

## Investigating the Pyrite oxidation and mineralogical characteristics of a coal washing waste dump, Alborz Sharghi, Shahrood, Iran

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**Abstract** In this research polished sections, x-ray diffraction (XRD), x-ray fluorescence (XRF) and atomic absorption spectrometry (AAS) were applied to investigate the pyrite oxidation in a coal washing waste dump as the greatest concern of producing acid mine drainage. Furthermore, mineralogical and geochemical characteristics of wastes samples were appraised in order to find the proportion of toxic materials. Polished sections show the presence of pyrite and its variations with depth. The AAS results quantitatively show that the pyrite content increases with depth. The amounts of toxic materials in the waste samples, measured by XRF analyses, were less than standard acceptable limits.

**Key Words** Pyrite oxidation, Acid mine drainage, Mineralogical characterizing, Coal washing waste dump, Alborz Sharghi

### Introduction

Acid mine drainage (AMD) that emerges from sulphide rich waste-dumps is an unusual focus of environmental impact in aquatic systems (Maria Valente *et al.* 2009). The oxidative dissolution of these mine wastes give rise to acidic, metal-enriched mine drainage (Johnson and Hallberg 2005). Due to the variety of the coal structure and its complicated formation conditions, concentration of non-metallic elements (Bi, As, Se, etc), metals (Cu, B, Br, Fe, Na, etc) and rare earth elements (La, Ce, Eu, etc) are frequent accompaniments with coal. To better understand the generation of such waters as well as to describe its properties and to evaluate its impact, the use of diversified analyses is imposed. The generation of AMD has been described in lots of papers (e.g., Johnson 2003). In brief, oxidation of sulphide minerals and in particular Pyrite, as the most abundant sulphide mineral on the earth, in the presence of oxygen and water (Johnson and Hallberg 2005), is the most important factor in producing AMD. So, the first step in any environmental survey of an area is to evaluate the proportion of sulphide minerals especially pyrite and their oxidation. The next step is the appraisal of the AMD effects in the vicinity. Most of the time, water samples are analysed to assess the environmental impacts of the AMD. Water quality is generally ascertained based on physical, chemical, and biological indicators such as pH, electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), hardness, turbidity and contaminant concentrations and based on guidelines provided by agencies such as the World Health Organization (WHO 1984) and the Bureau of Indian Standards (BIS

1991; Debasis *et al.* 2008). A variety of different methods has been used to examine water samples in previous works including AAS (Khan *et al.* 2005), ICPAES or ICPMS depending on concentration (Alderton *et al.* 2005). The important changes in the quality of a water resource affected by the AMD is the change in pH and the change in the concentration of some toxic materials (such as Arsenic, Germanium, Lanthanides, Cadmium, Aluminium, Cobalt, Mercury, Molybdenum, Manganese, Nickel, Lead, Selenium, Zinc and Copper). These metals can be dissolved by the AMD through its way to the aquatic systems. The waste dump, from which AMD is generating, is the best source to expose these toxic materials to this acidic solvent water. Therefore the amounts of metals, metalloids and other dangerous substances for the environment must be measured in such dumps and compared to the acceptable standard limits. Then, depending on this information, further surveys can be designed for improving the knowledge of environmental situation in the vicinity.

### Site description

Alborz Sharghi coal field consists of sandstone, thin bedded coaly shale of Shemshak formation and alluvial deposits. The coal seams are bounded by dolomite limestone on the lower part (Elica formation) and by thick layers of limestone (Lar formation) on the upper part (Doulati Ardejani *et al.* 2010). There are four forms of sulphur in coal including monosulphide ( $S^=$ ), sulphate sulphur ( $SO_4^-$ ), pyritic sulphur ( $S_2^-$ ), and organically bound sulphur (Golightly and Simon 1823). The extracted coal from the region, are washed in the Alborz

Sharghi coal washing plant which is located north-east of Damghan and 57Km from Shahrood (Sadeghi Amirshahidi *et al.* 2011). The input feed of the washing plant is more than 650,000 ton per year and the recovery of the planet is 50%. Therefore, half of input feed are dumped as low grade waste materials (containing metals, metalloids and other toxic materials, and also sulphide minerals). There are two methods of coal washing used in the Alborz Sharghi Co., the first one is using jig machine and second one is flotation process. Hence, we have two kinds of waste dumps and our investigations are made on jig machine waste dump.

