Potential of Mining Waste from Metallic Mineral Industry for Carbon Sequestration

Sharifah Nur Munirah Syed Hasan and Faradiella Mohd Kusin
Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

Email: faradiella@upm.edu.my

Abstract. Anthropogenic carbon dioxide emission mainly from metallic mining industry is the major gases that increase greenhouse gases. Mining wastes that are discarded from mining operation might have potential as a solid buffer in storing atmospheric carbon dioxide for long term by mineral carbonation. Therefore, this study was conducted to identify the major minerals in the waste rocks at waste dump and stockpile of a gold mine, and to determine the potential of silicate minerals from gold mining wastes for mineral carbonation process. Waste rocks sample from the waste dump and stockpile were obtained and were analyzed using X-ray diffractometer. Findings indicated that quartz, mica, dolomite, and calcite are the major minerals found in the waste rocks. Results also demonstrated that carbonate minerals such as dolomite, calcite, and siderite are in stable form that are considered a reservoir for carbon storage. Silicates minerals such as chlorite, pyroxene, mica, and amphiboles that are present at both waste dump and stockpile contain magnesium, calcium, and iron silicates ions, which can facilitate the formation of carbonate minerals. Thus, the presence of potential minerals from gold mining wastes provides a great possibility for carbon sequestration that can encourage evaluation of carbon footprint in mining industry.

1. Introduction
The removal of soil and rocks through extraction and processing of materials from mining industry to gain access to buried ore, includes the leftover materials such as solids, water, and gases that are called waste materials or residues. This process releases carbon dioxide (CO₂) which contributes to high accumulation of anthropogenic greenhouse gases (GHGs) in the atmosphere [1,2], and yields large amount of waste that has little or no economic value. However, mining wastes in a positive approach can help to mitigate environmental pollution due to its potential for CO₂ storage in reducing anthropogenic GHG emission to the atmosphere. Therefore, the process of passive CO₂ sequestration or carbon capture and storage (CCS) is required to stabilize CO₂ in the atmosphere which involves trapping CO₂ from the gas streams into geological formations such as soil and rocks in carbonate form by natural carbonation reaction [3,4,5]. Carbonate minerals that form in the soil include formation of stable carbonate or bicarbonate to capture carbon through weathering of primary minerals that release ions such as hydrogen (H⁺), magnesium (Mg²⁺), and calcium (Ca²⁺), reacting with CO₂ [1,4,5,6,7,8]. This natural process of carbonation provides a great potential for carbon storage of mining residue in reducing GHG emission. Furthermore, mining waste from different types of mining production might have potential for CO₂ sequestration and also provide economic benefits that involve minimal cost technology [3,6,9].
1.1. Theory of calculating carbon sequestration

Waste rock might have potential to sequester CO$_2$ s via mineral weathering in order to mitigate climate change. Waste rock is a coarse material that consists of different sizes of particles which is produced from mineral excavation alongside overburden that frequently has low mineral value [2,10]. This material is often stored in heaps or dumps and disposed of in stockpiles on the mine site, where the sizes of dumps or stockpiles are very huge and signify complex geotechnical constructions [11]. Mine waste rocks from ultramafic-hosted ore deposits are commonly preferred for carbonation mineralization due to high amount of magnesium silicates from final product of mining process and contains primary ultramafic minerals such as olivine (Mg$_2$SiO$_4$) and weathered minerals such as serpentine [Mg$_3$(OH)$_4$(Si$_3$O$_5$)] [12]. This minerals release magnesium ions and react with carbonate and bicarbonate ions to form carbonate minerals via carbonation reaction as shown in the following reactions (1) [8,13]:

$$2\text{Mg}_2\text{SiO}_4\text{(olivine)} + \text{H}_2\text{CO}_3 \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4\text{(lizardite)} + \text{MgCO}_3\text{(magnesium carbonate)}$$  \hspace{1cm} (1)

Moreover, ultramafic rocks in mine tailings also allow carbon sequestration to occur through formation of magnesium and/or calcium carbonates from natural weathering process [14]. For instance, during rock weathering, carbonation reaction of calcium silicates in metamorphic rocks produces wollastonite (CaSiO$_3$) minerals (reaction 2), which increase carbon uptake [8,13,15]. As a result of rock weathering, it accelerates carbonation of calcium silicates, which occur naturally and promote carbon sequestration.

$$\text{CaSiO}_3\text{(wollastonite)} + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3\text{(calcium carbonate)} + \text{H}_4\text{SiO}_4$$  \hspace{1cm} (2)

