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Tadaaki Shimizu, Takayuki Takahashi, Hiroko Narisawa, Yasuyuki Murakami, Liuyun Li, and Heejon Kim, "CO2 Looping Cycle for CO2 Separation" in "10th International Conference on Circulating Fluidized Beds and Fluidization Technology - CFB-10", T. Knowlton, PSRI Eds, ECI Symposium Series, (2013). http://dc.engconfintl.org/cfb10/32

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CaO LOOPING CYCLE FOR CO_2 SEPARATION

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ABSTRACT

A dual fluidized bed process using CaO-based solid sorbent is considered to be a promising technology to separate CO_2 from flue gas with low energy penalty. As reactor for CaO-looping cycle, both bubbling fluidized bed and “fast” fluidized bed are available, thus four possible combinations, (bubbling or fast absorber)x(bubbling or fast regenerator), are conceivable for this process. In this work, the authors discuss favorable combination of reactor type from viewpoints of heat removal from carbonation reactor and on energy penalty associated with dilution of pure oxygen by CO_2 in the regenerator. As conclusion, suitable combination was found to be bubbling bed absorber and fast regenerator. Design of bench-scale experimental apparatus of the present system was also carried out. Bubbling bed absorber was designed to achieve 86 % CO_2 removal efficiency from flue gas. Preliminary operating results of solid circulation at room temperature are also presented.

INTRODUCTION

It is well known that the concentration of CO_2 in the atmosphere has been increasing and the greenhouse effect (global warming) is anticipated. Fossil fuel combustion such as coal-fired power plant is one of the major sources of CO_2. An approach to reduce CO_2 emission into the atmosphere is the separation of CO_2 from flue gas of conventional air-blown combustion system followed by CO_2 storage in the ground. Attempts have been made to separate CO_2 from flue gas using absorption by amine solution (1) and adsorption by solids such as zeolite (2). Another way is to burn fuel using pure oxygen, which is separated from air in advance, to make the flue gas pure CO_2 (1). For combustion using O_2, pure O_2 is usually diluted with recycled CO_2 to control the temperature in the combustion chamber. CaO-looping cycle has been developed as a CO_2 separation process with low energy penalty (3); CaO particles capture CO_2 from flue gas in one reactor (absorber) and produced $CaCO_3$ is decomposed to CaO in another reactor (regenerator) by supplying heat through fuel combustion in O_2/CO_2 atmosphere,.

Since CaO-looping process needs continuous solid transportation between absorber and regenerator, fluidized bed solid circulation system is considered to be suitable for reactor system. There are two types of fluidized beds which can be used as reactor,

bubbling fluidized bed and “fast” fluidized bed. In the fast fluidized bed, all of the particles are entrained to the top of the reactor in high-velocity gas stream. In literature, different combinations of reactor type have been employed not only for experiments but also for simulation of reactors; bubbling bed absorber (3, 4, 5), fast bed absorber (6, 7, 8, 9), bubbling regenerator (9), and fast bed regenerator (4, 5, 7, 8). Both bubbling bed and fast bed can be used to capture CO_2 in the absorber if sufficient gas-to-solid contact time is to be given. However, for put this concept into practice, one must take account of heat removal from the exothermic reaction in the absorber to maintain bed temperature. In general, reactor size is determined not only by reaction rate but also installation of heat transfer surface. Thus the design of heat transfer surface is necessary.

The objective of the present work is to discuss suitable combination of reactor type for the CaO-looping process. Design of heat transfer surface was conducted for both fast fluidized bed absorber and bubbling bed absorber. Then design of a bench-scale experimental apparatus was then carried out based on the selection of reactor type. Also preliminary experiments were carried out to measure solid circulation rate in the system under a room temperature condition.

REACTOR DESIGN AND SELECTION OF REACTOR TYPE

Absorber Design

First, material and heat balances of CaO-looping process were calculated. Fig.1 shows an example of material balance and heat balance of this process of total gross electricity output of 350 MW. In order to avoid hot-spot formation within the regenerator, in which coal particles are burned in high O_2 concentration atmosphere, fed O_2 (pure) was assumed to be diluted by CO_2 at a ratio of CO_2/O_2=1. From the material balance, feed rates of gases were calculated to design horizontal cross sectional area of absorber and regenerator. Fig.2 shows enthalpy-temperature diagram of heat source and heat sink for secondary steam cycle denoted as “$Steam_2$” in Fig.1-b. The heat from the absorber and sensible heat of CO_2 stream from regenerator is assumed to produce subcritical steam as a separated steam cycle from existing steam cycle of air-blown combustor (denoted as “$Steam_1$”). From the heat removal requirement and temperature difference between steam and heat source, the required heat transfer surface area was calculated.

