Numerical simulation and experimental study on hematite production by oxidation of mill scale

M T Aldiramadan¹, J Nabilah², M Ridwan¹ and D S Khaerudini³

¹ Department of Chemistry, University of Indonesia, Depok, Jawa Barat, 16424, Indonesia
² Department of Physics, State University of Jakarta, Jalan Rawamangun Muka, Jakarta Timur, 13220, Indonesia
³ Research Center for Physics, Indonesian Institute of Sciences (LIPI), Kawasan PUSPIPTEK Serpong, Tangerang Selatan, 15314, Indonesia

Email: deni.shidqi.khaerudini@lipi.go.id

Abstract. Mill scale is a waste product from steel hot rolling processes and containing a high amount of FeO and Fe₂O₃. It is crucial to recycle and reuse this waste for the recovery into a metallic iron or its single oxide derivative. One of the end products of mill scale oxidation is hematite which has multitude of uses in various application. In this present study, mill scale is converted to hematite by roasting a mixture of mill scale at a specific set of conditions at 900°C for a varied time under ambient air environment by addition of pelletized limestone as a heat storage media. In this work, the Dimensionless Degree of Oxidation Prediction Model (DDOPM) has been constructed to gain hematite purity approach in the resulting powder by using Matlab. The Buckingham Pi Theorem is used to find dimensionless parameters considering the effect of different parameters including the geometric factor of tubular horizontal furnace used, characteristic of mill scale, ambient air factor, and thermal characteristics of limestone. The degree of oxidation from experimental result was obtained from XRF analysis and compared to the result of DDOPM to show the correlation between the experimental and numerical.

1. Introduction

Mill scale is a steel-making by-product from steel hot rolling processes and is composed of iron oxides and metallic iron with varying oil and grease contents [1]. It was formed during the continuous casting and rolling mill processes when steel is submitted to thermal gradients in oxidant temperatures, promoting the growth of the iron oxide layer at the surface of steel [2]. Mill scale was separated from the steel through some processes such as flame cleaning, water spray, pickling, and blasting [3]. The oil component in the rolling mill scale makes recycling difficult, and its direct re-use in sintering may lead to environmental pollution [1].

It was estimated that in 2020, the capacity of steel production in Indonesia was reaching 13.67 million tons every year [4]. Around 35-40 kg of mill scale was produced for every ton of hot-rolled product [1]. Therefore, 546.8 tons of mill scale was estimated to be generated every year. Legodi et al. [1] reported that the bulk of mill scale waste was dumped in landfills by a steel manufacturing company in the Republic of South Africa. Leaching minor percentages of heavy metals into soil and groundwater is threatening the environment [1]. The mill scale also needs to be pretreated before it can be re-utilized.
Therefore, it is increasingly encouraging to treat these solid wastes more sustainably to be re-utilized as a functional material.

One way to treat mill scale is to oxidize it into its highest level of oxide, i.e., hematite (Fe₂O₃). As the mill scale is the multi-oxide component with the amount of iron oxide varied depends on its location of steel production. Thus, oxidation into pure hematite would be economically beneficial because hematite is a functional material in various applications. Hematite is commonly used in synthetic pigments, such as in paints, ceramics, and porcelain [5]. Hematite nanomaterials have been investigated intensively as a promising anode material for Li-ion batteries due to their advantages including high theoretical capacity, low cost, environmental friendliness, and high resistance to corrosion [6]. It has also been a catalyst for many industrially essential reactions, such as synthesis of NH₃, high-temperature water gas shift reaction, and natural gas desulfurization [7].

Many studies in the literature deal with different methods for preparing hematite [1, 8–11]. Jikar et al. [12–13] have successfully prepared hematite from a ferrous mill scale by calcination under a 100 % oxygen environment at a temperature higher than 900°C. Pure oxygen was consumed and wasted in this process. A way to improve this method is to use the oxygen from ambient air. Another problem is that calcination under an ambient air environment needed longer time due to slower oxygen flow rate. This problem can be overcome by either increasing the holding time, which takes more energy (electricity), or employing heat storage media (passive heating) to extend its heating time for oxidation to be occurred even after the furnace (active heating) was turned off.

Heat storage is a technology that stores thermal energy over a particular time and releases the stored energy at a later time [14]. Heat storage by increasing the temperature of the material is known as sensible heat storage. Materials used for an efficient, sensible heat storage system should have high specific heat capacity, low thermal conductivity, long-term stability in terms of thermal cycling, and be compatible with the material where storage takes place [15]. Brick, concrete, granite, sandstone, and limestone are common material used as a heat storage media [16]. Limestone was selected as the heat storage material due to its low conductivity, high specific heat, low cost, and abundantly available in Indonesia.

