The high efficiency air separation technology “HIGH TEMPERATURE PRESSURE SWING ADSORPTION” for oxy‐fuel combustion

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1 Introduction/Backgrounds

The activities to reduce CO_2 emissions against global warming 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 plants. Therefore it is an important task for industrial sectors to find a way to use fossil fuels more efficiently. Natural gas is considered as a clean fuel, offering important environmental benefits when compared to other fossil fuels. Among fossil fuels, natural gas produces relatively small amount of CO_2 per unit calorific value. Other superior environmental qualities over coal or oil are that emissions of sulphur dioxide are negligible, and also that the level of nitrous oxide emissions is lower. Natural Gas is expected to play an important role in meeting our nation's future energy needs

We, Tokyo Gas Co., Ltd. have historically contributed to reduce CO_2 emissions by exchanging fuels that have larger CO_2 emissions coefficients, such as heavy oil and coal, to natural gas. We also have a long history in developing and introducing high efficiency combustion instruments such as regenerative burner [1][2] in attempts to reduce CO_2 emissions..

We believe that the innovative energy saving technology is necessary for natural gas to continue to be one of the primal energies. We argue that oxy-fuel combustion can be one of such innovative energy saving technologies. Oxy-fuel combustion is the process of burning a fuel using pure oxygen or oxygen-enriched gas instead of air as the primary oxidant. When the oxygen concentration is raised above 20.9% present in air, the air is considered oxygen-enriched. And the chemical reaction between fuels and oxygen-enriched air is called “oxygen-enriched combustion,” while between fuels and pure oxygen it is called “pure oxygen combustion.” In this paper, I describe the merits of oxy-fuel combustion, and “HIGH TEMPERATURE PRESSURE SWING ADSORPTION”, what is the technology of reducing the oxygen production cost.

2 Objectives

The features of oxy-fuel combustion are;

① Oxy-fuel combustion produces approximately 75% less flue gas than air fuel combustion.
② Higher flame temperatures are possible, because nitrogen component of air is not heated.
③ Because the flue gas volume is reduced and flame temperatures are high, less heat is lost in the flue gas.
④ Nitrogen from air is not allowed in, thus thermal NOx production is greatly reduced.
⑤ The exhaust gas consists primarily of CO_2 and H_2O, suitable for sequestration.

Although oxy-fuel combustion has advantages mentioned above, there remains following problems to be solved.

① It costs a lot to produce oxygen.
② Firing with pure oxygen would result in too high flame temperature, inadaptable with burners for air fuel combustion.
③ Reduced flue gas volume will decrease in efficiency of convective heat transfer and make temperature distribution in furnace uneven.
④ The invasion of the external air into the furnace combined with high flame temperature result in producing large amount of NOx.

Especially, cutting O_2 production cost is the most important task to popularize oxygen-fuel combustion. Two major existing O_2 production methods are PSA using zeolite and cryogenic separation, and their electrical consumption rates are $0.4kWh/m^3N\text{-}O_2$ and $0.32kWh/m^3N\text{-}O_2$ respectively. In order to widespread oxygen-fuel combustion, it is necessary to establish O_2 production method with higher efficiency at lower cost. The objective of this paper is to consider energy-saving effect of oxy-fuel combustion and « HIGH

TEMPERATURE PRESSURE SWING ADSORPTION », which is a highly efficient method of O_2 production. This method has a ptential to reduce electrical consumption rate of O_2 production to 0.2kWh/m^3N-O_2.

3 Development

3.1 Characteristics of oxy-fuel combustion

In this chapter, characteristics of oxy-fuel combustion are described in detail. Combustion is the chemical reaction between fuel and oxygen. The vast majority of combustion processes use air as an oxidizer in combustion with a fuel such as natural gas, fuel oil, propane, and other hydrocarbons. Usually air is the primal source of oxygen for industrial furnaces or boilers. While readily available for, air contains only about 21% oxygen and the rest is mainly nitrogen. Hot exhaust gases represent the largest source of heat losses in most industrial furnaces. It is recognized that pre-heating of the combustion air with heat exchanger provides the potential for energy saving. Since nitrogen does not contribute to the combustion process, it introduces a major source of inefficiency to the combustion process. The nitrogen in the air substantially increases the mass of the flue gas and the heat loss from the industrial furnaces or the boiler stack. Some nitrogen is converted to oxides of nitrogen, which is a major source of air pollution, and it contributes to the formation of ozone and photochemical smog.

Oxy-fuel combustion is the process of burning a fuel using pure oxygen instead of air as the primary oxidant. Here are the characteristics of oxy-fuel combustion

①Oxy-fuel combustion produces approximately 75% less flue gas than air fuel combustion.

In case of air fuel combustion, it is clear that the large part of exhaust gas consists of nitrogen, and it is heated up to high temperature after combustion. It is known that the performance of many air-fuel combustion processes can be improved by enriching the combustion air with oxygen. Replacing air with oxygen drops volume of exhaust gas and heat loss by 75% in the flue gas when compared to air-fuel combustion. Thus it results in an overall improvement in efficiency. (Fig.1)

②Higher flame temperatures are possible, because nitrogen component of air is not heated.

