

The review of recent carbonate minerals processing technology

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Abstract. Carbonate is one of the groups of minerals that can be found in relatively large amount in the earth crust. The common carbonate minerals are calcium carbonate (calcite, aragonite, depending on its crystal structure), magnesium carbonate (magnesite), calcium-magnesium carbonate (dolomite), and barium carbonate (barite). A large amount of calcite can be found in many places in Indonesia such as Padalarang, Sukabumi, and Tasikmalaya (West Java Province). Dolomite can be found in a large amount in Gresik, Lamongan, and Tuban (East Java Province). Magnesite is quite rare in Indonesia, and up to the recent years it can only be found in Padamarang Island (South East Sulawesi Province). The carbonate has been being exploited through open pit mining activity. Traditionally, calcite can be ground to produce material for brick production, be carved to produce craft product, or be roasted to produce lime for many applications such as raw materials for cement, flux for metal smelting, etc. Meanwhile, dolomite has traditionally been used as a raw material to make brick for local buildings and to make fertilizer for coconut oil plant. Carbonate minerals actually consist of important elements needed by modern application. Calcium is one of the elements needed in artificial bone formation, slow release fertilizer synthesis, dielectric material production, etc. Magnesium is an important material in automotive industry to produce the alloy for vehicle main parts. It is also used as alloying element in the production of special steel for special purpose. Magnesium oxide can be used to produce slow release fertilizer, catalyst and any other modern applications. The aim of this review article is to present in brief the recent technology in processing carbonate minerals. This review covers both the technology that has been industrially proven and the technology that is still in research and development stage. One of the industrially proven technologies to process carbonate mineral is the production of magnesium metals from dolomite. The discussion is emphasized to the requirements of certain aspects prior to the application of this technology in Indonesia. Other technologies that are still in research and development stage are also presented and discussed. The discussion is aimed to find further possible research and development in carbonate processing.

1. Introduction

Carbonate is a type of mineral that consists of CO_3 component in its molecule structure. The sub molecular structure of CO_3 is presented in Figure 1. The figure shows that atom carbon is surrounded by three atoms of oxygen. The structure is actually built by covalent bond between carbon and those oxygen atoms [1]. One of the oxygen atoms shares two electrons with carbon, whereas the other one shares one electron for each oxygen atom. This structure leaves two negative charges for carbonate sub molecule. A carbonate molecule is built through ionic bond between this negative charge and the positive charge from certain metallic element.



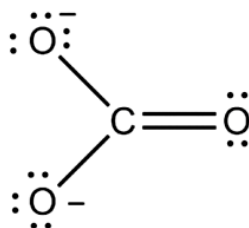


Figure 1. Molecular structure of CO₃ in carbonate mineral.

2. Carbonate deposit in Indonesia

Carbonate can be found in a relatively large amount in the earth crust. The common carbonate minerals are calcium carbonate (calcite, aragonite, depending on its crystal structure), magnesium carbonate (magnesite), calcium-magnesium carbonate (dolomite), and barium carbonate (barite) [2,3]. Among any other carbonate deposits in Indonesia, calcite and dolomite are the most common carbonate deposits that can be found in Indonesia. A large amount of calcite can be found in many places in Indonesia from west part of Indonesia, Sumatra and Java Island, until east part of Indonesia, such as Western Papua Province. Dolomite can be found in a large amount in Gresik, Lamongan, and Tuban (East Java Province). Magnesite is quite rare in Indonesia, and up to the recent years it can only be found in Padamarang Island (South East Sulawesi Province) [4].

3. Conventional utilization of carbonate minerals

Among carbonate minerals, calcite is the most common one that is often used conventionally. Calcite is heated and mixed with other materials to make the composite for construction structures like roads and buildings [5,6]. Calcite is not the only carbonate mineral that is used as construction material. Another carbonate mineral, such as dolomite, is also used as construction material [7]. It seems that as long as the carbonate is available in a large amount, the possibility of any carbonate minerals to be used in the construction of the infrastructure is high.

Calcite is also used as flux in the smelting industries such as iron and steel, aluminium, copper, nickel, and tin refineries [8]. The flux has a role to control the acidity and the melting point of slag during smelting process. Controlling slag acidity and melting point is important to maintain the refractory of the furnace and to reduce the energy cost.

4. Modern utilization of carbonate minerals

The conventional industries that process carbonate rock usually only treat the rock through physical process, such as crushing, milling, drying, compositing, and shape forming through compaction. On the other hand, modern processing of carbonate involves chemical treatment such as leaching, roasting, calcinations, smelting, alloying, and any other new processing method. Therefore, the product of chemical treatment is obviously different with that of physical treatment. Dolomite is one of the carbonate mineral that is often treated through chemical treatment in order to separate and utilize magnesium within dolomite, whether it is utilized as metal oxide or as metallic element.

