Process Analysis of the Effective Utilization of Molten Slag Heat by Direct Blast Furnace Cement Production System

Hadi PURWANTO,1) Eiki KASAI2) and Tomohiro AKIYAMA3)

1) Faculty of Engineering, International Islamic University Malaysia, Jalan Gombak 53100 Kuala Lumpur, Malaysia.
2) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577 Japan.
3) Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628 Japan. E-mail: takiyama@eng.hokudai.ac.jp

(Received on December 10, 2009; accepted on March 17, 2010)

This paper principally presents a process analysis of the production systems of blast furnace cement (BFC) based on exergy analysis and its carbon dioxide emission. The analysis was first carried out by using exergy balances of actual operating data in the cement industry. The results revealed that a large sum of net exergy losses was found on the conventional BFC production; this was contrary to the preliminary expectations. In the BFC production, the recovery of the thermal exergy of the molten slag should reduce the total exergy losses by up to 20%. In contrast, the emission of CO$_2$—488.2 kg/ton—in BFC production was lower than 797.5 kg/ton emission in portland cement production; this was because portland cement consumes more carbonaceous fuels such as coal. In conclusion, to reduce exergy loss, save energy and minimize CO$_2$ emission, it is imperative that the BFC production process should be improved with the recovery of the thermal exergy of the molten slag. This means thermal combination of portland cement and BFC for the effective use of waste heat, in which waste heat in the conventional BFC process is recovered and used for limestone decomposition in the clinker production to produce BFC.

KEY WORDS: CO$_2$ emission; waste heat recovery; exergy; blast furnace slag; cement production.

1. Introduction

In the last decade, energy and environmental problems, especially pertaining to greenhouse effect gases resulting from the utilization of fossil fuel energy, have attracted worldwide attention. In 2008, Japan dealt with this challenge to reduce CO$_2$ emission by 20% at 2020 in comparison to that in 1990; it was in accordance with the Kyoto protocol. However, the amount of emission exhibits an opposite trend, i.e., some increase was seen in 2007. To ensure the effectiveness of actions to cope with the global warming, it is essential to evaluate the energy flow in the present energy-consuming industry. This will promote the effective utilization of energy, identification of the most energy-consuming industries, and formulation of strategies for the future.

Cement production is well-known as an energy-consuming industry involving high-temperature processes such as a rotary kiln in which the calcination and burning of the cement materials occur at a high temperature over 1780 K. Needless to say, the calcination process (CaCO$_3$→CaO+CO$_2$) emits CO$_2$, which is generated from both the thermal decomposition of limestone and combustion of the fossil and other carbonaceous fuels. In the cement industry, a large amount of blast furnace slag has been used as a raw material and its product is often called as ‘blast furnace cement’ (BFC). The BFC is particularly effective in the reducing of CO$_2$ generation because decomposition process of limestone can be omitted. BFC is a mixture of cement clinker and water-granulated BF slag. The granulated BF slag is produced by quenching the molten BF slag by impinging water without heat recovery. Therefore, although BFC is well known as an environmental-friendly material, its production process provides scope to save energy further by recovering a significant amount of waste energy at 1780 K.

Based on the abovementioned viewpoints, energy evaluation of the cement production process is essential for energy saving and CO$_2$ emission reduction. Exergy is an essential thermodynamic concept that has been widely applied in the design/evaluation of thermal plants, and it contributes significantly toward improving the system efficiency and thermo-economy. However, to the best of our knowledge, a comparative exergy analysis of the two cement production systems—portland cement (PC) and BFC—is not yet reported. Therefore, the purpose of this study is to evaluate the exergy of PC cement against the exergy of BFC without heat recovery from molten slag. The results will identify the areas of energy degradation, thereby promoting the effective use of energy and enable the proposal of energy saving and reduction of CO$_2$ emission.
2. Method

The conventional enthalpy method is not suited for drawing enthalpy flow diagram. Generally, while calculating enthalpy, we use the standard conditions of 298.15 K \((T_0)\) and 0.101325 MPa \((P_0)\) and define the enthalpy of all elements as zero. This is termed the standard formation of enthalpy or standard heat formation and is denoted as \(\Delta H^0\) (kJ/mol). Based on this definition, the \(\Delta H^0\) values of compounds are always negative. For example, in the case of carbon, the enthalpy of carbon element is zero and that of \(\text{CO}_2\) is negative \((-393.5\ \text{kJ/mol})\). However, in the enthalpy balance sheet of thermal/chemical plants, the use of negative values for enthalpy inflow and outflow is rather inconvenient. Therefore, in this study, we employed the so-called ‘modified enthalpy’ for the analysis of the cement process by changing the definition of a standard substance.3)

