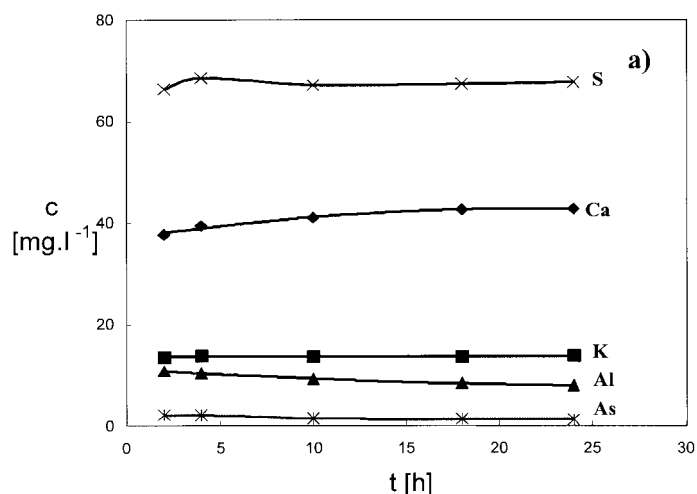


FIGURE 3 (a and b) Element concentrations in fly ash leachates (mg/L) as a function of contact time in the Czech national regulatory leaching test.

The pH was varied between 4.0 and 7.8 and it was found that the largest amounts of metals were extracted at pH = 4–5. However, at low pH the carbonate content of samples was partially dissolved as well. Since only the environmentally mobile fraction was to be determined, leaching at pH = 6.5 was selected.

During leaching the pH was found to increase due to the alkaline nature of the fly ash. This pH shift was measured as a function of the buffer capacity of the  $\text{NH}_4\text{OAc}$  solution. The concentration of the leaching solution was varied between 0.25 and 2.0 M at pH = 6.5. It was found that the complete ion exchange reaction had taken place using a 2.0 M  $\text{NH}_4\text{OAc}$  solution for all metals investigated.

Also the contact time is important in the case of slow dissolution processes. The leaching time was systematically varied between 2 and 24 h. Already after 4 h the

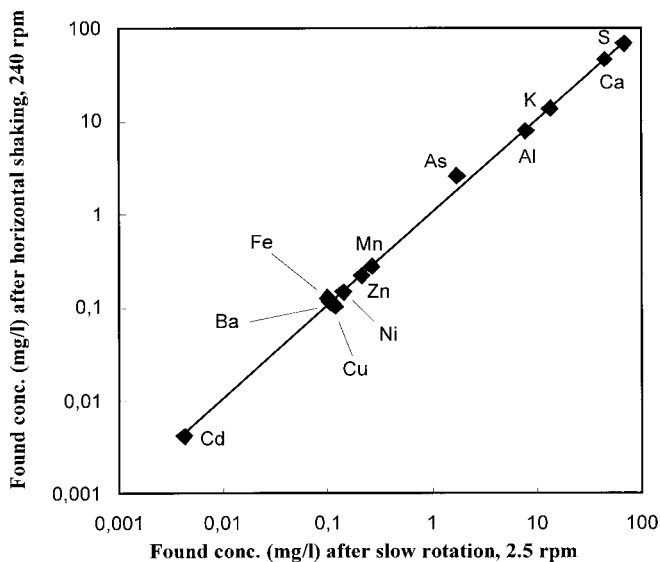


FIGURE 4 Effect of different agitation modes on the leachability of selected elements in the Czech national regulatory leaching test. Concentrations in leachates in mg/L.

TABLE III Performance characteristics of the national Czech leaching test in an interlaboratory study with fly ash [30], showing the within-laboratory RSD (repeatability) and the between-laboratory RSD (reproducibility). For each parameter four replicate results were submitted by 8–10 laboratories

Parameter	Unit	Mean	Repeatability $RSD_r$ (%)	Reproducibility $RSD_R$ (%)
pH	–	4.63	0.03 (absolute)	0.14 (absolute)
Conductivity	mS/m	43.0	1.0	15
Ca	mg/L	45.3	1.4	5.9
K	mg/L	13.4	2.2	24
Al	mg/L	8.46	2.9	16
As	mg/L	1.50	3.8	24
Ba	mg/L	0.12	5.0	16
Cd	mg/L	0.0075	30	30
Fe	mg/L	0.14	13	35
Cu	mg/L	0.15	6.0	23
Mn	mg/L	0.28	7.0	8.9
Ni	mg/L	0.13	46	46
Zn	mg/L	0.23	8.8	40
Fluoride	mg/L	5.1	4.4	27
NH <sub>4</sub> <sup>+</sup> ions	mg/L	0.48	4.7	43
Sulphate	mg/L	213	4.4	8.4

yield was close to the maximum; between 16 and 24 h no further increase was observed. For further experiments 16 h leaching time was applied.

