

Clean Technology : Limit and Limitation

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ABSTRACT

The limiting value of pollutant emissions from COREX & Romelt processes, non-recovery coke ovens and coke less cupola have been calculated using equilibrium analysis. The results show that main pollutants present after full utilization of the exit gases from all the processes are sulfur dioxide and nitric oxide. The former is dependent on the volatile sulfur present in the fuel and later depends on temperature of combustion and amount of air used for combustion. Lowering of combustion temperature and closer control of combustion can reduce NO load significantly.

Key Words : Limits of emission, clean technology development, thermodynamic analysis.

INTRODUCTION

Awareness about the undesirable effect of pollutants emitted by industries on human health and eco-system and stringent restrictions put forth by regulatory bodies like pollution control boards have led to development of clean technologies. The technologies whose pollutant emission levels are below the norm set by the regulating bodies are considered as clean technology. With better understanding of the effect of pollutants on the eco-system and human health, the norms change and in general it becomes more stringent from year to year. As the norm changes, new clean technologies are developed. But obviously, there is a theoretical limit up to which the levels of pollutant emission can be brought down. The limit is determined by equilibrium thermodynamics for chemical pollutant and velocity of gas, particle size and its density for emission of suspended particles. Besides emission of pollutants in air, industries produce effluents and solid wastes. Effluents are treated before its usage for recycling or gardening or discharge in water bodies like river and sea. Again the theoretical limit of toxic elements and compounds in treated effluent is determined by equilibrium thermodynamics and in principle can be brought down to very low levels. Solid wastes generated in the process sometimes contain hazardous materials which can be recovered and used like zinc in steel plant dust. The theoretical limit for this also is determined by equilibrium thermodynamics. If the solid wastes cannot be treated, it is stored in safe places so that there is no contamination of the surrounding or water bodies including ground water. Although significant effort is being made for usage of solid wastes, it does not form a part of clean technology yet.

It is apparent that the theoretical limit of pollutant emission in air and water and hazardous waste discharge in land is of little importance since the practical limit is set by technological factors and economic considerations. But technology always strives to attain the theoretical limit and economic considerations depend on the importance given to human health and preservation of eco-system. With time, importance given to human health and eco-system is increasing in every society. So there is a need to know the limit of pollutant emission.

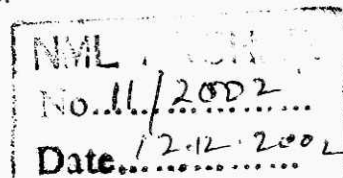
In the case of iron making by blast furnace route, coke ovens and sintering plants are the two most polluting units. So clean technologies in hot metal production aim at eliminating these two units from iron making complex. Although a number of smelting reduction processes which can produce hot metal are in the pilot plant or semi-commercial plant stages, at present two clean technologies are commercially available. These are COREX and Romelt process. Three COREX plants, POSCO in South Korea, Saldana in South Africa and JVSL in India are operating. Although no commercial plant of Romelt process is operating, but NMDC plans to start the first Romelt plant at Bailadila for processing iron ore slimes. In by-product coke ovens, there are three major sources of emission of pollutants. These are leakage from the ovens, water quenching of coke and by product recovery plant. Out of the three, first and last one are considered as a major bottleneck. The clean technology of coke making is the non-recovery coke oven which completely eliminates the by-product plant. In cast iron foundries, coke is the main source of fuel in cupola and this is the source of pollutant as well. The clean technologies in this area are induction furnace and coke-less cupola where coke is replaced by natural gas or light diesel oil. Induction furnace does not produce pollutant which comes from fossil fuels, but the thermal power plants which produce electricity for induction furnace operation emit the pollutants. Besides no satisfactory solution has been found yet for the disposal of solid waste, i.e. fly ash generated in thermal power plant. So the usage of electricity in iron foundry essentially shifts the generation of pollutant from one location to another only.

The present article aims at finding out the limit of pollutant emission from the clean technology of iron making, coke making and cokeless cupola.

THEORY

Both COREX and Romelt use non-coking coal as reducing agent. Figs.1 and 2 show the schematic diagrams of both the processes. The basic differences between the two processes are the following:

- (1) COREX has two reactors, a reduction shaft and a melter gasifier, and thereby it is a two step process but Romelt is a one step process having only one reactor.
- (2) COREX operates with lump ores or pellets but Romelt can operate with fines as well. Later is suitable for treating waste.



- (3) COREX operates at high pressure of about 3 atm. above gauge but Romelt operates at slightly negative pressure.
- (4) Finally, the exit gas from COREX has a high calorific value of about 7000 - 8000 kJ/nm³ and is used as source of heat for any purpose including power generation. On the other hand exit gas from Romelt has high sensible heat which is recovered for steam and power generation.

So if one neglects the detail of the process the exit gas that finally escapes from the process to the atmosphere is the product of combustion of coal and thereby it is similar to that produced in a thermal power plant with the following differences:

- (1) In the case of COREX and Romelt, part of oxygen for oxidation of carbon and hydrogen comes from iron oxide and rest part from the oxygen used in the process and air used to burn the gases. About 50% of total oxygen comes from the iron ore and process oxygen and rest from air. On the other hand in thermal power plants coal is burnt in air. So nitrogen content of exit gas is higher in the later case.
- (2) Secondly, in the case of combustion of coal, all sulfur present in coal burns to form sulfur dioxide but in the case of both COREX and Romelt processes, a significant part of sulfur comes out with metal and slag and rest part comes out with gas.

