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Installation and Operation of High Purity CO Gas Recovery Plant

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Installation and Operation of High Purity CO Gas Recovery Plant*



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1 Introduction

BOF (basic oxygen furnace) gas has a high CO content and low contents of undecomposed hydrocarbon and sulfur compounds, and, as a result, has, in recent years, been considered promising as a source of CO for so-called C1 chemistry and other applications. However, separation of CO from BOF gas requires separation of CO gas from N_2 gas. Because these compounds have similar physical characteristics, separation by physical methods, such as the cryogenic separation method or adsorption method, was considered difficult. As a result, conventional CO gas separation techniques, such as the COSORB method (toluene $\cdot CuAlCl_4 + CO \rightleftarrows CO \cdot CuAlCl_4 +$ toluene), which use a liquid adsorbent, have been practically used, but this method requires strict pretreatment of raw materials and is not suitable for medium- and small-scale facilities due to costs involved. Under such circumstances, Kawasaki Steel, in cooperation with Osaka Oxygen Kogyo, Ltd., developed a system for separating CO from BOF gas by the PSA process, using a 2-stage adsorption operation. This method is called the **COPISA** method (CO pressure-induced selective adsorption), as mentioned in previous reports.[1-4] Kawasaki Steel achieved successful results in a pilot plant test conducted at its Chiba Works.

Since the market scale for CO as an industrial gas was small at about 100 000 m^3 annually, however, the feasibility of establishing a commercial CO gas plant depended on the promotion of new sources of demand. At about this time, a plan was being formulated at the Mizushima Factory of Mitsubishi Gas Chemical Co., Inc., which adjoins Kawasaki Steel's Mizushima Works, for the construction of a plant for the production of trimellitic anhydride ($C_6H_3(CO)_2 \cdot OCOOH$) utilizing metaxylene. The Mizushima Works drafted a plan for construction of the No. 1 commercial COPISA plant with the aim of supplying the Mitsubishi Gas Chemical Plant with high purity CO gas. The CO gas manufactured by the Kawasaki Steel plant, it was planned, would also be used in the basic oxygen furnace steelmaking at the Mizushima Works as a substitute for argon gas for bubbling. In the following, the outline and operation of the No. 1 commercial COPISA plant are described.

2 Background of the Plan

In the Mizushima area, common use of natural resources and energy by enterprises in the industrial complex has been energetically promoted for some time, and the Mizushima Works has been supplying, by pipeline, oxygen gas, nitrogen gas, and byproduct gas to various enterprises in the complex area. Further, in

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recent years, in the sale of gases to the makers of industrial gases such as liquefied oxygen, nitrogen and argon gases, and in the manufacture and supply of city gas to city gas makers, the Mizushima Works has even reached the stage of replacing gas making operations for these gas makers. Cooperation among industries in the complex in terms of utilizing these resources and energy is now being studied with the aim of achieving still higher levels.[5] The recent supply of CO gas to Mitsubishi Gas Chemical Co., Inc. is the first step in a new stage of the supply of raw materials to the synthetic chemical industry.

3 Related Circumstances

Mitsubishi Gas Chemical Co., Inc. adjacent to the Mizushima Works, had previously developed a manufacturing process for trimellitic anhydride (TMA), a raw material for highgrade plastics; Mitsubishi's unique techniques use metaxylene (MX), a then comparatively little used chemical raw material. Mitsubishi Gas Chemical Co., Inc. was planning, at that time, to construct a TMA factory in the Mizushima Area. The process, however, requires high purity CO gas for the step of manufacturing dimethylbenzaldehyde (DBAL) from MX,[5] as shown in **Fig. 1**.

