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Review of CO₂ Reduction Technologies using Mineral Carbonation of Iron and Steel Making Slag in Malaysia

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Abstract. Climate change, greenhouse gas effect, and global warming is envisioning to turn more awful and more terrible by year. Since the leading cause of global warming is uncontrolled CO₂ in atmosphere. The amount of unused steel slag is expected to increment later on, steel industries is one of the mechanical industries that contribute the CO₂ emission. That because this businesses deliver carbon in light of powers reductant and substantial volume of steel. The changes of atmosphere these day is truly developing concern and that make steel creator are confronted with test of discovering methods for bringing down CO₂ emission. Malaysia is working decidedly in the diminishment of CO₂ gas. There are a few techniques in decreasing the amount of CO₂ in the air as underlined by the Intergovernmental Panel of Climate Change (IPCC), an organization under the United Country however CCS is an extremely encouraging innovation to moderate CO₂ emission in air. Mineral carbonation is another technique to store carbon dioxide permanently, long term stability and vast capacity.

1. Introduction

As per Malaysian Iron and Steel Industry Federation (MISIF), around 7.5 million tons of steel had been created in year 2014 [1]. In Malaysia around 750 tons of steel were delivered every day and roughly 7.5 tons of slag were produced, from the exploration completed in the Asian nation, roughly 10% of steel slag was produced from the industries of steel [2]. There are a few strategies in lessening the amount of CO₂ in the air underlined by the Intergovernmental Panel of Climate Change (IPCC), an office under the United Country. Those are CO₂ capture and storage (CCS), renewable carbon free energy (RE), Sources (solar), high efficiency of energy conversion and savings (ECS), policies and



legislation (PL) and High Efficiency of Energy Conversion & Savings (ECS) are all the more concentrating on the lessening of CO₂ produced, not to the diminishment of CO₂ radiated [3-4]. Policies and legislation (PL) is covering extensive variety of degrees and advances. Carbon Capture and Storage (CCS) is extremely encouraging innovation to relieve CO₂ emission in air. CO₂ capture and storage (CCS) are being examined broadly everywhere throughout the world.

The CCS technologies include capturing the CO₂ from the preparation of petroleum products and in addition the combustion of non-renewable energy sources, as in power generation. The CCS can likewise be connected to different procedures with high measure of CO₂ emitted [4]. The major components of a CCS process include separation of CO₂ from the exhausted gas, compression of CO₂ by high pressure, transportation of CO₂ from plant to stock yard and storage [9]. CO₂ storage, even with small amount of CO₂, would make an useful contribution to lowering emissions. Lately, the specialized writing on this field has extended quickly.

There are several CCS technologies namely biological storage (photosynthesis, soil carbon stock, ocean life storage etc), geological storage (underground or underwater), oil and gas reservoirs, enhanced oil recovery, chemical fixation, membrane flash process, artificial weathering, mineral carbonation and so on. The main concern of these techniques, besides applicability of them, is the temporary storage capability. For example, the CO₂ gas will stored in the sea, however about hundreds to thousands of years it will come back to the atmosphere. W J J Huijgen et al state, even though it has been brought out that the storage is not essentially be perpetual [10]. The inquiry stays with respect to whether re-discharge of CO₂ impacts future era. Extra shortcomings of ocean storage are the nearby change of pH of the water and its instigated consequences for the earth. In comparison to other CCS technologies, mineral carbonation have some advantages in term of storage stability, long term continuous monitoring not required, and economically feasible.

In term of material used for the carbonation, carbonation can be done either using natural resources or industrial waste. However, the utilization of natural resources such as olivines, mafic, peridotite, wollastonite and some others can contribute to some other environmental and public acceptance issues [11]. Thus, the use of industrial waste is very much preferable in CCS. Finding a suitable industrial waste for the carbonation process is very much essential for this work. Since the re-use of steel slag in Malaysia is all more concentrating on the development area such as construction sector, the reutilization of steel slag in carbon capture and storage technologies is especially imperative. In mechanical procedures, ball milling process is most likely the best options because of the low energy utilization. There are no much literatures on CCS technology in Malaysia. Most of the literature are focusing on the CCS in Malaysian forest soils, power plant generation, renewable energy and policies [12-15] and the use of steel slag in carbon capture and storage that may be extremely useful for Malaysia particularly and all different nations in the world generally

2. Steel making manufacturing and CO₂ emission

Steel industries is one of the huge mechanical industries in Malaysia that donate the CO₂ gas in atmosphere which danger the environment and earth . It is on account of this industries deliver carbon in view of powers reductance and expansive volume of steel. The change of climate these days is truly developing unease and that make steel producer are confronted with problem of discovering methods for bringing down CO₂ emission without genuinely influencing the process of productivity or adding to cost [6].

