

Water quality investigations in the vicinity of an active coal washing plant in Zirab, Mazandaran province, northern Iran

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Abstract This study aims to investigate the quality of water systems impacted by the Anjir Tangeh coal washing plant in the Mazandaran province, northern Iran. 22 water samples were taken from the tailings dam ponds, process water collection ponds, water from the Dalilam River and drainages discharging to this river passing near the plant. Water samples were analysed for pH, EC, major cations and anions and 70 trace elements concentrations. The type of water samples and the variation in their chemistry were determined according to Stiff, Piper and Ficklin diagrams respectively. Presence of carbonate rocks raised the pH of the water samples.

Key Words Coal washing plant, water quality, Natural alkaline mine drainage (NAMD), Dalilam River

Introduction

Water is a natural resource to basic human need and a precious national benefit. The coal produced by mining activity should be washed in order to raise its quality and remove any impurity. Coal mining and washing operations produce a number of environmental problems. Pollution problems in coal mines and subsequent coal washing program is generally due to the oxidation of pyrite. When pyrite is exposed to atmosphere and/or water, it undergoes rapid oxidation that produces acid waters (Atkins and Pooley 1982; Zhao *et al.* 2007). This process has detrimental effect on surface waters, groundwater aquifers and soils (Dinelli *et al.* 2001). The main chemical processes, which releases ions into solutions are hydrolysis, oxidation and reduction. Increased knowledge of geochemical processes that control water chemical composition in the Anjeer-Tangeh coal washing plant could lead to improved understanding of hydrochemical systems in such plants. Such improved understanding can contribute to effective management of water systems in coal washing plants.

This study was carried out to characterise the river, pond and drainage waters quality to evaluate the influence of major ions chemistry and to describe the changes in the water type and different controlling factors on the water geochemistry.

The study area is located in 45 km from South Qaem Shahr, 185 km from Tehran and 3 km in west of the Tehran-Qaem Shahr Road, north Iran. The coal washing plant is located in the Anjeer-Tangeh which lies between latitudes 36° 7' 55" N and 36° 8' 40" N, and longitudes 53° 1' 0" E and 53° 1' 20" E (fig. 1). The Zirab region is noted to be a major and old coal producer in Iran. Coal in the study area is mined by the Alborz Markazi coal company.

Karozd, Karsang and Kiasar are the most important coal mines in the Zirab region and these coal mines feed the coal washing plant.

The weather is very cold in winter and moderate and humid in summer. The mean annual precipitation at the Pol-e-Sefid region, near the study area has been 449.2 mm (Rainfall data of Mazandaran province 2009). The study area is located in Pol-e-Sefid 1:100,000 geological sheet. Coal seams in the Karozd mine are interbedded with Upper Triassic-Lower Jurassic argillites, siltstones and sandstones of the Shemshak formation. The coal seam is bounded by dolomite limestone on the lower part (Elica formation) and by thick layers of siliceous limestone (Tiz Kuh formation) on the upper part (Geological Survey of Iran 2002).

Dalilam River originated from the Alborz Mountains is the main stream passing next to the coal washing plant (fig. 1). This river is finally terminated to the Caspian Sea. The discharge of this river varies and increases from the dry season to during the wet season.

It has been estimated that up to 1.5 million tonnes of coal wash fines deposited in a land with 20000 m² area, over about 22 years, beside of the Dalilam River and this may increase the risk of acid drainage generation and metal transportation.

