



The high efficiency CO₂ separation using Chemical Looping Combustion and Oxy-Fuel Combustion

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1. Background

It is necessary to reduce CO₂ emissions against global warming, and the activities are expanding all over the world. In Japan, approximately 85% of primary energy consumption is reliant on non-renewable fossil fuels. And more than 30% of fossil fuels are used in industrial boilers, industrial furnaces and power generation stations.

Natural gas is considered as an environmentally friendly clean fuel, offering important environmental benefits when compared to other fossil fuels. Among fossil fuels, natural gas produces relatively small amount of CO₂ per unit calorific value. Furthermore, the superior environmental qualities over coal or oil are that emissions of sulphur dioxide are negligible or that the level of nitrous oxide emissions is lower. So, natural gas will play an important role in meeting our nation's future energy needs. We, Tokyo Gas Co., Ltd. has contributed to reduce CO₂ emissions by exchange fuels that have large CO₂ emissions coefficients such as heavy oil and coal to natural gas. And to develop and introduce high efficiency combustion technologies, such as FDI regenerative burner^{[1][2]}, Radiant tube burner, and oxygen combustion^{[3][4]} are also our significant environmental policies of CO₂ emissions reduction.

A trial calculation made by IPCC (Intergovernmental Panel on Climate Change) requires reducing the amount of CO₂ down to 50% by the year 2050. After the Great East Japan Earthquake on March 11, 2011, the introduction and operation of nuclear power plant is concerned and renewable energy such as wind and solar power is expected. Although the supply of these energies is not stable because it is affected by the weather, so a move away from natural gas is very difficult. Thus, innovation of technology for reducing CO₂ emissions is required in order to continue to use natural gas in the future.

2. Aim

It is necessary to take measures to reduce CO₂ emissions in order to that natural gas may become mainstay energy in the future. Technologies of reducing CO₂ emissions are stabilization and underground storage of CO₂. To actualize these technologies, the high efficiency CO₂ separation is requested. We pay attention to the following two technologies.

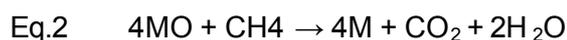
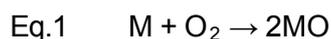
(1) “Chemical Looping Combustion (CLC)” for industrial boilers and comparatively low temperatures furnaces. (2) “Oxy-Fuel Combustion” for high temperature furnaces. Eventually we have considered these technologies applying to ironworks and chemical complexes.

Each exhaust gas components (which comes from the fuel reactor in case of CLC) is only CO₂ and H₂O, so that CO₂ separation can be facilitated. These technologies have been developed to apply to furnaces and boilers in order to enable the efficient CO₂ separation in the industrial field.

3. Chemical Looping Combustion

3-1. Principle of CLC

CLC is a novel combustion technology. It uses the redox of the metal, and the concept is very different from the combustion of the past. Fig. 1 shows the conceptual diagram of CLC. CLC consists of two reactions, one is oxidation of metallic particles another is reduction of oxidized metallic particles. The continuous reaction is occurred by cycling the metallic particle (oxygen carrier; OC). In the air reactor (AR), the oxygen of the air is strongly exothermically reacting with the OC from M to MO (shown in Eq.1). The metal oxide is transported into the fuel reactor (FR). Here it reacts with the fuel being reduced from MO to M (shown in Eq.2) in an endothermic or slightly exothermic reaction depending on the type of fuel and the type of the OC material [5].



In the FR, the reaction produces an exhaust gas consisting principally of only CO₂ and water vapor. The water vapor can be removed by condensation leaving the CO₂, an additional energy is not necessary for capturing CO₂. On the other hand, there is no local temperature peak like as burner flame because of the mild reaction in the AR, so thermal NO_x is hardly generated. Therefore CLC can achieve the zero combustion emissions. Furthermore, the exhaust gas from the AR is O₂-depleted air. CLC can generate N₂ gas by adjusting the amount of the air to the OC.

A pioneer of CLC is Professor Ishida of Tokyo Institute of Technology in Japan [6]. In 1980's he succeeded in the reaction experiment at 1200°C using Fe₂O₃ supported by alumina which diameter is about 100 μm. Now, this technology is studied actively in Europe. GDF SUEZ reported about CO₂ capturing for using CLC in power plant [7].

The size of the OC is generally about 50 ~ 200 μm. The candidates of the OC are Ni, Cu, Fe, Co, and Mn and those are supported by Al₂O₃, SiO₂, ZrO₂, and TiO₂ and so on. Fig. 2 shows two types of circulation system, one is externally-circulating fluidized bed and another is internally. Almost all researchers study the former. We have studied both types for industrial boilers and furnaces.