The steel industries and the carbon intensity of iron have diverse differs impressively production courses, unrefined steel for scrap/electric have going from 0.4 t CO₂/t circular segment heater (EAFs), 1.7-1.8 tCO₂/t rough steel for the integrated blast furnace(BF) basic oxygen furnace (BOF) to 2.5 tCO₂/t rough steel for coal based reduced iron directly (DRI) processes. [41, 52]

The indirect carbon capture and storage discharge from the all steel plant would bring down their CO₂ outflow. This outflow source from the utilization of power delivered. It could be change to power produced from sustainable power source, hydroelectric, or nuclear power plant [26]. Henceforth this

outcome will end up plainly close to zero of CO₂ emission for a piece or small scale process. Power decarbonised will frame if indirect CO₂ outflow from steel industries is diminish in future.

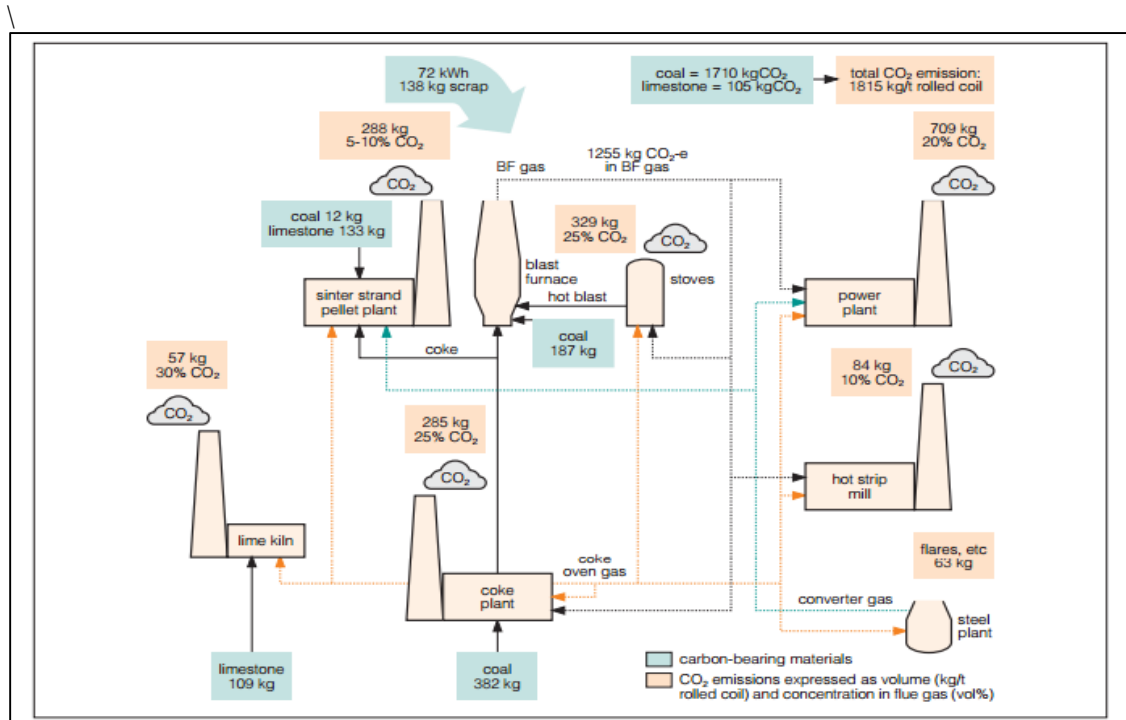


Fig. 1 CO₂ emission of typical steel mill [6]

