

Coal combustion in a dual-fluidized bed system

under Ca-Looping process conditions

(Ca ルーピングプロセス条件での 2 塔式循環流動層による石炭燃焼)

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### General introduction

#### 1.1 Background of research

With the rapid development of social civilization and industrial production, demand for energy has been increasing. Strong evidence suggests that this worldwide industrial evolution has increased both the average global temperature and the atmospheric CO<sub>2</sub> concentration. More than 30% of CO<sub>2</sub> has been estimated as coming from power plants [1]. Therefore, new combustion technologies must be used to solve this problem. As a global policy trend, the International Energy Agency has submitted a scenario for halving CO<sub>2</sub> emissions by 2050. Based on this scenario, CO<sub>2</sub> emissions reduction of 48 Gt/year will be necessary by 2050 to achieve a 50% reduction of emission in comparison to the baseline scenario by 2050 [2, 3]. A possible solution to reduce CO<sub>2</sub> emission to the atmosphere is the introduction of the carbon capture and storage (CCS) technology [4, 5].

#### 1.2 CO<sub>2</sub> capture processes

To capture CO<sub>2</sub> from power plants, four methods have been investigated intensively in the past few decades: pre-combustion capture, oxy-fuel combustion capture, post-combustion capture [6, 7], and chemical looping combustion. In Fig.1-1, CO<sub>2</sub> capture strategies of three kinds are presented [8].

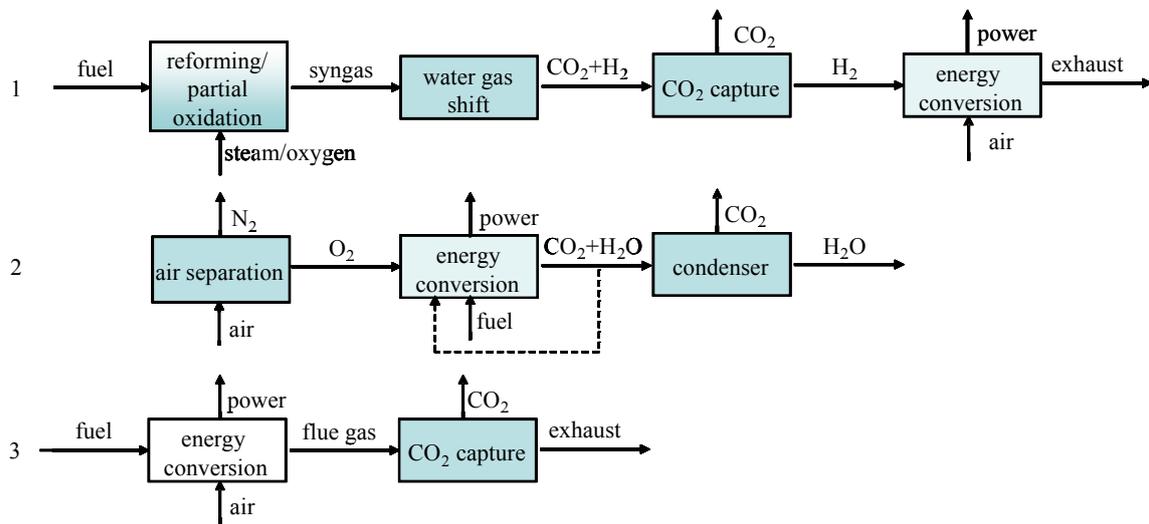


Fig.1-1. Principles of (1) pre-combustion capture, (2) oxy-fuel combustion and (3) post-combustion capture. White components are equal to the configuration without capture, light grey represents modifications to the configuration without capture, dark grey denotes new components [8].

In pre-combustion capture, CO<sub>2</sub> is removed from fuel before combustion. For this purpose, the integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) can be modified in power plants by adding processes to remove CO<sub>2</sub> from flue gases. Many commercial technologies based on liquid phase absorption can be implemented in coal gasification based plants. Decarbonization of the syngas stream benefits from high pressures and CO<sub>2</sub> concentrations, both of which constitute a strong driving force to lower the energy penalty necessary to capture CO<sub>2</sub> from power plant processes. Aside from liquid-phase absorption technologies, membrane technologies (either H<sub>2</sub> or CO<sub>2</sub> selective membranes) show high potential for pre-combustion carbon capture, but the cost of membrane integration and the efficiency losses accompanied by CO<sub>2</sub> separation are key factors for evaluation of the potential of membranes for pre-combustion capture of CO<sub>2</sub> [9].

In the oxy-fuel combustion process, the fuel is combusted with a mixture of oxygen and recirculated flue gas from power plants. Because of the absence of  $N_2$  from combustion gas, the flue gas from combustion consists mainly of  $CO_2$  and  $H_2O$ , the latter of which can be removed by condensation to obtain a high content ( $>90\%$ ) of  $CO_2$  gas stream. Nevertheless, production of pure oxygen entails a large energy penalty. The state-of-the-art separation process for oxygen is cryogenic air separation. Total efficiency losses of 8–12% have been estimated for a greenfield oxyfuel power plant, mainly because of the cryogenic air separation unit (ASU) [10,11].

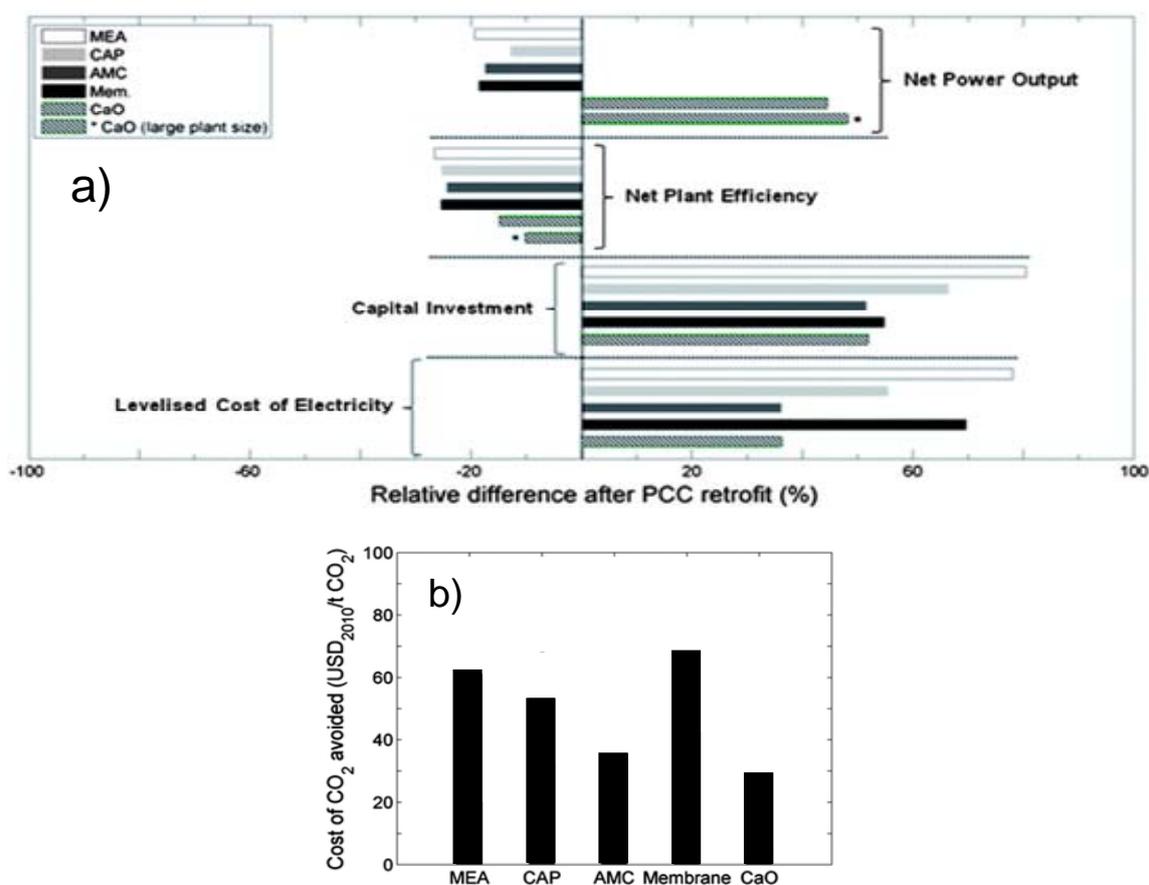


Fig. 1-2. a) Relative changes in the key techno-economic of a pulverized-coal power plant after PCC retrofit; b) Cost of  $CO_2$  avoided for the five PCC technologies considered here [12].

The separation of CO<sub>2</sub> from the flue gas in the back-pass of combustor, called post-combustion capture (PCC), is presented in Fig.1-2 [12]. Among these technologies are monoethanolamine (MEA), chilled ammonia process (CAP), alkali-metal (AMC), and membrane-based (Mem.) PCC, which all entail higher capital investment and a higher level listed cost of electricity than the Calcium Looping process presented in Fig. 1-2-a. Calcium looping exhibits the lowest cost of CO<sub>2</sub> avoided: 29 USD<sub>2010</sub> per tCO<sub>2</sub>, as presented in Fig. 1-2-b. The calcium looping (Cal) process was proposed in 1999 as a promising post-combustion technology for achieving CO<sub>2</sub> capture [13]. This dry absorption-desorption process uses solid CaO as an absorbent. In the Calcium Looping process, the CFB calciner and carbonator contribute to the total equipment costs. The reactions in the carbonator and in the calciner facilitate supercritical steam turbines and generate more electricity, which markedly decreases the extra capital requirement in comparison to MEA and CAP. Moreover, the waste bed material, such as limestone, provides excellent opportunities for use as a cheap raw material for cement manufacture [14, 15].

Chemical looping combustion has been discussed in the literature as an alternative to normal combustion [16, 17]. In recent years, chemical looping has been examined as a new carbon capture and storage technology for fossil fuels conversion. Two interconnected fluidized beds, a fuel reactor and an air reactor, are used. The fuel conversion process is separated into two steps using a solid catalyst, the so-called oxygen carrier, in the form of a

metal oxide,  $Me_xO_y$ . Oxides of Ni, Co, Fe, Cu, and Mn are used as oxygen-carrier materials. However, the oxygen carrier must have high reactivity with fuel and oxygen, ability to convert the fuel completely to  $CO_2$  and  $H_2O$ , low fragmentation and attrition, and low production cost. To date, more than 900 oxygen carriers have been investigated in the laboratory [18]. Nevertheless, it is too early to select any final winner because numerous very interesting materials are waiting to be tasted.

### 1.3 Calcium Looping (CaL) process

The study uses the CaL process is assessed as a promising post-combustion technology for  $CO_2$  capture [13]. This dry absorption-desorption process uses solid CaO as sorbent. It is based on a reversible reaction for absorption of  $CO_2$  by CaO (Eq. (1-1)) and decomposition of  $CaCO_3$  into CaO and  $CO_2$  (Eq. (1-2)) as shown below



The CaL process includes two reactors, as portrayed in Fig. 1-3 [13]. An absorption reaction Eq. (1-1) is conducted in one reactor (carbonator). A decomposition reaction is conducted in another reactor (regenerator). The carbonator is connected to the regenerator by solid transportation lines to recirculate the solid absorbent.

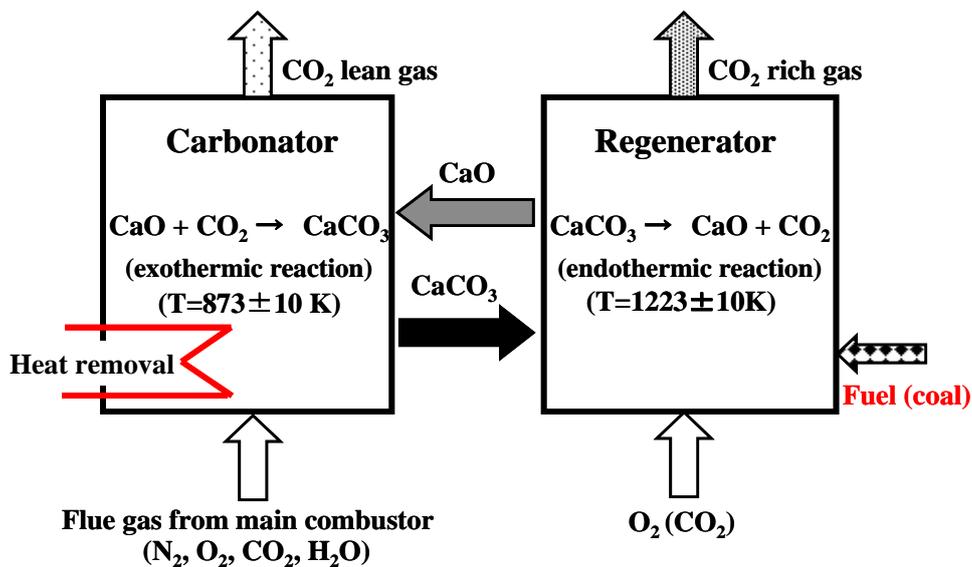


Fig. 1-3. Calcium Looping (CaL) process concept.

In the carbonator, the reaction temperature is fixed at approximately 873 K so that CaO is carbonated to CaCO<sub>3</sub>. The absorption reaction is exothermic. Therefore, the reaction heat must be removed from the carbonator to maintain the reaction temperature. The heat recovered from the carbonator is useful to produce high-temperature and high-pressure steam to drive a steam turbine used to recover energy.

The CaCO<sub>3</sub> produced in the carbonator is then transported to the regenerator. In the regenerator, the temperature is maintained at approximately 1223 K so that the CaCO<sub>3</sub> is regenerated to CaO, as in Eq. (1-2). The high-purity CO<sub>2</sub> is recovered. The CaCO<sub>3</sub> decomposition is an endothermic reaction. Therefore, the reaction heat must be supplied. The heat can be supplied by burning fuel with pure oxygen (oxy-fuel combustion) in the regenerator so that the flue gas consists only of CO<sub>2</sub> and H<sub>2</sub>O. Then the mixture of CO<sub>2</sub>

formed by decomposition and CO<sub>2</sub>-rich flue gas from oxy-fuel combustion is compressed for geological storage. The calcined CaO is recycled to the carbonator again. To avoid hot spot formation in the regenerator, part of the produced CO<sub>2</sub>-rich gas can be recirculated to the gas inlet to dilute the pure O<sub>2</sub>. A process design showed that about 440 J of heat was necessary to capture 1 mole of CO<sub>2</sub> from flue gas [13], although this heat requirement will increase concomitantly with increasing solid circulation rate and increasing CO<sub>2</sub> recycle rate to dilute pure O<sub>2</sub> because of increased heat carry over from the regenerator. This process has attracted a great deal of attention recently. Numerous reports have described fluidized bed experiments of CO<sub>2</sub> capture by CaO, as summarized below.

#### **1.4 Previous studies of CaL process**

The CaL process is expected to separate carbon dioxide from flue gas with a low energy penalty. To design, construct and operate this CO<sub>2</sub> capture process, many studies particularly addressing different research directions must be done. Two major directions are the following.

- 1) Selection of solid absorbent and improvement of capture rate and solid utilization efficiency
- 2) Continuous operation of CaL plants to prove the feasibility of this process

### 1.4.1 Development and improvement of sorbent

Particle attrition and declining reactivity and solid utilization efficiency after repeated carbonation–regeneration cycles are important shortcomings of sorbents. Some researchers using pilot-scale plants and laboratory scale plants have used different combinations of fluidized reactors (carbonator and regenerator) to mitigate those problems.

Sun et al. [19], based on many experiments and observations the SEM of the surface of particle under different condition of calciner, proved that the ultimate CaO utilization level depends on the operating conditions, especially the carbonation time. Salvador et al. [20] removed CO<sub>2</sub> in multiple carbonation–calcination cycles using a circulating fluidized bed combustor (CFBC) operated in bubbling FBC mode with three kinds of CaO. The result suggests that increased carbonation time in a sorbent with a higher reactivity to CO<sub>2</sub> and 100% CO<sub>2</sub> atmospheres may provide a possible reactivation method for some limestone and that the use of NaCl and Na<sub>2</sub>CO<sub>3</sub> for this purpose requires further investigation in an FBC environment. Alvarez and Abanades [21] reported that the critical product layer might be a constant characteristic value to explain the surface of CaO reacted with CO<sub>2</sub> in the internal surface of the sorbent. They showed that longer carbonation times will close large pores at the CaO surface. Lysikov et al. [22] first reported a study of the effects of thermal pretreatment in a long series of isothermal recarbonation–decomposition cycles, the type of precursor and the conditions of cycling influence the value of the residual CO<sub>2</sub> carrying capacity of CaO

sorbents.

Fan et al. [23] used a wet precipitation process and obtained synthetic precipitated calcium carbonate (PCC) with a large surface area. The CaO sorbent obtained from PCC (PCC-CaO) was less susceptible to pore plugging, and attained high than 90% conversion. Li et al. [24, 25] synthesized a new kind of Ca-based regenerable CO<sub>2</sub> absorbent, CaO/ Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. Compared with other Ca-based CO<sub>2</sub> absorbents, it has significantly improved CO<sub>2</sub> absorption capacity and cyclic reaction stability. Aihara et al. [26] used conventional powder method or a metal alkoxide method to produce solid reactants with CaO as the reactant and CaTiO<sub>3</sub> as the inert framework. Therefore, this method creates a synthetic sorbent by dispersing CaO across different inert matrixes. Lu et al. [27], through the simple calcination technique, developed a CaO sorbent derived from many metallic precursors such as calcium propionate, calcium acetate, calcium acetylacetonate hydrate, calcium oxalate, and calcium 2-ethylhexanoate.

Li et al. [28] and Sun et al. [29] reported that modification of dolomite using acetic acid or aqueous solutions of higher concentrations of Na<sub>2</sub>CO<sub>3</sub> or NaCl yielded a sorbent with significantly higher activity than the original sorbent. Unfortunately, these methods to deal with particles need long time reaction and cost high.