In a similar fashion, the protocols for the consecutive leaching steps were optimised, resulting in the following sequential extraction procedure:

*Fraction (1): Exchangeable metals:* add 20 mL of 2.0 M NH<sub>4</sub>OAc (pH = 6.5) solution to 0.5 g fly ash sample (L/S ratio:40) in a 30 mL centrifuge tube and extract by shaking for 16 h at ambient temperature. Separate the solid residue from the extract

by centrifugation (2500 rpm), decantate the supernatant liquid into a 50 ml volumetric flask and fill up with distilled, deionised (DDI) water.

*Fraction (2): Metals bound to carbonates:* add 20 mL of 0.75 M  $\text{CH}_3\text{COOH}$  ( $\text{pH} = 2.7$ ) solution to the residue from Fraction 1 in the centrifuge tube and extract the suspension by shaking for 16 h at ambient temperature. Separate the solid residue from the extract by centrifugation (2500 rpm), decantate the supernatant into a 50 mL volumetric flask and fill up with DDI water.

*Fraction (3): Metals bound to Fe/Mn oxides:* add 20 mL 0.25 M  $\text{NH}_2\text{OH HCl}$  solution ( $\text{pH} = 2$ ; adjusted with  $\text{HNO}_3$ ) to the residue from Fraction 2 in the centrifuge tube and extract the suspension by shaking for 16 h at ambient temperature. Separate the solid residue from the extract by centrifugation (2500 rpm), decantate the supernatant into a 50 mL volumetric flask and fill up with DDI water.

*Fraction (4): Metals bound to sulphide compounds:* carefully add 5 mL of an 8.8 M  $\text{H}_2\text{O}_2$  solution ( $\text{pH} = 2-3$ ; adjusted with  $\text{HNO}_3$ ) to the residue from Fraction 3 in a 30 mL centrifuge tube. Digest the suspension in a covered vessel at room temperature for 1 h. Continue the digestion for 1 h at  $85^\circ\text{C}$  on a water bath, and reduce the volume to a few mL. To the cool solution add 25 mL of 1 M  $\text{NH}_4\text{OAc}$  ( $\text{pH} = 2$ , adjusted with  $\text{HNO}_3$ ) and shake the suspension for 16 h at ambient temperature. Separate the solid residue from the extract by centrifugation (2500 rpm) and filtrate the supernatant liquid into a 50 mL volumetric flask. Conserve solutions by 0.5 mL concentrated  $\text{HNO}_3$ , fill up with DDI water and store at  $4^\circ\text{C}$  until analysis.

*Fraction (5): Metals bound to silicates, residue:* digest the residue from Fraction 4 at  $100^\circ\text{C}$  for 2 h with an acid mixture of 3.75 mL concentrated  $\text{HNO}_3$  and 2.5 mL concentrated  $\text{HClO}_4$ . Filter the solution into a 50 mL volumetric flask, fill up with DDI water and store at  $4^\circ\text{C}$  until analysis.

The sequential leaching approach was tested with incinerator fly ash CW6 and the results for four elements (Cu, Zn, Pb, and Cd) are shown in Table IV. The summed concentrations found in Fractions 1–5 are compared to the total element determination (average obtained by the six participating laboratories). For these elements there was a very good level of agreement between the two different approaches.

The leachability of the different elements proved to be different, and various distribution patterns were obtained. Copper compounds were found mostly in the environmentally mobile fraction (60%), while an additional 30% was distributed evenly between Fractions 2 and 4. Only 8.4% of the total Cu content was identified in the

TABLE IV Element concentrations in different fractions and percentage of total, determined with the sequential leaching method in city-waste incinerator fly ash CW6 ( $n = 3$ ). For comparison the bottom row shows the results of a total determination (average of 6 laboratories, 5 replicate measurements each)

