# Green processes in process metallurgy

# S. SUBRAMANIAN AND A. K. LAHIRI

Department of Metallurgy, Indian Institute of Science, Bangalore - 560 012, India

#### ABSTRACT

Environmental pollution ultimately governs the economic or industrial growth rate of the world. Ideal green processes, both conceptual and feasible are discussed and the advantages and limitations are brought out. Typical examples of novel techniques developed to combat pollution are presented. An integrated approach coupling energy saving with pollution control measures appears to be the best strategy.

## INTRODUCTION

The world model of Meadows et al <sup>11</sup> highlighted that the economic or industrial growth rate of the world cannot be sustained for long. Inevitably, environmental pollution may ultimately become the growth limiting factor. However, a number of scientists do not agree with their views. They reason that human innovativeness will be able to overcome the limitations. The quest for green or environmental friendly processes is an attempt in this direction.

The environmental pollution can be tackled in different ways. One method is the "add on" pollution control measure to the existing process or end of pipe solution. The second alternative is to change the process route or design the process such that it is environmental friendly. The basic difference between the two approaches is obvious. Pollution control is an after thought in the first approach whereas the second one is partly driven by it. Needless to emphasize, the development of green or environmental friendly processes requires an integrated approach. The present article examines the scenario for the green processes with respect to process metallurgy.

# Ideal Process — Conceptual and Feasible

Fig.1 schematically portrays the ideal green process. The process produces only the desired products and by-products. There is no waste effluent and pollutant discharge from the process. Water is completely recycled, only makeup water is added. Obviously it is an utopian concept.Metallurgical processes product large volumes of solid waste in the forms of tailing, red mud,

slag etc. Pyrometallurgical processes mostly use fossil fuels, consequently CO<sub>2</sub> is one of the major constituents of exhaust gases. Besides, effluents and gaseous pollutants cannot be completely eliminated and converted to useful products. However, there are indications that in future it may be plausible to consider this utopian concept seriously. Recently Akiyama et al <sup>[2]</sup> made a feasibility study of the blast furnace ironmaking system integrated with synthesis for reduction of carbondioxide emission. The study indicated that the system will reduce the green house effect gas emission and is superior from energy point of view.

The tailings are normally dumped in the tailing ponds and may be hazardous because of the presence of the heavy metals. Additionally, dust formation during dry seasons proves to be a nuisance to the nearby township. Hindustan Zinc Ltd. [3] and Kolar gold mines have successfully transformed the abandoned tailing dumps to large scale plantation, where a variety of plants such as eucalyptus, cassia, babool, kinker, casuarina, cactus etc. as well as grass are grown. In course of time, it will become good soil. Extensive work has been carried out on the processing and applications of red mud <sup>[4]</sup>. The multifarious uses of red mud apart from those for constructional purposes include manufacture of reinforced products, absorbent for toxic metals and waste gases, fertilizer additive to name a few. It is worthy of mention that as a consequence the potential for almost complete utilization of red mud exists. Recently<sup>[5]</sup>, a variety of plant species having capacity to bioaccumulate metals like cadmium, cobalt, copper, lead, manganese, nickel and zinc have been identified. In some cases the concentration of accumulated metals could be greater than 2%. Growing such plants under intensive crop conditions and harvesting the dry matter is a possible method of metal removal and recovery and polishing the soils. Even some plant tissues are effective in absorbing metals dissolved in aqueous medium. Roots of tomato and tobacco <sup>[6]</sup> absorb strontium from solution containing SrCl, at pm level with distribution coefficient of more than 500 and the mtal can be recovered from the bio-mass by pH adjustment. Farkas <sup>[7]</sup> developed a method of recovering transition metals from dilute electroplating and rinse water solution. The final discharge contains less than 0.5 ppm metal. some plants like mustard take toxic selenium salts and convert them into volatile gas dimethyl selenide which is 500-700 times less toxic than the inorganic salts <sup>[8]</sup>. Cyanide, thiocyanate and heavy metal concentration in waste water are reduced to trace levels using biodegradation techniques at Homestake Mines U.S.A. The water receiving streams now support aquatic species such as trout <sup>[9]</sup>.

The usage of slag for cement production and other standard applications is well known and widely practised now a days. Even the basic slag of L-D converter has been successfully used as soil conditioner and was found toincrease the farm productivity <sup>110]</sup>. Furthermore, Thoburn <sup>111]</sup> while discussing the evolution of gas cleaning in pyrometallurgy concluded that for non-ferrous applications where acid is produced or where it is economical to use wet scrubbig and absorption system, it is not unreasonable to consider the possibility of zero emissions. It s quite likely that in the distant future the utopian concept shown in Fig. 1. may be approached. However, for the present, Fig. 2. depicts a more feasible process. The plant discharges inert waste, effluent and exhaust gases but the level of pollutants in each of them is well within the present day permissible limit.