Anthony and Granatstein [30] demonstrated that, for the CaL process, with optimum carbonation temperature lower than 973 K and calcination temperature about 1173 K, CaSO<sub>4</sub> is formed dominantly under oxidizing conditions. Along with the CaSO<sub>4</sub> formation, the

reactivity of sorbent is lost irreversibly and the sorbent particles must be replaced. Manovic et al. [31] proposed that SO<sub>2</sub> be controlled before the flue gas enters the carbonator. Installing a flue gas desulfurization unit before the calciner can reduce this effect. It should be noted that sulfation is a problem in a post-combustion carbonator that one might expect to resolve.

To develop a successful sorbent, not only chemical reactivity measurement but also economic evaluation must be conducted. Natural limestone is widely regarded as the cheapest sorbent. Therefore, useful synthetic sorbents are likely to be a combination of simple processes such as precipitation methods and simple materials.

Other researchers have specifically examined the attrition and fragmentation of the sorbent. Anthony et al. believed that calcination is not the only cause of these difficulties; a sulfur reaction is also regarded as another important reason. The affect of sorbent attrition is mainly that of sulfation rather than repeated carbonation–calcination cycles [30, 31]. Fennell et al. [32] and Jia et al. [33] observed during bench-scale and pilot-scale experiments that limestone has a high attrition rate during the first calcination. However, the attrition rate decreased after repeated calcination–carbonation cycles. Moreover, it differed considerably among limestones. Some tests of mechanical stability of particle attrition revealed that the shrinkage of sorbent particles was attributable not only to attrition but also to particle densification [34, 35].

However, knowledge of attrition and fragmentation remain insufficient. Further study is necessary to predict the loss of attrition during continuous experiments using bench-scale or

pilot-scale plants.

#### **1.4.2 Development of CO<sub>2</sub> capture equipment**

The CaL process has attracted a great deal of attention recently. Experimental works of continuous CO<sub>2</sub> capture by CaO-based sorbents have been conducted using dual-fluidized bed systems of various scales, as presented in Table 1-1.

Fang et al. [36] built a dual fluidized bed reactor hot model for CO<sub>2</sub> capture with calcium-based sorbent. The heat support for reactions was electric furnaces, with CO<sub>2</sub> capture efficiency of nearly 95%, but the conversion of CaO to CaCO<sub>3</sub> in the carbonator was nearly 70.4%. Oxy-fuel combustion of biomass and coal in the regenerator with flue gas recirculation to achieve high-concentration CO<sub>2</sub> in the off-gas was regarded as the first demonstration of this technology using a pilot-scale dual fluidized bed system by Lu et al. [37]. Charitos et al. [38] designed a carbonate looping Dual Fluidized Bed (DFB) and investigated critical parameters affecting the CO<sub>2</sub> capture efficiency of the process, including the CaO looping rate, the carbonator space time, and the carbonator temperature. Abanades et al. used two interconnected CFB reactors as a carbonator and regenerator in continuous mode and reported that the capture efficiency reached 70–97% under realistic flue gas conditions in the carbonator reactor [39], and emphasized that the similarity between process conditions and those existing in CFBC power plants should allow a rapid scaling up of this technology

Table 1-1 Dual-fluidized bed systems used for the research and development of CaL process

Reference	Plant size	Carbonator	Regenerator	Solid	Fuel/Heating	Gas to carbonator	Gas to regenerator
Fang [36]	Lab.-scale	BFB	BFB	Ca-based sorbent	electric heater	Air+CO <sub>2</sub>	Air
Lu [37]	Small pilot	FB	CFB	limestone	biomass/coal	Air+CO <sub>2</sub>	Air/O <sub>2</sub> -enriched air
Charitos [38]	10 kW <sub>th</sub>	BFB	riser	limestone	electric heater/natural gas	N <sub>2</sub> +CO <sub>2</sub>	Air
Abanades[39], Alonso[40], Rodriguez [41]	30 kW <sub>th</sub>	CFB	CFB	limestone	coal	Air+CO <sub>2</sub>	Air
Dieter H [42]	200 kW <sub>th</sub>	Turbulent	CFB	limestone	wood pellets	synthetic flue gas	O <sub>2</sub> -enriched air
Kremer [43]	1 MW <sub>th</sub>	CFB	CFB	limestone	propane/coal	synthetic flue gas	O <sub>2</sub> -enriched air
Arias[44], Sanchez-Biezma [45]	1.7 MW <sub>th</sub>	CFB	CFB	limestone	coal	synthetic flue gas	Air/ (O <sub>2</sub> +CO <sub>2</sub> )

[40]. The effect of the average carrying capacity of the CaO circulating particles, the temperature and the gas velocity on the CO<sub>2</sub> capture efficiency were investigated. Almost complete calcination was achieved by burning coal. The bed inventory of CaO and the fraction of active CaO in the bed were interpreted by Rodríguez et al. [41] as the most important parameters affecting the CO<sub>2</sub> capture efficiency. Dieter et al. [42] demonstrated the CaL process on a pilot scale in realistic process conditions with a sorbent regenerator combusting wood pellets with an oxygen–air atmosphere (O<sub>2</sub>: 50 vol.%). Their results showed that the presence of water vapor in flue gas significantly improves the CO<sub>2</sub> capture efficiency. Kremer et al. [43] tested a 1-MW<sub>th</sub> pilot plant for continuous CO<sub>2</sub> capture at Technische Universität Darmstadt. The total CO<sub>2</sub> capture rate was high than 90%, although the heat for the endothermic calcination reaction in the calciner was provided by combustion of pulverized coal. In the next step, they expect to change the fluidizing gas from nitrogen to CO<sub>2</sub> atmosphere in calciner to modify the resident time of the sorbent in the calciner to operate the internal calciner circulation. Arias et al. [44] demonstrated CO<sub>2</sub> capture efficiencies over 90% with operating conditions in the reactors resembling those expected in large CaL CO<sub>2</sub> capture systems (i.e. reactor temperature, gas velocities, solid compositions, circulation rates, and reaction atmospheres). A certain O<sub>2</sub> excess at the exit of the combustion–calciner reactor was greater than 5 vol.% to ensure high coal combustion efficiency in the calciner. CO<sub>2</sub> capture efficiency and calciner temperature of the 1.7 MW<sub>th</sub>

pilot la Pereda was reported by Sánchez-Biezma [45]. Charitos et al. [46], through comparison of experimental data of two CaL process (INCAR-CSIC in Spain and IFK in Germany), concluded that a slightly overstoichiometric flow of active CaO was necessary to capture a certain molar flow of CO<sub>2</sub>, but for the INCAR-CSIC regenerator, air-fired coal combustion was used to supply additional heat, CH<sub>4</sub> combustion with O<sub>2</sub> (40%) enhanced air was realized in the IFK regenerator. Dual-fluidized bed reactor systems were proposed to capture CO<sub>2</sub>, with emphasis on the carbonate looping process [47–49]. Furthermore, modelling of dual-fluidized bed systems has been conducted for CO<sub>2</sub> capture [50–52].

Although these devices have already been designed to use coal as fuel, previous works related to the CaL process have particularly addressed CO<sub>2</sub> capture. Only a small amount of attention has been devoted to coal combustion behavior and the carryover of unburned char to the carbonator with recirculated solid sorbent.

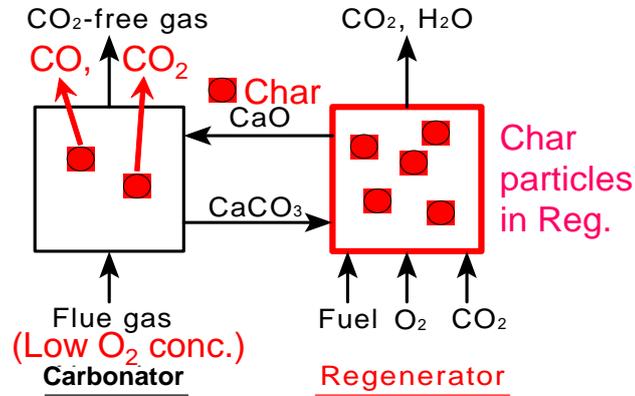
### **1.4.3 Problems of using coal as fuel in the Calcium Looping process**

In this process, coal is to be burned to provide heat for the endothermic reaction in the regenerator feeding pure oxygen (as an O<sub>2</sub>–CO<sub>2</sub> mixture). Therefore, the char behavior in this dual-fluidized bed system is regarded as playing an important role in determining the quality of both CO<sub>2</sub>-free flue gas from the carbonator and high-purity CO<sub>2</sub> from the regenerator. Coal fed into the regenerator forms char particles, most of which are consumed by combustion.

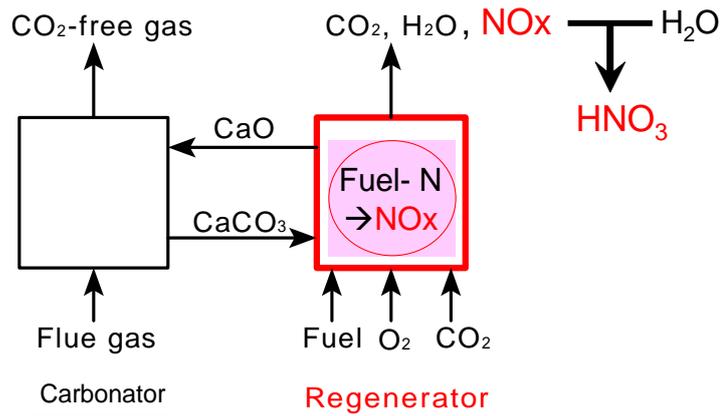
Nevertheless some char particles always exist in the circulating CaO particles. Those particles are transported to the carbonator because oxygen consumption in the regenerator through gas–solid reaction requires a certain hold-up of the solid reactant.

Shown as Fig. (1-4-(a)), the char particles transported to the carbonator with CaO particles may form CO through the reaction with oxygen in the fed flue gas. Due to the low reaction temperature in the carbonator, the CO that is formed is likely to be released to the atmosphere without being oxidized to CO<sub>2</sub>, thereby polluting the environment. Even if CO is oxidized to CO<sub>2</sub> or if char is oxidized directly to CO<sub>2</sub>, the resultant CO<sub>2</sub> will consume free CaO in the carbonator. Therefore, a greater CaO supply from the regenerator seems to be necessary to maintain CO<sub>2</sub> capture efficiency in the carbonator because activity of the sorbent decreases concomitantly with increasing conversion of CaO to CaCO<sub>3</sub>. Furthermore, capture of CO<sub>2</sub> formed by char combustion in the carbonator will result in the increased formation of CaCO<sub>3</sub>. Because of the greater requirement of CaO and extra formation of CaCO<sub>3</sub>, more fuel and pure oxygen will be consumed to regenerate CaO from CaCO<sub>3</sub> in the regenerator. Thereby, the energy penalty is anticipated to increase. If the char concentration can be reduced, then such formation CO and CO<sub>2</sub> can be mitigated. However, when the char concentration in the regenerator is low, then the consumption of oxygen by char decreases and high O<sub>2</sub> concentration in the produced CO<sub>2</sub> is anticipated. The increase in unreacted O<sub>2</sub> in the produced CO<sub>2</sub> will increase power consumption during CO<sub>2</sub> compression because of

increased non-condensable gas.



(a) Char transportation from regenerator to carbonator and formation of CO and CO<sub>2</sub>



(b) NO<sub>x</sub> formation in regenerator

Fig. 1-4. Anticipated problems with coal combustion in the CaL process regenerator.

In addition, coal is burned in this process to provide heat for the endothermic reaction in the regenerator. With coal combustion, NO<sub>x</sub> (NO and NO<sub>2</sub>) can be formed in the regenerator (Fig. 1-4-(b)). NO in the flue gas can be oxidized to form NO<sub>2</sub> at lower temperatures. When NO<sub>2</sub> is absorbed by water during gas compression or water condensation, it may form nitric

acid ( $\text{HNO}_3$ ). The acid might damage the compressor or condenser. Consequently,  $\text{NO}_x$  formation during combustion is of great concern.

However, if the study of char combustion behavior conducted under CaL process using  $\text{CaO}$  as bed material, then it is not easy to determine the char combustion rate in the carbonator by measuring  $\text{CO}_2$  emissions because  $\text{CaO}$ -based sorbents capture  $\text{CO}_2$  formed in the carbonator and the sorbents released  $\text{CO}_2$  in the regenerator, as shown in the schematic depicted in Fig.1-5-(a). Therefore, it is necessary to use inert bed material to determine  $\text{CO}_2$  formation from the carbonator (Fig.1-5-(b)). For this study, quartz sand will be used as the bed material.

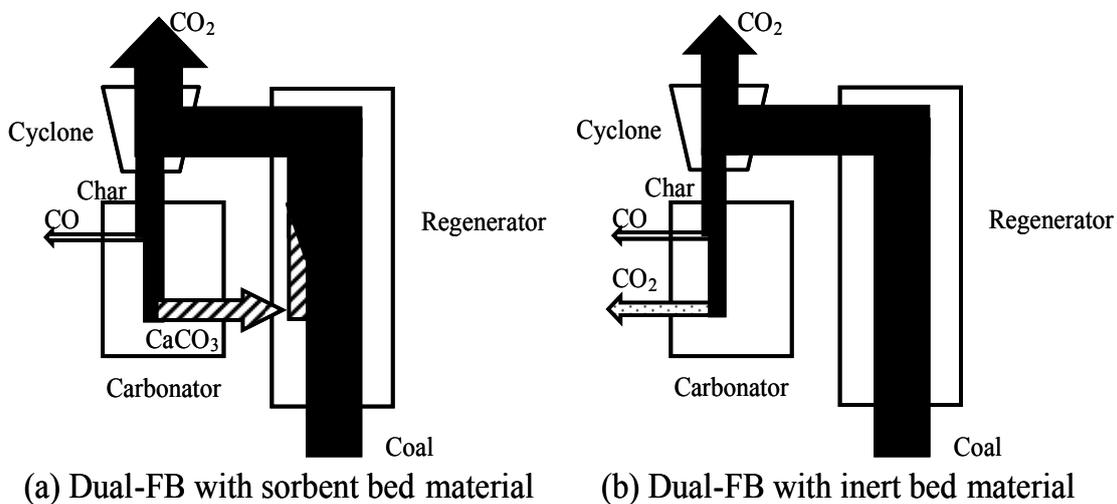


Fig. 1-5. Schematic diagrams of material flow of carbon in (a) dual-fluidized bed with sorbent bed, (b) dual-fluidized bed with inert bed material.

### 1.5 Main objectives of this research

The present work specifically examines the char combustion behavior in the dual-fluidized

bed system.

This work includes several important points: (1) Testing of the regenerator residence time, (2) Evaluation of CO and NO<sub>x</sub> emissions, (3) Effect of diluents of O<sub>2</sub> on CO and NO<sub>x</sub> emissions, (4) Effect of char on NO<sub>x</sub> formation.

### **1.5.1 Testing of regenerator residence time**

Sufficient reaction time and temperature are necessary for CaCO<sub>3</sub> calcination. Therefore, residence time control of solids in the regenerator is probable important. This residence time is determined by the circulation rate of bed material and solid hold-up in the regenerator, the former of which is determined so that the required CaO feeding rate to capture CO<sub>2</sub> in the carbonator to be attained. Therefore, the residence time control can be attained only by controlling solid hold-up in the regenerator. As a method to control the solid hold-up in the regenerator, staged gas feed, primarily air supply from the bottom of the calciner and secondary air supply to the middle part of the regenerator, is proposed [53].

In this study, the circulation rate and the residence time of solids in the regenerator (calciner) are measured to ascertain suitable operation conditions. The effect of gas feed staging to the regenerator on the solid residence time is evaluated.

### **1.5.2 Evaluation of CO and NO<sub>x</sub> emissions**

Burning different kinds of coal must be done to evaluate char formation and NO<sub>x</sub> emission in the regenerator. Moreover, discussing the transportation of unreacted char from regenerator to carbonator is necessary because different coals have different volatile matter contents. High-volatility coals yield less char, which is highly porous and reactive. The concentration of char in the bed material is expected to be low for high-volatility coals. However, volatile matter (combustible gas) will be generated quickly in the bottom of regenerator when coal is fed into the regenerator. Therefore, much heat will be generated there: hot spot might be formed at the bottom, although the temperature at the top might be lower for complete calcination.

In contrast, low-volatility coals form more char with low reactivity. That low reactivity and less volatile matter formation are beneficial for the suppression of hot spots in the regenerator. However, the char concentration will be high. For that reason, more char will be transported to the carbonator and will react with low O<sub>2</sub> concentration, forming CO there.

The objective of this work is to determine the effect of fuel characteristics (fixed carbon content) on CO emissions from the carbonator and NO<sub>x</sub> emission from regenerator.

### **1.5.3 Effect of diluent of O<sub>2</sub> on CO and NO<sub>x</sub> emissions**

As discussed above, CO emissions from the carbonator are regarded as strongly dependent

on char transportation from the regenerator. Furthermore, char concentration in the regenerator is expected to affect the emissions of NO<sub>x</sub> from the regenerator. In this study, the coal combustion behavior is investigated using a bench-scale dual-fluidized bed system in O<sub>2</sub>-enriched atmosphere. N<sub>2</sub> and CO<sub>2</sub> were used to dilute oxygen. The effect of diluents of O<sub>2</sub> on emissions of CO from the carbonator and NO<sub>x</sub> from the regenerator shall be clarified in this work.

#### **1.5.4 Effect of char on NO<sub>x</sub> formation**

To clarify the effect of char on the NO<sub>x</sub> formation in regenerator, reactors of two types with different solid circulating mode were used. One is the dual-fluidized bed (Dual-FB), the combination of a fast fluidized bed regenerator and a bubbling bed carbonator, a part of char was consumed in the carbonator. Another is the circulating fluidized bed combustor (single-CFBC) with simple controlling conditions to make unburned char circling from the combustor back to the combustor directly, which was operated by another research group in Shimizu Lab of Niigata University. The function of char on NO<sub>x</sub> formation will be clarified through two reactors burning the same coals under the same combustion conditions (temperature and fluidizing gas).