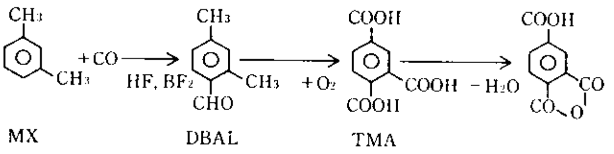

Fig. 1 TMA process from MX and CO

The high purity CO gas which is used in this reaction is under particularly severe restrictions on H_2O (dew point) and O_2 (because of generation of H_2O by reaction with H_2), because the catalysts HF and BF_3 are decomposed by H_2O. Thus the following conditions must be met:

CO purity: 98% or above
CO pressure: 25 kgf/cm^2·g or above
CO dew point: −60°C or below (H_2O, 10 ppm or below)
O_2: 1 ppm or below

As a measure for obtaining this level of purity in CO gas, it was first planned to use the methyl formic acid process, using methanol as raw material, with CO and H_2 produced by the following processes:

$$2CH_3OH \longrightarrow HCOOCH_3 + 2H_2$$
$$HCOOCH_3 \longrightarrow CH_3OH + CO$$

The production flow chart for these processes is shown in **Fig. 2**.[5] In the processes, raw-material methanol accounts for about 90% of variable production costs,

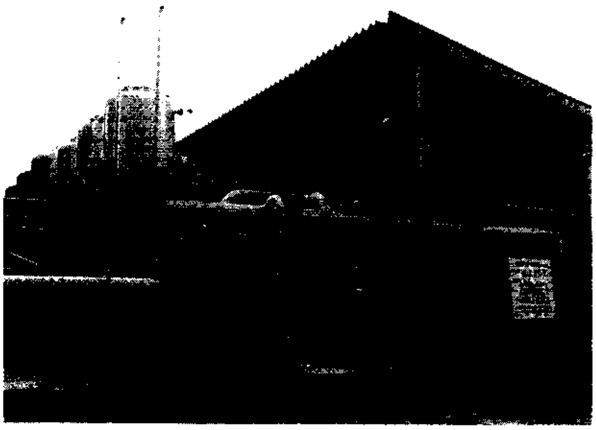

Photo 1 COPISA at Mizushima Works

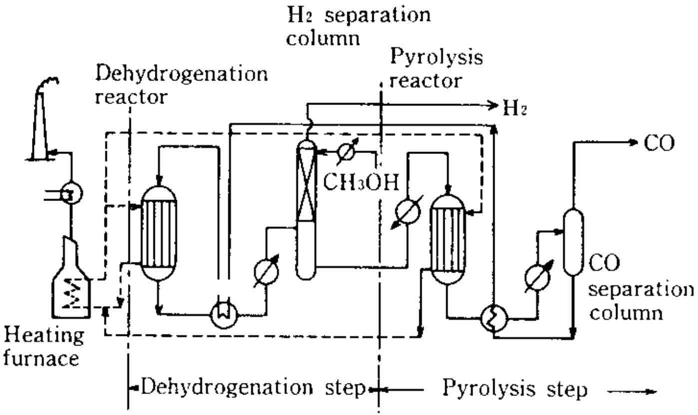

Fig. 2 Flowsheet of CO production by methyl formic acid process

whereas in the COPISA process, electric power is the principal cost item, although it is predicted to be reduced to about 50% of the total on a variable cost basis. Therefore, after taking into consideration the effective utilization of these resources and energy among the enterprises in the complex area, sourcing of CO gas from the COPISA commercial No. 1 plant was decided. Further, it was found that, besides the CO gas supply to Mitsubishi Gas Chemical Co., Inc., CO gas can, as already mentioned, be used as a substitute for the argon gas used in bubbling in the LD-KGC process at the Mizushima Works. It was decided, therefore, to construct facilities with a production capacity capable of coping with the CO gas requirements of the steelworks. The external view of the facility is shown in **Photo 1**.

4 Outline of COPISA Process

The total-balance flow chart of COPISA is shown in **Fig. 3**; the total flow chart is shown in **Fig. 4**. Separation and refining of high purity CO from BOF gas in the present facilities consists, broadly speaking, of the following processes:

(1) Pretreatment process ⟶ (2) CO_2 separation process ⟶ (3) N_2 separation process ⟶ (4) Refining process (de-O_2 and de-H_2O).