The Fig. 1 above demonstrates the important CO₂ emission of typical steel mill process delivering hot rolled coil. The biggest wellspring of CO₂ is the on location control plant. The BF taken after by the sinter/pellet and coking plants are the biggest producers of CO₂ on the iron making side. Consequently to limit this impact, the innovation alleviation should be considered. Production of iron and steel likewise prompt the production of steel making slag as result. Essential utilization of slag are, as a bond material of cement, road base course material, material for structural designing and development work, silicate-calcium compost, crude material for high-level glass and numerous more [25]. However, the utilization of steel slag has been constrained by its propensity to self-corruption, caused by nearness of free lime in the slag and its hydration capacity joined by volume changes, the lessening of open work ventures and other reused materials, for example, reused roadbed materials and fly fiery debris, additionally progress toward becoming contender of the slag in the fields. Fig. 2 and Fig. 3 shows the total production of crude steel in Malaysia and the total production of crude steel in Asia and world. Both figure shows that the production of crude steel in Malaysia and Asia are worrying and necessity to overcome to lowest CO₂ emission.

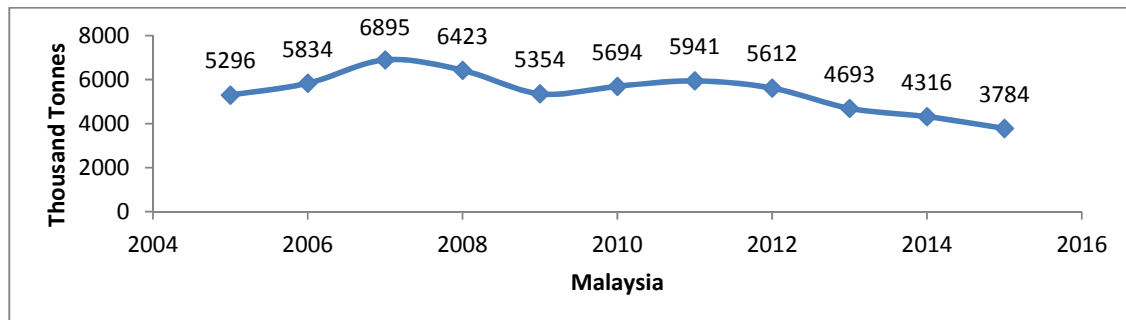


Fig. 2 Total production of crude steel in Malaysia

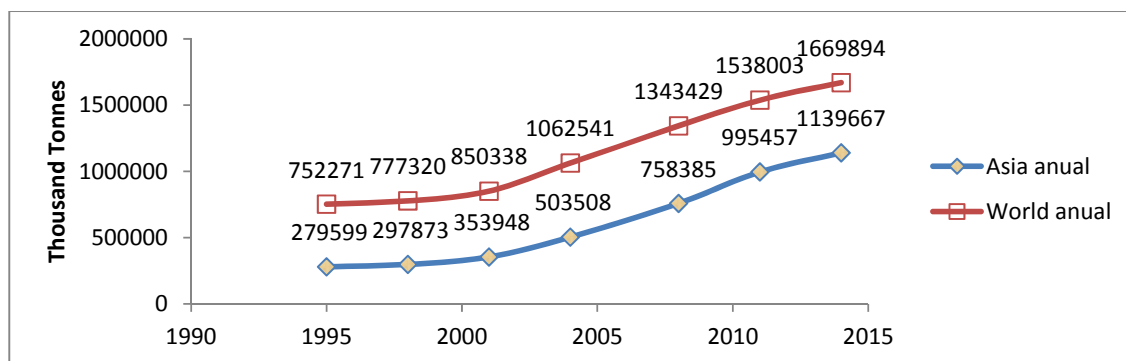


Fig. 3 Total production of Crude steel in Asia and World

3. Physical and chemical characteristics of steel slag

Steel making industry can take control of its vaporous CO₂ outflow with the strong of something created alongside steel slag, which is a rich wellspring of basic oxides, for example, CaO and MgO. The first parts of iron and steel slag are limestone (CaO) and silica (SiO₂), CaO, Fe₂O₃, FeO, Al₂O₃, P₂O₅, SiO₂, MgO and MnO [17]. Utilizing mineral processing innovation, the part of iron and steel slag can be isolated and reused for sintering, blast furnace and steel making. Steel slag contain high of CaO, MgO, and MnO which can diminish iron and steel making cost on the grounds that can be utilized as substitution for part of limestones, dolomite and manganese mineral. The chemical part of steel slag diverse with the furnace sort, steel evaluations, and pre-treatment technique [19-21]. Some steel slags contain higher measure of P₂O₅ and S than iron concentration. This may impact the quick reusing of the steel slags to the iron and steel making process. Various applications using the physical and compound characteristics of slag have been created and are being put to use in a wide extent of fields. The chemical composition of the steel slags from different sources is showed up in Table 1. Table 2 records the link between the characteristics and application fields of steel slag.

