ORIGINAL ARTICLE

Mineralogical Composition of Iron Ore Mining Waste and Associated Risk Assessment

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ABSTRACT

Introduction: Mining activities have often been associated with water-, soil- and air-related contaminants. An investigation has been undertaken on the distribution of mineral, major and trace elements of iron ore mining waste. This paper attempts to evaluate the chemical and mineralogical composition of the iron ore mining waste and its association with the potential ecological risks. **Methods:** Samples of mine waste were collected from eleven locations within an iron ore mine. The samples were subjected to mineralogical analysis using X-Ray diffraction and chemical composition using scanning electron microscopic with energy dispersive X-ray for its microstructure and major oxides. Metallic (major and trace) elements of the samples were also identified, and the potential ecological risk was estimated. **Results:** The major mineral composition of 60-90% and moderate amount of SiO₂ between 3.3-40.1%. Fe, Al and Mg were the major metallic elements in the samples. The potential ecological risk and the total risk index due to Zn, As, Cr and Cu was found to be at low risk. **Conclusion:** Despite being at low-risk, the extent of contamination should be monitored to prevent severe ecological damage due to mining activities.

Keywords: Mineralogy; Iron ore; Heavy metal; Contamination; Ecological health

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INTRODUCTION

Mining is an important sector in Malaysia that has contributed to significant gross domestic product (GDP) growth for the country. Minerals mining in Malaysia includes metallic and non-metallic minerals such as bauxite, coal, silica, antimony, barite, copper, clays, lead, gold, silver, iron, limestone, and tin which are essential minerals for the production of secondary minerals or other products. However, mining activities may result in environmental degradation due to some minerals exploitation through the mineral exploration, discovery, processing and distribution (1-3). Mining operations include vegetation destruction, grinding, blasting, and transportation from the pit to the dump site prior to further storage. Minerals of low value, e.g. mining waste or rock fragments have been discarded, adding up to the accumulation and origin of contaminants, while the valuable or high-grade minerals are extracted. Environmental degradation such as habitat destruction, soil erosion, turbidity increase, hydrology disruption are among the severe effects of mining activities (4-6).

Mining may induce an environmental hazard that can impair the quality of soil and water, which can end up affecting human and other organisms (7). The impacts if are not taken care of, the damages are irremediable and can be toxicity effect can be permanent or persistent in human and environment. For instance, contamination associated with heavy metals in soil may cause adverse health effects as heavy metals could pose long-term implications according to the persistence and biodegradability of heavy metal stressor. In order to evaluate the extent of hazards or risks due to the presence of heavy metals, several indices have been extensively used in different regions of the world such as geo-accumulation index (Igeo) and the potential ecological risk index (PERI) (8-10). Elements of heavy metals have been found widespread in most mining soils and sediments include As, Al, Cu, Cr, Zn, Fe, Mn, Sr and Cr. Severe impacts can be expected as a result of metallic contamination if their presence is uncontrolled. According to Diami (10), contamination of heavy metals from mining may pose health effects on adults and children on the long term. Consequently, there has been growing concern

about the toxicity effect from mining pollution and its impact on human health and environmental quality (11-14). Therefore, this study attempts to evaluate the mineralogical and chemical composition of iron ore mining waste and provide assessment of the potential ecological risk associated with the degree of contamination due to the iron ore mining.

MATERIALS AND METHODS

Sample collection

Iron ore mining waste was collected from an iron ore mining site in Jerantut, Pahang, Malaysia. The samples were collected from eleven locations in the vicinity of the iron ore mining site. The types of samples collected were rock samples (haematite and magnetite rocks), waste of processed minerals (stockpiles of grade A and grade B iron ores), iron ore sludge, tailing ponds sludge, waste dump and mine tailings. The samples were collected as representative samples from each location and were obtained as composite samples. In total, about 30 kg of iron ore rocks, 16 kg of stockpiles, 20 kg of waste dump, 10 kg of iron ore waste grade A and B, and 30 kg of mine tailings (sediment and sludge) were collected from the mining site. Based on the types of samples, i.e. rocks, soil, sediment or sludge, the samples the prepared accordingly for the subsequent chemical and mineralogical analyses.