Dolomite is carbonate mineral that contains magnesium as well as calcite. The existence of magnesium makes dolomite be used as magnesium source for human, animal and plants, since magnesium is one of important elements needed by living creatures. Dolomite is conventionally used as fertilizer for plants that need a huge amount of magnesium such as coconut palm trees. Magnesium has a role to aid the photosynthesis process in the plant [9], and it increases the efficiency of nitrogen utilization in plants body system [10]. Dolomite, which contains magnesium, is used as base material in drug manufacturing. Human body needs magnesium to maintain certain functions of the enzyme. Magnesium becomes the cofactor in more than 300 enzymes that regulate diverse biochemical reactions in the body, including protein synthesis, muscle and nerve transmission, neuromuscular conduction,

signal transduction, blood glucose control, and blood pressure regulation [11]. Magnesium, with calcium, is a structural integrity element in the bone, muscle and many body organs [12].

Manufacturing industries also need magnesium to make certain metal that needs certain requirement of physical properties. Magnesite as a direct magnesium carbonate mineral can only be found in limited amount in Padamarang Island, South East Sulawesi Province. The magnesite on this island cannot be exploited due to the island's status as Conservation Island [13]. Therefore in Indonesia, magnesium in a large amount can only be obtained from dolomite mineral. Magnesium is needed in automotive industry to build automotive engine. Certain types of magnesium based material has been produced. At first, magnesium was not used in many automotive industries due to its poor corrosion resistant and low strength at high temperature, but further research and development can overcome this disadvantage. The alloying of magnesium with aluminium, strontium, calcium and rare earth elements increases the high temperature strength, creep resistance, corrosion resistance, and cast-ability [14]. Nowadays, magnesium alloy has become the suitable metal in automotive industry [15].

5. Modern processing of carbonate rock

5.1. Roasting of calcite or dolomite rock

Roasting of carbonates is meant to eliminate carbon dioxide from carbonate mineral. In case of calcite and dolomite, the roasting equation can be written as follows.

- $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- $\text{CaMg}(\text{CO}_3)_2 \rightarrow \text{CaO} + \text{MgO} + \text{CO}_2$

The product of roasting is usually sent to the industries that need calcium or magnesium oxide as one of raw materials in their production process. Some of the industries are iron and steel refinery, paper mill factory, drug manufacturer, etc.

5.2. High temperature extraction process of magnesium carbonate

5.2.1. *Reduction and vaporization of magnesium carbonate.* The goal of reduction and vaporization is to separate magnesium from other components that are classified as impurities. The reaction of reduction and vaporization can be written as follows:

- $\text{MgO} + \text{Si(s)} \rightarrow \text{Mg(g)} + \text{SiO}_2$

The free energy of this reaction is quite positive but the manipulation of atmospheric pressure can lead to the vaporization of magnesium in gas phase so that it can be easily separated from other impurities such as CaO , Fe_2O_3 , Al_2O_3 , SiO_2 etc, which is maintained as solid phase [16].

5.2.2. *Electrolysis of magnesium salt.* The solid magnesium oxide has to be converted to solid magnesium salt, such as magnesium chloride, in order to be able to be electrolyzed in an electrolytic cell. It is a kind of electroplating process that takes place at high temperature, at the temperature above liquidus temperature of magnesium salt. The below equation is the example of chemical equation taking place at cathode of the cell [17].

- $\text{Mg}^{2+}_{(\text{l})} + 2\text{e}^- \rightarrow \text{Mg(s)}$

The positive ion of magnesium is neutralized by electron and this leads to the deposition of magnesium atom at cathode. The anode used in this electrolytic cell is usually carbon electrode. The reaction happening at anode is:

- $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

The product of cathodic reaction is chlorine gas. This kind of reaction will take place very rapidly at very low atmospheric pressure.

6. Physical metallurgy of magnesium metal

As single metal, magnesium is classified as light material. The weight of magnesium is 75% lighter than steel and 33% lighter than aluminium [18]. Thus, this metal is commonly used to construct something that needs to be light and strong such cars, ship, and plane. Although magnesium is lighter than aluminium, the price of magnesium metal is higher than that of aluminium. Therefore, magnesium is preferred to be alloyed with aluminium to obtain material that is lighter than aluminium at low price. Aluminium itself is the material commonly used in the application that needs light but strong material such as vehicle engine [19].

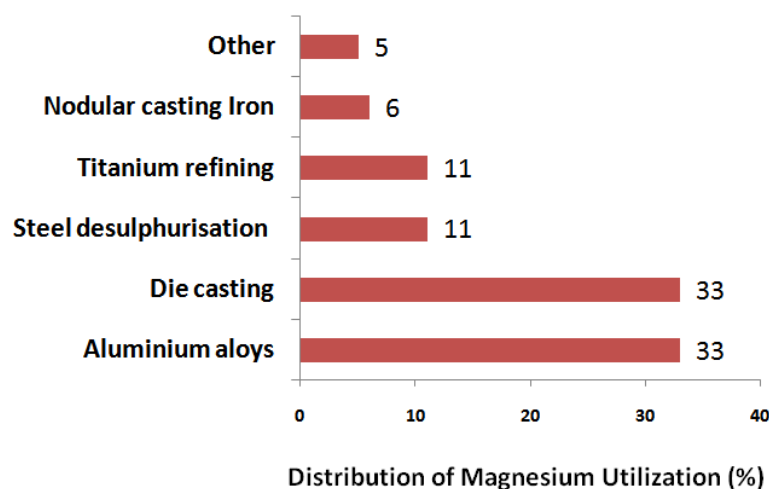


Figure 2. Distribution of Magnesium Utilization [18] (with modified graphic type).

