Arsenic and Heavy Metals Contamination in Small Scale Mining, Selogiri Area, Wonogiri Regency, Central Java, Indonesia

T. M. Htun¹, I W. Warmada¹, A. Harijoko¹, R. Saputra¹, L. D. Setijadji², K. Watanabe², A. Imai² *1 Departmenf of Geological Engineering, Faculty of Engineering, Gadjah Mada University, Indonesia 2 Department of Earth Resources Engineering, Kyushu University Corresponding author: warmada@mail.ugm.ac.id*

ABSTRACT: Different types of waste waters effluents may be produced as a result of mining. They arise due to the extraction or preparation of the mineral deposits or from the disposal of associated spoil. Generally the major pollutants are suspended solids, dissolved salts or acidity. In the latter case acid mine drainage refers to the oxidations of the sulphide minerals, notably pyrite, which are exposed in the mine or are present in the spoil. The primary oxidation products of pyrite are ferric and ferrous sulphates, and sulphuric acid. In Selogiri, there are many local gold mines where acidic waters were produced by heaps of pyrite discard. Treatment plants, tailings and dumps are also located in this area. Fairly high contents of Pb, Zn, Cd, and As are reflected in the tailing of the contamination source of the amalgamation site. Potential risk maps have been compiled for four elements: Zn, Pb, Cd and As. Among those, the state of geochemical pollution is serious for Cd, Pb, and Zn, As which are the main elements contained in the orebodies. Due to the mining activities in these area, the problems of the potential harmful elements contamination such as As, Cd, Pb, Zn, Cu, Co, and Ni in the mill tailing, water and stream sediments due to acid mine drainage had to be investigated as part of the environmental management programme.

KEYWORDS: Selogiri, mining district, pollution, maps, risk

1. Introduction

The Selogiri area in Central Java, Indonesia is one of the gold prospecting in Indonesia. Since ten years ago, there are many local gold mines with an estimated product of about 10 g per day in some mines and the estimated gold grade is 9 g/t by using amalgamation and complex adit and shaft entry method (Soe *et al.*, 2004; Soe, 2005). There has been extensive gold mining activity in Selogiri area since 1990s, resulting in impacts on the environment. This is due both to increasing production and to inadequate processing technologies. There is a growing awareness of the relationships between animal and human health and the distribution of chemical substances in the environment.

Environmental geochemistry research is concentrated on anthropogenic accumulations of potentially harmful elements (PHEs) such as As, Cd, Hg and Pb and other elements that may be classified as carcinogens, neurotoxins or irritants; some others may cause reproductive failure of birth defects. Occurrences of high As concentrations in drinking water are relatively rare, most case being associated with sources of natural sulphide minerals, such as pyrite and arsenopyrite; hence, high As levels may be produced by the disposal of associated mine wastes. The As concentrations in unpolluted fresh waters typically range from 1 to 10 μ gl⁻¹ rising to 100-5000 μ gl⁻¹ in areas of sulphide mineralization and mining. WHO (1993) recently reduced its recommended limit for As in drinking water from 50 to 10 μ gl⁻¹ in response to evidence from toxicological studies.

In this paper, to understand the As and heavy metals contamination problem by studying the source of As and heavy metals (with a focus on natural geologic processes versus manmade activities), release of As and heavy metals on a mine site (i.e., rocks, tailings, water and stream sediments) and measuring the intensity and extension of contaminated area.



Fig. 1: Location map of the study area

Both mining processes and natural weathering of these material releases the elements of minerals into the water phase. There are two main processes that transform the elements from solid phase to aqueous species. Biological mediated oxidation of sulfide minerals produces acid and iron in solution Equation 1

$$FeS_2 + 7/2 O_2 + H_2O \rightarrow Fe^{2+} + 2 SO_4^{2-} + 2 H^+$$
 (1)

The abiotic actions may further dissolve the solids, due to low pH and oxidation-reduction reactions Equations 2 and 3.

$$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 14Fe^{2+} + 2 SO_4^{2-} + 16 H^+$$
(2)

$$Fe^{2\tau} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3\tau} + \frac{1}{2}H_2O$$
 (3)

Under acidic conditions arsenic is co-dissolved with the major elements and transformed into an aqueous species when pH is below 4

2. Geology and ore deposit model in Selogiri area

The Selogiri is located administratively included in the Wonogiri, Central Java province (Fig. 1). It is belonging to western part of Southern Mountain in Central Java, which consists of a series of mixed and flysh-like deposits with a total thickness of about 4500 m (Bothe, 1929 vide Rahardjo, *et al.*, 1993). These rocks overlied unconformably the Pre-Tertiary metamorphic rocks and Eocene sedimentary formation of the Jiwo Hill complex, which was covered by limestone formation (Gamping-Wungkal Formation). The series of mixed and flysh-like deposits can be devided into Oligocene-Lower Miocene of Kebo-Butak Formation, Sambipitu Formation of Early-Middle Miocene age, and Oyo Formation of Middle Miocene age. These formations are covered unconformably by Middle Miocene-Pliocene limestone of Wonosari Formation, Late Miocene of Kepek Formation, and Quaternary alluvial deposits (Fig. 2).