The exit gas basically consists of carbon dioxide, nitrogen and steam. The pollutants present in the exit gas are oxides of nitrogen, sulfur dioxide, cyanides, ammonia etc.. The limit of these is calculated from thermodynamic analysis of the system C-H-O-N-S where the proportion of various elements are in the range that is encountered in the above mentioned two processes. Sulfur dioxide from exit gas can be removed by treating it with limestone to produce gypsum. So the thermodynamic limit of this treatment or minimum concentration of sulfur dioxide in the treated gas can be obtained from equilibrium analysis of the CaO-S-O-C-H-N system.

In case of non-recovery coke ovens, the volatile matters that come out during coking is burnt to generate heat. The sensible heat of this gas is used for power production. So the product of combustion and pollutants presents in it are same as in previous case and can be found out from thermodynamic analysis of the system C-H-O-N-S where the proportion of various elements are in the range that is present in the combustion product of volatile matter of coking coal.

In case of coke less cupola, natural gas is used as fuel and the final exit gas is again product of combustion of natural gas in air. So thermodynamic analysis of the system C-H-O-N-S where the proportion of various elements are in the range that is present in the exit gas from cupola will give the limit of pollutant.

In the COREX process, the exit gas has a high calorific value and is scrubbed before using it for power generation or other purposes (Fig.1). Since this is a reducing gas, amount of ammonia, hydrogen sulfide, hydrocyanic acid and organic compounds are more in it^[1]. The soluble products present in the gas dissolve in water. Besides

some of the organic compounds like tar, phenol etc. which are present in minor amounts also get trapped in water. The level of pollutants in water are brought below the norm set by regulatory bodies using multistage chemical and biological treatments in effluent treatment plant. The theoretical limit of chemical treatment can be calculated using appropriate thermodynamic analysis.

Among all the pollutants, suspended solid has maximum visibility as well as social impact and, therefore, its reduction to a very low value is essential for clean technology. If the reactors used in the process operate below atmospheric pressure, the emission through the leakage in the reactor and during charging is very low. This concept is used both in Romelt and non-recovery coke ovens to reduce the fugitive emission of suspended solids. Since major amount of suspended solid is carried by the exit gas, gas cleaning system consisting of cyclone, bag filters, scrubbers, and electrostatic precipitator are always used to reduce it below the permitted level. Theoretically, emission of suspended particles of measurable size can be made to almost zero, using these techniques.

The solid waste generated in COREX and Romelt is the slag, sludge and dust. These are not hazardous and technology of using them are well known. The solid waste generated in coke less cupola is slag whose amount is much less than that in conventional coke fired cupola and this is not a hazardous product and can be safely disposed of or used.

RESULTS AND DISCUSSION

Calculations have been carried out for following three cases: (1) gases burnt with stoichiometric amount of air (2) burnt with 10% excess air (3) burnt with 10% less air. Normally gases are burnt with excess air, but incomplete mixing of gases sometimes result in incomplete combustion, so calculation were carried out for case (3) also. All calculations were carried out using Factsage software. Fig.3 shows the theoretical limit of the amounts of NO, SO₂ and SO₃ that are finally discharged in the atmosphere per ton of coal in COREX and Romelt processes when the final combustion is done with the stoichiometric amount of oxygen. It shows that the amount of NO and SO₃ are strongly dependent on the temperature of thermodynamic calculation. Depending on the temperature of calculation, discharge of NO can vary from a less than a gram to more than 1kg per ton of coal. Theoretical combustion temperature of COREX gas or exit temperature of Romelt gas from the process is quite high, more than 1800K. So if equilibrium is attained at that temperature, NO formed will be as indicated in the figures. As temperature of flue gas decreases, amount of NO should come down as per equilibrium results shown in Fig.3. But the rate of decomposition of NO is determined by its concentration which is very low, about 200 ppm at 1800K. Besides reaction rate constant decreases exponentially with decrease of temperature. Hence, once NO is formed, its decomposition at lower temperature is not likely due to kinetic factors. Thereby the pollutant discharge rate will correspond to that of combustion temperature. The concentration of SO₂ is determined by the sulfur content of coal and fraction of it absorbed by slag and metal. The result shows that sulfur which is not absorbed by slag or metal comes out as SO₂. At lower temperatures,

