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**Carbon capture potential of mining and
industrial waste in Peru, South America:
Case studies for Junin region, Peru.**

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I. Abstract

Mineral carbonation is a greenhouse gas removal technology that offers a viable long-term solution to carbon capture; this technology relies on the reactive characteristics of the feedstocks to store carbon dioxide accumulated from the atmosphere. Waste materials from the mining and industry sector, often considered non-valuable resources, have been investigated due to their suitability for sequestering CO₂. Ultramafic and mafic rocks and cement kiln dust, for example, are natural and artificial silicate sources that have high contents of calcium oxide (CaO) and magnesium oxide (MgO); these oxides release calcium and magnesium cations that could form carbonates. This suitable composition represents a significant carbon capture potential by mineral carbonation pathway that could also be accelerated to accumulate CO₂. In this paper, it was investigated the potential carbon sequestration capacity of different waste materials through three case studies located in the Junin region, Peru. The results point out that serpentines quarries could sequester between 382.01 kgCO₂-581.1 kgCO₂ per ton of waste rock by mineral carbonation. Moreover, waste rocks from Corihuarmi mine could store 7.72 kgCO₂ per ton of rock material and 22.86 kgCO₂/t by mineral carbonation and enhanced weathering respectively. Cement kiln dust, generated in Cordorcocha cement plant, has a sequestration capacity between 524.40 kgCO₂ - 786.60 kgCO₂ per ton of cement kiln dust. These results suggest a potential alternative to achieve negative emissions of the mining and industry sector. Likewise, it could be considered a potential option to complement current Peru's response capacity to reduce GHG emissions.

II. Introduction

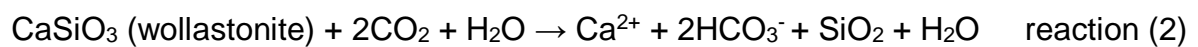
Greenhouse gases (GHGs) have increased steadily over the 40 years with a direct warming impact on the global temperature. CO₂ emissions from industrial processes and fossil fuel combustion contributed 78% of the total GHGs increase from 1970-2010 (IPCC, 2018). Limiting global warming below 2.0 °C annually relative to pre-industrial levels, target reassured by the Paris Agreement in 2015 (UNFCCC, 2015), requires mitigation pathways that aim to reduce and also remove the CO₂ accumulated. The mineralization of CO₂ is a greenhouse gas removal technology (GGRTs) (Mazzotti et al., 2005; Matter et al., 2016) that attempts carbon dioxide removal (CDR) by mineral carbonation and enhanced weathering (IPCC, 2018).

Mineral carbonation involves the reaction of CO₂ with rich-silicate minerals to yield carbonates (Renforth, 2011), more chemically stable form to store CO₂ (Rackley, 2010), this silicate weathering process has a natural slow occurrence on earth. However, the acceleration to fix CO₂ could achieve an effective large-scale CDR (Dunsmore, 1992; Lackner et al., 1995; Seifritz, 1990). Suitable silicate sources are presented naturally in silicate rocks or artificially as waste materials from the industrial sector (Renforth et al., 2011). Mine waste material might represent a potential CO₂ capture capacity due to its readily available alkalinity composition (Mazzotti et al., 2005). Renforth (2019), showed that alkaline materials could offset the harmful emissions by storing 2.9-8.5 billion tonnes of CO₂ per year by 2100.

The mining sector is one of the main drivers of the Peruvian economy, and it is present in 10.51% of the national territory (OSINERMING, 2017). Mining activities and industrial processes emit 10,715 Gg CO₂eq, which represent 6.25% of the total country's greenhouse gasses emissions (GHG). Peru has a central pledge to reduce 30% of its annual CO₂ emissions in a scenario Business As Usual (BAU) by 2030 (MINAM, 2016). Hence, it is necessary to implement additional measures to reinforce Peru's response to climate change. Here, we assess the potential carbon capture role of mine and industrial waste materials generated in Peru by the carbonation pathway.

2.1. Mineral carbonation process

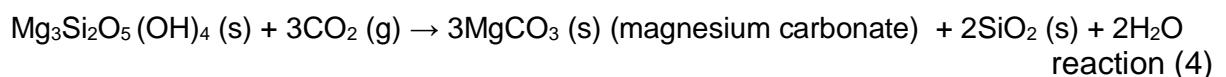
The weathering process starts with the hydration of CO₂ that forms carbonic acid (Martin, 2017) (reaction 1). This carbonic acid breaks silicate rocks and releases base cations (Ca²⁺, Mg²⁺) and bicarbonate and carbonate ions (Beerling, 2017). Wollastonite (CaSiO₃), for example, releases Ca²⁺ cations and bicarbonate ions, trapping 2 moles of CO₂ per mole of calcium (reaction 2). Then, these are transferred to the ocean and contribute to increasing the alkalinity (Renforth and Henderson, 2017).



The enhanced weathering process (EW), occurs when an additional mineral dissolution takes place, and the calcium and magnesium cations precipitate to form carbonate minerals (reaction 3) (Lefebvre et al., 2019).



Serpentine [Mg₃(OH)₄(Si₃O₅)] (reaction 4) and olivine (Mg₂SiO₄), for example, release magnesium ions that react with carbonate and bicarbonate ions that form carbonate minerals (Renforth et al., 2011).



Sources of metal oxides, such as serpentine and olivine, are founded naturally in mafic and ultramafic rocks. Calcium oxide is present in mafic rocks such as basalt or gabbro, with an estimated content of 10% of CaO by weight (Goff and Lackner, 1998). Moreover, the industry sector offers an essential artificial silicate material streams that have carbonation reactions (table 1) (e.g. cement waste and slag) (Maroto-Valer, 2010; Renforth et al., 2011) and could contribute to CO₂ sequestration. Thermodynamically, these reactions are exothermic. At standard condition, 25° C and 0.1 MPa, serpentine, releases 64 kJ/mol CO₂ and olivine 89 kJ/mol CO₂ (Maroto-Valer, 2010).

Table 1. Occurrence and carbonation reaction of different minerals and materials.

