

Geochemical characterisation of a pyrite containing coal washing refuse pile produced by the Anjir Tangeh coal washing plant in Zirab, Mazandaran province, Northern Iran

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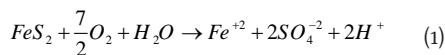
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Abstract Over the past 22 years, coal washing operation in the Anjir Tangeh plant, in Zirab, northern Iran has produced large piles of refuse materials containing pyrite. This paper presents the geochemical characterisation of these refuse materials to evaluate pyrite oxidation. Three trenches were made at about 4 m depth on a specific part of the refuse pile surface. Altogether, 25 solid samples were taken in 0.5 m intervals and geochemically analysed. Results show pyrite oxidation at low depths and subsequent leaching of the oxidation products. Presence of carbonate rocks raised pH of the drainages arising from refuse pile.

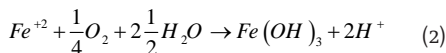
Key Words Coal refuse pile, Anjir Tangeh, coal washing plant, pyrite oxidation, geochemical analyses

Introduction

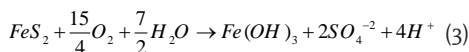
AMD is generated by the oxidation of pyrite and marcasite in coal mining activities (Kim and Chon 2001; Zhao *et al.* 2007, Doulati Ardejani *et al.* 2008 and 2010). Pyrite oxidation rate depends on temperature, pH, acidophilic Fe organisms, humidity and the availability of oxygen in the coal refuse pile, which is mainly controlled by diffusion process. Acidic water produced, acts as a corrosive agent and reacts with the country rock, resulting in the further leaching of many elements (Sullivan and Yelton 1988). Thus, AMD is characterised by low pH, high SO_4^{2-} , Fe, Al and variable concentrations of various elements. Due to pyrite oxidation, sulphuric acid is formed according to Eq. (1) (Stumm and Morgan 1996):



Fe(II) may be further oxidised to Fe(III) hydroxide according to Eq. (2):



Overall stoichiometric reaction describing pyrite oxidation and AMD generation for pH values greater than 3.5 is as Eq. (3):



Geochemical behaviour of Fe and Al mainly controls the mobility of metals through adsorption and co-precipitation in the acidic sulphate water (Bigham and Nordstrom 2000; Lee and Chon 2006). In the present study, the materials and pyrite containing coal refuse pile at the Anjir

Tangeh-Zirab, northern Iran was geochemically and mineralogically analysed.

Methods

Site description

The Anjir Tangeh coal washing plant is located in the Zirab city, 45 km from south of Qaem shahr and 3 km of the Qaem shahr-Tehran road within 681655 E – 681877 E and 4001040 N – 4001440 N, in the Mazandaran province, northern Iran (fig. 1). The climate is humid with sum annual precipitation of 449.2 mm and annual temperature of 15.5 °C. Annual potential evaporation is 99.2 mm, typically (Rainfall data of Mazandaran province 2009). Refuse pile consists of waste from about 22 years of coal washing processing and dumped in the plant area. Approximately 21 Mt dry solids have been produced from the coal processing by gravimetric separation (jigs). Approximately 5 m high pile in 2010 covers an area of about 2 ha. The refuse pile was deposited without concern for environmental issues and was subjected to weathering processes.

Sampling

Surface of the oxidised wastes was coloured median-Gray. Three trenches namely D, E and F were excavated in the refuse pile from surface to depth of 3.8, 4 and 3 m respectively. Samples were collected in July 2010 from the surface and various depths in each trench. Altogether 25 solid samples, 1 kg each in weight were taken in 0.5 m intervals from coal refuse pile (tab. 1).

Geochemical analysis

Paste pH was measured with an electrode after

shaking of prepared sample in deionised water for 1 h. Paste pH and major ions (HCO_3^- , CO_3^{2-} , Cl^- and SO_4^{2-}) concentration were analysed in the water laboratory of the Semnan Science and Technology Park, Iran. Total reduced inorganic pyrite was determined from the organic pyrite according to the method presented by ASTM (Gladfelter and Dickelhoof 1976; Doulati Ardejani *et al.* 2010). HCl acid was used to dissolve sulphates. Pyrite was extracted from the coal using HNO_3 . An AA- 670 Shimadzu atomic absorption at Shahrood University of Technology was used to measure iron in the so-

lution phase. 54 elemental compositions of the solid materials were determined by an inductively coupled plasma mass spectrometer (ICP-MS) by ACME Analytical Laboratories Ltd., Canada. Acid digestion method was used to dissolve solid samples prior to analysis with ICP-MS.

Mineralogical analysis

Four samples taken from F profile were sent to the mineral processing lab of Shahrood University of Technology for polished sections preparation.