The adiabatic flame temperature of air-fuel combustion is approximately 1950℃. Enrichment of the combustion air increases both the flame temperature and the thermal efficiency considerably. In oxy-fuel combustion, the adiabatic flame temperature reaches approximately 2800℃. (Fig.2)

③Because the flue gas volume is reduced and flame temperatures are high, less heat is lost in the flue gas.

In proportion to the enrichment rate of the combustion air, both the flame temperature and the thermal efficiency increase and the flue gas volume decrease. Relation between oxygen-enriched rate and fuel saving rate is shown in Fig.3. A higher temperature of flue gas is evaluated as higher efficiency of energy conservation.

The increase of concentration of CO_2 and H_2O in the flue gas increases efficiency of heat transfer. The benefits of oxygen-enriched or oxy-fuel combustion in conjunction with high flame radiation substantially increases the thermal efficiency of furnaces.

④Nitrogen from air is not allowed in, thus thermal NOx production is greatly reduced.

The relation between oxygen enriched rate and NOx formation is shown Fig.4. It shows the predicted equilibrium of thermal NOx formation from the combustion of a fuel under theoretical frame temperature. This study is meaningful in understanding the tendency of NOx formation. As a result of oxygen enrichment, the partial pressure of oxygen increases while that of nitrogen decreases. This leads to a radical increase in the adiabatic flame temperature, thus resulting in a great increase of NOx formation. When the oxygen enriched rate in over 60 %, partial pressure of nitrogen drastically decreases and so as NOx concentration. Theoretically, under pure oxygen combustion there is no NOx formation.

⑤The exhaust gas consists primarily of CO_2 and H_2O, suitable for sequestration.

Oxy-fuel combustion produces a nitrogen free flue gas, of which the main components are water vapour and a high concentration of CO_2. This makes it easy to further concentrate the flue gas to an almost pure stream of CO_2.

