Analysis of Industrial Metabolic Flux in Blast Furnace Ironmaking System

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Abstract. Based on the method of industrial metabolic analysis, the methods is given in this paper. Taking the blast furnace ironmaking process of an iron and steel enterprise as an example, the material metabolic analysis of blast furnace ironmaking process is carried out. By using the calculation method of metabolic flux, the regulation model of industrial metabolic flux based on the principle of flux balance is constructed, and the material metabolic communication in the process of blast furnace ironmaking is carried out and quantity prediction. On this basis, the control method of material flux in blast furnace ironmaking process is put forward, which can provide energy saving and emission reduction measures for enterprises.

1. Introduction

In 1989, R.A. Frosch, an American environmental ecologist, put forward the concept of industrial metabolism for the first time by linking the material and energy flow in industrial production with the process of biological metabolism and the process of recycling and regeneration of ecosystem[1]. Material flow analysis has always been the mainstream method of industrial metabolism research and the basis of industrial metabolism research. In 1998, the U.S. Bureau of Mineral Resources completed the assessment of reserves and distribution of related minerals and the analysis of industrial metabolism of metal resources at the national level through material flow analysis of As, Cd, Pb, Zn and other metals[2]. The report of Material and Energy Flow in the United States in 2000 further established the important position of material flow analysis method in industrial metabolism research subsequently.

In China, the academian of the Academy of Engineering and Professor Lu Zhongwu of Northeast University were the first to carry out industrial ecology research[4]. Professor Liu Fei of Chongqing University was the first to clarify the scientific connotation of green manufacturing in China. Overseas, improved input-output process model (IOPM) such as Karen of Massachusetts Institute of Technology is a representative input-output list analysis method[5]. Graedel, director of Yale University Industrial Ecology Center, professor of Geophysics and chemical engineering, and Allenby, professor of environmental engineering at Arizona State University co-published the first monograph on industrial ecology. Material flow analysis is an important tool for industrial ecology research. At present, most of the research is based on mathematical statistics. There are some deficiencies in explaining the physical and chemical process-based material and energy operation law in manufacturing system. Most of the research objects are macro-manufacturing systems such as specific industries, industrial parks, regional countries, etc. Discussions often focus on macro-level, which is difficult to solve micro-scale problems.
2. Metabolism Analysis of Blast Furnace Ironmaking System
In the process of blast furnace ironmaking, the main distribution in the furnace can be roughly divided into five areas, namely, lump zone, melting zone, dripping zone, slag belt and tuyere zone. The main reducing agents in blast furnace ironmaking are CO, H₂ and solid carbon. The reduction order of iron oxides is as follows: 3Fe₂O₃→2Fe₃O₄→6FeO→6Fe.

2.1. Reduction of Iron Oxides in Blast Furnace
Reduction of iron oxides with CO and H₂. After the ore enters the furnace from the top, when the temperature does not exceed 900℃-1000℃, the oxygen in the iron oxide is captured by CO and H₂ in the gas to produce CO₂ and H₂. When the temperature is less than 800℃, CO is used as reducing agent. When the temperature is higher than 800℃, H₂ is used as reducing agent.

With the ore decreasing in the furnace, indirect reduction is the first step, and the residual iron oxide mainly exists in the form of FeO. Because solid carbon reacts with iron oxide in solid state, the contact surface is very small and the direct reaction is limited greatly, it is generally considered that direct reduction reacts through gas phase.

In the above reaction, the superficial reaction between FeO and CO, in fact, the gas product CO₂ reacts almost entirely with carbon in the high temperature zone of the lower part of the blast furnace, directly consuming carbon. CO only plays a role in transferring oxygen.

2.2. Reduction of Non-Iron Elements in Blast Furnace
In addition to iron, there are other non-ferrous elements in blast furnace, such as Mn, Si, P, and so on. Mn is a common element in blast furnace smelting. Mn in blast furnace is brought in by MnO, and some iron ores contain a small amount of manganese. The reduction of manganese oxides in blast furnaces is also from high to low, and then to metal manganese, in the order of: MnO₂→Mn₂O₃→Mn₃O₄→MnO→Mn. Among them, manganese dioxide to manganese oxide can be obtained by indirect reduction, while MnO is a very stable compound. Therefore, Mn cannot be obtained by indirect reduction in blast furnace, but by direct reduction. The starting temperature of direct reduction of MnO is between 1100℃ and 1200℃. At this time, MnO has formed silicate primary slag with gangue, so MnO is obtained by direct reduction of MnO in liquid primary slag.