For calculating the modified enthalpy, we consider \(T_0\) and \(P_0\) as the standard conditions and the most stable materials in the atmosphere, such as \(\text{CO}_2\), as standard substances. Based on this definition, the enthalpy of element \(C\) is 393.5 kJ/mol and that of \(\text{CO}_2\) is zero at \(T_0 \) and \(P_0\). The enthalpies of the most stable substances such as \(\text{O}_2\), \(\text{N}_2\), \(\text{H}_2\text{O}\), \(\text{FeO}\), \(\text{CaCO}_3\), and \(\text{Al}_2\text{O}_3\) can also be determined by following this method.

The above mentioned method yields the modified standard enthalpy of any material; hence, the enthalpy of all materials is either positive or zero. When the molar specific heat at constant pressure is denoted as \(C_p\), the enthalpy is given by the following equations:

\[
H(T) - H(298.15) = \int_{298.15}^{T} C_p(T) \, dT = C'_{av,p}(T)(T - 298.15) \quad \ldots \ldots \ldots (1)
\]

\[
C'_{av,p} = \int_{298.15}^{T} \frac{C_p(T) \, dT}{(T - 298.15)} \quad \ldots \ldots \ldots \ldots \ldots (2)
\]

where \(H\) is enthalpy (kJ), \(T\) is temperature (K) and \(C'_{av}\) is defined as the average specific heat at constant pressure (kJ/mol K) and obtained by modifying the following basic equation of \(C_p\):

\[
C_p(T) = a + bT + cT^{-2} + dT^2 \quad \ldots \ldots \ldots \ldots \ldots (3)
\]

\[
C'_{av,p}(T) = A + BT + CT^{-2} + DT^2 \quad \ldots \ldots \ldots \ldots \ldots (4)
\]

where \(A, B, C, \) and \(D\) are the constants of the average specific heat modified from \(a, b, c, \) and \(d,\) respectively. The thermodynamic database of the thermochemical properties of inorganic substances provides the values of \(a, b, c, \) and \(d,\) as functions of temperature.\(^{10}\) Therefore, the modification of the original data on specific heats into corresponding average specific heat values will be useful in calculating the enthalpy balance of substances. The values of the constants in the modified specific heat of some substances involved in cement production are given in Appendix 1.

prior to the calculation of the enthalpy flow, it is imperative to verify the material balances of operating data in the cement process. The enthalpy flow in the process is defined as the sum of four types of enthalpy; chemical enthalpy, thermal exergy, pressure exergy, and mixing exergy, follows the equation:

\[
\varepsilon = \sum n_i \varepsilon_i^0 + \left( \sum n_i C_p \right)\left( T - T_0 - T_0 \ln(T/T_0) \right) + RT_0 \sum n_i \ln \left( n_i / \sum n_i \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots (5)
\]

where, \(\varepsilon\) is enthalpy (kJ), \(C_p\) is specific heat constant (kJ/mol K), \(T\) is temperature (K), \(P\) is pressure (kg/m^2s^2) and \(R\) is gas constant (J/mol K).

The numerical calculation is performed by using a computer program that considers the temperature dependency of the average specific heat of each substance. Before calculating enthalpy, a closed system is set up by creating a boundary surface for a combination of processes pertaining to cement production. After the heat and mass balances of the operating data are verified, the net enthalpy loss (EXL) is evaluated by the following equation:

\[
\text{exergy loss (EXL)} = \text{exergy output (} \varepsilon_{\text{out}} \text{)} - \text{exergy input (} \varepsilon_{\text{in}} \text{)} \quad \ldots \ldots \ldots \ldots \ldots \ldots (6)
\]

