EVALUATION OF ACID MINE DRAINAGE GENERATING POTENTIAL OF A LOW-GRADE ROCK DUMP FROM MIDUK MINE ACCORDING TO CHEMICAL STATIC METHODS, MINERALOGICAL STUDIES AND MULTIVARIATE STATISTICAL ANALYSES

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Abstract: The oxidation of sulfide minerals especially pyrite is the main source of acid production in mine waste rocks. Other sulfide minerals including chalcopyrite, covellite, and galena may also be responsible for acid production. Huge waste rock dumps with high sulfide content may generate lot of acidic drainages as a result of oxidation and hydrolysis processes. Accordingly, acid production and neutralization potential of waste rocks were evaluated based on common Acid-Base Accounting (ABA) and Net Acid Generation (NAG) methods at dump No.7 of Miduk Mine. The results of chemical methods were compared with the mineralogical studies. Mineralogical analyses including X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro analysis (EPMA) were employed to comprehensively study primary sulfides and secondary minerals. There was a strong possibility to generate acid mine drainage (AMD) with very high metal content in dump No. 7. According to the results of NAPP and NAG pH, all samples were classified as potential acid forming (PAF). The lowest and the highest NAPP were detected in samples HB1 and HC1S (200.08 and 654.14 kgH$_2$SO$_4$/t, respectively). Regarding paste pH and NAG pH, all samples were categorized as extremely acid forming (EAF) and acid forming (AF) materials. Due to high pyrite oxidation, the share of sulfate sulfur was ranged between 1.28 and 7.28 wt. According to both hierarchical cluster analysis (HCA) and principal component analysis (PCA), pH has an important role in the dissolution of waste materials. In addition, there is a strong positive correlation between Fe, Pb and As; indicating that they may have similar sources of soluble secondary minerals in the rock material. The results of the present study could be applied in the prediction of AMD generation for mine waste management projects.

Keywords: Acid mine drainage (AMD); Static tests; SEM; EPMA; Multivariate statistical analysis.

1- INTRODUCTION

Environmental liability and social responsibility play important roles in future mine operations. Firm environmental protection regulations and increasing social awareness about potential hazards of mining activities will limit development of mining projects. Low-grade ore rock dumps with a high content of pyrite are typically spread around the mine area and openly exposed to the atmospheric conditions. Acid mine drainage (AMD) is identified with a pH value of less than 5, and an elevated content of sulfate and potential hazardous metallic or non-metallic elements (Doulati Ardejani et al. 2005; Nordstrom 2011). Direct or indirect oxidation of sulfide minerals, especially pyrite, respectively by oxygen or ferric iron, generates AMD in presence of water. The oxidation of one mole pyrite by oxygen (Reactions 1) or ferric ion (Reaction 2) can produce 4 and 16 moles of sulfuric acid, respectively.

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$$FeS_2 + 3.75O_2 + 3.5H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad\quad (1)$$
$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad\quad (2)$$

The formation of secondary minerals by AMD dilution or neutralization can also load acidic leachate to the environment. According to the dissolution-equilibration and hydrolysis reactions, the precipitation of ferric iron hydroxyl sulfates (jarosite-alunite group and schwertmannite), is responsible for releasing acid and trace elements (Reactions 3 and 4).

$$HFe(SO_4)_2 + 3H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad\quad (3)$$
$$Fe_{16}O_{16}(OH)_{10}(SO_4)_3 + 6H_2O \Rightarrow 16FeO(OH) + 3SO_4^{2-} + 6H^+ \quad\quad (4)$$