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### Coal Combustion in O<sub>2</sub>/N<sub>2</sub> atmosphere using a dual-fluidized bed system under Calcium

#### Looping process conditions

##### 2.1. Introduction

Chapter 1 presented discussion of the problems of using coal as a fuel in the Calcium Looping process. CO formation in the carbonator is likely to be released to the atmosphere, thereby polluting the environment. Moreover, CO<sub>2</sub> formation in the carbonator will consume free CaO. Therefore, the objective of this work is to evaluate the formation of CO and CO<sub>2</sub> within the carbonator caused by transportation of unreacted char particles from the regenerator. In addition, the evaluation of NO<sub>x</sub> formation in the regenerator is of concern because NO<sub>x</sub> can be converted to nitric acid during compression. In this work, a bench-scale solid circulation system was operated at elevated temperatures. Coal of three different kinds was burned in an inert quartz sand bed to evaluate CO and CO<sub>2</sub> formation without being affected by reactive CaO particles.

##### 2.2. Experiment

In this work, a laboratory-scale dual-fluidized bed solid circulation system was built and operated. First, the solid circulation rate and solid residence time in the regenerator (calciner) were measured to determine a suitable operation condition. The effect of gas feed staging to

the regenerator on the solid residence time was evaluated. After establishing stable solid circulation with known solid residence time in the carbonator, coal combustion experiments were conducted. To observe combustion behavior, inert quartz sand of 0.15 mm average size was used as the bed material for all experiments.

### **2.2.1 Experimental apparatus**

A laboratory-scale twin fluidized bed CO<sub>2</sub> separation reactor was built as presented schematically in Fig. 2-1. For the regenerator, a fast fluidized bed is regarded as suitable for oxyfuel combustion at high temperatures because vigorous solid mixing in the fast bed is expected to suppress hot-spot formation. For the carbonator, a bubbling fluidized bed is regarded as beneficial to achieve the necessary heat recovery [1]. The inner diameter of the fast bed regenerator was 2.2 cm. The height from the distributor at the bottom to the gas exit at the top was 1.93 m. The total pressure drop of regenerator ( $\Delta Pr$ ) was measured continuously as an indicator of total solid hold-up in the regenerator. A primary cyclone was installed at the top of the regenerator to capture particles from the regenerator and to transport the captured particles to the carbonator. The inner diameter of bubbling fluidized bed carbonator was 9.3 cm. Its height was 0.60 m. In the carbonator, an overflow tube was installed at 0.30 m above the gas distributor to keep the bed height constant. Particles from the carbonator were recirculated to the bottom of the regenerator through a loopseal. The reactors

were heated by electric heaters to attain the desired temperature.

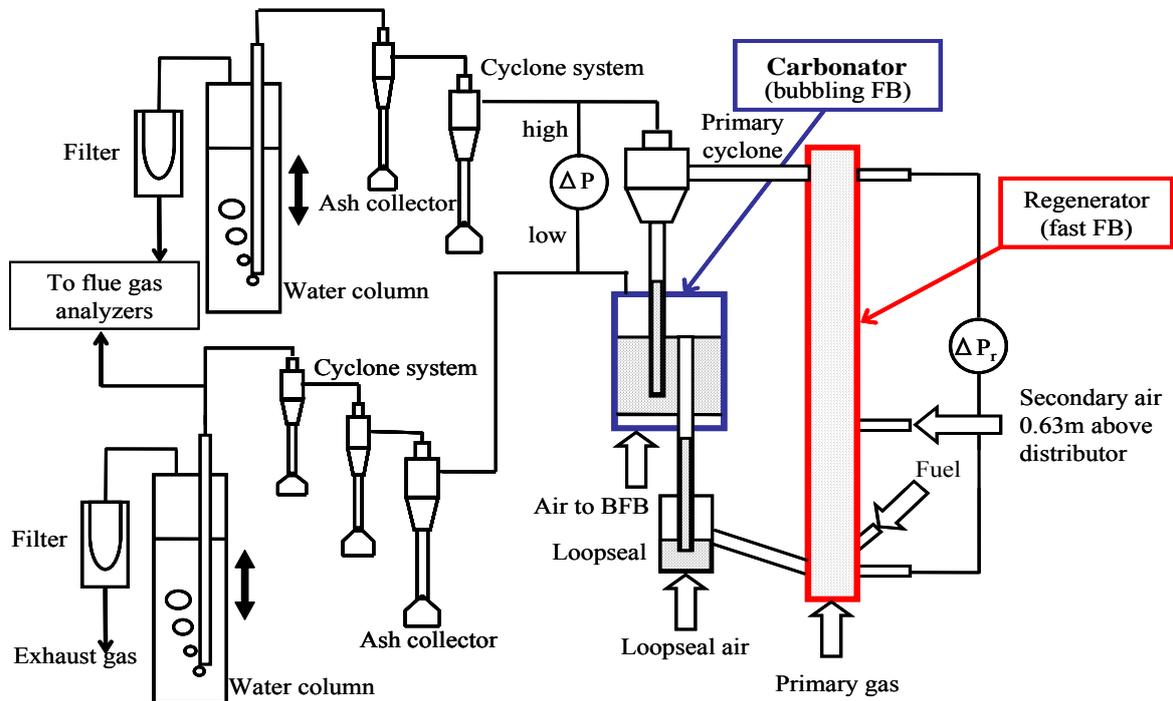


Fig. 2-1. Schematic diagram of experimental apparatus ( $\Delta P_r$ , total pressure drop of regenerator;  $\Delta P$ , pressure difference between exit of primary cyclone of regenerator and exit of carbonator).

This system had two separate gas outlets, a gas exit of primary cyclone of the regenerator and a gas exit at the top of the carbonator. Because the bottom of the primary cyclone was connected to the carbonator by a vertical standpipe, it was necessary to control the pressure balance between these two reactors in order to maintain stable solid circulation without gas leakage between two reactors. For this purpose, the pressure difference between the exit of primary cyclone of regenerator and the exit of carbonator ( $\Delta P$ ) was adjusted by changing the depth of the gas exit in the water columns that were installed at the end of the back-pass. By keeping  $\Delta P$  at 1–2 kPa, stable solid circulation without gas leakage was attained for the

present solid circulation system.

### **2.2.2 Measurement of solid circulation rate and solid residence time in the regenerator**

First, the solid circulation rate was measured under elevated temperature conditions without fuel combustion. Control of the solid residence time by staged gas feed to the regenerator was attempted. Primary gas was injected through the bottom of the regenerator. The secondary gas was injected at 0.63 m above the primary gas distributor. The ratio of the primary gas feed to total gas feed (PG/TG ratio) was varied from 1 (single-stage gas feed) to 0.5, in which PG included loopseal gas, primary gas, and fuel feeder gas. To maintain the solid circulation rate and fuel feed constant, feed rates of loopseal gas and fuel feeder gas were kept constant and solely primary gas feed rate was changed to vary PG/TG ratio. Air was used as the fluidizing gas for both the regenerator and carbonator. The temperature in the regenerator was maintained at  $973 \pm 20$  K. The superficial gas velocity above the secondary gas inlet was fixed at 2.75 m/s at this temperature. The carbonator temperature was maintained at  $873 \pm 10$  K; the superficial gas velocity was 0.16 m/s at this temperature.

Two techniques were used to measure the solid circulation rate. One was a transient method to observe the change in solid hold-up after stopping solid circulation. Another was a tracer injection method during steady solid circulation.

#### *Method 1: Transient method*

Particle circulation was stopped by stopping gas feed to the loopseal; the gas feed to the loopseal was switched to the regenerator to maintain the total gas feed rate in the regenerator constant. Then the change in pressure drop of regenerator was measured. Since the relationship between the pressure drop across the regenerator  $\Delta P_r$  and the total amount of particles in regenerator  $W_s$  is given by Eq. (2-1)

$$\Delta P_r = gW_s / S_r. \quad (2-1)$$

the pressure drop across the regenerator decreased with the decrease in solids in the regenerator due to the carry-over of bed material after stopping solid circulation.

As explained later, the pressure drop across regenerator decreased with time according to the Eq. (2-2) as

$$\ln(\Delta P_r) = \ln(\Delta P_{r,0}) - \alpha t. \quad (2-2)$$

where  $\alpha$  stands for the decay constant and  $\Delta P_{r,0}$  represents pressure drop at  $t = 0$ . The inverse of  $\alpha$  gives the average residence time of solids in the regenerator. The relation given as Eq. (2-2) shows that the decreasing rate of pressure drop across regenerator was proportional to the pressure drop itself, i.e., the solid carry-over rate was proportional to the total amount of solids in the regenerator. Because the pressure drop across regenerator is given by total amount of particles in regenerator, the cross sectional area of regenerator  $S_r$ , and acceleration of gravity  $g$ , the relation between pressure drop across the regenerator and solid carry-over rate is given as

$$d\Delta P_r / dt = (g / S_r) (dW_s / dt) = -\alpha\Delta P_r. \quad (2-3)$$

With solid feed, the change in the total amount of solids in the regenerator is given by the balance between solid feed rate  $r_f$  and the solid carry-over rate as

$$dW_s / dt = r_f - \alpha\Delta P_r S_r / g. \quad (2-4)$$

Under steady-state (constant pressure drop) conditions, the solid feed rate to the regenerator is equal to the solid carry-over rate. Therefore, the solid circulation rate under steady state  $r_c$  is given as

$$r_c = \alpha\Delta P_r S_r / g. \quad (2-5)$$

*Method 2: Measurement of solid down-flow velocity in standpipe by tracer injection*

A batch of cold quartz sand was injected into the overflow tube in the carbonator under steady solid circulating conditions. Temperature of the downflowing solids in the standpipe was measured continuously using three thermocouples (Fig. 2-2). When cold tracer particles reached a thermocouple, a change in temperature was observed. Time lag  $\Delta t$  of the temperature change peak is the time of the particle movement from one thermocouple to the next thermocouple. Consequently, the descending velocity  $V_d$  of particles is given by  $\Delta t$  and the distance between two thermocouples  $L$  as

$$V_d = L / \Delta t. \quad (2-6)$$

The particle circulation rate  $r_c$  is given by the descending velocity, the bulk density of the

particles  $\rho_b$ , and the cross sectional area of standpipe  $S_p$  as

$$r_c = S_p \rho_b V_d. \quad (2-7)$$

During the experiments, the pressure difference between two temperature measurement points was measured to ensure that the thermocouples were placed in the moving bed, not in the vacant region above the upper surface of the moving bed.

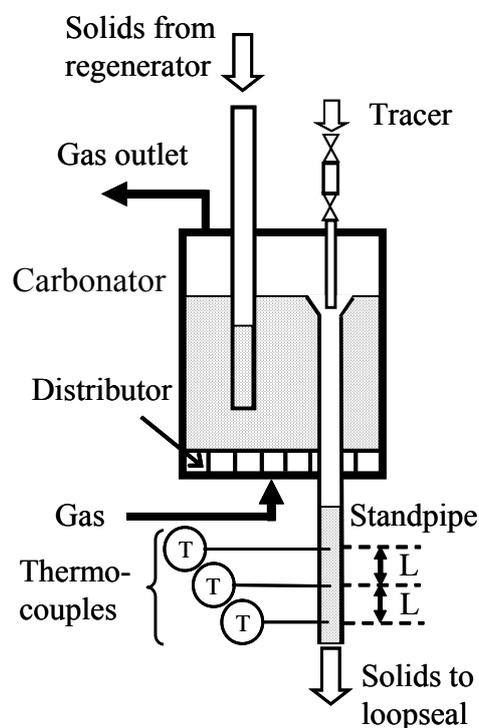


Fig. 2-2. Schematic diagram of the testing method (carbonator and standpipe).

### 2.2.3 Coal combustion experiments

In this study, coal of three kinds with different volatile matter contents was used as fuel, high-volatility bituminous (HVB), medium-volatility bituminous (MVB), and semi-anthracite

(SA). The coal particle size was 297–1000  $\mu\text{m}$ . Analyses of those coals are presented in [Table 2-1](#).

The fuel was burned in an oxygen-enriched atmosphere in the regenerator under a staged gas feeding condition. The ratio of primary gas to total gas (PG/TG ratio) was fixed at 0.5 to attain longer residence time of solids, as shown later. The regenerator temperature was maintained at  $1223 \pm 10$  K. That in the carbonator was kept at  $873 \pm 10$  K. The oxygen-enriched air was produced by mixing pure oxygen and air. The overall oxygen concentration in the gas fed into the regenerator, including primary gas, secondary gas, loopseal gas, and pneumatic conveying gas, was 30% by volume. As a matter of principle, the staged gas feed with oxygen-enrichment has wide freedom of choice of oxygen concentration in each feed gas as well as gas staging ratio. In this work, oxygen enrichment of the primary gas ( $\text{O}_2$  concentration 51%) was adopted to enhance fuel burning in solid dense region at the bottom of the regenerator except for one experiment. For the case of oxygen enrichment to solely primary gas, air was used as the secondary gas, loopseal gas and pneumatic conveying gas. For one experiment, oxygen enrichment to the secondary gas was also conducted. For this case, the ratio of pure oxygen addition to primary gas to secondary gas was varied from 1:0 to 0:1.

Fuel was fed continuously through a rotary feeder, conveyed pneumatically in the air stream, and injected into the bottom of the regenerator. During coal feeding, the coal feed rate

was controlled to attain the desired O<sub>2</sub> concentration in the flue gas from the regenerator (typically at 2–5%). The CO and CO<sub>2</sub> concentrations in the flue gas from the carbonator were measured using NDIR absorption to evaluate the amount of char combustion in the carbonator. The flue gas from the regenerator was also analyzed for O<sub>2</sub> and NO<sub>x</sub> using a magnetic oxygen analyzer for O<sub>2</sub> and chemical luminescence for NO<sub>x</sub>. Some flue gas from the regenerator was stored in Tedler gas bags. Concentrations of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> in the gas were measured using gas chromatography with a thermal conductivity detector.

**Table 2-1** Analyses of fuels

	Ultimate analysis (daf.%)					Proximate analysis (wt.%)			
	C	H	O	N	S	Ash	V.M. <sup>a</sup>	F.C. <sup>b</sup>	Moisture
High-volatility bituminous coal (HVB)	78.1	6.3	13.4	1.3	1.0	14.3	39.2	41.2	5.3
Medium-volatility bituminous coal (MVB)	85.9	4.9	7.0	1.7	0.5	15.0	26.3	56.2	2.5
Semi-anthracite (SA)	89.7	4.2	3.6	1.9	0.7	10.9	15.5	70.7	2.8

<sup>a</sup> Volatile matter; <sup>b</sup> Fixed carbon

## 2.3. Results and discussion

### 2.3.1 Solid circulation rate and solid residence time in the regenerator

As a method to control the solid hold-up in the regenerator, a staged gas feed was proposed.

Figure 2-3 portrays the decrease in pressure drop across the regenerator after stopping solid circulation by stopping gas feed to the loopseal. After stopping solid circulation, the pressure

drop decreased with time because of the carry-over of bed material. The straight-line relation between time and  $\log(\Delta P_r)$  shows that the decay of the pressure drop was well approximated by first-order decay equation (Eq. (2-2)). In addition, this relation shows that the solid circulation rate was proportional to the pressure drop across the regenerator. From the slope of the line portrayed in Fig. 2-3, the average residence time of solids in the regenerator was calculated. Under a single-stage gas feed condition ( $P_G/T_G=1$ ), the residence time was as short as 12 s. The gas velocity of 2.75 m/s under a single stage gas feed condition was regarded as sufficiently higher than the terminal velocity (about 0.7 m/s) of the present bed material. The decrease in the primary gas feed rate to  $P_G/T_G=0.7$  had no influence on the residence time. However, an additional decrease in the primary gas feed rate to  $P_G/T_G=0.5$  increased the residence time to about 40 s. The control of gas feed staging was found to be an effective modification to control the solid residence time.

Figure 2-4 presents a typical result of the response of the thermocouples when a batch of cold sand was fed into the standpipe where hot recycled solids were flowing. When the cold sand tracer reached a thermocouple, decreased temperature was observed. Such a negative temperature peak appeared at first at the thermocouple located at the top, then at the next one located at 10 cm below the top one, and finally appeared at the bottom one located at 20 cm below the top. With the progress of time, the cold tracer particles were heated by the surrounding hot solids, thereby the height of the negative temperature peak became smaller.

Nevertheless, the clear negative peak remained visible at the thermocouple located at the lowest position. From the time lag of the appearance of the peak time,  $\Delta t$ , the solid circulation rate was estimated using Eqs. (2-6) and (2-7).

Results of circulation rate measurement by tracer injection method are depicted in Fig. 2-5 which presents a comparison with the solid circulation rate estimated from the solid residence time by Eq. (2-5). Although the results obtained using the tracer injection showed wide scattering of the data, both techniques showed similar results. When the solid circulation rate was compared at a given pressure drop across the regenerator, i.e., at a given total solid hold-up in the regenerator, a decrease in primary gas feed ratio from single-stage mode to slight staging of PG/TG = 0.7 had no influence on the solid circulation rate. Further decrease in the primary gas ratio to PG/TG = 0.5 decreased the solid circulation rate at a given pressure drop across the regenerator. This low solid circulation rate at a given solid hold-up at a gas staging condition of PG/TG = 0.5 indicates that the residence time of solids in the regenerator was lengthy as

$$\tau = W_s/r_c = \Delta P_r S_r / g r_c. \quad (2-8)$$

A staged gas feed was identified as a promising modification that can control the solid residence time in the regenerator only by changing gas feed.