Table 1. Chemical composition of steel slag (oxides %)

COUNTRY	Type Of Slag	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃
Malaysia(Ah medzade & Sengoz, 2009)[22]	EAF	55.2	11	17	4	3.1	0.16	0.75	0.85

Thailand(Pen polcharoen, 2005)[23]	BFS	10.5	24	47	3.4	1.3	0.48	4.12	-
China(Xuequan, Hong, Xinkai, & Husen, 1999)[24]	Steel Slag	48.2	12	8.5	2.6	6.4	-	-	0.43
Japan(Shen & Forssberg, 2003)[25]	BOF	44.3	14	18	1.5	6.4	-	-	-
	EAF	38	19	15	7	6	-	-	-

Table 2. Characteristic and applications of steel slag [26]

Characteristics	Applications
Hard, wear resistant, Adhesive, rough	Aggregates for road and hydraulic construction Waste
Porous, alkaline	Waste water treatment
FeOx, Fe components	Iron reclamation
CaO, MgO, FeO, MnO components	Fluxing agent
Cementitious components (C ₃ S, C ₂ S and C ₄ AF)	Cement and concrete production
CaO, MgO components ,FeO,	CO ₂ capture and flue gas desulfurization
FeO, CaO, SiO ₂ components ,Fertilizer	Raw material for cement clinker
Fertilizer components (CaO, SiO ₂ , MgO, FeO)	Fertilizer and soil improvement

4. Mineral carbonation

Mineral carbonation has been proposed as one of the central procedures for CO₂ sequestration. Mineral carbonation Technology (MCT) is a system whereby CO₂ is chemically reacted with calcium or possibly magnesium-containing minerals to form stable carbonate materials which don't cause any whole deal hazard or watching obligations [5]. Mineral carbonation contemplates are huge with respect to utilizing CO₂ for mechanical purposes [6-7]. One imperative preferred standpoint of CO₂ sequestration by mineral carbonation include the actually liberal and in every way that really matters enduring catching of CO₂ as carbonated minerals by using rich mineral assets, for instance, Mg-silicates [27]. There are a few potential materials that can be utilized as a sorbent. These materials are ordered into minerals and waste materials. The major idea driving the mineral sequestration is the guideline of principle of natural rock weathering [6]. Throughout weathering, Ca and Mg silicate mineral-bearing rock materials respond actually with the encompassing CO₂ to change into strong carbonates which are then put away in the ground forever [7-8]. As of now the most explored mineral assets are olivine, serpentine and wollastonite. The carbonation of common minerals normally requires a high temperature and high weight since regular minerals more often than not requires a high temperature and high weight since characteristic minerals are thermodynamically steady. For squander material and additionally certain mechanical waste, steel slag has gotten a great deal of consideration, for example, electric arc furnace (EAF) dust, blast, furnace slag and waste cement have been assessed for use as crude materials for mineral carbonation. (28-37).

4.1 Methods

Catching carbon dioxide in carbonates can be accomplished through different process. Under the mineral carbonation, there are a few systems, for example, natural carbonation, heat and treatment,

aging, aqueous carbonation and mechanical activation. Mineral carbonation prepare ideas that have been contemplated can generally be isolated into direct and indirect methods as shows in Fig. 4 and Fig. 5

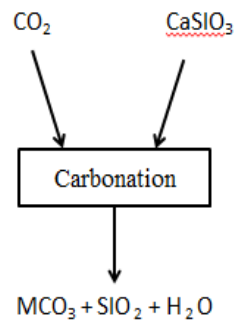


Fig. 4 Direct carbonation

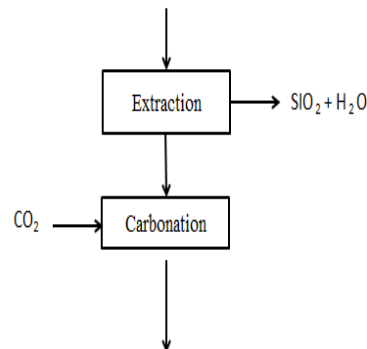
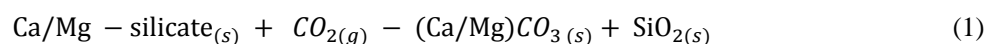