4.1 Pretreatment Process

In this process, the pressure of the feed gas (BOF gas) is raised and the dust is removed. The BOF gas is supplied to the subsequent de-CO_2-PSA (pressure swing adsorption) process. Equipment consists of an BOF gas compressor and a dust collector. A feature of the COPSIA system as a PSA unit is its comparatively low operation pressure. Since the necessary supply pressure for the BOF gas is about 0.5 to 1.5 $kg/cm^2 \cdot g$, a BOF gas compressor of the reciprocating type, a Roots blower, or screw type device can be used.

4.2 CO_2 Separation Process

In this process, CO_2 in the feed gas is selectively adsorbed and separated, and CO and N_2 are sent on to the subsequent process. Equipment consists of the de-CO_2-PSA and evacuation gas vacuum pump. The de-CO_2-PSA is composed of two or three adsorption columns filled with adsorbents such as activated carbon, which has a selective adsorbing property with respect to CO_2. The adsorption cycle is discussed in the following:

(1) Adsorption
The gas is passed through adsorption columns which have completed regeneration, and CO_2 is adsorped and separated. To prevent CO_2 from leaking into the gases (mainly CO and N_2) being passed through the column, the adsorption step ends before the CO_2 break-through point (saturation and adsorption point) is reached.

(2) Depressurization
The pressure in the adsorption columns where the adsorption step has ended is reduced to atmospheric pressure.

(3) Evacuation
After the pressure in the adsorption columns has been reduced, the gas is evacuated to a sub-atmospheric pressure by the evacuation vacuum pump.

(4) Purge by Waste Gas
After depressurization, CO_2 is further desorbed and regenerated by purging with a gas that contains no CO_2. As the purge gas in this case, a waste gas from the de-N_2-PSA (discussed below) is used. The gas