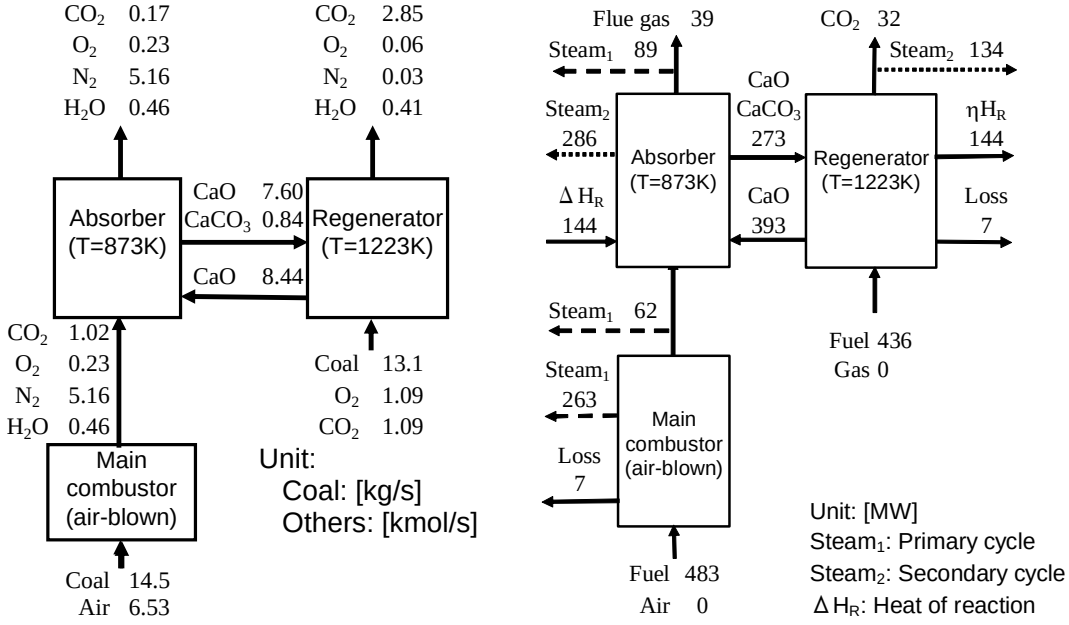
Heat transfer design in a fast bed absorber was carried. Heat transfer coefficient of reactor wall (h [W/m^{2}K]) is empirically given as a function of suspension density (ρ_{susp} [kg/m^3]) as (10, 11):

$$h = a\rho_{susp}^{0.5} \qquad (a = 30 - 40) \qquad (1)$$

$$h = 58\ \rho_{susp}^{0.36}. \qquad (2)$$

Both equations give similar results. When ρ_{susp} is assumed to be 55 kg/m^3, h is estimated to be 260 (eq.1) – 245 (eq.2) W/m^{2}K. At this suspension density, total pressure drop across a fast bed riser of a height of 50 m is 27 kPa, which is nearly the same as that of bubbling bed absorber, thus an advantage of fast bed, lower pressure drop, is lost under the present suspension density condition. Also it should be mentioned that this suspension density of 55 kg/m^3 is far higher than solid loading in the gas at the exit of the absorber: the solid loading in the gas at the exit should be 1.2 kg/m^3 to attain solid/gas material flow ratio shown in Fig.1. A measure to enhance

internal solid circulation in the riser is thus required. Therefore, this suspension density of 55 kg/m^3 is considered to be maximum conceivable value.



(a)Material flow (b) Heat flow

Fig.1 An example of material and heat balance of a CaO-looping cycle of total gross electricity output of 350 MW with dilution of pure O_2 by CO_2 at CO_2/O_2=1.

Heat transfer surface design in a fast bed was conducted assuming a bed-to-wall heat transfer coefficient of h = 250 W/m^{2}K. The overall heat transfer resistance is the sum of heat transfer resistances, i.e., tube-to-steam/water heat transfer resistance, conductive resistance in tube wall, and bed-to-wall heat transfer resistance. Thus the overall heat transfer coefficient was calculated separately in water preheater, evaporator, reheater, and superheater regioms (Table 1). The detail of calculation is available elsewhere (3). In order to avoid erosion of heat transfer surface, flat panel heat transfer exchangers are employed in fast beds when heat transfer surfaces are to be installed in addition to reactor wall.