Si in pig iron mainly comes from SiO₂ in ores and coke ash. SiO₂ is a stable compound with high heat of formation and low decomposition pressure, which is more difficult to reduce than Fe and Mn. The reduction of Si can only be carried out in the form of direct reduction in the lower high temperature zone of blast furnace (above 1300℃). Because SiO₂ absorbs a lot of heat during reduction, only a small amount of silicon is reduced in blast furnace. The reduced silicon can be dissolved in pig iron or FeSi can be formed and dissolved in pig iron.

Phosphorus in charge exists in the form of calcium phosphate [(CaO)₃-P₂O₅], and sometimes in the form of iron phosphate [(FeO)₃-P₂O₅-8H₂O]. Calcium phosphate is a very stable compound. It enters the slag first in the blast furnace. The reduction rate of phosphorus can reach 60% when carbon is used as reducing agent at 1100℃-1300℃.
3. Metabolic Flux Analysis of Blast Furnace Ironmaking System

The steady-state rate of metabolite output from the input metabolic bottom logistics through the node after manufacturing process is called industrial metabolic flux. A set of dynamic differential equations, i.e. the equilibrium equation of industrial metabolic flux, is established to describe the steady-state equilibrium relationship between the rate of change of node metabolite intensity with time and all metabolic flux in industrial metabolic network, as shown in equation (1):

\[ \frac{dX}{dt} = N \cdot V \]  

In the formula: N-flux coefficient matrix; V-Industrial metabolic flux matrix; X-Industrial metabolic intensity of nodal metabolites.

The calculation of cell metabolic flux follows the Michaelis-Menten flux law, and the metabolic flux is

\[ v(x) = \frac{v_{max} X}{K_{m} + X} \]  

In the formula: \( v_{max} \)-maximum flux; \( K_{m} \)-Michaelis constant.

The equation is obtained by logarithmic transformation and Taylor series expansion.

\[ \ln(v) \approx \ln(a) + g \cdot Y \]  

In the formula: \( a \)-natural logarithm of metabolic flux; \( Y=\ln(X) \); \( g \)-kinetic series; \( a \)-velocity constant.

By Cartesian transformation, the following results are obtained:

\[ v \approx a \cdot X \]  

By substituting equation (4) into equation (1), the dynamic differential equation is constructed as follows:

\[ \dot{X}_t = \alpha_i \prod_{j=1}^{n+m} X_{ij}^{a_{ij}} - \beta_i \prod_{j=1}^{n+m} X_{ij}^{h_{ij}} \]
In the formula: $\dot{X}_t$-dependent variable; $X_1, \ldots, X_n$-related variable; $X_{n+1}, \ldots, X_{n+m}$-independent variable; $\alpha_i, \beta_i$-velocity constant; $g_{ij}, h_{ij}$-dynamic series.

Assuming that the intermediate metabolites in the system are in a quasi-steady state, the metabolic flux of each reaction pathway can be obtained in tables 1.