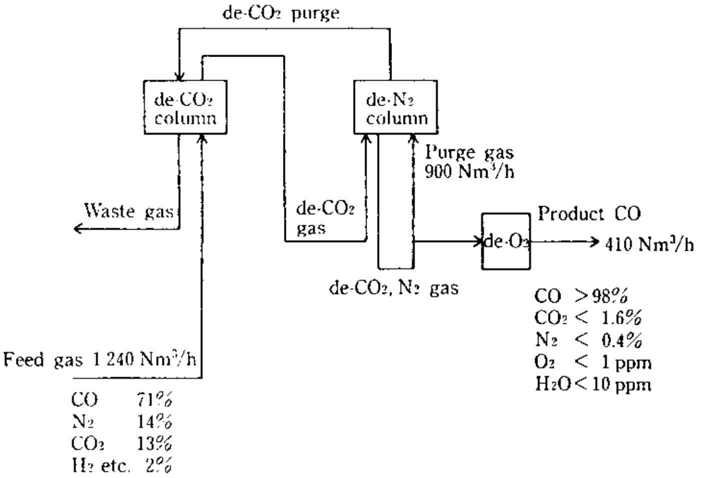

Fig. 3 Typical balance of COPISA

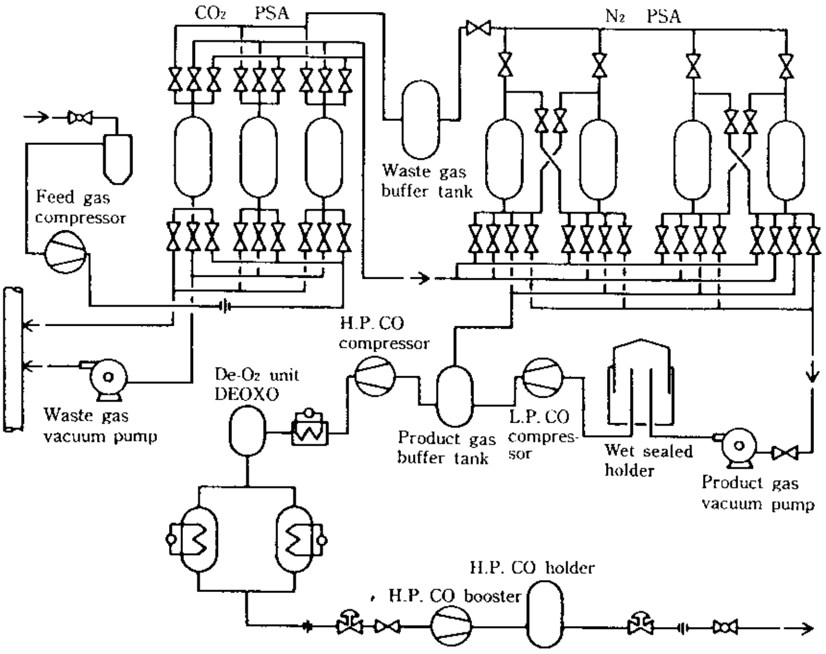

Fig. 4 Schematic flow of COPISA

flow during purging is as follows:

De-CO_2-PSA (during adsorption) ⟶ de-N_2-PSA (during adsorption) ⟶ waste gas buffer tank ⟶ de-CO_2-PSA (during purge) ⟶ evacuation vacuum pump

(5) Pressurization by Feed Gas

Adsorption columns in a vacuum state, when purging by waste gas and regeneration are complete, are slowly pressurized with feed gas until adsorption pressure is reached.

The steps (1) to (4), described above, comprise the complete CO_2-PSA adsorption and regeneration cycle. The de-CO_2-PSA can be operated with two columns, from the viewpoint of of cycle structure, but in commercial operation, three columns are used in alternation.

4.3 N_2 Separation Process

The gas leaving the de-CO_2-PSA is obtained by adsorbing and removing CO_2 from the feed gas; its composition is 82% CO, 16% N_2, and about 2%($H_2 + O_2$). The gas thus obtained is sent to the de-N_2-PSA (Fig. 3). The de-N_2-PSA is filled with a zeolitebased adsorbent which has a selective adsorption capacity of a CO/N_2 ratio of about 2.5 to 3.0, as shown in **Fig. 5**. Through a synergistic effect involving the partial pressure ratio of the gas ($CO:N_2 = 5:1$), high density CO is adsorbed in the de-N_2-PSA (= adsorption step). Further, to obtain CO of high purity, 98% or above as a target, a portion of the product CO (98%) gas is used for purging the adsorption columns which have just completed adsorption, thereby raising the purity of the adsorbed CO gas to 98% (= purging step).

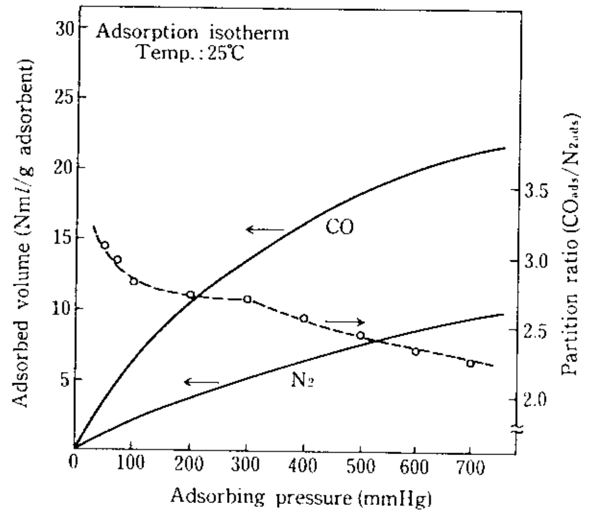

Fig. 5 Adsorption isotherm of de-N_2 PSA

In the de-N_2-PSA, the product gas is obtained at the adsorption side differently from the case with the ordinary PSA. Therefore, the product gas is recovered under reduced pressure by the vacuum pump. The adsorption cycle of the N_2-PSA is discussed in the following:

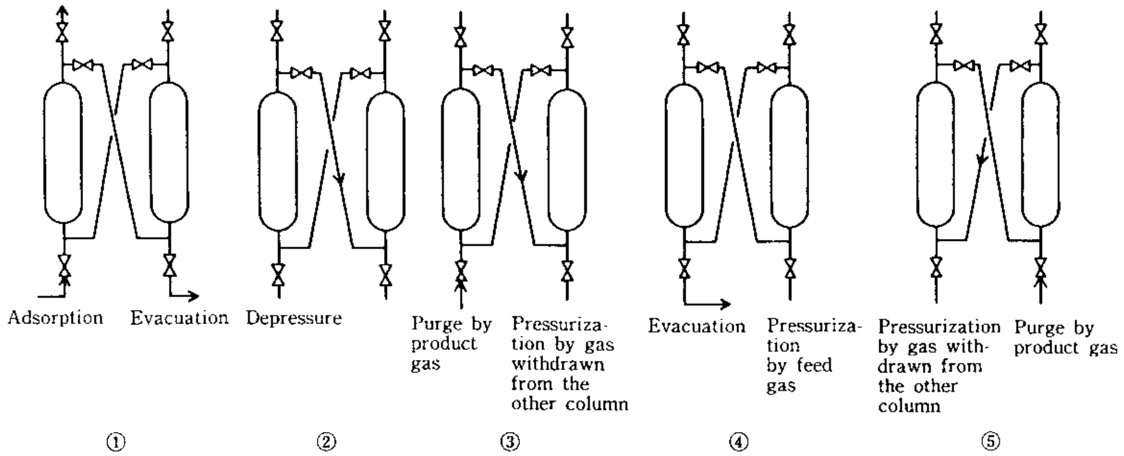

Fig. 6 Operation of de-N_2 PSA

(1) Adsorption (**Fig. 6** ①)
The gas from the de-CO_2-PSA is passed through the N_2-PSA, and CO gas is mainly adsorbed in this step. Since the product gas is obtained at the adsorption side, adsorption is performed near the CO breakthrough point. Gas which has passed through the de-N_2-PSA and mainly consists of N_2 and CO is used as a purge gas in the de-CO_2-PSA, in purging by waste gas.

(BOF gas) → de-CO_2-PSA (adsorption) → de-N_2-PSA (adsorption) → de-CO_2-PSA (purge by waste gas) → evacuation vacuum pump → waste-gas main pipe

(2) Depressurization (Fig. 6 ②)
Residual pressure in the adsorption column, after completion of adsorption, is evacuated into another adsorption column which forms a pair with the first column and where evacuation is complete; in this manner the product gas is recovered.

(3) Purge by Product Gas (Fig. 6 ③)
A portion of the product CO gas is fed to the adsorption column where depressurization is complete, thereby raising the concentration of adsorbed CO gas to the design purity level (98%). The CO gas to be used in purging is a portion of the CO recovered by evacuation from the adsorption column which is in a product-CO recovery state (Fig. 3). The purge gas which has passed through the adsorption column is, as in depressurization, recovered into a adsorption column, which forms a pair with the first column, where the product gas is being pressurized. The flow of the product CO gas at this time is shown below.

De-N_2-PSA (CO recovery by evacuation) → CO recovery vacuum pump → wet-seal gas holder → product CO compressor (low pressure) → product gas buffer tank

→ de-N_2-PSA (purge by product gas) → de-N_2-PSA (pressurization by product gas)

→ Product CO compressor (high pressure) → refining unit → Product CO

(4) CO Recovery by Evacuation (Fig. 6 ④)
From the adsorption column, in which purging has been completed and CO of prescribed purity (98%) has been adsorped, the product CO gas is recovered, after vacuum desorption, by the product recovery vacuum pump. The flow of the product CO gas is the same as that shown above. That is, part of the product CO gas is used as a purging gas, and the remainder is sent to the refining unit through a high-pressure CO compressor.

