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A Brief Review on Limestone Deposits in Korea, Vietnam and Applications of Limestone

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Abstract

Precipitated Calcium Carbonate (PCC) can be utilized in energy-effective paper production. Limestone is a raw material for synthesizing PCC. Since the PCC production yield depends on the physicochemical properties of the limestone, a basic investigation of the raw limestone is required. This study provides a brief review of the origin of limestone, limestone distribution characteristics, and limestone deposits in Korea and Vietnam. Most limestones in Korea were formed in the Paleozoic era. On the other hand, limestones in Vietnam have various ages from the Precambrian to the Triassic. Limestone is the most largely produced mineral in Korea, but Vietnam has 5 times more amount of limestone reserves than Korea.

Key words : Review, limestone deposits, Korea, Vietnam, Applications

1. Introduction

Recently, researches on the synthesis of precipitated calcium carbonate (PCC) are actively focused in order to prevent the deepening of global warming and to recycle depleting resources(Wardhani et al., 2018; Zevenhoven et al., 2019; Habte et al., 2020; Abeywardena et al., 2020; Grimes et al., 2020; Adnyani et al., 2020). PCC is a polymorphs of CaCO3 including hexagonal calcite, orthorhombic aragonite, and hexagonal vaterite. In addition, crystal size and shape have great impacts on their application.

In this context, aragonite would be considerably more significant than the others listed above. Aragonite is a needle-like material with a large aspect ratio. Furthermore, their particle size distribution and shape can be experimentally controled during synthesis (Park et al., 2004). These characteristics have made aragonite to be preferred as an industrial raw material. For example, using aragonite PCC as a filler for recycled paper has not only improved whiteness, strength, and lifespan, but also reduced industrial byproducts such as wastewater. In addition, the refining-drying time is short, so the energy use can be cut down(Kim et al., 2009).

The PCC synthesis process consists of calcining limestone, hydration of quicklime, and carbonation of slaked lime. To perform this process more efficiently, the aragonite yield is important. According to KS E 3077(Korean Standard Test) ‘Testing method for hydraulic activity of limestone used to precipitated calcium carbonate’, hydration activity is defined as the difference between the initial temperature and the temperature 30 seconds after starting the reaction.

Previous studies have demonstrated that the higher the hydration activity of quicklime, the higher the yield of aragonite-type PCC(Kim et al., 2007; You et al, 2017). Also, Yang et al. (2014b) pointed that impurities within a limestone makes the hydration activity lower and that different crystallographic charac-

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Table 1. Major carbonate phase in geologic periods.

Era	Period		Dominant Carbonate Mineral	0 Ma
Cenozoic	Quaternary		Aragonite + High-Mg Calcite (Aragonite Sea)	2.58
	Neogene			23.03
	Paleogene		Low-Mg Calcite (Calcite Sea)	66.0
Mesozoic	Cretaceous			~145.0
	Jurassic			201.3
	Triassic		Aragonite + High-Mg Calcite (Aragonite Sea)	251.9
Paleozoic	Permian			298.9
	Carboniferous	Pennsylvanian		323.2
		Mississippian		358.9
	Devonian		Low-Mg Calcite (Calcite Sea)	419.2
	Silurian			443.8
	Ordovician			485.4
	Cambrian			

teristics of limestones with similar CaO content result in distinct hydration activity. You et al. (2017) and Yang et al. (2014a) showed that the geologically older limestone has the lower hydration activity in their samples. Since the hydration activity depends on the parameters such as impurity content, crystallinity, age, etc. of a limestone, a basic investigation of limestone must be preceded before synthesizing aragonite PCC. This study introduces a brief concept of limestone formation and compares the associated natural limestone resources in Korea and Vietnam.

2. The origin of limestone

Limestone is a sedimentary rock mainly composed of calcium carbonate, and contains SiO_2, Al_2O_3, Fe_2O_3 as impurities. Limestone is formed by chemical precipitation or biochemical precipitation. Biochemical limestone forms from the accumulation of marine organisms such as shells and corals. Chemical limestone is formed by a reaction shown in **Eq.(1)**.

$$H_2O+CO_2+CaCO_3 \leftrightarrow Ca^{2+}+2HCO_3^- \quad (1)$$

As can be seen from the above equation, the formation of carbonate minerals is greatly affected by carbon dioxide. When carbon dioxide is dissolved in water, reactions such as **Eq.(2)~(4)** occur, releasing hydrogen ions. Therefore, when the partial pressure of carbon dioxide in seawater is high(i.e. pH is low), dissolution of $CaCO_3$ occurs, but when the partial pressure of carbon dioxide is low, the generation rate of H+ ions decreases (i.e. the pH of seawater increases), resulting in precipitation of $CaCO_3$. Therefore, when the temperature of seawater increases and the pressure decreases, the partial pressure of CO_2 decreases, and eventually CaCO3 is precipitated because of the low solubility of carbonate minerals.

$$CO_2+H_2O \leftrightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 \leftrightarrow H^++HCO_3^- \quad (3)$$

$$HCO_3^- \leftrightarrow H^++CO_3^{2-} \quad (4)$$

Ions in sea water also influence the precipitation of calcite and aragonite. As seawater salinity increases (i.e. ionic strength increases), the solubility

Table 2. Paleozoic Stratigraphy in South Korea.