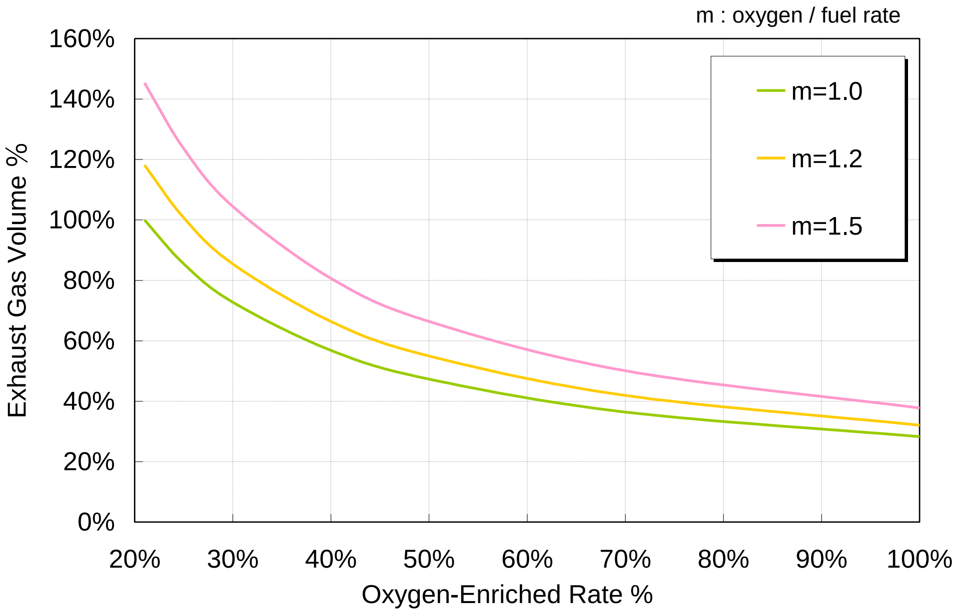


Fig.1 volume of exhaust gas

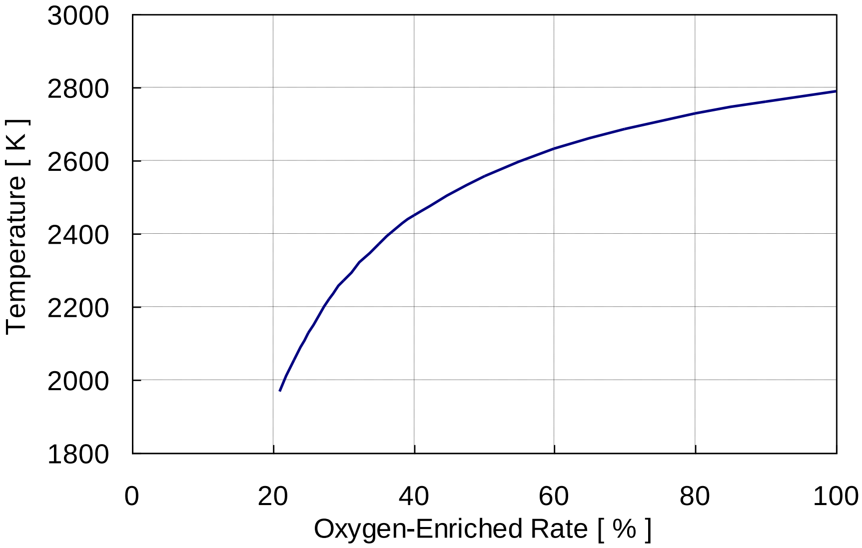


Fig.2 adiabatic flame temperature

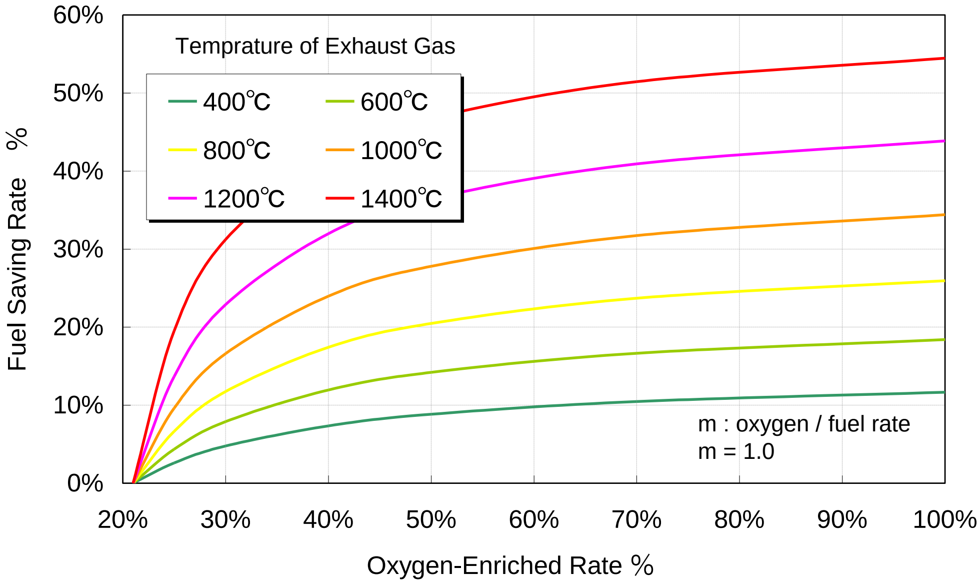


Fig.3 variation of fuel saving

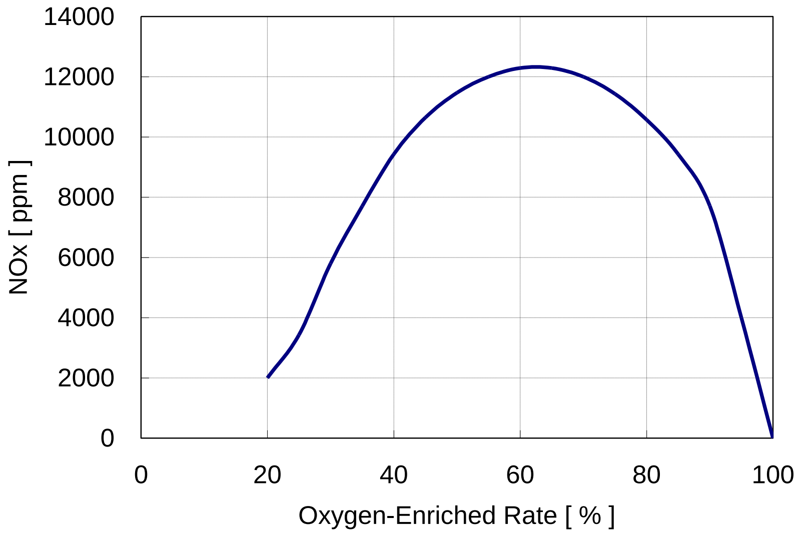


Fig.4 NOx formation and oxygen-enriched rate

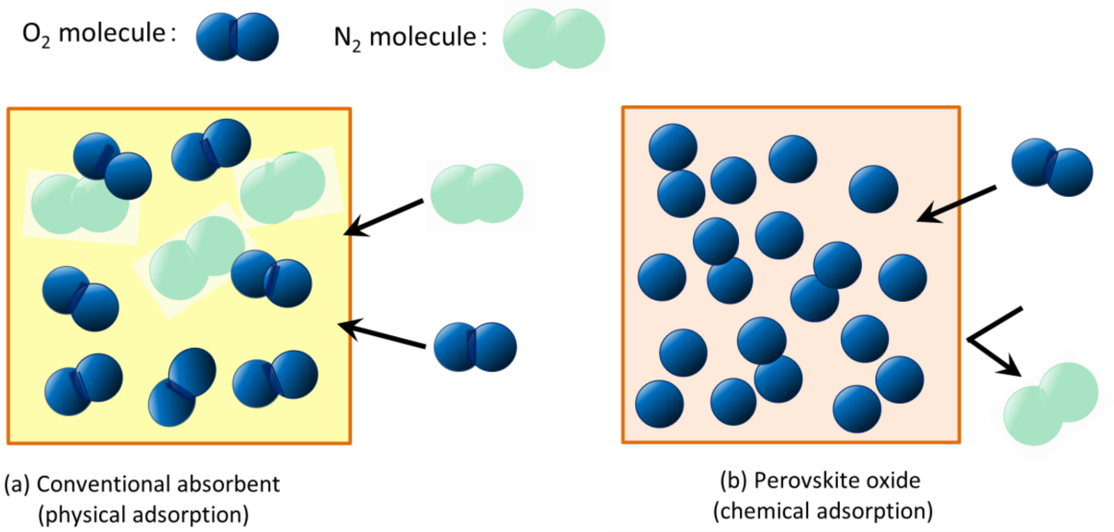
3.2 About Characteristic of HT-PSA

In this chapter, I describe the characteristics of "HIGH TEMPERATURE PRESSURE SWING ADSORPTION" (hereinafter referred to as the "HT-PSA") under development by Tokyo Gas Co.,Ltd.

HT-PSA is the method of O_2 production based on conventional PSA method, and perovskite oxides are used as O_2 adsorbent (In conventional PSA, zeolites are used as N_2 adsorbent.). By swinging pressure, perovskite oxides adsorb and desorb O_2 reversibly under the high temperature that is more than 600℃.　HT-PSA is an air separation technology using this property.

Perovskite oxides differ from conventional O_2 adsorbents in a way that it has 100% oxygen selectivity in theory. The image of the adsorption properties conventional adsorbents and perovskite oxides is shown in Fig.5.

