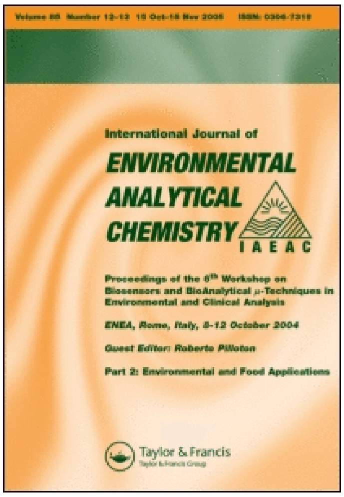

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COMPARISON BETWEEN DIFFERENT LEACHING/EXTRACTION TESTS FOR THE EVALUATION OF METAL RELEASE FROM FLY ASH

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A comparison of five different leaching/extraction tests, each characterized by different parameters such as liquid/solid ratio, pH, leachant, stirring conditions, duration time, has been performed on a highly homogenized fly ash reference material. Eight different elements (As, Cd, Cr, Cu, Ni, Pb, Se, Zn) have been considered in this study. The results show that, among all the considered experimental parameters, pH seems to have the greatest influence on metal release.

Keywords: Fly ash; trace elements; leaching test; availability test; sequential extraction; comparison

INTRODUCTION

Fly ashes are largely produced in incineration and power plants and their disposal poses a serious environmental problem [1–3] by the release of metals to soils and ground waters. It is important to consider that this is more related to the mobile fraction of metals than to their total content. In this view, leaching and extraction tests provide the necessary information for a correct evaluation of the ecocompatibility of the fly ashes.

Studies of leaching behaviour of metals from solid materials in general, and from fly ashes in particular, show that many factors influence the release both in the field and in the laboratory. Main factors are physical (particle size, particle homogeneity and porosity, temperature and others), chemical (pH, redox conditions, complexation phenomena, sorption processes and others) and biological

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ones (all factors affecting pH, redox capacity and complexation with organic matter).

A large number of leaching/extraction tests, characterized by different eachants, liquid/solid ratios, pH conditions and so on, has been developed both for research and regulatory controls [4–9]; the evaluation of the environmental risk related to waste reuse is based on the results of these tests [10–12]. The huge variety of these tests, providing different information, may lead to different waste management practices.

Therefore, the harmonization of the approaches in the existing leaching tests and the development of common procedures are of high priority [13]. Within this frame, the International Cooperation INCO Program of the European Union has financed a project dealing with the development and harmonization of the analytical procedures to quantitate leaching of inorganic and organic contaminants from fly ash. In particular, one of the principal aims of this project, named Analeach, is the comparison of the analytical procedures of existing leaching tests and, at the same time, the development of a common strategy for the use, validation and interpretation of leaching or extraction tests to assess environmental properties of fly ashes. Within the Analeach activities five different leaching/extraction tests have been applied on a highly homogenized fly ash reference material, in order to compare the results and to individuate the main experimental parameters affecting metal release.

EXPERIMENTAL

Instrumentation

Analyses of Cd, Cr, Cu, Ni, Pb, Zn have been performed with an Atomic Absorption Spectrometer Varian AA-40 controlled from a Varian DS-15 Data Station and equipped with a graphite tube atomizer Varian GTA-96 and a sampler dispenser for graphite tube atomizer PSD 707–2408. Hollow cathode lamps have been used as excitation sources. Analyses of As and Se have been performed by hydride generation, after a preliminary reduction step in a microwave oven according to a previously optimized procedure [14], with an Atomic Absorption Spectrometer Varian AA-40 controlled from a Varian DS-15 Data Station and equipped with a quartz cell, heated in an air:acetylene flame; the hydride was continously generated with a Varian vapor generation accessory Model VGA-76.

The instrumental parameters used for each element and the detection limits calculated according to the IUPAC rules are shown in Table I.