under equilibrium condition, part of it is converted to higher oxide SO_3 . The other gases including NO_2 present in the combustion product are insignificant. Fig.4 shows that if combustion takes place with 10% excess air, NO formation becomes much higher, about 8 kg per ton of coal but there is no significant change in the production of other pollutants. Ten percent excess air results in higher concentration of nitrogen and oxygen in flue gas, this leads to higher formation of NO. Fig.5 shows the result of incomplete combustion. If oxygen available is 10% less than stoichiometric requirement, NO formation comes down significantly, and ammonia is produced. Besides part of sulfur comes out as a highly toxic gas H_2S . Concentration of H_2S is quite low at high temperatures, about 1gm per ton of metal, but becomes significant, more than a kg, when temperature comes down to 1100K. At low temperatures, partial pressure of oxygen is low and thereby H_2S is more stable compared to SO_2 . Calculation shows that partial pressure of hydrogen is about 10^{-3} atm in the temperature range of 1100 to 1800K. So due to kinetic factors, actual concentration of H_2S in exit gas is likely to correspond to that of combustion temperature and the total discharge is expected to be low even when combustion is not complete. Comparison of NO production for three cases shown in Figs.3-5 clearly indicates that amount of NO in exit gas is strongly dependent on excess air in the system. To find out effect of excess air on NO formation, calculation was carried out with different percentages of excess air. Fig.6 shows that there is significant variation of NO formation when excess air varies from 1% less than stoichiometric to stoichiometric. This effect is more significant at lower temperatures. This sudden variation is due to rapid change in oxygen potential in this range (Fig. 7) and this leads to a variation of amount of H_2S produced as well.

The above results show that the major pollutants are NO and SO_2 and the value of the later is determined by sulfur content of coal and amount of sulfur absorbed by slag and metal. It is well known that during pyrolysis or devolatilization of coal, a part of sulfur present in coal comes out as H_2S , CS_2 etc. and remaining sulfur remains in coal char mostly as CaS. The later is released during burning of char. A major part of it is trapped as CaS in slag and dissolved sulfur in metal and only a small part of it comes out of the furnace as gaseous sulfur compounds. In COREX process, pyrolysis of coal takes place in the lumpy zone where all materials are in solid state. So sulfur present in the products of pyrolysis comes out of melter gasifier as gaseous sulfur compounds and finally ends up in the combustion product. Besides, a small fraction of sulfur present in coal char also comes out of melter gasifier as gas. On the other hand, in the Romelt process, lumpy coal falls directly into a foamy slag and devolatilization or pyrolysis of coal takes place in the slag phase. Thereby some amount of sulfur compounds present in pyrolysis product is expected to get trapped in slag. This indicates that in Romelt process, total sulfur from coal released in the exit gas is expected to be less than that of COREX process.

At present, complete post combustion has not been achieved in Romelt process. Maximum post combustion that has been achieved is about 85%^[2,3]. So the pollutant concentration in the exit gas is expected to be similar to that shown in Fig. 5. For the reasons mentioned earlier, pollutant formed is expected to be that corresponding to combustion temperature values.

Fig.8 shows the pollutant production in non-recovery coke oven when the combustion takes place with 10% excess air. The pollutants are again NO, SO₂ and SO₃ only. The amount of sulfur compounds depends on the volatile sulfur present in coal. NO formed is about 8 kg/ton of coal at 1800K. Interestingly, amount of NO formed is similar to that produced in COREX and Romelt process since the oxygen and nitrogen contents of the exit gas is similar in all the cases. Results of combustion with stoichiometric air and incomplete combustion is similar to the trend shown for COREX and Romelt process.

Fig.9 shows the pollutant emission from coke less cupola operated with natural gas where the exit gas from cupola burns with 10% excess of air. Calculation has been carried out for natural gas containing 0.1% sulfur. It shows that almost complete amount of sulfur comes out as SO₂. Amount of NO produced is more than 10kg per 1000nm³ of natural gas. This value is similar to that obtained from combustion of 1 ton of coal.

Thermodynamic calculation shows that if the combustion temperature is brought down or if exit gases attain equilibrium at lower temperatures, there can be significant reduction in NO emission. The later requires usage of catalysts and former requires change in technology where combustion and extraction of sensible heat of combustion is carried out in stages. Another alternative method for reduction of NO in flue gas is to avoid usage of excess air. Comparison of NO in Figs. 3 and 4 shows that 10% excess air increases amount of NO eight fold from about 1kg to 8 kg per ton of coal. So design of better burner whereby excess air requirement is eliminated will go a long way to reduce the NO emission.

