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Determination of trace elements in fly ash samples by FAAS after applying different digestion procedure

D. Bingöl[a,*], M. Akçay[b]

[a] Dumlupınar University, Department of Mining Engineering, Kütahya, Turkey
[b] Cumhuriyet University, Chemistry Department, Sivas, Turkey

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Abstract

The fly ash samples obtained from Kangal Power Plant were prepared for FAAS analysis by a new approach. The trace elements of the fly ash samples were leached with appropriate solvents under suitable conditions. The leaching method is known as an effective technique for substances dissolving very hard and refractory materials. The leaching effects of solvents and their mixtures were investigated on fly ash samples that are used largely in analysis of soil and sediment samples.

The fly ashes mainly consist of glassy aluminosilicates. The major components of the samples are SiO_2, Al_2O_3, CaO and Fe_2O_3. Therefore, decomposition of the silicate lattice of the fly ash is required for liberation of trace elements. The dissolution process can be completed by using a mineral acid such as concentrated HCl. This technique has an advantage that the fly ash can be dissolved without any oxidation at room temperature.

Maximum element recoveries were obtained by the procedure of 37% HCl leaching after the samples were treated with 2.0 ml of concentrated HF. It was also observed that maximum mass loss occurred in this procedure. The effect of the four leaching reagents, which are HCl, HNO_3, $HClO_4$ and $HNO_3 + HClO_4$, were investigated on fly ash samples that were treated with concentrated HF. An optimum leaching method was determined based on the confidence of analytical results and element recovery rates.

Keywords: Fly ash; Trace elements; Leaching; FAAS

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1. Introduction

Although many samples come to laboratory as solid state, the analytical measurements are generally made in solution of those samples. Yet, the solid sample must be decomposed totally and then dissolved.

The main objective is to develop a dissolving method that will be an alternative to conventional acid and heating methods for materials hard to dissolve allowing for reproducible/representative recovery of analyte.

There is an increasing interest in the information of trace element composition of fly ashes as the heavy metal transporters. The impossibility of total dissolution of fly ashes and very low level trace element concentrations prevent to reveal an analysis method accepted generally in these areas. The chemical treatments for decomposition and dissolution of biological samples, rocks, ores, sludges, glassy substances etc. are very important and these procedures could be the most critical stage in overall chemical analysis due to time consumption and confidence of analysis results [1–4].

The partial dissolving procedures can be used more than a total dissolving procedure for some geological and especially fly ash samples due to low chemical consumption, minimum contamination risks and speed [5–13].

It is expected that concentrated HF as solvent component will erode the structure of silicate and then the related elements will be leached with other solvent components. There is a growing need to exploit the unique properties of HF to

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[*] Corresponding author. Tel.: +90 274 2652031; fax: +90 274 2652066.
E-mail address: bdeniz@dumlupinar.edu.tr (D. Bingöl).

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dissolve fly ash samples in strong acid medium. The dissolution procedure is relatively fast when HF is used.

The investigation of solvent systems for effective trace elements recoveries from fly ash samples and the optimization of the leaching conditions are aimed in this study.

2. Experimental

2.1. Reagents and material

The fly ash samples were taken from of Kangal Power Plant vacuum line. The mineralogical analysis of the samples was performed by using a Rigaku D-Max III C model microprocessor XRD with K ray (35 kV and 15 mA).

Metal concentrations of solutions were determined using a Perkin Elmer 2380 Model FAAS. The absorption data obtained as the average of four measurements were evaluated on the basis of the least square regressed calibration graphs. The element concentration of fly ash samples was calculated by following Eq. (1) considering the leaching procedure:

$$\frac{(\mu\mathrm{g/ml}) \times 100\,\mathrm{ml}}{\mathrm{g}_{\text{sample weight}}} = \frac{\mu\mathrm{g}_{\text{element}}}{\mathrm{g}_{\text{sample}}} \qquad (1)$$

The analytical-grade reagents were used in all experiments and the solutions prepared with double distilled water. Suitable blanks for each stage of the leaching process were designed and all data were corrected from the blanks results.

