工學碩士 學位論文

제지슬러지소각재와 광물탄산화 방법을 이용한 이산화탄소 저장 연구

Study on carbon dioxide storage using paper sludge ash through mineral carbonation

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Abstract

광물탄산화는 이산화탄소를 칼슘, 마그네슘 등을 함유한 금속산화물과 반응시켜 영구적으로 저장하는 기술이다. 본 연구에서는 광물탄산화 방법으로 이산화탄소를 저장하기 위해 알칼리성 산업부산물인 제지슬러지소각재(PSA)를 원료로 선정하였다. 그리고 염산, 아세트산, 염화암모늄, 아세트산암모늄, 구연산나트륨, 물의 다양한 용제와 PSA를 반응시켜 간접탄산화 방법으로 이산화탄소를 저장하였고, 해수와 PSA를 반응시켜 직접탄산화 방법으로 이산화탄소를 저장하였다. 간접탄산화 방법의 경우 용출반응과 탄산화반응으로 나누어 실험을 진행하였고, 이를 통해 최적의 반응 조건을 도출하였다. 또한, 이산화탄소 저장 효율을 높이기 위해 알칼리 처리 또는 탄산화반응 시간을 조절하였다. 직접탄산화 방법의 경우 다양한 실험을 통해 해수와 PSA를 이용한 직접탄산화 반응의 최적 용매의 양(해수와 PSA의 혼합비)과 반응시간을 찾았고, PSA를 이용한 직접탄산화 반응에 해수와 초순수를 각각 용매로 사용했을 때의 이산화탄소 저장량을 비교하였다. 결과적으로 간접탄산화 방법에서 0.7M 염산을 고액비 2g/50mL

로 30분간 반응시켰을 때 PSA로부터 최대 54.1%의 칼슘이 용출되었다. 그리고 용출 실험을 통해 도출한 조건에서 아세트산과 PSA를 반응시켜 얻은 용출액에 수산화나트륨으로 알칼리 처리 후 탄산화 했을 때 최대 324kg CO_2/ton PSA를 저장할 수 있었다. 한편, 직접탄산화 방법에서 해수와 PSA의 적정 비율은 20g/100mL이었고, 최적 탄산화 반응 시간은 2시간이었다. 위 조건에서 해수와 PSA가 혼합된 슬러리를 탄산화 했을 때 최대 113kg CO_2/ton PSA를 저장하였다. 간접탄산화 후 회수한 고체는 일부 불순물을 제외하고 대부분 Calcite 형태의 고순도 탄산칼슘이었으며, 직접탄산화 후 회수한 고체는 Calcite 형태의 탄산칼슘과 소량의 탄산마그네슘을 포함하고 있었다.

KEY WORDS: Mineral carbonation 광물탄산화; Paper sludge ash 제지슬러지소각재; Carbon dioxide 이산화탄소; Sequestration 저장.

Chapter 1. Introduction

1.1 Concept of mineral carbonation

Since the Industrial Revolution, the carbon dioxide has been considered materials the greatest impact on climate change and it has been increased from 387ppm in 2005 to 400ppm in 2012(Climate Change Information Center, 2014). In addition, the climate change patterns will be continued because of carbon dioxide already emitted even if carbon dioxide emissions are non-existent in the world. If there are no additional policy, carbon dioxide concentration in the air is expected to increase up to 25~90% in 2030 compared to 2000(IPCC, 2007). Accordingly, research of developing Carbon Capture and Storage(CCS) technology has been carried out actively in the world.

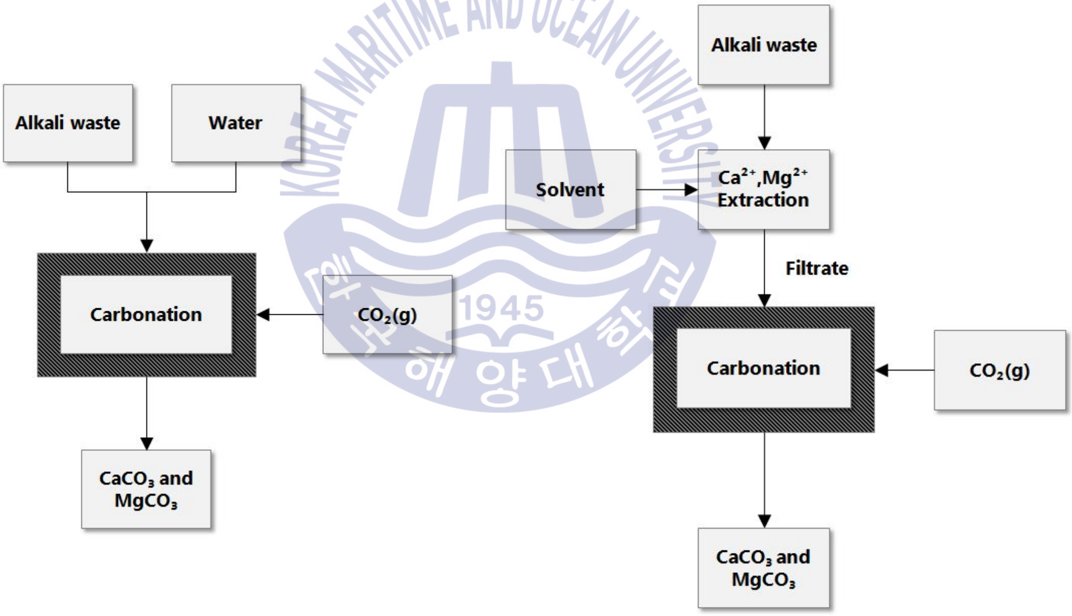
Mineral carbonation, one of the carbon capture and storage technology, is suitable for treatment of small amount of carbon dioxide unlike geological storage or marine storage to isolate on a large amount of carbon dioxide. Carbon dioxide can be disposed in the long term because carbonate produced after carbonation is thermodynamically stable and it is safe method without worry about exposing of gas in the air(Chae et al., 2009). After the concept of treatment carbon dioxide had been first reported in 1990(Seifritz, 1990), until now the research has been actively conducted mainly in the United States, the United Kingdom, Finland and Japan. Mineral carbonation is focused field in the world as much as established the international institute(Accelerated Carbonation for Environmental and Materials Engineering, ACEME) them as the main subject in 2006.

Mineral carbonation is technology to store carbon dioxide as insoluble carbonate by reacting with metal oxide like calcium and magnesium in the presence of water, the principle is the following equation(Eq. 1,2,3).

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (1)$$

$$CO_2(aq) + H_2O \rightarrow 2H^+ + CO_3^{2-} \qquad (2)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \qquad (3)$$



(a) (b)

Fig. 1 Processes of mineral carbonation using industrial waste (a) direct carbonation (b) indirect carbonation

Mineral carbonation can be classified to direct and indirect carbonation. The direct carbonation is single process to react carbon dioxide with raw materials(natural minerals or industrial waste) directly, and indirect carbonation is two step process to react carbon dioxide with filtrate extracted calcium or magnesium from raw materials using solvent(Han et al., 2011). A conceptual diagrams about two carbonation are shown in Fig. 1. The main factors affecting calcium extraction efficiency and carbonation efficiency can be mentioned the content of calcium or magnesium in raw material, form of them, particle size, pH of solution and water content, etc.

It can be used as a raw materials that natural minerals or industrial waste containing a large amount of calcium and magnesium. However, it is the best method in reality to use industrial waste containing components high reactivity with carbon dioxide as raw material of mineral carbonation because it is lack buried mines natural minerals such as wollastonite, serpentine and olivine(Han et al., 2011; Kim, 2009). In this study, carbon dioxide was stored using Paper Sludge Ash(PSA) which is one of industrial waste through two method of mineral carbonation and we tried to find its means comparing carbon dioxide storage in each methods.

1.2 Mineral carbonation using industrial waste

Recently, mineral carbonation researches using industrial wastes, which is a lot of advantages environmentally and economically are actively conducted in the world. The industrial wastes are estimated it is much more favorable as a raw materials because industrial waste can be easily obtained in the surrounding than natural minerals and they do not damage in environment also they can store a lot of carbon dioxide. And they can be reacted with carbon dioxide in mild conditions because industrial waste have higher reactive than natural minerals. Not only it can be stored carbon dioxide through mineral carbonation but also heavy metals in industrial waste can be stabilized so it can be buried safely or reused. In general, carbon dioxide storage capacity is proportional to the amount of calcium oxide and magnesium oxide contained in raw materials. And alkali industrial waste have a lot of storage capacity per weight because they contain a large amount of calcium oxide(Table 1).

Table 1 Theoretical carbon dioxide sequestration capacity of waste (Bonenfant et al., 2008; Santos et al., 2013; Jo et al., 2014; Montes-Hernandez et al., 2009; Huntzinger et al., 2009a)

Waste	CaO content (%)	Theoretical CO_2 sequestration capacity (kg CO_2/ton waste)
Slag	33~50	374~550
Cement waste	15~36	165~396
CKD	20~60	220~660
Coal ash	5~32	32~352

Mineral carbonation studies using industrial waste are mainly conducted from overseas rather than domestic. Currently, the research have been conducted to recycle of high purity recovered carbonate which is the final product in indirect carbonation, to reuse of waste solvents used in calcium extraction step and related papers have been published. Unlike natural minerals, when industrial waste containing a large amount of calcium oxide was used in mineral carbonation has been reported to be economical(Montes-Hernandez et al., 2009; Huntzinger et al., 2009a; Huntzinger & Eatmon, 2009b; Stolaroff et al., 2005). It is shown in Table 2 and Table 3 that summary included raw materials, particle size, reaction condition, carbon dioxide storage of recent carbonation research using industrial waste.

Table 2 Comparison of previous studies on direct mineral carbonation using industrial waste

Waste type	Particle size	CaO content (%)	T(℃)	L/S ratio (mL/g)	Reaction time	P_{CO2}	CO_2 flow rate	CO_2 sequestered		
								Conversion (%)	kg CO_2/ton waste	Experimental condition
Slag										
EAF LF	38-106 ㎛	32.8 58.1	20	10	~72h	atmospheric	5mL/min	58.2	247	LF, 16h
AOD* CC*	<500 ㎛	54.8 50	30-180	4-40	5-120min	2-30 bar	-	60	312	CC, 90℃, 60 min, 30 bar, 62.5 g/L
BHC	<44 ㎛	52.8	40-160	10	5 min-12 h	700, 1300 psig	-	68.3	283	BHC, 700 psig, 12h, 160 ˚C
BOF UF FA BHC	<44 ㎛	51.1 41.9 31.9 54.2	30-80	10	~240min	101.3 kPa	0.1L/min	72	270	BOF, 1h, 60℃
EAF AOD	<425 ㎛	35-50	30-50	0-0.6	0.5-24h	1-10 bar	-	-	300	AOD, 50℃, 3bar, 0.4L/kg
BOF	<44 ㎛	41.5	25	5-50	~120min	101.3 kPa	0.5-3 L/min	89.4	283	BOF, 25 ˚C, 20mL/g, 120 min, 1L/min
Cement waste										
CKD	-	34.5	ambient	1.63-3	~12day	ambient	45-60 mL/min	70	-	-
Coal ash										
Fly ash	40 ㎛	5	20-60	6.7-20	2h	10-40bar	-	82	26	-
Fly ash	0.9 mm	39.8	40	1.4-10	10h	2-6MPa	-	-	7.7	0.2mL/g
Fly ash	20 ㎛	7.2	ambient	5-10	until pH	ambient	2-10	-	8	2mL/min, 100g/L

					8.3		mL/min			
Others										
Paper mill waste	15 ㎛	83.2	30, 60	50	48h	10-40bar	-	84.5	218	30° C, 30bar
Red mud	5-50 ㎛	3	ambient	0.2-0.6	0.5-12h	3.5bar	-	82	53	0.35mL/g, 3.5h
12 wastes	250 ㎛	0.06-69.6	ambient	10	72h	2bar	-	26	-	with PSIA
Coal ash Waste ash	10 ㎛	24.9 30.5	30-80	40-80	60min	-	110mL/min	78.6	70.8	coal ash, 60mL/g, 75° C
Red gypsum	45-500 ㎛	32.2	25-300	5	60min	1-70bar	-	41	-	200° C, 70bar
SWIFA	-	36.3	21-91	0.1-0.8	3h	3bar	-	7-10	-	0.3mL/g

EAF: electric arc furnace slag

LF: ladle furnace slag

AOD: argon oxygen decarburization slag

CC: continuous casting slag

*: stainless steel slag

BHC: blended hydraulic slag cement (blend of Portland cement and fine granulated blast furnace slag, 90% BF slag content)

BOF: basic oxygen furnace

UF: ultra-fine slag

FA: fly-ash slag

CKD: cement kiln dust

PSIA: paper sludge incineration ash

SWIFA: solid waste incineration fly ash

Table 3 Comparison of previous studies on indirect mineral carbonation using industrial waste

