

# Abating Environmentally Harmful Waste Gases

S. Sridhar, Du Sichen, U.B. Pal, and S. Seetharaman

*A gas-purification method, based on the condensation of nitrogen, sulfur, and carbon-containing environmentally hazardous gases produced from industrial processes, is proposed in this article. The method, which utilizes the cooling capacity of waste nitrogen in the oxygen plant to condense the hazardous gases, is capable of removing hazardous impurities up to 99.98%. Theoretical calculations underlying the condensation process are presented employing gases produced in a blast furnace and coke oven in an integrated steel plant. The cooling power required for the condensation process is calculated using the waste nitrogen generated from an oxygen plant that generates captive oxygen for the steel plant. Design modifications that need to be made to the oxygen plant in order to utilize the cooling power of the waste nitrogen gas are also presented. As a case study, the advantages of the method are illustrated with purification of coke-oven gas. The economic impact and the investment aspects are also discussed.*

## INTRODUCTION

Environmental pollution is considered to be a major global problem. It is well known that the SO<sub>2</sub> gas produced in the extraction of metals, especially copper, as well as during coal gasification, has resulted in acid rain, seriously damaging vegetation and fish. Suitable alternatives to metallurgical coke are being investigated in view of the environmental hazards of H<sub>2</sub>S gas that is present in significant amounts in coke-oven gas. CO<sub>2</sub> gas produced in various combustion processes has been suspected to cause the greenhouse effect. Although various methods have been proposed to reduce the amount of such gases escaping into the atmosphere,

**Table I. Physical Properties of Some Compounds<sup>1</sup>**

Compound	Melting Point in K	Boiling Point in K
H <sub>2</sub>	13.86	20.2
O <sub>2</sub>	54.6	90.04
N <sub>2</sub>	63.14	77.2
CO	74	81.5
CH <sub>4</sub>	91	109
NO	109.4	121.2
COS	135	223
H <sub>2</sub> S	187.5	212.3
SO <sub>2</sub>	200.3	263
CO <sub>2</sub>	216.4	194.5*
NO <sub>2</sub>	261.8	294.2

\* sublimates

each has its inherent drawbacks. A complete solution to the problem does not presently exist.

## METHODS USED TODAY

The processes for SO<sub>2</sub> removal from industrial gases can be classified into wet and dry methods. The wet methods use various types of suspensions of adsorbents, both aqueous and non-aqueous, in gas scrubbers. The absorbing materials are generally based on calcium hydroxide, although other types of materials have also been proposed. In the dry methods, finely divided materials—usually metallic oxides such as CaO or compounds like dolomite—often are kept in gas filters. The disadvantages of these chemical

adsorbents are that the efficiency of the method is often dependent on kinetic factors such as residence time and temperature. Further, removal of the hazardous species from the flowing gas stream is often incomplete. Another important limitation is the disposal of the product material, which, by itself, is an environmental problem. The calcium-sulfur compounds that are formed by the reaction between CaO and sulfur-containing gases could be oxidized to gypsum, but the market for the same is limited to the construction industry. Hence, the surplus material often finds itself in large dumps. In wet scrubbers, some of the SO<sub>2</sub> pollutant is used in the production of sulfuric acid. The market for this acid is limited within the chemical and the fertilizer industries, however, and restricted mostly to the developed countries. Further, the production of the acid is economically profitable only if the SO<sub>2</sub> content in the gas is beyond a critical value. In the case of CO<sub>2</sub>, the steps taken today are more toward the minimization of the amount escaping into the atmosphere. The situation is very similar even in the case of NO<sub>x</sub>.

## PRINCIPLE OF THE SUGGESTED METHOD

The principle of the present method is to use a cryogenic technique to liquefy

**Table II. Vapor Pressure (mmHg) of Some Sulfides<sup>1</sup>**

Sulfides	Pressure (mmHg)						Melting Point (K)
	1	10	40	100	400	760	
H <sub>2</sub> S (K)	138.7 <sub>s</sub>	156.7 <sub>s</sub>	170.7 <sub>s</sub>	181.4 <sub>s</sub>	193	201.2	187.5
SO <sub>2</sub> (K)	177.5 <sub>s</sub>	192.5 <sub>s</sub>	196.2 <sub>s</sub>	226.1	250	263	199.8
COS (K)	140.6	159.7	174.7	187.1	190.3	232.1	134.2

The subscript s denotes the gas-solid (sulfide) equilibrium.

