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TECHNICAL ARTICLE

Geochemical and Mineralogical Characterization of a Pyritic Waste Pile at the Anjir Tangeh Coal Washing Plant, Zirab, Northern Iran

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Abstract Coal washing at the Anjir Tangeh plant, in Zirab, northern Iran, has produced more than 1.5 Mt of coal wastes. These waste materials were geochemically and mineralogically characterised to guide development of an appropriate remediation scheme. Three vertical trenches up to 4 m deep were excavated from the coal waste pile surface and 25 solid samples were collected at 0.5 m intervals. The samples were analysed for total concentrations of 54 elements, paste pH, SO_4^{-2}, CO_3^{-2}, and HCO_3^-. The lowest pH values were measured at a depth of 0.3 m. The upper portion (1 m) of one profile was moderately oxidised, while oxidation in the other two profiles did not extend more than 0.8 and 0.5 m beneath the pile surface. The waste piles have low acid-producing potential (15–21.87 kg $CaCO_3$/t) and high values of acid-neutralizing potential (0.06–96.2 kg $CaCO_3$/t). Fe, Al, S, Na, Mn, Pb, Zn, Cd, and Ag increased with increasing depth, while Mo, Sr, Zr, and Ni decreased with increasing depth. The results show pyrite oxidation at depth and subsequent leaching of the oxidation products. Mn, Zn, Cu, Pb, Ag, and Cd are the most important contaminants of concern at this site.

Keywords Acid-neutralizing potential · Acid producing potential · Pyrite oxidation · Trace element mobility

Introduction

The Alborz Markazi coalfield is one of the oldest and most significant coal production areas in Iran. Karmozd I, Karmozd II, Anjir Tangeh, Pol-E-Sefid, Keseliyan and Southern Zirab are the most important coal mines in the Zirab-Karmozd region of the Alborz Markazi coalfield. As is common around the world (Silva et al. 2011), the extracted coal from this region is washed in the Anjir Tangeh coal washing plant to increase the coal grade and remove impurities. Less than half of the input coal has been deposited as coal waste in a huge open-air dump in the plant area.

The waste dump minerals were subdivided into two groups: primary minerals (originally deposited within the waste dumps) and secondary minerals (formed within the dumps by precipitation from metal rich waters, derived from the acid mine drainage (AMD) processes, Jambor 2003). Gypsum, hydrous iron oxide (goethite), and hydrated iron sulphate (jarosite and shwertmannite) are the most common secondary minerals in coal wastes (Silva et al. 2011). Precipitation of sulphate minerals may remove metals from the water, but subsequent dissolution can increase concentrations of dissolved metals (Hakkou et al. 2008; Nordstrom and Alpers 1999).

The chemical composition of the coal waste pile was characterised to predict the likely long-term environmental impacts of the coal washing operation. The main goals of the research was to: to evaluate the acid production potential of

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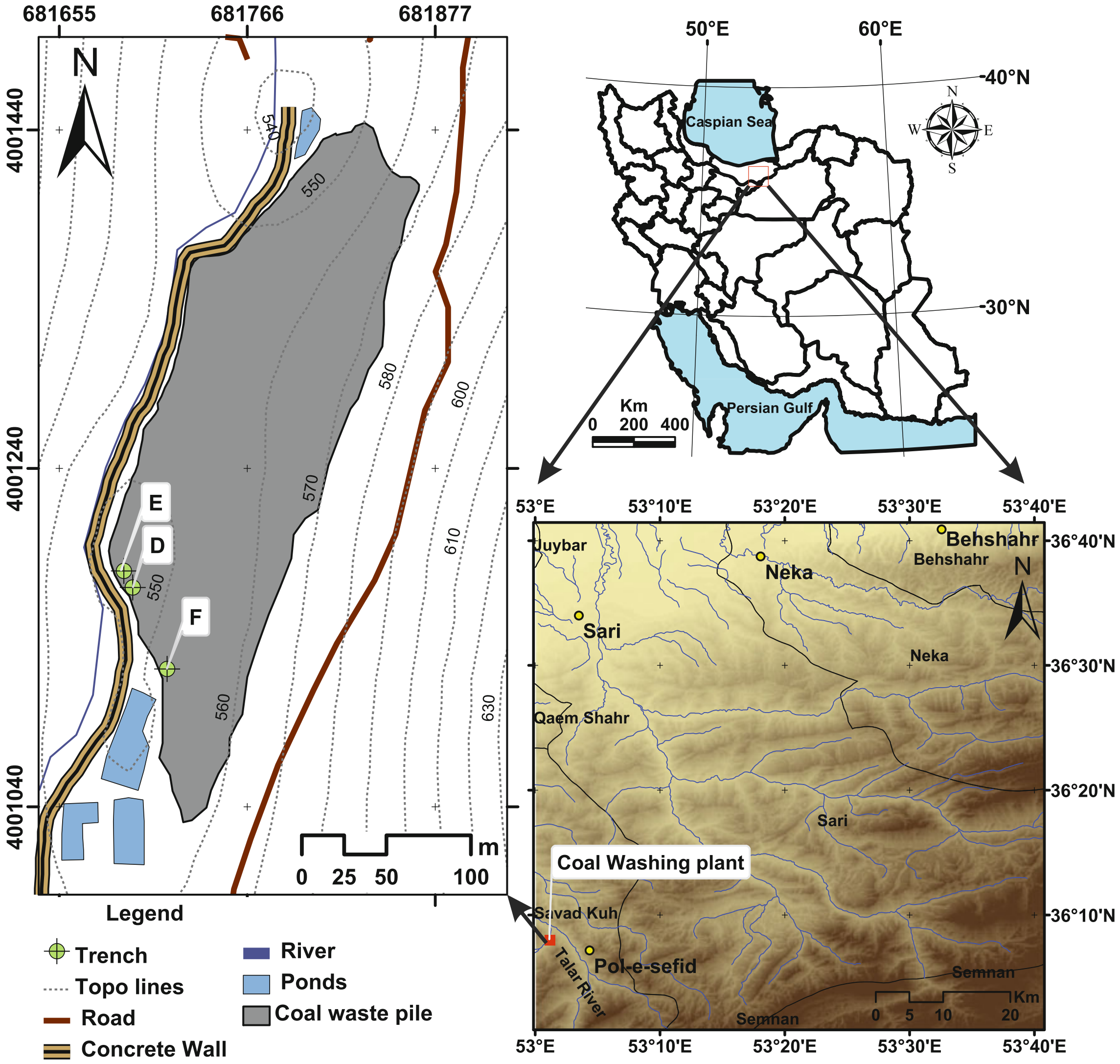


Fig. 1 Geographical situation of the coal waste pile in the Anjir Tangeh coal washing plant, northern Iran (modified after Shahhoseiny et al. 2011)

Fig. 2 **a** Coal waste pile in the Anjir Tangeh coal washing plant; **b** Ground instability in northern part of the pile