mineral/ material	formula	occurrence	carbonation reaction
Portlandite	$\text{Ca}(\text{OH})_2$	Portland cement	$\text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{H}_2\text{O}$
Larnite	Ca_2SiO_4	cement clinker	$\text{Ca}_2\text{SiO}_4 + 2\text{H}_2\text{CO}_3 = 2\text{CaCO}_3 + \text{H}_4\text{SiO}_4$
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	basic rocks	$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Jennite	$\text{Ca}_9\text{Si}_6\text{O}_{16}(\text{OH})_{2.6}\text{H}_2\text{O}$	hydrated cement	$\text{Ca}_{1.67}\text{SiO}_{1.57}(\text{OH})_{4.2} + 1.67\text{H}_2\text{CO}_3 = 1.67\text{CaCO}_3 + \text{H}_4\text{SiO}_4 + 1.77\text{H}_2\text{O}$
Rankinite	$\text{Ca}_3\text{Si}_2\text{O}_7$	cement clinker/slag	$\text{Ca}_3\text{Si}_2\text{O}_7 + 3\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = 3\text{CaCO}_3 + 2\text{H}_4\text{SiO}_4$
Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	slag	$\text{Ca}_2\text{MgSi}_2\text{O}_7 + 3\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{CaCO}_3 + \text{MgCO}_3 + 2\text{H}_4\text{SiO}_4$
Forsterite	Mg_2SiO_4	basic rocks; slag	$\text{Mg}_2\text{SiO}_4 + 2\text{H}_2\text{CO}_3 = 2\text{MgCO}_3 + \text{H}_4\text{SiO}_4$
Wollastonite	CaSiO_3	metamorphic rocks	$\text{CaSiO}_3 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{H}_4\text{SiO}_4$
Tobermorite	$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_{2.4}\text{H}_2\text{O}$	hydrated cement	$\text{Ca}_{0.83}\text{SiO}_{1.53}(\text{OH})_{2.6} + 0.83\text{H}_2\text{CO}_3 = 0.83\text{CaCO}_3 + \text{H}_4\text{SiO}_4 + 0.13\text{H}_2\text{O}$
Diopside	$\text{CaMgSi}_2\text{O}_6$	basic rocks	$\text{CaMgSi}_2\text{O}_6 + 2\text{H}_2\text{CO}_3 + 2\text{H}_2\text{O} = \text{CaCO}_3 + \text{MgCO}_3 + 2\text{H}_4\text{SiO}_4$
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	metamorphic rocks	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{H}_2\text{CO}_3 = 3\text{MgCO}_3 + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	metamorphic rocks	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 7\text{H}_2\text{CO}_3 + 8\text{H}_2\text{O} = 2\text{CaCO}_3 + 5\text{MgCO}_3 + 8\text{H}_4\text{SiO}_4$
Enstatite	MgSiO_3	basic rocks	$\text{MgSiO}_3 + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{MgCO}_3 + \text{H}_4\text{SiO}_4$
Laumontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$	metamorphic rocks	$\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 4\text{H}_2\text{O} + \text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CaCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{H}_4\text{SiO}_4$

Source: Adapted from Renforth et al., 2011

2.2. Natural and artificial silicate sources

2.2.1 Natural silicates

The development of this mineral carbonation technology has focused on the availability and suitability of waste silicate rich-materials. They have high carbonation potential (Mazzotti, 2005; Renforth et al., 2011) and offer a direct mitigation pathway for the emissions generated in the primary production of these products (Renforth, 2011). The use of waste material also provides a recycling perspective that benefits to the development of more sustainable processes (Beerling et al., 2018). Mine and industrial waste materials are available as natural and artificial silicate-rich sources, respectively.

They have been studied in the last decades for the potential contribution to carbon dioxide removal targets by the carbonation pathway.

The geochemistry and the availability of metal oxide bearing materials (primarily calcium and magnesium) define suitable mine waste materials. Mafic and ultramafic rocks, for example, have high amounts of calcium and magnesium and low content of alkali metals (e.g. sodium) (Mazzotti et al., 2005). During the weathering process, these components can precipitate in stable carbonate forms such as calcite (CaCO_3), magnesite (MgCO_3), aragonite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) (Renforth, 2011).

Table 2. Bulk chemical composition in the continental crust.

%wt	Bulk continental crust	Upper continental crust	Ultramafic rock	Ocean ridge basalt	Gabbro, basalt	Granite/Granodiorite	Limestone	Sandstone
SiO_2	61.60	64.91	42.99	49.41	48.55	72.08	6.63	86.20
Al_2O_3	11.06	10.76	2.78	12.36	11.53	10.14	0.56	2.92
Fe_2O_3	4.02	2.87	8.74	6.60	7.99	1.86	0.46	0.93
MgO	3.65	2.24	34.48	7.63	7.63	0.83	0.66	1.16
CaO	5.39	4.12	3.50	11.75	10.35	1.26	53.16	1.82
Na_2O	2.00	2.18	0.51	1.70	1.70	2.12	0.51	1.44
K_2O	1.51	2.02	0.35	0.14	0.56	2.32	0.21	0.77
Total	89.21	89.09	93.35	89.58	88.31	90.61	62.19	95.24

Source: cited by Renforth, 2011 (Reimens and de Caritat, 1998).

Non-metallic mining processes, for example, aggregates for construction, involve the extraction of rich silicate rocks used as building stones (e.g. basalt, diabase). Basalt rocks have high calcium oxide with a CO_2 sequestration capacity of 0.08 kg CO_2 /kg of rock (Goff and Lackner, 1998). Large basalt quarries are spread globally in countries such as USA (e.g. Columbia Plateau, Washington/Oregon), the UK (e.g. the Great Whin Sill and related rock, Northumberland/Southern Scotland) (Mazzotti et al., 2005) and Brazil (e.g. Parana Basin, Sao Paulo) (Lefebvre et al., 2019). For instance, 60 million tonnes (Mt) of igneous rocks are extracted annually in the UK, 70% of them used as aggregates (BGS, 2005). Whereas in the US, it is reported an annual extraction of 1.73 Gt of crushed stones, 24 wt% represented by igneous rocks (Willet, 2007). There is limited available data of the global production of aggregates due to regional consumption of this material. However, igneous quarries approximately produce 3.3 Gt of crushed rocks annually (Renforth, 2011), which is related to the estimations for carbonation of natural silicates made by IPCC (Mazzotti et al., 2005). In Brazil, the Parana Basin basalt quarry could provide suitable crushed rocks for

carbonation with a sequestration rate of 2.4 Mt CO_{2eq} through the application of crushed basalt in agricultural soils by enhancing weathering (Lefebvre et al., 2019).

Metallic mining activities generate different types of waste classified as waste rock, barren rock, which is material removed to expose the shallow ore, and tailings, the material produced during the mineral upgrading processes (BRGM, 2001). These waste materials show chemical and geological characteristics that depend on the type of deposits; the hosted rock, the technology applied during the ore processing; the nature of the mineral extracted and the design of the waste disposal (BRGM, 2001; Renforth, 2011; US EPA, 2011). Ultramafic and mafic mines from ore deposits produce a considerable amount of waste that is stored and stockpiled on the mine area, which represents low mineral and economic value (Harrison et al., 2013; Power et al., 2014). These ultramafic and mafic waste have an abundance of silicates, especially Mg-silicates in their composition. For instance, minerals such as serpentine in the polyform of lizardite and antigorite [Mg₃Si₂O₅ (OH)₄]; olivine as fosterite [Mg₂SiO₄] and also brucite [Mg(OH)₂] (Power et al., 2014). Thus, the Mg-bearing minerals react naturally with the atmospheric CO₂ and store them within the tailings by the carbonation pathway (Harrison et al., 2013). Clinton Creek, an abandoned asbestos located in Yukon, Canada had generated 11Mt of tailings, which had a passive carbonation rate of 6,200 gCO₂/m²/year due to the presence of 88wt% of chrysotile (Power et al., 2014). This passive carbonation process with no human intervention, driven by factors such as the rate of CO₂ or the environmental conditions, store significant quantities of CO₂ and have the potential to be accelerated at large mines to offset GHG emissions of the mining activities (Harrison et al., 2013; Pronost et al., 2011, Power et al., 2014). An investigation in the acceleration of carbonation of brucite of the tailings of Mount Keith Nickel Mine (MKM) at laboratory scale determined that the carbonation process would store a total of 1-3 Mt of CO₂, which accounts for 22-57% of the annual mine emissions (Harrison et al., 2013).