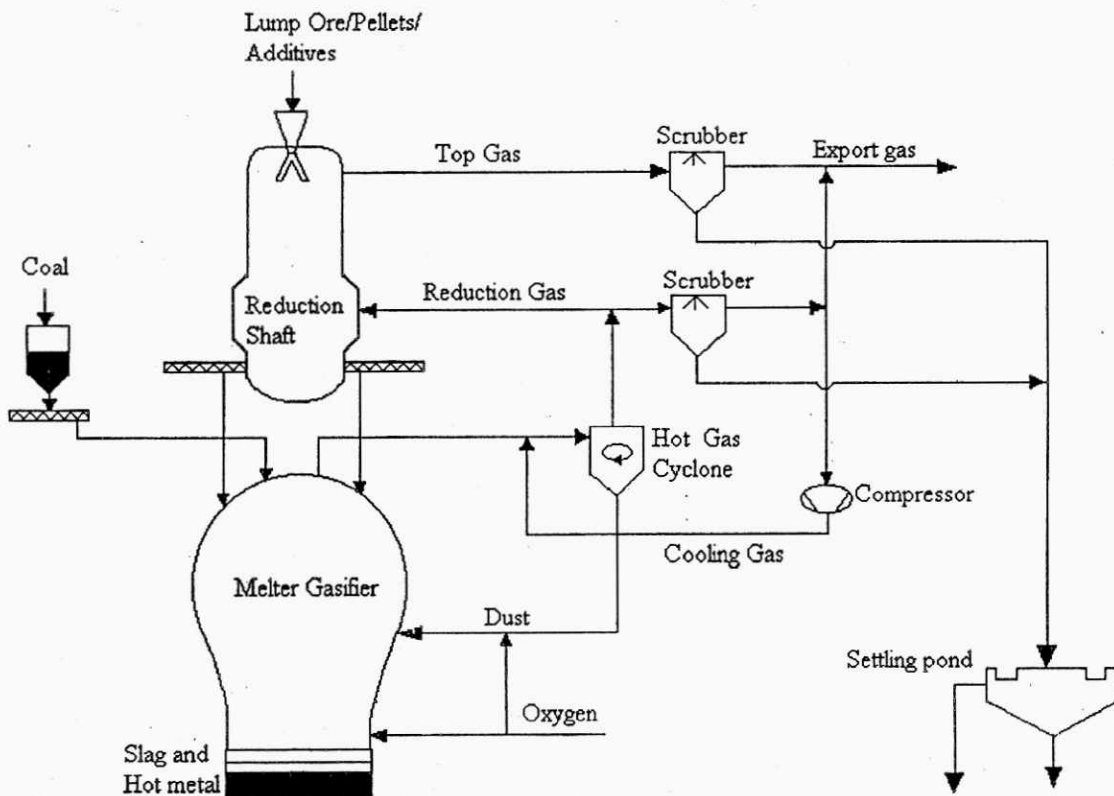


Fig. 1: Flow sheet of COREX Process.

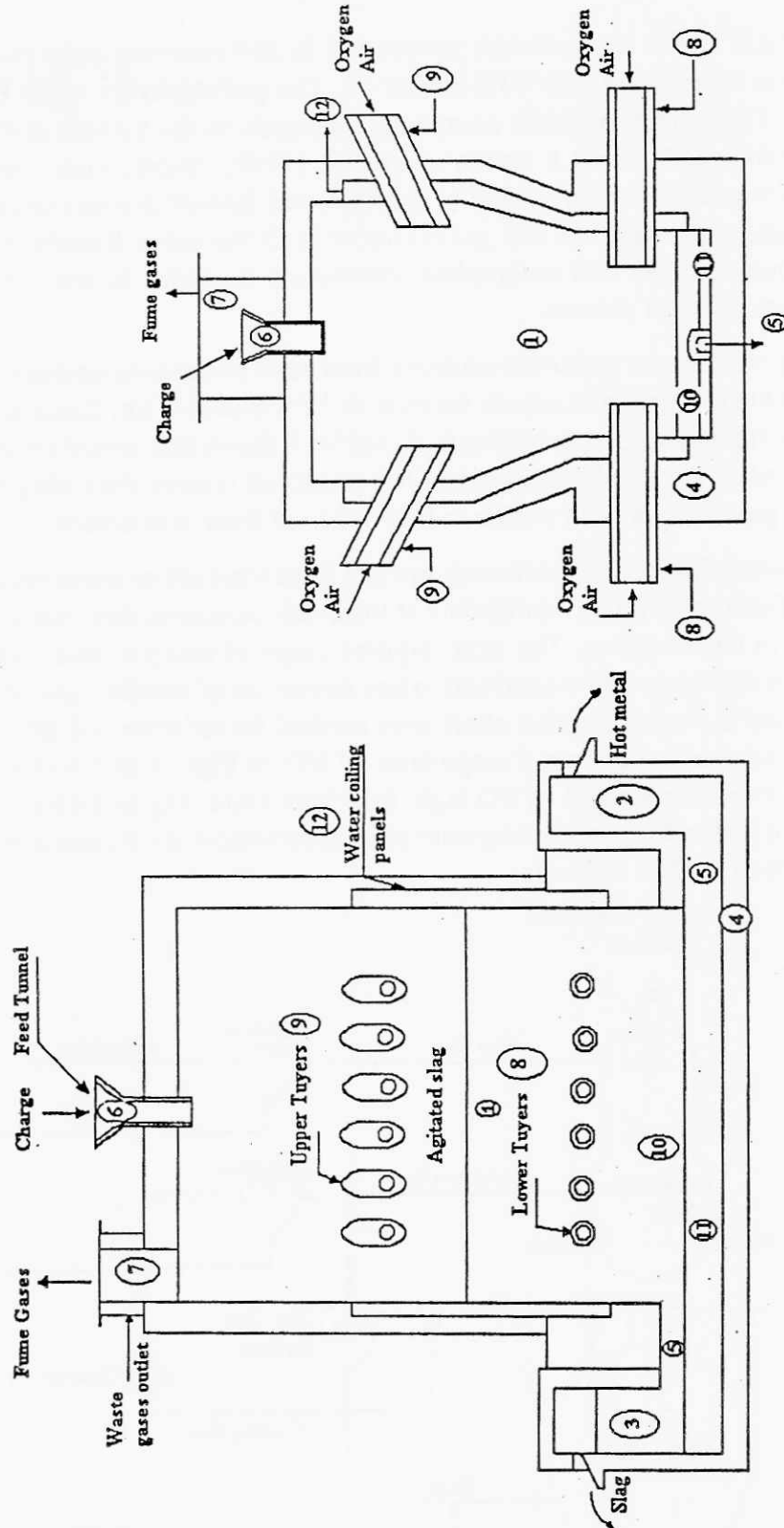


Fig. 2: Schematic Diagram of Romelt Plant. 1- Agitated Slag; 2- Siphon for Hot Metal tapping; 3- Siphon for removal of slag; 4- Hearth with refractory lining; 5- Orifice; 6- Feed Tunnel; 7- Waste gases outlet; 8- Lower Tuyers; 9- Upper Tuyers; 10- Calm Slag; 11- Hot Metal; 12- Water Cooling Panels.