The generation of AMD and associated leaching of metals is the worst environmental risk imposing high costs in metal mining (Jamieson et al. 2015; Dold 2017). In Canada, the reclamation costs of acid-generating tailings impoundment range typically between 100 and 250 thousands of dollars per hectare, while those of non-acid generating tailings are between 2 and 20 thousand of dollar per hectare (Bouzahzah et al. 2014). Due to the high remediation costs of acid generating materials, the acid generating potential of mine wastes must be accurately predicted by mine operators, as early as possible. The prediction of acid generating potential is essential during mine development in order to select appropriate waste management and remediation scenarios. The prediction methods of acid generating potential include two main groups of static and kinetic tests. The static tests are fast and cost effective. The tests, including acid-base accounting (ABA) and direct sulfide oxidation by hydrogen peroxide, have been applied to evaluate short-term acid generating potential of mine dump (Plante et a. 2012; Shahhoseiny et al., 2013; Celebi and Oncel 2016; Abrosimova et al. 2015). The main aim of the present study was to predict the acid generating potential of rock materials using static methods such as paste pH, ABA, and net acid generation (NAG) tests in a low-grade ore rock dump, to evaluate the association of trace elements with secondary water soluble minerals in dump No. 7 of Miduk mine.

2- METHODS

The Miduk copper complex is located near the Miduk village, 45 km North-East of Shahr-e-Babak which lies between longitudes 55° 9' and 55° 11' E, and latitudes 30° 24' 30" N to 30° 26' 30" N. The mine has been active since 1996 having produced more than 24 million metric tons of waste rock and low-grade ore in 2017. The climatic condition of the mine area is classified as "arid" with mean annual values of 13.17 °C, 253.8 mm, and 39.5% for air temperature, precipitation, and relative humidity, respectively. Dump No. 7 with a height and a length of about 100 m and 300 m, containing high sulfide minerals, has been abandoned since 2008. Three vertical trenches of HA, HB, and HC were excavated in a line with a horizontal spacing of 25 m on top area of the dump. The sampling intervals of 0.5 m was almost constant from the surface up to the depth of 3 m, for each trench. However, sampling intervals varied according to general appearances of oxidation zones such as color and texture. The most oxidized zone of rock materials with dark reddish-brown color was observed at the upper part of HC from surface up to the depth of 0.2 m. Samples of HC1S and HC1 were taken at the depth of 0 and 0.2 m of HC. Altogether, 19 samples (each sample with a weight of 1 kg), were taken from HA (6 samples), HB (6 samples), and HC (7 samples). Part of each sample with a size fraction of lower than 2 mm was used for geochemical and mineralogical analyses, and chemical tests. This part of sample was pulverized to particles smaller than 75 μm by an agate mortar. Total sulfur content was determined by ELTERA CS-2000 equipment. Total reduced inorganic form of pyrite was determined according to ASTM D2492 (ASTM, 2012). The bulk elemental composition of

samples was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300) after a whole rock digestion with HF/multi-acid (HF-HCl-HClO4-HNO3). The pH value of the paste was measured for samples based on procedure of AMIRA P3874 (Smart et al., 2002). The leachate was extracted from prepared paste using a vacuum pum p with a high pressure of 80 KPa. After filtration, all leachates were divided into two parts. One part after acidification with pure HNO3 (up to the pH below 2) was analyzed for the determination of major and trace elements using ICP-OES. The un-acidified part of leachate was used for measurement of pH, ORP (oxidation-reduction potential), electrical conductivity (EC) and major ions. The acidity, SO_4^{2-}, and Cl^- values were determined by NaOH titration, $BaCl_2$ turbidimetry, and argentometric titration (APHA, 1998), respectively. The maximum potential acidity (MPA) of rock materials was calculated by multiplying total sulfur of each sample by 30.6 (MPA = 30.6×%Stotal; kg H2SO4/t). The acid neutralizing capacity (ANC) is measured using back-titration of HCl mixture of sample with a strong base (NaOH) based on fizz rating (Smart et al. 2002). The net acid-producing potential (NAPP) of sample is calculated by subtracting ANC from MPA (NAPP = MPA - ANC kg H2SO4/t). In the single addition net acid generation (NAG) test, a 2.5 g (less than 75 µm) of the sample is reacted with 250 ml of 15% H2O2 in a 500 ml conical-flask under a fume hood according to AMIRA P387A method (Smart et al., 2002). The NAG is determined by back-titration of the final solution to pH values of 4.5 and 7 (Yucel and Baba, 2016). The pH of final solution is immediately measured to evaluate the NAG pH. A positive NAPP with a value of less than 4.4 for NAG pH represents material as potentially acid-forming (PAF). However, a negative NAPP with a high NAG pH (higher than 4.4) indicates the materials as non-acid forming (NAF). The mineralogical studies of samples were performed by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron microprobe analyser (EPMA). The XRD analysis was performed using a computer-controlled Bruker AXS, D8 Advance diffractometer. Both transmitted and reflected lights were employed to identify lithological and mineralogical types. A polished section was then used for further mineralogical analyses by SEM-EDS (CamScan MV2300 model) and EPMA (CAMECA SX-100 model). The Pearson correlation analysis (CA), hierarchy cluster analysis (HCA), and principal component analysis (PCA) were carried out using IBM SPSS 22. The normality of all variables was checked using the Kolmogorov-Smirnov test. The principal components accounting for the most significant variance were extracted based on the eigenvectors with the highest eigenvalues. The HCA was performed based on Ward's method and the squared Euclidean distance (Guler et al., 2002).