2.2.2 Artificial silicate sources

The industrial sector offers a considerable waste stream that is suitable for mineral carbonation due to the readily available calcium silicate composition. For example, bottom ash, fly ash and cement waste have a wide range of calcium content from 20% -65% by weight (Fernández Bertos et al., 2004; Iizuka et al., 2004; Johnson, 2000). The manufacturing of Portland cement generates cement kiln dust (CKD), a fine

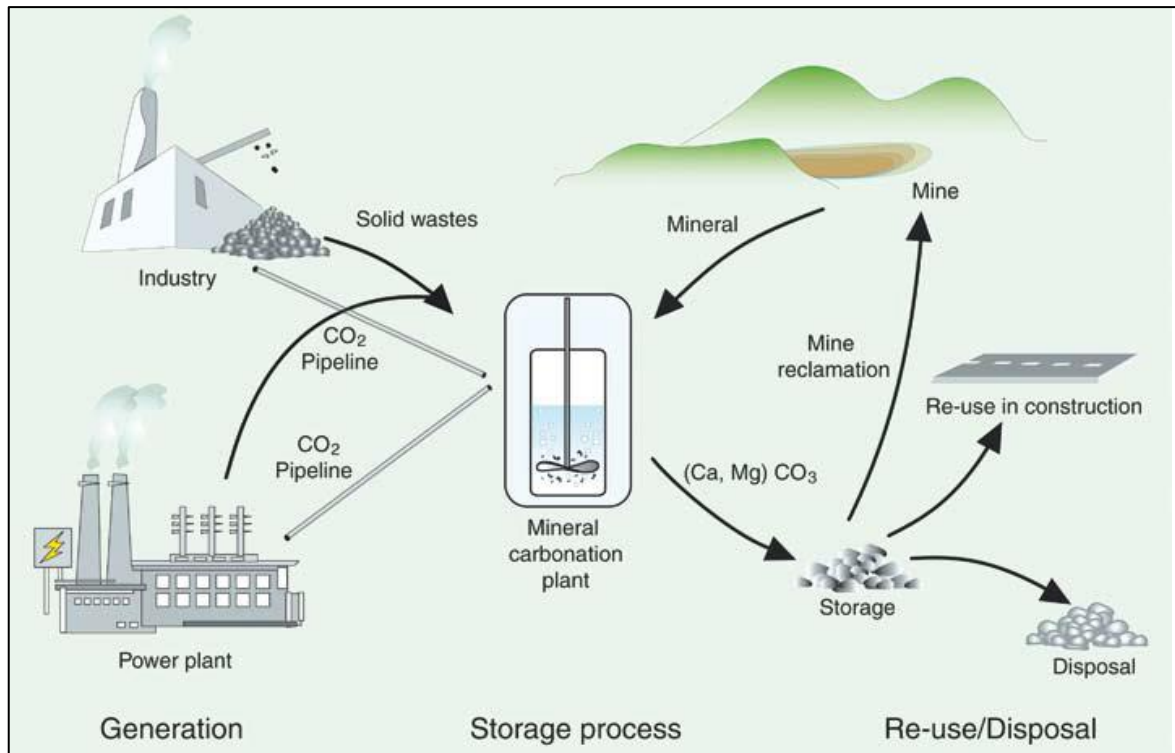
powder produced during the burning process of clinker production (Siddique, 2014). According to the United States Environmental Pollution Agency – USEPA (1993), 52% of these waste is disposed in a landfill, 43% in piles and 1% in ponds. This residue is composed primarily by calcium oxide, silica and alumina, similar chemical composition than the raw materials used for the production of Portland cement (Corish and Coleman, 1995). The output estimated for 1t of cement is approximately 150-200kg of cement kiln dust (Van Oss and Padovani, 2003); globally it is produced nearly 30 million tons of CKD per year (Dyer et al., 1999). It was estimated a sequestration potential of over 60% through the reaction of CO₂ with three CKD types by batch and column experiments, and these yielded CaCO₃ as primary carbonate (Huntzinger et al., 2009a). A carbonation potential of 330 ± 12 and enhanced weathering potential of 530 ± 21 kgCO₂ per ton of CKD was also estimated by the Steinoor formula (Renforth, 2019), which can contribute to the negative emissions required. Currently, the cement industry accounts for 8% of the global anthropogenic CO₂ emissions (Lehne and Preston, 2018), this negative contribution needs to be reduced in a minimum of 16% of its GHG emission by 2030 to be in line with the Paris Agreement (IEA, 2017).

2.3. Mineral carbonation approaches

2.3.1 In situ and ex-situ mineral carbonation

The application of mineral carbonation or enhance weathering involves different approaches broadly categorized as in situ and ex-situ mineral carbonation. In situ approaches are closely linked with CO₂ capture and geological storage (CCGS), which stands for the direct injection of CO₂ into underground reservoirs (e.g. mafic and ultramafic rocks) (Matter and Kelemen, 2009; Maroto-Valer, 2010). In contrast, ex-situ approaches (figure 1) comprise suitable feedstock rocks (crushed, grinded or and milled) that would entail additional requirements such as transportation or energy (Rigopoulos et al., 2018). The latter is one of the main challenges for the implementation as a viable option of this greenhouse gas removal technology, according to the IPCC. Depending on the type of source, the energy demand would include mining, transport, grinding, activation or disposal of carbonates (Mazzetti et al., 2005). For instance, the energy required for a crushing step is 2kWh/t, which increase the cost and also increase the CO₂ emissions (Gerdemann et al., 2007). The

exploitation of available waste material (e.g. ultramafic and mafic waste, quarry fines) arise as an alternative to overcome this constraint (Rigopoulos et al., 2018).



Source: Energy Research Centre of the Netherlands (ECN). Extracted from: Mazzetti et al., 2005

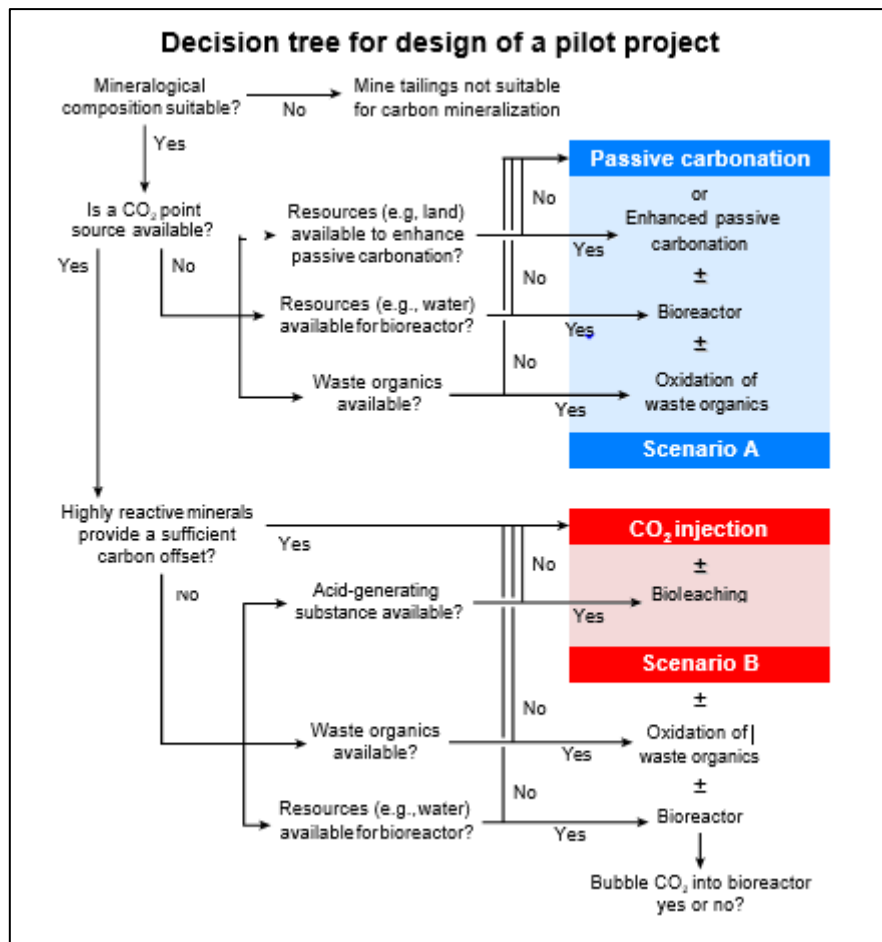
Figure 1. Ex-situ mineral carbonation fluxes.