TABLE I Instrumental parameters and detection limits of the analyzed elements

Element	*As*	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Se*	*Zn*
Instrumental technique	HG-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	HG-AAS	FAAS
Wavelength (nm)	193.7	228.8	357.9	324.8	232	217	196	213.9
Analytical Working Range (μg/L)	1–7	0.2–3	1–20	1–20	3–80	2–25	1–7	0.1–2
Detection limit (μg/L)	0.08	0.45	0.36	0.27	5.5	2.5	0.02	20

A pressurized CEM microwave digestion system Model MDS-81D has been used for the preliminary reduction step and for the total digestion of samples. Teflon CEM digestion vessels have been used as containers with a CEM capping station.

The following apparatus have been used for sequential extractions: PTFE centrifuge tubes; AIC 4233R refrigerated centrifuge; home made vertical rotary shaker.

A Metrohm automatic titrator (719 S Titrino) has been used both for the pH-stat test and the availability test.

Filtrations have been performed using a Millipore vacuum filtration device using a membrane filter (pore size = 0.45 μm).

Reagents

All reagents and standard solutions for AAS (1000 mg L^{-1}) were Merck analytical grade or suprapur grade. Deionised water (Milli-Q Millipore) has been used for all dilutions.

Sample characteristics

A fly ash reference material has been used for all the experiments.

The material originates from the incineration of the city waste of the city of Milan and has been collected at the largest incineration plant of Milan. The material represents the fine particles collected prior to the plant outlet.

Following drying at ambient temperature (to conserve the more volatile organic compounds), the material has been passed through a jaw crusher and sieved through a 90 μm sieve. The fraction less than 90 μm has been collected in a mixing drum and homogenized for two weeks.

Ten subsamples, of about 3g each, were taken from the homogenizing drum and the bulk homogeneity was tested by XRF-spectrometry for Si, Al, Ti, Ca, Mg, K, S, P, Fe, Mn, Cr, Ni, Zn, Cu and Pb.

TABLE II Principal experimental parameters of the leaching/extraction tests

test	*n° of steps*	*Leachant*	*L/S ratio*	*pH*	*stirring conditions*	*test duration*	*sample weight*	*Ref.*
Availability test	2	demineralized water (with addition of HNO_3)		under control	magnetic stirring		1g	[4]
			1st step: 100	1st step: 7		1st step: 3h		
			2nd step: 100	2nd step:4		2nd step: 18h		
European leaching test	2	demineralized water	1st step : 2	not under control	end over end tumbler	1st step: 6h	10g	[5]
			2nd step: 8			2nd step: 18h		
Italian leaching test	1	demineralized water (with addition of acetic acid)	20	partially under control ($pH \geq 5$; maximum amount of added acid cannot exceed 20% of leachant)	jar test	24h (+4h)	1g	[6]
pH – stat test	1	demineralized water (with addition of HNO_3)	10	under control	magnetic stirring	24h	5g	[7]
Sequential extraction	3	1st step: acetic acid	1st step: 40	not under control	end over end tumbler	1st step: 16h	0,5g	[8]
		2nd step: hydroxylammonium chloride	2nd step: 40			2nd step : 16h		
		3rd step: ammonium acetate	3rd step: 50			3rd step: 16h		

All tested elements showed variabilities due to sample inhomogeneities less than 2% and the material was therefore judged to be homogeneous and bottled.

Leaching/extraction test procedures

The main experimental differences in the considered tests are evidenced in Table II, where the most relevant experimental parameters are shown for each test.

All tests have been performed in four replicates, with the exception of the pH-stat test in which only one replicate has been done; a procedural blank for each test has also been evaluated.

In most cases the solid residue has been separated from the leachate by filtration; in the case of sequential extraction, the supernatant has been separated after centrifugation.

In all cases the leachates have been stored at 4°C or immediately analyzed.

PET containers have been used both for eaching/extraction tests and for the storage.