### Materials and Methods

Seventeen samples were collected from different depths of three trenches dug in the jig machine waste-dump (trenches were dug with loader and Samples were extracted from one wall of each trench applying shovel). Samples were oven dried at 105 degrees of centigrade for 72 hours in the mineral processing laboratory at Amirkabir University of Technology. Then grinding process was done applying jaw crusher, cone crusher and roll crusher respectively. After that sieve analysis was done using five sieves with different sizes (30, 60, 100, 140 and 200 Mesh). We used polished sections, X-ray diffraction (XRD), X-ray fluorescence (XRF) and atomic absorption spectrometry to investigate mineralogical characteristics of waste materials, pyrite oxidation and pollutant generation.

### Mineralogical Analyses

At first, polished sections were created from powder with different sizes of S36 sample (sample from trench 3 at depth of 200Cm), to find out the best size for qualitative investigating the pyrite oxidation process at various depths of the waste dump (fig. 1). As shown in fig. 1, although pyrite is obviously noticeable in all sections, the polished section created from powder above 200Mesh was the best section for investigating the changes in amount of the pyrite in different depths. After realizing the best size, polished sections were created from powder above 200Mesh for all samples.

X-ray diffraction analyses were carried out on any six samples of trench 2 at the Amirkabir University of Technology using PHILIPPS 1140. Powder above 140Mesh was used for this experiment.

### Quantitative Analyses

Those points on which XRD analyses had been done were selected for X-ray fluorescence analyses. XRF analyses were performed at Amirkabir University of Technology applying X'UNIQUE II and for this experiment again, powder above 140Mesh was used. A method presented by ASTM

(Gladfelter and Dickerhoof 1976) was employed to determine organic pyrite from the non-organic pyrite. Hydrochloric Acid (HCl) was used to dissolve sulphates and then the pyrite was extracted from the remained acid aqueous solution using Nitric Acid (HNO<sub>3</sub>). An AA-670 Shimadzu atomic absorption at Shahrood University of Technology was used to measure iron in the solution. It was then employed to determine the concentration of pyrite that remained in the waste particles.

## Results and Discussion

### Polished sections

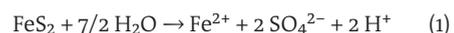
Study of polished sections indicates the pyrite depletion in surface samples, where oxygen as a potential oxidant is available, and presence of pyrite in deeper samples where the amount of oxygen is lower (fig.2). At the dump surface, the rate of pyrite oxidation is very high because of the availability of oxygen, and therefore the amount of remained pyrite is very low. Due to the reduction in oxygen diffusion with depth, the rate of pyrite oxidation decreases at deeper parts of waste dump (Doulati Ardejani *et al.* 2010). Therefore the pyrite content increases with depth.

### X-Ray Diffraction (XRD)

In all samples, Quartz, Chlorite, Gypsum, Illite and Tarascovite were determined. Cristobalite was specified just in two superficial samples (S21 and S22). Fig. 3 shows the results of XRD analysis for sample from trench 2 at the depth of 120Cm (S24). Pyrite was not seen in XRD analyses because the percentage of pyrite is less than 5% (in XRD analyses only minerals with minimum concentration of 5% can be determined). The noticeable point of these analyses is the existence of Illite which presents some elements in its structure such as Fe, K and Mg. The Fe could come from the hematite, and/or magnetite, and/or pyrite, and/or the electrolyte which contains Fe<sup>2+</sup> and Fe<sup>3+</sup> (Yolanda De Abreu *et al.* 2007). Due to polished sections, the absence of hematite and magnetite led us to the conclusion that the Fe in the illite has come from the pyrite or the electrolyte which is produced by the pyrite oxidation.

### X-Ray Fluorescence (XRF)

A number of XRF analyses results are shown in tab 1. It is considerable that the concentration of Fe<sup>3+</sup> (Fe<sub>2</sub>O<sub>3</sub>) in two samples from 160 and 200 Cm depth is very low while in four shallower samples, the content of Fe<sup>3+</sup> is higher. It can be assumed as an evidence of pyrite oxidation in shallower depth. The reaction describing oxidation of pyrite by O<sub>2</sub> is shown in Eq.1:



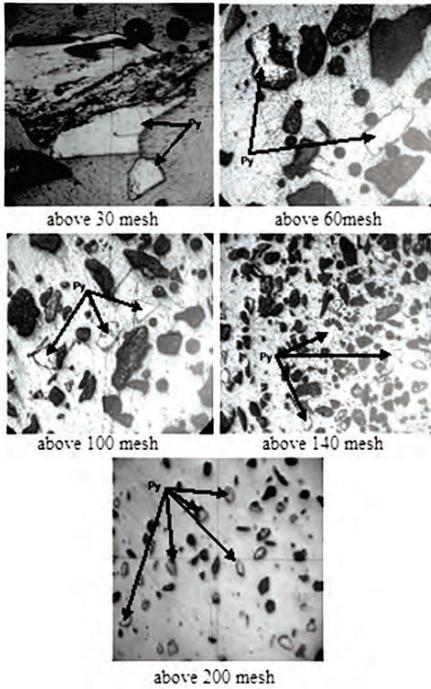


Figure 1 Polished sections which are created from powder with different sizes of sample No. S36 (Sample from trench 3 at the depth of 2m). (Py= pyrite).