Waste type	Particle size	CaO content (%)	Ca extraction						Carbonation						
			T (℃)	L/S ratio (mL/g)	Reaction time	Solvent	Ca extraction (%)	Ca or Mg Conc. in extract	pH adjust with	T (℃)	P_{CO2}	CO_2 flow rate	Conversion (%)	CO_2 sequestered (kg CO_2/ton waste)	Purity of $CaCO_3$ (%)
Slag															
blast furnace slag	<10 ㎛	40.6	70	20	2h	20vol% CH_3COOH	-	-	50wt% NaOH	30–70	30 bar	1L/min	74	227	-
steel slag	250–425 ㎛	16	25	50	0.5h	0.29M HCl	85	-	NaOH	ambient	-	1mL/min	83	-	98
steelmaking slag	<125 ㎛	44.9	30	200	1h	1M NH_4NO_3 NH_4Cl CH_3COONH_4	73	-	-	30	-	1L/min	-	-	-
converter slag	<64 ㎛	44.5	40–90	16	1h	1N NH_4Cl	59.5	0.29 mol/L	-	40	-	CO_2 + N_2 (13% CO_2) 17 sccm	80	-	98
steelmaking slag	38–250 ㎛	40	60	10	2h	2M NH_4Cl	-	15,000 mg/L	28% NH_4OH	20–80	10–40 bar	-	-	138	96
blast furnace	<200 mesh	47.2	ambient	10	1h	0.1M CH_3CO	-	4,017 mg/L	1M NaOH	ambie	-	1.5mL/min	-	90	-

slag						OH + 0.1wt% EDTA				nt					
Cement waste															
waste cement	<0.15 mm	35.7	20	20	4h	0.5M, 1.0M CH_3COONH_4 NH_4NO_3 NH_4Cl	24-69	2,479-8,899 mg/L	-	ambient	-	15vol.% CO_2 + 85vol.% N_2 40mL/min, 200mL/min	-	180	98
concrete waste	60-100 mesh	16223 mg/kg	25	50	15min	0.15~0.98M HCl	-	475 mg/L	NaOH KOH LiOH	25	-	1mL/min	-	-	-
waste cement powder	<200 mesh	23.1	ambient	10	1h	0.1M CH_3COOH + 0.1wt% EDTA	-	4,931 mg/L	1M NaOH	ambient	-	1.5 mL/min	-	60	-
portland cement	<0.075 mm	56.3	25	5	24h	1M NH_4Cl 0.01M HCl 1M CH_3COOH DI water	5-35	635-28,904 mg/L	-	ambient	-	4mL/min	25	-	95
waste concrete	<0.15 mm	20.3		5			2-10	212-2,978 mg/L					5		
ordinary Portland cement	<0.075 mm	56.3	ambient	20	24h	0.2-2.0 M NaCl	-	943-1,248 mg/L	-	ambient	-	40mL/min	63	-	-
Coal ash															
fly ash		27	25	10	1.5h	brine	-	97,700	0.07		1.36	-	-		90

								mg/L	-0.08 M NaOH		MPa				
fly ash	<22 ㎛	-	ambient	10	1h	6% CH_3COOH	-	Ca: 14,000 mg/L Mg: 7,000 mg/L	-	60	10 bar	-	-	-	-
fly ash	20 ㎛	7.2	ambient	10	24h	DI water	10	-	-	ambient	-	2mL/min	-	264	-
Others														8	
FGD gypsum	<74 ㎛	32.5	ambient	1-5.7	5min	NH_4OH	-	-	-	ambient	-	1-4L/min	95		>90

FGD gypsum: Flue gas desulfurization gypsum

1.3 International research trend

The major alkali industrial wastes used in mineral carbonation research were slag, cement waste and fly ash. Recently, the researches have been reported to use municipal waste incinerator ash, oil shale ash. It is as follows that summarizing of mineral carbonation research trends in industrial waste by category.

1.3.1 Slag

Slag is generated in the process of smelting iron, the mineral carbonation research is most conducted using slag. It is contained 34~50% of calcium oxide, also it has high possibility to store caron dioxide through carbonation reaction because it appears strong alkalinity reacting with water(Eloneva et al., 2008). However, it needs a lot of energy consumption required for the pre-treatment such as crushing. The research using slag was conducted mainly in Finland, Taiwan, China, Belgium, Canada and Japan, direct and indirect carbonation was actively conducted both. Recent years, indirect carbonation researches getting a high purity carbonate and high carbon storage efficiency was conducted, and solvents like ammonium chloride, acetic acid was used to extract calcium from slag. In most studies, slag was grinded at 10-425㎛ particle size before carbonation.

1.3.1.1 Direct carbonation

The researchers have tried in variety to find a conditions to increase efficiency. They used to regulate water contents, temperature and initial carbon dioxide pressure(Chang et al., 2011a; Chang et al., 2011b; Baciocchi et al., 2010), also compared carbon storage efficiency slurry of slag with thin-film of slag(Santos et al., 2013). Santos et al. (2013) carried out direct carbonation experiment of the following two method using stainless steel slag:

To pressurize the carbon dioxide in slurry

To carbonate in thin-film slag at atmospheric pressure.

As a results, the carbonation efficiency was up to 55% at 90° C, 9bar in slurry, on the other hands, efficiency was only up to 37% in thin-film. They concluded that carbonation of slag slurry can be obtained high carbonation efficiency as well as it can be easier to apply industrial site in a continuous process rather than thin-film.

Chang et al. (2011a) conducted direct carbonation using several slag samples with different particle size and calcium content thereby changing carbon dioxide flow rate. They got the result that the flow rate decreased, the carbon storage increased. And carbon storage increased as particle size of slag were smaller and its calcium content were higher, the maximum carbon storage was 270kg CO_2/ton slag. According to Chang et al. (2011b), examined the effect of water content, carbonation efficiency was very low without water but the efficiency was increased up to 57.5% when liquid to solid ratio was 10mL/g. Then the efficiency was almost not changed even if water content was further increased. They explained that a large amount of water makes a barriers of mass transfer, and then dissolution rate of calcium decreased due to decrease of ionic strength, finally it could interfere with the carbonation reaction. Chang et al. (2011a) and Chang et al. (2011b) also observed effect of temperature on the carbonation, in the overall trend, as temperature was higher the carbonation efficiency was increased. In a low temperature(30~60° C), as temperature was higher the carbonation efficiency was increased, but it was showed opposite tendency in high temperature(60~80° C). Because two main factors, affecting carbonation efficiency, were shown opposite trends according to temperature. In other words, the temperature was increased, the dissolution rate of calcium was faster but, carbon dioxide solubility was decreased above a certain temperature.

Baciocchi et al. (2010) carried out direct carbonation using stainless steel slag to observe effect of carbon dioxide pressure (1~10bar) on carbonation efficiency. When slag was reacted at 50° C during 2 hours, carbonation efficiency was maximum 30%, the difference of carbonation efficiency was not great according to carbon dioxide pressure. The conditions, most affecting in carbonation efficiency, was particle size of slag.

Chang et al. (2013) stored 283kg CO_2/ton slag by reacting slag with wastewater produced steel making process after pass through pre-treatment that all of the calcium carbonate in slag was calcined and they was converted to calcium oxide above 850° C.

1.3.1.2 Indirect carbonation

Indirect carbonation can be divided into calcium extraction step and carbonation step. The most important factors in calcium extraction step is solvents type, particle size of slag and solid to liquid ratio. It can be affected economics of technology(Kunzler et al., 2011; Said et al., 2013). And the pH is the main factor to effect on carbonation step(Eloneva et al., 2008; Kunzler et al., 2011). Indirect carbonation efficiency using slag was 74~83% and the purity of carbonate was 96~98%. It was mainly used as solvents in indirect carbonation that acid such as acetic acid, hydrochloric acid(Eloneva et al., 2008; Kunzler et al., 2011; Kodama et al., 2008) and ammonium salts such as ammonium chloride, ammonium acetate, ammonium nitrate(Said et al., 2013; Sun et al., 2011). When acid was used as solvents, it was problem that carbonation do not occur, whereas calcium extraction efficiency was very high. However it was solved to increase pH by injecting base in calcium filtrate(Eloneva et al., 2008; Kunzler et al., 2011). For example, Kunzler et al. (2011) conducted carbonation experiment at room temperature and atmosphere pressure after calcium extraction experiment was conducted at various solid to liquid ratio, concentration of hydrochloric acid and temperature. As a results, optimum calcium extraction condition was 50mL/g of liquid to solid ratio, 0.29M concentration of hydrochloric acid, and temperature was not affected calcium extraction efficiency. And then pH of calcium filtrate was adjusted using sodium hydroxide, carbonation efficiency was 83% and carbonate was recovered a purity of 98% or more. There is meaningful that calcium was extracted in a short time using low concentration of solvent and it was shown possibility of high carbonation efficiency at ambient temperature, pressure.

Also, there was study that calcium was extracted from slag using acetic acid and then, carbonation was conducted to dissolve calcium acetate solid, obtained by heating and drying filtrate.(Eloneva et al., 2008). In this case, the process of increasing pH by injecting sodium hydroxide was required to generate carbonation reaction in calcium acetate solution. Although pH was acting as a decisive factor in carbonation but, temperature and pressure could not be affected. Carbonation efficiency was maximum 74%.

When ammonium salts are used in carbonation, it can selectively extract calcium from slag also, it can be recovered high purity of calcium carbonate. In addition, it has advantage to reuse waste ammonium salts solvents. For example, study of Kodama et al. (2008), comparing results of indirect carbonation using hydrochloric acid, acetic acid and ammonium chloride as a solvents with slag, was shown advantage of ammonium salts. When hydrochloric acid and acetic acid was used in calcium extraction, the efficiency was higher than using ammonium chloride. However, carbonation reaction was not occur because pH of filtrate was low. On the other hands, using a ammonium salts, the carbonation efficiency was 80% and 98% purity of calcium carbonate was recovered. They proposed the following two mechanism for calcium extraction and carbonation.

$$4NH_4Cl(aq) + 2CaO \cdot SiO_2(s) \rightarrow 2CaCl_2(aq) + SiO_2(s)\downarrow + 4NH_3(aq) + 2H_2O(l) \qquad (4)$$

$$4NH_3(aq) + 2CO_2(aq) + 2CaCl_2(aq) + 2H_2O(l) \rightarrow 2CaCO_3(s)\downarrow + 4NH_4Cl(aq) \qquad (5)$$

As shown above equation, ammonium chloride is consumed to extract calcium(Eq. 4), it is recovered in carbonation step(Eq. 5). As such possibility of reuse ammonium salts are shown that indirect carbonation can become eco-friendly and economical way using that.

Sun et al. (2011) extracted calcium from slag using ammonium chloride and then, they conducted carbonation by adjusting pH of filtrate up to pH 9 using ammonia solution. The carbonation efficiency was increased as the temperature was higher, but carbon dioxide pressure had little effect. In this results, carbonation efficiency was high and they recovered high purity of carbonate(about 96 wt%). Based on the recovered solid, it could be stored 138kg CO_2/ton slag and if it was included dissolved $Mg(HCO_3)_2$, it could be stored maximum 211kg CO_2/ton slag.

1.3.2 Cement wastes

Cement wastes include cement kiln dust(CKD) generated cement manufacturing process, and waste cement or waste concrete generated after crushing. These have common to generate cement industrial but, there are difference of carbon dioxide storage through mineral carbonation because it is different to particle size, form of calcium compound according to waste type. CKD and waste cement are more economical than slag and waste concrete because these do not need pre-treatment like crushing. The research using cement waste was conducted in the United States, Brazil, Japan. Waste concrete and waste cement were mainly used as raw materials, and there was study using CKD.

1.3.2.1 Direct carbonation

There was study that conducted direct carbonation using CKD at ambient temperature, pressure during 2~12 days by batch type, column type, and obtained 70% of carbonation efficiency(Huntzinger et al., 2009a; Huntzinger & Eatmon, 2009b). CKD is a very suitable for mineral carbonation because CKD has a lot of calcium oxide and their particle size is fine. Huntzinger et al. (2009a), Huntzinger and Eatmon (2009b) obtained a high carbonation efficiency through previously mentioned two kinds of research without consumption of energy at room temperature and atmospheric pressure. However, it is difficult to apply industrial site because reaction time was too long at 2 days or 12 days.

Teramura et al. (2000) conducted direct carbonation using waste concrete. They mixed waste concrete powder with water(water content 50%), and then tried to make building materials(brick) by reacting slurry with carbon dioxide at 0.4MPa pressure. As a results, carbonation reaction was completed within 1 hour, the efficiency was about 96%.

1.3.2.2 Indirect carbonation

Acid and ammonium salts was mainly used as a solvents like indirect carbonation of slag. The base was used to adjust pH after calcium extraction reaction using acid.

Kunzler et al. (2011) conducted indirect carbonation using hydrochloric acid and waste concrete. Calcium concentration in filtrate was decreased up to 99% when the filtrate was carbonated after adjusting of pH about 12 using base(sodium hydroxide, potassium hydroxide, lithium hydroxide). In the experiment using ammonium salts, they obtained high purity of calcium carbonate by extracting calcium selectively, and the carbonation efficiency was very high.

1.3.3 Fly ash

Fly ash stands for ash generated after combustion of coal in coal-fired power plant. And it can be classified fly ash, bottom ash according to occurrence location. They have particle size average 20~30㎛, and composed of silica more than 50%(Korean Coal Ash Recycling Association, 2015). Fly ash is being recycled in concrete remicon admixture, fertilizers and cement clinker. Although mineral carbonation research using fly ash was conducted by a new recycling method, carbon dioxide storage was not so much compared to other industrial waste because calcium and magnesium contents in fly ash are relatively few. To improve efficiency, various studies were conducted in United States, Australia, France by method of direct carbonation.