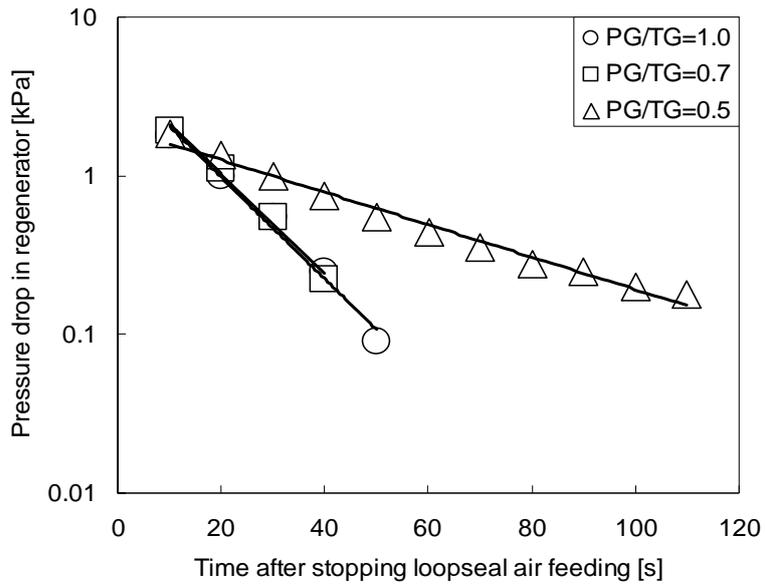


Fig. 2-3. Decrease in pressure drop across the regenerator after stopping loopseal gas feed.

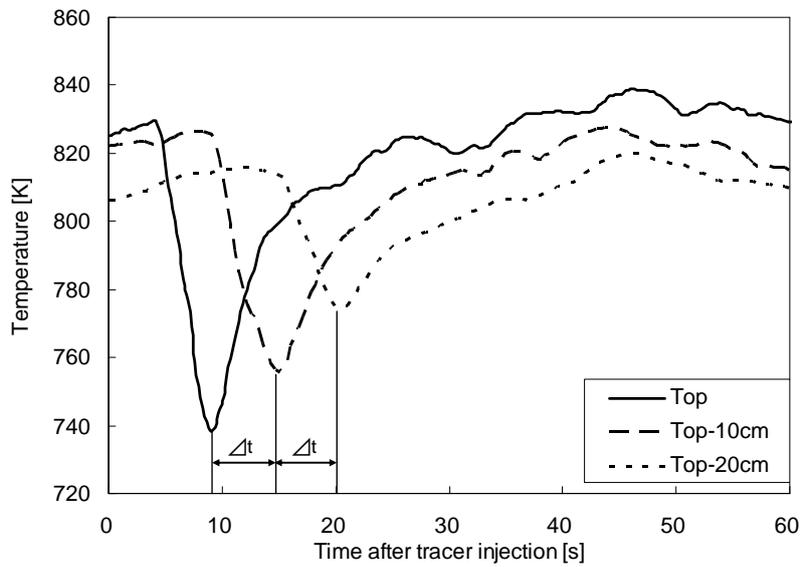


Fig. 2-4. Response of temperature in standpipe after injecting tracer (cold sand).

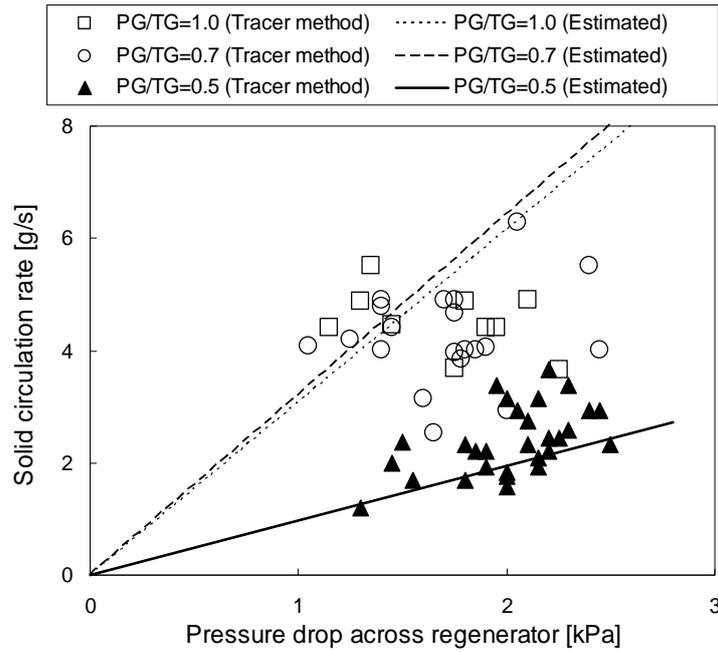


Fig. 2-5. Comparison of bed material circulation rates measured using tracer injection (keys) and those estimated from the solid residence time (lines).

## 2.3.2 Coal combustion

### 2.3.2.1 Coal combustion with oxygen enrichment to only primary gas

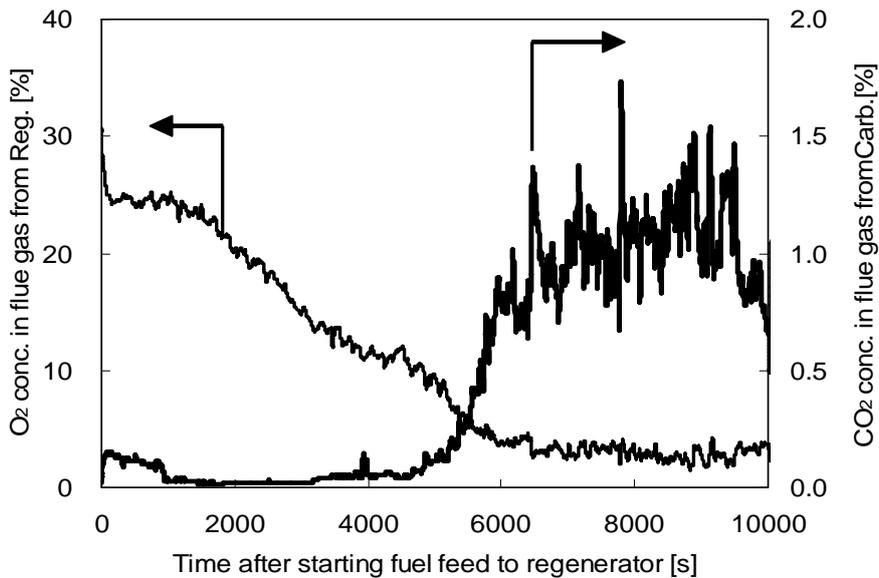


Fig. 2-6. Typical transient change in O<sub>2</sub> concentration in flue gas from the regenerator (Reg.) and CO<sub>2</sub> concentration in flue gas from the carbonator (Carb.) after starting the fuel feed to the regenerator (Fuel: HVB).

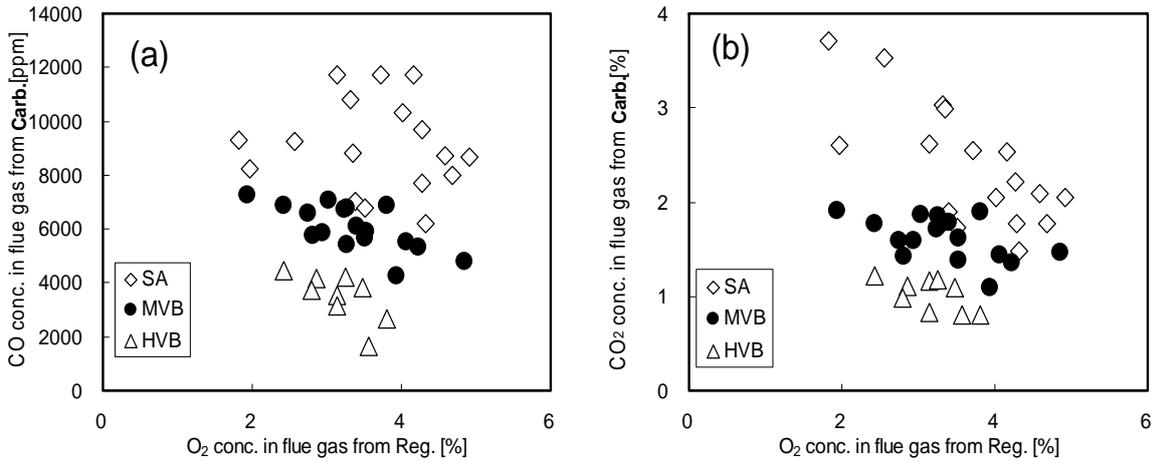
During coal combustion, formation of CO and CO<sub>2</sub> in the carbonator from the unburned char transported from the regenerator was evaluated. Inert sand was used as bed material instead of CaO. [Figure 2-6](#) shows typical transient changes in O<sub>2</sub> concentration in the flue gas from the regenerator and CO<sub>2</sub> concentration in the flue gas from the carbonator after starting coal feed into regenerator. Oxygen concentration in regenerator flue gas decreased while coal feed rate increased little-by-little until the temperature in the regenerator reached  $1223 \pm 10\text{K}$  and O<sub>2</sub> concentration in regenerator flue gas reached a desired value (2–5%). Simultaneously char particles accumulated in the bed material so that desired oxygen consumption in the regenerator was attained. The produced char particles were also transported to the carbonator. Therefore, they formed CO and CO<sub>2</sub> there. In [Fig. 2-6](#), the system was found to attain stable condition with nearly constant oxygen consumption in the regenerator and CO<sub>2</sub> formation in the carbonator at about 6000 s. In the following sections, combustion behavior of coal under steady state combustion will be shown.

There were two possible sources of CO<sub>2</sub> and CO in the gas from the carbonator. One was combustion of char in the carbonator. The other was leakage of flue gas from the regenerator. Therefore, gas leakage from the regenerator to the carbonator was evaluated using gas tracer technique. Inert helium was mixed with the feed gas to the regenerator. The He concentration in the produced gas was measured using gas chromatography with a thermal conductivity detector. [Table 2-2](#) shows a typical result. The helium concentration in the regenerator flue gas

was 1.83%, whereas that in the carbonator flue gas was only 0.01%. However, CO<sub>2</sub> concentration in the regenerator flue gas was about 24% whereas that in the carbonator flue gas was 2.4%. If the main source of CO<sub>2</sub> in the flue gas from the carbonator was attributable to the gas leakage, then concentration of CO<sub>2</sub> in the carbonator flue gas must be about 0.1 % (1/183 of 24%). Such high CO<sub>2</sub> concentration of 2.4% in the carbonator flue gas cannot be explained by gas leakage. A similar discussion is applicable to the source of CO in the carbonator flue gas. Therefore, it was concluded that CO<sub>2</sub> and CO found in the carbonator flue gas derived from combustion of unreacted char transported from the regenerator.

**Table 2-2** Evaluation of gas leakage from regenerator to carbonator measured using He tracer (Semi-anthracite coal, O<sub>2</sub> in flue gas from regenerator = 3.6%)

Component	Concentration in flue gas [Vol.%]	
	Regenerator flue gas	Carbonator flue gas
CO <sub>2</sub>	23.93	2.43
CO	0.08	0.76
He	1.83	0.01



**Fig. 2-7.** Effect of fuel type on CO and CO<sub>2</sub> emissions in flue gas from carbonator (a, CO; b, CO<sub>2</sub>).

Figure 2-7 shows the change in CO and CO<sub>2</sub> concentrations in the flue gas from the carbonator with the change in O<sub>2</sub> concentration in the flue gas from the regenerator for coal of three kinds. Flue gas O<sub>2</sub> concentration was controlled by changing fuel feed rate without changing gas feed rate to keep the fluidization condition constant. With decreasing O<sub>2</sub> concentration in the flue gas from the regenerator, CO and CO<sub>2</sub> emissions from the carbonator increased. This increased CO and CO<sub>2</sub> is attributable to the increased char hold-up in the regenerator: higher carbon loading is necessary to decrease O<sub>2</sub> concentration in the flue gas, i.e., to enhance oxygen consumption in the regenerator. Consequently, more char particles are transported to the carbonator with circulating solids when lower O<sub>2</sub> concentration in the produced gas was attained.

The results presented in Fig. 2-7 also show that more CO and CO<sub>2</sub> were formed in the carbonator when high carbon content fuel was burned. The amount of remaining char in the circulating solids was affected by the volatile matter contents in coal. High-volatility coal yields less char. In addition, the char from high-volatility coal is highly porous and reactive. Therefore, less char hold-up in the regenerator was sufficient to attain required oxygen consumption in the regenerator; the portion of the oxygen consumed by the volatile matter increases, whereas low char concentration was sufficient to attain oxygen consumption because of the high reactivity. In contrast, low-volatility coals formed more char, of which the reactivity was low. Therefore, higher char hold-up is necessary and more char transportation

to the carbonator occurred.

Higher emissions of CO and CO<sub>2</sub> observed for lower volatile matter fuel are disadvantageous for pollution control and reduction of the energy penalty. Since carbon monoxide is an air pollutant, emissions of CO to the atmosphere must be avoided. Formation of CO<sub>2</sub> in the carbonator will consume free CaO to form CaCO<sub>3</sub>. Therefore, increased CaCO<sub>3</sub> formation is anticipated to increase the requirement of CaO feed rate to the carbonator and the necessity of extra fuel and pure oxygen fed to the regenerator to decompose extra CaCO<sub>3</sub>. However, the low reactivity and less volatile matter formation are regarded as beneficial for suppression of hot spots in the regenerator operated under high-temperature and high-oxygen partial pressure conditions. Although higher oxygen concentration in the feed gas is beneficial for suppressing the energy penalty because it will reduce the heat loss from the regenerator in the form of sensible heat of the diluents (recirculated CO<sub>2</sub>) [1], combustion of coal in higher oxygen concentration atmosphere has a risk of ash fusion due to high combustion rate. For the engineering design of the regenerator, both carry over of unreacted char and prevention of ash fusion should be taken into consideration.

Fig. 2-8 shows the effect of fuel type on conversion of fuel-N to NO<sub>x</sub> in the regenerator. Conversion of fuel-N to NO<sub>x</sub> increased concomitantly with increasing oxygen concentration in the flue gas. In addition, it increased concomitantly with increasing volatile matter content of fuel. These results are explainable qualitatively by the influence of fuel type and operating

conditions on char hold-up in the regenerator. With increasing volatile matter contents of coal, the char hold-up in the regenerator decreased, as indicated by the decrease in CO and CO<sub>2</sub> formation in the carbonator. Additionally, increased O<sub>2</sub> concentration in the regenerator flue gas reflects the reduced char hold-up in the regenerator. Char is a reductant of NO as well as a catalyst of NO reduction by reducing gases such as CO [2-6]. Therefore, the increased char hold-up in the regenerator is regarded as beneficial for reducing NO<sub>x</sub> in the regenerator. The importance of char hold-up in the regenerator for the emissions of NO<sub>x</sub> is also reflected by the strong correlation between conversion of fuel-N to NO<sub>x</sub> in the regenerator and formation of CO and CO<sub>2</sub> in the carbonator (Fig. 2-9). Conversion of fuel-N to NO<sub>x</sub> in the regenerator can be expressed as a function of total concentration of CO and CO<sub>2</sub> in the gas from the carbonator irrespective of the coal type and flue gas oxygen concentration.

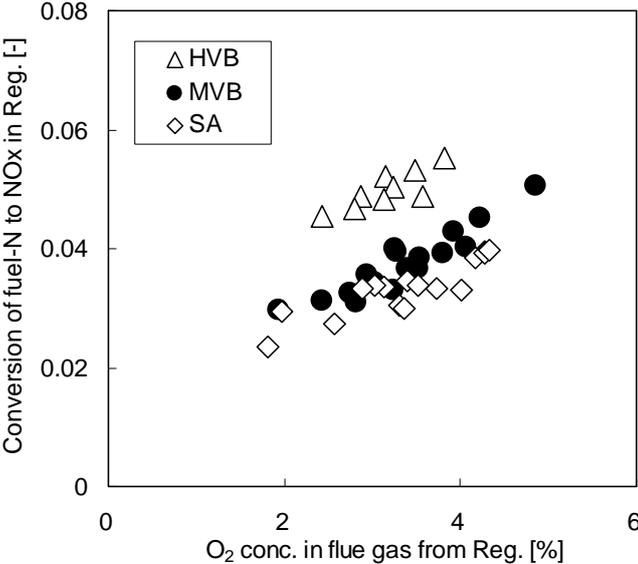


Fig. 2-8. Effect of fuel type on conversion of fuel-N to NO<sub>x</sub> in the regenerator.

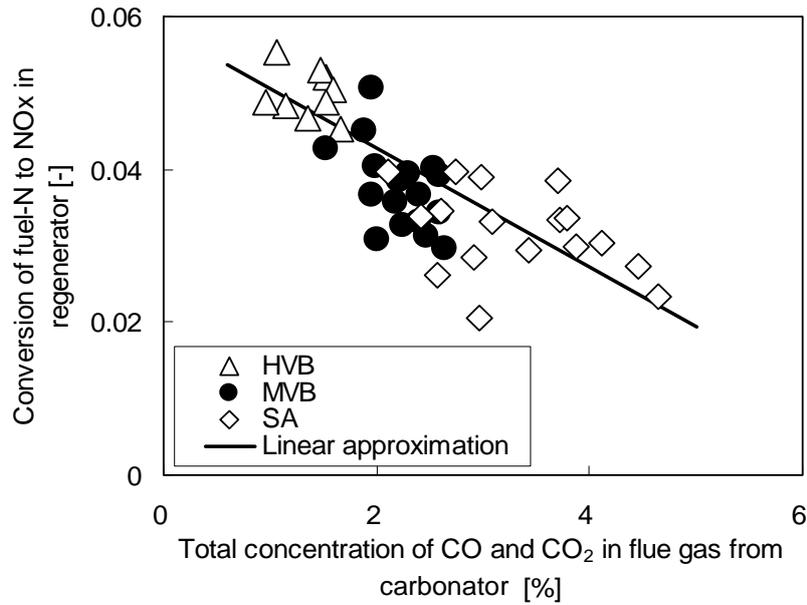


Fig. 2-9. Relation between total concentration of CO and CO<sub>2</sub> in flue gas from carbonator and conversion of fuel-N to NO<sub>x</sub> in the regenerator.