In this equation, the fuel and raw materials account for the energy input, whereas the product and waste, such as waste gas and dust, account for the energy output. Exergy loss will always be equal to zero or negative. The net EXL indicates the degradation of energy in the process. Thermodynamically, the exergy in the process is not always conserved even if the heat and mass are perfectly conserved, because the entropy always increases in an irreversible process. The net EXL in the cement process is unique and extremely important for evaluating the cement production process comparatively. The net EXL in each process within a cement production system is calculated and summed up for evaluating the system. Moreover, the exergy efficiency of the system is calculated by using the following equation:

\[
\text{exergy efficiency (}\varepsilon_{\text{eff}}\text{)} = \frac{\text{exergy out (} \varepsilon_{\text{out}} \text{)} - \text{exergy waste (} \varepsilon_{\text{waste}} \text{)}}{\text{exergy input (} \varepsilon_{\text{in}} \text{)}} \times 100 \%
\]

\...........................................(7)

In addition, the \(\text{CO}_2\) gas emission in the two cement production systems is comparatively evaluated from both the fuel consumed and raw materials used. Limestone, which is the main raw material for cement production, releases \(\text{CO}_2\) due to thermal decomposition. The fossil fuel, which is used as a heat source in this process, also causes \(\text{CO}_2\) emission during its combustion.

3. Process Descriptions

3.1. Portland Cement Production

The Portland cement production process comprises three unit processes: material preparation (grinding, drying, and mixing), clinker production, and clinker crushing. The process of clinker production consumes the largest amount of energy since it involves the high-temperature processes of firing and decomposition of limestone. Figure 1 illustrates a new suspension pre-heater (NSP) kiln, which is industrially used for cement production at one cement com-

© 2010 ISIJ

1320
pany, Japan. The NSP kiln has four cyclones in its upper section to recover heat from the hot gas, heat the raw material to approximately 173 K, and calcinate limestone into lime before it enters the rotary kiln. Within the rotary kiln, the calcinated material is transformed into clinker at a temperature of 1773 K through several chemical reactions. The clinker is then quenched by air blowing and stored in a silo. Among the three unit processes, clinker production is the most exergy consuming step in PC production; it accounts for approximately 94.3% of the total exergy loss in the overall system in comparison to the material preparation and clinker crushing processes. In this study, a practically-operated clinker process of the scale of 100-ton clinker production per hour is analyzed. Note that the main raw materials are limestone and coal, the secondary raw materials are fly ash, silica, iron ore, dust, sludge, and bone as well as used tire. The detailed compositions of the raw materials are provided in Table 1.

3.2. Blast Furnace Cement Production

In Japan, the most common treatment of molten BF slag involves the use of a considerable amount of water to produce glassy granulated slag. The molten BF slag at 1773 K is quenched by water impingement and immersion. The product is a granular slag with a size of 3–5 mm; it exhibits very limited crystal formation since it is highly cementitious in nature. The slag obtained is then dried, mixed with PC, and used as commercially available BFC. The drawback of this process is that a considerable amount of water, approximately 10 ton water per ton molten slag, is required. In addition, after the granulation, the water temperature is very low; therefore, its sensible heat cannot be recovered. The chemical composition of the BF slag used for producing the BFC is as follows: 33.7% SiO2, 41.7% CaO, 14.4% Al2O3, 0.41% Fe2O3, 6.4% MgO, 0.98% S, 0.5% MnO, and 1.1% TiO2.

The BFC is produced by mixing the water-quenched slag with the PC clinker. The blending ratio of the cement clinker to the granulated slag in the commercial BFC at Nittetsu Cement Co. Ltd. is 60 to 40 mass%. Thus, the exergy analysis of BFC production is conducted by considering the EXL in the two processes of clinker production and water-cooling of molten slag.

4. Results and Discussion

4.1. Material and Heat Balances of Clinker Production

The operating data on clinker production at a capacity of 100 ton/h at the Muroran Works of Nittetsu Cement Co., Ltd. are employed. The material balance of clinker production based on chemical compounds is given in Table 2. The element balances for the detailed calculation of exergy are provided in Appendix 2. The input and output elements are in excellent agreement; in other words, the difference between them is enough negligible for starting enthalpy flow analysis.