(5) Pressurization by Product Gas (Fig. 6 ⑤)
Into the adsorption column which has completed CO recovery by evacuation and is in the vacuum state (100 to 50 Torr), another adsorption column, which forms a pair with the first, introduces the residual gas remaining at the time of completion of adsorption, and then a purge gas is introduced, thereby pressurizing the first adsorption column.

As mentioned above, two adsorption columns in the de-N_2-PSA operate as a pair. When one adsorption column is in the purge state, the other adsorption column recovers the purge gas, thereby enhancing the CO recovery ratio. For this reason, a minimum of four adsorption columns is used in the N_2 separation process.

4.4 Refining Process

In this process, oxygen and moisture are removed from the 98% purity CO gas, which has been recovered from the N_2 separation process, to produce the CO ($O_2 < 1$ ppm and $H_2O < 10$ ppm), which is used as a chemical raw material.

(1) Deoxidation

To remove oxygen from CO, it is necessary to convert O_2 into CO_2 by the following reaction, using a catalyst after preheating:

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

The CO_2 gas formed here is permissible as an impurity, assuming the CO gas has the prescribed purity of 98%. Therefore, no CO_2 removal equipment is required.

(2) Dehydration

Since the high purity CO gas recovered from the de-N_2-PSA passes through a water-seal-type vacuum pump and wet-seal gas holder, the gas is in a moisture-saturated state. Therefore, moisture is removed by adsorption using molecular sieves.

5 Specifications of Facilities

Basic specifications of the COPISA at the Mizushima Works are shown in **Table 1**. Specifications of component equipment are almost the same as those for the pilot plant at the Chiba Works. The planned balance of the Mizushima COPISA plant is shown in Fig. 3.

5.1 Feed Gas Compressor

The necessary pressure of the feed gas is 0.5 to 1.5 kg/cm^2·g. Considering durability against dust in the BOF gas and adaptability to partial load operation, an oil-screw-type compressor was adopted in the present facility, along with a compression process method of dust removal.

5.2 De-CO_2-PSA

As the adsorbent in the de-CO_2-PSA, zeolite or activated carbon can be used in view of their adsorption characteristics for CO_2, but in the present facilities, activated carbon, which possesses a high CO_2 removal ratio, is used.

Table 1 Design points of COPISA

		Feed Gas	Product CO
Design volume (Nm^3/h)		1 240	410
Design components	CO	≥71%	≥98%
	N_2	≤14%	≤1.6%
	CO_2	≤13%	≤0.4%
	O_2	≤ 2%	≤1 ppm
	H_2O (Dew point)	sat.	≤10 ppm (D.P.< −60°C)

Table 2 Operation modes of COPISA

Operation modes (%)	Product CO (Nm^2/h)	Cycle time (s)
100	410	120
90	369	133
80	328	150
60	246	200
40	164	300

5.3 De-N_2-PSA

As the adsorbent in the de-N_2-PSA, reformed natural zeolite is used; the selective adsorption characteristics of this adsorbent for CO/N_2 were confirmed at Chiba pilot plant. (See Fig. 5)

5.4 Vacuum Pump

Purging by waste gas in the de-CO_2-PSA and CO recovery in the de-N_2-PSA are both conducted under a vacuum of about 50 to 100 Torr. As vacuum pumps in these operations (an evacuation vacuum pump for the de-CO_2-PSA and a CO recovery vacuum pump for the de-N_2-PSA), water-seal type vacuum pumps are used, taking into consideration the degree of vacuum required, durability, and degree of sealing. Incidentally, the plant performs adsorption at a low pressure of 0.5 to 1.5 kg/cm^2·g, and, therefore, compression power requirements are relatively small; power consumption by vacuum pumps accounts for about 70% of the total.