Determination of the total element content in the samples

The total element concentration has been determined after digestion of 0.2 g of sample with 1.5 mL HNO_3 65% + 1 mL HF 48% + 1.5 mL $HClO_4$ 60% solution, in a microwave oven. After cooling, 1.5 mL of H_3BO_3 (1 mol L^{-1}) have been added to each sample and a further treatment in microwave oven has been performed.

The digested extracts have been immediately analyzed or stored at +4°C in PET containers.

Evaluation of the analytical performances of the laboratory

The analytical performances of the laboratory and the analytical variability associated to measurements has been evaluated using available certified reference materials. In particular, the BCR CRM 601 (the only available CRM for sequential extraction procedures) and the NIST SRM 1633a have been used for sequential extraction and total determination, respectively. No certified reference materials are available for leaching, availability and pH-stat test.

Leaching and extraction tests

Within the frame of the Analeach project, a comparison between five different leaching and extraction tests has been carried out. The different tests have been applied on a highly homogenized fly ash reference material. The use of a reference material allows that differences in the results can be imputed to differences among the tests and not to inhomogeneities of the analyzed samples.

The considered tests were the following:

1) Regulatory availability test (NT ENVIR 003).
2) European leaching test (pr EN 12457 – option C).
3) Italian regulatory leaching test.
4) pH – stat test.
5) Sequential extraction (SM&T – three step procedure).

All these tests belong to the category of leaching tests; some of them have a specific name according to the operating conditions applied (pH – stat test, sequential extraction) or to the type of provided information (availability test).

1) Availability test

The availability test is used for measuring the potential release of components from solid materials and for distinguishing between extractable and not extractable substances [15]. The test aims to evaluate the maximum release of constituents in water, by using very high liquid/solid ratios to increase the diffusion of constituents from solids to bulk solution.

The considered test [4], applied in Countries of the Northern Europe, is performed in two steps: the first at neutral pH ($pH = 7$ for 3 hours) and the second at acidic pH ($pH = 4$ for 18 hours). The pH is under control and strictly mantained stable in both steps, by addition of HNO_3 1mol L^{-1} from an automatic titrator.

2–3) Leaching tests

Leaching could be defined as the dissolution of a soluble constituent from a solid phase into a leachant [16]. The most frequently used leachant is water in order to simulate real environmental conditions, even if organic solutions are used too. The leaching of materials is a complex process, depending on many factors and conditions under which the leaching test is carried out. The driving forces influencing the release of constituents from a solid material are the solubility of substances, the diffusion rate of the constituents inside the matrix and the wash off of the substances which lay on the surface of the matrix.

The European leaching test [5] is performed by adding deionised water to the sample, with a L/S ratio = 2 in the first step and a L/S ratio = 8 in the second step; in this test the pH is not under control.

On the contrary, in the Italian leaching test [6] the pH is partially under control, depending on the nature of the material, because, according to the normative protocol, the quantity of acid that can be added cannot exceed 20% of the leachant. The pH should be mantained constant at a value of pH = 5 by addition of acetic acid 0.5 mol L^{-1}, up to a maximum volume corresponding to 20% of the total leachant. In the case of particular materials it could happen that the addition of 20% of acid is not sufficient to mantain the pH = 5, and therefore the pH is only partially under control during the test. In Figure 1 is reported the pH trend during the Italian leaching test performed in this study. In this case the maximum allowed amount of acid was entirely added at the beginning of the test and it was not sufficient to mantain pH = 5. As it can be seen from figure 1, after two hours the pH reached a constant value of about 7.