### 2.3.2.2 Effect of oxygen enrichment of secondary gas

In the CaL process, pure oxygen is fed into the regenerator to burn fuel to supply heat for CaCO<sub>3</sub> decomposition. Under staged gas feed conditions, it is possible to change the ratio of pure oxygen supply as a primary gas to that as a secondary gas, keeping the stoichiometric oxygen ratio constant. In this work, the ratio of primary oxygen supply to the secondary oxygen supply was changed.

Figure 2-10 shows the change in CO and CO<sub>2</sub> concentration in flue gas from carbonator with the change in the O<sub>2</sub> enrichment of primary gas and secondary gas. First, all the pure O<sub>2</sub> for O<sub>2</sub> enrichment was fed into the primary gas (PG-O<sub>2</sub> : SG-O<sub>2</sub> = 1 : 0). Then the same amount of O<sub>2</sub> was fed into both the primary gas and secondary gas (PG-O<sub>2</sub> : SG-O<sub>2</sub> = 0.5 : 0.5). Finally, all the pure O<sub>2</sub> was fed into the secondary gas (PG-O<sub>2</sub> : SG-O<sub>2</sub> = 0 : 1). However,

no clear influence on the location of oxygen enrichment on the formation of CO<sub>2</sub> and CO in the carbonator was observed. Consequently, char transportation from the regenerator to the carbonator was unaffected by the location of the oxygen enrichment.

However, Fig. 2-11 shows that the location of the oxygen enrichment clearly influenced the formation of NO<sub>x</sub> in the regenerator. With increasing oxygen enrichment to the secondary gas, NO<sub>x</sub> emissions increased. This result is explainable by the change in location of NO<sub>x</sub> formation and reduction in the regenerator. It is widely accepted that NO<sub>x</sub> is formed in the lower part of the regenerator and that it is gradually reduced in the upper part during coal combustion using air [7]. If oxygen enrichment is conducted in the upper part, more combustion of fuel is expected to occur in the upper part. Thereby NO<sub>x</sub> reduction in the upper part is regarded as less. Consequently, more combustion in the lower part by oxygen enrichment of the primary gas is regarded as beneficial. Although oxygen enrichment of solely the primary gas is favorable for NO<sub>x</sub> abatement, it must be emphasized that overly high oxygen concentration in the bottom may lead hot-spot formation there. Optimization of the feed of oxygen in primary and secondary gases still demands further study.

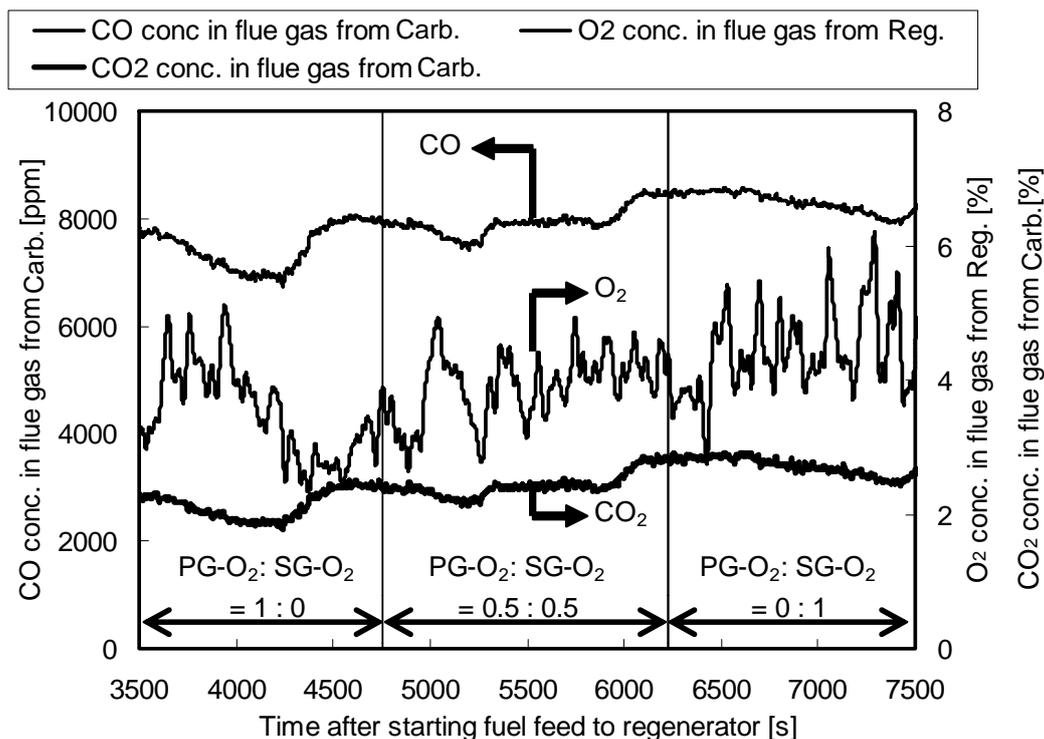


Fig. 2-10. Effect of ratio of pure O<sub>2</sub> enrichment of primary gas (PG-O<sub>2</sub>) to that of secondary gas (SG-O<sub>2</sub>) on the concentration of CO and CO<sub>2</sub> in flue gas from carbonator (Fuel : SA).

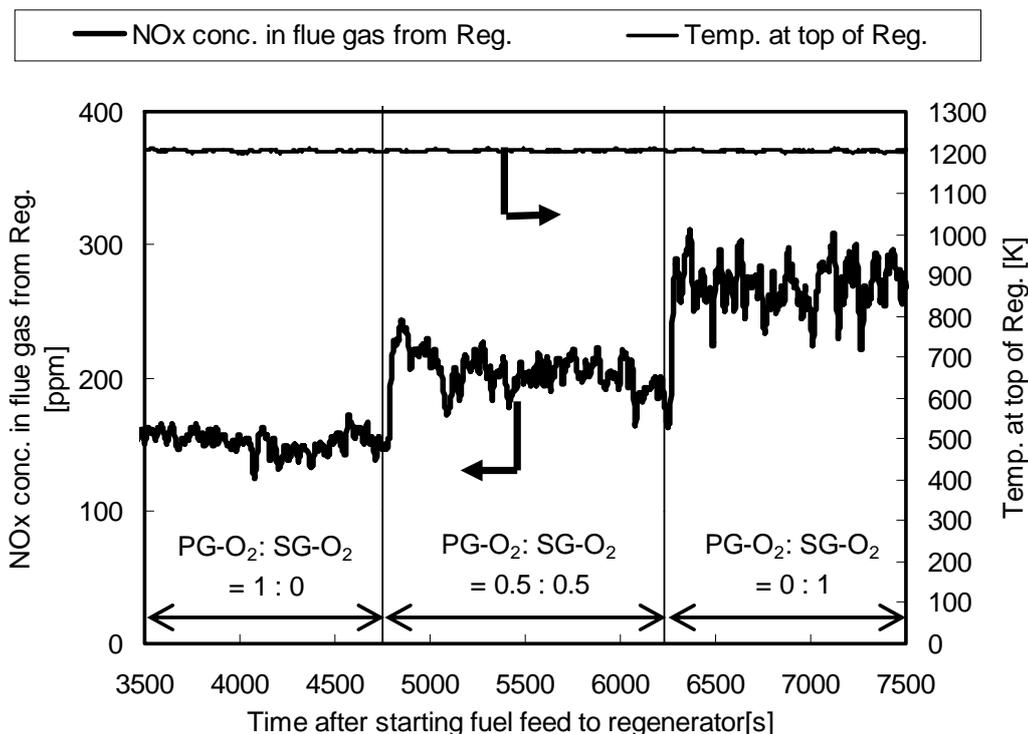


Fig. 2-11. Effect of ratio of pure O<sub>2</sub> enrichment of primary gas (PG-O<sub>2</sub>) to that of secondary gas (SG-O<sub>2</sub>) on the concentration of NO<sub>x</sub> in flue gas from the regenerator and temperature at the top of the regenerator (Fuel : SA).

## 2.4. Conclusion

A dual-fluidized bed solid circulation system was constructed and operated under Calcium Looping process temperature conditions. Two methods for measurement of the particles circulating rate were proposed. The residence time of solids in the regenerator is controllable using a two-stage gas feed, i.e., by changing the ratio of primary gas feed rate to the total gas flow rate. Coal combustion behavior in the regenerator was investigated by burning coal of three kinds with different volatile matter. High-volatility content coal was found to be favorable for suppressing formation of CO and CO<sub>2</sub> in the carbonator because of less char transportation from the regenerator, but such fuel released more NO<sub>x</sub> from regenerator than low-volatility fuels. Oxygen enrichment of solely the primary gas was found to be favorable for the suppression of NO<sub>x</sub> emissions.

## Nomenclature

$g$  acceleration of gravity (m/s<sup>2</sup>)

$L$  distance between two temperature measurement points (m)

$\Delta P$  pressure difference between exit of primary cyclone of regenerator and exit of carbonator (Pa)

$\Delta P_r$  total pressure drop of regenerator (Pa)

$r_c$  solid circulation rate under steady state (kg/s)

$r_f$  solid feed rate to regenerator (kg/s)

$S_r$  cross sectional area of regenerator (m<sup>2</sup>)

$S_p$  cross sectional area of standpipe (m<sup>2</sup>)

$t$  time (s)

$\Delta t$  time lag of temperature change peak between two measurement points (s)

$V_d$  descending velocity of solids in standpipe (m/s)

$W_s$  total amount of particle in regenerator (kg)

### **Greek letters**

$\alpha$  decay constant of pressure drop across regenerator after stopping solid circulation

(1/s)

$\rho_b$  bulk density of particles (kg/m<sup>3</sup>)

$\tau$  average residence time of solids in regenerator (s)

### **Abbreviations**

F.C. fixed carbon

HVB high-volatility bituminous coal

MVB medium-volatility bituminous coal

PG primary gas feed rate to regenerator

SA semi-anthracite

SG secondary gas feed to regenerator

TG total gas feed rate to regenerator

V.M. volatile matter

## References

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### **Coal combustion in a simulation atmosphere of flue gas recirculation from regenerator under Calcium Looping process conditions**

#### **3.1. Introduction**

In Chapter 2, coal combustion experiments were conducted under a temperature condition of the regenerator using an inert sand bed and oxygen-enriched air ( $O_2-N_2$  mixture), which revealed that unreacted char particles were transported from the regenerator to the carbonator. However, the effect of diluents of oxygen on char transportation from the regenerator to carbonator and  $NO_x$  formation in the regenerator remains unclear.

An  $O_2/CO_2$  atmosphere was adopted to simulate flue gas recycling to the regenerator, with the aim of obtaining the high  $CO_2$  concentration flue gas from the regenerator, and of avoiding hot-spot formation during combustion in an  $O_2$ -enriched atmosphere in the regenerator. The objective of this work is to evaluate the effects of diluents ( $CO_2$  or  $N_2$ ) of oxygen on the formation of CO and  $CO_2$  within the carbonator and  $NO_x$  formation in the regenerator while burning coal of three kinds using a bench-scale dual-fluidized bed experimental apparatus.

## **3.2. Experiment**

### **3.2.1 Experimental apparatus**

A dual-fluidized bed solid circulation system was employed for the present work. The detail of the experimental apparatus and procedure is described in Chapter 2. Coal of three kinds with different volatile matter contents was used as fuel, high-volatility bituminous (HVB), medium-volatility bituminous (MVB), and semi-anthracite (SA). Analyses of those coals are presented in Chapter 2. The coal particle size was 297–1000  $\mu\text{m}$ . To observe combustion behavior, inert quartz sand of 0.15 mm average size was used as the bed material for all experiments. By using inert sand bed, formation of  $\text{CO}_2$  in the carbonator could be evaluated by measuring  $\text{CO}_2$  concentration in the flue gas from the carbonator.

### **3.2.2 Coal combustion experiments**

The fuel was burned in an oxygen-enriched atmosphere in the regenerator under a staged gas feeding condition. The secondary gas was fed from a nozzle at 0.63 m above the bottom. The ratio of secondary gas to total gas (SG/TG ratio) was fixed at 0.5 to attain longer residence time of solids was obtained in Chapter 2. Coal was combusted in  $\text{O}_2/\text{N}_2$  and  $\text{O}_2/\text{CO}_2$  atmosphere conditions respectively shown in [Table 3-1](#). In each condition, the overall  $\text{O}_2$  concentration in the gas fed into the regenerator was 30% by volume. For  $\text{O}_2/\text{N}_2$  mixture, oxygen-enriched air ( $\text{O}_2$  concentration = 51%) was fed to the bottom of the regenerator as

primary gas, whereas air was used for the secondary gas, loopseal gas and gas for pneumatic conveying for fuel. O<sub>2</sub> / CO<sub>2</sub> atmosphere was adopted to simulate flue gas recycle to the regenerator. O<sub>2</sub> diluted by the CO<sub>2</sub> was fed as the loopseal gas, primary gas and secondary gas. Oxygen concentration in the secondary gas and loopseal gas was 21%. For pneumatic conveying of fuel, only CO<sub>2</sub> was employed for safety reason. Oxygen concentration in the primary gas from the bottom was 60% so that the concentration of the mixture of the primary gas and pneumatic conveying gas became the same as that for O<sub>2</sub> / N<sub>2</sub> mixture.

**Table 3-1** Gas feeding mode of regenerator (Secondary gas /Total gas = 0.5)

	Overall O <sub>2</sub> conc. in gas	Prim.	Sec.	Loopseal	Feeder
O <sub>2</sub> /N <sub>2</sub>	30 vol-%	Air+O <sub>2</sub>	Air	Air	Air
O <sub>2</sub> /CO <sub>2</sub>	30 vol-%	CO <sub>2</sub> +O <sub>2</sub>	CO <sub>2</sub> +O <sub>2</sub>	CO <sub>2</sub> +O <sub>2</sub>	CO <sub>2</sub>

Air was used as the fluidizing gas for the carbonator. When char particles are transported to the carbonator, they are oxidized to form CO and CO<sub>2</sub> there. By measuring concentrations of CO and CO<sub>2</sub> in the flue gas from the carbonator, char transportation can be evaluated. However, CO<sub>2</sub> and CO in the flue gas from the regenerator can also be transported to the carbonator with the circulating solids. Thus correction of the experimental results by eliminating gas leakage from the regenerator to the carbonator is needed. To evaluate gas leakage from the regenerator to the carbonator, a small amount of He was mixed with the feed

gas to the regenerator as tracer. The gas samples from the carbonator and the regenerator were analyzed by conventional analysis methods same as Chapter 2.

### 3.3. Results and discussion

#### 3.3.1 Char transportation from regenerator to carbonator

Table 3-2 shows typical results of gas leakage measurement using He tracer. Small amount of He was detected in the flue gas of the carbonator, i.e. a part of the CO<sub>2</sub> in the carbonator flue gas came from the gas leakage from regenerator to the carbonator. From the concentration of He in the carbonator flue gas and concentrations of CO<sub>2</sub> and He in the regenerator flue gas, the contribution of the gas leakage was eliminated and net formation of CO<sub>2</sub> in the carbonator was evaluated.

Table 3-2 Typical results of gas leakage from regenerator to carbonator measured using He tracer and correction of the CO<sub>2</sub> concentration in the carbonator flue gas (Unit: vol-%)

Fuel (Feed gas to regenerator)	Regenerator flue gas		Carbonator flue gas		
	Raw data		Raw data	After correction	
	CO <sub>2</sub>	He	CO <sub>2</sub>	He	CO <sub>2</sub>
SA (O <sub>2</sub> /N <sub>2</sub> ) [Chapter 2 Table 2-2]	23.93	1.83	2.43	0.01	2.30
SA (O <sub>2</sub> /CO <sub>2</sub> )	92.31	2.18	2.33	0.002	2.25
HVB (O <sub>2</sub> /CO <sub>2</sub> )	93.19	2.09	2.43	0.03	1.09

Fig. 3-1 shows the effect of fuel type, oxygen concentration of the regenerator flue gas, and diluents of fed gas to the regenerator. More CO and CO<sub>2</sub> were formed in carbonator when

higher carbon content fuel was combusted both in  $O_2 / N_2$  and  $O_2 / CO_2$  atmospheres. The amount of remaining char in the circulating solids was affected by the fixed carbon contents in coal; high fixed carbon content coal yields more char. In addition, CO and  $CO_2$  emission from the carbonator decreased with increasing the  $O_2$  concentration in the flue gas from the regenerator. This result is also explained by the decrease in unburned char in high  $O_2$  concentration atmosphere. However, the type of diluent gas ( $CO_2$  or  $N_2$ ) had negligible effect on the emissions of CO and  $CO_2$  from the carbonator, i.e. amount of char yield which was transported from the regenerator to the carbonator was not affected by the diluent.

### 3.3.2 NO<sub>x</sub> emissions from the regenerator

Fig. 3-2 shows the effect of fuel type and diluents gas ( $N_2$  or  $CO_2$ ) on NO<sub>x</sub> emissions from the regenerator. For high carbon content coal (SA), NO<sub>x</sub> emissions for  $O_2 / CO_2$  atmosphere were remarkably lower than those for  $O_2 / N_2$  atmosphere. With decreasing carbon content of fuel, the influence of diluents on the NO<sub>x</sub> formation decreased; for low carbon content coal (HVB), NO<sub>x</sub> emissions for  $O_2 / CO_2$  atmosphere were only slightly lower than those from  $O_2 / N_2$  atmosphere, comparing at a practical flue gas  $O_2$  concentration of 3%. Lower NO<sub>x</sub> emissions for  $O_2 / CO_2$  atmosphere than for  $O_2 / N_2$  atmosphere were also reported during circulating fluidized bed combustion of medium-volatility bituminous coal (FC/VM = 1.9) and anthracite (FC/VM = 9.0) [1]. These results suggest that the interaction between char and

CO<sub>2</sub> plays significant role in reducing NO<sub>x</sub> emissions.