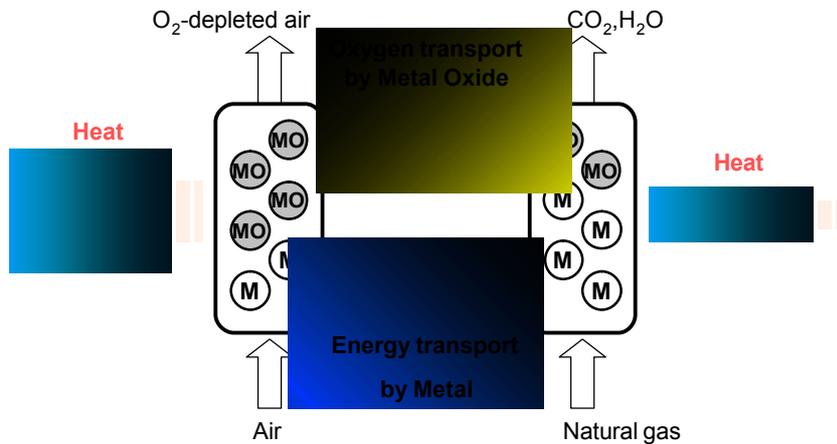


Fig. 1 The principle of chemical looping combustion.

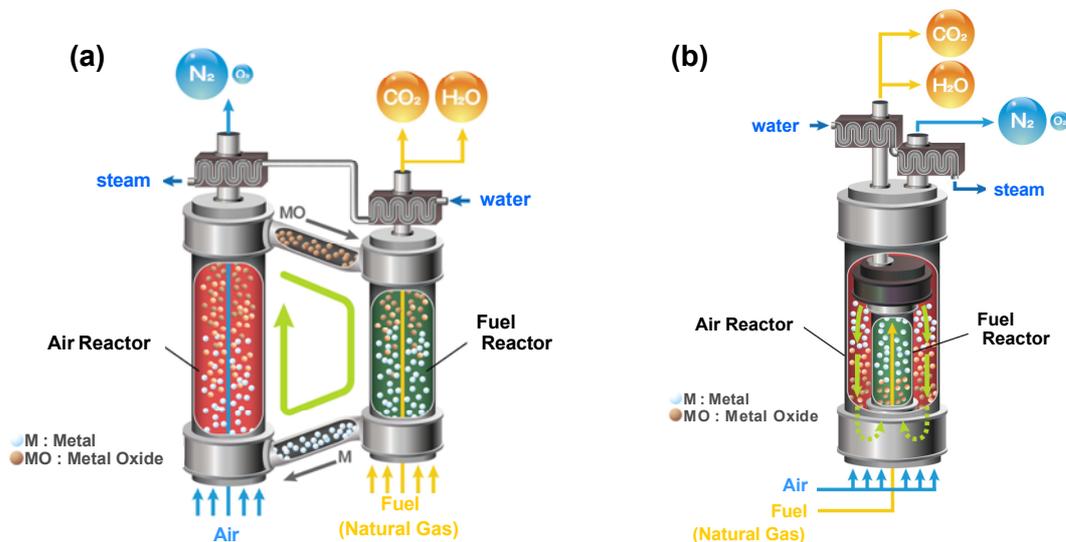


Fig. 2 The circulation systems for chemical looping combustion. (a) externally-circulation system (b) internally-circulation system

3-2. Test equipment

The redox reaction test was carried out with the switch type test equipment shown in Fig. 3 to clarify reaction characteristics in the AR or the FR. The test equipment was switch type and reaction gases were conducted at the bottom. The exhaust gas from each reaction was analyzed. Fe_2O_3 supported by alumina (Al_2O_3) was used as the OC which diameter is about $80 \mu\text{m}$ as shown in Fig. 4. This OC was developed by Ohba laboratory of Kanagawa Institute of Technology. The operating condition is shown in Table 1. The characteristics and the durability of the OC were evaluated.