Enthalpy flow in clinker production is shown in Fig. 2. It is found that approximately 70% of the input enthalpy in clinker production is effectively used in the process. It comprises the enthalpy input for the calcination (45%) and that for the preheating of a raw material (25%). As much as 30% of the input enthalpy is mostly wasted in the form of off-gas and clinker. Coal and other carbon-containing materials are combusted in the rotary kiln, and limestone thermally decomposes and undergoes calcination, after which it is fired to yield clinker. The NSP system emits dust and hot

| Composition | Component |
|-------------|-----------|
| mass%       | Limestone | Fly ash | Silica | Iron ore | Dust | Coal kiln | Coal calcination | Tire | Sludge | Bone | Air |
| CaCO3       | 98.6      |         |        |         |      | 1.46      | 1.44              |      |        |      | 3.13 |
| CaO         | 8.15      | 7.08    | 48.03  | 1.46    | 1.44  | 3.13      | 18.8              |      |        |      |     |
| SiO2        | 44.74     | 100     | 5.14   | 17.72   | 8.02  | 7.9       | 3.65              |      |        |      |     |
| Al2O3       | 32.84     | 1.75    | 25.32  | 5.89    | 5.79  | 1.68      | 0.68              |      |        |      |     |
| MgO         | 1         | 3.84    | 1      | 0.69    | 0.68  |           |                   |      |        |      |     |
| MnO         | 0.04      | 0.49    | 2.6    |         |       |           |                   |      |        |      |     |
| Fe2O3       | 0.4       | 5.83    | 84.34  | 6.33    | 1.04  | 1.03      |                   |      |        |      |     |
| H2O         | 0.2       |         |        |         |       | 0.75     | 1.59              | 0.75 | 82.61  | 3.59 |
| C           | 7.04      | 69.5    | 85.14  | 7.03    | 42.82 |           |                   |      |        |      |     |
| O2          | 6.94      |         | 0.94   | 4.53    | 18.39 | 21        |                   |      |        |      |     |
| N2          | 1.03      | 1       | 0.46   | 1.01    | 9.62  | 79        |                   |      |        |      |     |
| S           | 4.56      | 0.11    | 0.07   | 1.4     | 0.14  | 0.52      |                   |      |        |      |     |
| H2          | 3.67      | 3.6     | 3.13   | 1.03    | 6.06  |           |                   |      |        |      |     |

Table 1. Chemical compositions of raw materials for clinker.

Fig. 1. Schematic diagram of the NSP clinker production system consisting of a preheater and a rotary kiln. Here, note that tire, bone, and sludge are recycled as fuel or raw materials.

Fig. 2. Enthalpy flow in clinker production.
gas at 473 K from the rotary kiln; this hot gas is recycled and reused for preheating the raw materials. The clinker is finally discharged as a main product at 473 K and cooled to atmospheric conditions.

4.2. Enthalpy and Exergy Analysis in Cement Production Processes

Figure 3 illustrates a process-system diagram of the clinker production process at a capacity of 100 ton/h. The detailed description of this diagram; so-called ‘thermodynamic compass’, is reported elsewhere. Thus, only the principle of this method is explained here. In this diagram, a solid circle indicates a process; solid arrow, a material; white arrow, an intermediate energy; and dotted circle, a system boundary. The delta value is the difference between the output and input values. The input enthalpy and exergy are thermodynamically calculated based on the conditions of pressure, temperature, and compositions of the input materials. The input materials include coal and air under atmospheric conditions. The output enthalpy is obtained from the enthalpy calculations of clinker, off-gas, and dust as byproducts. The sum of the enthalpy and exergy in BFC production is calculated based on this mixing ratio. Process-system diagram of BFC production is shown in Fig. 4. Heat in the molten slag is assumed to be heat source in the process analysis. For simplicity, the calculation is performed by considering the production of 100 ton clinker as the basis so that the amount of slag can be adjusted. The enthalpy is balanced in the overall process of BFC production.

4.3. Comparison of Exergy Losses

EXL in cement production is usually caused by several reasons such as heat loss through walls, waste heat content in products, chemical reactions, cooling, and mixing. EXL is as 298.15 K, although the actual temperature of the discharged material is slightly different.

In the production of BFC, cement clinker and water granulated BFC are mixed with a mass ratio of 60% : 40%. The sum of the enthalpy and exergy in BFC production is calculated based on this mixing ratio. Process-system diagram of BFC production is shown in Fig. 4. Heat in the molten slag is assumed to be heat source in the process analysis. For simplicity, the calculation is performed by considering the production of 100 ton clinker as the basis so that the amount of slag can be adjusted. The molten BF slag and water at temperatures of 1 773 and 298 K, respectively, are employed as input materials for the water granulation process to produce granulated slag as the main product and water as the byproduct at atmospheric temperature.