1.3.3.1 Direct carbonation

Several researchers looked for the effect of solid to liquid ratio and carbon dioxide pressure on carbonation efficiency and carbonation rate. For example, Ukwattage et al. (2013) obtained the highest carbonation efficiency in direct carbonation when liquid to solid ratio was 0.2. They explained that it was important to decide appropriate liquid to solid ratio because it was difficult to diffuse carbon dioxide on surface of solid by blocking pores of solid if a large excess of water is added although water could dissolve calcium from raw materials and produced calcium hydroxide. Meanwhile, Montes-Hernandez et al. (2009) was conducted direct carbonation using fly ash in various conditions such as carbon dioxide pressure, temperature, solid to liquid ratio but, that conditions did not affect the carbonation efficiency.

Soong et al. (2006) carried out direct and indirect carbonation using fly ash and brine that has high concentration of calcium and magnesium. The solid weight was increased 21.9g/L through direct carbonation, and it was composed to 30% of calcium carbonate. Through indirect carbonation, the solid was recovered about 29.63g/L, it was composed to 90% of calcium carbonate and 9% sodium chloride. They calculated carbonation efficiency using solid weight because they determined that the increasing solid weight after carbonation was due to carbon dioxide. In carbonation reaction, calcium, magnesium concentration and pH are important factors. Therefore, carbonation efficiency can be increased to conduct carbonation if brine that has high concentration of calcium, magnesium will be mixed with alkali industrial waste that have high pH.

1.3.3.2 Indirect carbonation

Recently, there was a study that stored carbon dioxide using acetic acid and coal ash containing calcium oxide(29.7%), magnesium oxide(25.5%) through indirect carbonation(Sun et al., 2012). Calcium and magnesium were extracted by mixing acetic acid with coal ash, and then the filtrate was carbonated in the pressure vessel. As a results, carbon dioxide stored approximately 123kg CO_2/ton coal ash at 60° C, 10bar during 1 hour in addition, carbon dioxide was stored maximum 264kg CO_2/ton coal ash considering $Mg(HCO_3)_2$ in solution. That was considerable carbon storage compared to other studies using fly ash.

1.3.4 Others

The researches to store carbon dioxide have been conducted using other alkali industrial waste except for slag, cement waste, fly ash that used as raw materials meantimes.

Perez-lopez et al. (2008) stored 218kg CO_2/ton waste a way of direct carbonation using by-product produced in the paper making process at 30° C, 30bar during 48 hours. It was high corresponding to carbonation efficiency of 84.5%, and it was result of storing significant amount of carbon dioxide compared to the other industrial waste.

Yadave et al. (2010) conducted direct carbonation using 50㎛ or less red mud produced aluminium smelting process at room temperature, 3.5bar, and they stored maximum 53kg CO_2/ton red mud. At this time, red mud was mixed with sodium hydroxide solution in solid to liquid ratio of 0.2~0.6 before injection of carbon dioxide. In that study, carbon storage was relatively low because calcium and magnesium content was low at 3%, pH of red mud was low and calcium was presence of complex form.

Gunning et al. (2010) conducted direct carbonation using 250㎛ or less of alkali industrial waste produced cement, metal, paper and energy industry. They made a slurry mixing by-products with water, and then the slurry was carbonated in pressure vessel maintained carbon dioxide pressure at 2bar during 72 hours. As a results, carbonation efficiency was high at by-products containing a lot of calcium such as paper and cement waste. However, carbonation efficiency was low in bauxite and medical incineration ash although these was contained calcium about 20%. Based on this results, they concluded that the form of calcium can determine carbonation efficiency rather than calcium content. In other words, carbonation could be generated well when calcium presented in the form of calcium oxide or calcium hydroxide in industrial waste.

Mayoral et al. (2013) conducted direct carbonation using fly ash and bottom ash produced after combustion of lignite and waste. They performed in conditions of various pH, temperature, reaction time, liquid to solid ratio, and they examined the effect of sodium chloride and EDTA on carbonation. When the sodium chloride was injected, the carbonation efficiency did not change. However, when the EDTA was injected, the carbonation efficiency was decreased because EDTA could make calcium complex and calcium could not precipitate as calcium carbonate. As a results, when the sodium chloride and EDTA was not added, maximum 70.8kg CO_2/ton waste could be stored.

Azdarpour et al. (2014) conducted direct carbonation using red gypsum generated the process of manufacturing titanium oxide. Red gypsum has high content of calcium oxide(32.2%) and iron oxide(28.9%). The red gypsum, crushed 500㎛ or less, was mixed with 1M ammonia solution in high pressure vessel and it was carbonated in various conditions such as temperature, pressure. The particle size was smaller and carbon dioxide pressure was higher, the carbonation efficiency was increased. Also, carbonation efficiency was higher to increase temperature from 25° C to 200° C, however the efficiency was decreased at 200° C or more.

Li et al. (2007) conducted direct carbonation using municipal solid waste incineration ash. They carried out experiment by adjusting temperature(21~91° C) and liquid to solid ratio(0.1~0.8) to find effect of temperature and liquid to solid ratio on carbonation efficiency. As a results, carbonation efficiency was not changed although the higher temperature was, the faster reaction rate was. And the efficiency was highest when liquid to solid ratio was 0.3. As a results, 10% of carbon dioxide was stored at 21° C and 0.3 liquid to solid ratio.

1.4 Domestic research trends

1.4.1 Slag

Slag was most used in mineral carbonation researches of overseas, and it mainly used in indirect carbonation. The emissions of slag was reached 20,359,000 tons annually(by 2011), that has been increased every year according to the statistics of Korean Iron and Steel Association(Korean Iron & Steel Association, 2015). Most of slag has been recycled to raw materials of cement and aggregates for road. The researches in domestic using slag are as following.

There was study that used water as a weak solvents or recovered iron in slag prior to calcium extraction to obtain high purity of calcium carbonate through indirect carbonation.

Kim et al. (2009a) used slag that crushed and recovered iron using magnetic separator in mineral carbonation. They stored carbon dioxide after 100% of calcium was extracted by adjusting acetic acid concentration. Also, Kim et al. (2009b) extracted selectively calcium in steelmaking slag using water. They conducted carbonation to inject carbon dioxide in calcium filtrate of a strong base state, and recovered 99.9% purity of calcium carbonate.

There was study tried to indirect carbonation using various solvents. Baek et al. (2010) extracted calcium from slag or calcium oxide dust using sodium trimetaphosphate, sodium hexametaphosphate, polycarboxylic acid sodium, polycarboxylic acid ammonium, formic acid, succinic acid, sucrose fatty acid ester, sodium citrate, ammonium citrate, ammonium acetate as a solvents. And they could recover high purity of calcium carbonate through carbonation.

Also, Mun and Cho (2013) used hydrochloric acid, acetic acid, oxalic acid, citric acid and EDTA as a solvents to extract calcium from blast furnace slag. When acid with EDTA were used as a solvents the calcium extraction efficiency was higher than when acid and EDTA used as a solvents respectively, however it was not affected in carbonation. It was considered that the carbonation did not occur well because EDTA could extract efficiently calcium in slag, but it could create a strong bond with calcium.

Chung et al. (2013) conducted indirect carbonation by mixing steelmaking slag with acetic acid, sodium acetate, hydrochloric acid. They said that pH of calcium filtrate is suitable in the range of 3~5 and they carried out carbonation without additional pH adjustment because precipitation could be produced by adjusting pH. The 66% of initial calcium concentration was precipitated and recovered calcium carbonate had 99% purity.

Song et al. (2014) made magnesium hydroxide by injecting sodium hydroxide in the filtrate after they extracted magnesium from ferronickel slag using sulfuric acid. And then, carbon dioxide was pressurized in magnesium hydroxide suspension, and magnesium carbonate was recovered.

1.4.2 Cement wastes

Construction wastes in the country have been generated about 183,351 tons a day(by 2009), which is generated 65% by waste concrete(Ministry of Environment, 2010). According to statistics, emissions of cement wastes like waster concrete were expected to increase continuously. The research of mineral carbonation using cement wastes is as follows.

There was result that conducted indirect carbonation using waste cement and various ammonium salts(ammonium chloride, ammonium acetate, ammonium sulfate, ammonium nitrate) as a solvents(Jo et al., 2014). The 70% of calcium was extracted and calcium carbonate was recovered 98% or more of purity after carbonation. Finally, carbonation efficiency was higher in order of ammonium nitrate, ammonium acetate, ammonium chloride, ammonium sulfate. The carbon storage was maximum 180kg CO_2/ton waste.

Jo et al. (2012a) conducted indirect carbonation using portland cement, waste concrete, calcium oxide with ammonium chloride, acetic acid, hydrochloric acid as a solvents and then, they compared to each efficiency. As a results, carbonation efficiency was about 5% using filtrate extracted as acetic acid, hydrochloric acid, but the efficiency was maximum 90% when ammonium chloride was used as a solvents and it could be recovered high purity of calcium carbonate. The carbonation efficiency was higher in order of calcium oxide, portland cement and waste concrete. The more simple form of calcium was, the higher extraction and carbonation efficiency were.

Jo et al. (2012b) also, examined effect of salinity on carbonation reaction using portland cement. Calcium was extracted from portland cement by adjusting concentration of sodium chloride solution and then, carbon dioxide was injected in that slurry. The result of extraction, calcium was more extracted using sodium chloride than pure water. Also, carbonation efficiency was maximum 62.9% using sodium chloride as compared that efficiency was maximum 44.5% using pure water.

You et al. (2012) made as a fine powder state to crush waste concrete and then conducted a two following methods.

Dry carbonation: To pressurize carbon dioxide by adjusting water content at 15~20%

Wet carbonation: To inject carbon dioxide by adjusting water content at 10~50 times of raw materials

They can stored carbon dioxide using dry and wet carbonation method maximum 14%, 18% respectively.

Kim and Park (2014) conducted indirect carbonation using CKD with ammonium chloride, ammonium acetate as a solvents. They determined optimum calcium extraction conditions to carry out extraction experiment in conditions of solvents concentration, solid to liquid ratio, reaction time and temperature. When ammonium chloride was used a solvent, carbon storage was maximum 327kg CO_2/ton CKD and recovered high purity of calcium carbonate.

1.4.3 Fly ash

The study storing carbon dioxide was performed using fly ash and organic wastewater enhancers such as livestock wastewater, food waste leachate, landfill leachate(Choy et al., 2012). First, fly ash was mixed with organic wastewater enhancers after these were purified using liquid reducing agent and reduction catalyst and then, carbon dioxide was stored 22.6%.

Also, Jo et al. (2012) extracted calcium from fly ash using pure water and tap water then, they stored carbon dioxide by injecting in filtrate or slurry. As a results, carbon dioxide was stored maximum 8kg CO_2/ton fly ash at room temperature and atmospheric pressure.

1.4.4 Others

Lee et al. (2012) conducted carbonation using flue gas desulfurization gypsum generated from the thermoelectric power plant at room temperature and atmospheric pressure. The result of experiments, carbonation was completed approximately 95% within 10 minutes, recovered calcium carbonate was purity of 90% or more. At that time, the purity of calcium carbonate was increased when excess ammonia solution was added.

Also, Ahn et al. (2012) made a slurry by mixing water with municipal waste incineration bottom ash 150㎛ or less and then, they injected carbon dioxide. The carbon dioxide was stored about 16%.

Chapter 2. Indirect carbonation using various solvents

Natural minerals such as wollastonite, serpentine, olivine and alkali industrial waste like fly ash, slag cement waste are contained a large amount of calcium and magnesium(Jo et al., 2012). Therefore, these are suitable raw materials for mineral carbonation because they appear a strong alkalinity by reacting with water. However, it is difficult to put to practical use mineral carbonation using natural minerals due to economics and environmental problems. For that reason, the research which is carbon sequestration using industrial waste has been mainly conducted.

Paper sludge ash(PSA), one of the alkali industrial waste, is generated through paper making precess. It is also suitable for mineral carbonation because it is contained a large amount of calcium rather than other wastes by using chemicals including calcium compound to improve whiteness of paper and it has a fine particle size(Gunning et al., 2010). In the meantime, many researchers have used slag as a raw material for mineral carbonation. However, pre-treatment such as crushing is required because particle size of initial slag is large, on the other hands, PSA is not required pre-treatment because its particle size is very fine. For this reason, in this study, carbon sequestration research was conducted using PSA through indirect carbonation.

The main factors in indirect carbonation are pH of filtrate and calcium extraction efficiency. Among them, the pH is important factor that determines the amount of CO_3^{2-}. And carbon dioxide is presented CO_3^{2-} in solution when the pH of solution is about 9 or more(Fig. 2).

As a results, when the pH of calcium filtrate is higher than pH 9, carbon dioxide can react with calcium and calcium carbonate can be produced. Thus, it can be conditions for increasing carbon storage to maintain the high pH during carbonation.