Table 1 Depth samples descriptions of refuse pile.

Trench	Height (m)	Geographical situation (UTM)	Sampling Depth (m)	Number 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

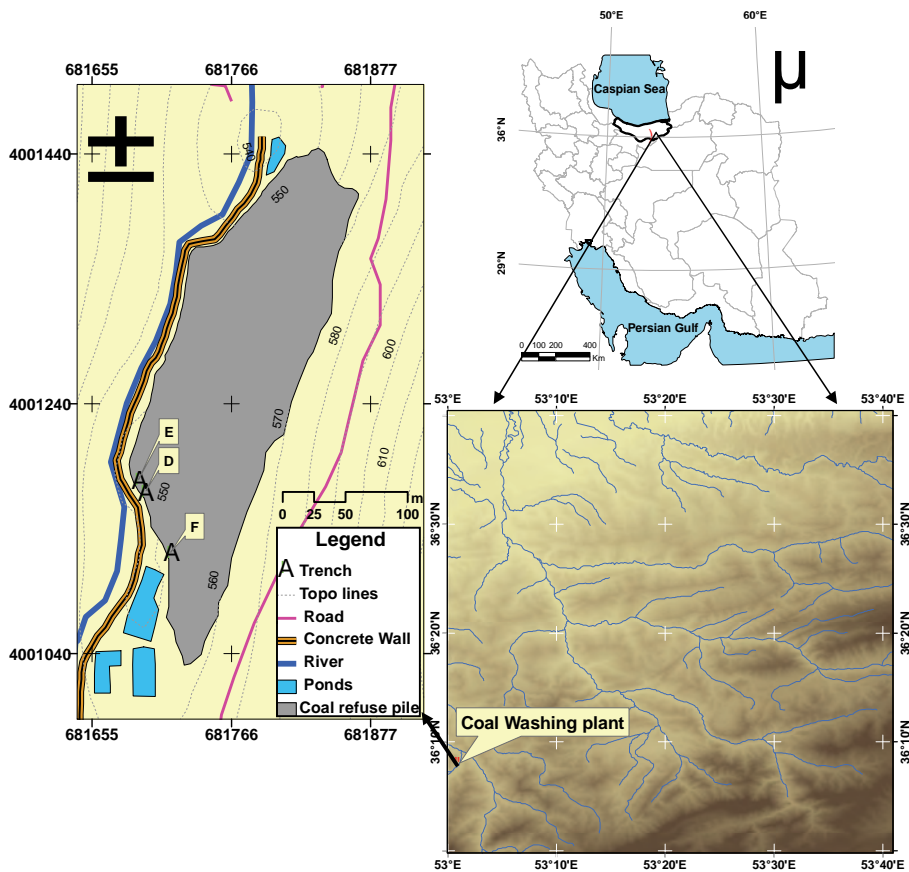


Figure 1 Geographical situation of the coal refuse pile in the Anjir-Tangeh coal washing plant, north of Iran.

Results

Results from the chemical analysis of the three trenches in the coal refuse pile are given in tab 2. Elements with very low concentrations (such as Be, Bi, Hf, In, Nb, Sb, Sn and Te) and below detection limit of ICP analysis (such as Ti, Au, B, Ge, Pd, Pt, Re, Ta, Tl and W) are not presented.

Polished section from the pile surface (fig. 2, a) indicates the lack of pyrite. Due to the reduction in oxygen diffusion with depth, the pyrite content decreased from the surface to a depth of 1 m (fig.

2, b) and 3 m (fig. 2, c) (Doulati Ardejani *et al.* 2010). Analysis of polished sections in profile F showed that the fraction of un-oxidised pyrite increased with depth. Pyrite content in waste pile versus depth is shown in fig. 2d. This figure shows that the rate of pyrite oxidation decreased sharply at lower depths up to 1 m in three profiles (D, E and F) where the oxygen concentration decreased considerably.

Average total sulphur concentration was 0.52 wt % in profile D, 0.48 wt % in E and 0.8 wt % in

Table 2 Minimum, mean and maximum values of geochemical parameters of coal refuse pile.