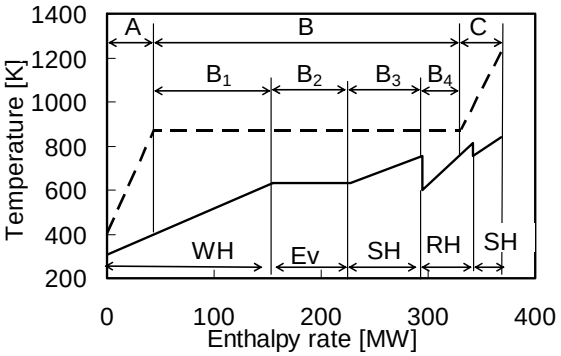


Fig.2 Enthalpy-temperature diagram of heat source and secondary steam cycle denoted as "Steam$_2$" in Fig.1-b. (Dash line: Heat source; Solid line: Heat sink; A, C: sensible heat of CO_2; B: heat recovery in absorber; WH: water preheat; EV: evaporation; SH: superheat; RH: reheat).

Fig.3 shows an example of estimated plant size and heat transfer panel requirement for the case of fast bed absorber combined with fast bed regenerator. The cross sectional area of absorber is determined by gas flow rate and superficial gas velocity. In this work, a superficial gas velocity of 6 m/s was assumed. Cross sectional area of absorber was 2.25 times of that of regenerator. This proportion is similar to the design by Ströhle (8) which gave an absorber/regenerator ratio of 2.6. To install heat transfer panels, rectangular horizontal cross section of 11 m x 7 m was assumed.

The reactor wall is used as water prehater. To attain required evaporation, reactor height of 50 m was found to be required. For evaporator, reheater, and superheater, flat panel heat transfer surfaces of 40 m in height and 7 m in width are assumed. Since both sides of flat panel can be used for heat transfer, a heat transfer surface area of 560 m^2 is available for one panel. Total 13 panels were calculated to be required, in which two panels are for evaporator, seven for reheater, and four for supereheater, respectively. Installing such large number of heat transfer panels in a fast bed is considered to be not easy. Therefore, the idea of employing fast bed for absorber is abandoned in this work.

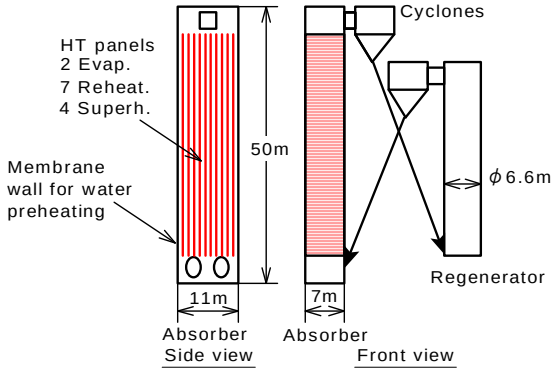


Fig.3 Estimated plant size and heat transfer panel requirement for the case of fast bed absorber combined with fast bed regenerator for total gross electricity output of 350 MW.

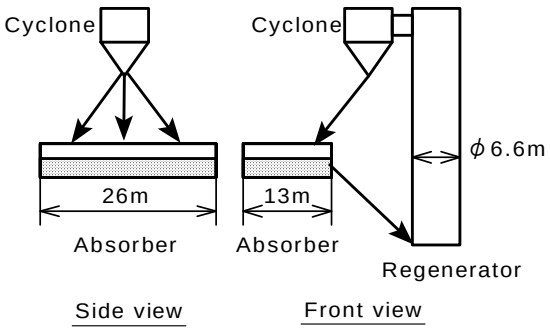


Fig.4 Estimated plant size and heat transfer panel requirement for the case of bubbling fluidized bed absorber combined with fast bed regenerator for total gross electricity output of 350 MW.

Table 1 Estimation of required heat transfer surface area for heat removal from fast bed absorber assuming bed-to-wall heat transfer coefficient of 250 W/m^2K

	Heat recovery rate [MW]	Overall heat transfer coefficient [W/m^2K]	Heat transfer area [m^2]
Water preheater	111	183	1753
Evaporator	72	218	1369
Reheater	68	101	3874
Superheater	36	85	2302

Bubbling fluidized bed absorber has already been designed in the authors' previous work (3). The cross sectional area was given by the volume flow rate and superficial gas velocity (assumed to be 1 m/s to suppress elutriation of solids). The bed height to install heat transfer tubes had been calculated to be 2.4 m and this height was higher than the bed height to capture CO_2. As shown in Fig. 4, considerably large cross sectional area is required because of low gas velocity. Stacked bed design may be required to reduce the plant size. Nevertheless, bubbling fluidized bed is considered to be suitable for absorber because the density of heat transfer surface can be higher than that of fast bed absorber.