Mineralogical and chemical analysis

All the samples were brought to the laboratory for further analysis. The rock samples the cleansed before being grounded to small fractions. Homogenous samples were then obtained and were subjected to further grinding to fine particles of < 1 mm. Soil samples were air-dried while the sludge was oven-dried prior to being grounded until the desired particle sizes were obtained. The samples were then analyzed using an X-ray diffractogram (XRD) for identification of mineral composition, which was conducted using a Bruker D8 Advance Model with Cu-Ka radiation over the range of 5° to 80° scattering angle at 1° / min rate. The detection limit for the instrument was between 1.2%. A Diffrac.EVA software was used to interpret the XRD data to identify the mineral phases in the samples. The scanning electron microscopic analysis with energy dispersive X-ray (SEM-EDX) using SEM instrument model Hitachi SU3500 was performed to observe the microstructure of the samples and to acquire the major chemical composition in the form of major oxide elements. About 1 g of homogeneous fine powder samples were used in the analysis which was heated at 2500°C for 15 minutes and observed at 100–150 µA current at 20 Kv.

Metallic element analysis

The elemental compositions of the bulk specimens of rock samples were identified using an X-ray fluorescence (XRF) spectroscopy. The samples were prepared by dissolving and diluting the samples by some analytes prior to the spectroscopic analysis. For the soil and sludge samples, the metallic composition were determined by an inductively coupled plasma -optimal emission spectroscopy (ICP-OES). The samples were subjected to acid digestion prior to the analysis, i.e. pre-digestion overnight and subsequent digestions following temperature increase from 40-140OC. Samples were then filtered and were then analyzed using an ICP-OES for the metallic elements.

Potential Ecological Risk Index

Potential ecological risk index (PERI) is a technique to identify the extent of contamination due to the presence of some metallic compound which is associated with the ecological, environmental and toxicity effects (15-18). The risk assessment was performed by evaluating the percentage of each contributing elements to the total risk index. The potential ecological risk index was calculated by using the following equation (1) :

$$E_{r}^{i} = T_{r}^{i} \bullet C_{r}^{i} = T_{r}^{i} \bullet \frac{D_{i}}{B_{i}}$$
(1)

The sum of all potential risk factors for all elements was defined as:

$$\Sigma E_{\mathbf{r}}^{\mathbf{i}} = \Sigma T_{\mathbf{r}}^{\mathbf{i}} (\mathbf{D}_{\mathbf{i}} / \mathbf{B}_{\mathbf{i}})$$
(2)

where,

 E_r^i is the potential ecological risk factor for a specific substance; T_r^i represents the toxicity coefficient for a specific element; C_r^i is the contamination factor; D_i is the mean content of the evaluated substance; B_i is the pre-industrial reference level adapted from Hakanson (17).

RESULTS

Chemical composition of iron ore mining waste

The chemical compositions of the iron ore mining waste samples were identified in the form of oxide elements which include Fe₂O₃, SiO₂, CaO, SO₃, TiO₂ and K₂O as shown in Table I. The largest portion of major oxide component in all samples was Fe₂O₂ (ferric oxide) in the range of 39.6-94.7%, followed by SiO₂ and CaO, and minor oxide composition of SO_3 , K_2O and TiO_2 . SiO_2 (quartz) was found in all samples between 3.3-40.1%, while CaO (calcium oxide) constituted about 0.6-15.2%. Minor oxide elements of potassium oxide, K₂O was found in the range of 0.1-5.3%, anatase, TiO, in the range of 0.7-1.9% and sulfur trioxide, SO, between 0.4-3.9%. The presence of these oxide elements was associated with the major minerals originating from the rocks and soils of the mining area.