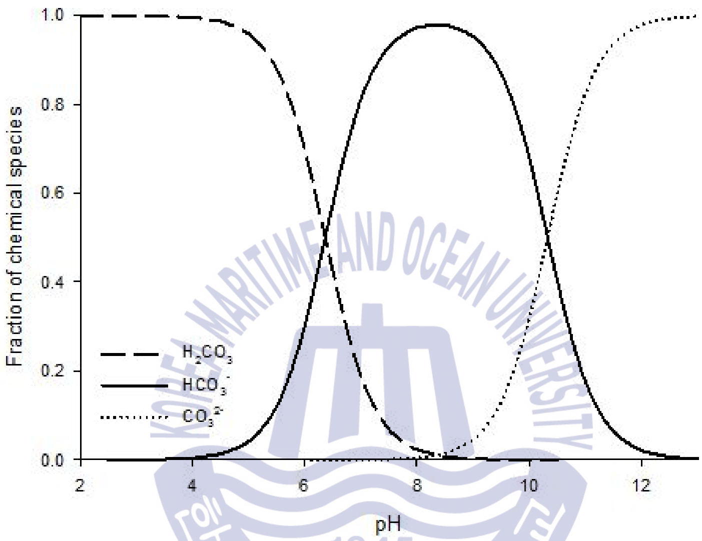


Fig. 2 Fraction of chemical species of CO_2

In this study, calcium in PSA was extracted using acids(acetic acid, hydrochloric acid), ammonium salts(ammonium chloride, ammonium acetate), others(sodium citrate, water) to sequestrate carbon dioxide through indirect carbonation and then, carbon dioxide was stored in that calcium filtrate. However, the solid was not generated or carbon storage was low in some solvents, we intended to increase carbon dioxide storage through additional treatment. Therefore, pH was adjusted highly by injecting base such as sodium hydroxide, ammonia solution in calcium filtrate prepared by reacting PSA with acid and ammonium salts. And carbon dioxide was stored by controling carbonation time to prevent dissolution of produced carbonate solid when PSA was reacted with other solvents(Fig. 3).

Finally in this study, carbon dioxide was stored through indirect carbonation in conditions requiring a low energy(room temperature, atmospheric pressure) using PSA and various solvents such as acids, ammonium salts, others. In addition, a large amount of carbon dioxide was efficiently stored through alkali treatment and time control.

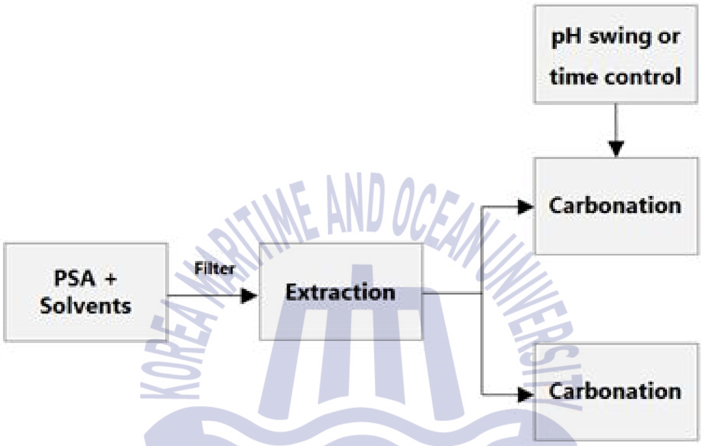


Fig. 3 Process of carbonation in this study

2.1 Materials and Methods

2.1.1 Materials

PSA, used in this study, was supplied in G company, Republic of Korea, and then, it was mixed equally. The reactor included agitator, carbon dioxide inlet, carbon dioxide outlet and sampling part was made in the 1L volume of pyrex to store carbon dioxide efficiently in atmospheric pressure. The solvents was used to extract calcium in PSA such as hydrochloric acid(Merk, 37%), acetic acid(Junsei, 99.7%), ammonium chloride(Junsei, 98.5%), ammonium acetate(Junsei, 95.0%), sodium citrate(Sigma Aldrich, 98.0%), pure water(Millipore, Milli-Q Academic A10) and base was used to adjust filtrate pH such as sodium hydroxide(Daejung, 50.0%), ammonia solution(Junsei, 28.0-30.0%). And 99% purity of carbon dioxide gas was used in carbonation. Finally, calcium concentration was measured using AAS(AA analysis 200, Perkin Elmer) and pH was measured using pH meter(Orion star 211, Thermo).

2.1.2 Methods

The extraction experiment was conducted to find optimum extraction conditions by reacting PSA with various solvents. And then, carbonation experiment was conducted using calcium filtrate in conditions derived from the extraction experiment. Detailed method is as follows.

2.1.2.1 Analysis of PSA

To analyze PSA composition, the X-ray diffraction(X'Pert-MPD system, Philips) and X-ray fluorescence analyzer(XRF-1700, Shimadzu) was used.

2.1.2.2 Extraction experiment

Extraction experiment was conducted according to solvents concentration and solid to liquid ratio. The solvents such as hydrochloric acid, acetic acid, ammonium chloride, ammonium acetate, sodium citrate was used in this experiment in the range of 0.1, 0.3, 0.5, 0.7, 1.0, 1.5M solvent concentration and 1, 2, 5g/50mL solid to liquid ratio. PSA and solvent was mixed depending on the each conditions at 25° C, 250rpm during 30 minutes then the mixture was filtered using 0.45㎛ membrane filter and calcium concentration, the pH of filtrate was measured. Calcium extraction efficiency was determined by the following Eq. (6) based on the measured calcium concentration.

Calcium extraction efficiency (%) =

$$\frac{C_{Ca}}{C_{CaO} \times W_i \times V_i \times 10^3} \times 100 \qquad (6)$$

C_{Ca} : Measured calcium concentration (mg/L)

C_{CaO} : CaO content of PSA (fraction)

W_i : Initial PSA weight (g)

V_i : Initial solution volume (L)

2.1.2.3 Carbonation experiment using calcium filtrate – extracted with acid

The carbonation experiment was conducted using 1L calcium filtrate manufactured at 0.7M solvent concentration and 2g/50mL solid to liquid ratio depending on the extraction experiment using hydrochloric acid and acetic acid. In this case, calcium extraction efficiency was relatively high however, carbon dioxide was difficult to exist in the form of CO_3^{2-}. because pH was low below 6. Therefore, carbon dioxide was stored by injecting sodium hydroxide to increase filtrate pH above 13. Finally, the carbon storage was compared to each case(with alkali treatment and without alkali treatment).

Sodium hydroxide was injected 20% excess of calcium concentration for convert the calcium in filtrate to calcium hydroxide. The experiment was carried out under the same conditions at 1atm, 25° C, stirring speed 250rpm, carbon dioxide flow rate 0.1L/min, during 30 minutes. And the sample was collected to measure calcium concentration and pH during carbonation at intervals of 0, 2, 4, 6, 8, 10, 12, 14, 20, 25, 30 minutes.

2.1.2.4 Carbonation experiment using calcium filtrate – extracted with ammonium salts

The carbonation experiment was conducted using 1L calcium filtrate manufactured at 0.3M solvent concentration and 1g/50mL solid to liquid ratio depending on the extraction experiment using ammonium chloride and ammonium acetate. In that case, the calcium extraction efficiency was lower than extraction using acid, but the pH was high as 10. And ammonia solution, the same kind of solvents(ammonium chloride, ammonium acetate), was injected for alkali treatment by considering reuse of waste solvent because it is possible to restore that ammonium salts used in extraction and carbonation.

The experiment was carried out with alkali treatment solution and without alkali treatment solution under the same conditions at 1atm, 25° C, stirring speed 250rpm, carbon dioxide flow rate 0.1L/min, during 30 minutes. However, the concentration of ammonia solution was determined 5 times of the remained calcium concentration when carbonation was conducted without alkali treatment during 30 minutes because ammonia could be easily volatilized into the air. And the sample was collected to measure calcium concentration and pH during carbonation at intervals of 0, 2, 4, 6, 8, 10, 12, 14, 20, 25, 30 minutes.

2.1.2.5 Carbonation experiment using calcium filtrate – extracted with other solvents

The carbonation experiment was conducted using 1L calcium filtrate manufactured at 0.3M solvent concentration and 1g/50mL solid to liquid ratio depending on the extraction experiment using sodium citrate. The carbonation experiment was carried out at 1atm, 25° C, stirring speed

250rpm, carbon dioxide flow rate 0.1L/min, during 30 minutes. And the sample was collected to measure calcium concentration and pH during carbonation at intervals of 0, 2, 4, 6, 8, 10, 12, 14, 20, 25, 30 minutes. The pH of filtrate was very high as 13, but produced solid was dissolved during carbonation. Therefore, carbonation time was controled based on the time to increase calcium concentration. Finally, solid could be recovered when time was controled 10 minuets and 2 minuets using sodium citrate and water, respectively.

2.1.2.6 Analysis of recovered solid

Recovered solid after carbonation was filtered using 0.45㎛ membrane filter paper and it was dried at 105° C during 12 hours. Then, solid weight was measured also, it was analyzed components and purity using XRD, XRF. Finally, carbon storage was calculated by the following Eq. (7).

Carbon storage (kg CO_2/ton PSA) =

$$\frac{W_f}{W_i} \times \frac{MW_{CO_2}}{MW_{CaCO_3}} \times P \times 10^3 \qquad (7)$$

W_i : Initial PSA weight (g)

W_f : Final solid weight (g)

MW_{CO2} : Molecular weight of CO_2 (g/mol)

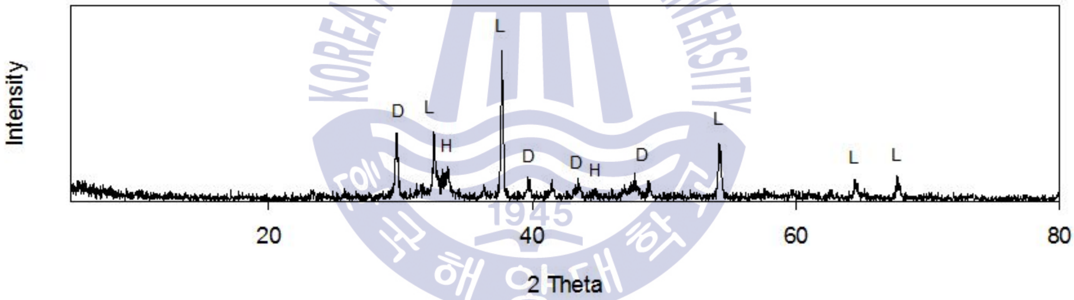
MW_{CaCO3} : Molecular weight of $CaCO_3$ (g/mol)

P : Purity of recovered solid

2.2 Results and Discussion

2.2.1 Analysis of PSA

PSA was contained 67% of calcium and it was contained in order of silicon, aluminium, magnesium(Table 4). PSA was contained calcium component very high because a reagents containing calcium were used in paper making process to improve paper quality. The calcium in PSA was primarily composed of Lime(CaO), Dolomite($Ca_{0.94}Mg_{0.06}CO_3$), Hibschite($Al_2Ca_3H_{3.36}O_{12}Si_{2.16}$)(Fig. 4). Also, complex of calcium component like Hibschite, Dolomite was contained relatively high proportion because of a number of used reagents.



L: Lime(CaO), D: Dolomite($Ca_{0.94}Mg_{0.06}CO_3$), H: Hibschite($Al_2Ca_3H_{3.36}O_{12}Si_{2.16}$)

Fig. 4 Result of XRD analysis

Table 4 Result of XRF analysis

Components	CaO	SiO_2	Al_2O_3	MgO	SO_3	Fe_2O_3	P_2O_5
Contents (%)	67.21	15.02	6.62	4.37	2.72	1.77	0.53

2.2.2 Extraction experiment

Generally, the calcium extraction efficiency was decreased as solid to liquid ratio was higher in all solvent. And calcium extraction efficiency was increased as solvent concentration was higher. When hydrochloric acid and acetic acid was used in extraction, the calcium extraction efficiency was 54.1% and 50.9%, respectively at 0.7M solvent concentration, 2g/50mL solid to liquid ratio. And filtrate pH was 3.9, 5.4, respectively(Fig. 5). In case of using ammonium chloride, ammonium acetate, the calcium extraction efficiency was 30.8%, 30.2%, respectively at 0.3M solvent concentration and 1g/50mL solid to liquid ratio. And filtrate pH was 9.91, 10.2, respectively(Fig. 5). And calcium was extracted about 28% in condition of 0.3M solvent concentration and 1g/50mL solid to liquid ratio using sodium citrate as a solvent. The filtrate pH was high as 13. Although solvent concentration was increased, calcium extraction efficiency was little changed.

After calcium was extracted, the remaining solid was mainly contained calcium carbonate. As a results, calcium carbonate, contained initial PSA in the form of Dolomite, was remained and other components were reacted such as Lime, Hibschite with solvent compared to initial PSA. The case of using ammonium salts and sodium citrate, calcium extraction efficiency was lower than using acid because these could be reacted with simple materials like Lime. On the other hands, in the case of using acid as a solvent, calcium extraction efficiency was the highest by dissolving complex materials because of their low pH. In conclusion, when acid was used in calcium extraction, the condition of 0.7M solvent concentration and 2g/50mL solid to liquid ratio was selected and when ammonium salts, sodium citrate was used in calcium extraction, the condition of 0.3M solvent concentration and 1g/50mL solid to liquid ratio was selected, then carbonation experiment was conducted.