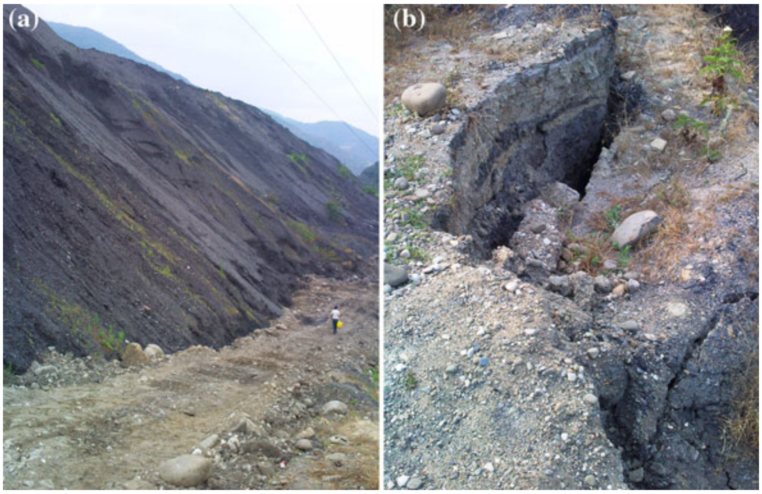


Table 1 Depth samples descriptions of waste pile (modified after Shahhoseiny et al. 2011)

Trench	Height (m)	Geographical location (UTM)	Sampling depth (m)	No. of samples
D	548	681682, 4001169	0, 0.3, 0.8, 1.3, 1.8, 2.3, 2.8, 3.3, 3.8	9
E	549	681681, 4001175	0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4	9
F	550	681685, 4001121	0, 0.5, 1, 1.5, 2, 2.5, 3	7

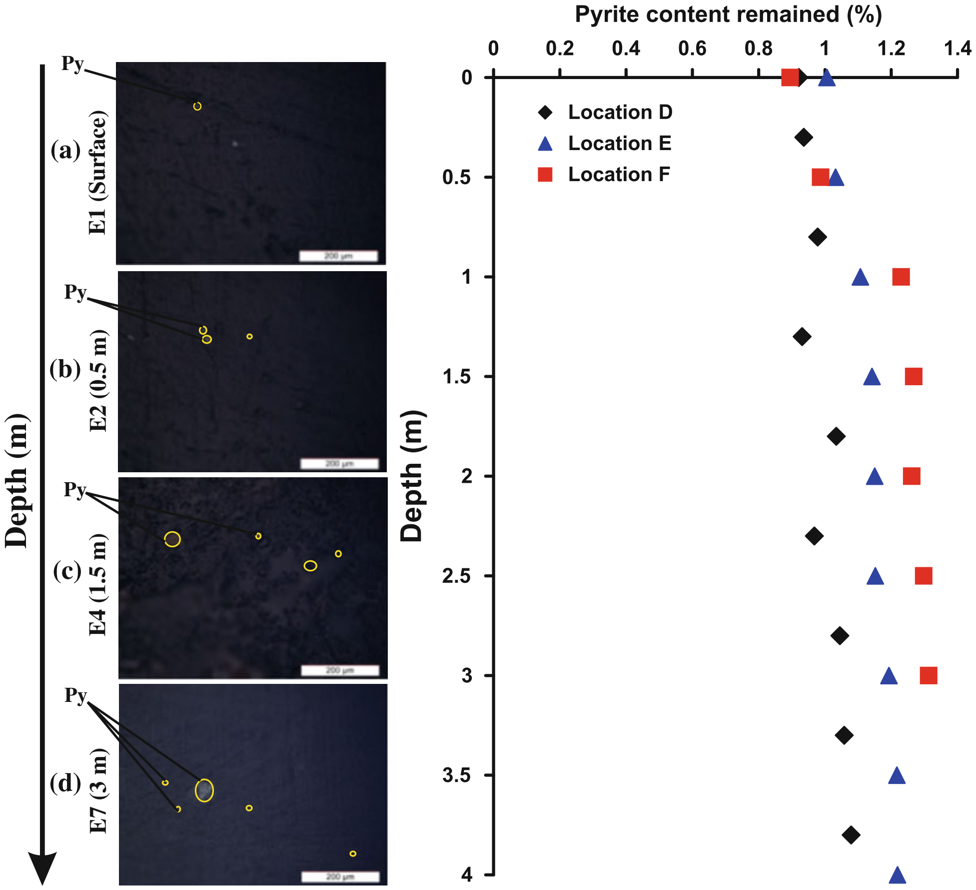


Fig. 3 Polished sections of E profile solid samples in the waste pile, showing pyrite depletion in the samples at shallower depths of the pile. (**a**) The pile surface, (**b**) at a depth of 0.5 m, (**c**) at a depth of 1.5 m, (**d**) at a depth of 3 m, (**e**) concentration of pyrite remained (wt%) versus depth. Py: pyrite, *Filled diamonds* indicate D, *filled triangles* indicate E, *filled squares* indicate F profiles (modified after Shahhoseiny et al. 2011)

the coal waste pile, determine the extent of pyrite oxidation, determine the mobility of Fe, S, and trace elements, and provide new data for further reclamation plans.

Site Description

The Anjir Tangeh coal washing plant is located in the city of Zirab in the province of Mazandaran in northern Iran (Fig. 1). The Zirab-Karmozd coal deposit is interbedded with Upper Triassic–Lower Jurassic shales, sandstones, and siltstones of the Shemshak formation. The coal deposit is bounded by thick layers of dolomite (Elika formation) below and by dolomite limestone (Tiz Kuh formation) above (Geological Survey of Iran 2002). From 1989 to 2011, the coal washing plant has produced and dumped more than 1.5 Mt of coal waste in the plant area. The waste pile, which is approximately few tens of metres in height, covers an area of about 2 ha in 2010. It seems that the waste pile has been deposited without concern for environmental issues (Fig. 2).

The receiving stream is the Dalilam River, which originates in the Alborz Mountains, flows past the coal washing plant, and later joins the Talar, the major river of this region. The Talar River discharges into the Caspian Sea. The Dalilam River flow rate varies seasonally. Little information is available about groundwater in the study area, which is used for agricultural activities; however, potable water is obtained from a spring. The weather is very cold in winter and moderate and humid in summer with an average annual precipitation of 449.2 mm and an average temperature of 15.5 °C. Typical annual potential evaporation is 99.2 mm (Rainfall data of Mazandaran province 2008).

Table 2 Concentration of pyrite in solid samples of waste pile (modified after Shahhoseiny et al. 2011)

Location D			Location E			Location F		
Sample	Depth (m)	FeS_2 (wt%)	Sample	Depth (m)	FeS_2 (wt%)	Sample	Depth (m)	FeS_2 (wt%)
D1	0	0.92	E1	0	1.01	F1	0	0.90
D2	0.3	0.94	E2	0.5	1.03	F2	0.5	0.99
D3	0.8	0.98	E3	1	1.11	F3	1	1.23
D4	1.3	0.93	E4	1.5	1.14	F4	1.5	1.27
D5	1.8	1.03	E5	2	1.15	F5	2	1.26
D6	2.3	0.97	E6	2.5	1.15	F6	2.5	1.30
D7	2.8	1.05	E7	3	1.19	F7	3	1.31
D8	3.3	1.06	E8	3.5	1.22	–		–
D9	3.8	1.08	E9	4	1.22	–		–

Materials and Methods

Sampling and Sample Preparation

The surface of the oxidised wastes is grey in colour. Three trenches (D, E, F) were excavated in the waste pile from the surface to a depth of 3.8, 4, and 3 m respectively. Samples were collected in July 2010 from the surface and various depths in each trench. Sampling locations are indicated in Fig. 1. A Garmin geographical positioning system unit was used to record geographical coordinates (latitude/longitude) of the sampling points. Altogether 25 solid samples, 1 kg each in weight were taken in 0.5 m intervals from the coal waste pile (Table 1) and placed in separate plastic bottles. All samples were dried at room temperature and then sieved into size fractions of 20, 30, 60, 100, 140, and 200 meshes in the mineral processing laboratory of Shahrood University of Technology. The samples were divided into two parts for mineralogical and geochemical analysis.