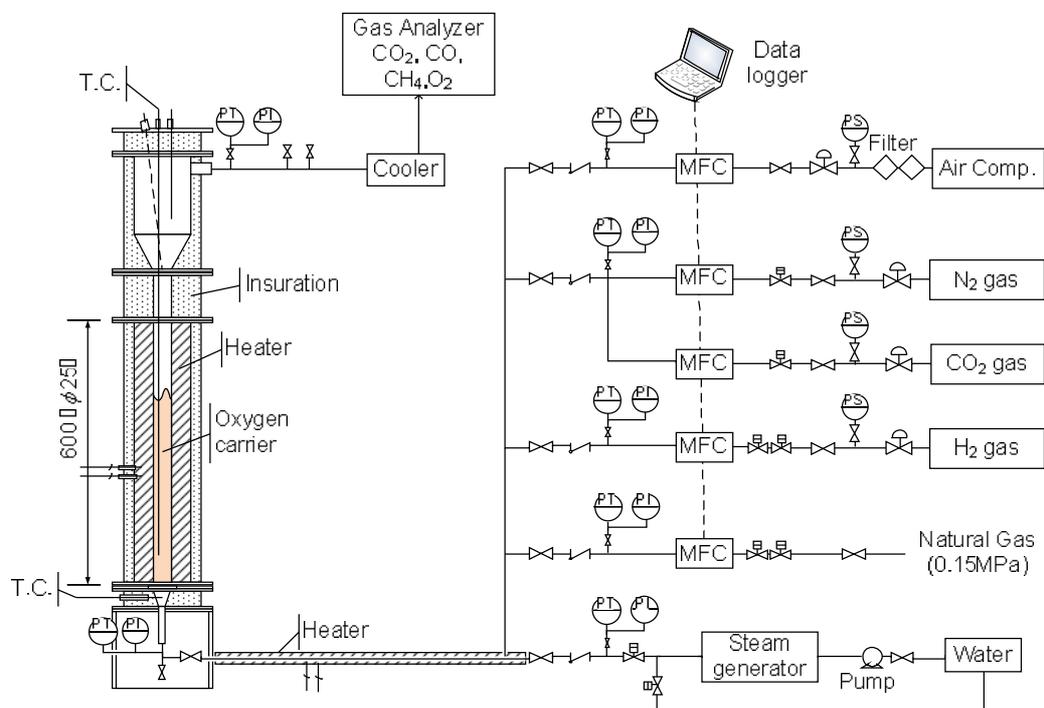


Fig. 3 The schematic diagram of chemical looping combustion test equipment

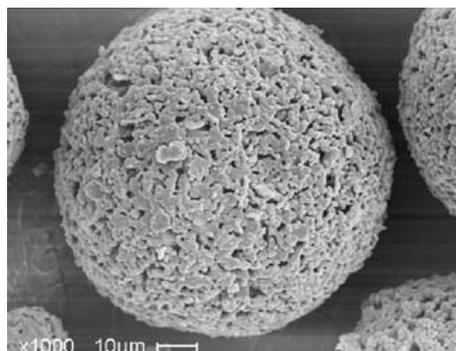


Fig. 4 SEM image of Fe_2O_3 supported by Al_2O_3

Table 1 The operating condition for the redox reaction test.

Parameters	Operating Condition
Reactor size	$\phi 25.4\text{mm} \times 600\text{mm}$
Oxygen carrier components	Fe_2O_3 / Alumina (25:75)
Fill ration and the height of OC	250g (300mm)
Reaction temperature	900°C(1173K)
Oxidation gas	Air
Reduction gas	*Natural gas / N_2 Balance (Natural gas 16.6%)
Purge Gas	N_2

3-3. Experimental results

Test conditions and experimental results are shown in Table 2 and experimental result in case 3-1 is shown in Fig. 5. Each test was carried out after the OC was completely oxidized by the air and the reactor was completely purged by N₂ gas. The time when reduction gas was injected was set to 0 second.

The reduction reaction began soon after injecting reduction gas. Natural gas was almost converted to CO₂ and H₂O but a part of natural gas remained with CH₄. The reaction rate was over 98 [Vol. %]. In the beginning of oxidation reaction, because of the carbon deposition on the OC in reduction reaction CO₂ concentration in the exhaust gas was increased. In this time, the OC reacted with all of oxygen in the air so O₂ concentration in exhaust gas was 0% for a while the components of the exhaust gas were only N₂ and Ar. We confirmed that CLC could product heat and nitrogen gas (co-production).

Fig. 6 shows a comparison of the reduction reaction rate for the residence time. The reduction reaction depends on the residence time. The lattice oxygen utilization ratio is shown in Table 2. Though the residence time is same, if the lattice oxygen utilization ratio increase, the reaction rate is worse. It is because of the lack of the OC which has enough Lattice oxygen. In each case, the oxidation reaction rate was 100 %. Therefore the reaction velocity of oxidation is faster than that of reduction. It is more than 4 times. For designing the CLC system, it is important for the FR to increase a residence time and an amount of the OC circulation rate.

The experimental result of the evaluation of the OC durability by continuous redox test (63 times) is shown in Fig. 7. It can be confirmed that the peak of CO₂ concentration remains unchanged, so the activity of the OC was kept in this term.

Table 2 The test condition for the redox reaction test.

		case 1-1	case 1-2	case 2-1	case 2-2	case 3-1	case 3-2
Volume flow	liter/min	1.2		0.48		0.24	
Reduction time	s	30	180	75	450	150	900
Amount of reduction gas	liter	0.1	0.6	0.1	0.6	0.1	0.6
Velocity	cm/s	12.3	12.3	4.9	4.9	2.5	2.5
Residence time	s	2.44	2.44	6.09	6.09	12.18	12.18
Reduction reaction rate	-	63.0%	45.7%	85.7%	54.0%	97.6%	77.2%
Lattice oxygen utilization ratio	%	8.39%	40.0%	12.4%	49.1%	14.0%	70.2%