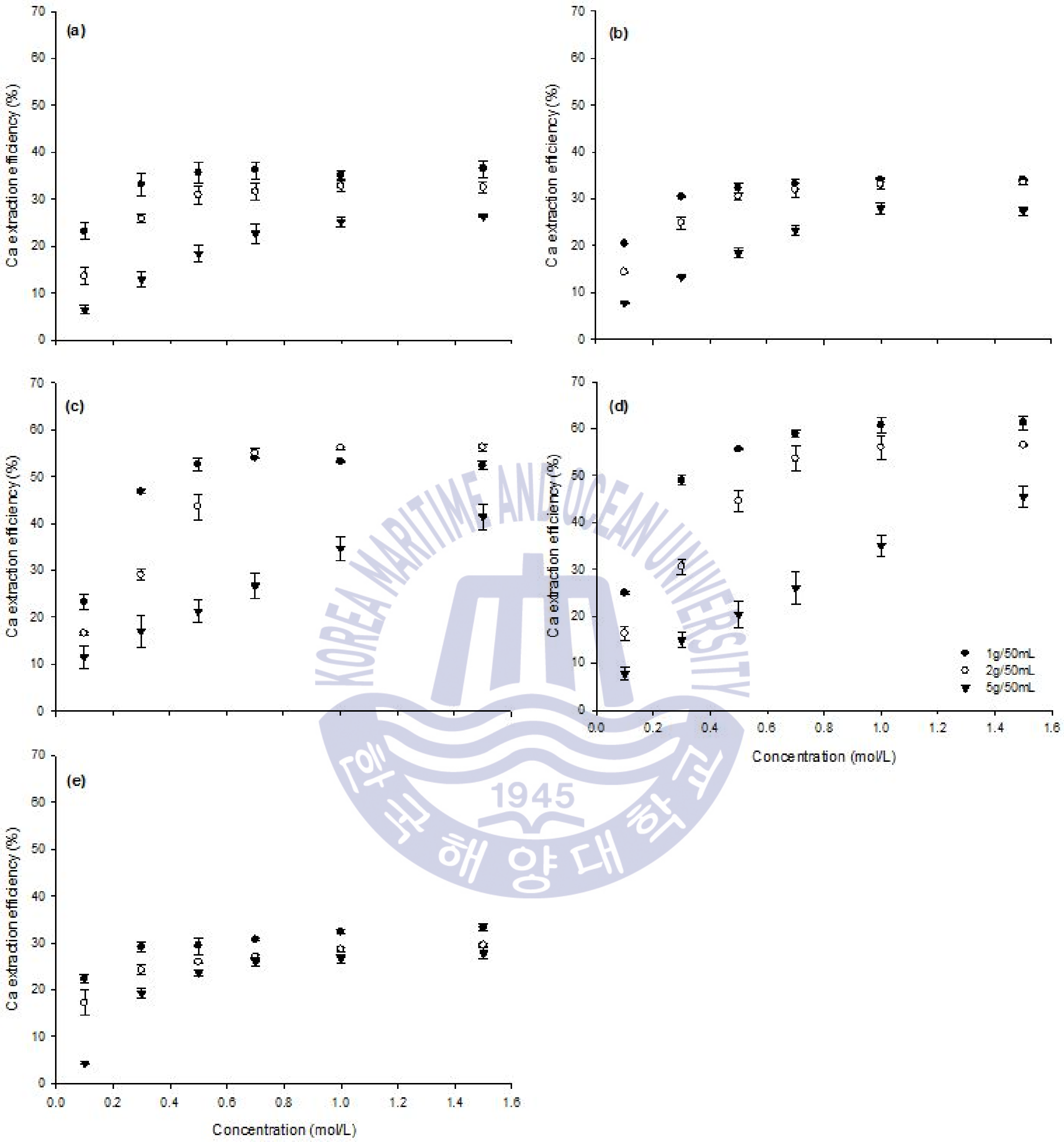


Fig. 5 Calcium extraction efficiency according to solvent concentration using (a) ammonium chloride (b) ammonium acetate (c) hydrochloric acid (d) acetic acid (e) sodium citrate

2.2.3 Carbonation experiment using calcium filtrate – extracted with acid

Calcium filtrate, prepared using hydrochloric acid, acetic acid had high calcium extraction efficiency but, carbonation reaction was not occur because their of low pH. As a result, after carbonation calcium concentration and pH were not changed also, solid was not produced.

On the other hand, the alkali suspension which was mixed calcium filtrate prepared using hydrochloric acid, acetic acid with sodium hydroxide had high pH as over 13. Before injecting a sodium hydroxide, the initial calcium concentration was 13,124mg/L, 13,052mg/L and then, the calcium was converted $Ca(OH)_2$ by injecting sodium hydroxide and their concentration was 1,300mg/L, 2,055mg/L, after carbonation reaction was started the calcium concentration was decreased at 117mg/L, 170mg/L(filtrate prepared using hydrochloric acid, acetic acid, respectively). During the carbonation, calcium concentration was maintained about 100mg/L because calcium presented in the form of $Ca(OH)_2$ was directly reacted with carbon dioxide(Fig. 5). Finally, after completion of the reaction, 32.54g, 32.73g of white solid was recovered in filtrate using hydrochloric acid, acetic acid, respectively.

In this case, the carbonation reaction is performed as follows: (Eq. 8,9)

$$Ca^{2+} + 2OH^{-} \rightarrow Ca(OH)_2(s) \qquad K_{sp} = 5.5 \times 10^{-6} \qquad (8)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3(s) + H_2O \qquad (9)$$

The solubility product(K_{sp}) of $CaCO_3$ is 3.3×10^{-9}, which is lower than solubility product of $Ca(OH)_2$ about 10^3 times therefore, reaction could be performed to produce calcium carbonate. As the carbonation reaction was proceeded, calcium which was presented in $Ca(OH)_2$ was precipitated $CaCO_3$ by reacting with carbon dioxide. And the pH could be maintained because OH^- ion injected in excess was reacted a neutralization with H^+ ion generated by dissolving carbon dioxide. Therefore, injected carbon dioxide could be presented in the form of CO_3^{2-} while pH was maintained highly as a result, solid could be produced by reacting carbon dioxide with calcium ion. Carbonation was carried out during 25 minutes maintained high pH, carbonation was completed after 25 minutes because OH^- ion had exhausted(Fig. 6). As a result, without alkali treatment, carbon dioxide could not be stored because of low pH. And with alkali treatment, injected sodium hydroxide in filtrate white solid could be recovered maximum 32.73g.

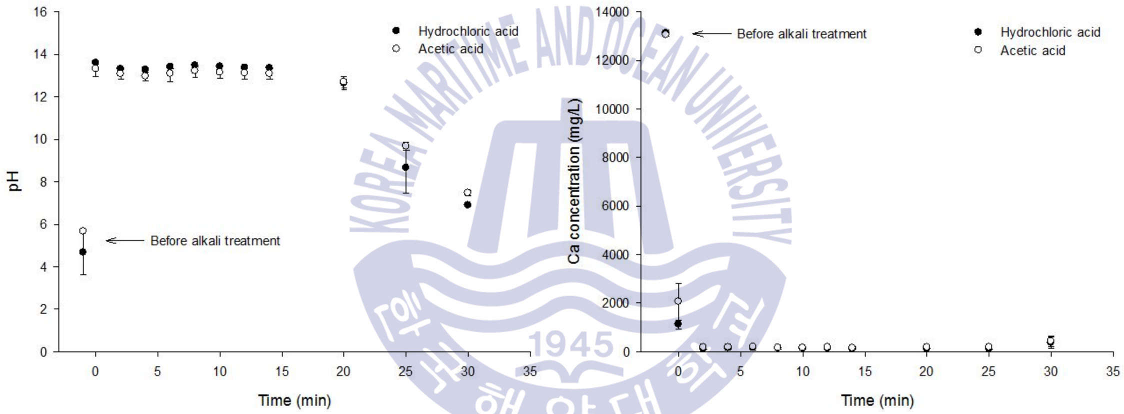


Fig. 6 Change of pH and calcium concentration using acid with sodium hydroxide

2.2.4 Carbonation experiment using calcium filtrate - extracted with ammonium salts

Initial pH of filtrate was relatively high as 10 because of ammonia ion, generated by reacting ammonium salts with PSA. As the carbonation reaction was proceeded, pH was decreased gradually by buffering capacity of ammonia(Fig. 7). After carbon dioxide was injected, pH of solution was decreased at 8.3 within 8-10 minutes and pH was maintained constant at 7. At the same time, calcium concentration was consistently decreased from 4,100mg/L to 400-600mg/L after 10 minutes. And calcium concentration was increased about 200mg/L by dissolving solid after 30 minutes.

After pH was decreased carbon dioxide could not react with calcium because they presented in the form of HCO_3^- in solution. Thus, carbonation reaction was hardly proceeded after 10 minutes and calcium concentration was kept constant. Finally, 6.15g, 5.59g of solid was recovered when the filtrate using ammonium chloride, ammonium acetate was carbonated, respectively. The remained calcium concentration was 612.4mg/L, 866.1mg/L using ammonium chloride, ammonium acetate, respectively after carbonation was completed. According to results, a significant of calcium was remained, and carbon storage could be increased if that calcium would be reacted with carbon dioxide.

When carbonation was conducted using filtrate prepared by reacting PSA with ammonium salts, the solvent could be recovered in the following equation(Kodama et al., 2008) (Eq. 10,11)

$$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O \qquad (10)$$

$$CaCl_2 + 2NH_3 + H_2O + CO_2 \rightarrow CaCO_3(s) + 2NH_4Cl \qquad (11)$$

Therefore, ammonia solution, which was caused buffering effect and the same material with ammonium salts was injected in filtrate to react sufficiently calcium with carbon dioxide by increasing time that pH remains high. And experiment was conducted in the same method. When ammonia solution was injected, initial pH was slight increased as much as 0.2 however, pH was decreased at 8.3 within 15 minutes(Fig. 7). The pH decrease rate was slower than before. In addition, the final calcium concentration was 129mg/L, 185mg/L(using calcium filtrate by prepared

PSA with ammonium chloride, ammonium acetate, respectively). It was the reduced concentration than without alkali treatment.

It was expected that the time, pH remained high, was prolonged than previous experiment because ammonia concentration in solution was increased by injecting ammonia solution in filtrate. Carbon dioxide could be sufficiently reacted with calcium ion when the pH was maintained high. Finally, When ammonia solution was injected, 7.67g, 7.98g of solid was recovered using filtrate prepared by PSA with ammonium chloride, ammonium acetate, respectively. It was the increased amount of solid.

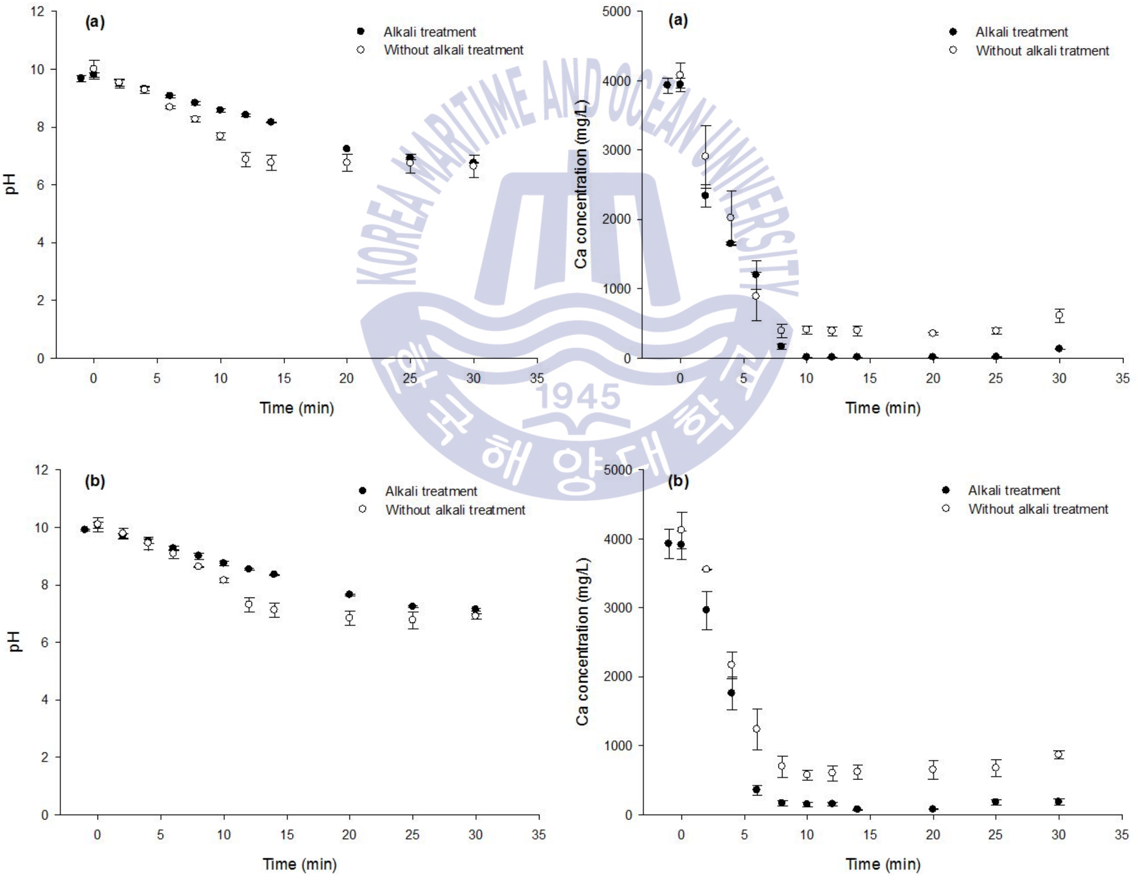


Fig. 7 Change of pH and calcium concentration using ammonium salts (a) ammonium chloride, (b) ammonium acetate

However, it was possible to lose injected ammonia solution in the air because it had volatile. Ammonia solution would be able to effect on the carbonation efficiency if it is prevented to loss of ammonia solution by sealing the reactor. As a result, it was a positive effect on carbon storage to add a ammonia solution.