2.3.2 Acceleration of mineral carbonation

Strategies for accelerating the carbonation process of ultramafic and mafic mine waste aim to enhance the mineral dissolution and facilitate the precipitation of carbonates in tailings storage facilities (TSFs). Bioleaching, increasing passive carbonation, CO₂ injection, oxidation of waste organic and bioreactor are strategies that can be applied in ultramafic and mafic mine waste and have been applied successfully at laboratory scale (Power et al., 2014). However, there are vital considerations to contemplate for the implementation of them under natural conditions. For instance, tailing permeability, acid-generating substances, land availability, the carbon content of waste organic and the rate of carbonate minerals could limit the sequestration target (Power et al., 2014).

Power et al., (2014) proposed case studies to assess the efficacy of five strategies for acceleration mineral carbonation in mine tailings. The decision tree generated (figure 2) outlines the benefits of combining approaches and also considers vital factors such as the source of CO₂. Scenario A, for example, discusses enhanced passive carbonation, bioreactor and use waste organics as strategies of acceleration. At the

same time, scenario B involves the combination of bioleaching and CO₂ injection, which based on the elevated $p\text{CO}_2$ of the mine tailings (Power et al., 2014).



Source: Power et al., 2014

Figure 2. Decision tree for a pilot case.

In the case of quarries fines, enhancing rock weathering (ERW) is the technical approach that consists of spreading milling silicate rock dust (e.g. basalt) on croplands to accelerate the weathering process. This approach is estimated to capture 0.3 tCO₂ per tonne of basalt (Smith et al., 2015); an application rate of 10-20t basalt/ha might store 12-21 MtCO₂ pa in the UK (Beerling et al., 2018). In Brazil, 20 t/ha of basalt was applied to agriculture soils, with a result of sequestration potential between 1.3 – 2.4 Mt CO₂eq (Lefebvre et al., 2019). Increasing in crop production, nutrient availability (e.g. phosphate), soil health, food security and the decrease of chemical pesticides application are part of the additional benefits of the rock dust approach (Beerling et al., 2018; Manning and Theodoro, 2020; Wright et al., 2014). Globally, China, the US and India have great potential to develop this technology due to the vast extension of

croplands and warm weather that might accelerate the chemical reactions (Beerling et al., 2018).

Artificial silicate waste material from the industry sector is also considered among the available silicate waste that, combined with the other approaches, can contribute to store CO₂. Cement kiln dust often is used for agricultural purposes, landfill disposal and stockpiled (Fernandez Bertos et al., 2004). In waste piles, CKD sequesters CO₂ at ambient temperature, and pressure with values greater than 70% of carbonation extend, CaCO₃ was the primary stable carbonate precipitated (Huntzinger et al., 2009b). Hence, there is need to expand the understanding of the carbonation pathway of CKD in the environment (Renforth et al., 2011) and the key factors that affect their carbonation rate (Huntzinger et al., 2009b; Lutyński and Pierzyna, 2017).

III. Methodology

3.1. Junin Region

Geographically located in the centre of Peru, Junin region has an extension of 44,197.23 km² (INGEMMET, 2018a) that includes highland and Amazonian zones in its territory, it also covers the eastern slope of the Andes in Peru (INGEMMET, 2018b). The average temperature is 11 °C in the highlands. In the Amazonian zones, it can reach 25 °C, and the weather range between cold to tropical according to the altitude. This region comprises six morphological-structural units: the western range, the inter-Andean depression, the eastern range, the sub-Andean belt, the Shira range and the Amazonian plain (INGEMMET, 2018b).

3.1.1. Geological characteristics

Junin region involves a series of metamorphic, sedimentary and igneous rocks with ages from the Neoproterozoic to the Holocene distributed across the regional territory. The composition is mainly granite, monzonitic, granodioritic, dioritic, and tonalitic quartz rocks (INGEMMET, 2018b). Basalt and andesite rocks are present in isolated outcrops in few lithologic groups (e.g. Cabanillas group, Pacococha formation) (Cobbing et al., 1996, León et al., 1998). The stratigraphic sequences contain several formations with a moderate degree of metamorphism (INGEMMET, 2018b).

The tapo mafic-ultramafic complex, one of the few ultramafic complex presents in the Peruvian territory, is located in Tarma province. This complex has an extension of 5 km long and 1-2 km wide and takes place at 3750-4200 metres above sea level (Tassirani et al., 2010). It consists of serpentized peridotites and metabasites with chromite dissemination and podiform chromitite. This massif lies over the deposits of the Ambo group (Tassirani et al., 2011). The petrology mostly altered to serpentinites (Tassirani et al., 2010) comprises antigorite and lizardite polymorphs (INGEMMET, 2018b). The primary mineral present is chromite (Tassirani et al., 2010).

3.1.2. Mining and industrial sector

15.76% of the Junin's territory, an equivalent of 699,879 hectares, is currently conceded as mining concessions for metallic and non-metallic mining activities. Junin represents 13.6% of the total rocks and industrial minerals available in Peru (INGEMMET, 2018a). Aggregates, clays, dolomites, bentonites and serpentines are principal minerals extracted. They are supplied to the local market, especially to the

construction sector. Latest prospective studies estimated 63,223.42 million metric tonnes of available non-metallic resources (INGEMMET, 2018b). Ore veins, skarn and porphyry deposits of copper, lead, zinc, silver and gold are present in the region; 15 mining units are operating (INGEMMET, 2018a) as open-pit mining models. Despite the high economic interest of these metallic mining activities, the contamination of water bodies and soils is a fundamental concern of the local communities. The release of a high content of heavy metals due to acid mine drainage (AMD), for example, has a direct negative impact on their livelihood (Quispe-Zuniga et al., 2019). The industry sector in Junin is mainly represented by Condorcocha cement plant that produces Portland cement and covers 45% of the national cement demand (UNACEM, 2019).

3.2. Data collection and selection of case studies

Data were collected from official government sources such as the Peruvian Geological Survey represented by INGEMMET, the Ministry of Energy and Mines (MINEM, Spanish abbreviation) and the Ministry of Environment (MINAM). In case of non-metallic mining activities, information of occurrences or quarries, extracted materials and chemical characterizations were found in prospective regional studies and complemented with the current mining registration. As for metallic mining activities, mining units were documented in official sources from the mining concession holders.