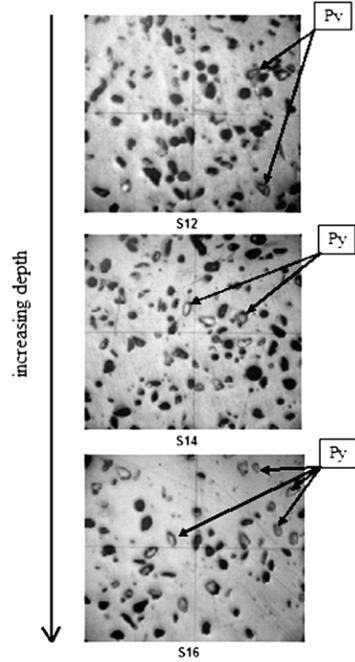


Figure 2 Polished sections from different depths of trench No.1 showing the increment of pyrite content with depth. (S12: depth=0.4m; S14: depth=1.2m; S16: depth=2m).

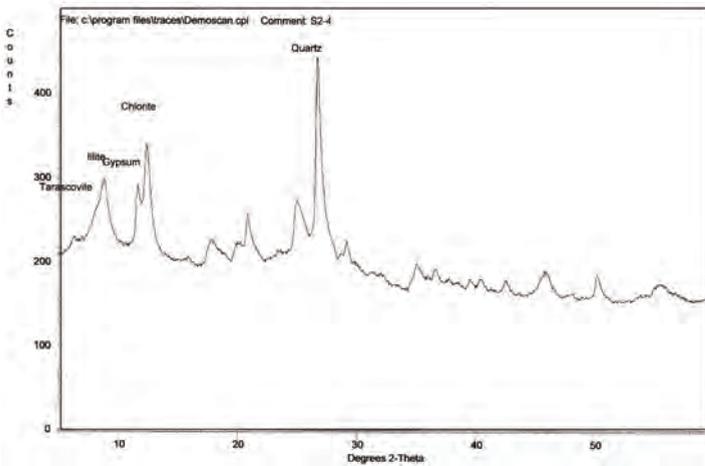
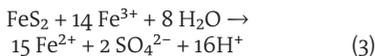
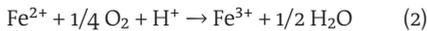


Figure 3 XRD pattern for sample from trench 2 at the depth of 1.2m (S24).

$Fe^{2+}$  produced by the pyrite oxidation (Eq.1) forms  $Fe^{3+}$  by Eq. 2:



The higher amount of  $Fe^{3+}$  in samples from shallower depth shows that these reactions were completed.  $Fe^{3+}$  produced by the oxidation of ferrous iron, may react with pyrite (Eq. 3) to produce additional  $Fe^{2+}$ ,  $SO_4^{2-}$  and  $H^+$  (Doulati Ardejani *et al.* 2005). This reaction has an important role in pyrite oxidation just in presence of the lithotrophic bacteria *Thiobacillus ferrooxidans*

**Table 1** A number of XRF results (Elements calculated as oxide).

Sample No:	S21	S22	S23	S24	S25	S26
Depth (m):	0	0.4	0.8	1.2	1.6	2
elements						
SO3	2.08	1.098	2.22	2.45	1.90	2.68
Al2O3	15.6	16.8	16.7	16.9	17.4	18.4
GeO2	<	<	<	<	<	<
Fe2O3	4.21	5.7	5.5	6.1	3.99	2.97
As2O3	<2e	<2e	<2e	<	<2e	<
MnO	0.056	0.118	0.073	0.024	0.041	0.035
Ar	<	<	<	<	<	<
CdO	<	<	<2e	<	<	<
Cr2O3	<	<	<	<	<	<
CuO	0.029	0.018	0.014	0.011	0.0101	0.0099
PbO	<	<	<	<	<	<
Hg	<	<	<	<	<	<
NiO	<	0.013	<	<	<	<
SeO2	<	<	<	<	<	<
ZnO	0.017	0.016	0.012	0.0111	0.021	0.0092
MoO3	<	<	<	<	<	<
Sum La...Lu	0.014	0.021	0.020	0.033	0.020	0.023
L.O.I	37.56	35.61	35.81	32.97	35.86	30.11

< means that the concentration is less than 10 ppm

<2e means that concentration is less than 2\*Std Err

(Singer and Stumm, 1970). At first, it seems that the low amounts of Fe<sup>3+</sup> in deeper samples is because of the consumption of Fe<sup>3+</sup> in pyrite oxidation (Eq. 3), but according to the results of polished sections studies, which shows that the amount of pyrite remained in deeper samples are high, we can realize that the rate of reaction between pyrite and Fe<sup>3+</sup> is very low. Therefore high concentration of Fe<sup>3+</sup> in surface samples is because of pyrite oxidation in these samples. Lower concentration of Fe<sup>3+</sup> in deeper points is a result of the reduction in oxygen diffusion with depth and subsequent decreasing of pyrite oxidation.