According to the geological succession of the Southern Mountain area, Selogiri area consisted of two Tertiery formations of rocks, i.e., sandstone as a member of Kebo-Butak Formation and igneous rocks as the members of Mandalika Formation. The most prospective host for mineralization lies on the Mandalika Formation, Oligo-Miocene in age (Surono et al,

1992) that is composed of andesite to decite lava and tuff and diorite intrusive. The Selogiri area is on the undulating hill of G.Randu Kuning, G. Tumbu, and Kalipuru with elevations range from 150 up to 222 m on the top of G. Tumbu.



Fig. 2: Geological map of Selogiri area and its vicinity showing mapped major faults (after Prasetyanto, 1997). Box: location of the samples collection.

Mineralization type was characterized by the present of potassic alteration (biotite-chlorite) and overprinted by phyllic alteration (quartz-sericite-pyrite) which is occurred in andesite host rocks. The altered andesite hosted quartz-calcite stockwork and disseminated (pyrite and chalcopyrite) copper-gold mineralization. The local mines were found in this intrusion. Andesite at G. Tumbu, was found with stockworks quartz veins. It was altered by hydrothermal fluids from later stages of solidification. There are four main veins formation which are composed of chalcopyrite, magnetite, and quartz (Fig. 3). Along fissures, there are secondary azurite and malachite deposits which are altered from chalcopyrite and copper rich ore from quartz veins and the stockworks mineralized quartz veins were found. Galena and sphalerite are also noted in this places associated with the stockwork. In G. Tumbu and G. Randu Kuning yielded 7.34g/t Au and with low 0.34% Cu but elevated Pb and Zn (Prihatmoko, 2005).



Fig. 3: Gold and copper mineralization zones in Selogiri mine (Soe, 2005)

3. Results and discussions

The natural As contents in Selogiri area, according to bulk-rocks and bulk-ores geochemistry (XRF & INAA) analyses results, the host rock (mainly andesite) contain 8-59 ppm As; it's contents elevate into hundreds of ppm due to alteration. There is 3 samples had 873 ppm (contaminated by ore mineral arsenopyrite and arsenian pyrite). The greatest concentrations of these minerals occur in mineralized areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. Among the other trace elements contamination, the highest contents Pb contains 2890 ppm, Zn contains 54400 ppm and Cd contains 202 ppm.

The another major source of As and Zn, Pb and Cd contamination is tailing materials from the amalgamation units that contain As of more than 5 ppm and up to almost 385 ppm. For Zn contains more than 75 ppm and up to 4520 ppm, Pb contains more than 20 ppm and up to more than 10000 ppm and Cd contains more than 1 ppm and up to 10 ppm. Studying the distribution of As and heavy metals anomalies in tailings is therefore an effective way to understand the process and extent of As and heavy metals contamination in the area.

From the tailing results, As and heavy metals contamination was established class margins for As, Pb, Zn and Cd classification that is used for mapping the As, Pb, Zn and Cd anomalies (approximately 1 sample = 0.9 km^2). In the study area location of the amalgamation units are grouped into three villages names, i.e., Nglenggong, Jendi and Keloran. On contrary, high level of As and heavy metals anomalies are mainly located at an operating amalgamation site at Keloran. The anomalies maps are shown in the figures (Fig.4-7). These anomalies remarkably show the background tailing effluents produced as the result of mining due to the extraction of the mineral deposits.



Fig. 4: As contents in tailing, Selogiri mine, Central Java, Indonesia

From the tailing sites (i.e., contamination source) sulfide oxidation and acid- generation rates can increase substantially. In addition, tailings particles are more likely to be distributed by wind and water than their more coarse-grained equivalents in waste rock piles. Therefore some of the surface water samples from the stream around these tailing sites show low field pH values as 2-3. It was attributable to acid mine drainage. The water from the stream,

irrigation and wells are suspected to be contaminated by As and heavy metals and these water samples are still under detected.



Fig. 5: Pb contents in tailing, Selogiri mine, Central Java, Indonesia



Fig. 6: Zn contents in tailing, Selogiri mine, Central Java, Indonesia



Fig. 7: Cd contents in tailing, Selogiri mine, Central Java, Indonesia

4. Conclusions

Our study shows that significant background source of geologic context of the Selogiri area and another important contaminated source of tailing (amalgamation sites). According to these analytical results, mineral dissolution reactions tend to be most rapid under extremes of pH and Eh. Iron oxides dissolve under strongly acidic conditions and under strongly reducing conditions. The trace elements, including As, present either as adsorbed (labile) As or as irreversibly bound (non-labile) As will also tend to be released during this dissolution. Sulphide oxidation, particularly pyrite oxidation, can also be an important source of As especially where these minerals are freshly exposed as a result of a lowering of the water table. This can occur locally in and around mines and on a more regional scale in aquifers. In extreme cases, this can lead to highly acidic ground waters rich in SO_4 , Fe and other trace metals. The prediction of water quality that results from mining and mineral processing activities has therefore become a high priority in the permitting of mining activities worldwide, in order to prevent the formation of the environmental effect of deleterious drainage water.

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