(a)The conventional adsorbents adsorb O_2 molecules and a few N_2 molecules. On the other hand, (b)the perovskite oxides chemically adsorb only O_2 molecules by weak oxidation reaction. The advantage of this technology is this strong oxygen selectivity.



(a) Conventional absorbent
(physical adsorption)

(b) Perovskite oxide
(chemical adsorption)

Fig.5 the adsorption properties of conventional adsorbents and perovskite oxides

The relation between separation factor of O_2 and electric consumption rate is shown in Fig.6. Fig.6 shows that as separation factor of O_2 becomes large, electric consumption rate becomes lower. This proves that HT-PSA has the advantage over cryogenic separation and conventional PSA using N_2 adsorbents. The energy saving rate of HT-PSA is 50% compared to conventional PSA, and 40% to cryogenic separation.

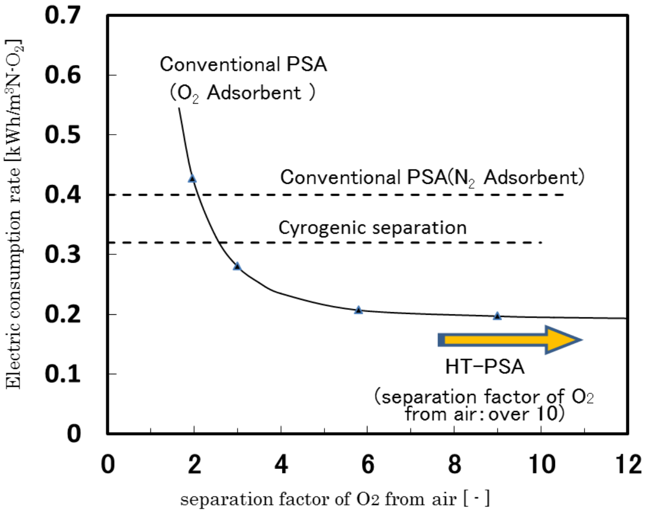


Fig.6 separation factor of O_2 vs electric consumption rate

The basic flow of HT-PSA is shown in Fig.7.