Fraction	Cu		Zn		Pb		Cd	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
1	1200 ± 60	59.6	12000 ± 420	45.9	2360 ± 870	24.8	307 ± 10	74.2
2	302 ± 2	15.0	7600 ± 1400	29.0	2300 ± 710	24.1	90 ± 3	21.7
3	30 ± 13	1.5	1760 ± 520	6.7	420 ± 150	4.4	9 ± 6	2.2
4	311 ± 5	15.5	2500 ± 760	9.4	1470 ± 80	15.5	5 ± 0.5	1.2
5	170 ± 15	8.4	2380 ± 290	9.0	2980 ± 440	31.2	3 ± 1.2	0.7
Σ1-5	2010 ± 70	100	26000 ± 2700	100	9500 ± 700	100	410 ± 30	100
Total analysis	1910 ± 380		27000 ± 4500		8300 ± 2900		430 ± 80	

residue Fraction 5. These findings show that copper compounds can be easily released into the environment under natural conditions. Zinc-compounds were concentrated in Fractions 1 and 2 (75%); the rest was distributed in Fractions 3–5. Of the amount of Pb-compounds 49% was found in the environmentally mobile fractions 1 and 2, while about 30% was concentrated in Fraction 5. Results for Cd compounds indicated a potentially great environmental impact: almost the total amount (96%) was found in the first two fractions. This means that, if the fly ash is dumped, Cd-ions will be easily transported into the environment. It should be stressed that the leaching properties are strongly dependent on the origin of the sample, and very different distribution patterns were obtained for other fly ash samples (not shown). The sequential leaching procedure is relatively time-consuming, but provides a wealth of information on the binding mode of the various elements, which is important for a full characterisation of the material, its environmental impact and potential for re-use.

### Leaching and Partitioning to Soil

The short- and medium-term leaching behaviour of elements from fly ash to soil was studied in a column leaching set-up, based on the Nordtest ENVIR 002 method. A thin (3 mm) layer of fly ash (CW 10 and CW3) was put on five different types of top soils (Solonitz, brown clay, acid sand, forest soil and black soil) and leached with lightly acidified water at pH = 4 and 5. The experiment was designed to mimic leaching from atmospherically deposited fly ash to soil by acid rain. A leachant volume of 12 mL was added dropwise with a typical percolation time of 24–48 h, reflecting an average month of rainfall [32]. This way, information was obtained on leaching from the fly ash matrix as well as retention by the different soil types. These processes can be influenced by many factors: pH, redox conditions, soil texture, humic acids, bacterial activity and the fly ash particle size distribution [33]. The major question to be answered was whether potentially toxic elements from atmospherically deposited fly ash can be a threat to groundwater quality.

The leachates were collected at the bottom of the column, filtered and stored at 4°C until analysis by ICP-OES (Thermo Jarrel Ash 9000). The elements determined were: As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn, K, Na, Ca, and Mg. Additionally, aliquots from the different soil samples were treated under the same conditions without added fly ash to establish the background. It was found that under the mildly acidic experimental conditions and using a L/S ratio of approx. 1.1, the minor amounts of heavy metals that were found in the leachates were mostly originating from the soil. Leaching from fly ash samples CW10 or CW3 contributed only marginally. Even in cases when leaching occurred from the fly ash, the metals were largely retained by the soil, the extent of retention depending on the soil type (for full details see ref. [32]). It was concluded that the short-term and medium-term risks from these types of ashes when deposited in thin layers are limited. In the long term, saturation effects and mobilisation reactions could still lead to an increased availability and pollution of deeper layers. Alkali and earth-alkali ions showed a high mobility and little retention in soil, and this aspect should be studied in more detail.

### Extraction and Analysis of Organic Compounds from Fly Ash

As numerous unidentified organic compounds were observed in preliminary fly ash extracts, a first part of this study was focused on the identification and total content

determination. The first measurements were targeted at polycyclic aromatic hydrocarbons (PAHs). Using Soxhlet extraction or accelerated solvent extraction (ASE), followed by volume reduction and HPLC with fluorescence detection, most of the 16 priority PAHs could be determined at the low ng/g level in fly ash samples CW3 and CW11. The profiles were different: in CW11 mostly lighter, 3–4 ring compounds were detected, while a more even distribution was found in CW3. Virtually no PAHs (LOD ca. 0.1 ng/g) could be detected in CW6 and CW10.