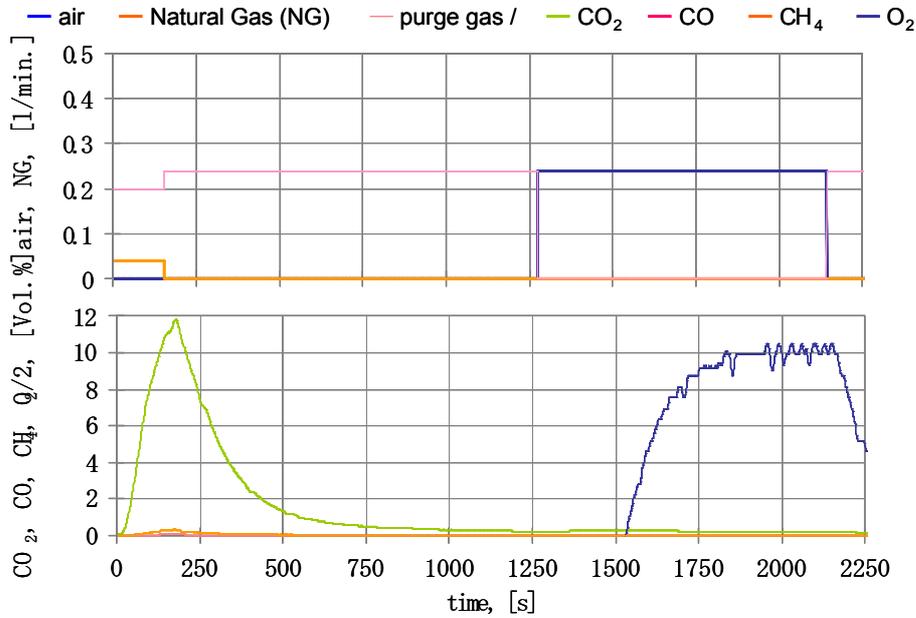


Fig. 5 The injection gas volume flow and the concentration of each gas in the exhaust gas in experimental case 3-1.

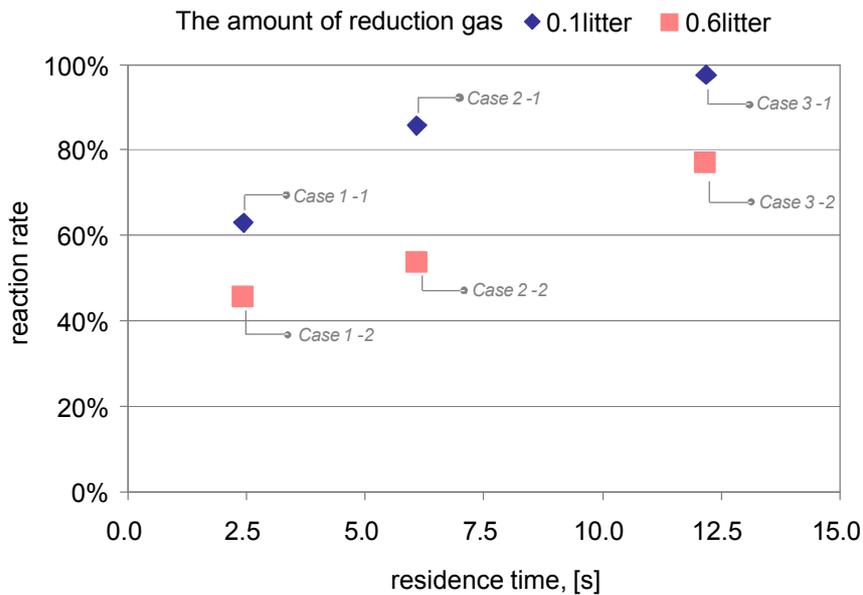


Fig. 6 The comparison of the reduction reaction rate with each residence time.

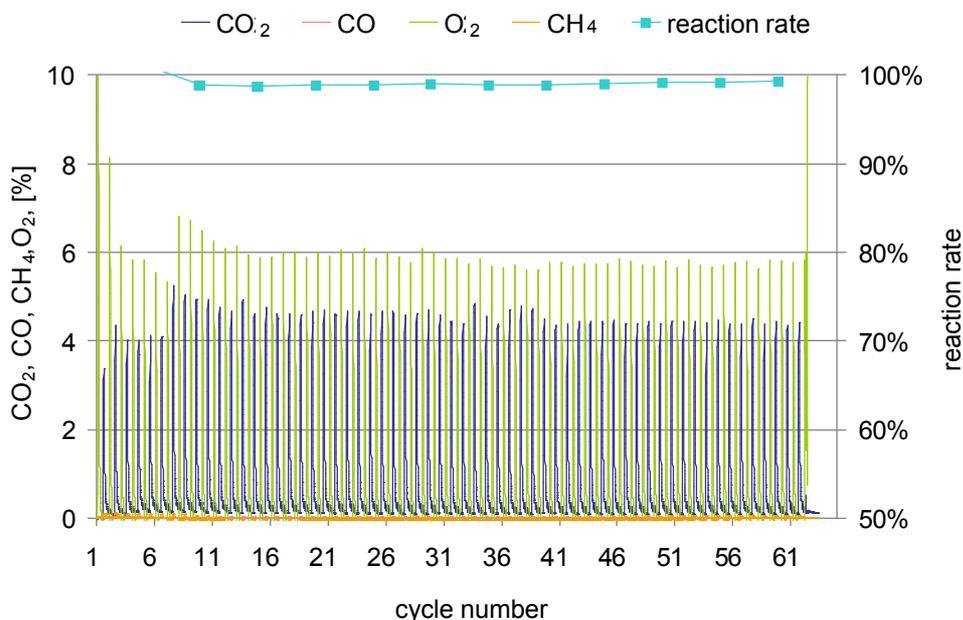


Fig. 7 The evaluation of the OC durability by continuous redox test (63 times).