Fig. 5 Indirect carbonation

4.1.1 Direct gas solid carbonation

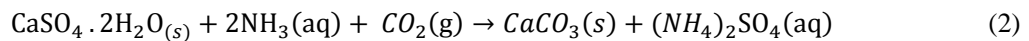
In the common carbonation process, the material that goes about as a sorbent will be presented to the CO_2 with no added substance or extra treatment for the response to occur. Gas-solid carbonation is a straightforward approach towards mineral carbonation. Shockingly, the response rates of such a procedure have been too moderate and the procedure experiences thermodynamic impediments and along these lines, not reasonable for the productive CO_2 sequestration. In Malaysia, mineral carbonation of red gypsum as a wellspring of calcium particle was concentrated to assess the possibility of utilizing it for CO_2 sequestration [31]. Direct carbonation technique is utilized to deliver solid carbonates in the exploration. Fresh red gypsum tests utilized as a part of this examination were gotten from landfill of Huntsman Tioxide, Kemaman, Terengganu, Malaysia. The composition arrangements of the red gypsum test were analyzed which demonstrates that the red gypsum is plainly ruled by CaO (32.2%), SO_3 (31.6%), and Fe_2O_3 (28.99%), and in addition TiO_2 (3.4%) together with some immaterial polluting influences. Plainly, the red gypsum is rich with Ca, a standout amongst the most ideal minerals for mineral carbonation. However experiment result demonstrated that the calcium and iron carbonates could be delivered through direct carbonation of red gypsum has low item immaculateness and carbonation productivity [32]. Past research from Reddy et al 2008, Baciocchi et al 2009, and Prigiobbe et al, 2009 additionally express that the direct gas–solid response of strong Ca/Mg silicate in equation 1 experiences moderate response rates and has for all intents and purposes been relinquished. Reaction kinetics, are moderate for Ca/Mg-silicates [25].



4.1.2 Direct aqueous carbonation

Aqueous carbonation process is the procedure that utilizing strong or weak acid, (HCL, CH_3COOH), base solution(NaOH), or chelating agents (EDTA, citrus extract), basic aqueous solutions or chelating operators to break down metal oxides, at that point respond it with vaporous CO_2 which at long last would prompt the form of carbonates. The direct aqueous mineral carbonation-route alluding to carbonation preformed in a solitary stride in a aqueous solution, gives off an impression of being the

most encouraging CO₂ mineralization other option to date [38]. Direct aqueous mineral carbonation can be additionally divided into two subcategories, contingent upon the kind of arrangement utilized. Be that as it may, it has been accounted for [39] that there are still upgrades to be made in regards to the previously mentioned arrangement. K song at el has examined impact effect of polyacrylic acid on direct aqueous mineral carbonation of flue gas desulfurization gypsum and expressed that the expansion of PAA brought down the general carbonation yield through the emission of CO₂(g), which hampered CO₂ disintegration [32]. The lower carbonation yield within the sight of PAA would thus be able to be ascribed to the loss of carbonate through the emission of CO₂(g). The direct aqueous carbonation of FGD gypsum can be expressed as far as the condition of every species, as in the following equation 2:



4.1.3 Indirect carbonation

At the point when the mineral carbonation process is partitioned into a few stages it is delegated as indirect carbonation. For example, the extraction of Ca as well as Mg from the feedstock, the dissolution of CO₂ (on account of aqueous carbonation) and the precipitation of carbonate materials occur as isolated strides and additionally in various reactors. In light of review of mineral carbonation utilizing indirect carbonation [], pH swing mineral carbonation is one of indirect carbonation. The research state that pH swing mineral carbonation have been fundamentally looked into, the cost is too high than others mineral carbonation technique, generally high carbonation effectiveness is accomplished through pH swing mineral carbonation and high purity carbonated are delivered by pH swing mineral carbonation [28].

4.2 Mechanical activation

Numerous methods have been utilized to treat the mineral metals that are environmentally worthy among which mechanical activation is an inventive procedure to make new surfaces and basic imperfections in solid state [21–33]. Mechanical activation was observed to be a positive pre-treatment process adding to altogether upgrade metal recuperations or enhanced material performances [34]. Think about others strategy, mechanical activation required less energy consumption [5, 37]. One of the previous study that utilizing mechanical activation is mechanical activation of chemically activated high phosphorous slag content concrete.