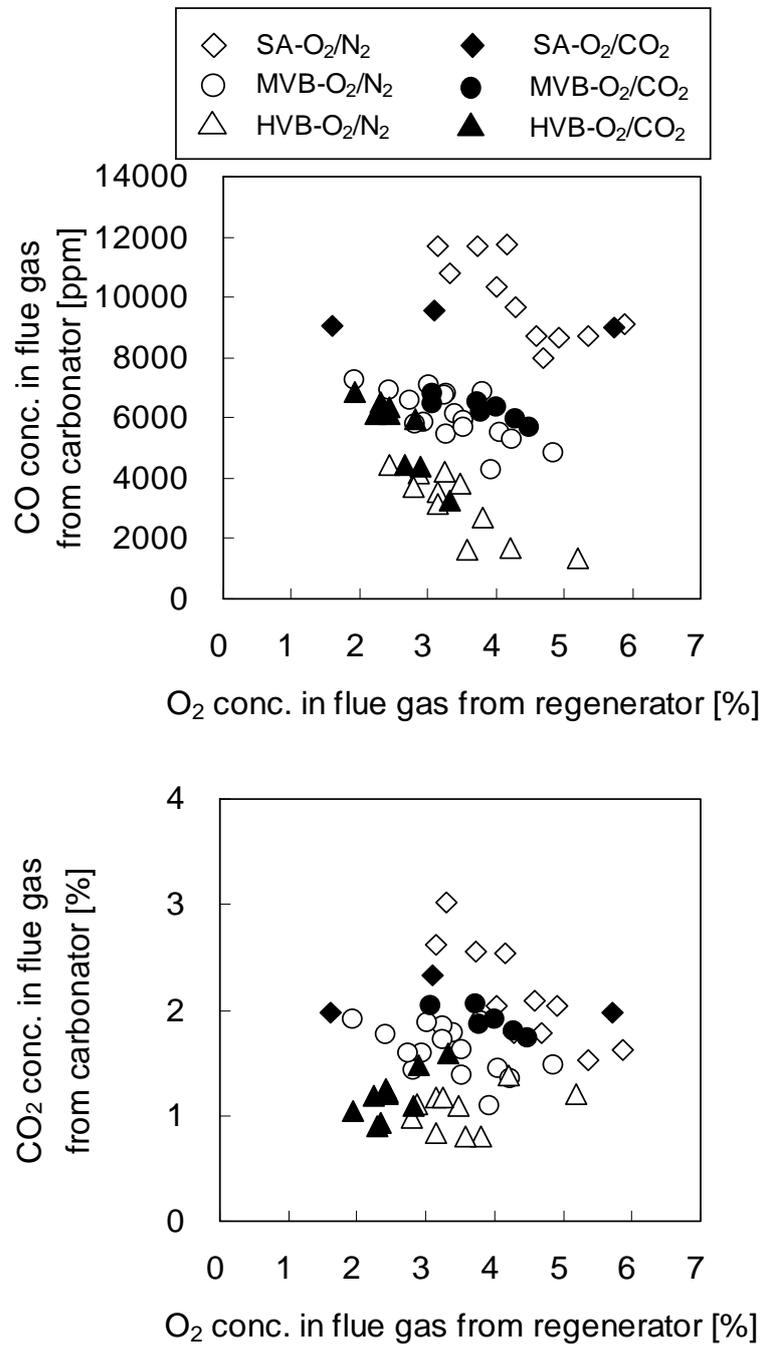


Fig. 3-1. Effect of fuel type on CO and CO<sub>2</sub> emissions from carbonator during coal combustion in regenerator using O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub> mixtures.

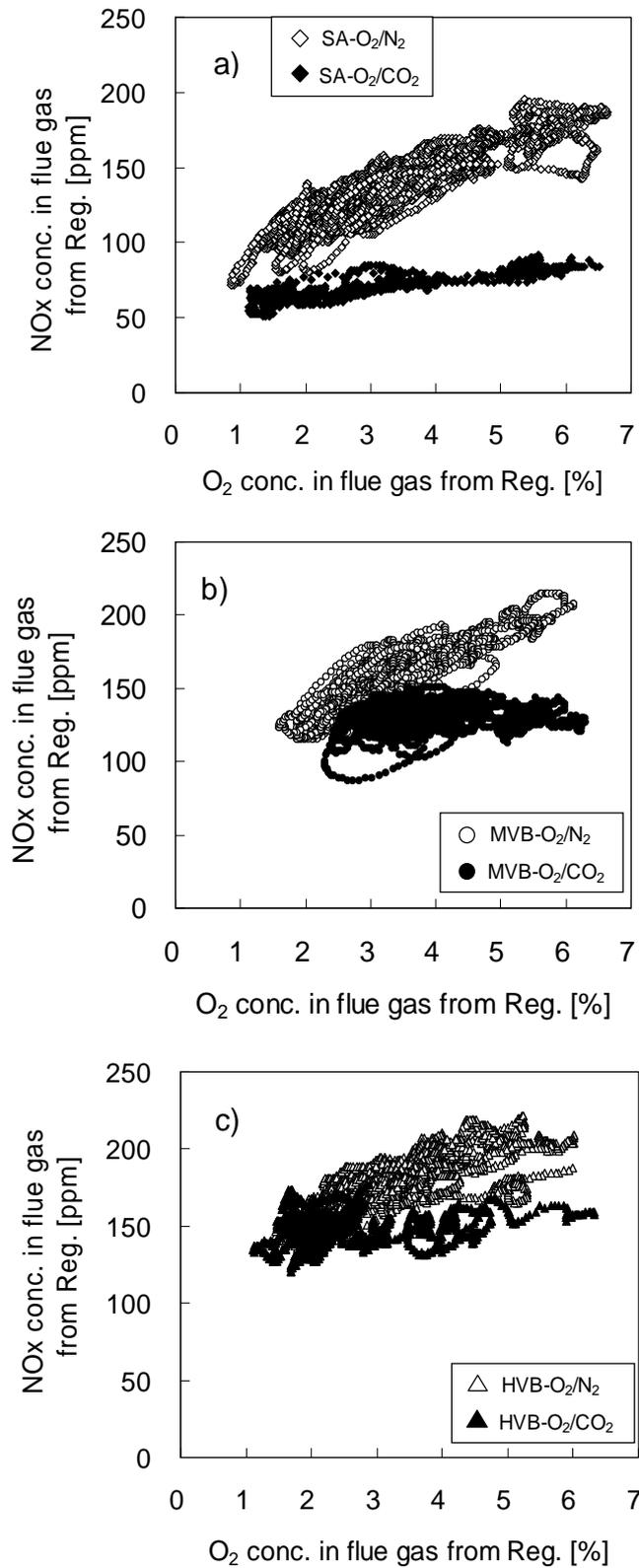


Fig. 3-2. Effect of fuel type on NOx emissions from regenerator during combustion in O<sub>2</sub>/ N<sub>2</sub> and O<sub>2</sub>/ CO<sub>2</sub> atmospheres (Fuel: a: SA; b: MVB; c: HVB).

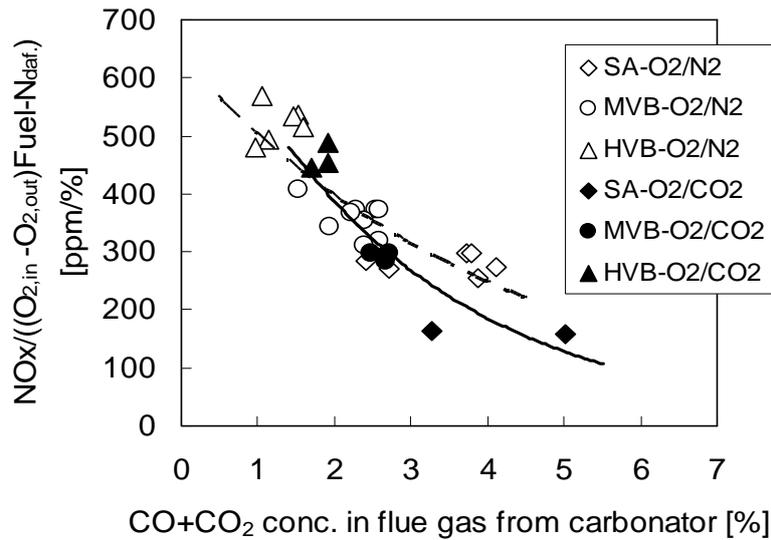


Fig. 3-3. Effect of char transportation on the NOx formation in regenerator in O<sub>2</sub> / N<sub>2</sub> and O<sub>2</sub> / CO<sub>2</sub> atmospheres (O<sub>2</sub> in flue gas of Reg. =3.5±0.5%).

Fig. 3-3 shows the effect of total formation of CO and CO<sub>2</sub> in the carbonator on the NOx formation in regenerator in O<sub>2</sub> / N<sub>2</sub> and O<sub>2</sub> / CO<sub>2</sub> atmospheres. Here NOx concentration (in [ppm]) was normalized by the O<sub>2</sub> consumption (difference in O<sub>2</sub> concentration between feed gas and flue gas, in [%]) and nitrogen content of fuel (Fuel-N<sub>daf</sub>, in [kg / kg-daf]). Formation of NOx in the regenerator decreased with increasing formation of CO and CO<sub>2</sub> in the carbonator for both diluents. These results also suggest the importance of NOx-char reactions in the regenerator. Char is known to be a reductant of NOx (Eq.(3-1)) as well as a catalyst to reduce NOx by CO (Eq. (3-2)) [2-4] as:



Thus increased char hold-up in the regenerator is considered to be favorable for NOx

reduction, though the formation of CO and CO<sub>2</sub> in the carbonator increases because of increased char concentration in the circulating solids. In addition, high CO<sub>2</sub> concentration is favorable for enhancing the catalytic reduction of NO<sub>x</sub> (Eq.(3-2)) because CO is formed through CO<sub>2</sub> reduction by solid carbon (Eq. (3-3) [5] as:



This reaction pathway gives an explanation of more remarkable effect of CO<sub>2</sub> on NO<sub>x</sub> reduction for higher carbon content fuel (Fig.3-2); the contribution of char to the reduction of NO<sub>x</sub> in the regenerator was more pronounced for higher carbon fuel, thus the NO<sub>x</sub> reduction by CO catalyzed by char was more enhanced by the presence of CO<sub>2</sub> for higher carbon fuel.

### 3.4. Conclusion

A dual-fluidized bed solid circulation system was operated under Calcium Looping process temperature conditions. Transportation of unburned char from the regenerator to the carbonator was found to be a source of CO<sub>2</sub> and CO formation in the carbonator. Effect of fuel type on CO<sub>2</sub> and CO formation in the carbonator was clearly observed. The type of oxygen diluent for the regenerator had no influence on char transportation. However, the diluent influenced NO<sub>x</sub> emissions, especially for high-carbon content fuel.

### Abbreviations

F.C. fixed carbon

HVB high-volatility bituminous coal

MVB medium-volatility bituminous coal

PG primary gas feed rate to regenerator

SA semi-anthracite

SG secondary gas feed to regenerator

TG total gas feed rate to regenerator

V.M. volatile matter

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Fuel 2001;80:1259-72.



### **Role of char in NO<sub>x</sub> formation during coal combustion at a regenerator temperature of the Calcium Looping process**

#### **4.1. Introduction**

In Chapter 2, emissions of NO<sub>x</sub> from the regenerator and emissions of CO and CO<sub>2</sub> from the carbonator were evaluated for coal combustion in an O<sub>2</sub>/N<sub>2</sub> atmosphere using a dual-fluidized bed system with inert bed material. NO<sub>x</sub> was formed in the regenerator during coal combustion. In addition, a certain amount of CO and CO<sub>2</sub> was detected in the flue gas from the carbonator. A relation was found between conversion of fuel-N to NO<sub>x</sub> in the regenerator and emissions of CO and CO<sub>2</sub> from the carbonator, suggesting that the amount of char in the regenerator affected NO<sub>x</sub> emissions.

The objective of this work is to evaluate the effect of char on NO<sub>x</sub> formation in the regenerator during coal combustion in oxygen-enriched air under regenerator temperature conditions of the CaL process. Reactor of two types were used: dual-fluidized bed system (dual-FB) and conventional single circulating fluidized bed combustor (single-CFBC), which was operated by another research group in Shimizu Lab of Niigata University. In dual-FB, some char was consumed in the carbonator (Fig. 4-1-(a)), whereas in single-CFBC, all of the fuel was burned in a single fluidized bed reactor by recycling the entrained char back to the combustor (Fig. 4-1-(b)). Coals of three different kinds were burned in an inert quartz sand

bed to evaluate CO and CO<sub>2</sub> formation without being affected by reactive CaO particles. By comparing the emissions of NO<sub>x</sub> from these two reactor systems, the role of char on NO<sub>x</sub> formation in the regenerator is discussed.

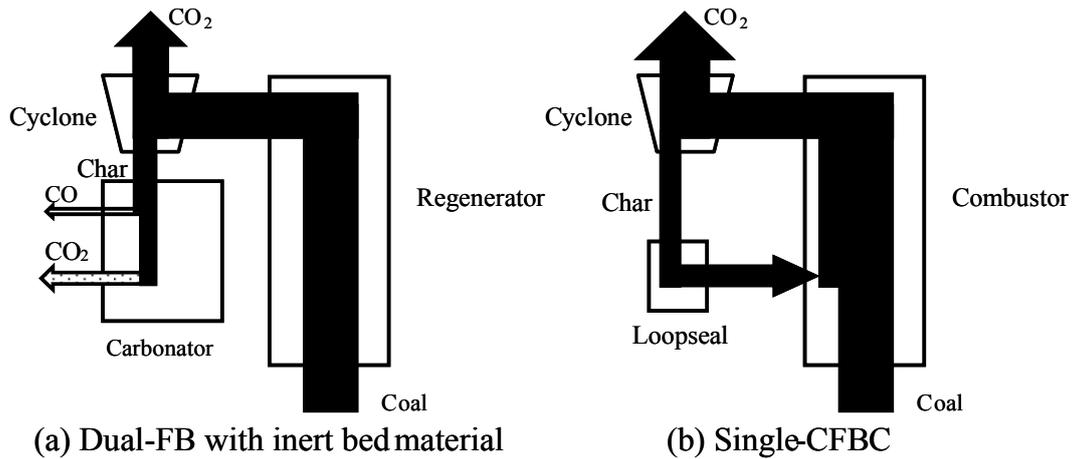
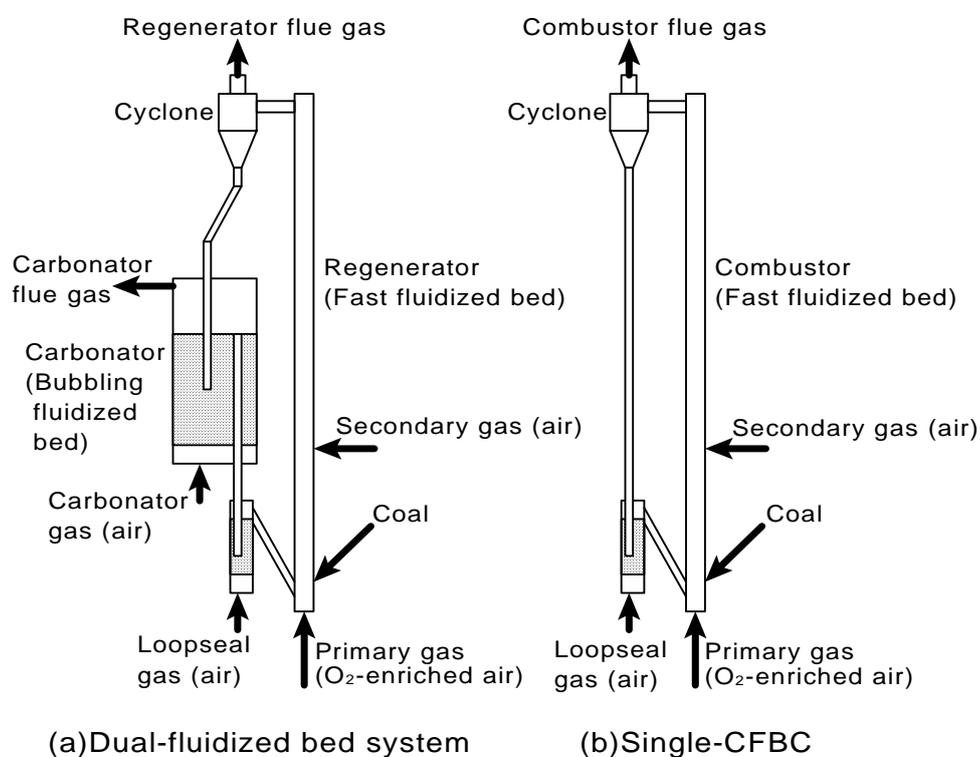


Fig. 4-1. Schematic diagrams of material flow of carbon in (a) dual-fluidized bed with inert bed material, and (b) conventional single circulating fluidized bed combustor [1].

## 4.2. Experiment

Fig.4-2 illustrates schematic diagrams of (a) dual-fluidized bed system and (b) single circulating fluidized bed combustor. The design of the fast fluidized bed for coal combustion was identical between dual-FB and single-CFBC. The difference between two reactor systems was the carbonator. The dual-FB was equipped with a bubbling fluidized bed carbonator, into which recirculated solids were introduced and a part of char in the solids was burned to form CO and CO<sub>2</sub>. The single-CFBC was equipped only loopseal that recirculates solids from cyclone to the bottom of the fast fluidized bed.

The detail of the dual-FB is described in Chapter 2. The inner diameter and the height of the regenerator of the dual-fluidized bed system were 2.2 cm and 1.93 m, respectively. Primary gas was introduced from the bottom of the fast fluidized bed. Secondary gas was introduced to the fast fluidized bed at 0.63 m above the distributor. Inert sand of average size of 0.15 mm was employed as bed material. The solids in the regenerator was transported to the upper part of the regenerator, separated from the flue gas by a cyclone, and introduced into the carbonator. The carbonator was a bubbling fluidized bed of 9.3 cm in inner diameter and the bed height was fixed at 0.30 m by an overflow tube. The particles from the overflow tube were introduced to the loopseal before they were recirculated back to the bottom of the regenerator.



**Fig.4-2.** Schematic diagrams of (a) dual-fluidized bed system and (b) single circulating fluidized bed combustor employed for the present experimental work[1].

