Content and Mobility Behavior of Iron and Manganese in Asphaltite Burning Residue Using ICP-OES

Isil Aydin^{a*}, Beniz Gunduz^b, Firat Aydin^c, Osman Akba^c, Abdurrahman Saydut^d, and Candan Hamamci^c

^a Dicle University, Pharmacy Faculty, Analytical Chemistry Department, Diyarbakır, Turkey

^b Selcuk University, Science Faculty, Chemistry Department, Konya, Turkey

^c Dicle University, Science Faculty, Chemistry Department, Diyarbakır, Turkey

^d Dicle University, Engineering Faculty, Mining Engineering Department, Diyarbakır, Turkey

INTRODUCTION

Fuel combustion products are one of the more important anthropogenic sources of emission of many metals and metalloids into the environment (1-5). In the burning process of fuel, minerals undergo thermal decomposition, fusion, disintegration, and agglomeration (6,7). The elements associated with sulfide minerals and organic matter are more volatile compared to those in different chemical forms, like oxides (8). The conventional method for identification and evaluation of the availability of heavy metals in ash samples is carried out by leaching of the samples via chemical extractants. Both single extraction and sequential extraction have been used (9-11). In this case, the most important information is the metal content, the chemical species, and the condition of metal migration from the studied material into the environment (12-14).

Asphaltites are formed by migration and later solidification of petroleum. The inorganic residue derived from the burning of asphaltite represents the noncombustible impurities originally present in asphaltite. Mineral matter is a complex mixture of inorganic minerals and elements except for carbon, hydrogen, oxygen, nitrogen, and sulphur (15-18). Chemical speciation of Fe and Mn is necessary for risk assessment of asphaltite burning residue (ABR). Mn is considered to be characteristic of fossil fuels from various sources (19,20). Among the heavy metals

ABSTRACT

The determination of inorganic pollutants leaching from solid waste, such as coal, asphaltite, oil shale, and ash, is an important topic for industrial applications and solid waste management. This study presents the concentration and fractionation of iron (Fe) and manganese (Mn) in asphaltite burning residue (ABR) and their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). A modified Tessier sequential extraction method was used for the fractionation of Fe and Mn in four forms (exchangeable, carbonates, bound to organic and sulfide, and residual content). Investigations on the Fe and Mn chemical fractions and their environmental mobility in ash solution systems were carried out. It was found that Mn in ABR (from Harbul-Silopi, Turkey) occurs in the following fractions: exchangeable (13.56%), associated with carbonates (28.94%), associated with organic matter and sulfides (17.48%), and residual content (40.08%). Fe occurs in the following fractions: exchangeable (11.11%), carbonates (27.68%), organic matter and sulfides (23.39%), and residual content (37.82%). Among these fractions, the exchangeable and carbonate-bound fractions are unstable and prone to leach out, while the organic matter-bound fractions and the residual fractions are considered to be relatively stable and of low bioavailability. The mobility fractions of Fe contain 38.79% and of Mn contain 42.50% of their total concentration in ABR under normal environmental conditions.

found in the environment, Mn presents one of the most insidious and widespread health hazards. Mn is an essential trace element known to be related particularly to the reproductive functions. Its deficiency may lead to negative effects such as brain damage, teratogenicity, skeletal abnormalities, and abnormal metabolism of lipids and carbohydrates. Miners exposed to chronic manganese overload show symptoms of the extrapyramidal system, surprisingly similar to those of patients with Parkinson's disease. For this reason, Mn can become a highly toxic heavy metal, emitted from industrial sources, which can seriously damage human health. It can also affect the ecosystem negatively, accumulating in the food chain (20,21). Different veins of asphaltic materials have different physical and chemical characteristics depending on the location of the asphaltic material, geological formation, and degree of metamorphism (22). The Harbul vein (in Silopi, SE Anatolia, Turkey) is the major source for asphaltites used by power plants in the production of electrical energy (23). Environmental contamination caused by the disposal of asphaltite burning residue, and also by other industrial applications, requires knowledge of their total metal concentrations in addition to the available metal fraction to other environmental components. The total metals concentration applied for environmental evaluations leads to an over-estimation of the contamination once it is well known that a significant fraction of the metals is immobilized in the solid matrix. In a natural environment, leaching of pollutants from an ash matrix is carried out by chelating agents in the form of

*Corresponding author.
E-mail: iaydin@dicle.edu.tr

humic acids (24,25). The structure of these complexes is affected significantly by the solubility and mobility of the metals in solid waste (26).