Mineral carbonation has the potential to sequester large amounts of carbon in stable carbonate minerals through natural weathering process of silicate such as magnesium and calcium silicates. However, Mg-silicates such as olivine and serpentine are preferred to be used in mineral carbonation in waste rock due to more reactive and accessible [11]. Estimation of carbon sequestration potential from mining waste is measured from cation content of magnesium oxide (MgO) and calcium oxide (CaO) in weight percent (wt%) which represents percentage of waste rock to be produced at mine site. 100% conversion rate is assumed where one tonne of MgO or CaO wt% can sequester one tonne of CO$_2$ based on the following equation 3, $R$ is the total amount of CO$_2$ sequestered [11]:

$$R = (\text{MgO/CaO wt%}) \times \text{(waste rock tonnage)}$$  \hspace{1cm} (3)

The maximum carbonation potential is calculated by assuming that all of Mg and/or Ca available in mining waste are converted to CaCO$_3$. For example, 1 mol of cations captures 1 mol of carbon from MgCO$_3$ mineral [8]. Therefore, 1 mole of cation can capture 1 mole of carbon dioxide from mining waste.

Thus, the objectives of this study were to: (1) to identify the major minerals in the waste rocks at waste dump and stockpile of a gold mine; and (2) determine the potential of silicate minerals from gold mining wastes for mineral carbonation process. Mineral compositions of other types of metallic mining waste are also discussed for their potential in carbon sequestration.

2. Materials and methods

2.1. X-ray diffraction analysis

Samples of rocks were obtained from a gold mine for field trial assessment. The rock samples were crushed and were grounded into fine particles using agate mortar and pestle. The fine samples were sieved to 1 mm size fraction using particle sieves because grain size of samples is a critical consideration that can affect results of X-ray diffraction (XRD) analysis [16]. Then, sieved samples were grounded in a very finely powder form using a special mortar and about 1 ± 0.5 g of fine powder samples were placed on special sample holder before being attached on X-ray machine [17]. Powder
samples were analyzed using XRD instrument (model Philips X’Pert Pro Pranalytical-PW3440/60, Netherlands) at 1°/min rate (0.02° step size) over the 5–50° scattering angle range [2,6], where the range of detection limit was between 1 to 2% [18]. This analysis was used to classify mineral characterization at the waste dump and stockpile within the gold mine [2,17]. Integrated intensity of peak areas from the single peak function was determined using Diffrac AT EVA software (v.9.0) and the d-spacing was identified using OriginPro 8 software (Originlab Corporation, Northampton, UK).

3. Results and discussion

3.1. Mineralogy of waste rocks and potential of silicate minerals from gold mine

Example from the case study of a gold mining is presented here. Potential feedstock for mineral carbonation found for this case study were the carbonate and silicate minerals as shown in Table 1. There were 15 types of minerals that were identified from XRD analysis of the waste rock samples at the waste dump and stockpile of the gold mine. There were four major minerals found in both the waste dump and stockpile samples which are quartz, mica, dolomite, and calcite, followed by other minerals such as kaolinite, pyroxene, goethite, anatase, chloride, illite, larosite, rutile, siderite, amphiboles, and opal. Major minerals were discovered widespread at both mining wastes due to parent rocks from the waste rock samples were originated from volcanic, sedimentary (e.g., limestone, carbonaceous shale, and conglomerate), and metamorphic rocks (e.g., phylite) [10]. Figure 1 and 2 indicate that the highest peak of quartz and mica were present in both types of mining wastes because these minerals were resistant to weathering [19]. Thus, quartz and mica minerals were considered as the common minerals found in all types of rocks.

From the XRD results, majority of minerals were present in the waste dump and stockpile except for minerals such as siderite, amphiboles, and rutile that were found at stockpile only, whereas opal mineral was only present at the waste dump (Table 1). Data in the table shows that silicate minerals such as chlorite, pyroxene, mica, and amphiboles that were present at the waste dump and stockpile are the potential feedstocks for mineral carbonation. These silicate minerals contain magnesium and/or calcium silicates ions, which can react with CO₂ to form stable carbonate mineral [7,11,13]. For instance, reaction of chlorite mineral with CO₂ will produce magnesite as shown in following reaction (4):

\[
\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \text{ (chlorite)} + 6\text{CO}_2 \rightarrow 6\text{MgCO}_3 \text{ (magnesite)} + 4\text{SiO}_2 + 4\text{H}_2\text{O}
\] (4)

The presence of magnesium and calcium silicates from chlorite, pyroxene, mica, and amphiboles minerals at the mining wastes are favorable for mineral carbonation processes. Therefore, this shows that the mineral components of the waste dump and stockpile of the gold mine have valuable potential of mineral carbonation for carbon sequestration.
Figure 1. Major minerals with d-spacing value from XRD analysis of waste rock at the waste dump.