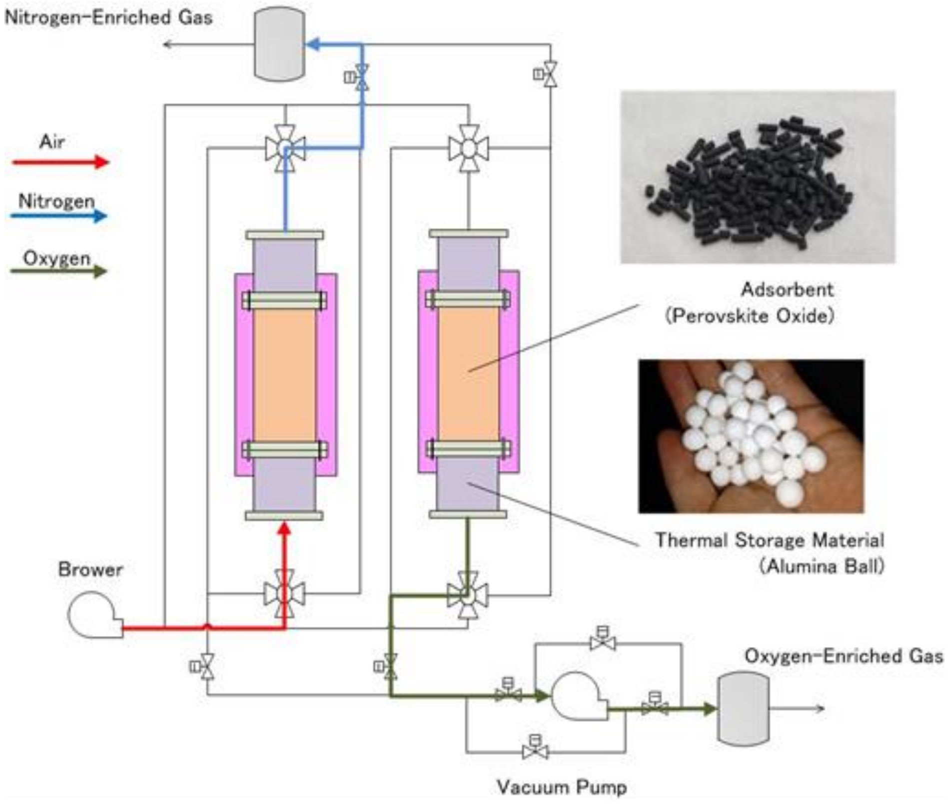


Fig.7 basis flow of HT-PSA

As shown in Fig.7, HT-PSA consists of twin adsorption tower heated about 600℃ by heater. In one adsorption tower, perovskite oxides adsorb O_2 from blower air. In another one, perovskite oxides desorb O_2 under reduced pressure by vacuum pump. Because it works at high temperature of over 600℃, we enhance the heat efficiency by heat recovery using thermal storage material at both ends of adsorption tower. The comparison of HT-PSA and conventional PSA using zeolites is shown in Table.1.

Table.1 comparison of conventional PSA and HT-PSA

	Conventional PSA	HT-PSA
Process	Pressure swing adsorption processes	
Adsorbent	Zeolite-type：attracts N_2	Perovskite-type：attracts O_2
Principle of adsorption	physical adsorption : limited selectivity	chemical adsorption : 100% selectivity
Electric power consumption rate	0.35～0.5 $kWh/m^3N\text{-}O_2$	0.2 $kWh/m^3N\text{-}O_2$ (target) ※
upper limit of the oxygen concentration	95.5 vol% (Upper limit)	>99 vol%
operating temperature	at ambient temperature	600℃
heat utilization	—	have a chance of heat utilization

※target at 80%-O_2 , by 1000m^3N/h machine

As shown in Table.1, both conventional PSA and HT-PSA separate air by swinging pressure. The difference is its adsorbents. The conventional PSA adsorbs N_2 molecules physically by zeolite, on the other hand HT-PSA adsorbs O_2 molecules chemically by perovskite oxides. As mentioned above, it is because HT-PSA has strong selectivity for O_2 molecules, and could produce high purity O_2. Unlike conventional PSA adsorbing N_2 which comprises 79% of the atmosphere, HT-PSA adsorbs O_2 which exists only 21% in the atmosphere. Therefore HT-PSA has advantages in adsorbent quantity and electric consumption rate.

We have worked in research and development on the configuration and composition of adsorbents, and examined the optimal operation status (adsorption and desorption time, inverter control of vacuum pump, and heat recovery etc.) by experiment with the use of pilot scale machine (rated 5$m^3N/h\text{-}O_2$). Based on this experiment results, we estimated electric consumption rate of 1000$m^3N/h\text{-}O_2$ machine.

In general, electric consumption rate is largely reduced as machine is scaled up. This is because the relatively smaller specific surface area makes heat release from tower wall smaller even if it is the same temperature. Furthermore, the adiabatic efficiency enhancement of vacuum pump and blower reduces electric consumption rate. The relation between the amount of O_2 generation and electric consumption rate is shown in Fig.8. If electric consumption rate of the pilot scale machine is 1.5$kWh/m^3N\text{-}O_2$, it is estimated that electric consumption rate of demonstration machine (500$m^3N/h\text{-}O_2$) and 1000$m^3N/h\text{-}O_2$ machine are 0.25kWh/m^3N and 0.20kWh/m^3N each.