The selection process of the case studies consisted of seeking suitable geological characteristics (e.g. parental rock, ultramafic and mafic rocks) that could have carbon capture potential (Figure 3). For example, in the case of aggregates, basalt and diabase rocks were the first target quarries due to their high sequestration potential. However, there was no specific characterization of the type of igneous rocks extracted as aggregates on the gathered data. After the geological suitability, the chemical composition was obtained from publicly available X-Ray Diffraction and ICP-OES analysis that was carried out on the selected case studies or from other mining operations that present geological similarities (INGEMMET, 2018b).

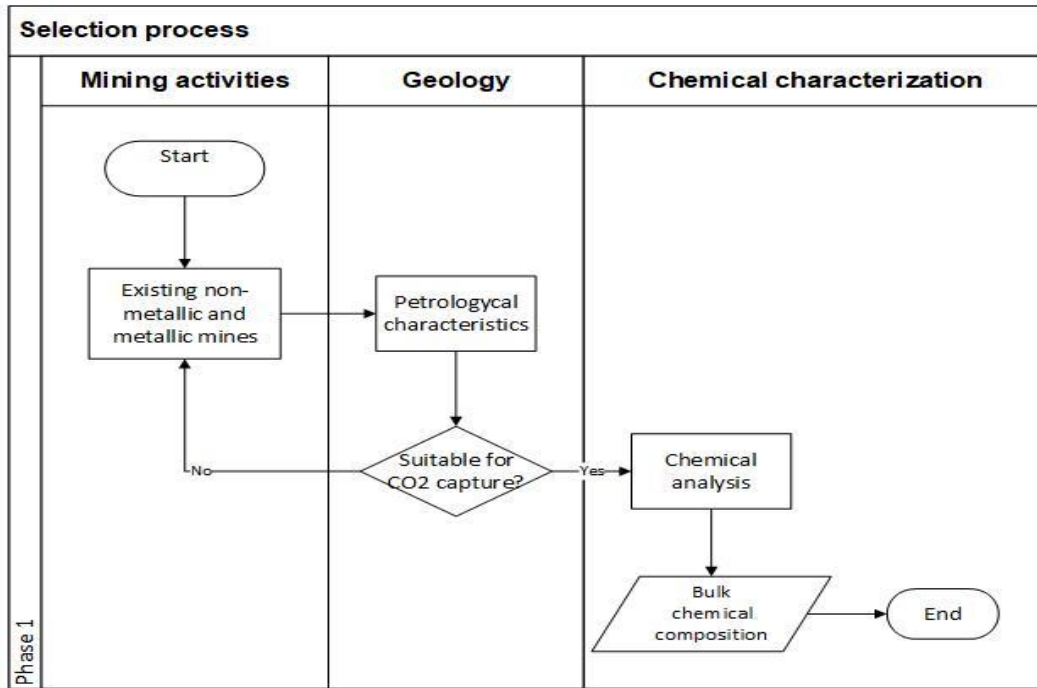


Figure 3. The selection process of case studies.

In case of non-metallic mining, it was selected serpentines quarries located on the ultramafic and mafic Tapo complex (Ambo group), which present a high content of magnesium oxide (MgO) and calcium oxide (CaO). Corihuarmi mine represents the metallic mining case study. This mine extracts gold (Au) and silver (Ag) from seven epithermal deposits (Minera IRL Limited, 2018). It has lithography composed by tobas and andesitic lava, and the stratigraphic unit is Caudalosa Formation (GEOCATMIN, 2020). Due to its association with the Andean Neogene Volcanism, this mine has geological and geochemical similarities to other deposits located in the same belt such as Yanacocha, Pierina and Sipan (ACS, 2017).

The chemical bulk composition information of the waste rock material for Corihuarmi mine was taken from one of these similar deposits as there was no specific available data from this mine. In the case of the artificial silicate waste source, Condorcocha cement plant, owned by UNACEM Company, was chosen due to its current production of five types of Portland cement (UNACEM, 2019). Figure 4 shows the location of the case studies.

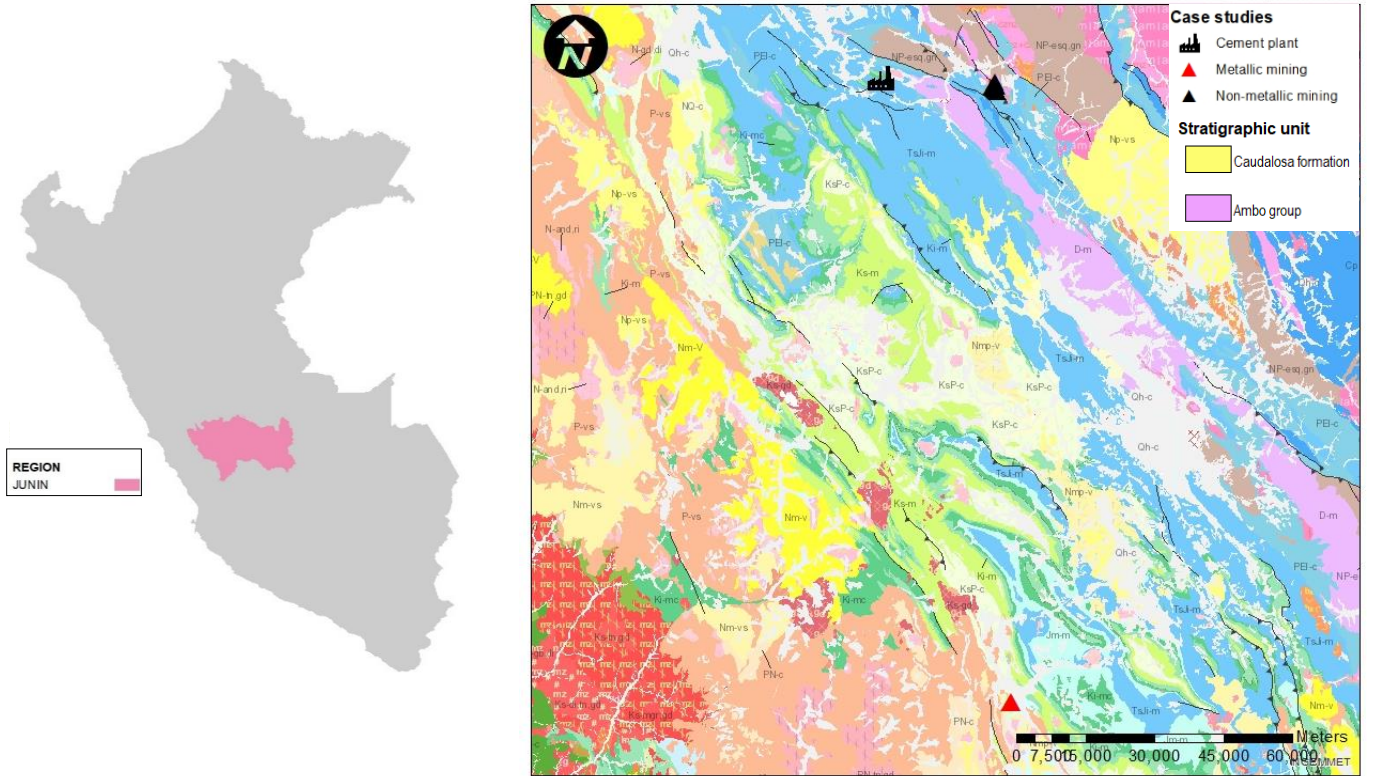


Figure 4. Location of the case studies.