Not only the physical properties, such as density, solid content, ignition loss and sieve analysis of fly ash, were determined, but also the major components (SiO_2, R_2O_3 –$Fe_2O_3 + Al_2O_3$– and CaO) of the fly ash were determined gravimetrically. The pH measurements were done by using HANNA 8521 pH-meter. The determination of the pH value of ash was made by mixing water and ash at the ratio of 1:100 and measuring the pH of mixture after waiting for 1 and 10 min. If pH is greater than 10 after 1-min wait, then it is said that the ash is basic. If pH is less than 7 after 10 min then it is said that the ash is acidic. If pH lies between 7 and 10 after 10 min then it is said that the ash is neutral [14]. Van der Sloot et al. indicated that ash pH can be determined by using the following Eq. (2):

$$(\mathrm{CaO} + \mathrm{MgO}) : (\mathrm{SO_3} + 0.04\mathrm{Al_2O_3}) \qquad (2)$$

On the basis of this ratio, ashes were classified as follows:

basic: ratio of >2.2; acidic: ratio of <1.1; neutral: ratio of 1.1–2.2.

2.2. Leaching procedures

Fly ash samples were dried at 105 °C for 2 h before leaching. The plastic beakers of 50 ml were used in leaching tests and these beakers were dried at the same temperature. A 1.000 g of fly ash was put into these plastic beakers and moistured with 2 ml of water in order to prevent the mass loss caused due to splashing when HF is directly added on the sample. Then, the different volumes of concentrated HF were added and stirred on the moistured sample aliquots. The beakers were kept on a hot plate (56–58 °C) until they get dry. After the samples dried, they were kept at 105 °C for 2 h in an oven. The leaching procedure was applied to HF-eroded samples with various concentrations of acids.

2.2.1. Determination of the optimum HF volume

The eroding procedure was performed with varied volumes of HF to determine the optimum HF volume. The concentrations of solutions were compared to each other.

2.2.1.1. Leaching with 1% HCl. The HF-eroded samples were washed with 1% HCl and filtered through a Gooch crucible with the aid of peristaltic pump. The filtrates were completed to 100 ml with 1% HCl. The mass losses were determined by drying and weighting the residue. The solutions were analyzed for trace elements through FAAS.

2.2.1.2. Leaching with 37% HCl. The eroded samples were washed in a total 6.0 ml of (three times with 2.0 ml) 37% HCl and filtrated as described above. The residue was washed with water, and the filtered material was combined and completed to 100 ml with water. The mass losses were determined by weighting the residue and the filtrates were analyzed for trace elements by using FAAS. This procedure was repeated nine times for the precision tests.

Table 1
Physical properties of fly ash studied

Properties (units)	Values
Density (g/cm^3)	2.22
Solid content (%)	99.62
The loss of ignition (1000 °C), solid matter %	2.47
The loss of ignition (1450 °C), solid matter %	3.52
pH	11.11

Table 2
Sieve analysis results of fly ash

Particle size (μm)	Σ (%)[a]
425–500	100
250–425	98.16
180–250	90.43
125–180	82.18
106–125	70.52
75–106	64.74
53–75	48.68
30–53	29.21
20–30	11.13
10–20	7.86
5–10	3.67
<5	2.36

[a] Σ, passing size.

Table 3
Results of XRF of fly ash

	Component									
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	TiO_2	Na_2O	P_2O_5	MnO
%	20.87	41.73	15.36	5.35	2.82	1.32	0.58	0.42	0.22	0.03

	Element													
	Sr	Ba	Cr	Zn	Pb	Ni	Zr	Rb	Cu	Co	Y	Ga	Th	Nb
μg/g	689.1	669.3	239.4	211.1	198.8	146.7	135.5	58.0	35.7	18.5	16.2	14.8	8.7	8.0

Table 4
FAAS results of the fly ash prepared by total digestion method

Acidic dissolving	Element concentrations (μg/g)						
	Cu	Ni	Co	Mn	Pb	Zn	Cr
[a]Confidence limits	55 ± 3	342 ± 12	75 ± 3	138 ± 3	52 ± 5	412 ± 35	176 ± 13

[a] Average of 17 experiments with 95% confidence interval.

2.2.2. *Leaching with various acids*

The procedure stated in the previous section was repeated with concentrated $HClO_4$, concentrated HNO_3 and mixture (3 ml + 3 ml) of the two, instead of 37% HCl. The mass loss and trace element concentrations of the solutions were determined for each test.

2.3. *Total digestion method*

Approximately 0.2000 or 0.5000 g fly ash aliquots were weighted in Teflon beakers, the mixture of $HNO_3 + HF + HClO_4$ was added to the samples, and the beakers were placed on a hot plate and evaporated. The treatment was repeated to get a spongeous mass. Then, the mass was dissolved in 1% (w/w) HCl and diluted to 100 ml with the same solvent [15].