2.2.5 Carbonation experiment using calcium filtrate – extracted with other solvents

The calcium filtrate prepared using sodium citrate, water had a similarity that pH was high as 13 or more. And their calcium concentration was 4,238mg/L, 1,067.6mg/L, respectively. The carbonation was taken place due to high pH however, produced solid was dissolved as the pH was lower. For the end of carbonation, the calcium concentration was increased as much as initial concentration and carbon dioxide was hardly stored(Fig. 8). It was important to prevent dissolving the solid by controling carbonation reaction time rather than alkali treatment.

When the filtrate prepared using water was carbonated, the pH was decreased rapidly within 5 minutes because it did not have a buffering capacity to maintain a pH highly. Thereafter, produced solid was dissolved within a short time and solid was not recovered after carbonation. In contrast, when the filtrate prepared using sodium citrate was carbonated, calcium concentration was little changed. After 8 minutes, calcium concentration was decreased. It was that the nucleation of calcium carbonate production rate was reduced due to citrate ion in solution(Tobler et al., 2015), the calcium concentration was little changed up to 6 minutes. And the calcium concentration was the lowest at 10 minutes, then it was increased. Final calcium concentration was similar to initial value, the solid was not recovered(Fig. 8).

The filtrate prepared using sodium citrate had a buffering capacity because base and calcium citrate was produced by reacting PSA with sodium citrate according to Eq. (12). Thereby, pH was decreased gradually and calcium carbonate was recovered as carbonation was proceeded(Eq. 13).

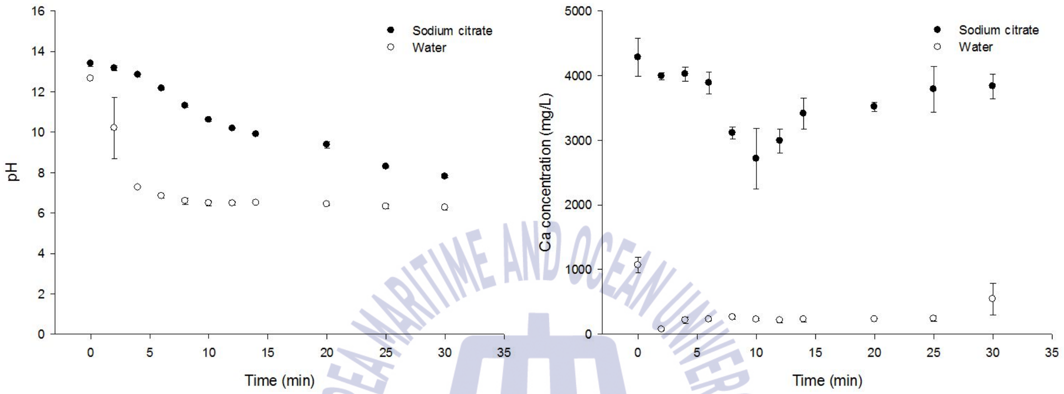


Fig. 8 Change of pH and calcium concentration during 30 minutes

$$3CaO + 2Na_3C_6H_5O_7 + 3H_2O \rightarrow Ca_3(C_6H_5O_7)_2 + 6NaOH \qquad (12)$$

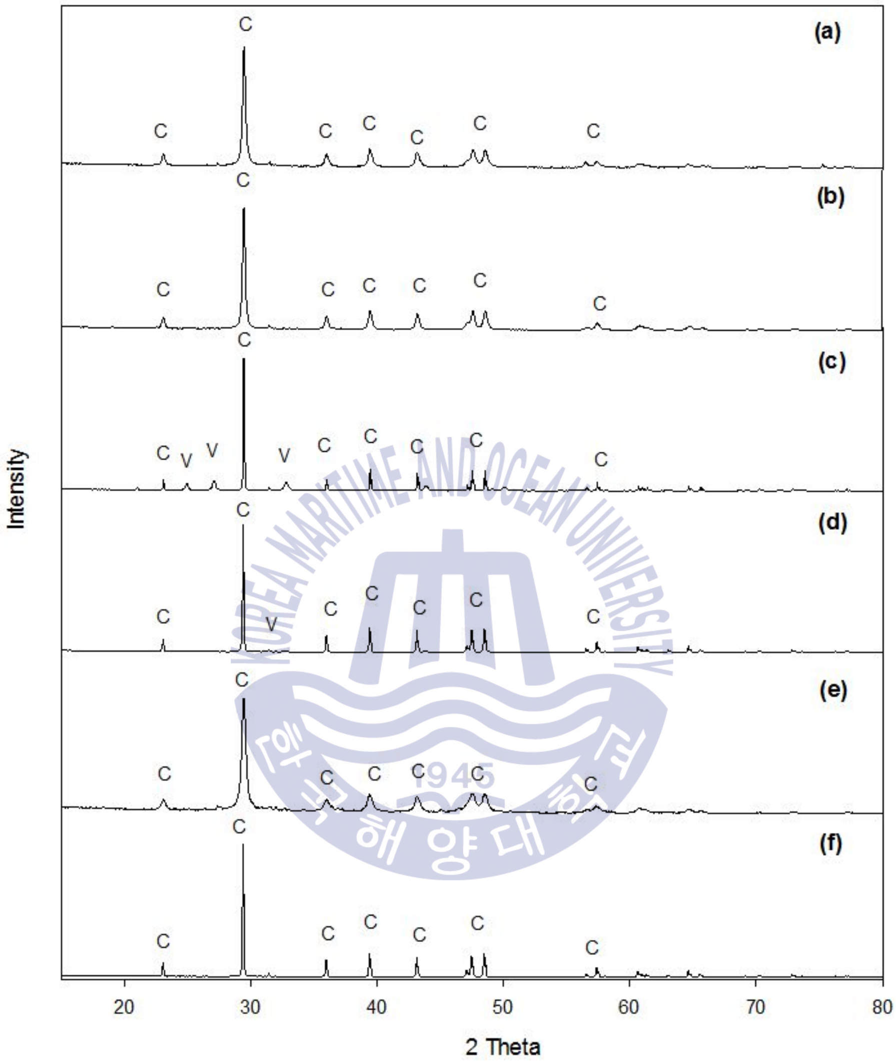
$$Ca_3(C_6H_5O_7)_2 + 6NaOH + 3CO_3^{2-} + 6H^+ \rightarrow 3CaCO_3(s) + 2Na_3C_6H_5O_7 + 6H_2O \qquad (13)$$

Westin and Rasmuson (2003) said that calcium precipitation reaction in the presence of citrate ion is preferably performed in the pH of 10–10.5. In low pH, carbon dioxide was presented in the form of HCO_3^- in that time, calcium could form a complex in combination with citrate ion because citrate ion was dominant than carbonate ion. Therefore, the calcium, precipitated in calcium carbonate, could be react with citrate. In this study, calcium concentration was increased based on carbonation reaction time at 10 minutes showed pH 10.6. In that reasons, carbonation reaction time was determined 10 minutes, 2 minutes using filtrate prepared by sodium citrate and water, respectively to prevent dissolving the solid and to maintain pH highly. As a consequence, 7.33g, 1.33g of solid could be recovered when the filtrate was carbonated using sodium citrate and water, respectively by controling carbonation time.

Sodium citrate was suitable solvent for the calcium extraction because the calcium extraction efficiency was relatively high and pH was very high. Also, it did not need additional alkali treatment because the filtrate using sodium citrate had buffering capacity. Thus, sodium citrate was very advantageous to the carbonation. However, citrate ion made a relatively strong bonding by reacting with calcium ion(Tobler et al., 2015). Accordingly, it is required to detailed study that carbonation reaction using sodium citrate as a solvent because it substantially affects to carbonation reaction or calcium carbonation yield by amount of citrate ion.

2.2.6 Analysis of recovered solid

It was analysis of recovered solid after carbonation(Fig. 9). When the filtrate prepared using hydrochloric acid, acetic acid was carbonated by injecting a sodium hydroxide, the recovered solid was calcium carbonate in the form of Calcite. The recovered solid through carbonation using filtrate prepared by ammonium salts with ammonia solution was calcium carbonate in the form of Calcite and Vaterite. In this result was consistent with Jo et al. (2014) study that calcium carbonate in the form of Vaterite could be produced at pH 8 or more in coexisting of ammonia ion. The recovered solid when sodium citrate was used as a solvent was calcium carbonate in the form of Calcite because citrate ion could inhibit the formation of Vaterite and Aragonite(Tobler et al., 2015). Also, in case of using water as a solvent, recovered solid was calcium carbonate in the form of Calcite because water was mainly reacted with calcium oxide in extraction step.



C: Calcite, V: Vaterite

Fig. 9 Results of XRD analysis recovered solid using (a) hydrochloric acid with Sodium hydroxide, (b) acetic acid with Sodium hydroxide, (c) ammonium chloride with ammonia solution, (d) ammonium acetate with ammonia solution, (e) sodium citrate with time control, (f) water with time control

To find out the purity of recovered solid, XRF analysis was conducted and the results were shown in Table 5. Except for using hydrochloric acid and sodium citrate, in most cases the purity of recovered solid was 90% or more. In particular, ammonium salts were known to extract calcium selectively(Sun et al., 2011). The results of analysis solid using ammonium salts as a solvent, purity was 99.8% or more. Ammonium salts had a favorable to recover high purity of calcium carbonate. Also, in case of using water as a solvent, purity of calcium carbonate was 99.5% because water mainly reacted with calcium oxide. On the other hand, purity of calcium carbonate recovered using acid and sodium citrate as a solvent was lower than using other solvent because of additionally injected base or other components extracted from PSA.

Table 5 Analysis of purity recovered solid after carbonation with pH swing or time control

	Hydrochloric acid	Acetic acid	Ammonium chloride	Ammonium acetate	Sodium citrate	Water
CaO	83.0	90.3	99.8	99.9	84.3	99.5
SiO_2	4.6	4.1	-	0.06	6.2	0.08
Na_2O	3.3	2.6	-	-	6.3	-
MgO	2.3	1.0	-	-	-	-
Al_2O_3	-	1.0	-	-	2.6	0.2

The result of storing carbon dioxide using various solvent, calcium extraction efficiency and carbon storage and efficiency were shown in Table 6. Calcium was extracted maximum 54.1% when PSA was reacted with hydrochloric acid.

Without additional treatment, except for ammonium salts carbon dioxide was not stored using other solvents. However, with additional treatment such as alkali treatment or carbonation time control carbon storage was increased in all solvents. And the most of recovered solid was high purity of calcium carbonate. Finally, in this study, carbon dioxide was stored maximum 324kg CO_2/ton PSA when acetic acid was used in extraction and additional treatment with sodium hydroxide.

Table 6 Calcium extraction efficiency and carbon dioxide storage according to solvent

Solvents	Ca extraction efficiency (%)	Without treatment		Additional treatment	
		Carbon storage (kg CO_2/tonPSA)	Carbon storage (%)	Carbon storage (kg CO_2/tonPSA)	Carbon storage (%)
Hydrochloric acid	54.1	-	-	297.0	56.5
Acetic acid	50.9	-	-	324.0	61.7
Ammonium chloride	30.8	135.3	25.7	168.4	32.0
Ammonium acetate	30.2	123	23.4	175.4	33.4
Sodium citrate	28.0	-	-	136.0	25.9
Water	11.0	-	-	29.1	5.5

2.3 Conclusion

In this study, carbon dioxide was stored through indirect carbonation using PSA with acid(hydrochloric acid, acetic acid), ammonium salts(ammonium chloride, ammonium acetate), other solvents(sodium citrate, water). Furthermore, it was conducted alkali treatment or controled carbonation time to improve the carbon storage. Finally, the results were obtained through in this study as follows.

In extraction reaction, acid which was low pH could be extracted calcium from PSA than ammonium salts, sodium citrate because PSA was contained a large amount of complex materials such as Dolomite, Hibschite. In carbonation reaction, carbon storage efficiency was low or carbon dioxide was hardly stored without additional treatment. And a large amount of carbon dioxide was stored with additional treatment. Also, recovered solid was high purity of calcium carbonate 90% or more except for some impurities. As a result, carbon dioxide was stored maximum 61.7% through additional treatment.

It is considered to be advantageous for energy savings because carbon dioxide was stored at mild conditions including room temperature and atmospheric pressure. Also, it is showed the possibility to store carbon dioxide using PSA through in this study, it is can be used as a method to store carbon dioxide as well as to recycle waste. In particular, it is confirmed that the carbon storage is further increased by conducting additional treatment differently according to the characteristics of solvents to improve carbon storage. In addition, some solvents such as ammonium salts, sodium citrate have advantage to reuse of waste solvents produced after carbonation because they can be restored. Thus, it is required to more deeply study about solvent.