3.3. CO₂ sequestration potential

Carbonation potential of the three waste sources was assessed by the modified Stenieur formula proposed by Renforth (2019) (equation 1):

$$C_{pot} = \frac{M_{CO_2}}{100} \times \left(\alpha \frac{CaO}{M_{CaO}} + \beta \frac{MgO}{M_{MgO}} + \gamma \frac{SO_3}{M_{SO_3}} - \delta \frac{P_2O_5}{M_{P_2O_5}} \right) \times 10^3 \quad \text{Equation (1)}$$

Where CaO, MgO, SO₃ and P₂O₅ represent the concentration of these elements expressed in wt % of oxides, M is the molecular mass of the oxides; coefficients α, β, γ, δ, are the relative contribution of the different oxides. The carbonation potential obtained is expressed in kilograms of CO₂ per tonne of waste material.

$$E_{pot} = \frac{M_{CO_2}}{100} \times \left(\alpha \frac{CaO}{M_{CaO}} + \beta \frac{MgO}{M_{MgO}} + \varepsilon \frac{Na_2O}{M_{Na_2O}} + \theta \frac{K_2O}{M_{K_2O}} + \gamma \frac{SO_3}{M_{SO_3}} - \delta \frac{P_2O_5}{M_{P_2O_5}} \right) \times 10^3 \times \eta \quad \text{Equation (2)}$$

Enhanced weathering potential (equation 2), expressed in kg of CO₂ per ton of waste, was calculated, where: η is the molar ratio of the carbon dioxide to divalent cation capture during enhanced weathering, 1.5 was the global average considered. The presence of phosphorus and sulphur would impact the carbonate system by reducing the potential of carbon sequestration (Renforth, 2019). The enhanced weathering

process assumes a complete dissolution of the cations released during the dissolution of the rocks and finally transferred to the ocean (Lefebvre et al., 2019). Table 3 represents the oxides values regarding the bulk chemical composition of the serpentine quarries and metallic mine waste.

Table 3. Bulk chemical composition

Serpentines quarries											
Name	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	LOI
Felipito I	2.48	0.06	6.39	0.81	35.51	0.07	0.47	0.00	38.33	0.04	14.93
San Felipe I	5.92	0.21	9.56	0.76	33.82	0.31	0.46	0.00	36.56	0.12	11.58
San Felipe II	0.52	0.53	5.77	0.76	37.61	0.06	0.49	0.00	39.50	<0.01	14.43
Felipito II	1.06	0.10	5.19	0.75	35.28	0.11	0.40	0.00	44.24	0.07	12.50
Tomasa II	4.14	0.46	13.17	0.70	30.51	0.23	0.41	0.00	37.20	1.67	11.39
Tomasa III	1.35	0.07	7.53	0.00	37.19	0.09	0.00	0.00	39.34	0.26	13.43
Tomasa IV	0.76	0.26	6.93	0.70	36.35	0.06	0.47	0.00	40.90	0.03	12.70
Rumicruz I	2.65	10.30	9.53	0.67	22.81	0.21	0.44	0.00	30.46	0.92	21.25
Rumicruz II	0.52	0.21	7.18	0.64	36.75	0.06	0.42	0.00	39.93	0.02	14.24
San Felipe III	1.03	0.29	8.00	0.57	36.20	0.13	0.33	0.00	38.62	0.35	13.80
San Felipe IV	0.84	0.42	10.68	0.53	34.94	0.04	0.35	0.00	36.81	<0.01	14.54
San Felipe VI	0.99	1.52	6.94	0.48	31.77	0.12	0.28	0.00	44.17	0.15	13.11
San Antonio	2.28	0.85	6.26	0.45	35.12	0.12	0.25	0.00	39.93	0.06	14.40
Corihuarmi metallic mine											
Alteration	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	LOI
Silicic	5.50	0.07	0.00	0.49	0.12	0.01	0.1	0.07	86.45	0.79	
Advance argillic	16.17	0.19	0.00	0.38	0.21	0.01	0.1	0.17	73.35	0.85	
Argillic	18.93	1.29	0.00	1.59	0.77	0.00	1.36	0.09	71.17	0.63	

Source: Adapted from INGEMMET (2018b) and MINAM (2006).

IV. Results

4.1. Non-metallic mining

Table 4. Sequestration potential of serpentines quarries

Serpentines quarries	Carbonation (kgCO ₂ /t)	Enhanced weathering (kgCO ₂ /t)
Felipito I	388.20	592.95
San Felipe I	370.90	566.56
San Felipe II	414.80	632.69
Felipito II	386.02	588.54
Tomasa II	336.74	514.42
Tomasa III	406.63	609.94
Tomasa IV	398.85	608.20
Rumicruz I	329.88	504.26
Rumicruz II	402.89	613.28
San Felipe III	397.58	603.90
San Felipe IV	384.71	584.44
San Felipe VI	358.81	544.53
San Antonio	390.10	590.95
Average	382.01	581.13
Annual production		N/A
Total estimated serpentine resources (t)		20,000.00
Waste produced ratio		1.00
Waste produced (t)		20,000.00
Potential CO ₂ emission offset (tCO ₂)	7,640.14	11,622.57

Thirteen serpentines quarries located on the ultramafic and mafic Tapo complex (Ambo group) present high content of magnesium oxide (MgO) and calcium oxide (CaO) (INGEMMET, 2018b). Table 4 shows that the sequestration potential by carbonation varies between 329.88 - 414.80 kgCO₂ per ton of this waste rock material, with an average of 382.01 kgCO₂/t; enhanced weathering ranges 504.26 - 632.69 kgCO₂/t with an average of 581.13 kgCO₂/t. Currently, there is no available data on the public domain of mining extraction activities in this zone. However, chromite was a mineral extracted from a residual concentration deposit in different periods in the zone (Mégard, 1996); these serpentines quarries form part of mining concessions conceded to private companies. The Peruvian Geological Survey-INGEMMET (2018b) estimated that serpentine resources are around 20,000 tons in 1.13 km² area. This calculation considered the specific serpentine weight (2.6) and the specific area (1.13 km²) where the serpentines quarries are located. The processing ratio of serpentine quarries is

considered approximately 1.00 (Cavallo, 2018) that implies a total waste material of 20,000 tones. Thus, this case study has a potential CO₂ emission offset between 7,640.14 tCO₂ -11,622.57 tCO₂ by mineral carbonation.

4.2. Metallic mining

Table 5. Sequestration potential of Corihuarmi waste mine

Waste rock alteration	Carbonation (kgCO ₂ /t)	Enhanced weathering (kgCO ₂ /t)
Silicic	1.64	6.96
Advance argillic	3.26	8.61
Argillic	18.25	53.00
Average	7.72	22.86
Stripping ratio (SR)	0.433	
Total waste 2017-2020(Mt)	4,734,511	
Potential CO ₂ emission offset (tCO ₂)	36,535.33	108,223.77

Corihuarmi mine currently comprises seven deposits of Au and Ag that are extracted by heap leaching process. Table 5 shows that the classification of the waste rocks is according to their alteration (silicic, advance argillic and argillic). This classification represents the type of rock alteration that affects the physical and chemical properties of the rocks by increasing or decreasing the acid-generating capacity of the host rocks (e.g. acid sulphate alterations) (Plumlee, 1999). The sequestration potential estimated was in a range of 1.64-18.25 kgCO₂ per ton of waste rock material with an average of 7.72 kgCO₂/t by carbonation. Whereas by enhanced weathering, the sequestration potential was 6.96-53.00 kgCO₂/t with an average of 22.86 kgCO₂/t; the argillic alteration has the highest sequestration capacity. The average stripping ratio (SR) of the mining extraction is 0.433, which represents a total waste production of 4,734,511 metric tons in the period 2017-2020 (ACS, 2017). Therefore, the potential CO₂ emission offset calculated would be between 36,535.33 -108,223.77 tons of CO₂.