Figure 2. Major minerals with d-spacing value from XRD analysis of waste rock at the stockpile.
Table 1. Summary of composition of minerals in waste rocks of a gold mine. Symbol of (✓) is referring to the presence of minerals in waste dump and stockpile.

| Minerals       | Chemical formula                        | Waste dump | Stockpile |
|---------------|-----------------------------------------|------------|-----------|
| Primary minerals |                                         |            |           |
| 1. Quartz      | SiO₂                                   | ✓          | ✓         |
| 2. Mica        | K(Mg₃Fe)₆(AlSi₃O₁₀)(OH)₂                 | ✓          | ✓         |
| 3. Pyroxene     | (Ca,Na)(Mg,Fe,Al)(Al,Si)₂O₆             | ✓          | ✓         |
| 4. Amphiboles   | NaCa₂(Mg,Fe,Al)₃(Al,Si)₂O₂(OH)₂         | ✓          | ✓         |
| Secondary minerals |                                       |            |           |
| 5. Dolomite    | CaMg(CO₃)₂                             | ✓          | ✓         |
| 6. Calcite     | CaCO₃                                  | ✓          | ✓         |
| 7. Siderite    | FeCO₃                                  | ✓          | ✓         |
| 8. Kaolinite   | Al₂Si₂O₅(OH)₄                          | ✓          | ✓         |
| 9. Chlorite    | Mg₆Si₄O₁₀(OH)₈                         | ✓          | ✓         |
| 10. Goethite   | HFeO₃                                  | ✓          | ✓         |
| 11. Illite      | (K,H₂O)(Al,Mg,Fe₂)(Si,Al)₄O₁₀[(OH)₂,(H₂O)] | ✓          | ✓         |
| 12. Anatase    | TiO₂                                   | ✓          | ✓         |
| 13. Rutile      | (Cu,Ag)₂₃(Pb,Bi)₂Si₃                  | ✓          | ✓         |
| 14. Rutile      | TiO₂                                   | ✓          | ✓         |
| 15. Opal       | SiO₂·nH₂O                              | ✓          | ✓         |

*aSilicates minerals, bCarbonate minerals.

3.2. Mineral composition of metal mining waste for carbon sequestration

Minerals are the largest components in soils approximately 45% to 49% of mineral portion, consisting of primary and secondary minerals. Primary minerals such as sand and silt are similar to parent minerals, while secondary minerals are produced from weathering of primary minerals that released ion such as hydrogen, magnesium and calcium ion and react with CO₂ to form stable carbonate mineral such as carbonates [6,7]. Table 2 shows the mineral compositions and its percentage of waste rock materials, which have the potential for carbonation reaction to increase carbon capture. In terms of mineral composition, waste rocks contain magnesium minerals that are potential for mineral carbonation such as brucite, nesquehonite, hydromagnesite, and landsfordite, which are hydrated during natural weathering process from the rocks [4,20]. In addition, alkaline earth silicate type of waste rocks such as ultramafic rock (e.g., peridotite, amphibolite, pyroxenite, and serpentine) and mafic rock (e.g., basalt and gabbro) [21,22,23], are more preferable for mineral carbonation reaction due to abundance of magnesium and calcium content that can bind with CO₂ and form a carbonate, which can reduce CO₂ in the atmosphere. Generally, the waste rocks have the potential feedstock for carbon sequestration due to high amount of magnesium and calcium content that can form a stable carbonate during mineral carbonation process.

Various metal mining wastes are potential to sequester more CO₂ permanently. For instance, metal mining waste from bauxite has a potential for carbon storage due to high concentration of divalent cations such as calcium oxide (CaO = 40%) from calcite (CaCO₃) and gypsum (CaSO₄·2H₂O) minerals [24] and magnesium oxide (MgO = 39.50%) from brucite [Mg(OH)₂], chrysotile [Mg₆Si₄O₁₀(OH)₈], talc [Mg₃Si₂O₅(OH)₂], and chlorite [Mg₆Si₄O₁₀(OH)₈] minerals [8] (Table 3). These minerals have potential to form carbonates such as CaCO₃ and MgCO₃ through mineral carbonation reactions. Bauxite also has high concentration of aluminum oxide (Al₂O₃ = 33.10%) which is from boehmite (Al₁O₃·H₂O), gibbsite (Al₂O₃·3H₂O), and kaolinite (Al₂O₃·2SiO₂·H₂O) minerals [25]: silica (SiO₂ = 23.80%) [2], and ferric oxide (Fe₂O₃ = 71.9%) from wustite (FeO), hematite (Fe₂O₃), magnetite (Fe₃O₄), and goethite (HFeO₃) minerals [6]. Other minerals composition such as chalcanthite [CaAl₂(SO₄)(OH)₄], chamosite [(Mg,Fe,Al)₃(Si,Al)₄(OH)₈], hydrogarnet [Ca₃AlFe(SiO₄)(OH)₈], and albite [(Na,Ca)(Al,Si)₃O₈ /NaAlSi₃O₈] also exists in bauxite mining residue.
Table 2. Characteristics and compositions of waste rock from mining industry for carbonation reaction.