	SiO ₂	TiO ₂	Fe ₂ O ₃	CaO	SO ₃	K ₂ O
Haematite Rock	8.9	0.7	84.7	0.6	2.8	1.3
Site 1 (Magnetite)	8.9	1.2	86.8	2.5	-	1.8
Stockpile A	3.6	0.8	93.6	1.1	0.4	-
Stockpile B	4.5	0.9	92.2	1.7	-	0.1
Site 2 (Stockpile)	3.3	0.7	94.7	0.7	-	0.1
Sludge Ore	19.4	0.8	61.8	9.6	3.9	0.9
Tailing Pond 1	24.0	1.4	62.9	7.1	1.3	1.4
Tailing Pond 2	21.4	0.9	61.1	11.5	2.1	1.5
Tailing Pond 3	40.1	1.9	39.6	10.2	1.4	5.3
Waste Dump	14.1	0.8	78.1	3.6	1.5	0.9
Mine Tailings	20.8	0.7	57.8	15.2	2.9	1.1

Table I : Major oxide elements of iron ore mining waste

Mineralogical composition

Mineralogical analysis of the samples suggested that the major minerals found were haematite (Fe_2O_2) , magnetite (Fe_3O_4) , anorthite $(CaAl_2(SiO_4)_2)$ and quartz (SiO₂) as depicted in the XRD peaks in Fig. 1. Haematite and magnetite were the major mineral phases detected which were identified to be >30% from the XRD analysis. The presence of the minerals were observed from the SEM images which demonstrate surface morphological structure of the scanned samples (Fig. 2). The presence of these minerals were represented by the flaky-shaped minerals (at magnification of 200x with 100 µm) and crystal-shaped minerals (at magnification of 500x with 80 µm) as seen in the SEM images in Fig. 2a and 2b, respectively. These images indicate samples that are enriched with Fe-based minerals which correspond with haematite and magnetite (21).

Metallic elements of iron ore mining waste

The concentrations of major and trace elements in the iron ore mining waste are tabulated in



Fig. 1: X-ray diffractogram patterns of iron ore mining waste sample.



Fig. 2 : SEM images of iron ore mining waste samples.

Table II, which were found to be in the order of Fe>Al>Mg>Ca>Ti>K>Ba>Mn>Zn>Sr>V>As>Cr>Cu. Based on Table II, Fe, Al and Mg were the major elements in the samples, having the mean concentration of 8001 mg/kg (in the range of 144-21758 mg/kg), 3325 mg/kg (406-6856 mg/kg) and 1222 mg/kg (183-3113 mg/kg), respectively. The mean concentration of other trace elements of Ca, Ti, Mn and Sr were 2.61 mg/kg, 2.89 mg/kg, 2.78 mg/kg and 1.16 mg/kg, respectively. Other elements such as K, Ba, Zn, V, As, Cr and Cu were recorded below 3 mg/kg. Fig. 3 shows the concentration distribution of the major elements of Fe, Al and Mg in the iron ore mining waste. Fe was notably found in greater amount in samples of haematite, the processed waste minerals, sludge and mine tailings.

Potential ecological risk index

In this study, the presence of trace elements in the samples such as As, Cr, Cu and Zn was evaluated for their potential ecological risk due to their potentially toxic behaviour. Table III shows the contribution from each element to the total ecological risk index, RI. The potential ecological risk index (E_r^i) for Zn, As, Cr and Cu were all found to be less than 4.00. Despite this, the contribution of each element to the total