Finally, it is possible to establish single plant leading to paper making process – paper sludge ash capture – carbon dioxide storage – reuse of recovered calcium carbonate in paper making process as well as it contributes to reduce green house gas emissions and to improve economic efficiency if the recovered calcium carbonate will be reused in paper making process.

Chapter 3. Direct carbonation using sea water

Sea water has calcium and magnesium ion which can participated in the carbonation reaction, and their average concentration is 411mg/L, 1290mg/L, respectively(Leggett & RaO, 2015). Also, sea water has buffering capacity because it contains a lot of cation such as sodium, potassium and anions such as carbonate, bicarbonate. The concentration of components contained in sea water were shown in Table 7.

Table 7 Concentration of elements in sea water (Leggett & Rao, 2015)

Element	Concentration (mg/L)
Na	10,800
Mg	1,290
Ca	411
K	392

The study that stored to carbon dioxide using sea water was hardly conducted, most studies were carried out with brine rather than sea water. For example, Soong et al. (2004) was conducted carbonation experiment using brine contained a large amount of calcium, potassium, sodium, magnesium ion at various pH, carbon dioxide pressure, temperature conditions after pH of brine was adjusted using potassium hydroxide. When the pH of brine was increased at 11, they could recover solid, which was mixed 95% of $CaCO_3$ and 5% of Fe_2CO_3. They reported that pH was the greatest effect on carbon storage, and carbon dioxide pressure and temperature did not have a significant effect on carbon storage. Druckenmiller et al. (2005) was conducted carbonation experiment using three types of brine at various temperature, carbon dioxide pressure, pH conditions. They also reported pH was the greatest effect on carbon storage. Meanwhile, Soong et al. (2006) was carried out carbonation by mixing brine with fly ash to adjust pH. After carbonation, the solid weight was increased about 21.9g/L, it was composed of 30% of calcium carbonate. They calculated carbonation efficiency through increased solid weight because they determined it was due to storage of carbon dioxide. According to previous three studies using brine, calcium, magnesium concentration and pH were the most important factor to affect the carbonation efficiency(Kim & Kim, 2015).

In this study, carbonation experiment was conducted at various sea water content and reaction time to find optimum conditions in carbonation using PSA and sea water through direct carbonation. Also, PSA was mixed with sea water, ultrapure water, respectively and then, carbon storage was compared to conduct carbonation experiment according to the solvent in optimum conditions obtained previous experiment. Sea water has calcium and magnesium ion which can participated in the carbonation reaction, and it has buffering capacity. For that reason, it is expected to be favorable if sea water will be used in carbonation. In addition, carbon dioxide was stored by mixing PSA with sea water to increase pH of sea water and provide calcium and magnesium.

3.1 Materials and Methods

3.1.1 Analysis of sea water and PSA

PSA, used in this study, was supplied domestic G company and stored in desiccator. Sea water was sampled at Busan coast and then, filtered 1 ㎛ glass fiber filter paper. Calcium and magnesium concentration in sea water was measured using AAS(AA200, Perkim Elmer), pH of slurry during carbonation was measured using pH meter(Orion star 211, Thermo). Also, XRF(XRF-1700, Shimadzu), XRD(X'Pert-MPD System, Philips) were conducted to analyze components of PSA.

The calcium, magnesium contained in PSA would be finally converted in the form of carbonate by reacting with carbon dioxide. However, it was possible to already present carbonate in PSA prior to the carbonation, TGA(TGA-7, Perkin Elmer) analysis was conducted to measure calcium carbonate and magnesium carbonate in initial PSA.

3.1.2 Carbonation experiment

Carbonation experiment using PSA and sea water was carried out in continuous flow system. The schematic of experiment for carbonation was shown Fig. 10. For experiment the reactor was manufactured. Volume of reactor was 1L and it had pyrex material also, carbon dioxide inlet, outlet, agitator were placed at the top. And 99% of carbon dioxide was used in carbonation, flow regulator and flow meter were installed near the reactor to control carbon dioxide flow rate.

The carbonation in conditions of various sea water content and reaction time was conducted then, the optimum conditions were determined. Finally, the experiment that compared carbon storage using sea water with ultrapure water was conducted.

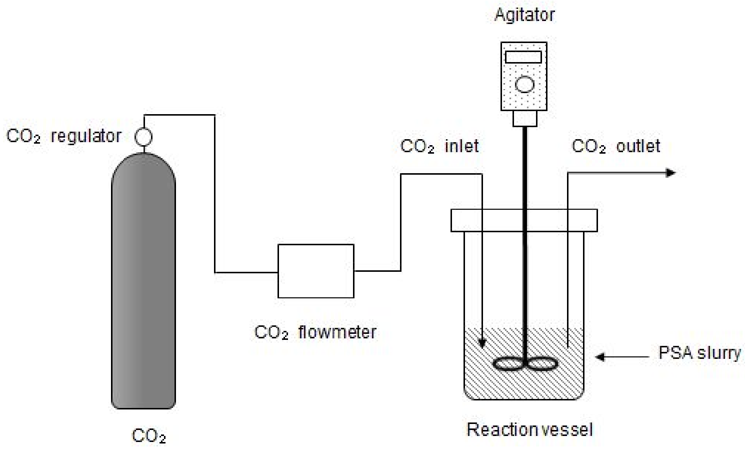


Fig. 10 Schematic of carbonation experiment

3.1.2.1 Sea water content determination

Volume of sea water was adjusted while fixing the amount of PSA to make a various conditions about sea water content. Slurry was made to mix 20g of PSA with a volume of sea water(40, 100, 200, 500, 1000mL) in vessel then, it was stirred at 250rpm during 5 minutes. Carbon dioxide was injected in slurry at 0.05L/min flow rate during 2 hours. After the carbonation was completed, slurry was filtered using 0.45 ㎛ membrane filter. Finally, the solid was dried at 105° C, 12 hours then, the weight was measured.

3.1.2.2 Reaction time determination

Carbonation reaction time was adjusted 10-300 minutes in order to determine optimum reaction time. Slurry was made to mix 20g of PSA with a volume of sea water 100mL in vessel then, it was stirred at 250rpm during 5 minutes. Carbon dioxide was injected in slurry at

0.05L/min flow rate during a constant time(10, 20, 30, 60, 120, 300 minutes). Later experiment methods was the same as “Sea water content determination” .

3.1.2.3 Carbonation experiment using sea water and ultrapure water

The carbonation was conducted using ultrapure water(Milli-Q Academic A10, Millipore) as a control in order to find effects of sea water on carbonation. Thus, the experiment was conducted in the same methods using two solvents(sea water, ultrapure water). Slurry was made to mix 20g of PSA with a volume of water 100mL in vessel then, it was stirred at 250rpm during 5 minutes. Carbon dioxide was injected in slurry at 0.05L/min flow rate during 2 hours. Later experiment methods was the same as “Sea water content determination” . The recovered solid was analyzed TGA to measure produced carbonate(calcium carbonate, magnesium carbonate) then, carbon storage was calculated using sea water, ultrapure water, respectively based on TGA analysis results. Also, components of solid was analyzed using XRD.

3.2 Results and Discussion

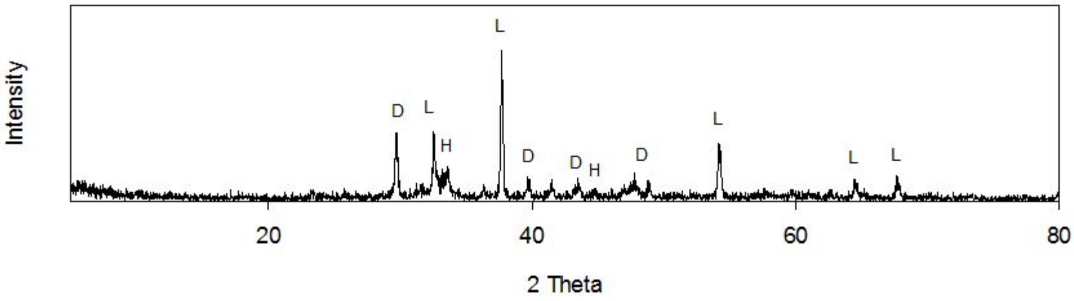
3.2.1 Analysis of sea water and PSA

The pH of sea water used in this experiment was 8.3, and calcium, magnesium concentration was 474mg/L, 1,322mg/L, respectively. This was similar to the average value of the document. In general, pH of surface sea water is average 8.3(Waters & Millero, 2013), but depending on component of salts and concentration. The average concentration of calcium and magnesium is 411mg/L, 1290mg/L, respectively(Leggett & RaO, 2015). PSA is a material suitable for direct carbonation without pre treatment because it has a lot of calcium as well as particle size of PSA is very fine. The calcium contained in PSA was very high as 67.2% according to XRF analysis result(Table 8). This was because calcium carbonate was used in paper making process as coating pigments and fillers to improve the quality of paper. However, magnesium content was low as 4.37% compared to calcium content.

Table 8 XRF analysis of PSA

Components	Content (%)
CaO	67.21
SiO_2	15.02
Al_2O_3	6.62
MgO	4.37
SO_2	2.72
Fe_2O_3	1.77
P_2O_5	0.53

The result of XRD analysis was shown in Fig. 11. The calcium in PSA was mainly composed of Lime(CaO), Dolomite($Ca_{0.94}Mg_{0.06}CO_3$) and Hischite($Al_2Ca_3H_{3.36}O_{12}Si_{2.16}$). Among them, Dolomite was remained because calcium carbonate used in paper making process could not be decomposed and it was combined with magnesium.



L: Lime(CaO), D: Dolomite($Ca_{0.94}Mg_{0.06}CO_3$), H: Hibschite($Al_2Ca_3H_{3.36}O_{12}Si_{2.16}$)

Fig. 11 XRD analysis of PSA

The result of TGA analysis conducted in order to calculate the carbonate in PSA was shown in Fig. 12. In TGA analysis, the cause of weight loss appears due to water evaporation at 25-105° C, decomposition of organic materials and magnesium carbonate at 105-500° C, decomposition of calcium carbonate at 500-780° C(Chang et al., 2011a). PSA used in this study was contained 0.069% of water, 2.72% of magnesium carbonate and 15.66% of calcium carbonate.

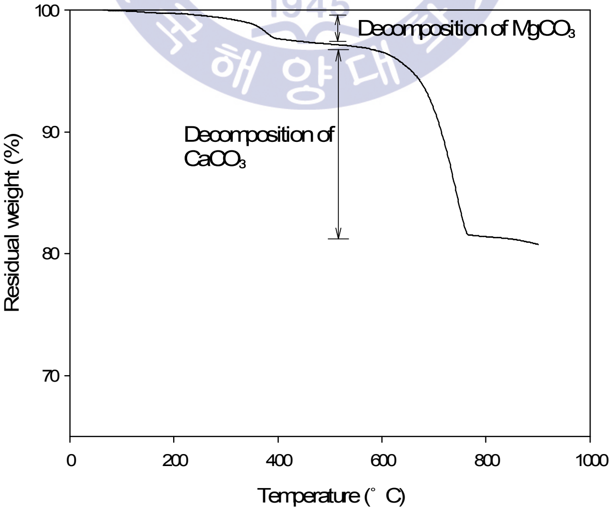


Fig. 12 TGA analysis of PSA before carbonation

3.2.2 Carbonation experiment

Until now, the researchers conducted a many carbonation experiments to improve carbonation efficiency by varying conditions of water content, reaction time, temperature and carbon dioxide pressure(Kim & Kim, 2015). In this study, carbonation was conducted method of continuous flow system at room temperature, atmospheric pressure to store carbon dioxide economically. Also, we tried to find a optimum conditions sea water content and reaction time that the greatest effect on the direct carbonation efficiency.

3.2.2.1 Sea water content determination

The increased solid weight was shown in Fig. 13 when 20g of PSA was carbonated by varying sea water content from 40mL to 1000mL. As the sea water content was higher, the weight of final solid was decreased. For example, the final solid weight was 26.9g, 23.0g when volume of sea water was 40mL, 1000mL, respectively. It meant that calcium carbonate and magnesium carbonate was produced more by accelerating carbonation reaction as the sea water content was lower. On the other hand, the final solid weight was 26.9g and 26.7g using sea water 40mL and 100mL, respectively. There was little differences.

According to Chang et al. (2011a) that examined the effect of water content using slag, when liquid to solid ratio was 10mL/g carbonation efficiency was increased up to 57.5% and the efficiency was very low in the state of without water. However, efficiency was little changed even if water content was further increased. Water was necessary for carbonation and extraction to dissolve carbon dioxide and extract calcium. However, carbonation could be prevented with the excess of water because calcium extraction rate was decreased by forming mass transfer barrier and decreasing ionic strength(Kim & Kim, 2015; Chang et al., 2011a). Ukwattage et al. (2013) obtained the highest carbonation efficiency at 0.2 of liquid to solid ratio through direct carbonation using fly ash, and carbonation efficiency was decreased as liquid ratio was higher. They explained it is important to determine optimum liquid to solid ratio because it was difficult to diffuse carbon dioxide into solid surface by blocking the pores if the excess of water was added. Although water play a role to dissolve calcium from raw materials and then, produce calcium hydroxide.