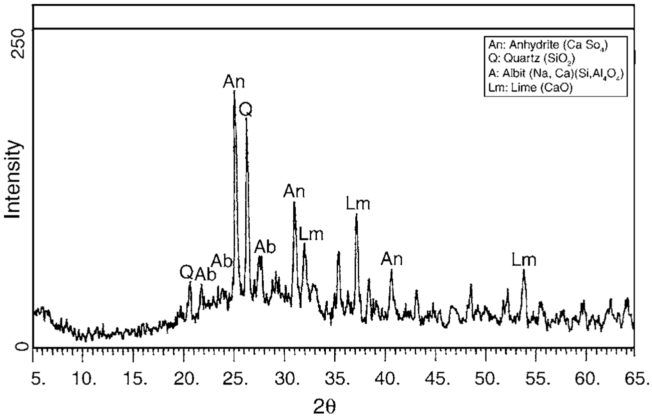

Fig. 1. X-ray diffractogram of fly ash.

3. Results and discussion

3.1. *Physical properties of fly ash*

The physical properties of fly ash sample studied are given in Table 1.

The pH value was calculated to be 4.18 from the results of XRF (X-Ray Flouresance Spectrometer), which indicates

Table 5
The major components of fly ash determined by XRF and gravimetrical methods

Method	SiO_2 (%)	R_2O_3 (%)	CaO (%)
XRF	41.73	20.71	20.87
Gravimetrical	38.94	27.00	23.60

Table 6
The mass loss of the samples and FAAS results of 1% HCl leaching after treating various volumes of HF

Sample no.	Volume HF (ml)	Mass loss (%)	Element concentrations (μg/g)						
			Cu	Ni	Co	Mn	Pb	Zn	Cr
A1	2	56.04	23.5	216	38.8	113	24.3	401	80.0
A2	4	42.10	24.9	238	26.9	116	20.0	307	75.0
A3	6	38.19	30.7	243	26.9	116	15.7	312	85.0
A4	8	48.58	30.7	254	34.8	112	20.0	405	95.0
A5	10	41.98	22.0	243	30.8	108	15.7	395	85.0

Table 7
The mass loss of the samples and FAAS results of 37% HCl leaching after treating various volumes of HF

Sample no.	Volume HF (ml)	Mass loss (%)	Element concentrations (µg/g)						
			Cu	Ni	Co	Mn	Pb	Zn	Cr
B1	2	65.96	33.6	318	44.2	121	80.9	303	108
B2	4	53.64	41.8	292	38.8	114	54.2	296	167
B3	6	58.46	43.7	286	44.2	116	34.2	292	154
B4	8	57.84	38.0	310	48.2	113	54.2	299	180
B5	10	56.04	36.5	310	44.2	108	54.2	298	173

Table 8
The mass loss of the samples and FAAS results the sample leaching with other concentrated acids and mixtures

	Mass loss (%)	Element concentrations (µg/g) ($\bar{x} \pm ts/\sqrt{N}$)[a]						
		Cu	Ni	Co	Mn	Pb	Zn	Cr
$HClO_4$	37 ± 3	27 ± 3	253 ± 8	36 ± 5	106 ± 3	59 ± 7	258 ± 4	97 ± 10
HNO_3	44 ± 4	33 ± 1	267 ± 8	53 ± 4	109 ± 3	58 ± 8	293 ± 51	99 ± 11
$HNO_3 + HClO_4$	52 ± 3	31 ± 3	272 ± 2	41 ± 5	105 ± 7	68 ± 9	267 ± 12	85 ± 19
HCl	59 ± 7	41 ± 3	302 ± 9	49 ± 6	109 ± 4	77 ± 6	294 ± 8	152 ± 14

[a] At HCl, average of nine experiments with 95% confidence interval. At other acids, average of five experiments with 95% confidence interval.

basicity according to Van der Sloot et al. [14] as given below.

$$\frac{20.87 + 2.82}{5.05 + (0.04 \times 15.36)} = 4.18$$

(> 2.2, therefore the fly ash is basic)

The results of sieve analysis for fly ash are also given in Table 2.

3.2. Chemical properties of fly ash

X-ray diffractogram of fly ash is shown in Fig. 1, and the results of XRF and results of FAAS are given in Tables 3 and 4, respectively.

It is clear that fly ash contains mainly quartz, lime, anhydride and albite mineral owing to this diffractogram. The Si in fly ash is in the form of quartz and albite, Ca is in the form of anhydrite, albit and lime, and Al is in the form of albite mineral.