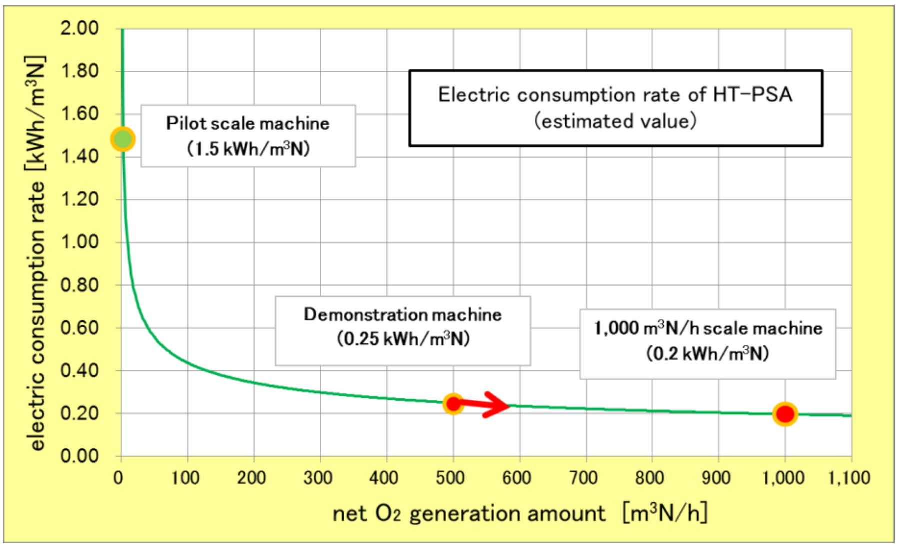


Fig.8 electric consumption rate of HT-PSA

3.3 Methods of Pilot scale machine tests

The abstracts and figure of the pilot scale machine is listed below. (Table.2 and Fig.9)

Table.2 abstracts of pilot scale machine

Adsorbents fill weight	Perovskite oxides：226 kg
Thermal storage material fill weight	Alumina ball ϕ 3 mm：300 kg
	Alumina ball ϕ 6mm：30kg
Adsorption tower bore・length	355 mm (350A)・1,750 mm
O_2 production volume	About 5,000 LN/h
Heating method	Electrical inner heater
Temperature in tower	700℃～900℃

Fig.9 figure of pilot scale machine

The sources of electrical power consumption in HT-PSA are ①Blower, ②Vacuum pump, and ③ Heater. ③Heater power for keeping temperature is split into exhaust loss and heat release from tower wall. In this test, we measured O_2 generation volume and power consumption of each by following methods (Table.3). Based on these results, we calculated the electrical consumption rate of pilot scale machine.

Table.3 each measurement method

Measurement item	Measurement methods
Blower	Calculated value from supply volume, average discharge pressure, and adiabatic efficiency
Vacuum pump	Measured value by power meter
Heater(Exhaust loss)	Calculated value from outlet flow volume and exhaust temperature
Heater(Heat release loss)	Difference between measured value of heater power consumption ,and exhaust loss value

As mentioned above, electric consumption rate is largely reduced as machine is scaled up. Therefore, it is estimated that if pilot scale machine achieves 1.5kWh/m^3N-O_2 electrical consumption rate, 1000m^3N/h machine could achieve 0.2kWh/m^3N-O_2. In this test, we targeted 1.5kWh/m^3N-O_2, and estimated profitability and energy saving of HT-PSA from the point of view of 1000m^3N/h machine electrical consumption and energy saving of oxy-fuel combustion.

4 Results

4.1 Electrical consumption rate

Fig.10 shows electrical consumption rate of pilot scale machine (measured value) and 1000m^3/h-O_2 machine (estimated value derived from this test). The left bar shows electrical consumption rate of pilot scale machine, and as it demonstrates, it achieved the target value of 1.5kWh/m^{3}N-O_2. The success factor is the reduction of power consumption of heater and vacuum pump. The power consumption of heater was largely reduced by heat recovery using the heat storage material. The power consumption of vacuum pump was reduced by avoiding high vacuum operation by inverter control.

The right bar in Fig.10 shows estimated value of electrical consumption value of 1000m^{3}N/h-O_2 machine. As mentioned above, both the heat release from tower wall and power consumption of vacuum pump decreased, and electrical consumption rate was reduced to 0.2kWh/m^{3}N-O_2.