The alloying of magnesium with aluminium makes the physical properties of the engine much better. For example, the tensile strength of aluminium metal with certain minor element such as silicon, copper and mangan is only 100-150 MPa, whereas aluminium that is alloyed with magnesium has minimum tensile strength 220 MPa [20]. Figure 2 shows the distribution of magnesium application in industries. The figure clearly shows that alloying magnesium with aluminium is among the largest application of magnesium.

Another largest application of magnesium is die-casting industry. Die-casting method is highly suitable to process lightweight metal such as magnesium and aluminium. The demand of magnesium being processed through die casting seems to increase. This indicates that some part of aluminium demand has been replaced by magnesium.

The refining of titanium needs huge amount of magnesium to convert titanium chloride into titanium metal [21]. Titanium processing industry is not as large as steel processing industry, which is indicated by the low utilization of magnesium.

Magnesium is also needed in steel desulphurization process in iron and steel industry. It is needed to eliminate silicon from steel melt solution [22]. The amount of silicon to be eliminated from steel melt is very low, so that the amount of magnesium needed for this process is not high.

Cast iron is the popular iron base material ever since the ancient era. Cast iron is the solid solution of iron with excessive carbon. The excessive carbon precipitates as graphite flake in the matrix of iron solid solution. The flake shape makes the total strength of cast iron low. Although the tensile stress of cast iron is quite high, ductility is very low. In order to increase its ductility, the flake shape graphite has

to be changed into nodular shape. Magnesium plays important role to change the shape of graphite from flake into nodular. Although magnesium plays important role to dramatically change mechanical property of cast iron, the amount of magnesium used for this purpose is very low [23].

7. The possibility of carbonate processing in indonesia

Conventional processing of carbonate such as mixing the carbonate with other materials to produce composite for civil construction, crushing and milling to make fertilizer for plants, and flux for smelting process obviously has been done in Indonesia. Calcite perhaps is the most suitable carbonate to be processed conventionally, since calcium is not needed to be produced in the elemental form. On the other hand, dolomite contains magnesium, which is needed in elemental form by various manufacturing industry. Nowadays, the automotive industry is urged to create vehicles that need less energy. Some innovation has been initiated to make the engine that is able to reduce the fuel consumption. It is widely known that the cars produced by Japanese companies need less fuel than those made by American or European companies. Obviously, Japanese companies have successfully created the engine that needs less fuel. Another innovation to decrease the energy consumption can be done by reducing the weight of materials. Magnesium is the lightweight material that can be used to reduce the total weight of the car. Unfortunately, the processing to produce magnesium metal is not easy. It needs a lot of energy and, since the process has to take place in ultra-low atmospheric pressure, it will require special equipment.

On the other hand, the modern application of carbonate minerals in the oxide form has been developing. These oxides can be used as raw materials to make slow release fertilizer, non-metallic biomaterial, drugs, etc. Since the final product is the oxide, it must have much less energy requirement than that of magnesium metal.

Slow release fertilizer is one of the possible products that uses these oxides as raw materials. Slow release fertilizer can play an important role in the food safety program in Indonesia. It can increase the efficiency of fertilizer application, and at the same time, it can reduce fertilizer cost, and also reduce the environment pollution that is caused by the application of conventional fertilizer. Unlike the production of magnesium metal, which is classified as the already proven technology, the production of oxide from carbonate mineral for slow release fertilizer synthesis is still in the research stage. There are still wide gaps that have to be filled in order to implement the utilization of these minerals to maintain food safety in Indonesia. These wide gaps certainly contain scientific aspect that has to be revealed during achieving those purposes. The revealing of the scientific aspect will be the basis of the development of the whole process until it reaches dissemination stage.

8. Conclusions and suggestions

Indonesia has a large amount of carbonate deposit in the form of calcite, dolomite and magnesite. Among them, calcite and dolomite are the largest carbonate minerals that can be found in Indonesia. Calcite and dolomite have been utilized through conventional ways to produce raw materials for construction and for synthesizing ordinary fertilizer. Dolomite contains magnesium metal that nowadays is needed by many manufacturing industries. The implementation of the industry to produce magnesium metal will need a large amount of energy and complicated equipment. This process technology is actually the already proven technology - in other words, the research opportunity in this area is low.

On the other hand, the demand of the oxides that can be resulted from carbonate minerals processing is quite high. The process needs less energy and less complicated equipment than that of magnesium metal production. Slow release fertilizer is one of the products that can be chosen to process carbonate mineral. Slow release fertilizer is the fertilizer that is made by changing the nutrient release rate of ordinary fertilizer. Slow release fertilizer can increase fertilizer efficiency and decrease environment pollution caused by the application of ordinary fertilizer. Thus, the research to study the mineral processing of carbonate to produce slow release fertilizer is suggested.

Acknowledgments

I acknowledge comments from the reviewer and the editor of GCGE2017.

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