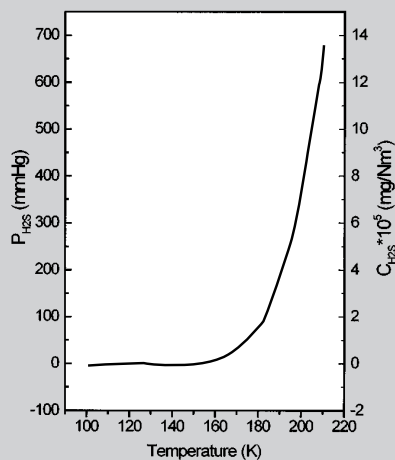


Figure 1. The concentration and vapor pressure of H<sub>2</sub>S in the gas phase as a function of temperature.

the hazardous species in the waste gases emanated from various processes. These species generally have higher melting and boiling points as compared to fuel gases such as hydrogen and carbon monoxide (see Table I).

Hence, a condensation temperature of around 110 K would selectively liquefy these gases and allow the pure fuel gases to be recovered. With the design of a good heat exchanger, the environmentally hazardous gases can be recovered to near 100%. Converting the condensed gases into useful forms can further enhance the process economy. For example, the liquid SO<sub>2</sub> recovered could be concentrated by fractional distillation and converted to sulfuric acid or allowed to react with H<sub>2</sub>S to form elemental sulfur, both of which are of economic value.

In order to examine the possibility of using the cryogenic method, the theoretical principles, suitable process-design schemes, and economic factors have to be considered.

## THEORETICAL CONSIDERATIONS

The theoretical considerations presented here will highlight sulfur abatement from metallurgical industries. Similar arguments hold even for CO<sub>2</sub> as well as NO<sub>2</sub>.

The main sulfur-containing components in the by-product and exhaust gases of the metallurgical industries are H<sub>2</sub>S, SO<sub>2</sub>, and COS. The equilibrium vapor pressures of these gases at different temperatures are presented

in Table II.

It is possible to calculate the equilibrium vapor pressures of the sulfur gases at different temperatures using the data in Table II. The equilibrium sulfide concentrations, C (mg/Nm<sup>3</sup>), can be calculated from the equilibrium partial pressures using Equation 1

$$C = (P/760)/22.4 \times 10^6 \times M \quad (1)$$

where M is the molecular weight of the corresponding sulfur-gas specie. The calculated equilibrium concentration of H<sub>2</sub>S in the gas is plotted in Figure 1 as a function of temperature.

It is seen that the concentration of H<sub>2</sub>S decreases dramatically as the temperature decreases. The concentrations of the sulfur species in the gas phase have been calculated assuming that the gas can be cooled to 108 K using liquid nitrogen from captive oxygen plants in the metallurgical industry. (The liquid oxygen plant is usually operated at 88 K<sup>2</sup>.) The results are presented in Table III.

The concentrations of the sulfur species in the gas phase can be reduced to very low levels using this method. Usually, the concentration<sup>3</sup> of H<sub>2</sub>S is 8–15 g/Nm<sup>3</sup> in the waste gas and, therefore, its content can be reduced by 99.9%, as shown in Table III.

## CASE STUDY: SULFUR GASES FROM IRON-MAKING

The sulfur gases in the iron industry come from coke ovens and, to a lesser degree, blast furnaces. The production rate and the composition of coke-oven and blast-furnace gases are listed in Table IV. This is based on statistics reported in the early 1980s by U.S. companies<sup>2</sup> (the ratio of coke to iron produced in the blast furnace is taken as 300–400 kg/t-Fe).

According to the same statistics,<sup>2</sup> the amount of oxygen consumption is 56.7

Table III. Equilibrium Vapor Pressure and Concentration of Sulfide in Gas Phase at 108 K

Sulfide	P mmHg	Concentration	
		P/760, atm.	mg/Nm <sup>3</sup>
H <sub>2</sub> S	4.78*10 <sup>-3</sup>	6.28*10 <sup>-6</sup>	9.53
SO <sub>2</sub>	2.98*10 <sup>-6</sup>	3.9*10 <sup>-9</sup>	0.011
COS	7.01*10 <sup>-3</sup>	9.23*10 <sup>-6</sup>	24.7

Nm<sup>3</sup>/t-steel. If one assumes that 20% more oxygen is required, it is apparent that production of liquid oxygen is 68 Nm<sup>3</sup>/t-steel, and production of liquid nitrogen is 272.2 Nm<sup>3</sup>/t-steel.