In the present study, the modified Tessier sequential extraction method (27) was applied for the determination of binding forms of iron and manganese in the asphaltite burning residue (ABR) and for evaluation of their leaching behavior in view of their potential environmental impact. The elemental determinations in the different leachates were performed by inductively coupled plasma optical emission spectrometry (ICP-OES).

EXPERIMENTAL

Instrumentation

A PerkinElmer Optima™ 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Inc., Shelton, CT, USA) was used for the determination of Fe and Mn in asphaltite burning residue (ABR). The ICP-OES operating conditions are listed in Table I. All of the procedures from sampling to analysis were also applied to the blanks in order to evaluate any metal contamination during the analytical procedure. A blank was simultaneously prepared and all procedures were applied before measurements.

Selection of the instrumental parameters and the optical wavelengths was based on obtaining good sensitivity, reasonable detection limits, and eliminating interferences (2). Internal standards were not used for this study. The direct calibration process was performed for Mn and Fe, and the respective calibration curve for each metal is shown in Figure 1 (a and b).

Reagents

The reagents used were of Suprapur® grade (Merck & Co., Darmstadt, Germany) or of analytical grade and used without further purification. Deionized water, obtained with a Milli-Q® system (Millipore Corporation, Bedford, MA, USA), was used throughout this study.

TABLE I
ICP-OES Operating Conditions of the PerkinElmer Optima 2100 DV

Parameters	
RF power	1450 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	0.2 L min ⁻¹
Nebulizer gas flow rate	0.8 L min ⁻¹
Sample flow rate	1.5 L min ⁻¹
View mode	Axial
Read	Peak area
Source equilibration time	15 s
Read delay	50 s
Replicates	3
Background correction	2-point (manual point correction)
Spray chamber	Scott type spray chamber
Nebulizer	Cross-Flow GemTip™ Nebulizer (HF resistant)
Detector	CCD
Purge gas	Nitrogen
Shear gas	Air
Gas	Argon
Analytical wavelengths	Fe 238.204 nm, Mn 257.610 nm

Fig. 1 (a and b). Calibration curve of Fe and Mn.

Sample Preparation

The asphaltite sample was obtained in lump form from the Harbul (Silopi) asphaltite field (Harbul vein $2.5 \cdot 10^7$ tonnes), located in the SE Anatolia region of Turkey. A sample amount of about 20.0 g was oven-dried with a Memmert ULM 500 drying oven (Germany) at 105 °C, crushed with a Retsch BB1/A jaw breaker (Germany), and ground in a Retsch SRZ rotor beater mill. The particle sizes of the samples were sifted to less than 300 μm . The heating value and the ash and sulfur concentrations of the samples were determined according to ASTM procedures (22). For analysis, 20.0 g of asphaltite was weighed into a porcelain crucible and subjected to the calcination step in a muffle furnace at 950 °C for about 6 hours.

Digestion Procedure

A Berghof MWS-3 microwave digestion system (Berghof, USA) was used for acid digestion of the asphaltite burning residue. The two-stage, five-step microwave acid digestion was applied. An amount of 0.3 g dried ABR sample was weighed and transferred into a pressure-resistant polytetrafluoroethylene (PTFE) vessel and an acid mixture of 10 mL HNO_3 + 3 mL HF added (5,8). The vessel was then sealed and mounted in a sleeve for one hour, then removed and cooled to room temperature in a water-bath. The method and acid composition of the first step were the same as used for the one-stage

digestion, except for the digestion program. An amount of 20 mL of H_3BO_3 was added to the sample, the vessel returned to the microwave digestion system, and the second stage applied using the conditions listed in Table II at 1000 W power. The reaction mixture was subjected to an evaporation module in order to remove the acids after the final digestion (11,14). Then the residue was dissolved in Milli-Q™ water, filtered, and the filtrate diluted to a fixed volume of 50 mL.