The enthalpy is balanced in the overall process of BFC production.
through walls is caused by imperfect thermal insulation and material transportation during the process. Clinker, dust, and off-gas are the final products of the process discharged at over 473 K before finally cooling to atmospheric conditions. In fact, the clinker temperature is 1 573 K before discharge and excess air is introduced for cooling it to 473 K. EXL also results from the transportation of hot air to the NSP for preheating the raw materials. The waste heat content in the product also causes EXL. Similar to other high-temperature industries, which involve chemical processes, the largest EXL in the cement process results from chemical reactions; in this case, the reaction is combustion. It is noteworthy that the clinker processing requires a high temperature of over 1 773 K, which is obtained by the combustion of carbon from coal with air.

Figure 5 shows the overall net exergy losses in the production of PC and BFC. The net EXL in the production of clinker for PC is approximately 1.7 GJ/ton-cement, and it is mainly in the form of chemical exergy. In the case of BFC, a large temperature exergy exists at the input; however, it is absent at the output. The water-cooling process for the molten slag from 1 773 K to atmospheric temperature causes temperature EXL, without any remainder in the product. Since this process involves the mixing of clinker and slag, the EXL caused by mixing is extremely small and therefore, negligible. The overall net EXL in BF cement is approximately 2 GJ/ton-cement or around 57% of the total input exergy (BF Cement A). This value is higher than that of the EXL for PC 45%. In other words, the exergy efficiencies for PC and BFC are 55% and 43%, respectively.

The percentage efficiency of the PC process is 12 points higher than that of the BFC process. This is because a considerable amount of exergy is wasted during the granulation of molten slag using water. Although heat and enthalpy are conserved, chemical reaction and cooling undoubtedly degrade the energy. It is noteworthy that the extremely large net EXL in BFC is caused by the cooling process. Therefore, it is desirable to consider a high-efficiency technique for exergy recovery from molten slag. Therefore, it is possible to increase the efficiency of BFC by recovering the exergy of the molten slag.

An alternative method to produce blast furnace cement is proposed by mixing the limestone with molten slag directly, so called direct blast furnace cement production. The image of the direct blast furnace cement production is given in Fig. 6. The image of the proposed process for the Direct blast furnace cement production.
rotating cup atomizer without water impingement to produce glassy slag.\textsuperscript{13} A rotary cup atomizer is set between calcination and rotary kiln furnace. Since granulation process is carried out in a closed system, there is no heat release from the slag outside the system. The remained heat of the slag at above 1 673 K is also used to support calcination process and clinker production. The glassy slag produced is directly fed into rotary kiln together with other materials. When the proposed process is applied and the thermal exergy of the molten slag is completely recovered, the total EXL for the production of BFC will be 1.6 GJ/ton or 20\% less EXL compared to the present BFC method as shown in Fig. 5 (BF Cement B). It can be understood that the proposed direct blast furnace cement process will promote energy recovery and avoid exergy loss by utilize both thermal energy and glassy slag.

4.4. Energy Requirement and CO\textsubscript{2} Gas Emission

The energy consumption in PC and BFC production are evaluated based on the amount of coal-based energy. The analysis is carried out using common basic-energy consumption in Japanese industries.\textsuperscript{14} One ton of PC consumes 105 kg coal, equivalent to approximately 2 985 MJ energy. The total consumption of electricity for the grinding process is 99 kW h/ton-cement; the individual consumptions are 28.6, 2.4, and 68 kW h/ton for raw material, coal, and clinker, respectively. The overall energy requirement for cement production is shown in Table 3. The results show that the energy requirements are 4 036.2 MJ/ton for PC and 2 666.0 MJ/ton for BFC using present technology (refer to Fig. 5-BF Cement A). Coal is the main energy source for the calcination process in the rotary kiln and electricity is mainly used for grinding. On comparing the results we observe that PC and BFC consume 75\% and 67\% of the energy from coal, respectively, and the remaining energy is derived from the electricity that is mainly used for grinding the raw material and clinker. In other words, BFC production consumes 34\% lesser energy than PC. This difference can be accounted for by the fact that a part of the raw material in BFC is the glassy slag that is directly mixed with the clinker.