3- FINDINGS AND ARGUMENT

The pyrite content of the rock materials in dump No. 7 varied between 5.8 and 24.47 wt%. Elements of S, Al, Fe, K, Mg, Na, P, Cu, and Ca were the most abundant elements of rock materials based on their median values. The paste pH values of rock materials were between 1.03 and 4.13. Elements and major ions of SO_4^{2-}, S, Fe, Al, Cl^-, Cu, Ca, Mg, Si, P, Na, Mn, and K were the most abundant in rock materials based on to their median values. Optical mineralogy revealed that pyrite particles between 50 and 500 microns were associated with quartz fragments (Figure 1).
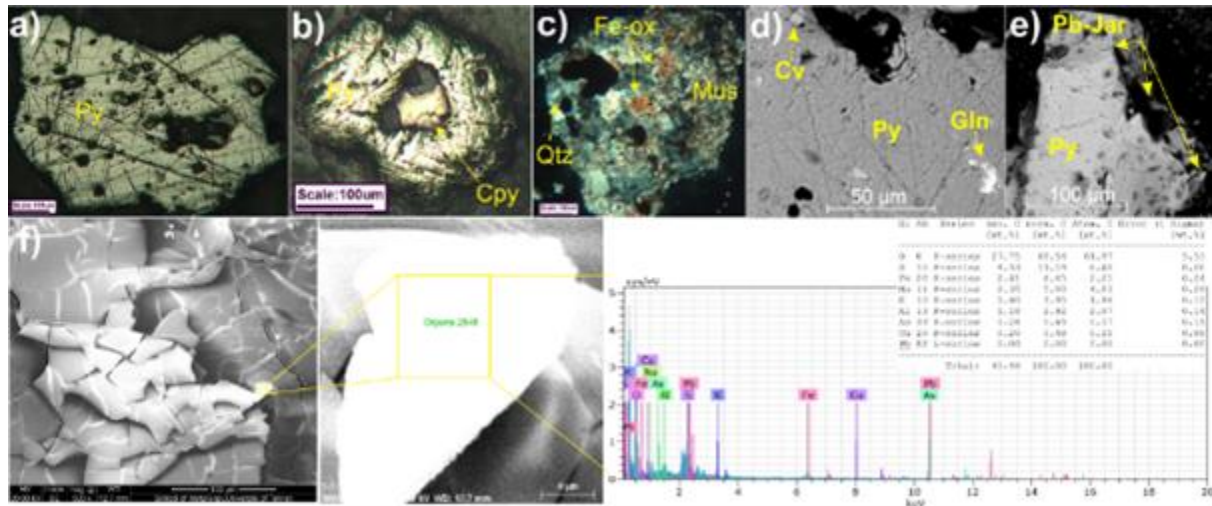
Fig 1. Selected photographs of optical mineralogy, EPMA, and SEM-EDS analyses a) an unaltered form of pyrite (py) with grain size of about 500 μm, b) the inclusion of chalcopyrite (cpy) with pyrite crystal, c) quartz (Qtz) and muscovite (Mus) gangues with Fe-oxyhydroxysulfate (Fe-ox) at the oxidized sample of HC1S in transmitted light, d) an oxidized form of pyrite (py) with the occurrence of Pb-jarosite (Pb-Jar) at its margin, e) pyrite grain with the inclusions of covellite (Cv) and galena (Gln), f) secondary mineral of jarosite associated with trace elements.