The enthalpy change corresponding to the process by which liquid oxygen and nitrogen are heated to 293 K can be estimated from the physical properties of the gases, including the critical temperature and pressure as well as the heat capacities and heat of vaporization. The authors' estimates lead to a value of 1.82 × 10<sup>5</sup> kJ/t-steel. This is shown in Figure 2. The estimated negative enthalpy changes of the coke-oven gas and the blast-furnace gas due to cooling to liquid-air temperatures are also plotted in Figure 2. It is seen that, in the case of the coke-oven gas, the heat absorbed by liquid oxygen and nitrogen produced in the oxygen plant of the steel industry is more than sufficient to condense the sulfide species in the gas phase. However, in the case of the blast-furnace gas, the heat absorbed by liquid oxygen and nitrogen can cool the gas to 210 K, which is only 3 K lower than the boiling point of H<sub>2</sub>S, as can be seen in Table I. This is due to the huge amount of the blast-furnace gas (1,350–1,890 Nm<sup>3</sup>/t-Fe). Even then, most of the SO<sub>2</sub> and CO<sub>2</sub> from the blast-furnace gas can be removed by the condensation method. In the case of the coke-oven gas, the sulfur content

Table IV. The Productive Rate and Composition of Gases

Gas	P.R.** m <sup>3</sup> /t-Fe	Composition (vol.%)							
		CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>
Coke O	148–179	2.2*	0.8	8.1	6.3	46.5	32.1	3.5	0.5
Blast F	1,350–1,890	11.5	—	60.0	27.5	1.0	—	—	—

\* Including H<sub>2</sub>S

\*\* Production Rate

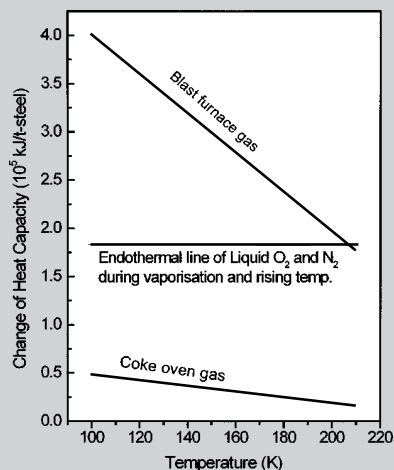


Figure 2. The heat balance during cooling of gases by liquid oxygen and nitrogen.

is much higher than that in the blast-furnace gas. Hence, the development of this method is of importance in both cases.

## DESIGN OF THE CONDENSATION PROCESS

Based on the above principles, a design for the adaptation of the condensation process to the existing industrial metallurgical processes was developed and patented.<sup>4</sup> Figure 3 describes the Heylandt air-separation system.<sup>5,6</sup> The installation is an example of how the present invention can be modified in order to utilize the existing, but unused, cooling capacity in an air-separation system for purifying industrial gases, such as the coke-oven gas. In normal practice, incoming air is pre-cooled by outgoing excess nitrogen at liquid-air temperature and enters the lower part of the column. As the air expands, it gets liquefied and the excess nitrogen escapes through the upper portion of the tower.

The cooling capacity of the outgoing nitrogen can be utilized to cool the furnace gases instead of the incoming air by means of heat exchangers, as shown in Figure 3. The outgoing furnace gas, cooled to nearly 113 K, in turn can cool the incoming air, thereby keeping the Heylandt system operating.

The heat exchangers suggested are dual regenerative exchangers. One of them operates with the furnace gases, enabling the preferential condensation of the hazardous gases, while the other uses the exit gases to cool the incoming

air. The intermittent functioning of these exchangers enable the condensed gases to be re-gasified so that the impure gases can be processed further. In the case of sulfur gases, for example, the Claus process or other appropriate methods can be applied.

## APPLICABILITY TO DESULFURIZATION OF COKE-OVEN GAS

The data for the coke-oven battery with 34 gates in a standard integrated steel plant was obtained from *The Making, Shaping and Treating of Steel*.<sup>2</sup> The products from the coke ovens per tonne of coal, retrieved from the same source, are presented in Table VI. From that data, it is possible to calculate the production rate of coke, coke-oven gas, and pure sulfur per year (330 days): coke:  $53.52 \times 34 \times 0.7/24 = 53$  tonne/hour, 420,000 tonne/year; coke-oven gas:  $2.48 \times 10^4 \text{ Nm}^3/\text{hour}$ ,  $1.96 \times 10^5 \text{ Nm}^3/\text{year}$ ; sulfur: 247 kg/hour, 1,960 tonne/year.

### The Oxygen Plant

The capacity of a modern oxygen plant operating to support an integrated steel plant is very high (2,300 tonnes of oxygen per day). The technical specifications of the KTD-41000 oxygen plant are shown in Table VII.