With regard to the environmental aspect, reduction in energy consumption leads to reduction in carbon gas emission. The comparison between the CO\textsubscript{2} gas emissions in the two cement processes is shown in Fig. 7. The CO\textsubscript{2} gas emitted by the cement industry originates from three sources: coal combustion, electricity, and limestone decomposition. In the case of coal and electricity, a conversion factor is used for calculating CO\textsubscript{2} emission; this factor is estimated based on the guidelines provided by the Japanese government.\textsuperscript{15} The results show that carbon gas is mainly emitted from the decomposition of limestone rather than from coal combustion and electricity. In BFC production (refer to Fig. 5-BF Cement A), where slag replaces a part of the limestone, the carbon gas emission reduces by about 25\% from 797.5 to 488.2 kg. The existing slag also contributes toward the reduction of carbon gas because of the reduction in the consumptions of coal and limestone.

5. Conclusions

The analysis first showed that a large amount of net energy losses (EXL) was found on the conventional blast furnace cement (BFC) production. The BFC production, the recovery of the thermal exergy of the molten slag should reduce the total EXL by up to 20\%. Most of the EXL in the BFC production is caused by the water granulation of molten slag.

Secondly, the CO\textsubscript{2} emissions in portland cement and BFC productions are approximately 800 and 490 kg/ton, respectively; the large CO\textsubscript{2} emission for portland cement is attributed to the utilization of more carbonaceous fuels for calcination process.

Next, the proposed direct blast-furnace-cement process by utilization of waste heat in the molten slag as an energy source for limestone decomposition will promote energy saving in the BFC production. The recovery of thermal energy from the molten slag will reduce the total EXL in BFC production by around 20\% of CO\textsubscript{2} emission.

In conclusion, the recovery of thermal energy in the molten slag is essential to prevent the degradation of energy in conventional BFC production. By effectively utilizing both thermal energy of molten slag and glassy slag produced from direct cement production process will promote energy recovery and reduce not only exergy loss but also CO\textsubscript{2} emission. When the BFC manufacturing plant locates next to an ironmaking plant, both ironmaking and cement production industries cooperate with the effective use of energy easily.

Acknowledgments

The authors gratefully acknowledge the Japan Society for Promotion of Science (P04150) for the support to the present study, The Ministry of Economic Trade and Industry of Japan for their financial support and Nittetsu Cement Co., Ltd. (Muroran Works), for providing the operating data.
REFERENCES
1) Kyoto Protocol, (in Japanese; Kyoto Giteisho) (2005). http://www.kyoto-protocol.jp/
2) E. Onuma, R. Waizumi and H. Muramatsu: *Cem. Concr.,* 703 (2005), 1.
3) T. Akiyama, R. Takahashi and J. Yagi: *ISIJ Int.,* 29 (1989), 447.
4) M. A. Rosen: *Exergy Int. J.,* 1 (2001), 180.
5) G. P. Verklavker and B. V. Kosoy: *Energy Convers. Manag.,* 42 (2001), 2053.
6) G. Bisio: *Energy,* 18 (1993), 971.
7) G. Van Gool: *Energy,* 17 (1992), 791.
8) M. M. Costa, R. Schaeffer and E. Worrell: *Energy,* 26 (2001), 363.
9) G. Bisio and L. Tagliafico: *Exergy Int. J.,* 2 (2002), 34.
10) I. Barin and O. Knacke: Thermochemical Properties of Inorganic Substances, Springer-Verlag, New York, (1973).
11) T. Akiyama, R. Takahashi and J. Yagi: *ISIJ Int.,* 29 (1989), 447.
12) T. Akiyama, K. Otsuka, T. Shimada, E. Kasai and J. Yagi: *ISIJ Int.,* 40 (2000), 286.
13) H. Purwanto, T. Mizuochi, H. Tobe, M. Takagi and T. Akiyama: *Mater. Trans.,* 45 (2004), 3286.
14) Japan Cement Association: Energy Consumption (2005). http://www.jacssoc.or.jp/
15) The Ministry of Environment Japan: Guideline for Calculating Greenhouse Gas Effect from Industry (in Japanese; Jigyosha Kara no Onshitsu Koka Gasu Haishutsu Santei Hoho Gaidorain) (2005). http://www.env.go.jp/press/press.php3?serial=4221

Appendix 1. Values of chemical enthalpy and exergy for major raw materials along with the information for calculating the average specific heat (M: molecular weight; A, B, C, D: constants; T1, T2: temperatures; L: latent heat).