Mechanical activation has noteworthy enhancing impact on the advance of hydration responses of chemically activated high phosphorous slag content cement. This thus significantly influences the microstructure and the compressive quality improvement of the cement [34]. Compare others method, mechanical activation required less energy consumption [5, 37]. One of the previous study that using mechanical activation is Mechanical activation of chemically activated high phosphorous slag content cement. Mechanical activation has significant improving effect on the progress of hydration reactions of chemically activated high phosphorous slag content cement. This in turn greatly affects the microstructure and the compressive strength development of the cement [34].

In Malaysia there is not much study and method using mechanical activation however, in industrial processes especially steel making industry, a traditional ball process is most likely the best option because of the the low energy consumption [37].Various techniques for mineral CO₂ sequestration have been suggested in many literatures such as the membrane flash process, pressurized gas/solid process, aqueous acid and alkaline solution process, mechanical activation and so on. However under mechanical activation technique, the use of mechanical grinding machines plays a significant role in enhancing the carbonation process. There are several types of grinding machines that typically used, for examples centrifugal mill, attrition mill, nutating mill, tumbling mill, planetary mill and vibrating mill. [40-48].

4.2.1 Effect of CO_2 absorption into steel slag using mechanical milling

As a progression of major investigation of CCS by the mechanical grinding technique, the reaction between CO_2 and numerous ground metal powders; Fe, Ni, Pb, Sn and Cu, are most component in steel slag were done at the first place to investigate the reaction behavior and mechanism, and to prove the possibility of utilization of this strategy to CCS. The specimen were chosen since they had moderately low proclivity of oxygen, as such, they were effortlessly diminished by hydrogen and generally simple to be gotten. An investigation using mechanical activation on past research studied the absorption of carbon dioxide onto metals and compound reagent calcium oxide under dry grinding which express that CO_2 not decomposed during the grinding but rather it happened on the new uncovered surface of the Fe powder produced by the grinding [6].

The absorption of CO_2 into Fe powder was quickened and upgraded with the grinding procedure by around 26 times in contrast with that without grinding process. Increment in the weight of Fe and rotational speed appeared to altogether influence the the rate of CO_2 absorption. However the underlying weight of CO_2 seemed to have no impact on the rate of CO_2 absorption into Fe powder. The absorption likewise seen on other specimens with the amount of CO_2 absorption tends to increment with the standard free energy of formation of each metal oxide. The grinding process by centrifugal mill did not crush the whole sample to finer particle, but only grazed the surface of the sample. The use of other type of grinding system that has higher impact intensity might lead to the enhancement of the CO_2 absorption into the metal powders. Fig. 6

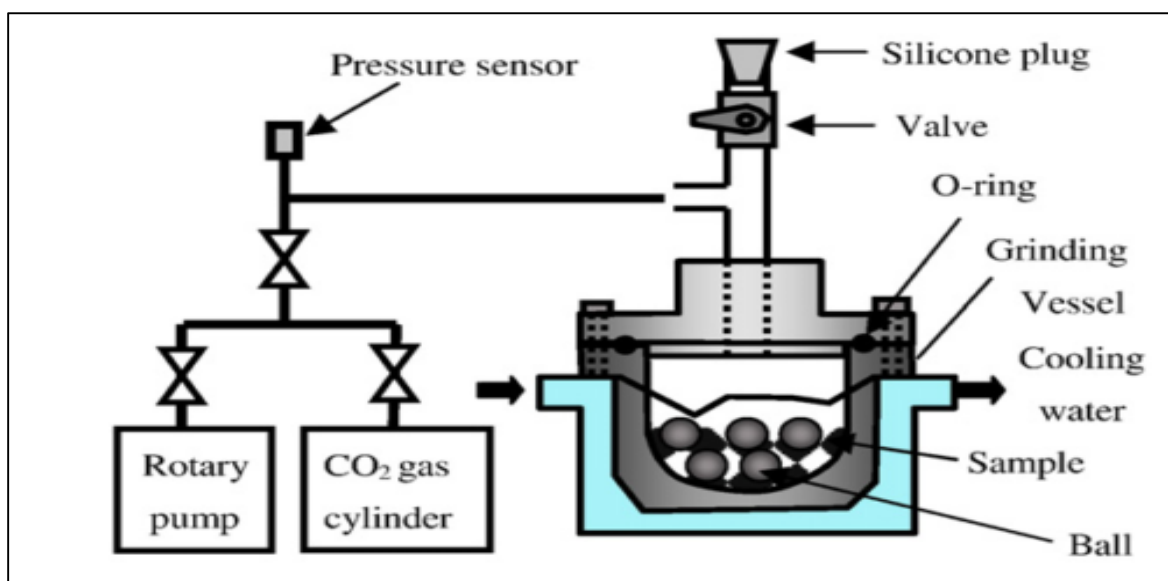


Fig. 6 Schematic Diagram of Experimental apparatus of dry grinding [5]