Location	D			E			F		
	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
pH	3.24	6.381	7.56	6.61	7.22	7.9	3.47	6.162	7.46
Major ions (mg/L)									
HCO₃⁻	1.25	1.263	1.375	1.25	2.194	3.75	1.25	1.607	2.5
CO₃⁻²	0	0	0	0	0	0	0	0	0
Cl⁻	2.25	2.972	5	0.375	4.625	12.5	2.5	3.321	5
SO₄⁻²	36.8	62.038	83.3	35.2	88.88	238.1	32.79	73.678	100.95
Major elements (wt %)									
Al	0.33	0.65	0.81	0.46	0.63	0.75	0.55	0.68	0.81
Ca	0.28	0.42	0.55	0.23	0.53	1.23	0.29	0.4	0.62
Fe	0.52	1.54	2.32	0.86	1.22	2.29	1.36	1.88	2.52
K	0.08	0.14	0.17	0.12	0.14	0.15	0.13	0.141	0.17
Mg	0.21	0.34	0.4	0.3	0.39	0.57	0.24	0.39	0.52
Na	0.023	0.0408	0.057	0.019	0.076	0.228	0.019	0.038	0.067
S	0.19	0.52	1.31	0.15	0.48	0.94	0.4	0.8	1.46
Trace elements (ppm)									
As	1.4	8.93	26.9	2	6.42	22.8	5	12.47	29.1
Ag*	51	66.11	87	51	64.44	79	62	74.28	109
Cd	0.1	0.151	0.24	0.09	0.12	0.16	0.09	0.152	0.26
Co	4.9	7.25	8.8	5.9	7.14	8.3	7	8.17	9.6
Cr	6.5	11.64	14.1	10.2	13.56	18.2	10.4	14.58	17.6
Cu	35.81	40.73	48.9	30.04	37.8	48.95	40.13	44.6	47.91
Ga	1.1	2.03	2.7	1.5	2.01	2.3	1.8	2.21	2.6
Mn	97	246.22	362	134	180.77	266	139	210.85	296
Mo	0.35	0.58	1.23	0.36	0.56	0.97	0.52	1.08	3.79
Ni	10.5	18.45	21.7	14.1	17.94	20.4	17.2	21.4	26.5
Pb	18.19	24.85	33.39	19.79	22.47	27.14	21.61	24.76	29.56
Rb	8.5	15.67		10.4	12.82	14.2	12.9	14.3	
Sr	35	56.6	93	35.5	63.82	98.8	51.4	56.1	61.1
U	0.4	0.48	0.6	0.4	0.48	0.5	0.4	0.45	0.6
Zn	28.9	47.13	76.1	28.3	38.85	48.9	33.5	46.38	67.8
Zr	3.1	3.85	4.6	3.4	4.63	5.8	3.7	4.65	5.6

* Concentration of Ag is given in ppb.

profile F (tab. 2), but the important factor that determines the reactivity of the fine grains in pile is the fraction of pyrite remained within the particles. It ranges from 0.895 to 1.313 wt % in three profiles.

Variations of pH values and SO_4^{-2} concentration with depth in solid samples from the three profiles are shown in fig 3. Maximum concentration of SO_4^{-2} , 83.3, 93.92 and 100.95 mg/L was observed at depth 0.8 m in D profile, 0.5 m in E profile and 3 m in F profile, respectively. Sulphate concentration produced by the oxidation of pyrite is evacuated progressively, in F profile due to rapid migration of water through the F profile. This may cause sulphate precipitation in solid phase.

The lowest pH values 3.24, 5 and 3.47 were measured at depth 0.3 m in D profile and pile surface in E and F profiles, respectively. Paste pH of soil samples in un-oxidised zone is likely to be near normal, while oxidised soil samples (between 0–1 m in three profiles) which include small amount of residual pyrite oxidation products (Fe-sulphates), show a low paste pH.

The refuse pile is also characterised by a significant proportion of aluminium and calcium. Aluminium (0.33–0.81 wt %) contents indicate the presence of alumina-silicate in clay minerals with coal. Calcium (0.23–1.23 wt %) exceeds magnesium (0.21–0.57 wt %), potassium (0.08–0.17 wt %) and sodium (0.019–0.076 wt %). Fe and Na increased with increasing depth of the pile. Elements including K and Mg show almost a constant

trend with depth. The highest concentrations of Al were observed in depths from 2 to 2.5 m.

Among the all elements, the main elements were Mn (97–362 ppm), Zn (28.3–76.1 ppm), Cu (30.04–48.9 ppm), Pb (18.19–33.39 ppm), As (1.4–29.1 ppm), Ni (10.5–26.5 ppm), Co (4.9–9.6 ppm), Cd (0.09–0.26 ppm). Elements including Au and U show almost a constant trend with depth. Concentrations of Mo, Sr, Zr and Ni decreased with increasing depth. Mn, Pb, Zn and Ag increased with increasing depth of the pile.