Regenerator Design

Regenerator should be basically adiabatic to suppress heat loss, thus one important operating parameter is dilution of fed oxygen by recycled CO_2 in order to prevent hot-spot formation. As shown in Fig.5, dilution by CO_2 decreases net efficiency

through increase power consumption of air separation unit (ASU) because CO_2 carries sensible heat away from the reactor and more fuel combustion is necessary with increasing CO_2 recycle. To reduce the risk of hot-spot formation at low recycle ratio of CO_2, fast bed is considered to be advantageous because of vigorous solid mixing near the reactor inlet.

BENCH SCALE REACTOR DESIGN

Design parameters and reactor size

As discussed above, one advantageous combination of reactor type for CaO-looping cycle is bubbling bed absorber and fast bed regenerator. A bench scale experimental apparatus is designed based on this combination. Material flow was calculated assuming that oxygen is diluted with the same amount of CO_2. Table 2 shows the design parameters. For the absorber, a bubbling bed of 93 mm in I.D. is adopted. For the regenerator, a fast bed of 22 mm in I.D. is adopted. The design size of sorbent particle is 0.3 mm, whose minimum fluidizing velocity at 873 K and terminal velocity at 1273 K are 0.026 m/s and 1.48 m/s in each atmosphere, respectively. Thus fluidization in absorber and transportation of particles in regenerator are expected to be attained. The design parameters such as the ratio of the cross sectional area of two reactors and gas velocities are different from that of large scale plant (Fig. 4) because of the height limitation of bench-scale unit. Nevertheless this reactor is expected to attain necessary CO_2 recovery and solid circulation as discussed later. The material flow rates are determined by scaling down the material flow shown Fig.1-a.

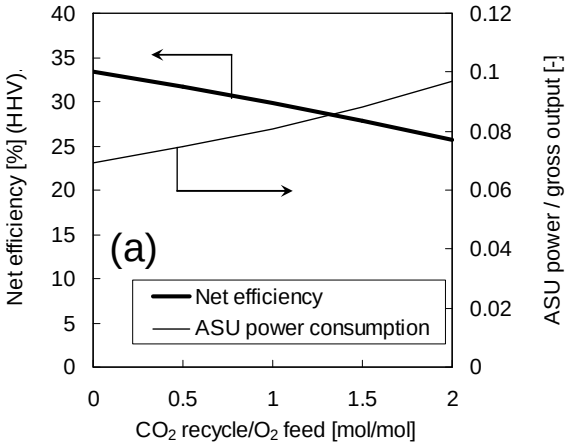


Fig.5 Estimation of the change in net efficiency and ASU power consumption with dilution of O_2 by recycled CO_2 at ambient temperature.

Table 2 Design parameters of CaO-looping bench scale plant

Absorber

ID [mm]	Gas feed rate [mol/s]	Gas velocity [m/s]	Inlet gas composition [%] CO_2	H_2O	O_2	N_2	Temperature [K]
93	0.0213	0.226	14.8	6.7	3.3	75.2	873

Regenerator

ID	Gas feed rate		Gas velocity		Coal feed rate	Temperature
	O_2	CO_2	Bottom	Top		
[mm]	[mol/s]	[mol/s]	[m/s]	[m/s]	[g/s]	[K]
22	0.0034	0.0034	1.79	2.75	0.041	1273

Solid circulation

CaO/Captured CO_2 [mol/mol]	CaO circulation rate [g/s]	Solid circulation/Gas flow rate in riser [kg/kg]
10	1.47	3.2

Estimation of CO_2 capture efficiency in absorber

In order to design the bed height of absorber, CO_2 capture efficiency was estimated using Kunii-Levenspiel model. The detail of the model is described elsewhere (3). The reaction of CaO with CO_2 is characterized by maximum utilization of CaO (D) and rate constant (k_R); change in CaO conversion (X) with time is given as follows:

$$dX/dt = k_R(D - X). \quad (3)$$

The maximum utilization of CaO is known to decrease after repeating carbonation – calcination cycles (3, 12). After a number of carbonation – calcination cycles, maximum conversion finally decreased to 0.17 (12). Thus D=0.17 was assumed. Reaction rate constant of k_R =25 m^3/kmol·s was assumed based on the author's previous work (3). The gas velocity is given in Table 2. The calculation result is shown in Fig.6. A CO_2 removal efficiency of 86% was calculated to be attained when a bed height of 0.30 m and bubble diameter of 4 cm was assumed. Thus the present experimental apparatus is expected to be suitable for CO_2 capture experiments.