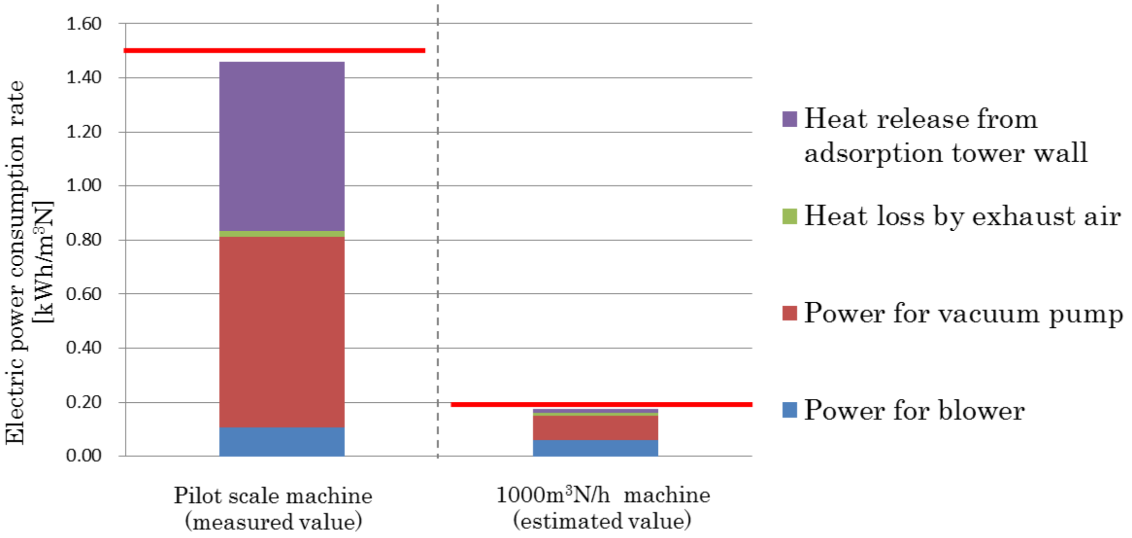


Fig.10 electrical consumption rate of pilot scale machine and 1000m^{3}N/h machine

4.2 Profitability

In this chapter, the profitability of oxy-fuel combustion using HT-PSA in the global market is described. Its profitability relies on exhaust temperature and proportion of fuel cost to electric cost. In countries where fuel cost is high and electric cost is low, oxy-fuel combustion using HT-PSA could largely reduce running costs of furnaces. In reverse, if fuel cost is low and electric cost is high, oxy-fuel combustion is unsuitable. And because high exhaust temperature enlarges exhaust loss, oxy-fuel combustion can reduce exhaust loss largely under high exhaust temperature.

I classified the countries all over the world into three groups according to the proportion of O_2 cost (electrical consumption rate of O_2 production × electric cost) to fuel cost (hereinafter referred to as Oxy-Fuel ratio). I examined the profitability of oxy-fuel combustion using HT-PSA in each group. The detail of three groups is shown in Table.4.

Table.4 detail of three groups classified by Oxy-Fuel ratio

	Group1	Group2	Group3
Representative Countries	South-Eastern Asia etc.	Japan, Europe etc.	North American etc.
Oxy-Fuel ratio	0.008-0.015	0.02-0.10	0.30-0.35

Fig.11 shows the relation between Oxy-Fuel ratio and cost saving with respect to each exhaust temperature. It shows that oxy-fuel combustion using HT-PSA could reduce running costs under almost all exhaust temperature conditions in the group1 including South-Eastern Asian nations, and group2 including Japan and European nations. In the group1 (especially low electric cost), 25-30% of cost down is estimated under 800-1000℃ exhaust temperature, which is the most realistic. On the other hand, in the group3 (greatly low fuel cost), it is estimated that oxy-fuel combustion is profitable only under very high exhaust temperature conditions.

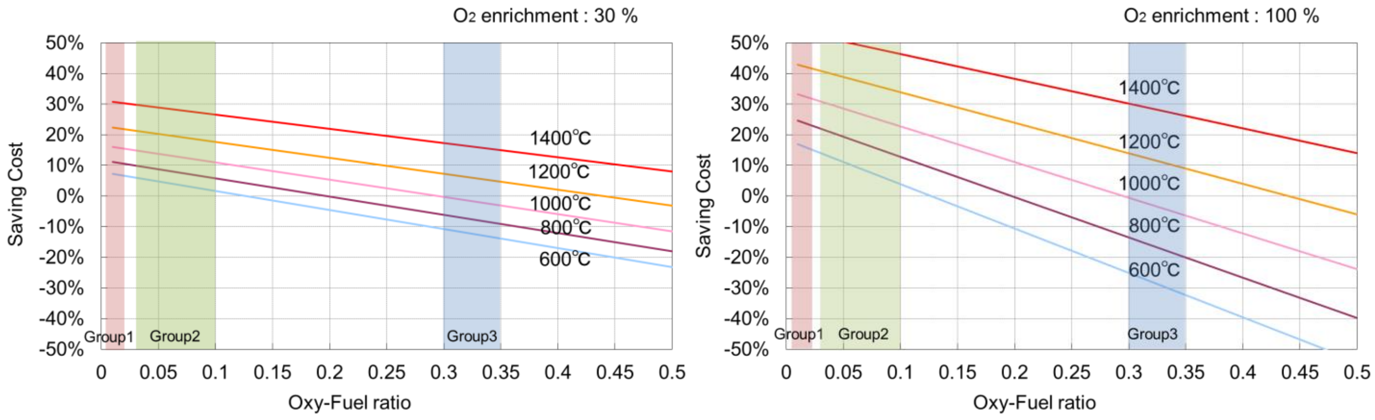


Fig.11 profitable line of oxy-fuel combustion (O_2 enrichment 30% and 100%)

4.3 Energy saving in actual conditions

In this chapter, I examine the energy saving results of oxy-fuel combustion using an actual furnace. As mentioned above, the reduction of exhaust loss by oxy-fuel combustion can conserve energy. In practice, increase of flame temperature and brightness can also conserve energy by the promotion of heat transfer.