4.3. Cement kiln dust

Table 6. Sequestration potential of cement kiln dust (CKD)

Condorcocha cement plant	Carbonation (kgCO ₂ /t)	Enhanced weathering (kgCO ₂ /t)
Cement kiln dust	524.40	524.40
CKD(kg)/t clinker	150.00	
Clinker production 2017- 2019(t)	4,680,380	
CKD produced(t)	702,057	
Potential CO ₂ emission offset (tCO ₂)	368,156.38	552,234.57
GHG emitted 2017-2019 (tCO ₂ eq)	4,078,836	
% CO ₂ offset	9.03	13.54

Condorcocha cement plant, owned by UNACEM Company, currently produces five types of Portland cement and clinker (UNACEM, 2019). The composition of the clinker material is similar to the typical cement composition. Thus, the bulk chemical characterization used for CKD was the typical Portland cement type I that contains 63.9 wt % of CaO and 2.1 wt % of MgO (Adaska & Taubert, 2008). Table 6 shows that CKD has a carbonation potential of 524.40 kgCO₂ per ton of CKD 786.60 kgCO₂/t by enhanced weathering. According to Van Oss and Padovani (2003), the CKD generation rate is between 15-20% of the clinker production. It was considered a rate of 150 kg CKD per ton of clinker produced. In the period 2017-2019, Condorcocha cement plant produced 4,680,380 tons of clinker (UNACEM, 2019), which indicates 702,057 tons of cement kiln dust generated during that period. Therefore, the potential CO₂ emission offset estimated is between 368,156.38 tCO₂- 552,234.57 tCO₂ mineral carbonation. UNACEM (2019) reported that Cordorcocha cement plant emitted 4,078,836 tCO₂eq in the period 2017-2019. By considering CKD as a CO₂ mitigation pathway, the percentage of CO₂ offset could be around 9.03% -13.54% of the current GHG emitted.

V. Discussion

5.1. Mining waste removal potential

The suitability of waste rock material for CO₂ sequestration is defined by their mineralogy, geochemical composition and their reactivity for long term CO₂ storing as carbonates (Power et al., 2014). Ultramafic and mafic mine waste, one of the most reactive rocks, are primarily composed by serpentines polymorphs and olivine groups that have a high content of MgO. Serpentine quarries, located in the ultramafic and mafic Tapo complex, have a high MgO content between 22.81 - 37.61 wt % and an average carbonation potential estimated ranged between 382.01 - 581.13 kgCO₂/t. These values correlate satisfactorily with magnesium oxide content of ultramafic and mafic rock waste investigated in three different mine sites and reviewed by Power et al. (2014). The mineralogical data showed the presence of major minerals such as chrysolite (88 wt %), antigorite and lizardite (81 wt %); MgO content between 33-40 wt % and their carbonation rate was from 374 to 6200 gCO₂/m²/ year. (Power et al., 2014). In contrast, Corihuarmi metallic mine waste showed low CaO and MgO content (e.g. CaO ranged 0.07- 1.29 wt %), which also implied low carbonation potential values from 7.72 kgCO₂/t to 28.86 kgCO₂/t. Metallic mine activities are commonly associated with the presence of sulphide minerals that leads to acid-sulphate alterations on the host rocks (Plumee, 1999). For instance, Smuda et al. (2007) determined the mineralogy and geochemical composition of waste rock material from the Excelsior polymetallic mine, located in the central Andes in Peru. This investigation found that 70-80% of the total waste volume was represented by Quartz-pyrite rocks, 15-20% by volcanic rocks and 5% by carbonate rocks; the CaO concentration ranged between 0.35 – 5.98 wt %; MgO content ranged between 0.67 -2.57 wt %. The characterization for Corihuarmi waste considered silicic, advanced argillic and argillic alterations that suggest the acid-sulphide conversions of the rocks minerals (e.g. feldspars into clays minerals) and low CaO and MgO content from 0.07- 1.29 wt % and 0.01 wt % in average respectively. This highly sulfidic mine rock waste would affect the suitability of this material as feedstock for mineral carbonation.

As the rate of carbon mineralization is low naturally, approaches for accelerating this process attempt to increase the accumulation of CO₂ in a shorter period. The findings suggest that the serpentine quarries waste and Corihuarmi mine waste could reach 581.13 kgCO₂/t and 22.86 kgCO₂/t respectively by enhanced weathering. Power et al.,

(2014) proposed strategies for accelerating carbon mineralization in mine waste that target processes such as the rate of mineral dissolution, the supply of CO₂ and carbonation precipitation. For example, the scenario A suggest that suitable mine waste, where a CO₂ point source is no available, would consider, enhanced passive carbonation, bioreactor or oxidation of waste organic as the most suitable strategies for enhanced carbonation. These approaches depend on the availability of resources such as water and waste organics. In the case of the serpentine quarries case study, these strategies would be appropriate; however, it is plausible that several limitations would influence the suitability of them. For instance, there is no update data regarding the current exploitation of serpentine in the zone, which limit the information of the tailings storage facilities (TSF) and the deposition of the tailings to the atmosphere. Another possible limitation is the freshwater available for the bioreactor strategy. In the case of the metallic mine waste, the mineralogical composition suggest a low rate for mineral carbonation. However, Savage et al. (2019) suggest that the enhanced of the carbonation process could increase the acid buffering capacity of the metallic mine waste. The precipitation of stable carbonates may increase the alkaline environment, therefore, prevent sulphide alterations. The extension of carbonation mineralization could reduce Acid Mine Drainage (AMD), a significant issue in metallic mines activities.

Quantities of natural rich silicate rocks for carbon capture by mineral carbonation would probably be insufficient for offsetting all the anthropogenic CO₂ present in the atmosphere (Power et al., 2014). Furthermore, it is fundamental to consider the balance between the CO₂ sequestration potential and the CO₂ emissions of this carbonation process to obtain a more accurate CO₂ offset. The finding of these studies suggests that serpentines quarries could offset between 7640.14 tCO₂- 11622.57 tCO₂ by considering 1.00 the waste ratio in a total of 20,000.00 tons of available resources. Nemat et al., (2016) expressed that serpentine could be present in considerable amounts in chromite mines and their waste can be used with low cost for different purposes previous beneficiation treatments. Similarly, for ex-situ mineral carbonation of CO₂, transportation and energy requirements were considered main drivers that affect the carbon capture efficiency of this approach (Lefebvre et al., 2019; Rigopoulos et al., 2018). Although the serpentine estimated resources are low, Tapo massif, where the serpentine quarries are located, had historical chromite extraction (Mégard, 1996). These previous mining activities would indicate a potential increment of suitable ultramafic and mafic waste for mineral carbonation. Metallic waste rocks could offset

36,535.33 tCO₂ -108,223.77 tCO₂ according to 0.433 stripping ratio. The latter is a factor that determines the amount of waste generated to extract the ore. The waste management often implies long-term monitoring due to the heterogeneous geotechnical composition of this waste, often store in tailing or dumps. Economically, waste management represents around 1.5%–3.5% of the total operational cost (Hitch et al., 2009). Despite the low carbonation rate and the mineralogical suitable of Corihuarmi rock waste, mineral carbonation could represent economic values in the growing carbon market, and it could also signify an additional input on reducing the carbon footprint of the mining operations.