When analyzing the same extracts with gas chromatography-mass spectrometry (GC-MS), a large number of other compounds was also detected. Some of these were easily identified based on their mass spectra and confirmation with known standards. For instance the incinerator ash CW6 contained relatively high levels of chlorinated compounds such as hexachlorobenzene, pentachlorobenzene and PCBs. Most peaks, however, corresponded to unknown compounds and as a follow-up a more systematic study was carried out to optimise extraction methods. Also, since selected ion monitoring cannot be used when scanning for unknown compounds, it was necessary to find ways to reduce blank interferences.

Seven different extraction methods: shaking, Soxhlet, microwave assisted extraction, ultrasonic extraction (USE), ASE, and supercritical fluid extraction (SFE) and four extraction solvents: acetone, acetonitrile, cyclohexane and a dichloromethane/methanol mixture (80/20, v/v) were compared in a systematic way [34]. The performance of each of the extraction methods was evaluated using standard reference sediment materials from the SETOC proficiency testing scheme. Recoveries were studied based on spiked materials.

As fly ash test materials we used brown-coal fly ash (CW10), fly ash from a city-waste incinerator (CW6) and fly ash from an industrial waste-amended sludge (CW3). The extracts obtained were concentrated to 1 mL acetonitrile and subsequently analysed by GC-MS (injection volume 1  $\mu$ L). Analytes were identified based on their full-scan electron impact mass spectra, mass spectral library searches and expert interpretation. Positive and negative chemical ionisation were found useful for confirmation of molecular masses and/or structures of the identified substances. The identified compounds were then quantitated based on standard calibrant solutions. Numerous organics were detected in each of the three fly ash materials tested, and ca. 50 substances were unambiguously identified. Among the major compound classes detected were aliphatic and cyclic hydrocarbons, sulphur containing analytes, chlorinated and alkyl-substituted benzenes, and phthalates. Semi-quantitative analysis of aliphatic hydrocarbons suggested that these compounds are present in brown-coal fly ash in the 5–70  $\mu$ g/g range. For spiked PAHs the best extraction efficiency was obtained with Soxhlet extraction. A major disadvantage of the Soxhlet method was the presence of abundant, strongly interfering matrix impurities concentrated from the large volumes (150 mL) of solvents used. Microwave-assisted extraction and accelerated solvent extraction showed lower extraction efficiencies. Disappointingly low yields were obtained with SFE. Finally, ultrasonic extraction with acetonitrile was concluded to be the best compromise extraction technique (broad range of extracted compounds, acceptable yields and low blanks). However, there is no single best solvent for extraction of all classes of organic compounds and for specific analytes other solvents could be superior.

Acid treatment of fly ash prior to extraction increases the extraction yields of organic compounds [15]. Therefore, in a separate experiment the materials were first treated with 1M HCl and dried at 30°C overnight prior to USE with acetonitrile. Images of



fly ash material CW10 obtained by electron scanning microscopy showed clear evidence that the acid destroyed the structure of individual grains. The amount of individual compounds extracted from fly ash significantly increased with the duration of the acid treatment, 2 h of contact time being a suggested optimum.

Fly ash extracts obtained by USE with acetonitrile were also analysed by large volume injection GC-MS (LVI-GC-MS). A programmable temperature vapouriser operating in solvent vent mode was used to inject 10  $\mu$ L aliquots of fly ash extracts. Over one hundred compounds were detected in each sample, however, only about 20% could be identified from their electron impact mass spectra. A full list of (tentatively) identified compounds is given elsewhere [23]. Four target compounds were selected for further optimisation of extraction conditions: pentachlorobenzene (QCB), hexachlorobenzene (HCB) and *o*-, and *m*-terphenyl (TPH) isomers. This selection was based on the toxicity and the abundance of the compounds. Monitoring of QCB and HCB in fly ash leachates from municipal waste incineration is environmentally relevant as these two compounds are included in a European Union list of proposed priority pollutants. A typical municipal waste contains poly(vinylchloride) plastic, therefore the presence of chlorinated compounds in fly ash generated by its incineration can be expected.