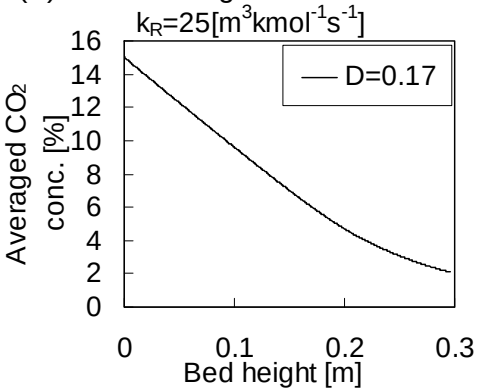


Fig.6 Estimated CO_2 capture in bubbling fluidized bed operated under a condition shown in Table 2 assuming a bubble diameter of 4 cm.

PRELIMINARY OPERATION RESULTS OF BENCH SCALE REACTOR

A bench-scale reactor of CaO-looping cycle was constructed and operated at room temperature. The objective of the cold-experiments was to confirm whether required solid circulation rate could be attained. Schematic diagram of the experimental apparatus is shown in Fig.7. The experimental apparatus consisted of riser reactor (22 mm in I.D. and 1.93 m in height) and bubbling fluidized bed reactor (93 mm in I.D.), both of which were made of stainless steel. The gas exit at the top of the riser is connected to a cyclone in which particles were separated from the gas then the captured particles were transported to the bubbling fluidized bed by gravity. Particles in the bubbling fluidized bed were drained from an overflow tube. The fluidizing bed height (i.e. height of overflow tube) was 0.30 m above gas distributor. The particles flowed through a standpipe whose bottom is connected to a loopseal. The particles from the loopseal were fed into the bottom of the riser. The bed material was quartz sand of average size of 0.15 mm. Under the present cold model experiments, gas velocities were 1.75 m/s, 0.050 m/s, and 0.067 m/s in the riser, in the bubbling bed, and in the loopseal, respectively.

In order to measure the solid circulation rate, the standpipe was equipped with three thermocouples at an interval of 10 cm and with a tracer injection system from the top. As tracer, heated bed material was employed. A batch of tracer was injected from the top of the standpipe. The change in temperature with time after tracer injection was continuously measured. When the tracer particles passed the location of the thermocouple, a peak of the temperature was observed (Fig.8). From the time lag (t_D) of the peaks and the distance between two thermocouples (L), the descending velocity (U_D) of solids in the standpipe is given as:

$$U_D = L/t_D. \quad (4)$$

By assuming that the solids in the standpipe forms moving bed without bubbles and the solid density in the standpipe is identical to the bulk density of the solids (ρ_b), the solid circulation rate (G_s) is given as a product of descending velocity, bulk density, and cross sectional are of loopseal (A_s) as follows:

$$G_s = A_s \rho_b U_D . \quad (5)$$

Fig.9 shows the solid circulation rate that attained at a pressure drop across the riser of about 3 kPa. Solid circulation rate under the present condition was 3 – 4 g/s, which is considered to sufficient for CO_2 capture experiments in the present test apparatus (Table 2). The present measurement method can be applied for hot experiments. For hot experiments, cold limestone particles can be used as tracer because circulating particles from the bubbling bed absorber are sufficiently hot (about 873 K) and the temperature decrease due to tracer can be easily detected.

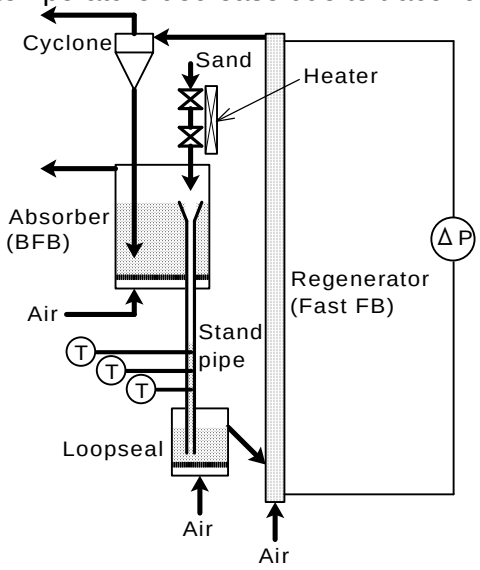


Fig.7 Bench-scale fluidized bed solid circulation system for cold experiments.