**Tables 1. Stable Metabolic Flux at the End of Blast Furnace Ironmaking Reaction Cycle**

| Industrial metabolites | metabolic flux $X_i$ | Reaction equation | Stable period flux kg/t·h |
|------------------------|----------------------|-------------------|--------------------------|
| Fe$_2$O$_3$            | X$_1$                | $3\text{Fe}_2\text{O}_3+\text{CO}=2\text{Fe}_3\text{O}_4+\text{CO}_2$ | 19.44                    |
|                        |                      | $3\text{Fe}_2\text{O}_3+\text{H}_2=2\text{Fe}_3\text{O}_4+\text{H}_2\text{O}$ |                         |
| FeO                    | X$_2$                | Fe$_2$O$_3$+CO=Fe+CO$_2$ | 9.68                       |
|                        |                      | Fe$_2$O$_3$+H$_2$=Fe+H$_2$O |                         |
|                        |                      | Fe$_2$O$_3$+C=Fe+CO |                         |
|                        |                      | Fe$_2$O$_3$+CO=3FeO+CO$_2$ |                         |
|                        |                      | Fe$_2$O$_3$+H$_2$=3FeO+H$_2$O |                         |
| Fe$_3$O$_4$            | X$_3$                | Fe$_3$O$_4$+CO=3FeO+CO$_2$ | 28.17                     |
|                        |                      | Fe$_3$O$_4$+H$_2$=3FeO+H$_2$O |                         |
|                        |                      | 3Fe$_2$O$_3$+CO=2Fe$_3$O$_4$+CO$_2$ |                         |
|                        |                      | 3Fe$_2$O$_3$+H$_2$=2Fe$_3$O$_4$+H$_2$O |                         |
| CO                     | X$_4$                | 3Fe$_2$O$_3$+CO=2Fe$_3$O$_4$+CO$_2$ | 1423.27                   |
|                        |                      | Fe$_2$O$_3$+CO=Fe+CO$_2$ |                         |
|                        |                      | Fe$_2$O$_3$+H$_2$=Fe+H$_2$O |                         |
|                        |                      | Fe$_2$O$_3$+C=Fe+CO |                         |
|                        |                      | CO$_2$+C=2CO,2CO+O$_2$=2CO$_2$ |                         |
|                        |                      | MnO+O=C=Mn+CO |                         |
|                        |                      | MnO$_2$+2C=Mn+2CO |                         |
| H$_2$                  | X$_5$                | 3Fe$_2$O$_3$+H$_2$=2Fe$_3$O$_4$+H$_2$O | 0.61                      |
|                        |                      | Fe$_2$O$_3$+H$_2$=3FeO+H$_2$O |                         |
|                        |                      | H$_2$+O$_2$=2H$_2$O |                         |
|                        |                      | MnO$_2$+H$_2$=Mn+O+H$_2$O |                         |
| O$_2$                  | X$_6$                | 2CO+O$_2$=2CO$_2$,H$_2$O=2H$_2$O | 11.71                     |
| C                      | X$_7$                | CO$_2$+C=2CO,FeO+C=Fe+CO | 30.01                     |
|                        |                      | MnO$_2$+2C=Mn+2CO |                         |
| MnO$_2$                | X$_8$                | MnO$_2$+2C=Mn+2CO | 2.81                      |
| Mno                    | X$_9$                | MnO+O=C=Mn+CO | 1.54                      |
|                        |                      | MnO$_2$+H$_2$=MnO+H$_2$O |                         |
| H$_2$O                 | X$_10$               | H$_2$+O$_2$=2H$_2$O | 0.91                      |
|                        |                      | MnO$_2$+H$_2$=MnO+H$_2$O |                         |
|                        |                      | 3Fe$_2$O$_3$+H$_2$=2Fe$_3$O$_4$+H$_2$O |                         |
|                        |                      | FeO+H$_2$=Fe+H$_2$O |                         |
|                        |                      | Fe$_2$O$_3$+H$_2$=3FeO+H$_2$O |                         |
| Ca$_3$(PO$_4$)$_2$     | X$_11$               | 2Ca$_3$(PO$_4$)$_2$+3SiO$_2$+10C=3Ca$_3$SiO$_4$+4P+10CO | 0.04                      |
| Ca$_5$SiO$_4$          | X$_12$               | 2Ca$_5$(PO$_4$)$_2$+3SiO$_2$+10C=3Ca$_3$SiO$_4$+4P+10CO | 1.22                      |
| Fe                     | X$_13$               | FeO+CO=Fe+CO$_2$,FeO+O=C=Fe+CO | 927.06                    |
|                        |                      | FeO+H$_2$=Fe+H$_2$O |                         |
| Mn                     | X$_14$               | MnO+O=C=Mn+CO | 0.80                      |
|                        |                      | MnO$_2$+2C=Mn+2CO |                         |
CO$_2$ & X$_{15}$ & $3\text{Fe}_2\text{O}_3$+CO=$2\text{Fe}_3\text{O}_4$+CO$_2$ & 1248.60 \\
FeO+CO=Fe+CO$_2$ \\
$\text{Fe}_3\text{O}_4$+CO=$3\text{FeO}$+CO$_2$ \\
CO$_2$+C=2CO, 2CO+O$_2$=2CO$_2$

4. Conclusions and Prospects
Through the prediction calculation, it can be seen that the metabolic flux of blast furnace gas in the process of blast furnace ironmaking is very large, mainly CO and CO$_2$. At the same time, these two gases are also the raw materials needed for ironmaking, and their reuse can be considered. The metabolic flux of flux is relatively small, so the flux can be increased appropriately and the slag removal rate can be increased as much as possible to improve production efficiency.

Establishing the differential dynamics equation of metabolic flux and forecasting the steady-state flux will play a fundamental role in the follow-up flux regulation and control, and achieve the goal of efficient production, energy saving and emission reduction.

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