Modified Tessier Sequential Extraction Procedure

The modified Tessier sequential extraction procedure was used to study the iron and manganese distribution in the Silopi asphaltite burning residue (3,20,27). The

operating conditions of the method are listed in Table III.

Fraction 1 – Exchangeable

Approximately 1 g asphaltite burning residue was extracted with 10 mL of 1M ammonium acetate (pH=7). After 1 hour of shaking at 200 rpm at room temperature, the sample was centrifuged for 10 minutes at 5000 rpm. The liquid phase was decanted and diluted to 50 mL with ultrapure water.

Fraction 2 – Carbonate

To the residue of fraction 1, 10 mL of 1M acetic acid was added (pH=5). After 1 hour of shaking at 200 rpm, it was centrifuged for 10 minutes at 5000 rpm at room temperature. The liquid phase was decanted and diluted to 50 mL with ultrapure water.

Fraction 3 – Bound to Organic and Sulfide

The residue from fraction 2 was treated with 5 mL of a 30% solution of H_2O_2 (pH=2 with HNO_3) and shaken at 35 °C and 200 rpm for 3 hours. After centrifugation at 10,000 rpm, the samples were paper-filtered and diluted to 100 mL with ultrapure water.

Fraction 4 – Residual Content

A mixture of *aqua regia* (HCl/HNO_3 , 3:1) was added to the filtered residue from fraction 3. After microwave destruction, the samples were paper filtered and diluted to 100 mL with ultrapure water.

TABLE II
Operating Conditions for the
Two-Stage Microwave Digestion

Step 1			
T°C	140	160	190
Ta (min) ^a	5	5	3
Time (min) ^b	5	10	20
Step 2			
T°C	160	100	
Ta (min) ^a	3	2	
Time (min) ^b	15	15	

^a Waiting time at desired temperature.

^b The time between the two successive temperatures.

TABLE III
Operating Conditions Required for the Modified Tessier Sequential Extraction Method

Fraction	Nominal Fraction	Extractant	Extraction Conditions
1	Exchangeable	1M ammonium acetate (pH=7)	Shaken 1 h, 25 °C
2	Carbonates	1M acetic acid (pH=5)	Shaken 1 h, 25 °C
3	Bound to organic and sulfide	30% solution of H_2O_2 (pH=2 with HNO_3)	Shaken 3 h, 35 °C
4	Residual content	HCl/HNO_3 (3:1)	Acid digestion

Accuracy of the Analytical Method

The certified reference material (CRM) NIST-1633b Coal Fly Ash (National Institute of Standards and Technology, Gaithersburg, MD, USA) was used to check the accuracy of the analytical method used. The results are listed in Table IV.

RESULTS AND DISCUSSION

This study presents the concentration and fractionation of Fe and Mn in the inorganic residue derived from the burning of asphaltite and represents its noncombustible impurities. Table V lists the elemental analysis of the studied asphaltite. The reagents used in the various stages of analysis selectively leach certain fractions of the ABR.

Microwave-acid digestion (MW-AD), followed by inductively coupled plasma optical emission spectrometry (ICP-OES), was examined for the determination of total Fe and Mn. Dry ashing was used for the almost complete elimination of the organic materials prior to analyte determination. The burning temperature of 950 °C was found to be the best as a result of the trade-off between the overall iron and manganese recovery yield (10). In this research, wet acid digestion (HCl, HNO₃, H₃BO₃) was used for the Fe and Mn determinations. Crystallization of CaF₂ was avoided by the addition of boric acid. The two-stage, five-step microwave digestion method was carried out as detailed above in Table II.