Fig. 7 shows the example of schematic diagram of the experimental apparatus in Malaysia. It is mainly composed of stirrer, pressure sensor (SDL 700), pressure gauge, tank, motor, CO_2 gas cylinder, and rotary pump, this machine required low energy to operate because using simple stirrer to mixture the CO_2 and slag sample. Both experiments show how mechanical activation process can absorb CO_2 gas without using much energy.

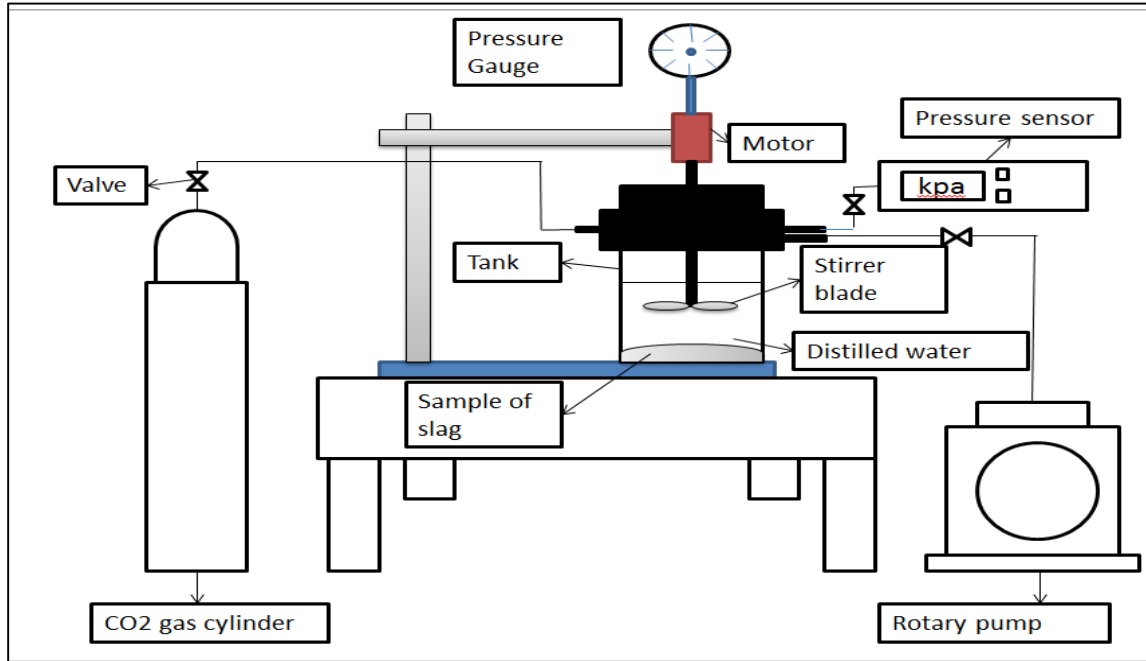


Fig. 7 Schematic Diagram of Experimental Apparatus of Mechanical Stirrer in Malaysia [52]

Conclusion

Malaysia is working positively in the reduction of CO₂ gas in line with the commitment for the 40% reduction in CO₂ intensity by GDP compared to 2005 [2,5]. Carbon storage technology must be increased in order to achieve further reduction of CO₂ gas emission. It can be concluded that the among techniques using additives for reactivity rising gave better results than those not using additives and for that, studies were performed with the purpose of a better understanding on the reactions complexity regarding the carbonation techniques. Compared to the developed countries, the utilization rate of steel slag is still very low in Malaysia. Therefore, large-scale utilization is a substantial resolution to the environmental problems arisen by steel slag dump, thus, CCS is a very promising technology to mitigate CO₂ concentration in atmosphere. Mineral carbonation is a potentially attractive sequestration technology for the permanent and safe storage of CO₂.

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