| Percentage of mineral present | Waste rock | References |
|-------------------------------|------------|------------|
| Forsterite = 64.7%             | References |
| Lizardite = 29.6%              | References |
| Magnetite = 4.2%               | References |
| Quartz = 0.3%                  | References |
| Brucite = 2.5%                 | References |
| Mineral composition            | Mg-rich minerals | References |
| Brucite                        | References |
| Nesquehonite                   | References |
| Hydromagnesite                 | References |
| Lansfordite                    | References |
| Mg-silicates                   | References |
| Olivine                        | References |
| Chrysotile                     | References |
| Talc                           | References |
| Chlorite                       | References |
| Phlogopite                     | References |
| Fe minerals                    | References |
| Magnetite                      | References |
| Ca-rich                        | References |
| Albite                         | References |
| Type of rock                   | Ultramafic rock | References |
| Peridotite                     | References |
| Amphibolite                    | References |
| Pyroxenite                     | References |
| Serpentinite                   | References |
| Mafic rock                     | References |
| Basalt                         | References |
| Gabbro                         | References |

Iron ore also has high possibility to be used for carbon sequestration due to the presence of secondary mineral phases, such as iron oxides (FeO), which can form stable iron carbonate (FeCO$_3$) from mineral carbonation process. For example, mineral composition from iron ore residue consists of 41.10% of MgO, 5% of CaO [22], and 16.04% of FeO from minerals such as siderite (FeCO$_3$) and goethite (HFeO$_2$) [26] (Table 3). Further mineral compositions of iron contain 67.33% of ferric oxide (Fe$_2$O$_3$) from both hematite (Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$) minerals [27]; 5.79% of quartz (SiO$_2$) mineral [23], and other minerals including pyrite (FeS$_2$), ilmenite (FeTiO$_3$), and chamosite (Mg,Fe,Al)$_6$(Si,Al)$_4$(OH)$_8$. Therefore, high concentration of carbonate minerals in iron and bauxite can increase carbon capture and storage, thus reducing carbon dioxide emission to the atmosphere. Other metal mining waste from gold, tin, and manganese mining might also have potential for CO$_2$ sequestration but the composition of the divalent cations are not known from the available literature.
Table 3. Percentages of estimated divalent cation content of metal mining wastes expressed in oxides.

| Metallic mineral | MgO  | CaO  | FeO   |
|------------------|------|------|-------|
| Bauxite          | 39.50\textsuperscript{a} | 40\textsuperscript{c} | unknown |
| Iron             | 41.10\textsuperscript{b} | 5\textsuperscript{b} | 16.04\textsuperscript{d} |
| Gold             | unknown | unknown | unknown |
| Tin              | unknown | unknown | unknown |
| Manganese        | unknown | unknown | Unknown |

\textsuperscript{[8], [22], [24], [26].}

4. Conclusions
Metallic mineral from mining industry is highlighted in this study due to their potential to mitigate the release of CO$_2$ to the atmosphere through mineral carbonation processes. Extraction of gold for instance, are mined from mafic and ultramafic rocks for economic purposes, however natural weathering of the waste rocks results in the formation of carbonates that encourage carbon sequestration processes. Gold mining wastes have a great potential for carbon sequestration in reducing CO$_2$ in the atmosphere. The major minerals that were discovered at the waste dump and stockpile of the gold mine include the quartz, mica, dolomite, and calcite. Calcite, dolomite, and siderite are considered a reservoir for carbon capture and storage because these minerals were in stable carbonate forms. The presence of silicate minerals such as chlorite, pyroxene, mica, and amphiboles at the waste dump and stockpile are the potential feedstocks for carbon sequestration because these minerals are rich in calcium and magnesium that are essential for mineral carbonation processes.

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