| Substance | Enthalpy kcal/mol | Exergy kcal/mol | M  | A  | B  | C  | D  | T1 | T2 | L kcal/mol |
|-----------|-------------------|-----------------|----|----|----|----|----|----|----|------------|
| CaO       | 42.5              | 26.37           | 56.0794 | 11.86 | 1.06 | -1.66 | 0  | 29815 | 2888 | 0          |
| FeO       | 0                 | 0               | 100.09 | 24.89 | 5.24 | -6.2  | 0  | 29815 | 1000 | 0          |
| MgO       | 0                 | 0               | 101.961 | 24.821 | 6.278 | -6.953 | 0  | 29815 | 1000 | 0          |
| Fe        | 0                 | 101.961 | 28.004 | 21.97 | -11.56 | 0  | 800  | 2327 | 0          |
| Mn        | 281.1             | 12.14         | 40.3141 | 11.707 | 0.751 | -2.734 | 0  | 29815 | 3068 | 0          |
| SiO2      | 0                 | 0               | 70.9574 | 11.11 | 1.94 | -0.68  | 0  | 29815 | 2000 | 0          |
| Fe2O3     | 0                 | 0               | 159.692 | 23.49 | 18.6 | -0.352 | 0  | 29815 | 953  | 0.16       |
| Fe2O      | 0                 | 0               | 159.692 | 36    | 0    | 0     | 0  | 953   | 1063 | 0          |
| Fe2O3     | 0                 | 0               | 159.692 | 31.71 | 1.76 | 0     | 0  | 1055  | 1730 | 0          |
| Fe        | 98.65             | 87.99          | 55.847 | 6.734 | -1.749 | -0.692 | 5.985 | 29815 | 800  | 0          |
| Fe        | 98.65             | 87.99          | 55.847 | -62.667 | 61.14 | 1.48 | 0  | 800   | 1000 | 0          |
| Fe        | 98.65             | 87.99          | 55.847 | -153.419 | 166.429 | 0  | 1000 | 1042 | 0          |
| Fe        | 98.65             | 87.99          | 55.847 | 465.166 | -427.222 | 0  | 1042 | 1060 | 0          |
| Fe        | 98.65             | 87.99          | 55.847 | -134.305 | 79.862 | -696.012 | 0  | 1060 | 1184 | 0.215     |
| Fe        | 98.65             | 87.99          | 55.847 | 5.754  | 1.968 | 0   | 0  | 1184  | 1655 | 0.2       |
| C         | 94.05             | 98.12          | 12.011 | 0.026 | 9.307 | -0.354 | -4.155 | 29815 | 1100 | 0          |
| C         | 94.05             | 98.12          | 12.011 | 0.041 | 7.575 | 0.0174 | 0   | 29815 | 368  | 0          |
| S         | 70.86             | 144.07         | 32     | 3.54  | 5.75  | 0.174 | 0  | 29815 | 368  | 0          |
| H2O       | 0                 | 0               | 18.015 | 18.015 | 0    | 0     | 0  | 29815 | 37315 | 0          |
| Mn        | 124.45            | 110.21         | 54.938 | 6.03   | 3.56 | -0.443 | 0  | 29815 | 1410 | 0.43       |
| Mn        | 124.45            | 110.21         | 54.938 | 11.3   | 0    | 0     | 0  | 1410  | 1617 | 3.2       |

Appendix 2. Element balances for clinker production.

Element balances-1

| Element | Si | Al | Fe | Ca | Mg | Mn | C | H | O | S | N | Total |
|---------|----|----|----|----|----|----|---|---|---|---|---|-------|
| Input   | 0  | 11.62 | 2.85 | 2.29 | 56.04 | 1.16 | 0.06 | 25.21 | 0.7 | 118.23 | 0.6 | 123.62 | 342.43 |
| Output  | 0  | 11.62 | 2.85 | 2.29 | 56.04 | 1.16 | 0.06 | 25.21 | 0.7 | 117.82 | 0.6 | 123.62 | 341.48 |

Element balances-2

| Element | Si | Al | Fe | Ca | Mg | Mn | C | H | O | S | N | Total |
|---------|----|----|----|----|----|----|---|---|---|---|---|-------|
| Input   | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0     |
| Output  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0     |

© 2010 ISIJ