3-4. Discussion

The high purity CO₂ separation without additional energy has been confirmed; however the problem that the reactivity of the OC is poor still remains. Furthermore nitrogen gas production with heat generation has been confirmed. Thus if CLC-Boiler that the industrial boiler is applied CLC technology can supply steam and N₂ gas, the high efficiency CO₂ separation can be achieved by replacing existing boiler and N₂ generator to CLC-Boiler.

The size of CLC-Boiler has been estimated based on the redox test. Our target capacity of the CLC-Boiler is 10 ton/hr. The reaction time of reduction is 12 seconds and is much slower than that of oxidation. The height of the FR is over 4 times higher than that of the AR if each diameter is equal.

Korea Institute of Energy Research (KIER) has selected Ni as the OC [8]. Ni has a good reactivity and the reaction velocity is about 10 times faster than Fe, however it is identified as carcinogens. We have tried to estimate the CLC-boiler size by reference to the CLC test equipment of KIER again. As a result, the size of the FR is equal to the AR. Therefore the size depend on the reactivity of the OC, the CLC-Boiler using exiting OC (Fe) is not available for industrial fields. Hence the development of the exceptionally-reactive OC is required.

Many researchers say that the Chemical Looping System (CLS) can generate hydrogen gas with Fe₂O₃ / FeO [9]. We have discussed that the new combustion system which uses CLS and CLC shown in Fig. 8 is applied to the material and energy-intensive industries, such as ironworks and chemical complexes.

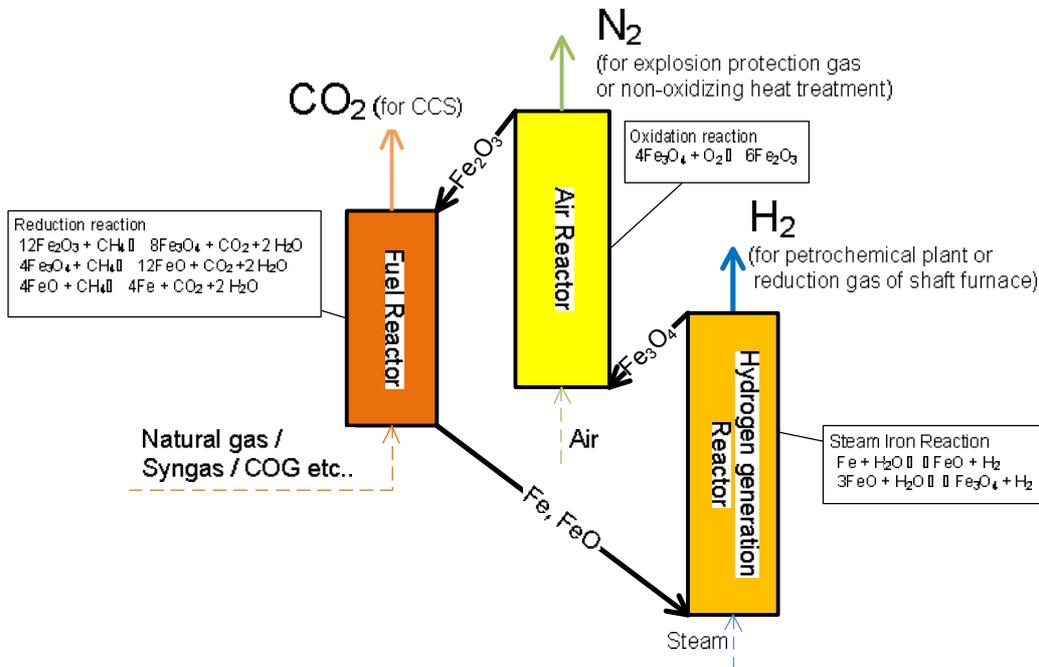


Fig. 8 New combustion system using Chemical Looping System for heat, N₂ and H₂ production.