The experimental condition, gas feed staging and oxygen enrichment in the regenerator, was chosen so that circulating solids could attain long residence time and low NO<sub>x</sub> emissions, as described elsewhere in Chapter 2. The fluidizing gas for the regenerator was oxygen-enriched air. The ratio of primary gas (including gas from the bottom, loopseal gas, and the gas for pneumatic transportation of fuel) to the total gas feed rate was fixed at 0.5. All of the pure oxygen for oxygen enrichment was mixed to the primary gas fed from the bottom of the regenerator. For the secondary gas, air was used. The overall oxygen concentration in the gas fed into the fast fluidized bed, including primary gas, secondary gas, loopseal gas, and pneumatic conveying gas, was 30% by volume. The temperature in the regenerator was measured at two points, 0.33 m and 1.23 m above the distributor. These temperatures were controlled within a range 1213 – 1233 K by using electric furnaces. The superficial gas velocity above the secondary gas inlet was fixed at 2.75 m/s at this temperature. For carbonator, air was fed as fluidizing gas. The carbonator temperature was maintained at 873 K. The superficial gas velocity was 0.16 m/s at this temperature. The operating condition of the combustor (fast fluidized bed) of the present single-CFBC was identical to the regenerator of the dual-fluidized bed system.

In this study, coal of three kinds with different volatile matter contents was used as fuel, high-volatility bituminous (HVB), medium-volatility bituminous (MVB), and semi-anthracite (SA). The coal particle size was 297–1000 μm. Analyses of those coals are presented in

Chapter 2 (Table 2-1). Fuel was fed continuously through a rotary feeder, conveyed pneumatically in the air stream, and injected into the bottom of the regenerator. During coal feeding, the coal feed rate was controlled to attain the desired O<sub>2</sub> concentration in the flue gas from the regenerator (typically at 2–5%).

The CO and CO<sub>2</sub> concentrations in the flue gas from the carbonator were measured using NDIR absorption to evaluate the amount of char combustion in the carbonator. The flue gas from the fast fluidized bed was also analyzed for O<sub>2</sub> and NO<sub>x</sub> using a magnetic oxygen analyzer for O<sub>2</sub> and chemical luminescence for NO<sub>x</sub>. Some flue gas from the fast fluidized bed was stored in Tedler gas bags. Concentrations of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> in the gas were measured using gas chromatography with a thermal conductivity detector.

#### **4.3. Evaluation of char burn-up in the carbonator and in the regenerator of dual-FB system**

In the present dual-FB system, particles were transported to the carbonator and oxidized to form CO<sub>2</sub> and CO there. In contrast, char particles were oxidized solely in the fast fluidized bed of the present single-CFBC. Thus amount of char burned in the regenerator of the dual-FB is lower than that in the single-CFBC. In this work, overall char combustion rates in the regenerator and carbonator of the dual-FB were evaluated from the concentrations of CO<sub>2</sub> and CO in the flue gases and feed rates of air to the system. To simplify the calculation, the

following assumptions were adopted as depicted in Fig. 4-3.

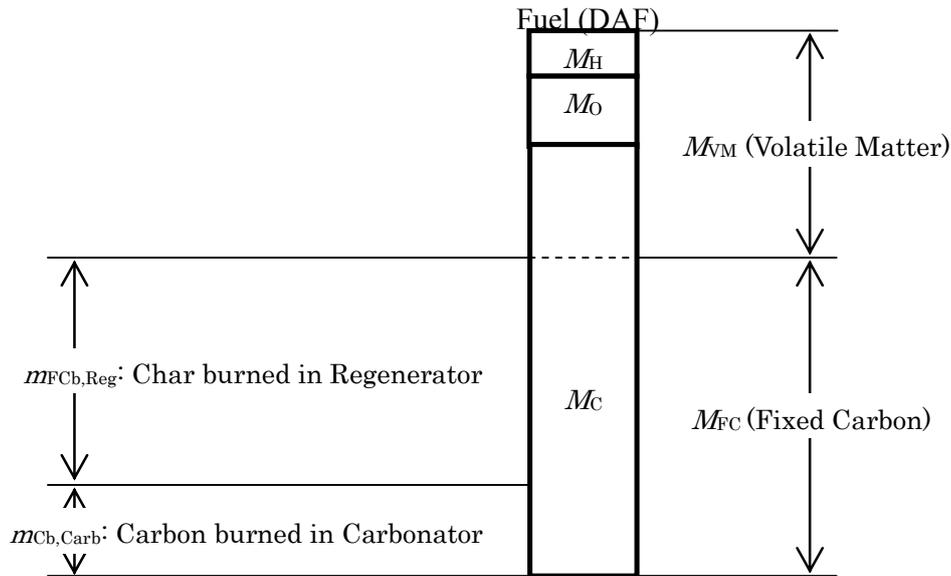


Fig.4-3. Schematic diagram of relationship among carbon burned in carbonator, char (solid carbon) burned in regenerator, ultimate analysis of fuel (contents of C, H, and O in combustible part of fuel), and proximate analysis of fuel (FC and VM contents) assumed for the analysis of carbon flow of present dual-fluidized bed system.

- When coal is introduced in the combustor, coal is decomposed to form char and volatile matter.
- Char consists of only carbon. Char yield is the same as that of fixed carbon (Chapter 2 Table 2-1).
- The rest part of carbon and other combustible components (H and O) are converted to volatile matter.
- Fuel is completely burned up in these systems, i.e. loss of carbon by fly ash entrainment is negligible.
- Gas leakage between regenerator and carbonator is negligible.
- For single-CFBC, combustion occurred only in the fast fluidized bed and combustion in

the loopseal was negligible.

For the dual-fluidized bed system, a part of char is transported from the regenerator to the carbonator and the transported char was oxidized to CO and CO<sub>2</sub>. With formation of CO in the carbonator, total gas flow rate of the flue gas from the carbonator slightly increases in comparison to the air feed rate,  $f_{IN,Air}$ . Thus the molar fraction of CO in the flue gas from the carbonator,  $y_{OUT,CO}$  [mol/mol], is given by CO formation rate in the carbonator,  $f_{OUT,CO}$ , and  $f_{IN,Air}$ , as:

$$y_{OUT,CO} = \frac{f_{OUT,CO}}{f_{IN,Air} + \frac{1}{2} f_{OUT,CO}}. \quad (4-1)$$

Thus CO formation rate in the carbonator is given as:

$$f_{OUT,CO} = \frac{2y_{OUT,CO}f_{IN,Air}}{2 - y_{OUT,CO}}. \quad (4-2)$$

Similarly, CO<sub>2</sub> formation rate in the carbonator,  $f_{OUT,CO_2}$ , is given by the molar fraction of CO<sub>2</sub>,  $y_{OUT,CO_2}$ ,  $f_{OUT,CO}$ , and  $f_{IN,Air}$  as:

$$f_{OUT,CO_2} = y_{OUT,CO_2} \left( 1 + \frac{y_{OUT,CO}}{(2 - y_{OUT,CO})} \right) f_{IN,Air}. \quad (4-3)$$

In the regenerator, formation rate of CO was not taken into consideration because CO concentration in the flue gas from the regenerator was negligible in comparison to CO<sub>2</sub> concentration. Flow rate of CO<sub>2</sub> in the flue gas from regenerator,  $F_{OUT,CO_2}$ , is given by molar fraction of CO<sub>2</sub> in the flue gas,  $Y_{OUT,CO_2}$  [mol/mol], molar fraction of N<sub>2</sub> in the flue gas,  $Y_{OUT,N_2}$ , and total air flow rate to the regenerator,  $F_{IN,Air}$ , as:

$$F_{OUT,CO_2} = \frac{Y_{OUT,CO_2}}{Y_{OUT,N_2}} F_{IN,N_2} = \frac{Y_{OUT,CO_2}}{Y_{OUT,N_2}} \left( \frac{79}{100} F_{IN,Air} \right). \quad (4-4)$$

Fraction of carbon oxidized in the carbonator in total carbon burn-up in this dual-fluidized bed system,  $Z_{C,Carb}$ , is thus given as:

$$Z_{C,Carb} = \frac{f_{OUT,CO_2} + f_{OUT,CO}}{f_{OUT,CO_2} + f_{OUT,CO} + F_{OUT,CO_2}} \quad (4-5)$$

Fig. 4-3 illustrates the relationship among the fractions of carbon burned respectively in the regenerator and in the carbonator, ultimate analysis of fuel (content of C, H, and O in combustible part of fuel), and proximate analysis of fuel. For 1 kg of combustible part of coal,  $M_{C,FC}$  [kg] of carbon is converted to char (solid carbon). The rest of the carbon ( $M_C - M_{FC}$ ) is converted to volatile matter with hydrogen and oxygen in the fuel. A fraction of carbon converted to char in the regenerator is partly oxidized in the regenerator and unreacted part is transported to the carbonator as discussed above. Thus the fraction of carbon consumed in the carbonator,  $m_{Cb,Carb}$ , is given by carbon content in the fuel and  $Z_{C,Carb}$  as:

$$m_{Cb,Carb} = Z_{C,Carb} M_C \quad (4-6)$$

The fraction of char burned in the regenerator,  $m_{FCb,Reg}$ , is given by fixed carbon content and  $m_{Cb,Carb}$ , as:

$$m_{FCb,Reg} = M_{FC} - m_{Cb,Carb} = M_{FC} - Z_{C,Carb} M_C \quad (4-7)$$

During the operation, oxygen concentration of flue gas from the regenerator was controlled at a desired range (typically 2 – 5 %) by changing the coal feed rate. With the entrainment of char to the carbonator, more fuel feed was needed than the case without char entrainment. Thus contribution of volatile matter to the total oxygen consumption increased with

increasing char entrainment. The ratio of  $m_{\text{FCb,Reg}}$  to volatile matter content of fuel,  $m_{\text{FCb,Reg}}/M_{\text{VM}}$ , gives the net ratio of fixed carbon to the volatile matter both of which actually burned in the regenerator. In other words, carbon consumption in the carbonator changed the ratio of fixed carbon to the volatile matter of fuel burned in the regenerator without changing char property and volatile matter composition.

In the present single-CFBC, the entrained char particles were captured by the cyclone and recycled back to the combustor. Therefore, the ratio of fixed carbon to the volatile matter both of which actually burned in the regenerator was the same as that of the fuel ( $= M_{\text{FC}}/M_{\text{VM}}$ ).

#### **4.4. Results and Discussion**

##### **4.4.1 Comparison of NO<sub>x</sub> emission behavior between dual-fluidized bed system and single-CFBC**

Figure 4-4 shows NO<sub>x</sub> emission per unit oxygen concentration difference between the inlet gas and the outlet gas of fast fluidized bed (i.e. oxygen consumption in the fast fluidized bed). The emissions of NO<sub>x</sub> from the regenerator of dual-FB were found to be higher than those from the combustor of single-CFBC. The difference in NO<sub>x</sub> emissions between dual-FB and single-CFBC was more remarkable for higher carbon content fuel. For high-volatility bituminous coal, however, the difference in NO<sub>x</sub> emissions between two reactors was nearly within the range of scattering of the data.

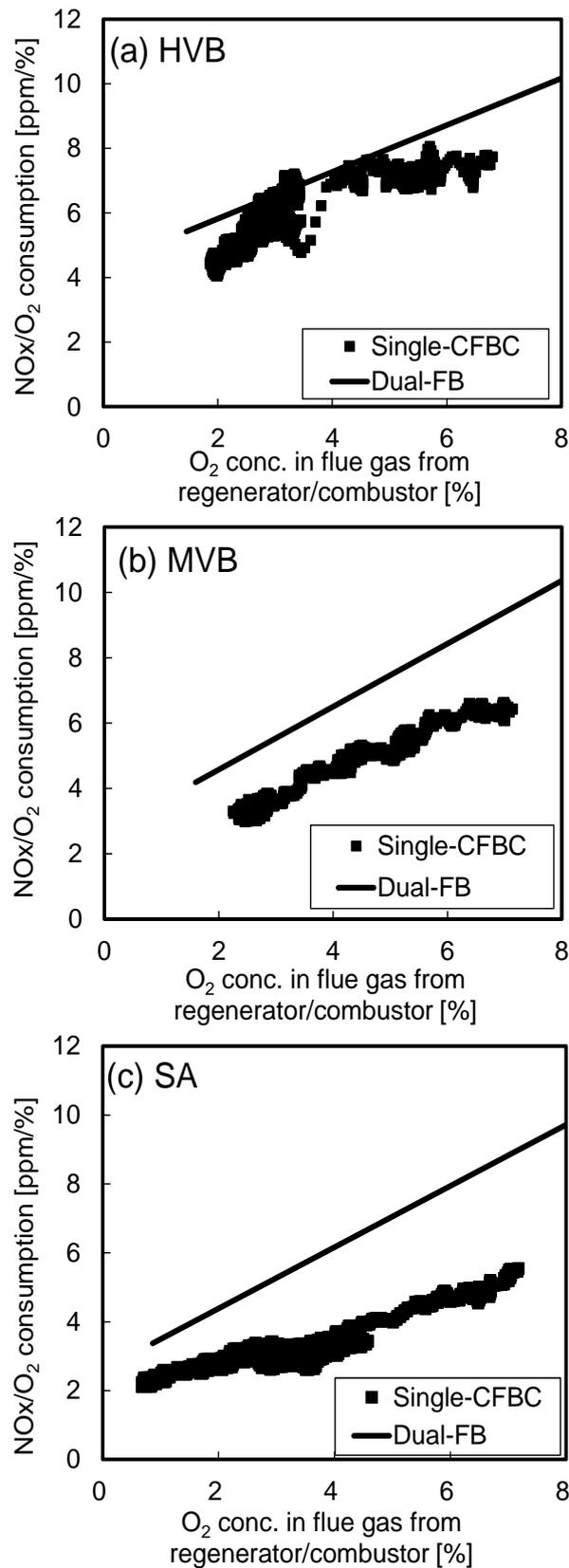


Fig.4-4. Comparison of NOx emissions from regenerator / combustor per unit oxygen consumption between dual-fluidized bed system and single-CFBC [1] for three coals with different coal rank. ((a) HVB; (b) MVB; (c) SA).

Figure 4-5 shows the conversion of fuel-N to NO<sub>x</sub>. The conversion to NO<sub>x</sub> was found to decrease with increasing fixed carbon content of fuel. A similar trend has already been reported in the study of Chapter 2 for this dual-fluidized bed system. Also it was reported that the char transportation from the regenerator to the carbonator of the dual-fluidized bed system had significant influence on NO<sub>x</sub> emissions from the regenerator; NO<sub>x</sub> emissions decreased with increasing char transportation to the carbonator were detailed in Chapter 2.

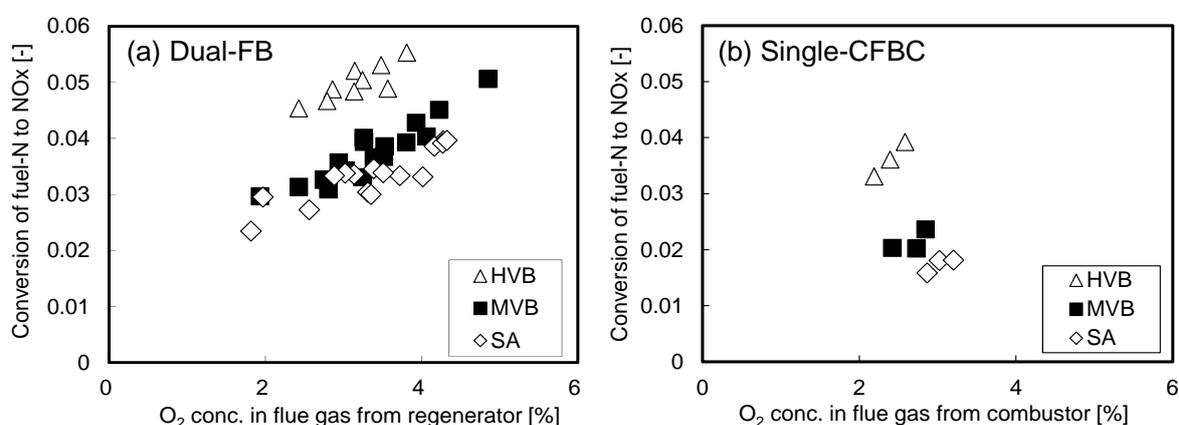


Fig.4-5. Effect of fuel type on conversion of fuel-N to NO<sub>x</sub> during coal combustion in regenerator / combustor ((a) Dual-fluidized bed combustor [Chapter 2 (Fig.2-8)]; (b) Single circulating fluidized bed combustor[1]).

The effects of reactor type and fuel type on NO<sub>x</sub> emissions mentioned above strongly suggest that char hold-up in the fast fluidized beds (regenerator and combustor) has strong influence on the emissions of NO<sub>x</sub>. Char is a reductant of NO as well as a catalyst of NO reduction by reducing gases such as CO [2 – 6]. Therefore, the increased char hold-up in the regenerator / combustor is regarded as beneficial for reducing NO<sub>x</sub>. The contribution of char

combustion in the regenerator of the dual-FB is less than that in combustor of single-CFBC because a part of the char is transported from the regenerator to the carbonator and consumed there. Thus higher NO<sub>x</sub> emissions from dual-FB can be qualitatively explained by the decreased contribution of char combustion in the regenerator. For quantitative discussion, the decrease in char combustion in the regenerator for the dual-FB system was calculated.

Figure 4-6-(a) shows the effect of coal type on the fraction of carbon combustion in the carbonator to total carbon burn-up in the dual-fluidized bed system,  $Z_{C,Carb}$ , observed for the dual-FB system. Although scattering of the data was observed, a trend was found that the carbon combustion in the carbonator increased with increasing carbon content of fuel. These results are attributable to the increased fixed carbon (char) yield with increasing carbon content of fuel. For high-fixed carbon content fuel, more char is formed with devolatilization. With increasing char formation in the regenerator, char transportation from the regenerator to the carbonator with circulating bed material increased.