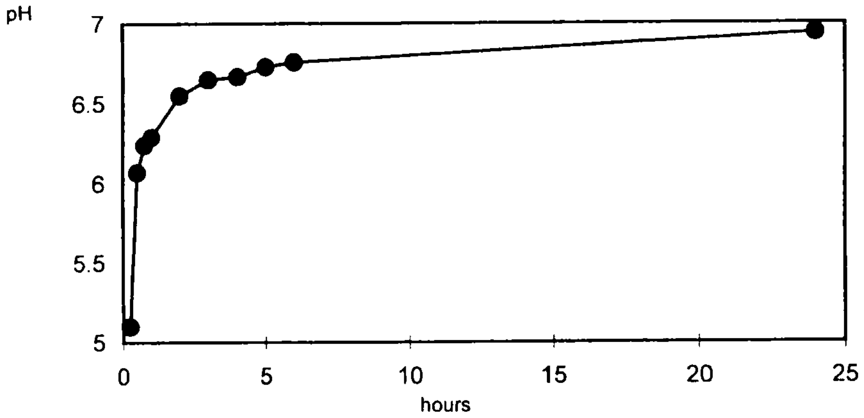

FIGURE 1 pH trend during the Italian leaching test

4) *pH-stat test*

Within the frame of the European Committee of Normalization (CEN), a group of experts is involved in the standardization of a pH-stat test procedure.

In this study, the draft proposed by the working group (draft CEN/TC 292/WG6, 9/7/1997) [7] has been considered.

The pH-stat test consists in an extraction performed at a fixed pH in a wide range of pH values (usually from pH=3 to pH=12). The pH is mantained constant along the test by addition of HNO_3 or NaOH (depending on the natural pH of the material) from an automatic titrator.

5) Sequential extraction

The fifth test applied was the SM&T three step sequential extraction procedure, proposed for the fractionation of metals in sediments [8]; nowadays it is largely applied both to sediments and soils [17–19]. This test was included in order to evaluate its applicability to fly ash materials.

RESULTS AND DISCUSSION

The results obtained for each element are shown in Figures 2a and 2b. The full line corresponds to the total content, while the dotted line corresponds to the sum of the results of the two steps of the availability test. It is worth stressing that the sum of the results practically coincides with the results of the second step of the availability test, as only a little amount of metals was extracted during the first step.

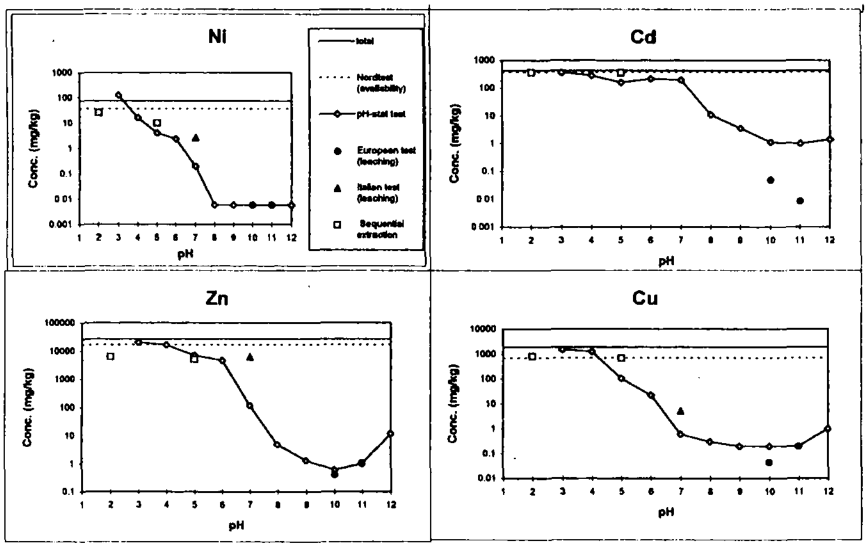

FIGURE 2A Results of the leaching/extraction tests for Ni, Cd, Cu and Zn

The results of all the other tests are plotted as function of the pH, under which they have been carried out. Actually, the only tests performed under pH control