### Organic Compounds in Fly Ash: Intercomparison

An interlaboratory study with six participating laboratories was organised on the determination of organic compounds in city-waste incinerator ash CW6. Based on the experiences described above an extraction protocol was developed which included two sequential ultrasonic extraction steps of 1 h each with acetonitrile. Target compounds were HCB, QCB, *o*-terphenyl (*o*-TPH) and *m*-terphenyl (*m*-TPH). Propazine was to be spiked to the fly ash samples as an internal standard. Four replicates were required; participants were free to choose their own GC-MS conditions. The final results of the intercomparison are listed in Table V, which shows the means obtained in each laboratory, the intralaboratory- and the interlaboratory standard deviation. The results were discussed at a technical meeting and it was concluded that the level of comparability obtained was quite encouraging, given the low analyte levels and

TABLE V Results of the interlaboratory comparison for organic compounds, availability test on city-waste incinerator fly ash (CW6). Concentrations in mg/kg fly ash

Partner #	QCB		HCB		<i>o</i> -TPH		<i>m</i> -TPH	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	0.016	0.010	0.019	0.008	0.062	0.010	0.0041	0.0012
2	0.037	0.007	0.042	0.006	0.072	0.004	–	–
3	0.034	0.003	0.033	0.003	0.085	0.004	0.0035	0.001
6	0.033	0.001	0.028 <sup>a</sup>	0.003	0.091	0.007	0.0010	0.0001
7	0.029	0.006	0.058	0.010	0.190 <sup>b</sup>	0.028	0.0072	0.0015
8	0.021	0.005	0.022	0.006	0.048	0.001	0.0058	0.0041
Mean of all analyses	0.028		0.034		0.072		0.0044	
SD of all analyses	0.008		0.014		0.017 <sup>c</sup>		0.0024	
RSD (%) of all analyses	29		43		24		55	

<sup>a</sup>after rejection of one outlying replicate, T-test at confidence level  $\alpha = 0.05$ ; <sup>b</sup>outlying laboratory according to Hampel test,  $|x_{\text{med}} - x_i| = |d_i|$ ; calculate median of  $|d_i|$ , MAD; outlier if  $|d_i| > 4.5 \cdot \text{MAD}$ ; <sup>c</sup>average calculated after rejection of outlying laboratory means (see note b)

the fact that such an intercomparison had not been carried out before. One possible explanation for the observed systematic differences between laboratories appears to be related to the temperature of the sonicating bath; this will be the subject of future studies.

### **Leaching of Organic Compounds from Fly Ash with Water; Method Development**

The ultrasonic extraction procedure with acetonitrile as described above can be regarded as an availability test, suitable to determine the maximum potentially leachable fraction of a given component from fly ash. In addition, a water-based leaching test was developed in order to gain insight into the fraction that can be leached from the solid matrix under natural leaching conditions. Such a procedure should simulate field conditions, but some adjustments will be necessary in order to mimic long-term environmental processes on a more practical timescale. The method should be robust, preferably simple to perform, with maximum control of all parameters for optimum intra- and interlaboratory reproducibility.

Fly ash CW6 was used as test material. In the optimised procedure, 5 g sample was first sonicated with 100 mL of distilled water (L/S 20) for 8 h. The temperature of the water bath was maintained below 45°C throughout the sonication. After filtration over acetocellulose the process was repeated with a new 100 mL volume of water. Of the combined aqueous phases a 70 mL aliquot was subsequently preconcentrated on a C-18 membrane extraction disk and the adsorbed compounds were eluted with 10 mL of ethylacetate. After volume reduction to 1 mL a 100 µL aliquot was analysed by large volume injection GC-MS using a programmable temperature vapouriser injector (PTV) operating in a solvent vent mode.

Water is of course not the most efficient extraction medium for relatively nonpolar compounds, and the extracted amounts are much smaller than with organic solvents. Large volume injection was essential for analysing water-based leachates. Once the target compounds are confirmed by MS detection in the full-scan mode the MS detector can be operated in the more sensitive selective ion monitoring (SIM) mode. This allows reduction of the injection volume down to 10 µL.

The most important parameter affecting recoveries of target compounds was found to be the extraction time. Increasing the extraction time from 4 to 8 h increased the leached amount of target compounds four to ten times. This can be explained by crumbling of the fly ash particles to smaller fragments during sonication. Another possible cause can be the increased temperature of the ultrasonic bath (45°C).