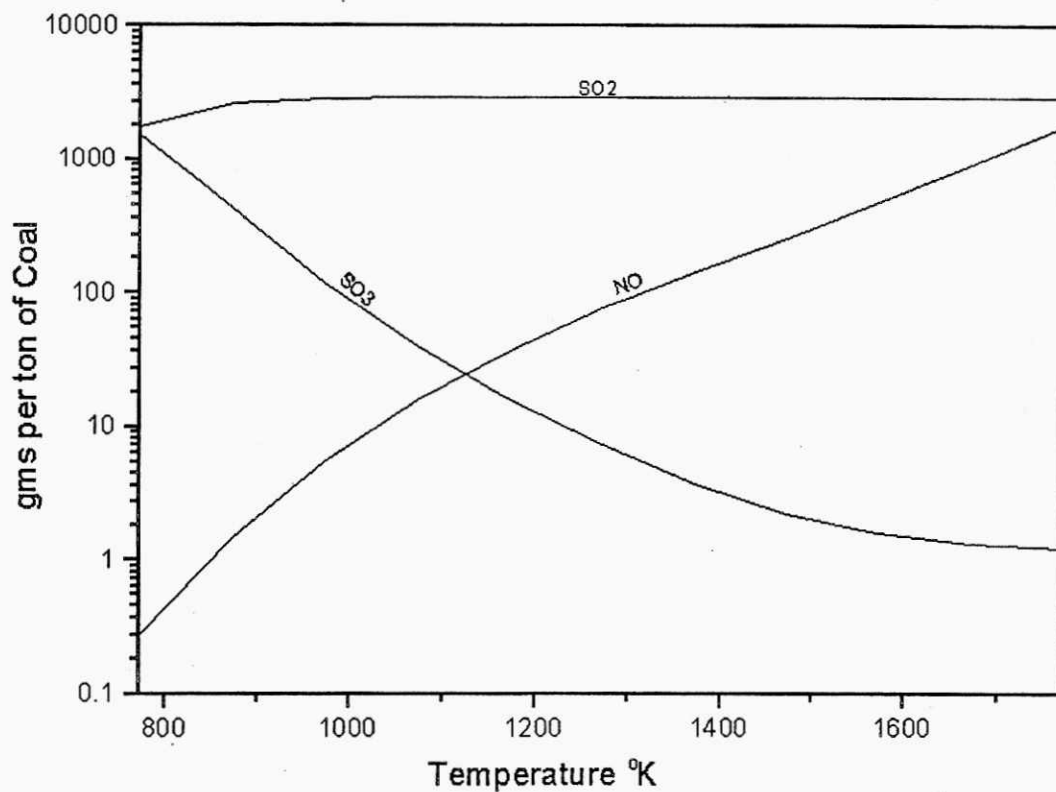


Fig. 3: Amount of pollutants produced per ton of coal for Corex and Romelt Process. Combustion of exit gases with stoichiometric amount of air.