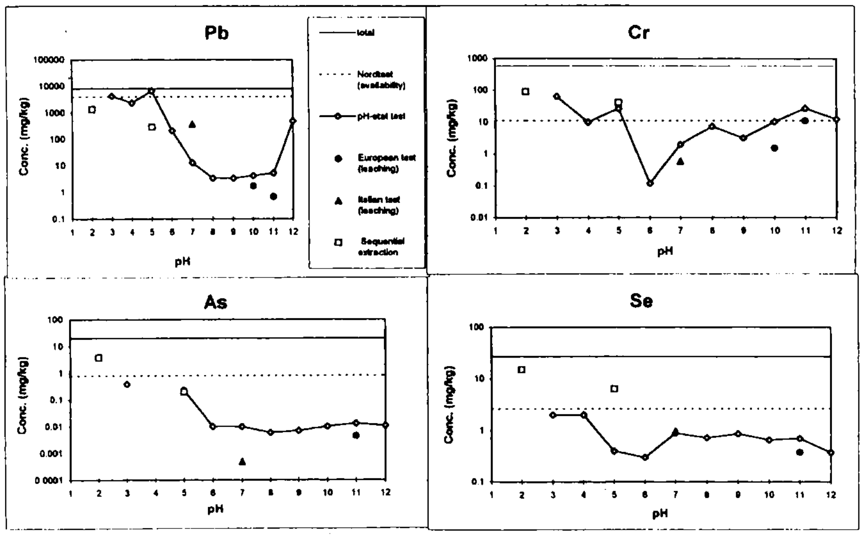

FIGURE 2B Results of the leaching/extraction tests for Pb, Cr, As and Se

all along the experiment were the pH-stat test and the availability test; for the other tests, the reported pH value corresponds to the pH measured at the end of the experiment.

In particular, the full circles correspond to the two steps of the European leaching test (the final pH of the first step was around 10 whereas the final pH of the second step was around 11), the full triangle to the Italian leaching test, the empty rhombi to the pH-stat results and the empty squares to the sequential extraction procedure; in this last case, the result obtained in the first step is plotted at pH=5, whereas at pH=2 is reported the sum of the results obtained in the three steps.

The total content is obviously the highest value for each element and in the case of some elements the results obtained with the availability test are very close to the results obtained for the total content. This means that in this material the maximum extractable fraction of Cd, Zn, Ni, Pb and to a lesser extent Cu, represents a significant percentage of the total content.

If considering the two leaching tests (Italian and European), there is a large difference in the results: the lowest release for all elements is generally observed when the European leaching test is applied, whereas the results of the Italian leaching test fall in an intermediate position between those of the availability test and those of the European leaching test.

TABLE III Results of the two leaching tests (European and Italian)

Element	*As*	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Se*	*Zn*
1st step of the European leaching test (mg/kg)	<0.0005	0.052±0.006	1.55 ± 0.3	0.044 ± 0.006	<0.006	$(1.8 \pm 0.3)^{*}\ 10^{-3}$	$(1.5 \pm 0.3)^{*}\ 10^{-3}$	0.58 ± 0.21
Second step of the European leaching test (mg/kg)	$(43.8 \pm 0.02)^{*}\ 10^{-3}$	0.010 ± 0.001	11.4 ± 1.3	0.195 ± 0.047	<0.006	0.69 ± 0.10	$(375 \pm 66)^{*}\ 10^{-3}$	1.04 ± 0.11
Cumulative results of the European leaching test (mg/kg)	$(43.8 \pm 0.02)^{*}\ 10^{-3}$	0.062 ± 0.007	13.0 ± 1.6	0.24 ± 0.05	<0.006	0.69 ± 0.10	0.38 ± 0.07	1.6 ± 0.2
Results of the Italian leaching test (mg/kg)	<0.0005	466 ± 18	0.60 ± 0.23	8.3 ± 5.3	2.72 ± 0.58	388 ± 86	0.97 ± 0.16	6.300 ± 1800

In Table III the results obtained by the two applied leaching tests are shown. As it can be seen, in some cases (Pb and Zn for instance) the Italian leaching test provides results three order of magnitude higher than those provided by the European leaching test; this means that an evaluation of the risk assessment for this material could be very different depending on the applied leaching test.