The results of oxygen-enriched combustion test are below. Table.5 shows exhaust loss and available heat per $1m^3N$ fuel of air combustion and oxygen-enriched combustion (O_2 28.3%) under 1125℃ exhaust temperature. It shows the reduction of exhaust loss by oxygen-enriched combustion can reduce energy consumption by 18%.

Table.5 exhaust loss, available heat and cost saving rate per $1m^3N$ fuel

O_2 enriched rate	Exhaust loss	Available heat	Energy saving rate
(%)	(MJ/m^3-f)	(MJ/m^3-f)	(%)
21	20.65	19.99	0
28.3	16.27	24.37	17.99

However, it was found that the energy saving rate was 34.1% in our test (Fig.12). This difference between calculated value and experimental value is thought to be due to the promotion of heat transfer by increase of flame temperature and brightness.　Although it is difficult to calculate the energy saving, the result of our test confirms the promotion of heat transfer has large energy saving effect.

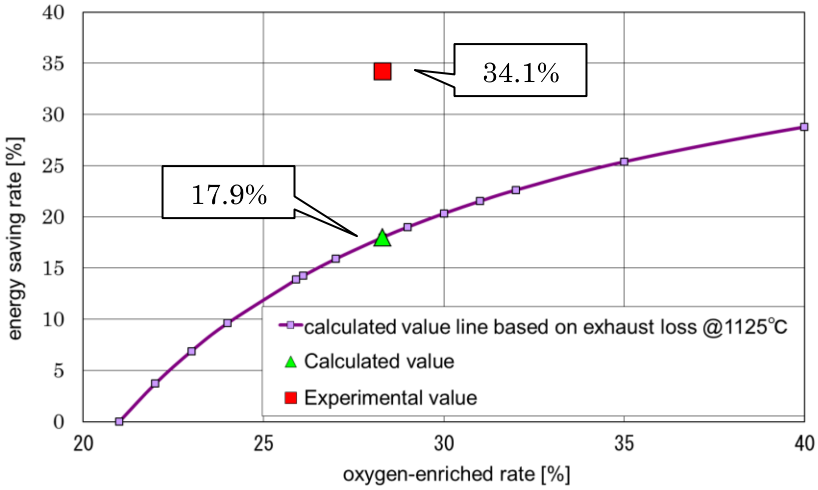


Fig.12 actual energy saving in comparison to calculated value based on exhaust loss

Fig.13 shows the flame of air-fuel combustion and oxygen-enriched combustion. The flame brightness of air-fuel combustion is extremely low and it cannot be seen in the picture. However, the flame brightness of oxygen-enriched combustion is high, and its flame shape is clearly confirmed in the picture. This brightness has great importance for heat transfer under high temperature above 1000℃.

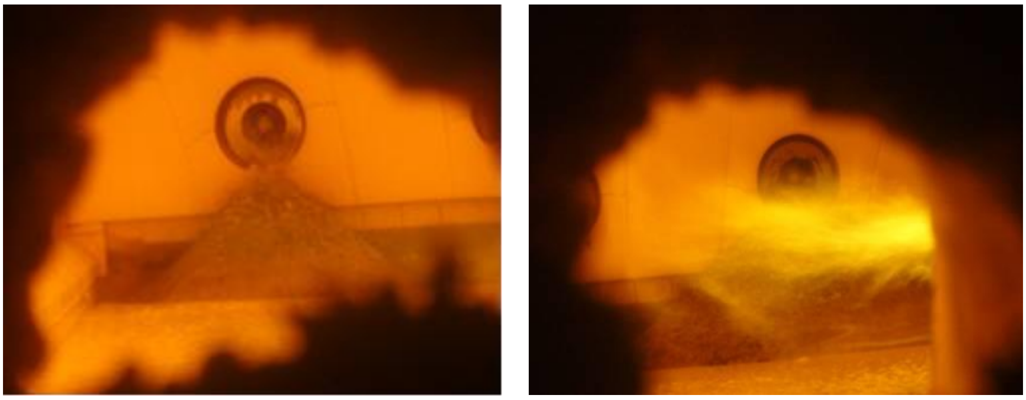


Fig.13 flame of air-fuel combustion (left) and oxygen-enriched combustion (right)

5 Summary

In this paper I described the energy saving effects of oxy-fuel combustion, and HT-PSA as the technology to reduce the oxygen production cost. We have conducted HT-PSA experiments by the pilot scale machine (5m^{3}N/h), and as a next step we are going to produce prototype machine (100m^{3}N/h) and demonstration machine (500m^{3}N/h) in order to advance this development.

In short, the energy saving effect is measured as below,

(Decreased use of fuel by oxy-fuel combustion) – (Increased use of power by oxygen production)

The former depends not only on reduction of exhaust loss but also promotion of heat transfer. Oxy-fuel combustion is especially useful under high exhaust temperature such as glass melting furnace.

And power for oxygen production will be greatly reduced by use of HT-PSA instead of conventional methods.

We believe that by completing HT-PSA development, we can promote the efficiency of natural gas usage and can spread the energy saving technology all over the world.

Reference

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