Results further indicate that the pick concentrations of Cu, Pb, Zn, Cd, Ni, Cr, Co, As, Ga, Rb, Zr, Mo, and Ag were observed in 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. Concentrations of these elements at different depths maybe attributed to their different geochemical behaviour, characteristics and different mobility. These elements are probably sequestered in the secondary minerals through co-precipitation and adsorption processes. Given the relative low solubility of sulphate minerals, this will likely retain these elements more effectively in the solid phase than soluble sulphate secondary minerals (Norton *et al.* 1991).

Conclusions

Geochemical and mineralogical studies together proved the pyrite oxidation process within the coal refuse pile. Solid material contains about 1–2 wt % pyrite and calcite and dolomite as major gangue minerals in coal refuse pile. Geochemical

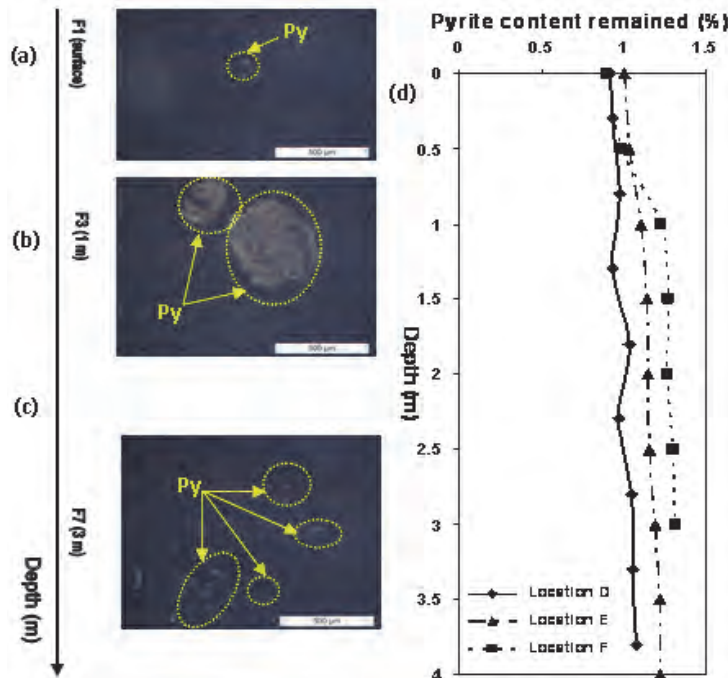


Figure 2 Polished sections of F profile solid samples in refuse pile, showing pyrite depletion of coal wastes. (a) pile surface, (b) at a depth of 1 m, (c) at the end of F profile (3m), (d) concentration of pyrite remained versus depth.

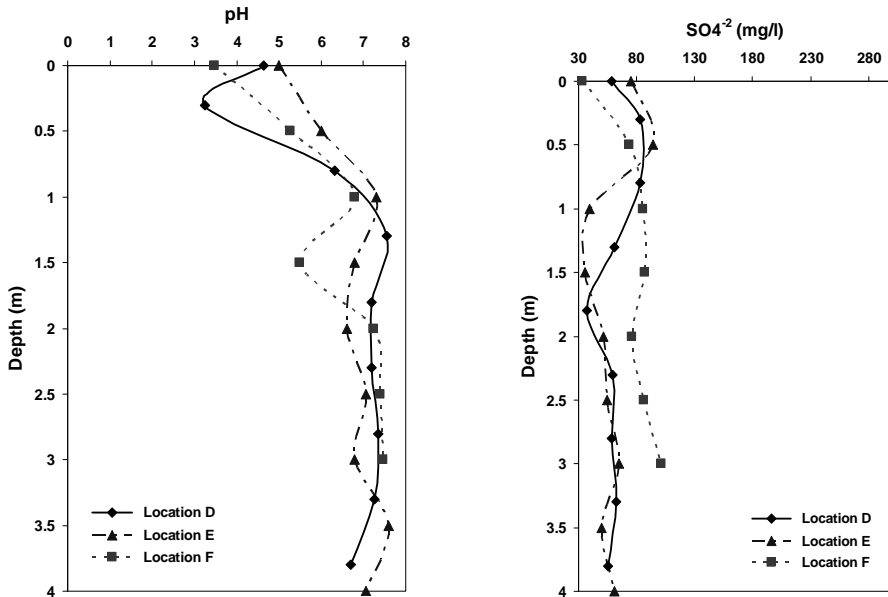


Figure 3 Depth variations of pH and Sulphate for D, E and F profiles from coal refuse pile.

analyses of coal samples for pyrite content that remained in the waste particles showed that the rate of pyrite oxidation decreased sharply at lower depths of up to 1 m, where the oxygen concentration decreased rapidly. Acid released from pyrite oxidation has been enough to deplete carbonate minerals in the spoil profile, so a zero concentration was detected for CO_3^{2-} ion.

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