<table>
<tr><td>Mesozoic</td><td>Triassic</td><td rowspan="8">Pyeongan Supergroup</td><td>Donggo Formation</td></tr>
<tr><td rowspan="18">Paleozoic</td><td rowspan="5">Permian</td><td>Gohan Formation</td></tr>
<tr><td>Dosagok Formation</td></tr>
<tr><td>Hambaeksan Formation</td></tr>
<tr><td>Jangseong Formation</td></tr>
<tr><td>Bamchi Formation</td></tr>
<tr><td rowspan="2">Carboniferous</td><td>Geumcheon Formation</td></tr>
<tr><td>Manhang Formation</td></tr>
<tr><td>Devonian</td><td colspan="2">Imjin System</td></tr>
<tr><td>Silurian</td><td colspan="2">Hoedongri Formation</td></tr>
<tr><td rowspan="5">Ordovician</td><td rowspan="9">Joseon Supergroup</td><td>Duwibong Formation</td></tr>
<tr><td>Jigunsan Formation</td></tr>
<tr><td>Makgol Formation</td></tr>
<tr><td>Dumugol Formation</td></tr>
<tr><td>Dongjeom Formation</td></tr>
<tr><td rowspan="4">Cambrian</td><td>Hwajeol Formation</td></tr>
<tr><td>Daegi Formation</td></tr>
<tr><td>Myobong Formation</td></tr>
<tr><td>Myeonsan Formation</td></tr>
</table>

of carbonate minerals increases, and the precipitation becomes difficult. In addition, Mg^{2+} ions in seawater prevent precipitation of calcite. This is because Mg^{2+} ions are well adsorbed on the surface of calcite and prefer to be substituted in the crystal structure, so the stability of the crystal decreases and eventually increase the solubility of calcite. On the other hand, aragonite is relatively less affected by Mg^{2+} ions. When the content of Mg^{2+} ions in seawater increases, aragonite precipitation is more preferred than calcite. Therefore, the types of carbonate rocks formed through geological history are different. During the period of rapid seafloor spreading, Mg^{2+} ions are adsorbed to the hot seafloor basalt, resulting in precipitation of calcite with low magnesium(S Boggs, 1995). The major carbonate mineral phases according to the geological age are shown in **Table 1.**

3. The Korean limestones

3.1. Distribution characteristics

According to the geological map of Korea, distribution area of limestone is about 1,899 km^2, but if including the limestone area covered by the alluvium, it accounts for 18% of Korea territory(Park et al., 2017). Limestones in Korea are mainly distributed in the early Paleozoic era, the Joseon Supergroup. In the Joseon Supergroup, clastic sedimentary rocks are embedded in carbonate rocks deposited in shallow sea environments. The Joseon Supergroup is divided into the Yeongwol, Taebaek, Yongtan, Pyeongchang, and Mungyeong Group according to lithology and geographical distribution. Among these, the Yeongwol Group is subdivided into the Sambangsan, Machari, Wagok, Mungok and Yeongheung Formations, and the Taebaek Group is subdivided into the Myeonsan, Myobong, Daegi, Sesong, Hwajeol, Dongjeom, Dumugol, Makgol, Jigunsan and Duwibong Formations(Jang et al., 2018). The stratigraphy of the Paleozoic era in Korea is summerized in **Table 2**(The Geological Society of Korea, 1999).

The Taebaek Group corresponds to Cambro-Ordovician. A limestone layer is located in the upper Myobong Formation. In the Daegi Formation, milky white, dark gray, and pink massive limestone, dolomite limestone and stratified limestone are the main lithofacies. The Hwajeol Formation includes gray limestone, flat pebble conglomerate, and has a structure in which lime and silica are arranged parallel to the bedding plane. The Dongjeom Formation is composed of calcareous mudstone, calcareous sandstone, and flat pebble conglomerate. The Dumugol Formation has nodular limestone, flat pebble conglomerate, and massive limestone. In the Makgol Formation, dark gray to light gray dolomitic limestone, dolomite, calcareous mudstone, and flat pebble conglomerate are distributed. The Jikunsan Formation has intercalated limestone in the shale layer. The Duwibong Formation is mainly composed of light gray massive limestone and dolomitic limestone, and partially dark-gray shale and flat pebble conglomerate are embedded.