Table II : Concentration of major and trace elements in iron ore mining waste

Site	Fe	Al	Mg	Ca	Ті	К	Ba	Mn	Zn	Sr	V	As	Cr	Cu
Haematite Rock	21758	nd	nd	0.47	3.22	0.63	1.20	1.87	0.39	nd	nd	nd	0.39	nd
Site 1 (Mag- netite)	6304	1836	2936	1.99	5.33	0.09	nd	3.17	0.62	0.65	nd	nd	nd	nd
Stockpile A	7935	406	183	1.06	4.69	nd	nd	2.88	nd	nd	nd	nd	0.96	nd
Stockpile B	10259	932	358	1.64	5.65	0.06	nd	2.84	nd	0.68	0.55	nd	nd	0.05
Site 2 (Stock- pile)	10592	5572	nd	0.66	nd	0.07	nd	2.88	0.47	nd	0.43	nd	0.84	4.05
Sludge	13630	710	nd	6.59	1.47	0.33	0.29	2.85	0.68	3.68	nd	0.40	nd	0.26
Tailing Pond 1	8683	5473	3113	4.46	1.99	0.32	0.31	3.04	1.79	1.88	nd	0.60	nd	0.31
Tailing Pond 2	310	5169	643	2.78	2.89	0.41	0.48	2.81	nd	1.30	nd	0.57	nd	nd
Tailing Pond 3	6445	6856	nd	4.61	1.84	0.43	nd	2.63	1.03	2.16	0.14	0.48	nd	nd
Waste Dump	144	9117	2050	2.51	2.24	1.03	nd	1.80	0.90	1.83	0.17	nd	nd	nd
Mine Tailing	7589	514	4164	1.99	2.51	0.36	nd	3.84	nd	0.62	0.24	nd	nd	nd
Guideline values:														
Canadian Council of Ministers of Environment	**	**	**	**	**	**	**	**	290	**	**	11	64	63
Australian Dep. of Envi- ronment and Conservation	**	**	**	**	**	**	**	500	200	**	**	20	400	100
Crust aver- age (24)	30890	77440	13510	29450	3117	28650	668	527	52	316	53	2	35	4.3
Crust aver- age (25)	50000	80000	270000	30000	5000	500	26000	430	900	70	350	150	2	60

All units in mg/kg; nd - not detected (below detection limit); ** not specified





Fig. 3 : Concentration distribution of Fe, Al and Mg in iron ore mining waste.

RI is depicted in Fig. 4. It can be seen that the highest contribution from As was found in the tailing ponds

Fig. 4 : Percentage of potential ecological risk index for single elements to the total RI.

and ore sludge, Cu was dominating in the processed waste minerals in the stockpiles and magnetite rocks, while Zn was dominant in the waste dump.

Site	Potential Ecological Risk Index (E ⁱ ,)				Total Ecological Risk Index			
					(RI)			
	Zn	As	Cr	Cu				
Haematite Rock	0.002	0.000	0.009	0.000	0.01			
Site 1 (Magnetite)	0.004	0.000	0.000	1.000	1.04			
Stockpile A	0.000	0.000	0.021	2.000	2.02			
Stockpile B	0.000	0.000	0.000	3.000	3.00			
Site 2 (Stockpile)	0.003	0.000	0.019	4.000	4.02			
Sludge Ore	0.004	0.267	0.000	0.026	0.30			
Tailing Pond 1	0.010	0.399	0.000	0.031	0.44			
Tailing Pond 2	0.000	0.380	0.000	0.000	0.38			
Tailing Pond 3	0.006	0.320	0.000	0.000	0.33			
Waste Dump	0.005	0.000	0.000	0.000	0.01			

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DISCUSSION

Chemical and mineralogical composition

Notably, iron oxide, Fe₂O₃ deposit was found dominating in all the iron ore mining waste samples. It can be anticipated that the iron oxides were derived from haematite and magnetite as these were the major Fe-based minerals found in most iron ores (19). Higher portion of Fe_2O_2 , i.e. > 90% were found in the processed waste minerals in the stockpile areas that contained grade A and grade B iron ores. Fe₂O₂ were found between 57-78% in other samples including the mine tailings, tailing ponds, sludge and waste dump, which were mostly in sediment form. Quartz, SiO₂ was found in relatively greater amount in clayey samples of tailing ponds and mine tailings compared to rock samples (20). CaO was found in greater amount in samples of mine tailings, tailing ponds and sludge. The CaO was mainly derived from anorthite mineral, $CaAl_{2}(SiO_{4})_{2}$ which is a Ca silicate mineral.