Mineralogical Analysis

The above 200 mesh sample fractions were embedded in epoxy resin and then prepared as standard polished sections in the mineral processing laboratory of Shahrood University of Technology. Optical microscopy (reflected and transmitted light) was used to characterise the pyrite mineral.

Geochemical Analysis

The less than 200 mesh sample fractions were ground in an agate mill and acid digested. The resulting solutions were then analysed for 54 bulk element concentrations by inductively coupled plasma-mass spectrometry (ICP-MS) at ACME Analytical Laboratories Ltd., Canada. The paste pH, electrical conductivity (EC), and major anion (HCO_3^-, CO_3^{-2}, Cl^-, and SO_4^{-2}) concentrations were analysed in the water laboratory of the Semnan Science and Technology Park, Iran. Paste pH is a method for estimating the acid

Table 3 Geochemical analysis of waste pile samples in the Anjit Tangeh coal washing plant; all concentrations are in mg/L; electrical conductivity is in µS/cm (modified after Shahhoseiny et al. 2011)

Parameter						
Samples	pH	EC × 103	SO_4^{-2}	CO_3^{-2}	HCO_3^-	Cl^-
Location D						
D1	4.6	6.2	58	0	1.2	2.5
D2	3.2	8.9	83	0	1.2	5
D3	6.3	8.7	83	0	1.2	2.5
D4	7.5	6.4	61	0	1.2	2.5
D5	7.1	4.2	36	0	1.2	4.5
D6	7.1	6.2	59	0	1.2	2.5
D7	7.3	6.2	58	0	1.2	2.5
D8	7.2	6.5	62	0	1.2	2.2
D9	6.6	5.9	55	0	1.3	2.5
Location E						
E1	5	25	75	0	1.1	12
E2	6	22	93	0	1.2	11
E3	7.3	4.3	39	0	1.2	2.5
E4	6.7	3.9	35	0	1.2	2.5
E5	6.6	5.6	51	0	2.5	2.5
E6	7	6	54	0	2	3.7
E7	6.7	6.7	64	0	2	0.3
E8	7.5	5.5	49	0	2	3.7
E9	7	6.5	60	0	2	2.5
Location F						
F1	3.4	3.9	32	0	1.2	5
F2	5.2	6.4	73	0	1.2	2.5
F3	6.8	7.5	85	0	1.2	2.5
F4	5.5	9.1	87	0	1.2	2.5
F5	7.2	8.1	76	0	2.5	2.5
F6	7.4	9.2	86	0	2.5	3.7
F7	7.4	10	100	0	1.2	4.5

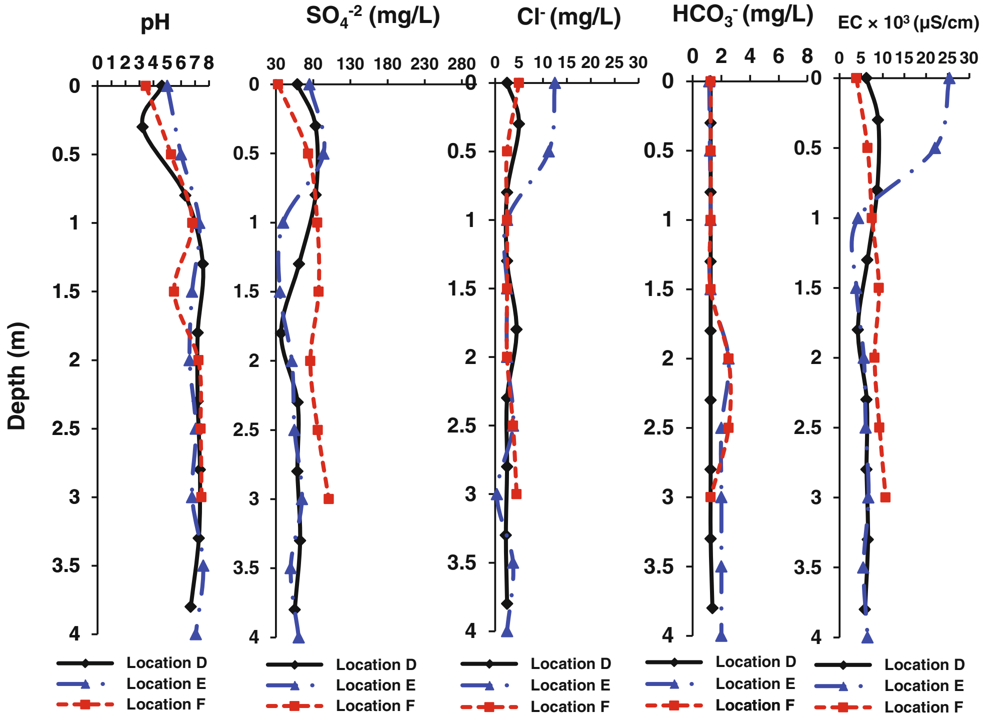


Fig. 4 Vertical depth profiles of pH, EC and major anions (SO_4^{-2}, HCO_3^- and Cl^-) variations for trenches D, E, and F of the coal waste pile at the Anjir Tangeh coal washing plant (modified after Shahhoseiny et al. 2011)

producing potential of soil samples (Sobek et al. 1978). An ORION 420A metre was used to measure the pH values of the paste. The concentrations of major anions in the paste samples were determined using a Palintest-Photometer 7000.

Total reduced inorganic pyrite was determined using the ASTM method (Doulati Ardejani et al. 2010; Gladfelter and Dickerhoof 1976). Hydrochloric acid (HCl) was used to dissolve the sulphate minerals. A 670 Shimadzu atomic absorption (AA) spectrometer at the Shahrood University of Technology was used to measure dissolved iron and the concentration of pyrite that remained in the coal waste particles after the pyrite was extracted from the coal using HNO_3.

AMD Evaluation

The maximum potential acidity (MPA) was calculated assuming that the total sulphur content was expressed as pyrite; the acid generation potential (PA) was calculated assuming that all of the pyrite was available for oxidation, and converted to calcite equivalents (kg $CaCO_3$/t) by multiplying by a factor of 31.25 (Sobek et al. 1978). The neutralization potential (NP) was determined by alkalinity titration. The net neutralization potential (NNP) is the difference between the MPA and NP. NNP is commonly used to indicate whether a material has potential to generate AMD. A positive NNP indicates that the sample may have sufficient NP to prevent acid generation. Conversely, a negative NNP indicates that the material may be acid generating.