Chalcopyrite, covellite, and galena were observed as interstitial allotriomorphic crystals within pyrite (Fig 1). The flaky shapes of muscovite and Fe-oxyhydroxide traces were detected in the oxidized part of the dump (sample of HC1S) (Fig 1). Strong oxidations and replacements by secondary products of jarosite were detected around the pyrite crystal in HC1S sample (Figure 1). The association of As and Pb with pyrite was confirmed by semi-quantitative analysis of EPMA-WDS. There was no evidence of As-bearing minerals in the samples. Pyrite was a primary carrier of As compared to other sulfide minerals. The jarosite rims around pyrite composed of moderate As (from 0 to 600 mg/kg) and relatively high Pb concentrations (from 1900 to 3100 mg/kg) (Figure 1). The XRD results indicated that pyrite, chalcocite, and chalcopyrite were main sulfide minerals of the rock materials. The secondary products of pyrite oxidation such as brochantite and jarosite were observed in the oxidized samples of the dump. Quartz, phyllosilicates (illite and muscovite), orthoclase and clay minerals were identified as major gangues of rock materials. Due to the scarcity of galena, it was not detected by XRD analysis in the rock materials. The ANC value was negative for all samples and the two samples of HC1S and HC1 had the lowest neutralization potential. The NAPP ranged between +200.08 and +654.1 kg H2SO4/t based on total content of S. Based on the NAPP values, AMD is generated in all samples for a long time due to the high content of total S and high content of pyrite. For a short or long term persisting of AMD, a sulfur content of 0.3 wt.% has been suggested. The behavior of rock materials was predicted by comparing the two values of paste pH and NAG pH (Figure 2). Based on the result of AMD prediction plot, all samples, except for HC2, were extremely acid-forming (EAF). Sample HC2 with a high NAG pH value (higher than 4) was acid-forming (AF). Sample HC1S had the highest NAG at the pH of 7 with a value of 205.75 kg H2SO4/t. Sample HB4 with an NAG value of 48 kg H2SO4/t had the lowest NAG at pH of 7. Based on correlation analysis, a strong negative correlation was observed between pH and elements of As, Fe, and Pb. It appears that these elements were highly mobile under low pH values. There was a positive correlation between Fe, Pb, As, and K, indicating their association with secondary water soluble minerals. Four major groups each representing a distinct facies

were classified by dendrogram. Cluster 1 included physico-chemical parameters of pH, EC, DO, sulfur, sulfate, chloride, Al, and Ni derived from the dissolution of secondary sulfates. Cluster 2 containing K, Sc, Co, Y, Bi, Cu, Ce and Na revealed the association of copper with rare earth elements.
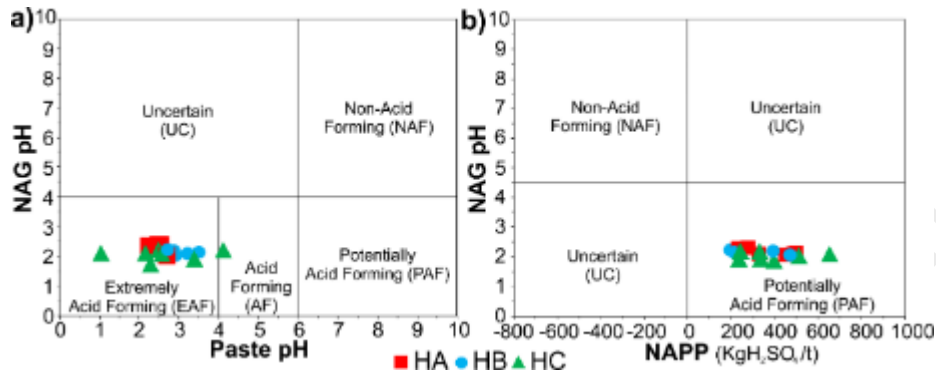