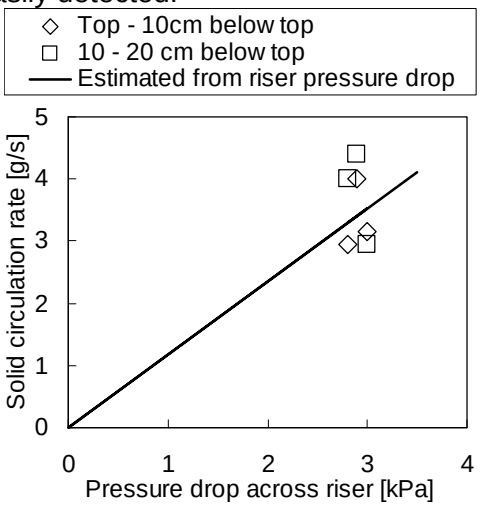


Fig.9 Comparison between solid circulation rate measured by tracer injection into the standpipe and estimation from riser pressure drop.

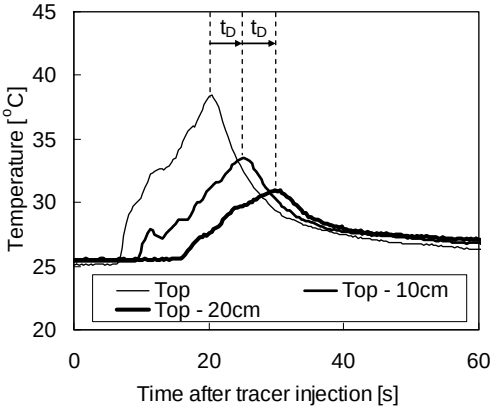


Fig.8 Typical temperature change in standpipe at different vertical position after injecting a batch of hot sand (tracer) into the standpipe.

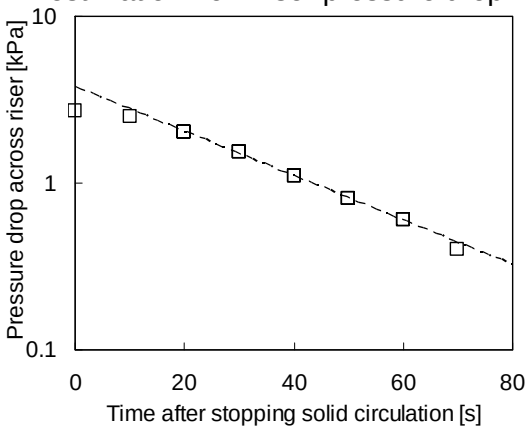


Fig.10 Decrease in pressure drop across riser after stopping solid circulation.

Another approach to measure the solid circulation rate is to measure the pressure drop across the riser (ΔP_R) after stopping solid circulation by stopping gas feed into

the loopseal. As shown in Fig.10, the pressure drop across the riser decreased with time (t) according to the first-order equation after stopping solid circulation as:

$$ln(\Delta P_R) = ln(\Delta P_{R,0}) - kt \quad (6)$$

where k is first-order decay constant. This relationship indicates that the decreasing rate of pressure drop across the riser is proportional to the pressure drop itself. By neglecting pressure drop due to gas flow, the pressure drop across the riser is given by total amount of solid in the riser (W_s), cross sectional area of riser (A_R) and acceleration of gravity (g). Thus the entrainment rate of solids is given as:

$$\frac{d\Delta P_R}{dt} = \frac{g}{A_R}\frac{dW_s}{dt} = -k\Delta P_R \,. \quad (7)$$

Under constant pressure drop condition, solid circulating rate is thus given as:

$$G_S = -\frac{dW_S}{dt} = kW_S = \frac{k\Delta P_R A_R}{g} \,. \quad (8)$$

As shown in Fig.9, solid circulation rate measured by tracer injection into the standpipe agreed well with that estimated by eq.8. Therefore, the solid circulation rate can be monitored by measuring the pressure drop across the riser.

CONCLUSION

Conceptual design of a CaO-looping cycle was carried out. To recover heat from absorber, bubbling fluidized bed is considered to be more suitable than fast bed. Experimental apparatus is designed and CO_2 capture efficiency in the absorber was estimated. Solid circulation rate was measured under a cold model condition and required solid circulation rate was attained.

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