Results and Discussion

Mineralogical Data

Pyrite was the primary sulphide mineral and was fine or coarse grained and cubic in polished sections of coal waste pile samples (Fig. 3). The polished section from the pile surface indicates a lack of pyrite (Fig. 3a). Due to reduced oxygen diffusion with depth, the pyrite content increased with depth. Pyrite crystals were only partially oxidised at shallow depths (Fig. 3b), less oxidised pyrite grains were observed in the E4 sample (Fig. 3c), and completely unoxidised grains occurred in the E7 through E9 samples (Fig. 3d).

Geochemical Data

Pyrite Oxidation

The important factor that determines the reactivity of the fine grains in the waste pile is the pyrite remaining. The content of pyrite remaining ranged from (0.921–1.079 wt%), (1.006–1.219 wt%) and (0.895–1.313 wt%) in D, E, and F profiles, respectively (Table 2) (Shahhoseiny et al. 2011). The minor difference between pyrite remaining at shallow and greater depth of each profile reflects the fact that little of the pyrite in the waste pile has oxidised.

The pyrite oxidation process has been more intense in profile F than D and E because oxygen can flow more easily through the coarse grained waste particles containing

Table 4 AMD evaluation results of samples in the Anjir Tangeh coal waste pile

Sample	S_{total} (wt%)	S_{pyrite} (wt%)	$S_{sulphate}$ (wt%)	$S_{Non\ pyritic}$ (wt%)	$S_{sulphate}/S_{pyrite}$	MPA total S (kg $CaCO_3$/t)	PA pyrite (kg $CaCO_3$/t)	NP (kg $CaCO_3$/t)	NNP total S (kg $CaCO_3$/t)	NNP pyrite (kg $CaCO_3$/t)
Location D										
D1	0.55	0.49	0.01	0.05	0.02	17.18	15.31	1.54	−15.64	−13.77
D2	0.79	0.5	0.02	0.27	0.04	24.68	15.62	0.06	−24.62	−15.56
D3	0.6	0.52	0.03	0.05	0.05	18.75	16.25	30.18	11.43	13.93
D4	0.55	0.5	0.02	0.03	0.04	17.18	15.62	49.37	32.19	33.75
D5	0.6	0.55	0.01	0.04	0.01	18.75	17.18	46.57	27.82	29.39
D6	0.55	0.52	0.01	0.02	0.01	17.18	16.25	46.53	29.35	30.28
D7	1.31	0.56	0.01	0.74	0.01	40.93	17.5	47.54	6.61	30.04
D8	0.6	0.57	0.02	0.01	0.03	18.75	17.81	47.11	28.36	29.29
D9	0.63	0.58	0.01	0.04	0.01	19.68	18.12	43.49	23.81	25.37
Location E										
E1	0.88	0.54	0.25	0.09	0.462	27.5	16.87	3.29	−24.21	−13.58
E2	0.94	0.55	0.31	0.08	0.563	29.37	17.18	21.05	−8.32	3.86
E3	0.68	0.59	0.013	0.077	0.022	21.25	18.43	47.82	26.57	29.39
E4	0.82	0.615	0.011	0.194	0.017	25.62	19.21	41.4	15.78	22.18
E5	0.69	0.616	0.017	0.057	0.027	21.56	19.25	74.9	53.34	55.65
E6	0.71	0.62	0.018	0.072	0.029	22.18	19.37	72.4	50.22	53.03
E7	0.77	0.64	0.021	0.109	0.032	24.06	20	66.1	42.04	46.1
E8	0.68	0.655	0.016	0.009	0.024	21.25	20.46	78.75	57.5	58.29
E9	0.83	0.657	0.02	0.153	0.03	25.93	20.53	72.2	46.27	51.67
Location F										
F1	0.5	0.48	0.011	0.009	0.022	15.62	15	0.1	−15.52	−14.9
F2	0.64	0.53	0.024	0.086	0.045	20	16.56	6.18	−13.82	−10.38
F3	1.46	0.66	0.028	0.772	0.042	45.62	20.62	41.55	−4.07	20.93
F4	0.92	0.683	0.029	0.208	0.042	28.75	21.34	9.8	−18.95	−11.54
F5	1.18	0.68	0.025	0.475	0.036	36.87	21.25	93.75	56.88	72.5
F6	0.9	0.69	0.029	0.181	0.042	28.12	21.56	96.2	68.08	74.64
F7	0.8	0.7	0.034	0.066	0.048	25	21.87	48.62	23.62	26.75

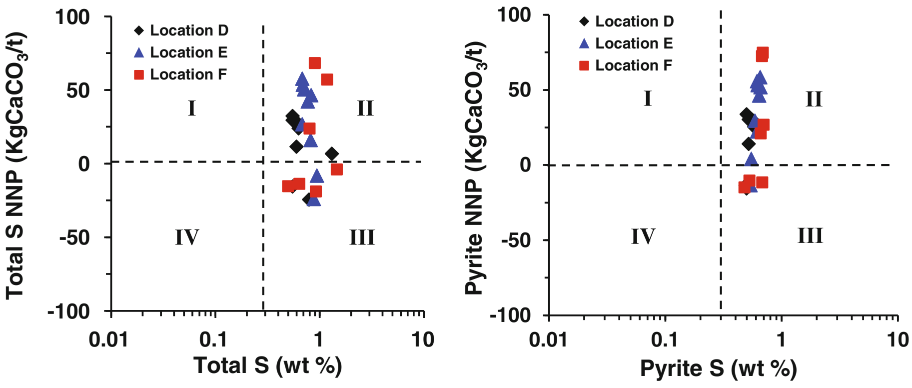


Fig. 5 **a** Total S NNP values versus total S content, **b** Pyritic NNP values versus pyritic S content. Field III: AMD possible but not persistent due to low S content; Field IV: AMD possible and persistent due to high S content; Fields I and II: AMD impossible. 0.3 wt% S as a limit above which AMD persists (Soregaroli and Lawrence 1997)

pyrite in profile F; oxidation has reached the upper 80, 50, and 100 cm of D, E, and F profiles, respectively (Fig. 3e). The rate of pyrite oxidation decreased sharply at lower depths, up to a depth of about 1 m, in the three profiles; below this depth, pyrite oxidation gradually decreased, and it had completely ceased at an approximate depth of 3 m.