To incorporate this oxygen plant into the present condensation-oxidation process, a part of the cold air at the exit of the expansion turbines needs to be used for the cooling of the coke-oven gas and cleaning the condensed deposits of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . This will alter the amounts of gases in Table VII to some extent. Assuming that the air requirement for the above is about 3%, the amount of gases produced can be estimated as oxygen ( $6,250 \text{ Nm}^3/\text{h}$ ,  $4.95 \times 10^7 \text{ Nm}^3/\text{year}$ ); nitrogen ( $6,870 \text{ Nm}^3/\text{h}$ ,  $5.44 \times 10^7 \text{ Nm}^3/\text{year}$ ); waste nitrogen ( $26,650 \text{ Nm}^3/\text{h}$ ,  $2.11 \times 10^8 \text{ Nm}^3/\text{year}$ ); and branch air ( $1,230 \text{ Nm}^3/\text{h}$ ,  $9.74 \times 10^6 \text{ Nm}^3/\text{year}$ ).

These two units can be employed in an integrated steel plant producing 900,000 tonne/year (oxygen:  $57.5 \text{ Nm}^3/\text{tonne steel}$ ; coke:  $450 \text{ kg/tonne iron}$ ).

### The Heat Exchangers

If the coke oven has to be cooled to 108 K, the reversible heat exchangers

ought to work at very low temperatures. If the hot and cold ends of the heat exchanger are at 290 K and 80 K, respectively, the heat exchanged,  $Q$ , can be calculated for a given flow rate as follows:

$$Q = \int_0^A k \cdot \Delta T \cdot dA \quad (2)$$

where  $A$  is the area and  $k$  is the heat-transfer coefficient. With an optimum design of a multi-channel-heat-exchanger system provided with fins to improve heat transfer, under forced convection, the value of  $k$  can be as high as  $35\text{--}350 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ .<sup>7</sup>

Assuming the temperature differences at the hot as well as the cold ends

Table V. Performances of High-Capacity Coke Ovens

Coking-chamber height	7.5 m
Length, face to face	16.48 m
Length between doors	15.60 m
Coking-chamber width, coke side	0.488 m
Coking-chamber width, pusher side	0.412 m
Number of twin flues	17
Working volume of oven	48.230 m <sup>3</sup>
Coal throughput per oven per day	53.520 t
Coking time	17 h

Table VI. Data per Tonne Coal

Products	Productivity
Blast furnace coke	600–800 kg
Coke freeze	50–100 kg
Coke-oven gas	296–358 Nm <sup>3</sup>
Tar	30.3–45.4 l
Ammonium sulfate	10–13.8 kg
Light oil	9.5–15.1 l

Table VII. The Performances of KTD-41000 Gaseous-Oxygen Generating Plant

Treatment Rate of Air	41,000 Nm <sup>3</sup> /h
Oxygen	
Gas-generation rate	6,440 Nm <sup>3</sup> /h
Temperature at exit of distillatory	93 K
Nitrogen	
Gas-generation rate	7,080 Nm <sup>3</sup> /h
Temperature at exit of distillatory	79 K
Waste nitrogen	
Gas-generation rate	27,480 Nm <sup>3</sup> /h
Temperature at exit of distillatory	80 K

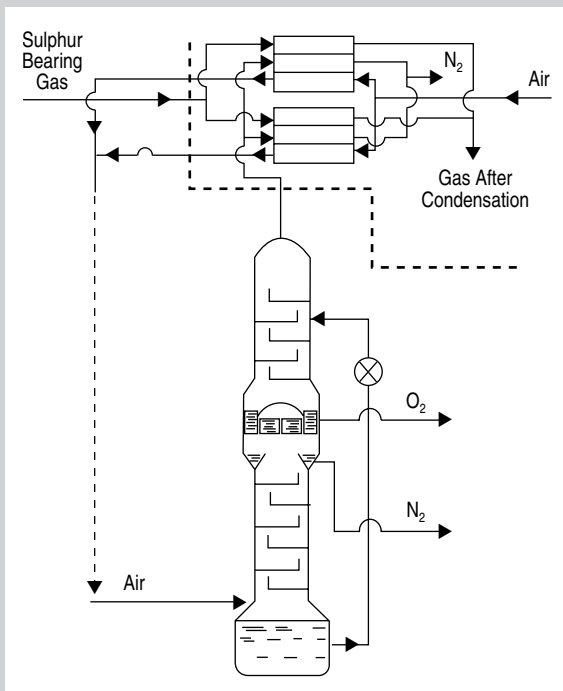


Figure 3. A Heylandt air separation system incorporated with the condensation unit.

oven to the oxygen plant, and pipeline modifications in the oxygen plant; and sulfur recovery (Clous system and Clous tail-gas treatment system). (These systems are commonly used today. Hence, there is no need for further investment.) The operation for the oxygen plant will increase slightly; some cost will be associated with energy loss during circulation, a part of the air will be used to flush the condensed  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , etc., so the oxygen-production rate will decrease a little.