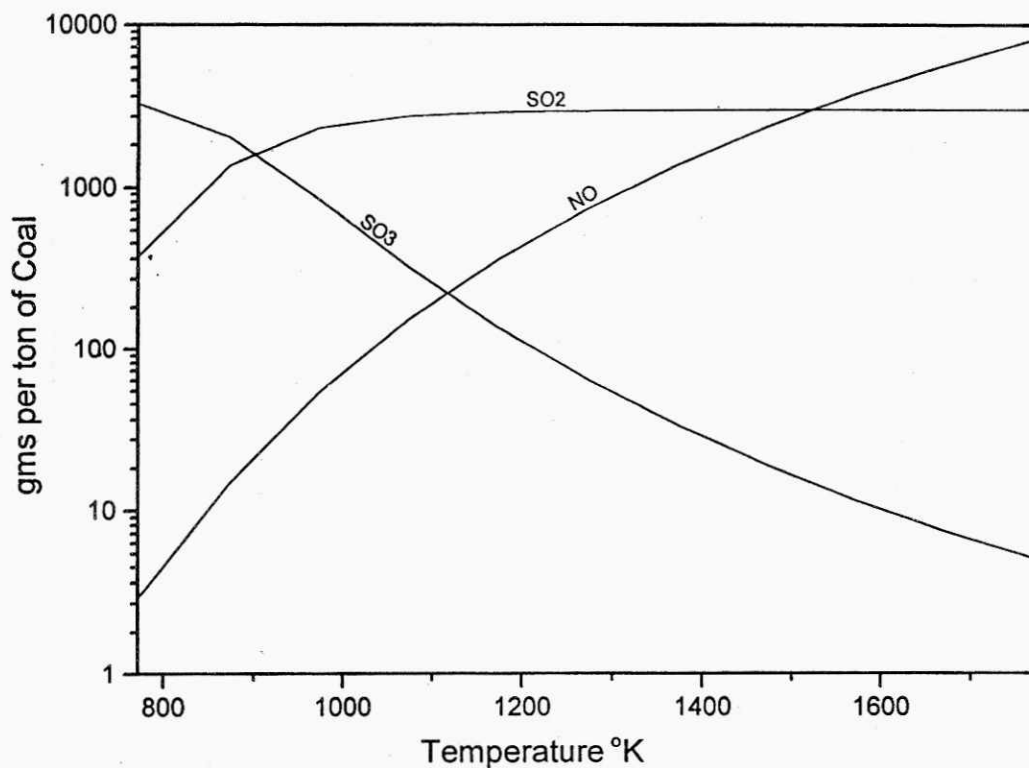


Fig. 4: Amount of pollutants produced per ton of coal for Corex and Romelt process. Combustion of exit gases with 10% excess air.

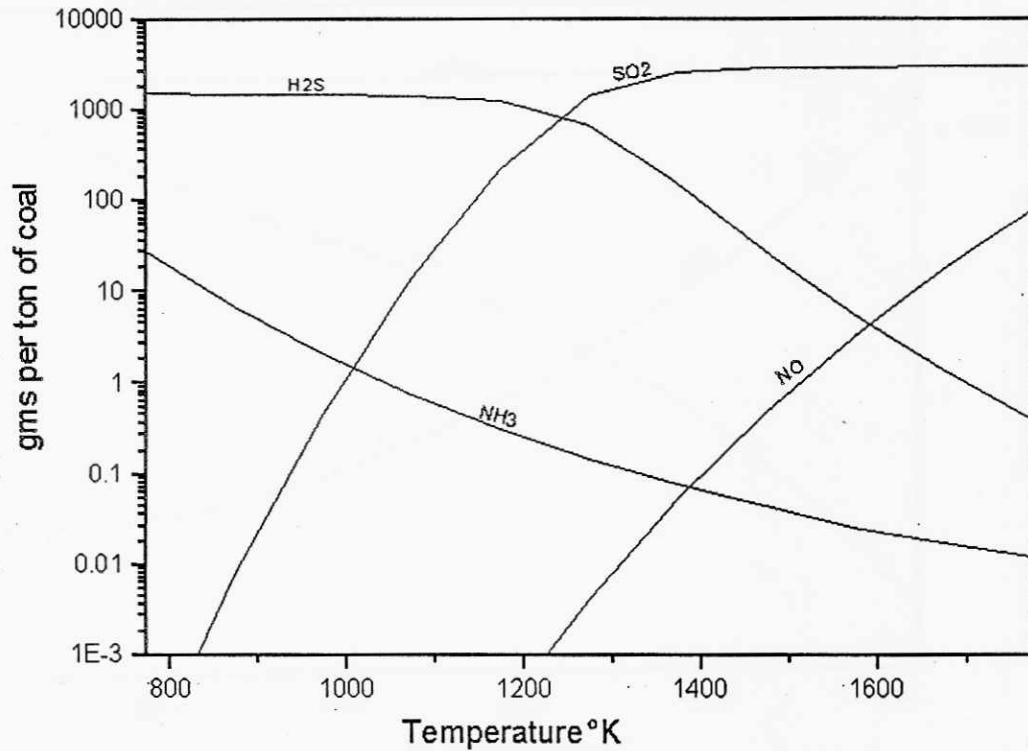


Fig. 5: Amount of pollutants produced per ton of coal for Corex and Romelt process. Combustion of exit gases with 10% less air.