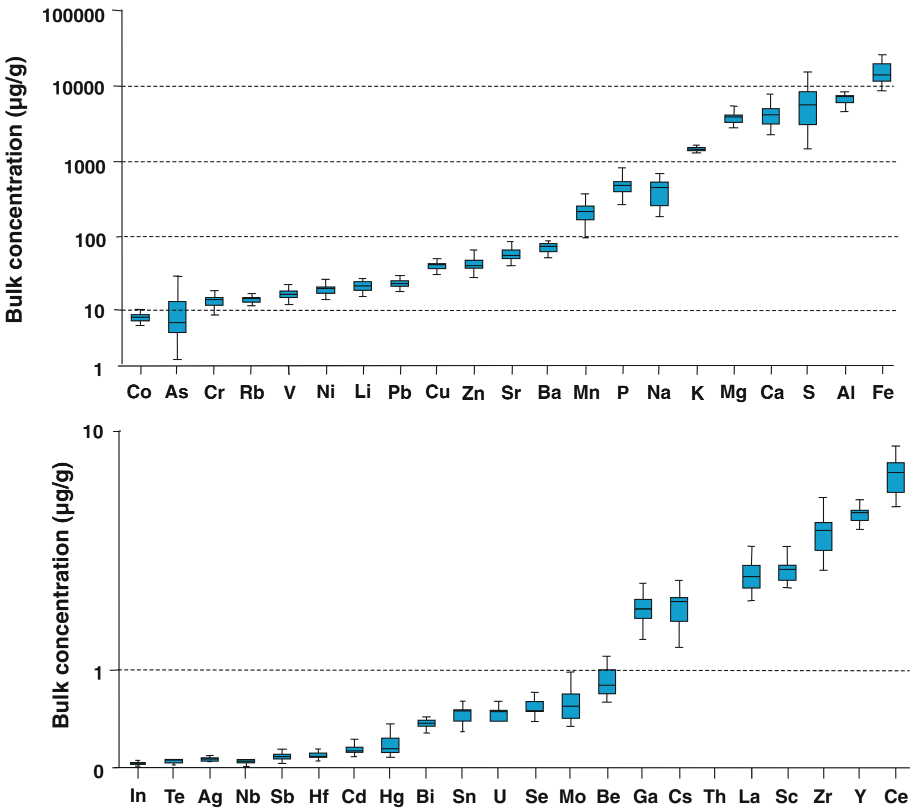


Fig. 6 Bulk concentrations of 43 elements in 25 solid samples of the coal waste pile in the Anjir Tangeh coal washing plant

pH Values and Major Anions

The results of the geochemical analysis for pH, EC and major anion concentrations in the coal waste pile samples are given in Table 3. Variations of pH, EC, SO_4^{-2}, HCO_3^-, and Cl^- concentrations with depth in the solid samples from the three profiles are shown in Fig. 4.

The maximum concentrations of SO_4^{-2}, 83.3, 93.92, and 100.95 mg/L, were observed at a depth of 0.8 m in profile D, 0.5 m in profile E and 3 m in profile F, respectively. The SO_4 concentration reflects pyrite oxidation and decreases with depth, inversely with the pyrite content remaining in the solid samples from profiles D and E. This trend is not observed in profile F, presumably because water migrates rapidly through profile F, reducing the possibility of sulphate precipitation in the solid phase at the upper layers of the waste profile. The lowest pH values (3.24, 5, and 3.47) were measured at 0.3 m in profile D and in the superficial part of profile E and F, respectively. According to the paste pH values, samples can be classified into two main groups: (1) an unoxidised zone (1–4 m) with near normal pH values in the 6.0–7.59 range, and (2) an oxidised zone (0–1 m in the three profiles) with pH values ranging from 3.24 to 6. The low pH in group 2 is consistent with the occurrence of the small amount of residual pyrite oxidation products (Fe-sulphates). The acid released by pyrite oxidation has depleted the concentration of carbonate minerals in the waste pile vertical profiles, so that a zero concentration was detected for CO_3^{2-} ion in the three profiles and the peak concentrations of HCO_3^- (1.3, 2.5, and 2.5 mg/L) was observed at 3.8, 2, and 2 m in profiles D, E and F, respectively. Li (2000) demonstrated that for mine wastes with a low sulphide content and low NP, the proportion of dissolved carbonates that effectively neutralise acid decreases when sulphide oxidation drops below a certain rate because bicarbonate ions are dissolved and flushed out of the material without acid neutralization. The maximum EC values (8.9×10^3, 25×10^3, and 10×10^3 µS/cm) was detected at depths of 0.3 m, the pile surface, and 3 m in profiles D, E, and F, respectively. EC decreased with depth in profiles D and E. However, it gradually increased versus depth in profile F. EC values correlate with SO_4^{-2} and Cl^- concentrations in profiles D and E (Fig. 4).

AMD Evaluation

The AMD evaluation results are given in Table 4. S_{Pyrite} values range between 0.49 and 0.58 wt%, 0.54 and 0.657 wt%, 0.48 and 0.7 wt% in profiles D, E, and F, respectively. S_{Pyrite} values are significantly higher in the fresh coal waste than in the weathered material, most probably due to pyrite oxidation. The NP values range from 0.06–49.37, 3.29–78.75, and 0.1–96.2 kg $CaCO_3$/t in profiles D, E, and F, respectively. All of the NNP of total S

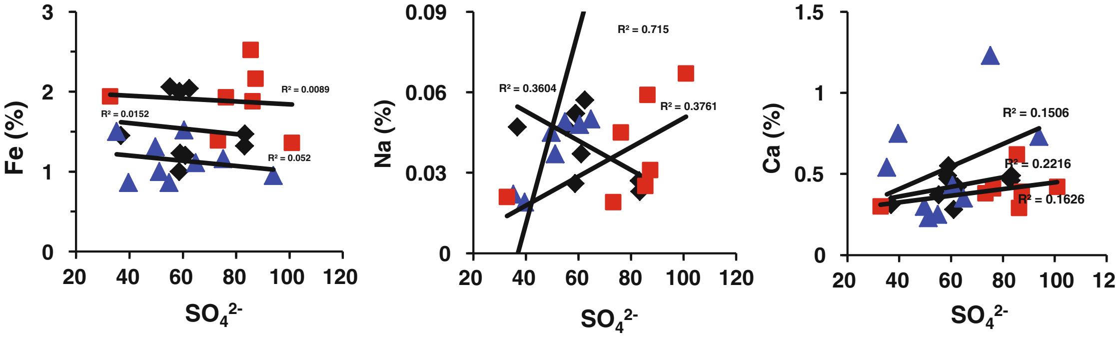
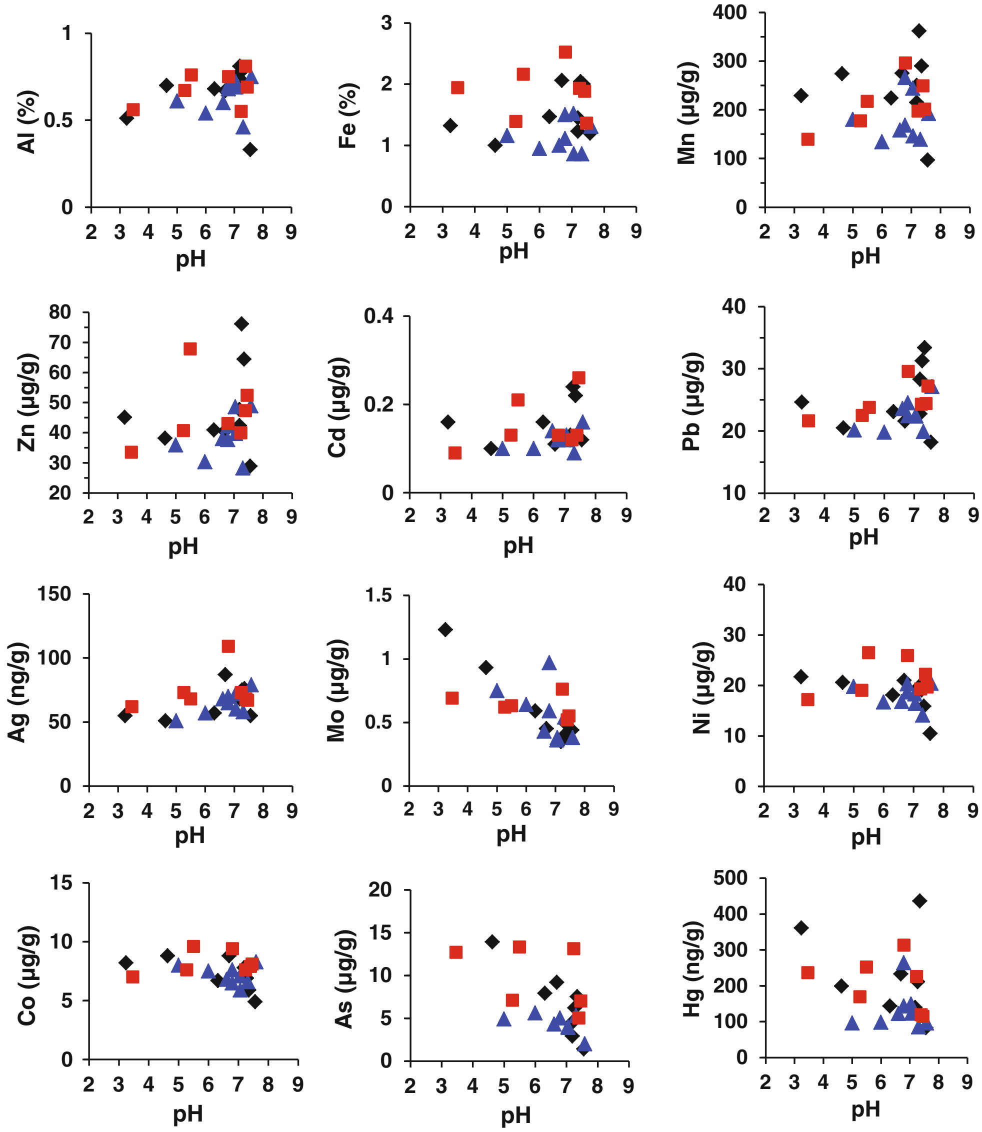