## ACKNOWLEDGEMENT

The authors are thankful to X. Xiao for his contribution to the process calculations.

## References

1. R.C. Weast, editor, *CRC Handbook of Chemistry and Physics*, 61st edition (Boca Raton, FL: CRC Press, 1980–1981).
2. T.L. William, Jr. et al., editors, *The Making, Shaping and Treating of Steel* (Pittsburgh, PA: AISE, 1985).
3. L.K. Arthur and C.R. Fred, *Gas Purification*, third edition (Houston, TX: Gulf Publishing Company Book Division, 1979).
4. S. Seetharaman, X. Xiao, and Du Sichen, Swedish patent 503 097 (1996).
5. G. Rosenblad, *Energiteknik I*, (Stockholm, Sweden: Almqvist & Wiksell Förlag AB, 1968).
6. *Ullman's Encyclopedia of Industrial Chemistry*, 5th edition, vol. B3, Chap. 20, Sect. 5.7 (Weinheim, Berlin: Wiley-VCH Verlag GmbH).
7. C. Kakac, *Heat Exchangers* (New York, NY: Hemisphere Publishing Co., 1981).

S. Sridhar is with the Department of Materials Science and Engineering at Carnegie Mellon University. Du Sichen and S. Seetharaman are with the Department of Materials Science and Engineering at the Royal Institute of Technology in Stockholm, Sweden. U.B. Pal is with the Department of Manufacturing Engineering at Boston University.

For more information, contact S. Sridhar, Carnegie Mellon University, Department of Materials Science and Engineering, Pittsburgh, PA 15213, USA; sridhar@andrew.cmu.edu.

of the heat exchanger to be 4 K, the temperature at the entry for the coke-oven gas as 303 K at the hot end, and temperature for air and waste nitrogen as 82 K at the cold end, the heat absorbed by air and waste nitrogen is estimated to be  $2,170 \text{ kJ}\cdot\text{s}^{-1}$ . The corresponding heat released by the coke-oven gas is estimated to be  $1,859.8 \text{ kJ}\cdot\text{s}^{-1}$ . The above calculation shows that the amount of the coke-oven gas can be increased by 18.5%. This means the coke-oven battery can be increased to accommodate 40 gates and the coke-oven gas that is produced will also have negligible amount of sulfur.

## Economic Rationale

This process offers economic as well as environmental benefits:

- The  $\text{H}_2\text{S}$  content in the coke-oven gas can be decreased from  $10 \text{ g}/\text{Nm}^3$  to  $2.5 \text{ mg}/\text{Nm}^3$ . The desulfurization capacity is 99.98%, which is better than the state-of the art today.
- The concentration of the condensate can be high to warrant economic recovery and utilization.
- These estimations are extremely conservative. If the energy associated with cold nitrogen as well as oxygen is fully accounted for, the capacity for the treatment of the coke-oven gas is likely to improve

further.

- Modifications in the existing steel plants are minimal. A heat-exchanger system must be added to the oxygen plant.
- The method can be applied to any gasification or waste-incineration process.

## CAPITAL AND OPERATION COSTS

The capital investment and the operation cost are discussed on the basis of a coke-oven battery with 40 gates: capital investment—condensation chamber, with two heat exchangers as described earlier ( $1.85 \text{ Nm}^3$  in volume,  $3,325 \text{ m}^2$  in surface area), two compressors for coke-oven gas, pipelines from the coke

## What's new at TMS On-Line?

The TMS web site brings you continual updates of the latest society information.  
What's new this month? Visit the TMS web site to find:

- The new TMS Document Center is here! The upgraded site provides faster service, easier navigation, and a host of new features [doc.tms.org](http://doc.tms.org)
- View the 2002 Electronic Materials Conference technical program on-line [www.tms.org/Meetings/Specialty/EMC02/EMC02.html](http://www.tms.org/Meetings/Specialty/EMC02/EMC02.html)
- The June issues of JOM, *Journal of Electronic Materials*, and *Metallurgical and Materials Transactions A and B* will be available on-line at the end of this month [doc.tms.org](http://doc.tms.org)
- The June issue of TMS e-News will be available on-line at the beginning of next month [www.tms.org/newsletter/newsletter.html](http://www.tms.org/newsletter/newsletter.html)

Visit the site regularly and click on "What's New" to find out the most up-to-date information on meetings, publications, membership activities, and more.

[www.tms.org](http://www.tms.org)