#### **New Technology**

In the last two decades, a number of technologies have been commercialized. Most of these are most environmental friendly than the earlier technologies. A few of them which are of relevance to iron and steel industry are COREX



Figure-1 : Ideal green process



Figure- 2 : Present day green process

process, non-recovery coke oven dry quenching of coke, as well as gas recovery system for BOF.

In the western world and Japan, there has been considerable public resistance against the installation of coke ovens which are considered as hazardous for the environment. This led to a search for alternative methods for producing hot metal using coal and oxygen. A number of such processes known as smelting reduction or SR processes are at various stages of development. the COREX process, one of the SR processes, has already been commercialized. The third Corex plant and first in India is going to be commissioned at Jindal Vijayanagar Steel Ltd., Hospet, shortly. This process is a two staged proess <sup>[12]</sup>. The ore, sinter or pellet are reduced to 90% or more degree of metalization in a reduction shaft at a pressure of about 3 atm. and 850°C. The hot reduced material along with partly calcined limestone are dirtectly transferred to the melter gasifier unit. This unit generates a highly reducing gas containing more than 95% Co + H<sub>2</sub> by burning coal with oxygen and melts the metalized pellets to produce hot metal and slag. A part of the reducing gas is used for reduction in reduction furnace and the rest is available as export gas. One of the possible uses of export gas is power generation. The export gas contains very low SO<sub>2</sub>, dust and NO<sub>x</sub> and even the pollutants namely, phenols, sulphides, cyanides and ammonia in waste water are very low and meet the environmental standards.

The non-recovery coke oven is essentially a modified version of the beehive coke oven where the volatile matter of coal is burnt for heat generation. The recent designs ensure uniform heating and coke quality. The coke produced in the non-recovery coke ovens like Kumbraj developed by the Central Fuel Research Institute (CFRI), Dhanbad, are comparable to that of by-product ovens and the emission level from these ovens are much less. Knoerzer and Cekela report that the emissions are well within the permissible levels <sup>[13]</sup>.

In conventional wet quenching of coke, a large amount of dust and chemical pollutants like  $H_2S$ ,  $NH_3$ , HCN etc. are emitted. This is effectively controlled in dry quenching where hot coke is cooled by circulation of nitrogen in a closed system consisting of a cooling chamber and waste heat boiler.

In non-ferrous extraction also new processes like Outokumpu, Mitsubishi, Kivcet, QSL etc. are clean processes and meet the environmental requirements. All these processes use oxygen to increase the  $SO_2$  percentage in waste gas and reduce its volume. As a result, the treatment of flue gases becomes easy.

In addition, technologies have been developed to recover the metal value

from metal-rich solid waste <sup>[14]</sup>. All these technologies are based on the present day understanding of causes for pollutant formation and methods of controlling them.

#### **Integrated Approach**

To make a process environment friendly, an integrated approach is essential. Emission and wastes are generated due to process chemistry, the design, the operating practice and maintenance procedures. Chadha<sup>[15]</sup> suggests that the classification of true causes of emission and wastes into the above mentioned four generic categories provides a simple but structured frame work for developing a pollution prevention solution. Fig. 3 shows the flow diagram for developing strategies for pollution prevention. Analysis of each part of the overall process for emission and waste assessment leads to identification of the true cause of emission and waste release. The analysis aims to identify the origin of generation, the cause of release i.e., adequacy or otherwise of preventive steps and total amount of release from each part. Once the major sources of pollution and cause for it are understood, the appropriate strategy for its prevention can be thought of in the form of : (1) modification of process chemistry or design change, (2) adoption of new process technology, (3) better strategy of operation and maintenance, (4) add on facilities such as off gas, effluent, waste treatment plant. The final strategy, of course, is etermined by the overall economics. Typical examples of change of process chemistry or process at Hoogovens and converter process at the International Nickel Company (INCO).

It is well known that recirculation of flue gases can reduce  $NO_x$  content by upto 80%. Hoogovens incorporated this in a demonstration project with flue gas recycle to get about 15% oxygen above the bed <sup>[16]</sup>. This reduced coke consumption by 10% without affecting productivity and at the same time reduced pollutants CO, SO<sub>2</sub> and NO<sub>x</sub>.