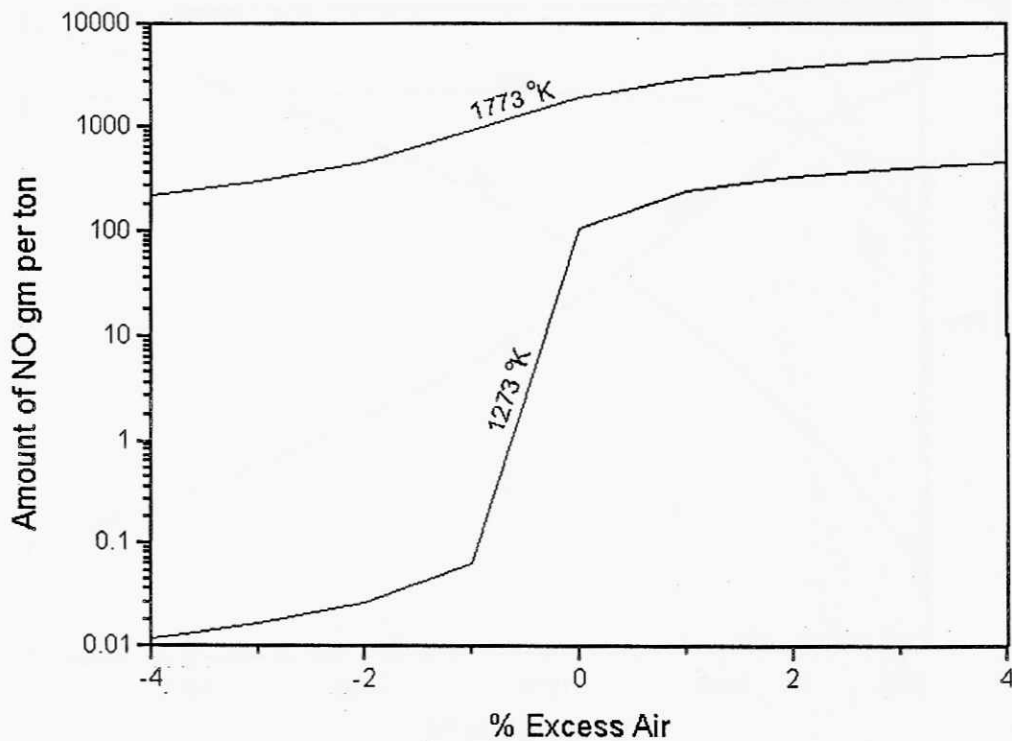


Fig. 6: Variation of amount of NO produced per ton of coal with percentage excess air for Corex and Romelt Processes.

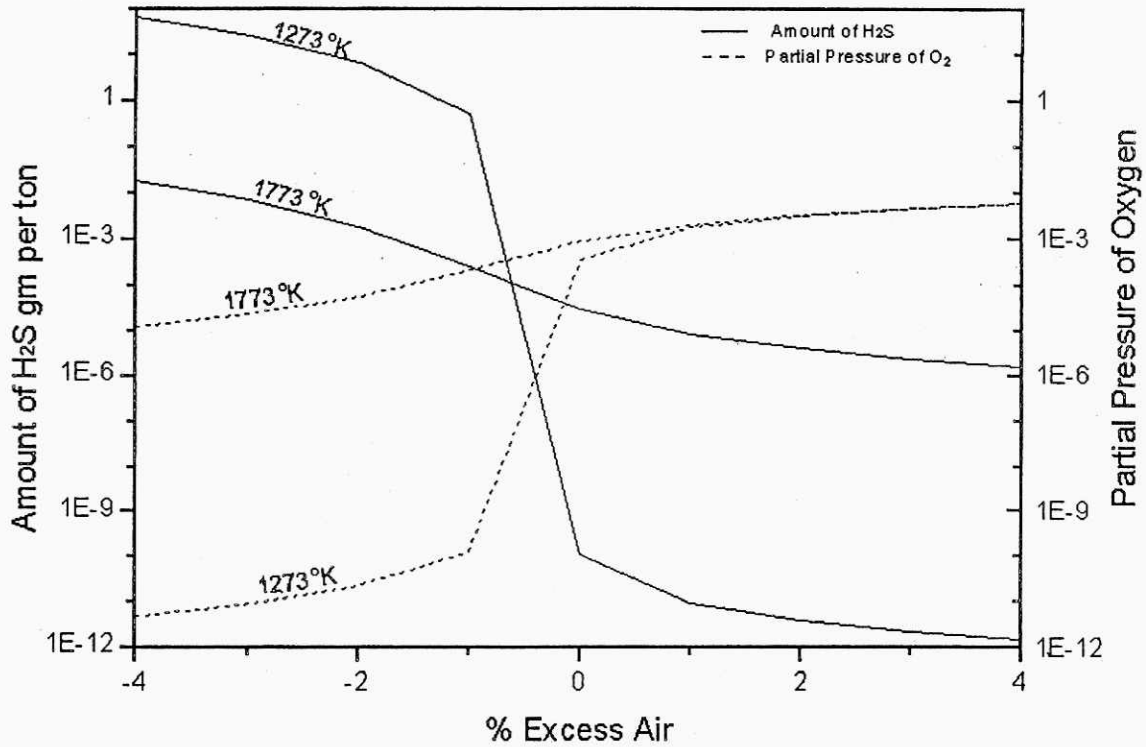


Fig. 7: Variation of amount of H₂S produced per ton of coal and oxygen potential with percentage excess air in Corex and Romelt Processes.