### **Leaching of Organic Compounds From Fly Ash with Water; Results**

For quantitative determinations 10 µL aliquots of fly ash leachate were analysed by GC-MS in SIM acquisition mode, monitoring five structure-specific ions for each target compound. The analytes were quantified from chromatographic signals obtained at the base peak (the most abundant ion in mass spectrum). Calibration curves constructed with standard solutions at concentrations between 2–40 µg/L showed good linearity for all analytes with correlation coefficients ( $r^2$ ) ranging from 0.9945–0.9977. The leached amounts of QCB and HCB were 1.1 and 3.1 ng/g fly ash, respectively, corresponding to 4–9% of the total available levels listed in Table V. Despite the fact that the leachable amounts represent only a fraction of the total

available amounts, these values should not be regarded as insignificant from an ecotoxicological point of view. For instance, the hexachlorobenzene level in CW6 (34 ng/g in availability test, see Table V) was found to exceed the maximum permissible risk level of 5 ng/g currently in use in the Netherlands [35]. The water-leachable fraction of HCB is of course lower (3.1 ng/g), but is still very close to this maximum and exceeds the recommended value of 0.5 ng/g [35] by two orders of magnitude.

### **Leaching Pathways of Organic Pollutants From Fly Ash; Field Study**

A field study was organised to investigate whether organic substances from fly ash from a brown coal fuelled power plant are being released into the environment. None of the fly ash dump sites utilized by the Novaky power plant in Slovakia has a sealed bottom, i.e., water used for transport of fly ash to the dump sites (ca. 6 000 000 m<sup>3</sup>/year) and rain water may carry away pollutants in a largely uncontrolled way. Routes of drain water, the degree of pollution of the groundwater, soils and river sediments in the area are not known. Excessive accumulation of individual toxic substances in deeper layers may result in a so-called “chemical time bomb” effect.

Analytical studies of fly ash from the disposal site Chalmová and sediments from the nearby Nitra river yielded important information about the fate of organic pollutants. Over two hundred compounds were detected in the fly ash samples, using ultrasonic extraction with acetonitrile and GC-MC. Of those compounds, ca. 30% were identified on the basis of their mass spectra (Wiley database). Surface water and sediments were sampled at six sites along the Nitra river: upstream, next to and downstream from the fly ash dump sites. By comparing the fly ash extracts with the sediment extracts, a group of compounds present in both environments was obtained. Aliphatic and aromatic hydrocarbons and their degradation products were major constituents. Most of these compounds were found at much higher levels at the river sampling sites next to and downstream from the dump sites in comparison to the upstream reference point. These preliminary results indicate that organic compounds are indeed being transported from the disposal site to adjacent surface waters of the Nitra river.

### **CONCLUSIONS**

Several leaching test protocols, including the European leaching test [4] and the pH-stat test [5] that are currently being discussed within CEN TC 292 and the EU-SMT network on leaching tests [8], were evaluated in a series of intercomparison exercises. The results and the difficulties encountered in practice resulted in a number of recommendations, which are hoped to be very valuable for further harmonisation efforts. It was found that the leached amounts depended extremely critically on the pH, and much less on other experimental conditions.

The fly ash materials tested contained large amounts of sulphur, which could hamper its re-use in concrete construction materials. An X-ray diffraction method was developed for the rapid screening of the total sulphur content. For sulphur (but not for nitrogen) most existing leaching tests for metals could be used without adaptation.

A five-step sequential leaching procedure was optimised for fly ash samples. This characterisation method can be used to interpret leaching behaviour in terms of element species and mode of binding to the matrix.

Column leaching experiments, aimed at mimicking the effects of (acid) rain on fly ash deposited on topsoil after atmospheric transport, showed little leaching, and the major fraction of the leached metal ions was retained by the soil. Alkali and earth alkali ions did show extensive leaching to deeper layers.

Fly ash materials were found to contain a large number of organic compounds and extraction methods for organics were optimised. An intercomparison on a selection of organic analytes yielded a reasonable level of agreement. In order to investigate possible mobilisation in the field, a leaching test based on demineralised water and ultrasonication was developed. A field study in the Nitra river basin showed a similar profile of organic compounds as in a nearby fly ash dumpsite, indicating mobility and a potential environmental impact from fly ash.

Test batches of two new fly ash reference materials were prepared and analysed for trace element content, particle size and homogeneity. These results could be used as a feasibility step for the future production of fly ash reference materials. Fly ashes of different origins often vary substantially in terms of composition, particle structure, contaminant levels and leaching behaviour. For the quality control of leaching tests in Central Europe, a browncoal-based fly ash reference material from the region would be of utmost importance. Reference materials need to be developed that can be certified for leachable fractions rather than total amounts. Such materials have been developed for other matrices [7], but are currently not available for fly ash leaching tests.

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