From the mineralogical analysis, haematite and magnetite were the major Fe oxide minerals in the iron ores. Quartz is a typical mineral found is most mining soils, while anorthite is a Ca-silicate mineral originated from mafic igneous rocks. Alongside, the haematite, magnetite, anorthite and quartz, there were other minerals found in the iron ore samples such as wollastonite (CaSiO₃), diopside (Ca(Mg,Al) (Si,Al)₂O₆) and johannsenite (Ca₄Mn₄Si₈O₂₄). These are all Ca silicate minerals that were adding up to the CaO compound in the samples.

The presence of these minerals explain the origin of some important metallic elements in the iron ores such as Fe and Al, and major components of Ca and Mg (2, 10). Essentially these metal elements are stable in the earth strata and within the geological structure of rocks. However, upon reactions with water and air they will become mobile into the environments and potentially causing contamination (25). For instance, leaching of Fe into water may cause orange-like or reddish-coloured water which can be very acidic. This can be harmful to the surrounding environments and aquatic lives upon contact with the water. This is also not visibly desirable as the impact may persist over long term.

Metallic elements and potential ecological risk index

Understanding metallic elements distribution will enable identification of potential ecological risks due to the presence of these constituents, apart from evaluating the quality of the mining waste. The concentration of Fe was found highest in the haematite sample and moderately found in the ore sludge and stockpiles of the processed waste minerals. As noted earlier, the Fe element was originating from haematite and magnetite minerals. While Al were moderately found in the waste dump and tailing ponds. It is likely that the Al was derived from Al-containing minerals such as the anorthite and diopside. Mg is believed to be derived from Ca-Mg silicate mineral such as diopside and other traces of Mg oxide minerals. Meanwhile, Mn can be associated with johannsenite mineral that was also found in some samples of the iron ore waste. Overall, it was found that most of the metallic content of the samples were below than the recommended acceptable range according to the guideline values of Canadian Council of Ministers of the Environment (22), Australian Department of Environment and Conservation for metallic content in soil and sediment (23), crust average value from Wedepohl (24), and Smith and Hyuck (25) (Table II).

On the other hand, ecological risk assessment is an evaluation on the extent of the risks due to the toxicity effect of some metallic or metalloid elements in the environment (11,15, 26). Findings indicated that there having a low ecological risk due the presence of trace elements in the samples such as As, Cr, Cu and Zn. Despite its low risk, the presence of metalloid As and metallic constituents of Cr, Cu and Zn should be monitored to minimize or prevent the environmental hazards, which can eventually threaten human health. Regardless of their toxicity level, the contribution of the trace elements to the potential ecological risk was ranked to be in the order of Cu>As>Cr>Zn. Of these elements, Cr were reported to be less volatile and has lower risk on the environment compared to As, Cr and Zn (27). It is worth noting that although metalloid As is a non-essential element for living organisms, however it can be very toxic and may cause environmental pollution (12, 13). Based on the classification of the risk index, the RI for all metallic/metalloid elements was classified as having low risk as the value was below 40 (18). The findings were also similar with a previous study on the extent of contamination at an iron ore mining site in the state of Pahang, Malaysia, that the same elements were detected but were not likely to cause serious environmental and health impacts (10). Therefore, it can be learned that the presence of these elements at current concentrations will not induce short- to medium-term risks on the ecological health. Further investigation can be undertaken to assess whether it may induce long-term impact on ecological and human health.

CONCLUSION

The mineralogy and the chemical composition of iron ore mining waste have been determined in association with its potential ecological risks. It was discovered that the major mineral composition of the iron ore mining waste were composed of quartz, anorthite, haematite and and magnetite. As anticipated the greatest percentage of chemical composition of the samples was Fe₂O₃ which constituted 60-94% of all major oxide components. The mean concentration of metallic elements were ranked in order of Fe>Al>Mg>Ca>Ti>K>Ba>Mn>Zn>Sr>V>As>Cr>Cu. All the metallic elements were below than the recommended guideline values. Trace elements of Zn, As, Cr and Cu have been evaluated for their potential ecological risks. The total ecological risk index indicated low ecological risk due to these elemental composition, suggesting that the current concentrations of these elements would not inflict ecological health. Findings from this study would be useful for current and future mitigation measures as a result of mining activities.

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