The Yeongwol Group is also a Cambro-Ordovician stratum, with dolomite dominating. Limestone is distributed in the Machari, Wagok, Mungok, and Yeongheung Formation. The Machari Formation includes stratified limestone, crystalline limestone, and dolomitic limestone. The Wagok Formation is mainly composed of massive light gray to gray dolomite and dolomite limestone, with gray to blue gray limestone intercalated. The Mungok Formation is composed of dark gray dolomite, dolomitic limestone, and flat pebble conglomerate. The Yeongheung Formation includes gray to dark gray dolomite and dolomitic limestone.

The upper Paleozoic layer also contains some limestone. The Hoedongri Formation in Jeongseon area is the Silurian Formation, consisting of fine-grained limestones of blue-gray, light gray to milky white, and few dolomitic limestones. Among the Carboniferous-Permian strata, limestone is distributed in the Manhang, Geumcheon, and Baamchi Formation of Pyeongan Supergroup(The Geological Society of Korea, 1999).

3.2. Limestone deposits

Domestic high-quality limestone deposits are divided into Jecheon-Danyang districts, Samcheok-Taebaek-Jeongseon districts, and Andong-Uljin districts. Limestone ores are classified into five categories according to the state of production, composition, crystallinity, and organization: (1) Crystalline limestone type, (2) Micro-crystalline calcite type, (3) Micro-crystalline marble type, (4) Coarse-crystalline marble type, (5) Mega-crystalline calcite type. Limestone in Jecheon-Danyang district is crystalline limestone and is composed of pure isometric calcite phase. Limestone in Samcheok-Taebaek region is a crystalline limestone type, but contains a lot of dolomite. The limestone in Jeongseon area is coarse-grained calcite type, and coarse calcite-type limestone is produced in mines in Taebaek, Yeongwol and Uljin area. The CaO content was the highest in Jecheon-Danyang district, and the MgO content was the highest in the mega-crystalline calcite type(Noh et al., 2004).

Korea has 166 Limestone deposits and total reserves are about 8.8 billion tons(Korea, S., 2018). The high-grade limestone with CaO content higher than 52% accounts for about 12% of this. In Korea, most limestones were formed in the Paleozoic Era, whereas Japanese limestones mainly have a chronology between the Mesozoic and Paleozoic, and high-quality limestones account for more than 90% of the total limestone. Therefore, as the demand for high-quality limestone increases, the amount of imports of limestone and calcium carbonate from countries such as Japan, China, and Malaysia is increasing.

4. The Vietnamese limestones

4.1. Distributional Characteristics

The Vietnamese limestone occupies 50,000-60,000 km^2 of the continent, which is 20% of Vietnam territory. Its age ranges from the Precambrian to the mid-Triassic, mostly from the Hue region to the northern regions(e.g., Van et al., 2005). Limestone zones cover half of several areas, including Binh (53.4%), Cao Bang (49.5%), Tuyen Quang (49.9%) and Ha Giang (38.0%). In particular, areas such as Mai Chau(Hoa Binh province), Moc Chau, Son La (Son La province), Tua Chua, Tam Duong (Lai Chau province), Dong Van, Meo Vac (Ha Giang) are completely limestone areas. Most Vietnamese limestones have biochemical origins.

Based on the location of limestone deposits, Viet-

Table 3. Overview of limestone and dolomite deposit in Vietnam(Prime Mininster, 2012).

Type of CaCO3	Number of deposits	Investigation		Scale (million tons)		
		Not yet	Yes	Reserve	Resource	Total
Dolomite	82	37	45	124	2,676	2,800
Limestone	351	77	274	12,557	32,180	44,738

nam's limestone can be divided into four regions. Northeastern limestone was found in Early Cambrian-Late Triassic geological formations, limestone deposits of this group are Na Hen, Suoi Co, Lang Bet, Hoang Thach, Uong Bi, etc. Northwestern limestone was found in Early Cambrian-Middle Triassic geological formations, and limestone deposits of this group are Ninh Xuan, Hoan Long, But Phong, Cam Van, and Dinh Thanh. Northern central limestone was found in Middle Devonian-Middle Triassic geological formations, and limestone deposits of this group are Quynh Xuan, Len Hai Vai, Ca Tang, and Ha Trang. Southern limestone was found in Middle-Late Permian geological formations. Limestone deposits of this group are Ta Thiet, Nui Com, Hang Tien, and Ba Hon.