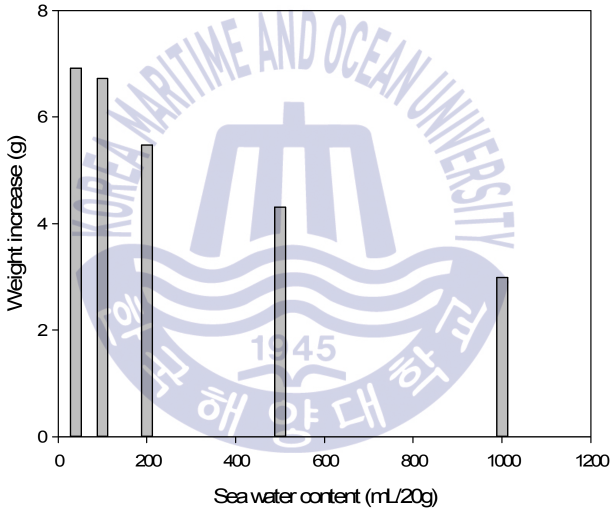


Fig. 13 Comparison of solid weight increase according to sea water content

In this study, carbon storage was increased as sea water content was lower however, sea water was required enough to be uniformly mixed PSA with sea water. As a result, when 20g of PSA was mixed with 40mL, 100mL of sea water, carbonation efficiency was not changed and it was difficult to agitate at sea water volume less than 100mL. Therefore, the optimum sea water content was determined in 20g/100mL, and then next experiment was conducted in this condition.

3.2.2.2 Reaction time determination

The sufficient reaction time is required to produce carbonate by reacting carbon dioxide with metal oxide. However, it is necessary to determine optimum reaction time because produced carbonate can be dissolved if the carbon dioxide was injected a long period.

The increased solid weight according to carbonation reaction time was shown in Fig. 14. As the reaction time was longer, the final solid weight was increased but, solid weight was decreased after 120 minutes. For example, the final solid weight was the lowest as 4.6g in 10 minutes on the other hands, it was the highest as 6.43g in 120 minutes. However, when the carbonation time was 300 minutes, the final solid weight was decreased as 5.7g, it was similar to that of 60 minutes. This was because if the reaction time was longer than 120 minutes, produced carbonate was dissolved.

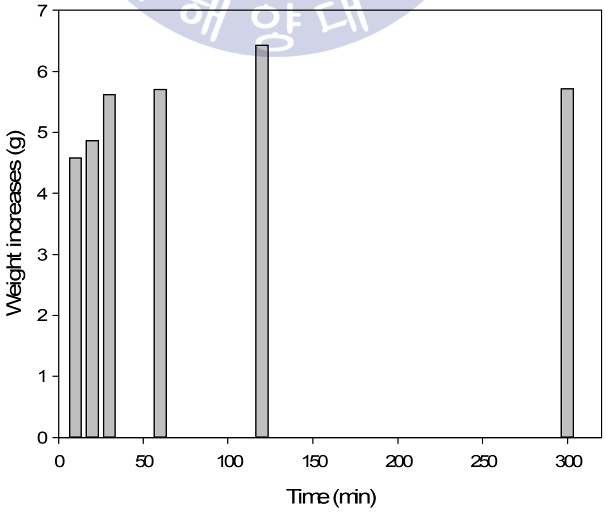


Fig. 14 Comparison of solid weight increase according to reaction time

In previous studies, the reaction time to obtain high carbonation efficiency was various according to type of alkali waste and experiment conditions. For example, Huntzinger et al. (2009a) conducted direct carbonation a column method using Cement Kiln Dust(CKD) at room temperature, atmospheric pressure and they obtained 70% of high carbonation efficiency. However, the reaction time was very long as 2-12 days. On the other hand, Teramura et al. (2000) obtained 96% of carbonation efficiency when they conducted direct carbonation using waste concrete at 50% of water content, 0.4MPa carbon dioxide pressure. The reaction was completed within 1 hour.

It was difficult to generalize the optimum carbonation time because it changed according to type of alkali waste, water content, carbon dioxide pressure. However, it was important to find appropriate reaction time because energy consumption could be increased and it could be difficult to apply in industrial field if the reaction time would be increased. As a result, the carbonation time was determined in 120 minutes.

3.2.2.3 Carbonation experiment using sea water and ultrapure water

A pH of slurry that stirred PSA with sea water and ultrapure water during 5 minutes was high more than 12.7 in both cases. However, it was decreased consistently as carbon dioxide was injected. In particular, the pH was changed more rapidly in case of using ultrapure water as a solvent. For example, pH was 11.3, 9.8 in case of using sea water and ultrapure water, respectively after carbonation was started 4 minutes. The time using sea water was longer than using ultrapure water to maintain high pH during carbonation because sea water had a buffering capacity. In high pH, since carbon dioxide is presented in the form of CO_3^{2-}, it can be produced insoluble carbonate by reacting with metal oxide. Therefore, a large amount of carbon dioxide could be stored as the pH would be maintained highly.

The final solid weight was 26.43g, 24.63g when carbonation was proceeded using sea water and ultrapure water, respectively. It meant that more carbon dioxide was stored to have a lot of increased solid using sea water. The result of TGA analysis using two solvents was shown in Fig. 15.

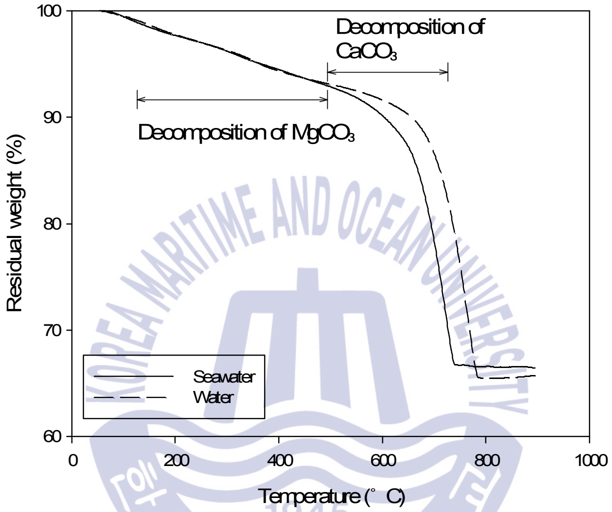


Fig. 15 TGA analysis of solid after carbonation

The weight loss was 6.49%, 6.35% in the range of 105-500° C using sea water, ultrapure water, respectively. It meant magnesium carbonate content in the solid after carbonation. Also, the weight loss was 25.92%, 26.38% in the range of 500-780° C using sea water, ultrapure water, respectively. It meant calcium carbonate content. And carbon storage by carbonation was calculated as following Eq. (14).

Carbon storage (kg CO_2/ton PSA) =

$$\{(W_f \cdot C_f) - (W_i \cdot C_i)\} \times \frac{MW_{co_2}}{MW_c} \times \frac{1}{W_i} \times 10^3 \qquad (14)$$

W_f : solid weight after carbonation (g)

C_f : $CaCO_3$ or $MgCO_3$ content after carbonation (%)

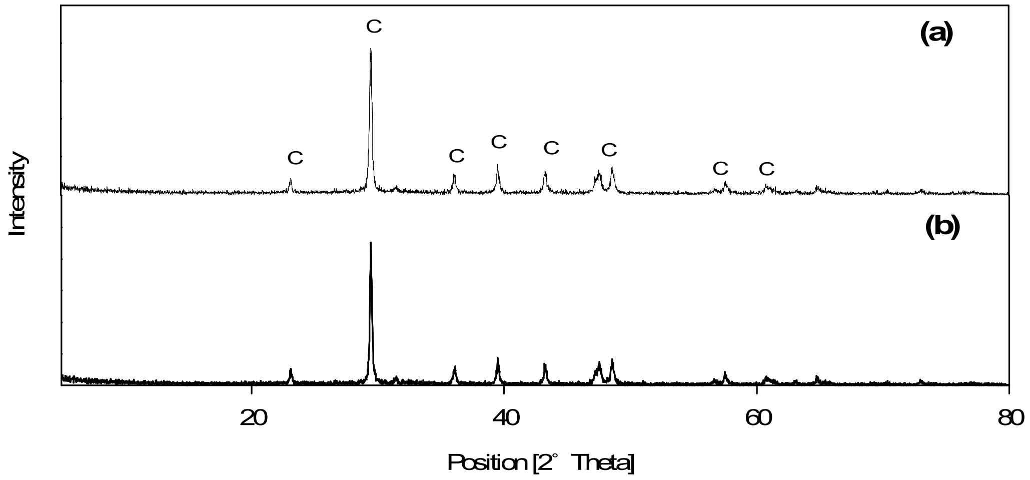
W_i : solid weight before carbonation (g)

C_i : $CaCO_3$ or $MgCO_3$ content before carbonation (%)

MW_{CO2} : molecular weight of CO_2 (g/mol)

MW_C : molecular weight of $CaCO_3$ or $MgCO_3$ (g/mol)

The Eq. (14) was established by considering to the weight of final solid weight after carbonation, the result of weight loss according to temperature after TGA analysis and the initial carbonate content before carbonation. The carbon storage was obtained by calculating carbonate separately in case of calcium carbonate and magnesium carbonate then, adding two value. As a result, when sea water and ultrapure water was used as solvent in direct carbonation, carbon storage was 113kg CO_2/ton PSA, 101kg CO_2/ton PSA, respectively. Carbon storage using sea water was higher as 10% than that of using ultrapure water. It was because pH of slurry using sea water was decreased more slowly than ultrapure water also, sea water had calcium, magnesium ion.



C: Calcite

Fig. 16 XRD analysis after carbonation: (a) sea water (b) ultrapure water

When the final solid carbonated using PSA with sea water was analyzed through XRD it had calcium carbonate in the form of Calcite but, material of amorphous form was not detected(Fig. 16). Before carbonation, calcium in PSA was presented in the form of Lime(CaO), Dolomite ($Ca_{0.94}$,$Mg_{0.06}CO_3$), Hibschite ($Al_2Ca_3H_{3.36}O_{12}Si_{2.16}$), and they were converted to Calcite after carbonation. On the other hand, the result of analysis final solid carbonated using ultrapure water, Lime and Hibschite were not detected but, only Calcite was detected.

3.3 Conclusion

In this study, it was found to optimum conditions of sea water content and reaction time through direct carbonation using sea water with PSA. And then, carbon storage was compared that using ultrapure water. The results were as follows.

The optimum sea water content was 5mL/g when PSA was carbonated at 25° C, 1atm, 0.05L/min flow rate during 2 hours. Also, the optimum reaction time was 2 hours in same conditions. In the above conditions, the carbon storage was 113, 101kg CO_2/ton PSA when PSA was carbonated using sea water and ultrapure water, respectively. Also, the final solid in both cases were composed of calcium carbonate in the form of Calcite.

Carbon dioxide was stored using sea water with PSA at room temperature, atmospheric pressure also, carbon storage in this result was not less than in previous studies. In addition, the carbonation process and raw materials were eco-friendly and economical. In other words, it had great significant in terms of commercialization because carbon dioxide was efficiently stored using PSA industrial waste and sea water readily available from coast and a large energy was not used for increasing temperature and pressure.

Finally, it is hope to conduct a next study that a larger scale of carbonation using sea water and PSA and utilizing the final solid after carbonation as the materials of marine structure.

Chapter 4. Comprehensive conclusion

In this study, carbon dioxide was stored using PSA through mineral carbonation. Until now, industrial wastes used in mineral carbonation studies are slag, cement waste and fly ash. These industrial wastes are generated a large amount in worldwide. Also, these are suitable for raw material of mineral carbonation because they are contained a lot of metal oxide which is a high reactive with carbon dioxide such as calcium oxide or magnesium oxide as well as they are shown a high alkalinity in contact with water. Recently, studies that conducted using various industrial wastes are increasing.

In direct carbonation method, carbon dioxide was stored in conditions of high temperature and high pressure at initial research step, in contrast most studies were conducted by injecting carbon dioxide in slurry at room temperature, atmospheric pressure to improve energy reduction and cost effectiveness, recently. In indirect carbonation method, there was a various attempt to find solvent extracting efficiently the calcium from industrial wastes. Further, waste solvent after carbonation was reused considering a secondary environmental problems. Also, the studies to obtain high purity of carbonate for recycling in industry have been conducted. It will be a method to solve economic issue, which is considered the biggest disadvantage of mineral carbonation. Future studies will be expected to conduct in the directions of low-cost, eco-friendly, high efficiency in other words, to save a cost and energy, to utilize recovered carbonate in industry, to reuse the solvent for reducing a environmental problems and to store a lot of carbon dioxide efficiently.

Since the concept of mineral carbonation technology was first proposed in the early 1990s, the study was started only after 2000s in the domestic although it has consistently conducted in the overseas. Thus, in the domestic, mineral carbonation technology is not widely known than overseas and the technology development is still insufficient. As mentioned earlier, in that technology, carbon dioxide can be stored stably in a relatively simple principle and it can be stored directly where it is emitted without capture, transportation steps although it has economic problem. Also, it has advantage of being able to recover the subsequent by-products at the same time, to recycle industrial wastes.

Future in domestic, mineral carbonation study will be required as minimal countermeasures for an uncertain future in carbon dioxide storage. As a result, it is important to secure the independent a mesoscale storage technology that can be shared a part of carbon dioxide reduction objective and it is essential to develop mineral carbonation technology for match domestic situation.

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