Fig. 7 Fe, Ca, and Na concentrations (wt%) plotted against SO_4^{-2} concentration (mg/L) in pile. *Filled diamonds* indicate D, *filled triangles* indicate E, *filled squares* indicate profile F samples

Fig. 8 Bulk contents of some elements in the coal waste samples as a function of the paste pH values. *Filled diamonds* indicate D, *filled triangles* indicate E, *filled squares* indicate profile F samples



values in D1 (−15.64), D2 (−24.62), E1 (−24.21), E2 (−8.32), F1 (−15.52), F2 (−13.82), F3 (−4.07), and F4 (−18.95) samples were negative, indicating that AMD process could occur, while NNP values of other samples in the coal waste pile were positive, indicating AMD generation was unlikely.

The maximum $S_{Sulphate}/S_{Pyrite}$ ratio was observed at depths of 0.8, 0.5 and 3 m in profiles D, E, and F, respectively (Table 4). The low $S_{Sulphate}/S_{Pyrite}$ ratio at higher depths in the bulk waste material suggests that although most of the total sulphur is in the pyrite state, a small fraction has been oxidised to sulphate. The total S and pyritic S were plotted against the NNP, similarly to Marescotti et al. (2007) and Soregaroli and Lawrence (1997) (Fig. 5). The D1 and D2 samples of profile D, the E1 sample of profile E, and the F1, F2, and F4 samples of profile F fell in Field III where AMD occurs due to high S contents (more than 0.3 wt%).

On the other hand, other samples fell in Field II (non-acid forming field). The AMD processes within the upper part of vertical profiles (0–1 m) in the coal waste pile corresponded to a "transition from an early to a maturing stage" (stage 2 early alteration: Jambor 2003; Marescotti et al. 2007) where most of the sulphides were at least partially altered. The presence of this stage indicated that the waters infiltrating from the upper part of the profiles were modified solutions that were oversaturated with respect to most transition and heavy metals. The lower part of the vertical profiles (1–4 m) is excluded from AMD processes due to insufficient AMD potential.

Major and Trace Elements

One of the major aims of this research was to determine the mobility of trace elements in the coal waste pile (Supplemental Tables 1 and 2, available in the electronically published version of this article). Elements with very low concentrations (such as Be, Bi, Hf, In, Nb, Sb, Sn, and Te) or below the detection limit of ICP analysis (such as Ti, Au, B, Ge, Pd, Pt, Re, Ta, Tl, and W) are not presented. Total S concentrations ranged from 0.55–1.31, 0.68–0.94, and 0.5–1.46 wt%, while Fe concentrations ranged from 1–2.06, 0.86–1.52, and 1.36–2.52 wt% in profiles D, E, and F, respectively. The Fe and S contents reflect the presence of pyrite.

Calcite, dolomite, and carbonaceous shales are major components of the coal waste pile. The aluminum (0.33–0.81 wt%) content indicate the presence of aluminosilicate in clay minerals. The waste pile are characterised by significant amounts of trace elements: Mn (97–362 µg/g), Ba (53.4–124.3 µg/g), Sr (35–98.8 µg/g), Zn (28.3–76.1 µg/g), Cu (30.04–48.9 µg/g), Pb (18.19–33.39 µg/g), Li (10.5–26.3 µg/g), and Ni (10.5–26.5 µg/g). Fe, Al, S, Mn, Ba, Sr, Zn, and Cu were the abundant major and trace elements (Fig. 6).

Newly Formed Minerals

Oxidation of pyrite in the coal waste pile and the weathering process introduces considerable amounts of aluminum, iron, magnesium, calcium, sodium, and potassium into solution. As the pore water in the weathering residue evaporates, these ions precipitate out as hydrous sulphates (efflorescent salts). Grains commonly are cemented to surrounding particles by secondary and tertiary gypsum at various depths (Boulet and Larocque 1997). The SO_4^{-2} concentration is positively correlated with Ca (r = 0.47) and negatively correlated with Na (r = −0.6) in the profile D samples (Fig. 7). The SO_4^{-2} is strongly positively correlated with Na (r = 0.84) and Ca (r = 0.38) in the profile

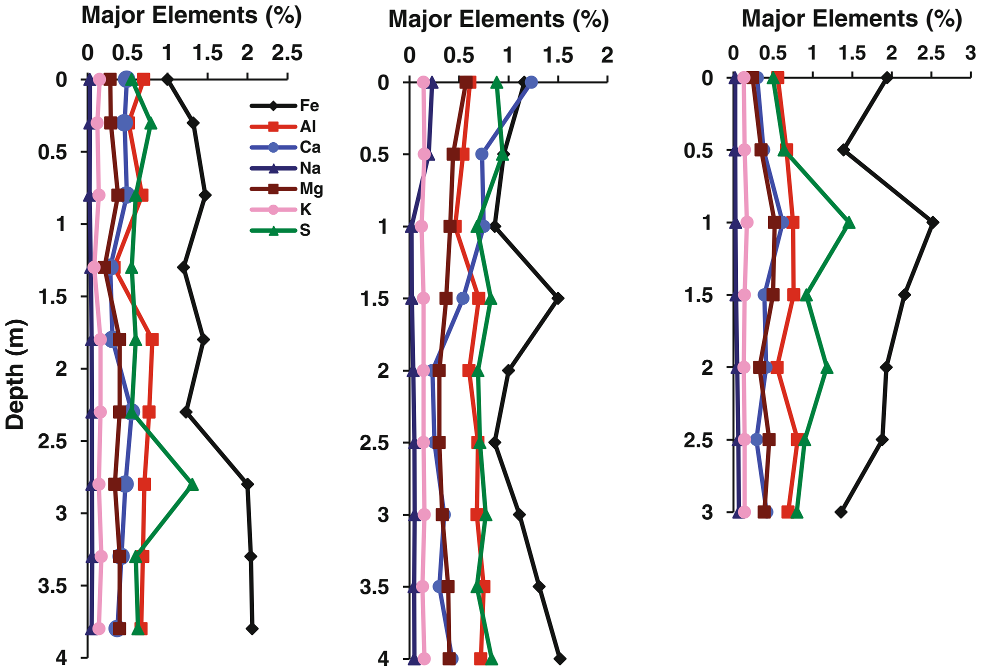


Fig. 9 Depth profiles of Fe, S, Al, Ca, Mg, Na and K (wt%), (**a**) for D, (**b**) E and (**c**) F profiles from the coal waste pile (Shahhoseiny et al. 2011)