Fig 2. The generation of AMD is predicted for the rock materials from dump No. 7 based on, a) Paste pH versus NAG pH and b) NAPP versus NAG pH (EAF: Immediate AMD generation, AF: rapid AMD generation, PAF: lag-tim Cluster 3 including Eh, ferrous iron, ferric iron, Fe, Pb, and As revealed same source of these parameters. Cluster 4 comprising Ca, Mn, V, Mg, Si, Zn, Cr, Cd and Sr derived from silicate gangues. Five principal components accounted for 91.29% of the total variance of the hydro geochemical data (Figure 3). PC1 accounted for 38.19% of total variance and is characterized by strong positive loadings for pH, EC, DO, sulfate, chloride, Al, Ni, P, and sulfur, and negative loadings for ferrous iron, ferric iron, Fe, Mg, Mn, Pb, and V. PC2 accounted for 20.17% of the total variance with positive loadings of Ca, Cd, Cr, Mn, Si, Sr, V and Zn, and negative loadings for Ce and Cu. PC3 accounted for 14.5% of the total variance and is recognized for positive loadings of Bi, Co, Cu, K, Sc and Y. PC4 accounted for 13.05% of total variance with positive loadings of Eh, ferric iron, As and Ni, and a negative loading of pH. PC5 with 5.36% of total variance only had a positive loading of Na. PC1 and PC4 may be responsible for the dissolution of pyrite oxidation products. PC2 and PC3 are characterized to be responsible for dissolution of gangues and copper sulfates.
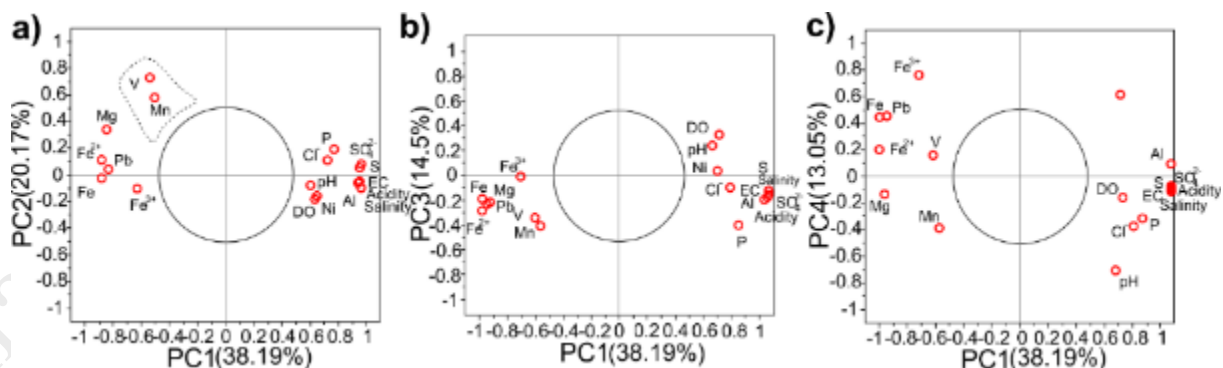

Fig 3. The graphical representation of principal components a) PC1/PC2, b) PC1/PC3, c) PC1/PC4.

4- CONCLUSIONS

Pyrite mineral between 5.1 and 24.4 (wt.%) was the most abundant sulfide mineral in the rock materials. Quartz, muscovite, kaolinite, and montmorillonite with low neutralization potential were the main gangues of the rock dump No. 7. The ANC value of all samples were negative. The MPA ranged between 142.2 and 481.9 kg H2SO4/t. According to the results of NAPP and NAG tests, the upper part of the dump No. 7 up to a depth of 3 m has a potential to generate AMD. The sulfate form of sulfur between 1.28 and 7.2 (wt.%) was related to the formation of secondary products of pyrite oxidation. The mobilization of Fe, As, and Pb is mainly controlled by the precipitation of jarosite-groups and surface adsorption on Fe-hydroxyl-sulfates. The copper content was high in the water leaching solution of the rock materials. Therefore, the extraction of the remaining copper from dump No. 7 should be investigated in future researches..

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