4. Oxy-Fuel combustion

4-1. Principle of Oxy-Fuel combustion and oxygen generation method

3 types of Oxy-Fuel combustion show in Fig. 9. (1) Oxygen-Enriched Combustion, (2) Under Flame Enrichment Combustion, (3) Oxy-Fuel Combustion. In order to separate CO₂ emissions effectively, (3) must be chosen but the special equipment is necessary. To solve this problem, we considered new concept Oxy-Fuel Combustion. This is applied with the usual air combustor because of low flame temperature compared with traditional oxy-fuel combustion. This is the system that makes a part of the flue gas recirculation and injects oxygen into flue gas and supplies burner as the pseudo-air as shown in Fig. 10. The exhaust gas becomes only CO₂ and H₂O. Therefore more than 90% concentration of CO₂ can be separated. It was confirmed that CO₂ concentration in exhaust gas was more than 95% [10].

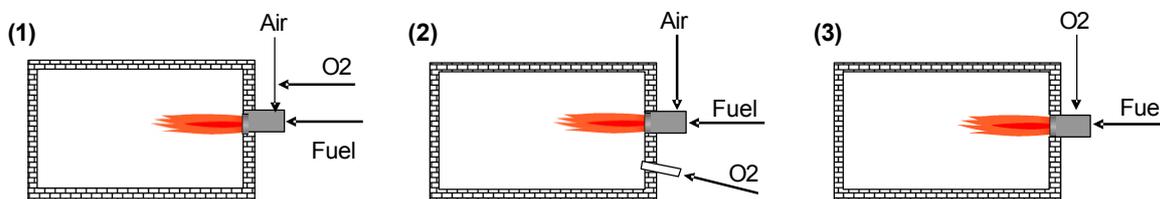


Fig. 9 3 types of Oxy-Fuel combustion (1) Oxygen-Enriched Combustion, (2) Under Flame Enrichment Combustion, (3) Oxy-Fuel Combustion

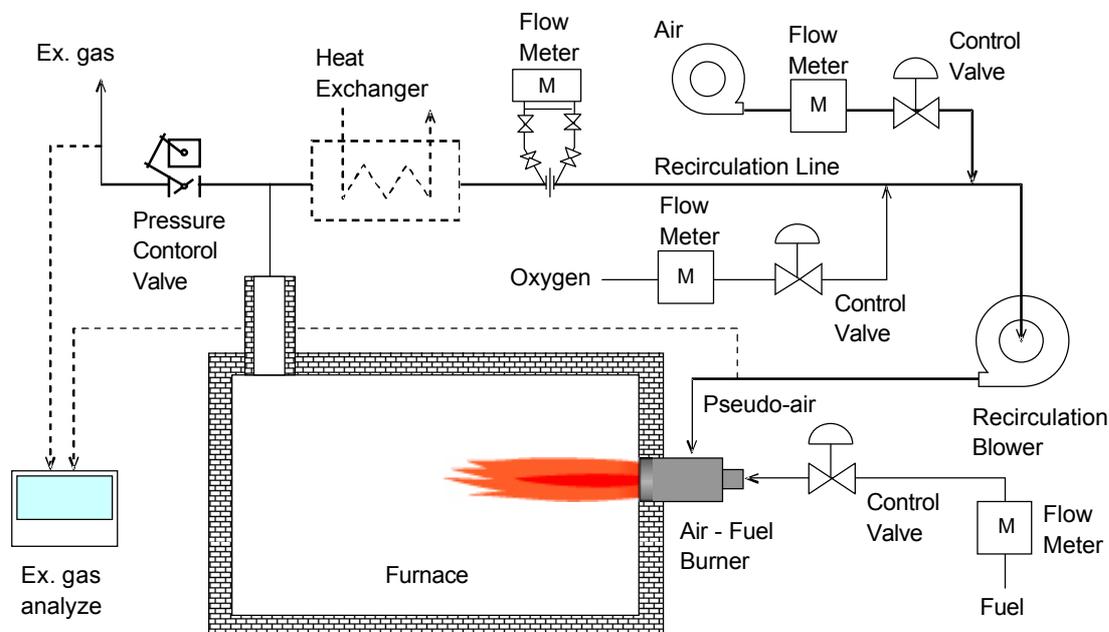


Fig. 10 The schematic diagram of the Oxy-Fuel combustion which uses the pseudo-air made of injection oxygen into flue gas.

The Oxy-Fuel Combustion has worked out already and has been known as the technology of decreasing CO₂ emissions. On the other hand, one of barriers of the introduction of the oxy-fuel combustion is the oxygen cost. There are the pressure swing adsorption (PSA) and the cryogenic distillation method as the oxygen generation method. These electric power consumption rates are not so good, that is 0.4 kWh/m³N-O₂ (or more) and 0.32 kWh/m³N-O₂ respectively at best. Therefore, the high efficiency oxygen PSA of the on-site type has been developed in cooperation with Adsorption Technology Industries, Ltd., Miura lab of Kyushu University and JNC Engineering Co., Ltd. The feature of this PSA is the utilization of perovskite-type metal oxides as the adsorbent material. The operating temperature is around 300 - 600 °C, and it depends on the material. It becomes high efficiency to recover exhaust heat. We call this PSA system HT-PSA (High Temperature - PSA).