The major components of fly ash were SiO_2, R_2O_3 and CaO and their concentrations were found gravimetrically and their XRF results are outlined comparatively in Table 5.

3.3. Results of the leaching experiments

The mass loss and FAAS results of the samples after treating with different volumes of concentrated HF leached with

Table 9
Significance tests between the methods

	HCl–$HClO_4$	HCl–HNO_3	HCl–($HNO_3 + HClO_4$)	$HClO_4$–HNO_3	$HClO_4$–($HNO_3 + HClO_4$)	HNO_3–($HNO_3 + HClO_4$)
Ni	+	+	+	+	+	●
Cu	+	+	●	+	●	●
Pb	+	+	●	●	●	+
Zn	+	●	+	●	●	+
Mn	●	●	●	●	●	●
Cr	+	+	+	●	●	●
Co	+	+	+	●	+	+

(+) If average of experimental > average of statistical, there is significant difference between the methods. (●) If average of experimental < average of statistical, no significance.

Table 10
Summary of standard errors of compared methods (µg/g)

	HCl–$HClO_4$ ($N = 14$)	HCl–HNO_3 ($N = 14$)	HCl–($HNO_3 + HClO_4$) ($N = 14$)	$HClO_4$–HNO_3 ($N = 10$)	$HClO_4$–($HNO_3 + HClO_4$) ($N = 10$)	HNO_3–($HNO_3 + HClO_4$) ($N = 10$)
Ni	10.1	10.2	11.0	6.4	8.1	8.3
Cu	3.3	3.0	10.5	2.0	2.6	2.0
Pb	6.9	7.3	7.6	6.1	6.6	7.1
Zn	8.9	25.3	10.4	29.2	7.3	1.8
Mn	4.3	4.4	27.4	2.4	4.3	4.4
Cr	15.6	15.6	17.1	8.8	12.4	12.8
Co	6.3	6.2	6.3	3.4	3.7	3.4

Table 11
The element recoveries by the leaching method

	Element						
	Cu	Ni	Co	Mn	Pb	Zn	Cr
Recovery (%)	75.3	88.3	65.2	78.9	147.3	71.4	86.4

1% HCl are given in Table 6 and those leached with 37% HCl are given in Table 7.

According to the results in Tables 6 and 7, maximum silicate destructions arise from 2.0 ml of concentrated HF treatments, and therefore this volume of HF was used in the subsequent experiments. The reason for the highest silicate destruction by using the least HF volume was not investigated in this study.

The elements, except Cu, could be recovered at high rates from the eroding samples by using 37% HCl as leach reagents. The maximum mass loss was also observed with this solvent.

The mass losses of the samples after treating with 2.0 ml of HF and leaching with various acids, and FAAS results are given in the way of confidence interval in Table 8. It is obvious that 37% HCl is a better leaching reagent according to the results given in Table 8.

The fly ash samples were also prepared by total digestion method to test the validity of the proposed sample preparing method for chemical analysis. The results of the total digestion method are given in Table 4.

The “Student *t* significance tests” were carried out to see the differences in the various leaching procedures. The results and pooled standard deviations of the experiments are presented in Tables 9 and 10, respectively.

The leaching effect of oxidative acids was found to be different from that of nonoxidatives (Table 10).

The usability of leaching procedure instead of total digestion was investigated as sample preparation technique on fly ash samples. The element leaching recoveries were defined as division of the element concentration obtained from the leaching procedure by the element concentration of total digestion method. The element leaching recoveries are given in Table 11.

It was concluded that the results of the proposed method are comparable with those of similar work studied previously.

4. Conclusions

An alternative leaching method was developed for total digestion procedure of fly ash. Maximum element recovery was obtained after the samples (1.0000 g) were eroded with 2.0 ml of concentrated HF and leached with a total 6.0 ml of (three times with 2.0 ml) 37% HCl. This procedure is accepted as an optimum method. The results of optimum leaching method are given in Table 8 with confidence limits. The best result was judged on the basis of the highest analytical value and good reliability. The precision (reproducibility) of the applied leaching method is comparable to total digestion method and the application of this approach is as easy as the classical method. The leaching procedure has important advantages over the total digestion method in terms of the solvent consumptions and environmental effects.

Analyte can be taken from solid samples in a representative and reproducible manner by means of contemporary technologies and can be analyzed correctly, reproducibly and sensitively with valid analytical methods.

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