5.5 Operation Control Method

In the present plant, partial load operation modes of 90%, 80%, 60%, and 40% have been set up against the 100% load (410 Nm^3/h). Since the adsorption and evacuation quantities per PSA cycle are constant, partial load operation involves prolonging the adsorption and evacuation cycle time as shown in **Table 2**. Operation of the present plant is conducted by remote-control from the central control room of the Oxygen Plant about 300 m away. Operating conditions are monitored by CRT screens.

6 Operating Condition

The present facilities have been in service since July 1985; changes in feed gas composition and product CO gas composition are shown in **Fig. 7**. Although the feed gas composition fluctuates depending upon steel blowing timing, a product CO gas purity of 98% or above has

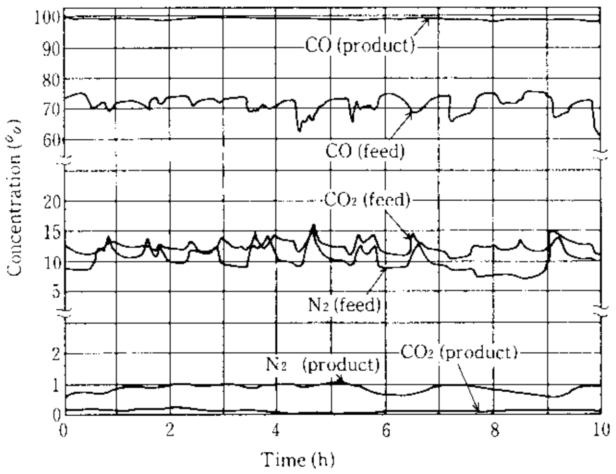

Fig. 7 Changes in feed gas and product gas compositions

been maintained. Impurities in the CO gas mainly consist of N_2; in this respect, the COPISA system differs from the COSORB method, in which impurities consist mainly of CO_2. A matter requiring caution in the operation and control of the present facilities is that, since the product gas is obtained at the adsorbed side in the present facilities, contrary to the case in an ordinary PSA, where CO is removed by vacuum depressurization, leakage at the PSA change-over valve may directly affect product purity.

With deoxidation equipment, excessive gas temperature caused by the preheater at the equipment inlet side may cause deposition of carbon in the following decomposition reaction:

$$2CO \longrightarrow C + CO_2$$

Therefore, careful temperture control is essential. Further, the catalysts for deoxidation are more easily affected by trace ingredients in the gas than the adsorbent used in the PSA proper, and thus pretreatment as appropriate to the catalysts used may become necessary.

The CO recovery ratio (ratio of product high-purity CO to CO in feed gas) in the present plant is about 45% according to the gas balance shown in Fig. 3. Unrecovered CO is evacuated as waste gas. As a result, the waste gas from the present plant has a calorific value of about 1 700 kcal/Nm^3, and is recovered into the BOF gas main pipe for reuse as fuel. Further, in the COPISA system, the CO recovery ratio improves as the CO concentration in the feed gas rises. In the Chiba Pilot Plant, a recovery ratio of more than 60% has been achieved for feed gas CO concentrations of 80 to 85%.

7 Conclusions

With the installation of CO separating and refining equipment at the Mizushima Works, pipeline-supply of high purity CO gas to the adjacent chemical plant began. This equipment uses CO_2 adsorbents such as activated carbon in its first stage and CO adsorbents such as zeolite in the second stage, thereby making it possible to separate and refine a CO gas of 98% purity from a mixed gas of CO and N_2, compounds with similar physical properties. The recovery ratio of CO with respect to CO in the feed BOF gas is about 45%.

This project has been realized, commercially, as a result of a combination of the development of a new process on the steel mill side and a new demand for CO on the chemical plant side. The projects gives an indication of the future orientation of the industrial complex and has opened the way for high-added-value utilization of steel mill byproduct gases.

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