The PSA is a technology used to separate O₂ from the air under pressure according to the O₂ molecular characteristics and affinity for an adsorbent material. Special adsorptive material (e.g., zeolites) is used as a molecular sieve. The process then swings to low pressure to desorb the adsorbent material. The performance of the PSA depends on the adsorbent material. The capacity of the PSA is from 10 m³N-O₂/h to 1,000m³N-O₂/h.

The cryogenic distillation method is a method of separating each gas species based on differences in volatilities of components in a boiling liquid mixture. The air is distilled to separate its components—notably oxygen, nitrogen, and argon—for industrial use. The capacity is more than 10,000 m³N-O₂/h and the purity of each gas is more than 99.999%.

4-2. Principle of HT-PSA

The schematic diagram of HT-PSA is shown in Fig. 11. The feature of HT-PSA is that the perovskite-type metal oxide (LSCF) is used as adsorbent material. The synthetic zeolite used to be selected. Fig. 12 shows the relation of the electric power consumption for O₂ generation to O₂ separation factor of adsorbent material. Theoretically, if the O₂ separation factor is over 3, the electric power consumption for PSA is better than the cryogenic distillation method. The separation factor of existent synthetic zeolite is 2 ~ 3 and that of perovskite-type metal oxides is more than 10. The operating temperature is higher but total electric power consumption for HT-PSA is very lower than existing one because of exhaust heat recovered in addition to O₂ separation factor. It is 0.2 kWh/m³N-O₂ on the PSA simulation.

According to the previous study by Adsorption Technology Industries, Ltd. and Miura lab of Kyushu University, it was indicated by small size test equipment test that the O₂ separation factor of LSCF was very good. Furthermore the durability of LSCF was confirmed by 3 months continuous test. The trial calculation of evaluating material balance and heat balance based on these tests showed the electric power consumption for O₂ generation by HT-PSA was 0.2 kWh/m³N-O₂.

The concentration of O₂ from HT-PSA is more than 99% however existing PSA is up to 95.5%. It is because that LSCF adsorbs only O₂ so it can completely separate O₂ from the air.

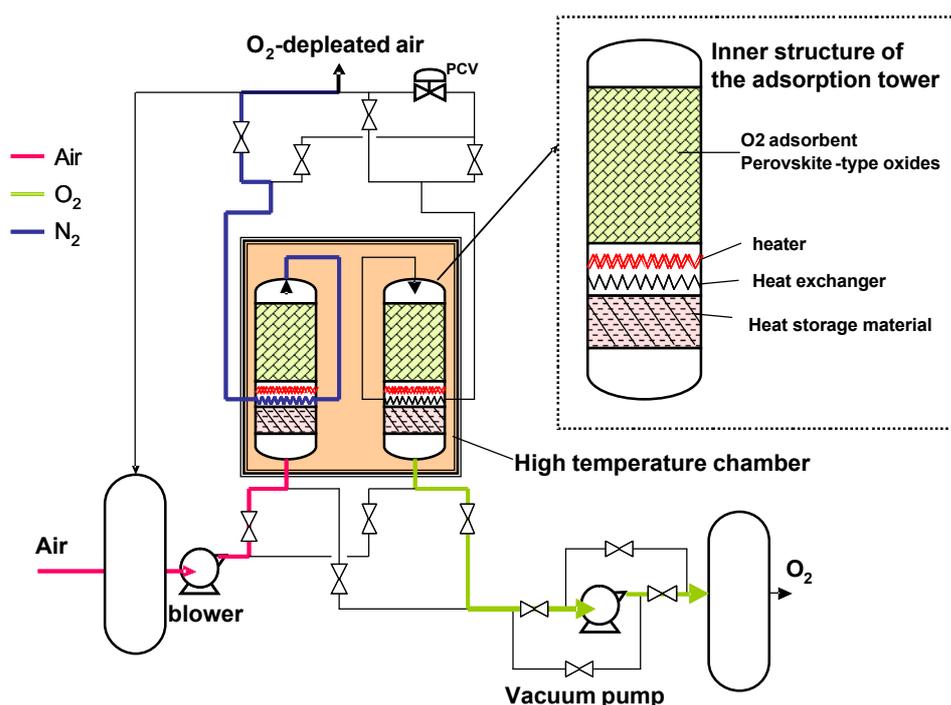


Fig. 11 The schematic diagram of HT-PSA which has heat recovery system.