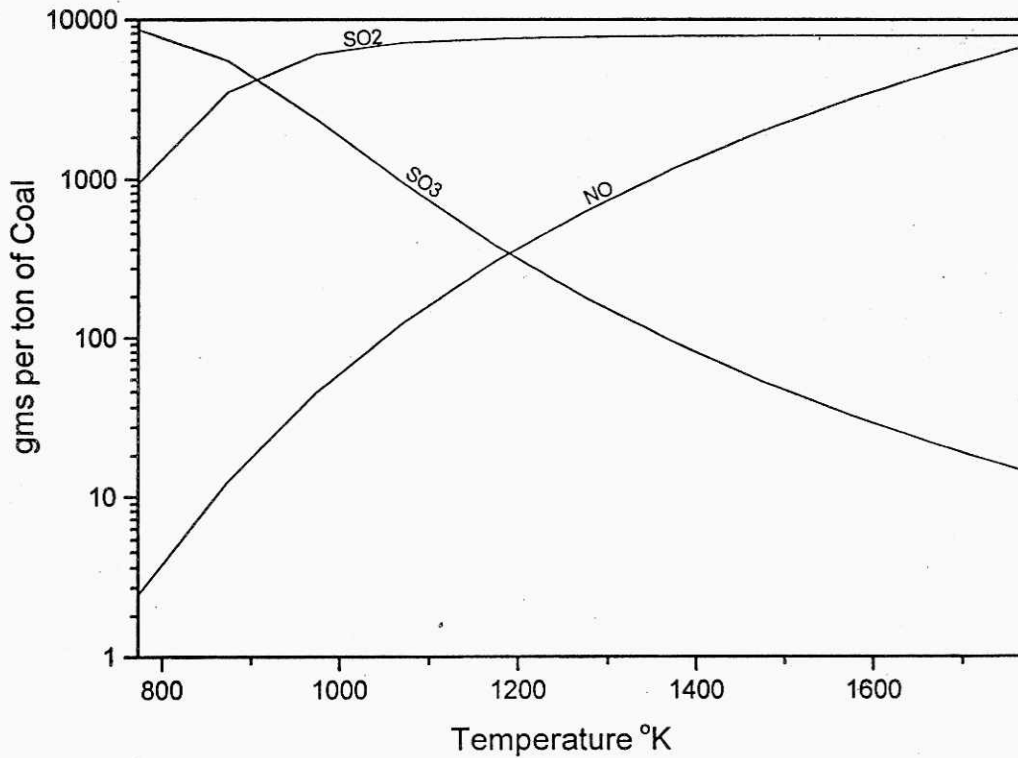


Fig. 8: Amount of pollutants produced in Non-Recovery Coke Oven per ton of coal.

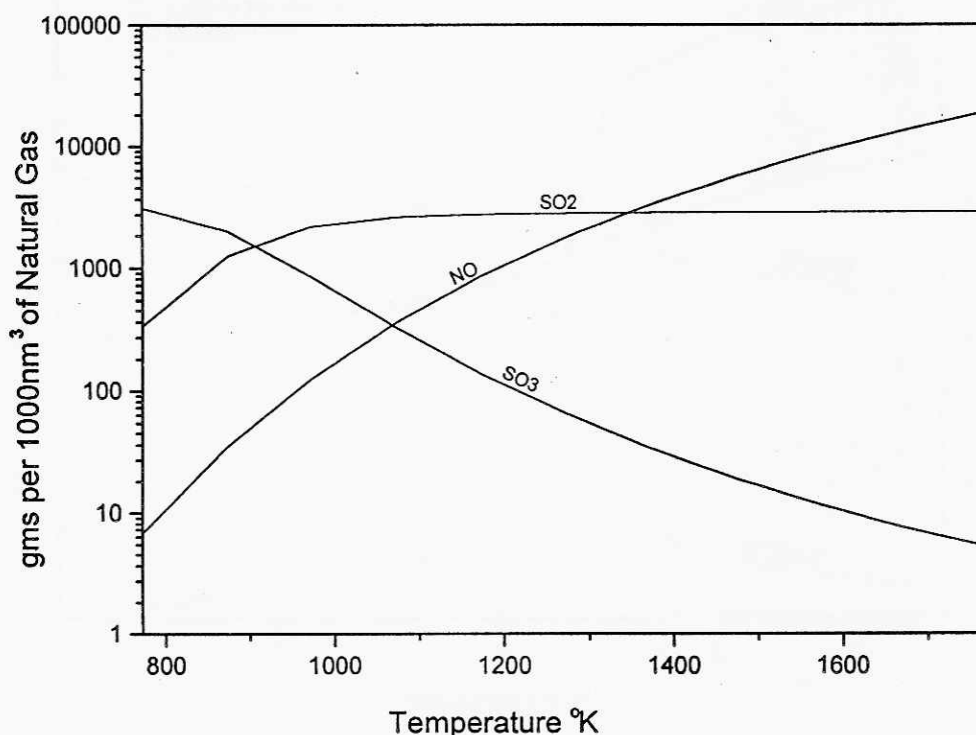


Fig. 9: Amount of pollutants produced in Cokeless Cupola per 1000nm³ of natural gas.

CONCLUSIONS

Gaseous pollutants from COREX, Romelt, non-recovery coke oven and coke less cupola are primarily SO₂ and NO. The former is mainly determined by volatile sulfur present in fuel. Theoretical minimum emission of these gases is quite significant.

Emission of NO is determined by the combustion temperature and excess air. Elimination of excess air can reduce NO emission by about eight times. Emission of NO in the flue gas can also be reduced by reducing combustion temperature or if flue gases are brought to equilibrium at lower temperatures using catalysts.

REFERENCES

- [1] A. K. Lahiri: *Proc. Int. Conf. on Environment Management in Metallurgical Industries, Varanasi, Dec. 2000*, R.C.Gupta (Ed.) Allied Publishers Ltd. (2000), p. 23.
- [2] P. Sandhir, V.P. Zhdan and J.S.Saluja : *Environmental and Waste Management in Iron and Steel Industries*, Amitava Bandopadhyay, N. G.Goswami and P. Ramachandrarao (Ed.) Published by NML, Jamshedpur, pp. 69-82.