It can be seen that the proposed ICP-OES procedure is the most simple and reliable analytical method for the elemental analysis of asphaltite burning residue due to its high selectivity and low interference problems. ICP-OES functions best when the samples are in the aqueous or solution phase. The total Fe and Mn concentrations

TABLE IV
Accuracy Assessment Through the Analysis of CRM NIST-1633b
Constituent Elements in Coal Fly Ash

Element	Certified	Found
Fe (wt %)	7.78 ± 0.23	8.01
Mn (mg kg ⁻¹)	131.8 ± 1.7	130.7 ± 2.4

found in the Silopi ABR were 5.13 wt% and 55.73 mg kg⁻¹, respectively.

Although assessment of the total concentration of Fe and Mn is still useful in many areas, knowledge of their speciation is of primary importance because their characteristic toxicity, mobility, bioavailability, and bioaccumulation depends on their different chemical fractions. Fractionation of Fe and Mn was carried out using the modified Tessier method based on the sequential extractions of the metals from the ABR, each releasing four forms of Fe and Mn: exchangeable (fraction 1), carbonates (fraction 2), bound to organic and sulfide (fraction 3), and residual fraction (fraction 4).

As can be seen in Table VI, the most abundant fraction of both Fe and Mn in ABR was in the residual fraction (fraction 4). The presence of Fe and Mn in the residual fraction is safer for the environment since it shows lowest possible mobility and bioavailability. The most abundant Fe fraction in the carbonates (fraction 2) was second, while in the organic matter and sul-

TABLE V
Elemental and Proximate Analysis of Harbul-Silopi Asphaltites

Elemental Analysis	Weight (%)
Carbon	54.079
Nitrogen	0.764
Hydrogen	5.122
Proximate Analysis	
Moisture	0.630
Ash	32.490
Fixed Carbon	20.140
Volatile matter	46.740
Heating value (kcal g ⁻¹)	6276.253

fide fraction (fraction 3), it was third. On the other hand, the prevailing Mn in the carbonate fraction was second, and in the organic matter and sulfides fraction it was third. The values for Fe and Mn were lowest in the exchangeable fraction (fraction 1).

The exchangeable fraction is the most dangerous for the environment. This fraction shows that the amount of Fe and Mn that could be released into the environment

TABLE VI
Concentration of Total and Fractions of Fe and Mn
in Asphaltite Burning Residue (ABR)

	Mn (mg/kg ⁻¹)	Mn (%)	Fe (wt%)	Fe(%)
Total	55.73 ± 1.14	100.00	5.13 ± 0.29	100.00
Exchangeable Fraction	7.56 ± 0.42	13.56	0.57 ± 0.05	11.11
Carbonate Fraction	16.13 ± 0.24	28.94	1.42 ± 0.12	27.68
Organic Matter and Sulfide Fraction	9.74 ± 0.58	17.48	1.20 ± 0.07	23.39
Residual	22.34 ± 0.97	40.08	1.94 ± 0.15	37.82

would increase if the environmental conditions became more acidic (10,28). The carbonate fraction also has an adverse impact on the environment, and under low pH conditions, Fe and Mn may be present as co-precipitates with carbonate minerals and strongly adsorbed metal forms on the ash surface. Fe and Mn in this fraction can be released easily by ion exchange processes and can also leach very easily when the environmental conditions become disturbed due to a change in pH (13).

The metals Fe and Mn in the exchangeable (fraction 1) and carbonate fractions (fraction 2) play a very important role in the evaluation of the environment and always act as a pollution indicator due to the metals' environmental mobility and bioavailability. The first fraction in ABR is the most labile form that can be easily leached into the environment when the ABR is rinsed by rain or other water bodies. Thus, it can be stated that this fraction is the most active part in nature which poses an environmental risk to human beings and all biological species (29,30).