With regard to the sequential extraction, the results at pH=2 (corresponding to the sum of the three steps) are very often similar to those of the availability test and in some case (Cd above all but also Se, Cu and Ni) to the total content. Furthermore, the difference between the results obtained in the first extraction step and the sum of the three extraction steps is generally low (with the exception of As). In case of three out of eight elements (Cd, Cu and Zn), the extracted amount of metal represents even more than 80% of the total amount extracted by the three step procedure. These results are in agreement with the nature of the sample. In fact, during the incineration process, volatilization of metals, followed by a partial condensation on the material surface, occurs. Due to this fact the metals are mostly physically adsorbed on the combustion particles and then they cannot be considered "strongly bonded" to the fly ash matrices. The results obtained by the pH-stat test seem to describe all situations, from the European leaching test to the availability test, depending on the experimental pH. Furthermore, they are very similar to those obtained by the other tests performed around the same pH, even if in the other tests the pH is not maintained rigorously under control all along the experiment.

An exception regards the results of the Italian leaching test, plotted at pH 7, that are almost always quite higher (with the exception of As) than those obtained by pH-stat test at pH 7. It must be taken into account that the experimental pH of the Italian leaching test is only partially under control; in this case, due to the high natural pH of the considered material, the amount of acetic acid, entirely added in the first minute of extraction, was not sufficient to reach and mantain the pH = 5. Actually, the experimental pH was ranging between 5 and about 7 for two hours, before reaching a constant value of about 7 (Figure 1). Due to this fact, the Italian leaching test results should be plotted between pH 6 and 7. Considering this shift there could be a good agreement also between pH-stat test and Italian leaching test. In case of Pb, Ni and Zn the results obtained by the Italian leaching test are very similar to those obtained at pH 6 by the pH-stat test. It will be interesting to evaluate the amount of the extracted metals during the first two hours of the Italian leaching test to check if the pH is the only parameter influencing the release or if the duration time plays also a role, even if minor. Furthermore, it must be taken into account the nature of the leachant applied in the Italian leaching test that may have also a complexation action.

In general, the lower the pH the higher the metal release with a partial exception of Pb, above all, and Zn for whom the release at pH 12 was higher than that at pH 11. These results reflect the amphoteric behaviour of these metals. A similar trend was also observed for Cu.

The chromium up and down trend seems to be peculiar respect to the trends of the other elements. However, considering the metal release as function of pH there is a good agreement among the tests. Furthermore, chromium is the only element, beside As, for which the results of the Italian leaching test are lower than pH-stat test at pH 7 and, here again, a better agreement could be reached plotting the results of the Italian leaching test somewhere between pH 6 and 7. This seems to confirm a real up and down chromium trend, probably as a function of the different equilibria of chromium species; speciation analysis could provide further confirmation.

It is not easily explainable the lowest arsenic release when the Italian leaching test is applied.

CONCLUSIONS

Five different tests have been applied, each characterized by different parameters, such as pH, L/S ratio, nature of leachant, duration time and stirring conditions. Results show that pH influences the metal release more than the other parameters. Differences in the experimental pH under which the tests are carried out seem to explain the differences in the results obtained by these tests.

Significant differences have been observed also between the two leaching tests. Both the European and Italian leaching tests are "compliance tests" used to evaluate the compliance of the wastes to guideline values or regulatory concentration limits. On the basis of the obtained results, it is of main importance that guideline values and regulatory concentration limits be defined also as function of the applied test.

The pH-stat test, providing information on metal release along a wide range of experimental pH values (from pH=3 to 12), allows a better assessment about the final disposal of the material and should be strongly recommended for the environmental risk assessment.

Finally, sequential extraction procedures usually provide useful additional information about the fractionation of metals in the matrix. In this case, however, pH plays a more mportant role than leachants and the pH-stat test and the sequential extraction procedure seem to provide similar information for most of metals.

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