5.2. Industrial waste CO₂ removal potential

Cement kiln dust, generated in the burning process of the clinker production, is characterized by a high alkali content, similar to the Portland cement. This waste is normally used for blended cement, agricultural amendment and an important part is frequently landfilled (Siddique, 2014). Considering a typical chemical content for Condorcocha cement plant, the results suggest a CKD production of 702 057 tons; this amount represents a potential CO₂ emission offset between 368,156.38 tCO₂ - 552,234.57 tCO₂ by carbonation pathway. Bertos et al. (2004) state cementitious byproducts have great carbonation potential due to their readily available calcium content in hydraulic, pozzolanic and lime bearing materials. Carbonation on these materials could be enhanced by exposure conditions and a constant relative humidity at 50-70%; this carbonation process could also influence the encapsulation of heavy metals. Furthermore, the clinker process is a considerable GHG emissions input to the operational process, CDK accounts for 2%-6% additional to the CO₂ emissions during clinker production (IPCC, 2000). Condorcocha Cement Plant calculated total GHG emissions in the period 2017-2019 4,078,836 tCO₂eq. Considering the potential CO₂ removal by carbonation, this would represent a CO₂ offset between 9.03-13.54 % of the current cement plant's GHG emissions. This cement company has policies aligned towards decreasing their GHG emissions. In 2018, they renewed their multi-cyclone system to a more efficient particle uptake in their kilns (UNACEM, 2019). In that sense, the untapped CO₂ removal potential of the cement kiln dust could represent an opportunity to reach negative GHG emissions.

5.3. Peru's GHG target emissions

According to Peru's GHG national inventory, the mining sector emits 6,197 Gg CO₂eq, whereas the industrial processes emit 4,518 Gg CO₂eq. These sources, essential components of the primary energy category, have high uncertainty regarding the availability and quality of data. It is estimated that the energy sector would represent 25% of the total GHG emission by 2030 (MINAM, 2016). Currently, strategies to reduce or mitigate the emissions of these sectors are focused on the adoption of clean energy sources, such as hydraulic or wind energy. Although these alternative fuel sources contribute to the developing of cleaner mining and industrial activities, it would be essential to evaluate other potential pathways to reach net-negative emissions. The mineral carbonation pathway depends on several process stages for its development; life cycle assessments are essential to identify the factors associated with the benefits and consuming steps (e.g. energy consumption, mining processing and disposal). Currently, this carbon capture and storage (CCS) technology represents demonstrable long term CO₂ storage that offers a potential permanent carbon dioxide removal alternative (Mazzotti et al., 2005).

VI. Conclusion

In this study, it was investigated the carbon capture potential of mining and industrial waste materials through mineral carbonation in the Junin region, Peru. The findings show that serpentines quarries have a carbonation potential between 382.01- 581.13 kgCO₂/ per ton of waste material. Therefore, it could offset between 7,640.14 tCO₂- 11,622.57 tCO₂ regarding the total resources estimated by the Peruvian geological survey-INGEMMET. In the case of Corihuarmi metallic mine, the carbonation potential ranges between 7.72 kgCO₂/t - 22.86 kgCO₂ per ton of waste rock; the emission offset calculated is 36,535.33 tCO₂ - 108,223.77 tCO₂ according to 4,734,511 Mt of total waste generated in the period 2017-2020. As for the artificial silicate waste material, cement kiln dust generated in Condorcocha cement plant has a sequestration potential between 524.40 kgCO₂/t - 524.40 kgCO₂ per ton of cement kiln dust; this could represent a CO₂ emission offset between 368,156.38 tCO₂- 552,234.57tCO₂ regarding a cement kiln dust production of 702,057 tons. Concerning the acceleration process of mineral carbonation, considerable strategies could be applied by taking into account factors such as the mineralogical suitability, geochemistry, quantity, waste management and the resources needed to implement those approaches. Likewise, these results offer a comprehensive starting point to consider mineral carbonation as a feasible alternative to offset the current GHG emissions of the mine and industrial sector in Peru. Finally, further studies should be carried out focused on integral life cycle analysis to estimate the requirements, costs and more accurate carbon capture potential regarding the GHG emitted during the particular processes of the waste material production.

VII. References

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VIII. Appendix

A. Carbonation potential calculations

Mining waste	Bulk chemistry												Molecular Mass					Carbonation n(kg CO ₂ /ton)	Enhanced weathering (kgCO ₂ /ton)	
	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	SO ₃	CO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅			SO ₃
Serpentine quarries																				
Felipito I	2.48	0.06	6.39	0.81	35.51	0.07	0.47	0.00	38.33	0.04	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	388.20	592.95
San Felipe I	5.92	0.21	9.56	0.76	33.82	0.31	0.46	0.00	36.56	0.12	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	370.90	566.56
San Felipe II	0.52	0.53	5.77	0.76	37.61	0.06	0.49	0.00	39.50	0.00	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	414.80	632.69
Felipito II	1.06	0.10	5.19	0.75	35.28	0.11	0.40	0.00	44.24	0.07	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	386.02	588.54
Tomasa II	4.14	0.46	13.17	0.70	30.51	0.23	0.41	0.00	37.20	1.67	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	336.74	514.42
Tomasa III	1.35	0.07	7.53	0.00	37.19	0.09	0.00	0.00	39.34	0.26	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	406.63	609.94
Tomasa IV	0.76	0.26	6.93	0.70	36.35	0.06	0.47	0.00	40.90	0.03	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	398.85	608.20
Rumicruz I	2.65	10.30	9.53	0.67	22.81	0.21	0.44	0.00	30.46	0.92	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	329.88	504.26
Rumicruz II	0.52	0.21	7.18	0.64	36.75	0.06	0.42	0.00	39.93	0.02	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	402.89	613.28
San Felipe III	1.03	0.29	8.00	0.57	36.20	0.13	0.33	0.00	38.62	0.35	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	397.58	603.90
San Felipe IV	0.84	0.42	10.68	0.53	34.94	0.04	0.35	0.00	36.81	0.01	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	384.71	584.44
San Felipe VI	0.99	1.52	6.94	0.48	31.77	0.12	0.28	0.00	44.17	0.15	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	358.81	544.53
San Antonio	2.28	0.85	6.26	0.45	35.12	0.12	0.25	0.00	39.93	0.06	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	390.10	590.95
Corihuarmi																				
Silicic Advance	5.50	0.07	0.0	0.49	0.12	0.01	0.1	0.07	86.45	0.79	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	1.64	6.96
argillic	16.17	0.19	0.0	0.38	0.21	0.01	0.1	0.17	73.35	0.85	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	3.26	8.61
Argillic	18.93	1.29	0.0	1.59	0.77	0.00	1.36	0.09	71.17	0.63	0.0	44.01	56.08	40.31	62	94.2	141.94	80.07	18.25	53.00
Cordorcocha																				
CKD	5.4	63.9	2.6	0.0	2.1	0.0	0.0	0.0	20.5	0.0	3.0	44.01	56.08	40.31	62	94.2	141.94	80.07	524.40	786.60