Fortunately, the amount and proportion of Fe and Mn in ABR that is bound to the organic and sulfide fraction (fraction 3) is low, which is consistent with its chemistry of being predominantly bound as sulfides that do not dissolve in the ABR at this stage. Sulfide solid phases are dissolved in various extraction fractions along the extraction sequence and not only in the "sulfide" fraction. This fraction shows the amount of Fe and Mn bound to the organic matter and sulfur which would be released into the environment if the conditions became oxidative. Most metals readily form compounds with sulfur. The sulfur-binding fraction is normally stable with respect to temperature and lower pH. Fe and Mn in this fraction are more stable and

will take part in the geochemical cycle less easily. Yet, they will become labile when the redox conditions change. Under oxidizing conditions, the organic materials and reducing sulfur compounds may be destroyed, and the metals associated with them can be leached into the environmental water system. The percentage of total Fe and Mn leached from the organic matter and sulfide fraction (fraction 3) was 23.39% and 17.48%, respectively.

Results of Using Modified Tessier Sequential Method in Residual Fraction

The strongest affinity of Fe and Mn was found in the residual fraction (fraction 4). The metals were held in a more stable fraction in which the movement of these heavy metals in the ABR profile would be negligible (31). The residual fraction represents the part of Fe and Mn that has strongest association with the crystalline structures of the minerals. However, it is not always easy to extract metals in this fraction. A much higher percentage of metals was noticed in the residual fraction using the modified Tessier scheme (28). The percentages of Fe and Mn in the residual fraction (37.82% and 40.08% of the total metal leached) were higher than in the other fractions. The mobilization of elements from the ashes is a relatively slow process, and an equilibrium between the solid and liquid phases may not be attained even after long leaching times. However, short-term leaching experiments are capable of giving critical information in considerably shorter interaction periods.

The results presented in this research imply that the modified Tessier sequential extraction method can be used to identify qualitative differences in the partitioning of Fe and Mn in the ABR samples collected from the Harbul vein, Silopi, Turkey. The sequential

extraction scheme recommended by the modified Tessier method is sufficiently repeatable and reproducible for application in fractionation studies. The advantages of the technique include a high degree of automation, good reproducibility, and short analysis time, which makes it the method of choice for the fractionation of Fe and Mn (10,30,31).

Quantitative evaluation of leachable Fe and Mn from ABR to surface waters under environmental conditions, in addition to metal contamination of the environment, is essential. Mn, which is mobile in environmental conditions (pH=5-7), is associated with the exchangeable fraction (pH=7) and also with the carbonate fraction. The other Mn fractions present in the residue are bound to mobile fractions and can migrate to the environment under specific conditions, i.e., aggressive environments and/or the presence of microorganisms (13).

This study further supports the fact that knowledge of the levels of toxic and potentially toxic elements, especially in the most mobile fractions, is an important tool for environmental risk assessment (1,10,29,31).

CONCLUSION

This study presents a modified Tessier sequential extraction method for the fractionation of Fe and Mn from asphaltite burning residue (ABR) in four forms (exchangeable, carbonates, bound to organic and sulfide, and residual content) and their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The 238.204 nm and 257.610 nm lines were used for Fe and Mn determination, respectively.

The proposed method provides quantitative knowledge of the Fe and Mn distribution in ABR and

their toxicity, mobility, leachability, bioaccumulation, and bioavailability. Assessment of the chemical, mineralogical, morphological, and leaching behavior of these ashes is important for their effective management.

The total Fe and Mn concentrations in the ABR (Harbul vein, Silopi, Turkey) were 5.13 wt% and 55.73 mg kg⁻¹, respectively. This investigation concludes that the most abundant fraction of both Fe and Mn in ABR is in the residual fraction. Relative abundances of the remaining Fe fractions in ash follow the order: Carbonate > Organic matter and sulfur > Exchangeable fraction. The remaining Mn fractions follow the order: Carbonate > Organic matter and sulfur > Exchangeable fraction.

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