Methods

Sampling and analysis

Twenty two water samples, including 4 samples from refuse pile drainages (H1, H2, H3, Leach), 5 samples from tailing dam and process water collection ponds (A, B, C, I, J), 1 sample from the settling pond, downstream of the pile (Po), 11 samples along the Dalilam River (W1 to W11) and 1 sample from spring (SPR) out of the plant area,

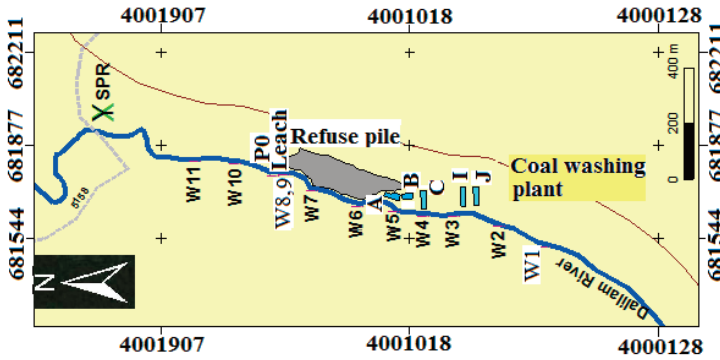


Figure 1 Geographical situation of the study area.

were collected. The drainage sites were selected based on the expected discharge locations of effluents from the refuse pile and pond sites. The river samples were collected along the river from upstream to downstream (end of the plant).

Water samples were collected in clean plastic bottles 250 mL each in capacity. In each location, two water samples were collected. One was for cations and anions analysis. The second one was for trace metals analysis. For water sampling, pre-cleaned sample bottles were immersed about 10 cm below the surface.

pH and electrical conductivity (EC) were measured in the field. Water samples were directly stored under cool conditions at about 5°C without acidification for anions and cations and with acidification for trace metal samples. A pH metre model Suntex SP-701 (Taiwan) was used to measure pH. An EC meter model WP-84 was utilised to measure electrical conductivity of the water samples.

The chemical analysis of water samples was performed using Palintest-Photometer 7000 for cations and anions in the water laboratory of the Semnan Science and Technology Park, Iran. Concentrations of 70 elements were determined using an inductively coupled plasma mass spectrometer (ICP-MS) by ACME Analytical Laboratories Ltd., Canada.

Statistical analysis for representation of hydro-chemical data

The Pearson’s correlation matrix was computed to find the relationships between two or more variables for both river and pond samples. The correlation matrix for all water samples collected in the study area is shown in tab. 1.

A strong negative correlation between pH and trace elements and major ions and strong positive correlation among trace elements (Co, Cu, Mn, Ni and Zn) and major ions (Ca⁺², K⁺, Mg⁺²) suggest

Table 1 Correlation between various parameters in all water samples.

	pH	EC	Ca	K	Mg	Na	SO ₄ ²⁻	HCO ₃ ⁻	Cl ⁻	Al	Co	Cu	Fe	Mn	Ni	Pb	Zn
pH	1																
EC	-.7**	1															
Ca	-.7**	.9**	1														
K	-.7**	.9**	.9**	1													
Mg	-.7**	.9**	.9**	.9**	1												
Na	-.4*	.3	.23	.24	.22	1											
SO ₄ ²⁻	-.7**	.9**	.9**	.9**	.9**	.28	1										
HCO ₃ ⁻	-.1	-.3	.6**	-.3	-.4*	.3	-.51*	1									
Cl ⁻	-.8**	.8**	.7**	.7**	.7**	.6**	.7**	-.01	1								
Al	.53*	-.3	-.3	-.30	-.35	-.1	-.29	-.2	-.4	1							
Co	-.5**	.8**	.8**	.8**	.8**	.18	.8**	-.54**	.6**	-.1	1						
Cu	-.32	.19	.07	.18	.08	.6**	.07	.48*	.4**	-.1	.04	1					
Fe	-.04	-.10	-.23	-.22	-.24	.7**	.404	.41	.27	.36	-.20	.5**	1				
Mn	-.7**	.6**	.5**	.52*	.5**	.7**	.5**	.28	.8**	-.3	.51*	.5**	.46*	1			
Ni	-.6**	.8**	.8**	.8**	.9**	.09	.9**	-.57**	.6**	-.2	.8**	-.04	-.3	.4*	1		
Pb	-.01	-.04	-.14	-.01	-.15	.5*	-.11	.32	0.1	.4*	-.13	.7**	.7**	.27	-.2	1	
Zn	-.5*	.5**	.44*	.50*	.48*	.5**	.46*	.13	.6**	-.2	.32	.8**	.38	.6**	.4	.5*	1

** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

that these ions are likely derived locally from water-rock interactions. Similarly, a strong positive correlation between SO_4^{2-} and Cl^- proposes that these anions are likely produced locally from water-rock interactions.