Fig.4-6-(b) shows the fraction of char burned in regenerator for unit mass of combustible part of coal,  $m_{FCb,Reg}$  [kg/kg-DAF coal]. The fraction of char burned in the regenerator was found to be lower than the char yield of the fuel. For semi-anthracite (SA), char yield was 82% (Chapter 2 Table 2-1) but  $m_{FCb,Reg}$  was only 65 – 70% at an oxygen concentration in flue gas of 3%. For high-volatility bituminous coal (HVB), the difference was less but still observed; char yield was 51% while  $m_{FCb,Reg}$  was about 45%.

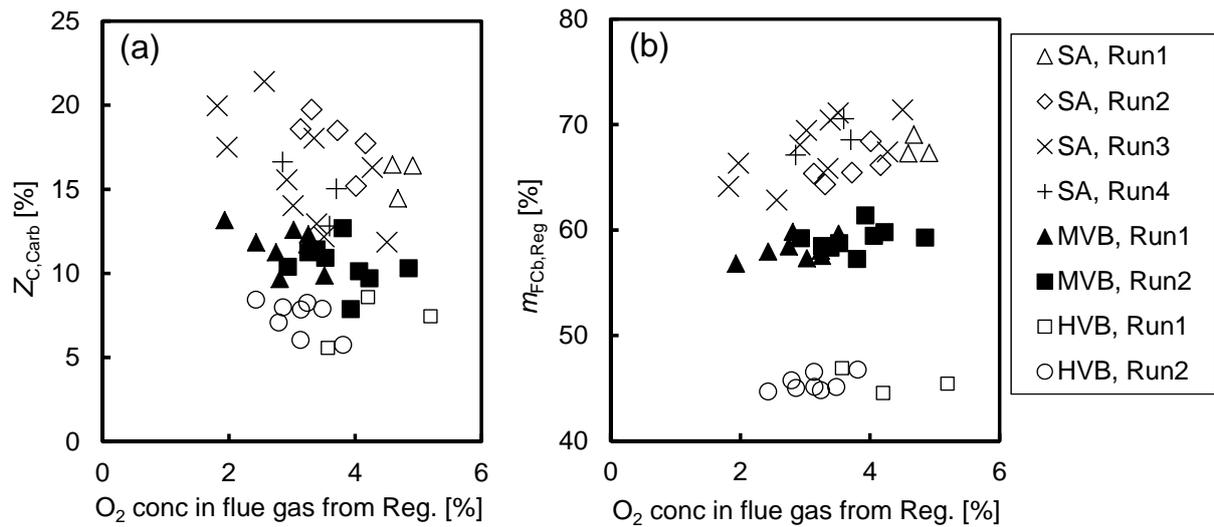


Fig.4-6. Effect of coal type on (a) fraction of carbon combustion in the carbonator to total carbon burn-up in the dual-fluidized bed system ( $Z_{C,Carb}$ ) and (b) fraction of char burned in the regenerator in the dual-fluidized bed system ( $m_{FCb,Reg}$ ).

Since volatile matter evolution is a rapid process in comparison to char combustion, volatile matter can be assumed to be completely burned in the regenerator. Thus the decrease in contribution of char combustion in the regenerator is considered to have an effect similar to the use of higher-volatility fuel. The ratio  $m_{FCb,Reg}/M_{VM}$  gives net FC/VM ratio of fuel actually burned in the regenerator. Fig.4-7 shows the relationship between  $m_{FCb,Reg}/M_{VM}$  and  $M_{FC}/M_{VM}$  (FC/VM ratio of fuel). For high-volatility fuel,  $m_{FCb,Reg}/M_{VM}$  was close to  $M_{FC}/M_{VM}$ . With increasing coal rank, the deviation between  $m_{FCb,Reg}/M_{VM}$  and  $M_{FC}/M_{VM}$  became more remarkable. This is attributable to the increased char transportation to the carbonator with increasing char yield of fuel.

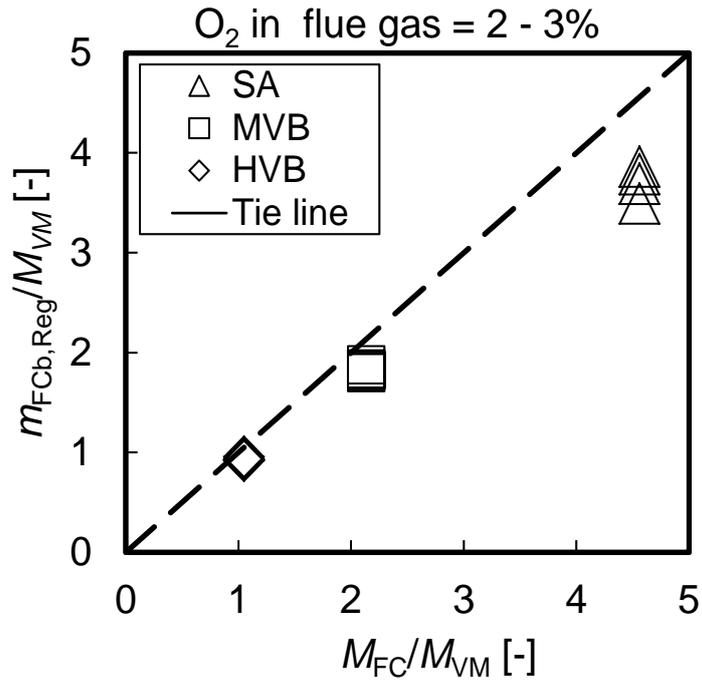


Fig.4-7. Relationship between ratio of char burned in regenerator to volatile matter content of fuel ( $=m_{FCb,Reg}/M_{VM}$ ) for dual-FB and ratio of fixed carbon content to volatile matter content of fuel. ( $O_2$  concentration in the flue gas from the regenerator = 2-3%).

#### 4.4.2 Relationship between conversion of fuel-N to NOx and the net FC/VM ratio

Figure 4-8 shows the relationship between conversion of fuel-N to NOx and  $FR_{net}$ , where  $FR_{net}$  is the net FC/VM ratio of fuel actually burned in the regenerator. For dual-FB,  $FR_{net}$  is given as  $m_{FCb,Reg}/M_{VM}$ , while  $FR_{net}$  is given as  $M_{FC}/M_{VM}$  for single-CFBC. For both reactors, the conversion of fuel-N to NOx,  $X_{NOx}$ , decreased with increasing  $FR_{net}$  and an empirical correlation was obtained as:

$$X_{NOx} = 0.04FR_{net}^{-0.5}. \quad (4-8)$$

This relationship indicates that the ratio of char to volatile matter plays an important role in NOx formation and reduction in the regenerator / combustor. The importance of char in NOx

reduction is in accordance with the concentration profile in the combustion chamber; it is widely accepted that NOx is formed in the lower part of the fast bed combustors and NOx is gradually reduced in the upper part during coal combustion using air [7–9]. In contrast, such pattern of NOx reduction along the combustor height was not observed for wood combustion, whose char yield is known to be very low [9]. Therefore, the hold-up of char in the upper part of combustion chamber is considered to have a strong influence on NOx reduction in the regenerator / combustor.

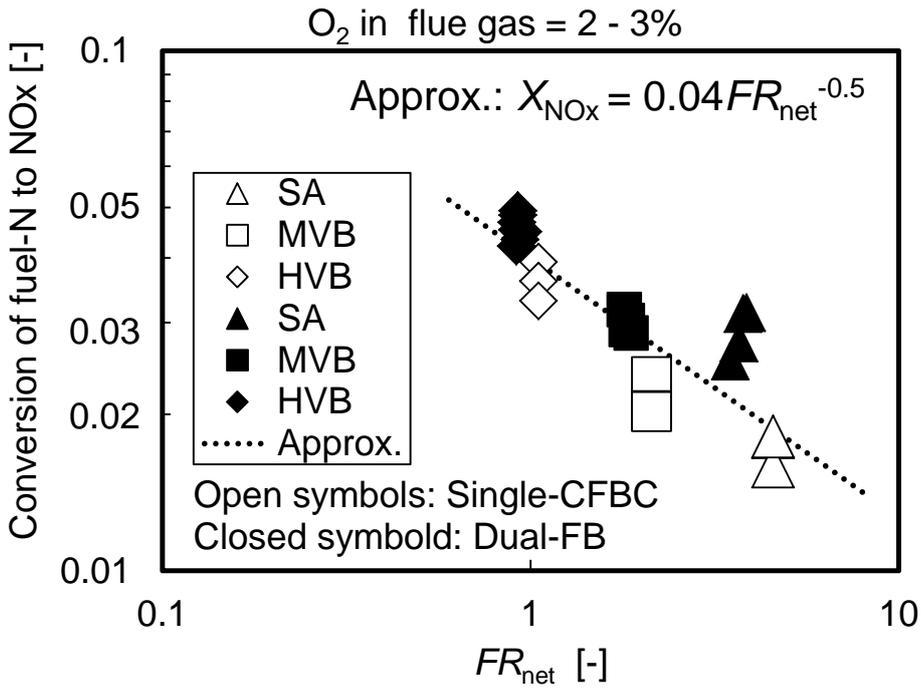


Fig.4-8. Relationship between the conversion of fuel-N to NOx and ratio of char burned in regenerator / combustor to volatile matter content of fuel ( $FR_{net} = m_{FCb,Reg} / M_{VM}$  for dual-FB,  $FR_{net} = M_{FC} / M_{VM}$  for single-CFBC [1]).

The relationship found in Fig.4-8 also suggests that the results of oxyfuel combustion using a single-CFBC can be used directly to predict NOx emissions from the dual-fluidized system

if char combustion in the carbonator is negligible. Even when char consumption is not negligible, the results of single-CFBC can be used for prediction if char transportation rate is to be known. For the prediction of char transportation, char burn-up rate should be known. The char burn-up rate can be measured by use of a batch fluidized bed reactor equipped with flue gas analyzer for CO<sub>2</sub> and CO, for example.

The present dual-fluidized bed system can be also applicable to the evaluation of the role of char in NO<sub>x</sub> emissions during combustion. Usually, the role of char is discussed in terms of coal type, namely fixed carbon content or coal rank of the fuel. For this purpose, coals with different fixed carbon contents are burned. However, use of the different coals also influences the chemical reactivity of char as well as volatile matter composition such as NH<sub>3</sub> and HCN. So the role of char cannot be separately discussed when different coals are used. The present dual-FB can control the contribution of char combustion to total fuel combustion using the same coal by changing char transportation to the carbonator and consumption there. Thus the effect of the overall char burn-up rate (or char hold-up) in the combustion chamber on NO<sub>x</sub> emissions can be evaluated, keeping char property and volatile matter composition the same.

#### **4.5. Conclusion**

Coal combustion experiments were carried out using two types of reactor with identical fast fluidized beds but with different solid circulation system. One reactor type was a conventional

single circulating fluidized bed combustor. In the conventional single-CFBC, the entrained char particles were recycled back to the bottom of the fast fluidized bed, thus all the char particles were burned in the fast fluidized bed. The other reactor was a dual-fluidized bed system equipped with another fluidized bed reactor called carbonator, in which a part of char was consumed, thus char combustion in the fast fluidized bed was reduced in comparison to the combustor of the single-CFBC. NO<sub>x</sub> emissions from single-CFBC were less than those from the regenerator of the dual-FB and this tendency was more remarkable for higher carbon content fuel. The fractions of char burned in the fast fluidized bed and carbonator were also determined from the compositions and flow rates of flue gases from these reactors. Conversion of fuel-N to NO<sub>x</sub> in the fast fluidized bed was found to decrease with increasing the ratio of char combustion to volatile matter combustion in the fast fluidized bed.

## **Nomenclature**

$f_{IN,Air}$ : Feed rate of air to carbonator [mol/s]

$f_{OUT,CO_2}$ : Flow rate of CO<sub>2</sub> as flue gas from carbonator (= CO<sub>2</sub> formation rate in carbonator)  
[mol/s]

$f_{OUT,CO}$ : Flow rate of CO as flue gas from carbonator (= CO formation rate in carbonator)  
[mol/s]

$F_{IN,Air}$ : Feed rate of air to regenerator [mol/s]

$F_{OUT,CO_2}$ : Flow rate of  $CO_2$  as flue gas from regenerator / combustor ( $CO_2$  formation rate in regenerator / combustor) [mol/s]

$FR_{net}$ : Ratio of char burned in regenerator / combustor to volatile matter content of fuel  
( $=m_{FCb,Reg}/M_{VM}$  for dual-FB,  $=M_{FC}/M_{VM}$  for single-CFBC) [-]

$m_{Cb,Carb}$ : Fraction of carbon burned in carbonator [kg/kg-DAF coal]

$m_{FCb,Reg}$ : Fraction of char burned in regenerator [kg/kg-DAF coal]

$M_C$ : Mass fraction of carbon in combustible part of fuel [kg/kg-DAF coal]

$M_{FC}$ : Mass fraction of carbon converted to char in combustible part of fuel = Fixed carbon content of combustible part of fuel [kg/kg-DAF coal]

$M_H$ : Mass fraction of hydrogen in combustible part of fuel [kg/kg-DAF coal]

$M_O$ : Mass fraction of oxygen in combustible part of fuel [kg/kg-DAF coal]

$M_{VM}$ : Volatile matter content of fuel [kg/kg-DAF coal]

$y_{OUT,CO}$ : Molar fraction of CO in flue gas from carbonator [mol/mol]

$y_{OUT,CO_2}$ : Molar fraction of  $CO_2$  in flue gas from carbonator [mol/mol]

$Y_{OUT,CO_2}$ : Molar fraction of  $CO_2$  in flue gas from regenerator / combustor [mol/mol]

$Y_{OUT,N_2}$ : Molar fraction of  $N_2$  in flue gas from regenerator / combustor [mol/mol]

$X_{NO_x}$ : Conversion of fuel-N to  $NO_x$  in the regenerator / combustor [mol/mol]

$Z_{C,Carb}$ : Fraction of carbon burned in carbonator to total carbon burn-up in dual-fluidized bed system [kg/kg]

## Abbreviations

F.C. fixed carbon

HVB high-volatility bituminous coal

MVB medium-volatility bituminous coal

SA semi-anthracite

V.M. volatile matter

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**Conclusion**

The CaL process is expected to separate carbon dioxide from flue gas with a low energy penalty. In this study, a combination of a fluidized bed carbonator and a fluidized bed regenerator is designed for CO<sub>2</sub> capture at atmospheric pressure using coal as a fuel to supply heat for CaCO<sub>3</sub> decomposition.

In the first chapter, literature surveys related to the CO<sub>2</sub> capture technologies were described. Difficulties related to the Cal Looping process using coal as fuel were presented. The respective purposes of the present studies described herein were also discussed.

The second chapter focuses on the coal combustion in an oxygen-enriched air using a dual-fluidized bed solid circulation system under conditions of the Calcium Looping process. Two methods for measuring the particles circulating rate were proposed. The effects of gas feed staging on the regenerator on the solid residence time were evaluated. By reducing the ratio of the primary gas feed rate to total gas feed rate to 0.5, the average solid residence time of about 40 s was attained. Under this gas feed condition, coal combustion experiments were conducted using three kinds of coal. Effects of volatile matter content of coal on CO and CO<sub>2</sub> formation in the carbonator and NO<sub>x</sub> emissions from the regenerator were investigated. High-volatile matter coal was found to be favorable to reduce CO and CO<sub>2</sub> formation in the carbonator, but the conversion of fuel-N to NO<sub>x</sub> of high-volatile matter coal was higher than

that of low-volatile matter coal. Oxygen enrichment of the primary gas alone was found to be favorable for the suppression of NO<sub>x</sub> emission.

In the third chapter, coal combustion in a mixture of O<sub>2</sub> and CO<sub>2</sub> was conducted by using a bench-scale dual-fluidized bed system. O<sub>2</sub>/CO<sub>2</sub> atmosphere was adopted to simulate flue gas recycle to the regenerator, with the aim of obtaining the high CO<sub>2</sub> concentration flue gas from regenerator, and avoiding hot-spot formation during combustion in O<sub>2</sub>-enriched atmosphere in regenerator. Formation of NO<sub>x</sub> in the regenerator and formation of CO and CO<sub>2</sub> in the carbonator were evaluated. By comparing the results of coal combustion in O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub> atmospheres, diluents of O<sub>2</sub> were found to have no effect on the formation of CO and CO<sub>2</sub> in the carbonator, although it affected NO<sub>x</sub> formation in the regenerator for high rank coal.

In the fourth chapter of this thesis, the results of NO<sub>x</sub> emission from the regenerator of dual-FB were compared with those obtained by another research group at Shimizu Lab of Niigata University, which used a circulating fluidized bed combustor (single-CFBC) with the same fast fluidized bed burning the same coals under the same combustion conditions (temperature and fluidized gas). For the dual-FB, simulating Calcium Looping process comprised a fast fluidized bed regenerator and a bubbling bed carbonator, a part of char was consumed in the carbonator, whereas for the conventional single-CFBC, all of fuel was burned in the single fluidized bed reactor by recycling the entrained char back to the combustor. In both systems, coal combustion in oxygen-enriched air was carried out under



In this thesis, the unburned char transportation rate from regenerator to carbonator and the NO<sub>x</sub> reduction by char hold-up in the regenerator in O<sub>2</sub>/CO<sub>2</sub> atmosphere have been already clarified. However, the CO formation from unburned char combustion in carbonator when the air as carbonator fluidized gas, and the NO<sub>x</sub> emissions from regenerator are still problems, shown as [Fig.5-1-\(a\)](#). Therefore, in next step, a proposal is shown as [Fig.5-1-\(b\)](#): if the unburned char moves from the regenerator to the carbonator, while changing the fluidized gas in the carbonator with low O<sub>2</sub> concentration or no oxygen to make unburned char not to combust in the carbonator. The char will circle with bed material back to the bottom of the regenerator. The returned char increases the amount of char hold-up in the regenerator, and then promotes the NO<sub>x</sub> reduction. In this way, both the CO emissions from the carbonator and the NO<sub>x</sub> emissions from the regenerator might be controlled.

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