E samples (Fig. 7). Furthermore, SO_4^{-2} and Na (r = 0.61), and SO_4^{-2} and Ca (r = 0.4) are positively correlated in profile F. There is no correlation between SO_4^{-2} and Fe in profiles D, E, and F samples though slight amounts of Fe are thought to be associated with sulphate phases in the waste pile.

Overall, the bulk concentration of Ca and Na increased with increasing SO_4^{-2} concentration in the solid phase pile samples indicating that these elements might be associated with sulphate minerals. Gypsum, hydrous iron oxide (goethite), and Fe-hydroxides are probably the most common secondary mineral results of pyrite oxidation in the oxidised zone of the waste pile. The relationships between the bulk contents of some elements with paste pH values are shown in Fig. 8. The bulk concentration of Mo (r = −0.16), Ni (r = −0.22), Co (r = −0.3), As (r = −0.46), and Hg (r = −0.31) show slightly negative correlations against paste pH in the waste pile samples.

The paste pH exhibits a somewhat positive correlation with Mn (r = 0.11), Zn (r = 0.18), Al (r = 0.21), Cd (r = 0.23), Pb (r = 0.31), and Ag (r = 0.37). No clear correlation was observed between Fe and paste pH, probably due to various compounds controlling its solubility over a wide range of pH. Bulk concentrations of metal cations (Mn, Zn, Al, Cd, Pb, and Ag) were low under acidic conditions (in oxidised zone) due to the enhancement of metal dissolution; metal liberation decreased at near neutral conditions (in the unoxidised zone). The oxidation of pyrite may release hosted trace elements, such as As, Hg, Se, or Pb to the environment (Finkelman 1994). The distributions of major elements (Fe, S, Al, Ca, Mg, Na, and K), and some trace and rare earth elements versus depth are shown

Fig. 10 Depth profiles of Mo, Sr, Zr, Ni, Mn, Pb, Zn, and Ag for profiles D, E, and F of the coal waste pile (Shahhoseiny et al. 2011)

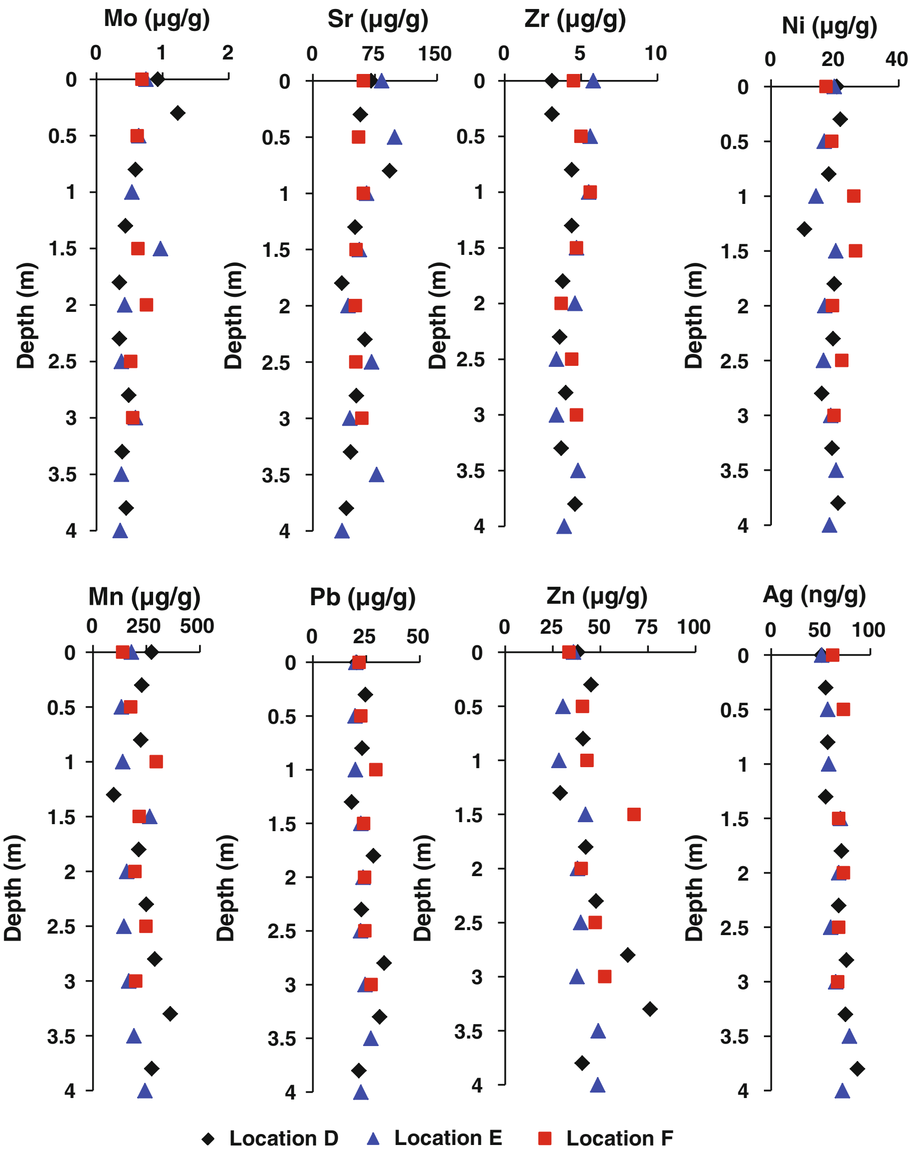
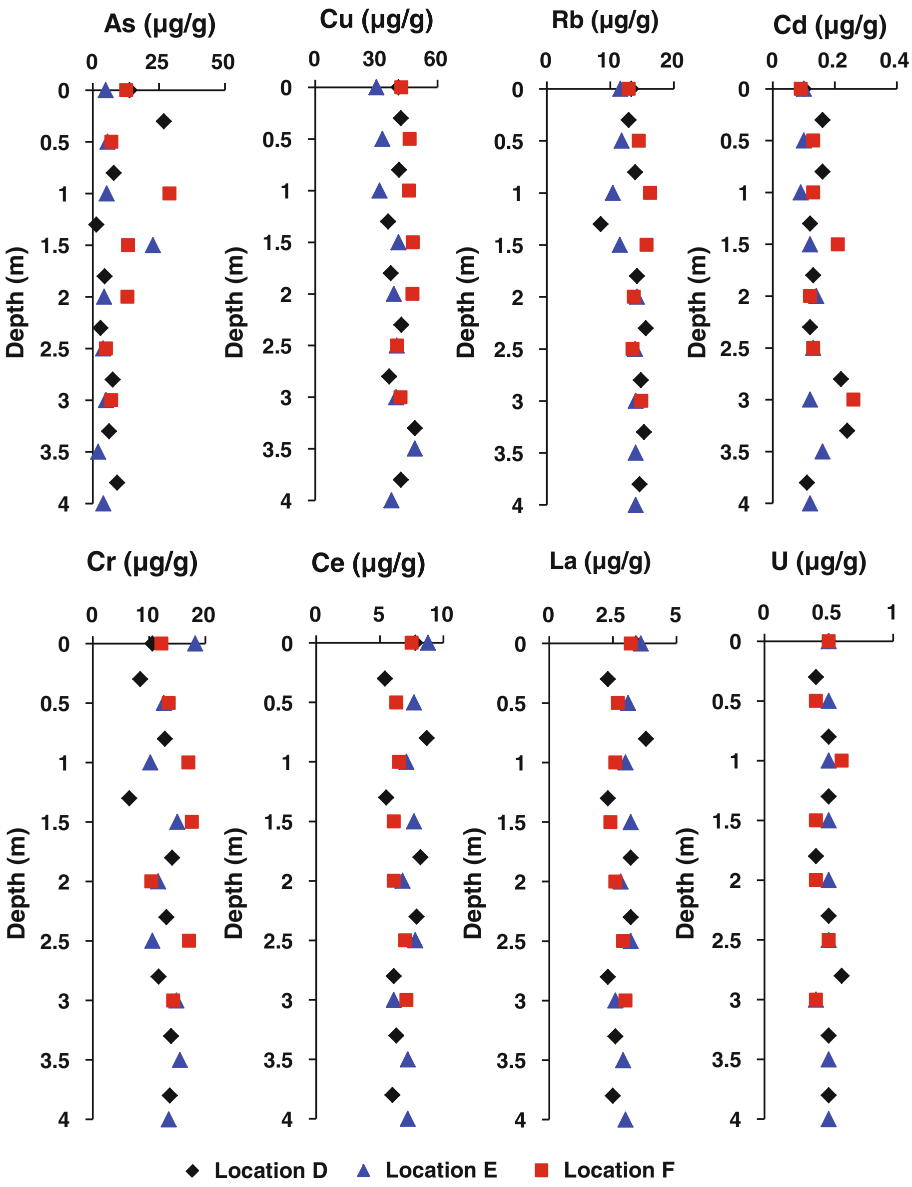