Strong correlations exist among the major elements K, Ca, Mg, SO_4 and EC. These relationships clearly identify the main elements contributing to the salinity of water samples.

Acid drainages produced are quickly buffered by dolomite and ankerite $[\text{Ca}(\text{Mg,Fe,Mn})(\text{CO}_3)_2]$. The dissolution of such minerals releases divalent metals (Ca^{+2} , Fe^{+2} , Mg^{+2} and Mn^{+2}) and bicarbonate (HCO_3^-) ions to solution phase (Balistrieri *et al.* 2002).

The strong correlation between Ca and HCO_3^- probably indicate that Ca and HCO_3^- might be associated with the presence of calcite and negative correlation between HCO_3^- and SO_4^{2-} ($r=-0.51$) indicate that acid waters also buffered by calcite.

The negative correlation between pH and SO_4^{2-} observed for all water samples ($r=-0.7$) which is attributed to the oxidation of sulphide minerals, mainly pyrite. The reverse relationship between Mg, Ca and HCO_3^- with pH value in water samples can be attributed to the decrease of Mg and Ca ions at high pH values due to the precipitation of calcite. HCO_3^- correlates directly with Na. The source of sodium in the water may be related to Na-silicates or clay minerals with coal.

Most of the metals are significantly negatively correlated with the pH in water samples. This is mainly due to an increase in the mobility of these elements with decrease in pH.

EC positively correlated with all major and some trace elements in river, pond and drainage waters, because total dissolved solid (TDS) strongly positively correlated with EC.

There is a positive correlation between Fe and SO_4^{2-} in water samples. Iron concentration is probably the result of both pyrite oxidation and dissolution of iron-bearing carbonates.

Most of the metals (Cu, Pb and Zn) are positively correlated with each other and it is possibly due to the same source of origin.

Water Types

Representation of water quality data with Stiff diagram

Stiff diagram (Todd 1959) is very useful in making quick comparison between waters from different sources. Although not given here, the concentration of major dissolved ions for each sampling point were plotted on Stiff pattern diagram. The type of the water samples was determined based on the highest concentrations of anions and cations represented in Stiff diagrams (tab. 2). Among anions, SO_4^{2-} is dominant in all ponds and drainages emanating from the coal refuse pile

Table 2 Water types of the area based on Stiff diagrams.

Source	Water sample	Water type
River	W1, W2, W3, W4, W5, W6, W10	Ca - HCO_3^-
	W7, W9	Ca - SO_4^{2-}
Drainage	W8, W11	Na - SO_4^{2-}
	H2, H3	Ca - HCO_3^-
	Leach, H1	Ca - SO_4^{2-}
Pond	A, B, C, I, J, P0	Ca - SO_4^{2-}
Spring	SPR	Ca - HCO_3^-

and discharging to the Dalilam reiver. However, nearly 50% of the river water samples collected away from the drainages impacted stream and downstream of the confluence of drainages with river. These samples fall into HCO_3^- facies. Among cations, Ca is dominant, followed by Na^+ in most water types.

Representation of water quality data with Piper diagram

One of the most helpful graphs for representing water quality analysis is the Piper diagram (Piper 1944; Todd 1959). This diagram allows displaying large numbers of analyses. Furthermore, the interpretation of the results of chemical analyses of water samples is easy using Piper diagram to discriminate the type of waters in terms of the major constituent cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and anions (Cl^- , SO_4^{2-} and $\text{HCO}_3^- + \text{CO}_3^{2-}$). Fig. 2 shows Piper diagram for illustration of the chemical analyses of the water samples taken from the study area.