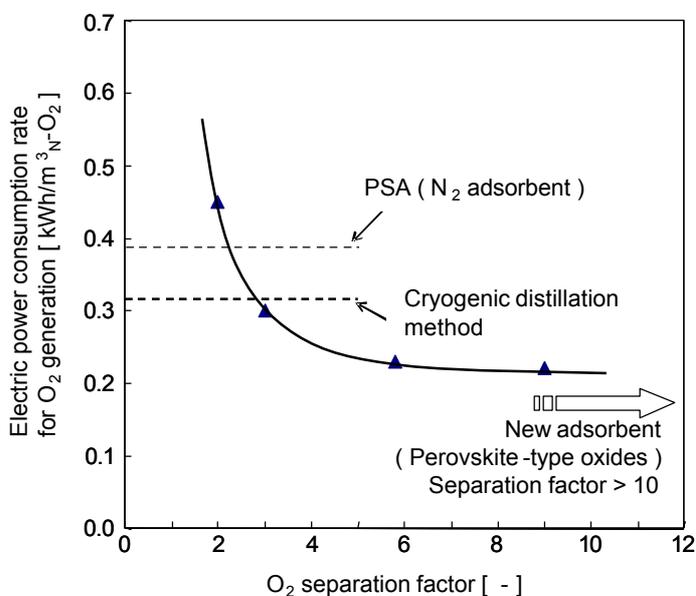


Fig. 12 The relation of electric power consumption rate for O₂ generation to O₂ separation factor.

4-3. Test equipment and experimental results

Fig. 13 shows the small size of HT-PSA test equipment. It has two adsorption towers and the production capacity of O₂ is 2.0 l/min. There is no exhaust heat recovery system. Adsorption towers are heated up to 600 °C by electric heater. Pressure of adsorption and desorption is 1.4 – 2.0 atm (abs) and 0.05 atm (abs) respectively. To clarify the basic property of HT-PSA, the concentration of product O₂ and O₂-depleted air had been analyzed with changing cycle-time and cycle-pattern.

The performance of HT-PSA expected by previous test was shown by the examination. Furthermore the probability of nitrogen gas generation was indicated. It was confirmed that the O₂ concentration in O₂-depleted air is less than 2.0% in the examination. To optimize the cycle-time and cycle-pattern can generate high purity N₂ in addition to generation of high purity O₂.

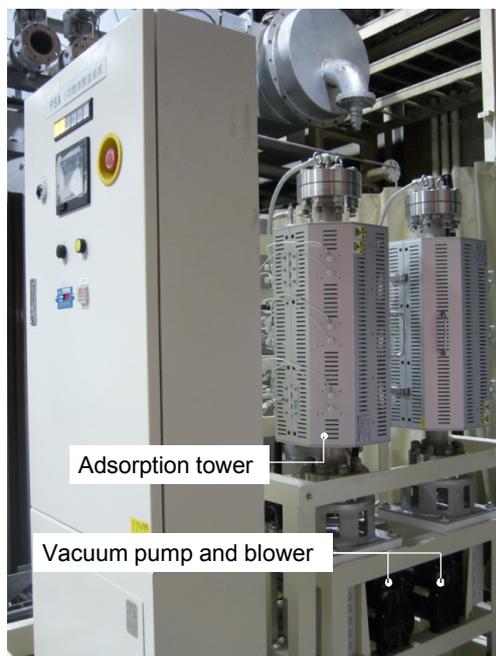


Fig. 13 The photo of the small size of HT-PSA test equipment

4-4. Discussion

The fundamental properties of HT-PSA have been verified in the present work however verification test of the electric power consumption have not been carried out. We plan to do the test after installation heat recovery systems.

The electric power consumption for O_2 generation is $0.2 \text{ kWh/m}^3\text{N-O}_2$. On the other hand, the possibility of nitrogen gas production was indicated in the present work. Thus it is expected that total electric power consumption for O_2 and N_2 production is less than $0.2 \text{ kWh/m}^3\text{N}$ if almost all of these production is consumed on-site.

5. Conclusion

We have developed CLC and Oxy-Fuel combustion for the high-degree application of natural gas and reducing CO_2 emissions.

The possibility of co-production which means producing heat and nitrogen gas with CO_2 separation by using CLC has been indicated in the redox test. Considering the hydrogen generation in addition to co-production, it is expected that CLC is applied to various industrial fields.

The previous study of WGC 2009 explained that Oxy-Fuel combustion allowed to separate CO_2 emissions and could be easily applied to furnaces. In this work, we tried to reduce the oxygen generation cost which is one of the significant problems of Oxy-Fuel combustion. As a result, we have indicated the possibility that the electric power consumption of O_2 generation using HT-PSA is $0.2 \text{ kWh/m}^3\text{N-O}_2$. Furthermore HT-PSA can generate high purity nitrogen gas. Therefore we will contribute to promotion of Oxy-Fuel

combustion and to the reduction of CO₂ emissions in industrial fields. Oxygen is a basic material for industry. There is possibility of application in various fields, such as industrial furnaces, coal gasification, ironworks, medical treatment, and so on...

We plan to discuss applying these technologies to ironworks and chemical complexes. We will also put CLC and HT-PSA into practical use until 2020 and contribute to reduce CO₂ emissions.

Acknowledgement

This work about CLC includes a part of results of co-development with Dr. Hatano (AIST), and a part of oxygen carrier was provided by Dr. Ohba (Kanagawa Institute of Technology). The authors would like to appreciate their supports.

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