Fig. 11 Depth profiles of As, Cu, Rb, Cd, Cr, Ce, La, and U for profiles D, E, and F of coal waste pile (Shahhoseiny et al. 2011)



in Figs. 9, 10 and 11. Elements including S and Fe increased with increasing depth because the leaching of S and Fe increases as pyrite oxidation proceeds in the waste pile. The peak concentrations of Fe were observed at 3.8, 1.5, and 1 m depth of profiles D, E, and F, respectively. Na increased with depth, K and Mg show an almost constant trend with increasing depth in profiles D and F, but in profile E, Ca, Mg, and Na initially decreased trend to depths 2, 2, and 1 m, respectively. The decrease in the concentrations of these elements with depth is unusual. This trend may be due to the mobility restrictions of a Ca- and Na-bearing complex, evaporation of Ca-, Na-, and Mg-rich pore waters near the surface, and generation of tertiary minerals, such as gypsum.

Elements including Ag, Al, Cu, Cd, Mn, Pb, Rb, and Zn increased with increasing depth. The bulk concentrations of these metals increased with increasing pH; this distribution can be explained by adsorption models (Al et al. 1997). Elemental U shows an almost constant trend with depth. Concentrations of Mo, Sr, Zr, Ni, Cr, Ce, and La decreased with increasing depth. Arsenic initially decreased with depth down to 2 m, then increased with depth. Co-precipitation or adsorption of As onto Fe-(oxy) hydroxides scavenging dissolved As ions in the oxidised zone could be responsible for this trend (Lee et al. 2005). The peak concentrations of As were observed at 0.3, 1.5, and 1 m depths of profiles D, E, and F, respectively. The highest concentrations of Al were observed at depths of 2–2.5 m in profile F. The peak concentrations of Cu, Pb, Zn, Cd, Ni, Cr, Co, As, Ga, Rb, Zr, Mo, and Ag were observed at depth intervals 3.3–3.5, 3–3.5, 3–3.5, 3–3.5, 3.4–3.5, 1.5–2, 3.5–4, 1–1.5, 1.5–2, 1.9–2, 1–1.2, 0.9–1.5, and 3.5–4 m, respectively.

Environmental Impacts and the Reclamation Process

Coal washing at Anjir Tangeh has produced large amounts of wastes that pose environmental hazards. They generally inhibit the growth of vegetation and are characterised by steep, eroded, unstable banks (Doulati Ardejani et al. 2011a). Although not discussed here, the drainage from these wastes has slightly affected water quality (Doulati Ardejani et al. 2011b) in downstream areas that are used for agricultural purposes, although their impact on the human population in the study area is not too serious. According to Doulati Ardejani et al. (2011a), the following approaches should be undertaken for environmental protection:

- The waste pile should be covered with soils and other amendments to promote the growth of plants. Alternatively, a plastic barrier could be constructed over the coal waste pile to limit the infiltration of water and transport of oxygen to the pyritic wastes.
- Steep slopes should be regraded and an appropriate water management system should be established to keep water from infiltrating the waste pile.

Conclusions

Together, the geochemical and mineralogical studies show how pyrite oxidation is proceeding within the coal waste pile. The solid material contains about 0.89–1.31 wt% pyrite; calcite and dolomite are the major gangue minerals. Geochemical analyses showed that the rate of pyrite oxidation decreases sharply at depths of up to 1 m, where the oxygen concentration decreases rapidly. Elements such as Mn (97–362 µg/g), Zn (28.3–76.1 µg/g), Cu (30.04–48.95 µg/g) and Pb (18.19–33.39 µg/g) are present in significant concentrations in the solid samples. All of the samples have a very high NP (0.06–96.2 kg $CaCO_3$/t). Samples D1, D2, E1, F1, and F2 in the oxidised zone (0–1 m) have some acid production potential because dissolution by atmospheric precipitation have leached carbonate minerals out of this zone. Variations in the geochemical depth profile for elements indicate that Mn, Zn, Pb, Cu, Ag, and Cd are more mobile than Mo, Ni, and As and As is immobilised by pyrite oxidation products (Fe-(oxy) hydroxides). Mn, Zn, and Cu may be associated with the pyrite oxidation in the Anjir Tangeh coal waste pile, while As may pose a long-time threat to the environment.

Development of a site rehabilitation and environmental management plan is necessary at Anjir Tangeh to limit further environmental impact. Reclamation techniques, including capping the waste piles with soils and other amendments to promote the growth of vegetation, should be employed. As another option, the coal waste pile could be covered with a plastic barrier to limit the infiltration of water and transport of oxygen to the reactive sulphide minerals in the waste. The result of this investigation will provide useful information for developing an appropriate remediation plan.

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