Based on the age of formation, Vietnam's limestone can be divided into four groups. They are Precambrian limestone, Middle Cambrian-Middle Devonian limestone, Middle Devonian limestone-Carboniferous/Permian limestone, and Carboniferous/ Permian limestone-Middle Triassic limestone (Van et al., 2005). The Precambrian limestone was formed more than 550 million years ago. They are widely distributed from the North to the middle of Vietnam. The Middle Cambrian-Middle Devonian limestone was formed 520-500 million years ago distributing in the North and Northwest of Vietnam. The Middle Devonian limestone-Carboniferous/Permian limestone was formed 350-280 million years ago. This limestone age exposes over the country from North to South. The Carboniferous/Permian limestone-Middle Triassic limestone was formed 280-235 million years ago. This limestone age distributes stretching from Northwest to Southeast of the North. Especially, Bac Son (C-P*bs*) and Dong Giao (T_2 *dg*) limestone formation are the most widely distributed and own the highest value.

4.2. Limestone deposits

Vietnam is rich in high-quality limestone reserves.

Fig. 1. Vietnam's limestone deposits.

There are 351 limestone deposits in Vietnam. Up to date, 274 limestone deposits have been investigated. In the 274 sites investigated, the reserves were counted at 47.5 billion tons. There are also 82 dolomite deposits, of which 37 have been investigated. Dolomite reserves are reported to contain 2.8 billion tonnes of reserves(**Table 3**). The distribution and reserves of limestone deposits in Vietnam are shown in **Fig 1.**(Mekong joint stock Company, 2017; Prime Minister, 2010).

Based on the scale, Vietnamese limestone deposits

Table 4. Characterization of some selected limestone samples in Vietnam(Nam and Drebenstedt, 2016).

Deposit	CaO [%]	MgO [%]	IgLoss	Density [%]	Humid [%]	Hardness [f]
But Son	52.6-54.5	0.3-1.84	42.4	2.7	0.18	7-8
Hoang Thach	47.3-54.7	0.2-6.6	37.1-44.0	2.7	0.23	7-8
Bim Son	50.2-54.7	0.4-0.9	42.4-43.9	2.7	0.84	5-12
Hoang Mai	53.0-54.7	0.8-2.4	42.7	2.7	0.7	7-8
Sao Mai	53.9	1.1	42.3	2.3-2.7	0.6	6-9

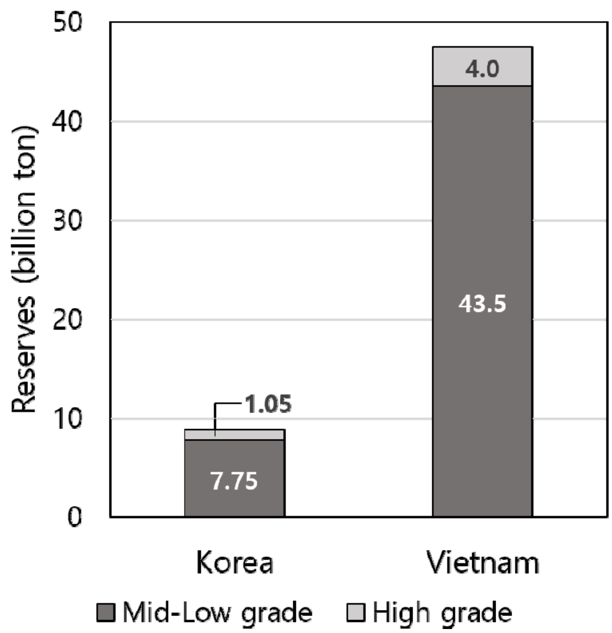

Fig. 2. The comparison of Korea and Vietnam's limestone reserves.

can be classified as large (>100 million tonnes or more), medium-sized (20 to 100 million tonnes), and small (less than 20 million tonnes). The number of large, medium and small deposits is 91, 92 and 91 respectively. There are 190 places where high quality limestone is buried, and the reserve is about 4 billion tons. However, some deposits are located in restricted areas that cannot be mined. The chemical composition and physical properties of some limestone deposits in Vietnam are shown in **Table 4.**

5. The Comparison of Korea and Vietnam

The Korean and Vietnamese limestone reserves are compared in **Fig. 2.** High-grade limestone ore in Korea accounts for 12% of total reserves. In vietnam, high-grade limestone is about 8.5% of total reserves. But in amount, Vietnam's reserves of high grade limestone are about four times more than that of Korea. Beside the reserves, Korean and Vietnamese limestone has different geological age. Korean limestone age is mostly Paleozoic, while Vietnamese limestone age varies from Precambrian from Triassic. Also, limestone distribution area in Vietnam is about 3 times larger than in Korea.

6. Conclusion

For the efficient PCC synthesis, the crystallinity and quality of limestone must be investigated, and its efficiency can be quantified through hydration activity. The geological age of limestone is presumed to be related to the crystallinity of limestone in previous studies. Therefore, further research on this will be needed. This study investigated the characteristics of Korean and Vietnamese limestone deposits, and this could be utilized on choosing the PCC raw materials. With the results, Vietnam is expected to be the good source of limestone for producing PCC. This research would be a cornerstone of Vietnam-Korea joint research.

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