River waters exhibit the highest variability, ranging from: Ca- SO_4^{2-} - HCO_3^- type (W1) to Ca-Mg-(Na+K)- SO_4^{2-} type (W11), along the river (fig. 2, tab. 3). Such multiple cations and anions water types Ca-Mg-(Na+K)- SO_4^{2-} are the product of mixing of waters from drainages and seepages that come to the river in different points along the river in vicinity of coal washing plant. These drainages are generated from coal refuse pile and process water ponds.

In the Dalilam River, Ca- HCO_3^- waters reflect bed rock mineralogy (carbonate rocks) based on Piper diagram. The pond waters exhibit Ca- SO_4^{2-} type dominated by Ca and SO_4^{2-} and resulted from the dissolution of calcite, dolomite and sulphides, especially pyrite.

The drainages and seepages also exhibit high variability in water type, from Ca- SO_4^{2-} type (H1), to Ca-Mg- (Na+K)- SO_4^{2-} type along the river. It is obvious that the Ca-Mg-(Na+K)- SO_4^{2-} water type that is most affected by AMD generally has low alkalinity and HCO_3^- values and high sulphate values. High sulphate ion concentration in drainage is commonly an indicator of pyrite oxidation

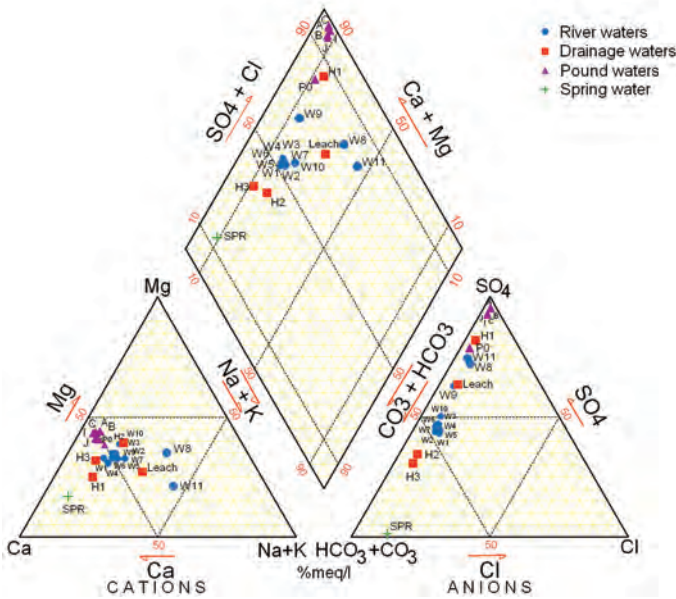


Figure 2 Piper diagram of water samples in the study area.

(Leach and H1 samples). The main reason for the high value of HCO_3^- is the presence of carbonate rocks, that neutralize the acidic drainages produced in the study area (H2 and H3). The spring water sample (SPR) exhibits Ca- HCO_3^- type dominated by Ca and reflects the mineral composition of the aquifer (carbonate rocks). The spring water is not affected by the coal washing operation.

Ficklin Diagram

Ficklin diagram is often used to interpret variations in mine drainages chemistry having different origins (Plumlee *et al.* 1999). The Ficklin plot is a scattergram in which the sum of the base met-

als zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), cobalt (Co), and nickel (Ni) is plotted against pH. These elements were selected rather than more common metals such as iron (Fe), aluminium (Al), and manganese (Mn) because they have proved the most diagnostic in differentiating between different geologic controls. Differences in the sum of Zn, Cu, Cd, Pb, Co and Ni concentrations for different samples allow in differentiating various geological controls on their resultant water chemistry. When plotted on a Ficklin diagram, all water samples classify as near-natural low metal waters (fig. 3). pH for all water samples collected in the study area range from 7.16 to 8.18. Among the sum of

Table 3 Water types from study site according to Piper diagram.