At INCO <sup>[17]</sup>, the change of flux from sand to coarser flux like gravel and quartz in nickel converter reduced the dust formation significantly. Rationalization of the complex by elimination of the number of dust collection points, redundant flues and equipment further reduced the dust pollution.

If we extend the concept of integrated approach then a cluster of interdependent processes could be made environmentally friendly instead of one. Fig. 4 shows such a concept. It is well known that coal based power plants generate fly ash which is likely to pose a serious problem. On the other hand COREX or

any other SR process generates gas and converts the coal ash to slag. The gas based power plants are more eco-friendly and the technology of production of slag cement is well established. So on the whole, the itnegrated flowsheet shown in Fig. 3. is expected to be more environmental friendly compared to individual plants.

#### **Economics**

In general the adoption of pollution control measures make the process costly. So environmental friendly processes are considered to be not always an



Figure- 3 : Flow diagram for developing strategies for pollution prevention



Figure- 4 : COREX — power-cement environmental friendly complex

economically viable option. In cases where by products or energy could be effectively recovered, the economics by and large becomes favorable. For example, recovery of  $SO_2$  from copper smelting plants or waste gas from BOF process which could be used for energy saving are economic. However economics is not a static concept and it depends on number of local and global factors Oda et al [18] narrate an example of this. A high temperature gas cleaning system was developed for oxygen converter in order that waste heat could be recovered from flue gases at 600°C or less. Although the performance of the system was found to be better than expected, it could not be immediately used because of dramatic changes in the global energy cost. In this context, it is worthy of mention that indirect benefits of pollution abatement and waste utilization on the well-being of the human race cannot be measured in terms of cost-analysis alone.

### CONCLUSION

The primary metal processing industries contribute significantly to industrial pollution. While zero-pollution is an utopian concept, an integrated approach incorporating pollution abatement and energy saving in the process flowsheet appears to be feasible.

#### REFERENCES

- [1] D.H. Meadows, D.L. Meadows, J. Randers and W.W. Behrens : The limits to growth, Earth Island Ltd. London, 1972.
- [2] R.T. Akiyama, H.Sato, A.Muramatsu and J.Yagi : ISIJ Inter., 33 (1993) 1136.
- [3] V.P. Kohad and M.R. Jakh: In "Pollution through Metallurgical opertions", Proc. of National Seminar NSPMOP-87, Ab. Rashid Chesti, Ed., 1991, p. 27.
- [4] P.M. Prasad, J.S. Kachhawaha, R.C.Gupta, T.R. Mankhand and J.M. Sharma, Processing and application of red mud, in "Proc. Light Metals: Science & Technology", Trans Tech. Pub. Ltd., Switzerland, 1985.
- [5] A.J.M. Baker, S.P. Mcgrath, C.M.D. Sidoli and R.D. Reeves: Resources, Conservation & Recycling 11 (1994) 41.
- [6] C.D.Scott: Biotechnology and Bio-engineering 39 (1992) 1064.
- [7] J.Farkas: J. Metals 37 (1875) 72.
- [8] M.Knott : New Scientist 148 (1995) 46.
- [9] J.L. Whitlock and G.r. Smith: Bio-hydrometallurgy (1989) 613.
- [10] A.S. Prasad and H.N. Prasad: Tata Tech. 20 (1995) 15.
- [11] W.J. Thoburn: In "Process gas handling and cleaning" Proc. Int. sym. held at Halifax, Aug. 1989, C.Twigge - Molecey, Ed., Pergamon Press, 1989, p3
- [12] S.K. Gupta and C.Bohm : Production of liquid iron using coal: H.S.Ray, D.N. Dey, R.K. Paramgura and A.K. Jouhari, Ed., Allied Publishers, 1994, p 3.
- [13] J.J. Knoerzer and V.W. Cekela : in "Proc. 2nd International Cokemaking Congress", 1992, p 435.
- [14] J. Kohl : MPT 6 (1992) 98
- [15] N. Chadha : Chem. Engg. Prog. Nov. (1994) 32.
- [16] J. Rengersen et al. Annual ATS Conf. Paris Dec. (1994).
- [17] A. Dutton, A.E.M. Warner and M.J. Humphris:in "Process gas handling and cleaning", Proc. of Int. symp. held at Halifax Aug. 1989, C. Twigge-Molecey, Ed., Pergamon Press, 1989, p. 183.
- [18] N.Oda, H.Maeno, T. Takawa, N.Suga and N. Matsuda ibid p. 48.