Acid mine drainages typically pose an additional risk to the environment by the fact that they often contain elevated concentrations of metals (Iron, Aluminium and possibly others) and metalloids (of which Arsenic is generally of greatest concern) (Barrie Johnson *et al.*, 2005). For this reason, in XRF analyses we measured the concentrations of metals and metalloids (i.e., Arsenic, Germanium, Lanthanides, Cadmium, Aluminium, Cobalt, Mercury, Molybdenum, Manganese, Nickel, Lead, Selenium, Zinc and Copper) in waste samples which are demonstrated in tab. 1. Considering the table contents, concentrations of all these toxic materials are very low (less than standard acceptable limits) except for the Aluminium. Due to the back ground value of Aluminium in the study area which is between 12% and 18% (Khodabakhsh *et al.* 2008), this amount of Aluminium in samples is logical.

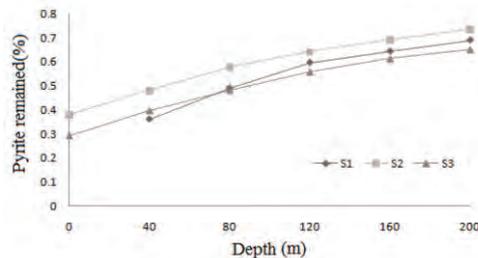
**Atomic Absorption Spectrometry (AAS)**

Concentration of pyrite that remained in different depths of the waste dump, obtained from AAS analyses, is shown in tab. 2. The results quantitatively show that the pyrite content increases with

depth. It means that the results of this analysis is in a very good agreement with results of polished sections studies where qualitatively shows the increasing of remained pyrite in the waste particles at deeper parts of the dump. As it has been explained before, increase of pyrite content is relative to decrease of oxygen diffusion with depth. Fig. 4 shows the concentration of pyrite that remained in particles versus depth at all three trenches.

**Table 2** Concentration of pyrite (%) that remained in different depths of the waste dump (Obtained from AAS analyses).

Depth(m):	0	0.4	0.8	1.2	1.6	2
Trench No						
S1	-	0.36	0.49	0.596	0.643	0.689
S2	0.379	0.48	0.578	0.64	0.689	0.735
S3	0.292	0.396	0.481	0.557	0.612	0.65



**Figure 4** Concentration of pyrite that remained in waste particles versus depth for all the trenches (Obtained from AAS analyses).

## Conclusions

Oxidation of pyrite cause the generation of acid mine drainage which is known as the most important threat for the environment in mining operations, especially tailing dumps. These acidic waters can typically dissolve metals, metalloids and other toxic materials and pose many environmental problems. Hence, study of pyrite content and its oxidation as a matter of AMD generation, and the mineralogical investigation of the waste dumps finding the amount of toxic materials, can help us to provide a mine plan which has the minimum harms for the environment.

Polished sections show the existence of pyrite and in particular increasing the amount of pyrite with depth. The pyrite oxidation is evidenced by such a trend as an effect of the reduction in oxygen diffusion with depth. Quartz, Chlorite, Gypsum, Illite and Tarascovite were determined in all samples by XRD analyses and pyrite did not observed in any of samples. The concentration of pyrite in waste samples is about 2% which is less than the minimum assay limit of XRD analysis (5 %). The existence of pyrite can be proved by the presence of Illite. XRF results showed an increase in Fe<sup>3+</sup> contents of samples with depth which confirm the increase of pyrite concentration in deeper points. The AAS results quantitatively show that the pyrite content increases with depth. All of these Outcomes are showing the pyrite oxidation, and therefore generation of AMD. In addition, the carbonate rocks in the study area (such as dolomite and limestone), will able to neutralise the acidic drainages produced in the area which reduce the ability of drainages to dissolve and transport toxic materials. Low amounts of metals, metalloids and other toxic materials (i.e., As, Ge, Ca, Al, Co, Hg, Mo, Mn, Ni, Pb, Se, Zn and Cu) measured by XRF analyses on one hand, and the presence of carbonate rocks on the other, show that the environmental condition of study area is not very concerning. Such investigations can be used for designing an environmental management program.

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