Location	Sample	Source	Water type
Dalilam River	W2, W3, W5, W6, W7 W10	Stream	Ca - Mg - (Na+K) - HCO_3^- - SO_4^{2-}
	W8, W9, W11	Stream	Ca - Mg - (Na+K) - SO_4^{2-}
	W1, W4	Stream	Ca - SO_4^{2-} - HCO_3^-
	Refuse pile	H1	Drainage
H2		Drainage	Ca - Mg - (Na+K) - HCO_3^-
H3		Drainage	Ca - HCO_3^-
Leach		drainage	Ca - Mg - (Na+K) - SO_4^{2-}
Plant area	A, B, C	Process water collection ponds	Ca - SO_4^{2-}
	P0	Settling pond	Ca - SO_4^{2-}
	I, J	Tailings dam	Ca - SO_4^{2-}
	In vicinity of the plant	SPR	Spring

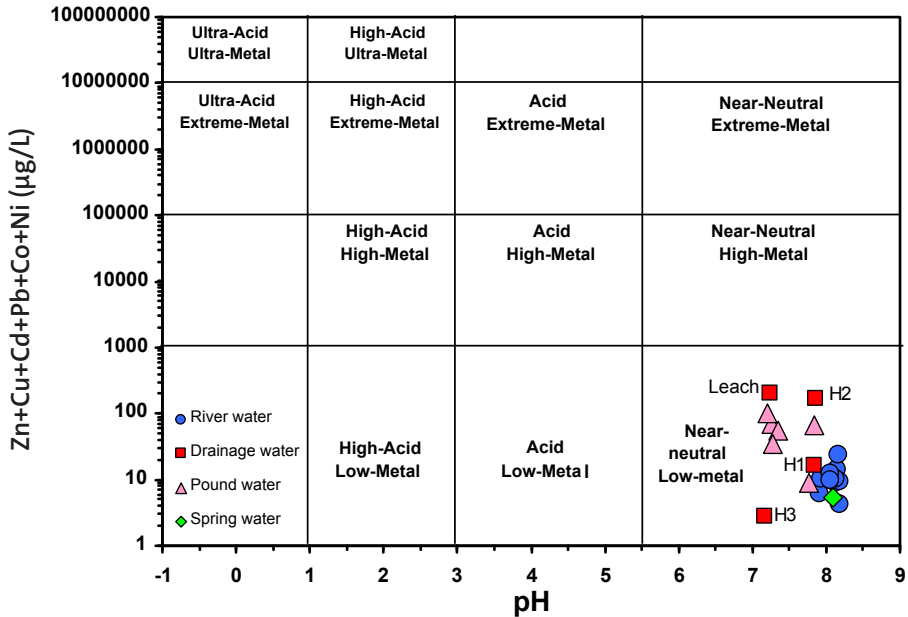


Figure 3 Ficklin diagram showing variations in aqueous base metal concentrations (given as the sum of base metals zinc, copper, cadmium, cobalt, nickel, and lead) as a function of pH for the study area.

base metals in drainage samples, Leach (199.44 µg/L) and H2 (168.83 µg/L) samples were higher than the others. H3 (2.8 µg/L) shows the lowest sum of base metals in drainages and all water samples in the study area.

Conclusions

Coal washing operations in the Anjir Tangeh, Zirab, north of Iran has slightly affected water quality in the surrounding area. A hydrogeochemical study has been carried out to investigate the impacts of the Anjir Tangeh plant on water bodies. According to Stiff and Piper diagrams, the most of water samples from the Dalilam River were classified into Ca-HCO₃⁻ type. Type of the pond water samples was determined to be Ca-SO₄⁻². The drainages from the coal refuse pile were placed in Ca-SO₄⁻² and Ca-HCO₃⁻ types. The drainages from the coal refuse pile may be recognised as the natural alkaline mine drainage (NAMD). Presence of carbonate rocks raised the pH of the water samples. Field investigations revealed that red and red brown precipitates of goethite and iron hydroxides were dominant from the pile leachates discharging to the Dalilam River. Drainages quality was largely influenced by the coal refuse pile mineralogy, weathering of the pile materials, process water input and local hydrological settings. Water samples with high pH, variable concentrations of SO₄⁻² and low trace metals were classified as near-natural and low-metal. The results of this study

provide useful information for developing an appropriate water remediation and pollution controlling strategies in the region.

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