Thus, the whole oxidation process can be mathematically modelled considering the effect of different parameters by using the Dimensionless Analysis Approach, i.e., Buckingham Pi Theorem [12]. The use of dimensionless analysis has been widely applied in processing metallurgy when more than two parameters influence its behavior [13]. Jikar et al. [12] attempted experimentation and mathematical modelling in this process with thirteen dimensionless groups and simplified it to a simple power-law equation with two dimensionless groups.

In this work, hematite was successfully prepared from mill scale. Pelletized limestone was added as heat storage media, and calcination is carried out under an ambient air environment at 900 °C. The attempt has been made to model ideal conditions in the tubular horizontal furnace (THF) and is modelled using the Buckingham Pi Theorem to estimate the degree of oxidation for predicting the output by assuming 20 input parameters. Subsequently, the supporting experimentation is also carried out, and the resulting powder was then characterized using X-ray fluorescence (XRF) to investigate the obtained hematite content. The affecting parameters on the degree of oxidation considered in the dimensionless analysis modelling are listed in table 1.

### 2. Formulation of Dimensionless Degree of Oxidation Prediction Model (DDOPM)

The degree of oxidation (O) is defined as %Fe₂O₃ content in the oxidized powder obtained by XRF (S2 Puma, Bruker) analysis. In this present study, it was assumed that the degree of oxidation is influenced by the different process parameters, as described in table 1, and its relationship is stated by:

\[
X = f(T, t, T_R, L_T, D_T, V, W_M, \rho_M, d_M, S_M, P_O, \rho_O, \eta, W_C, D_C, S_C, \rho_C, \kappa, P_C)
\]  

It also considered that \(\rho_O, \eta,\) and \(P_C\) are a function of temperature [17, 18].
Table 1. List of variables input of physical and material parameters.

| No | Variables                          | Symbol | SI Unit       | Dimensions                  |
|----|------------------------------------|--------|---------------|-----------------------------|
| 1  | Holding Temperature                | T      | K             | $[M^1L^0T^0θ^0]$           |
| 2  | Holding time                       | t      | s             | $[M^0L^0T^1θ^0]$           |
| 3  | Heating rate                       | $T_R$  | Ks$^{-1}$     | $[M^0L^0T^{-1}θ^0]$        |
| 4  | Length of the tube                 | $L_T$  | m             | $[M^0L^1T^0θ^0]$           |
| 5  | Diameter of the tube               | $D_T$  | m             | $[M^0L^1T^0θ^0]$           |
| 6  | Crucible volume                    | $V$    | m$^3$         | $[M^0L^3T^0θ^0]$           |
| 7  | Weight of mill scale               | $W_M$  | Kg            | $[M^1L^0T^0θ^0]$           |
| 8  | Apparent density of mill scale     | $ρ_M$  | Kgm$^{-3}$    | $[M^1L^{-3}T^0θ^0]$        |
| 9  | Mill scale particle size           | $d_M$  | m             | $[M^0L^1T^0θ^0]$           |
| 10 | Specific surface area of mill scale powder | $S_M$ | m$^2$Kg$^{-1}$ | $[M^{-1}L^2T^0θ^0]$       |
|    |                                    |        |               |                             |
| 11 | Oxygen purity                      | $P_O$  | Kgm$^{-3}$    | $[M^1L^{-3}T^0θ^0]$        |
| 12 | Density of oxygen                  | $ρ_O$  | Kgm$^{-3}$    | $[M^1L^{-3}T^0θ^0]$        |
| 13 | Viscosity of oxygen                | $η$    | Kgm$^{-1}$s$^{-1}$ | $[M^0L^{-1}T^1θ^0]$        |
|    |                                    |        |               |                             |
| 14 | Weight of limestone                | $W_C$  | Kg            | $[M^1L^0T^0θ^0]$           |
| 15 | Limestone pellet diameter           | $D_C$  | m             | $[M^0L^1T^0θ^0]$           |
| 16 | Surface area of limestone pellet   | $S_C$  | m$^2$Kg$^{-1}$ | $[M^{-1}L^2T^0θ^0]$       |
| 17 | Apparent density of limestone      | $ρ_C$  | Kgm$^{-3}$    | $[M^1L^{-3}T^0θ^0]$        |
| 18 | Specific heat capacity of limestone| $C_P$  | Jkg$^{-1}$K$^{-1}$ | $[M^0L^2T^{-2}θ^{-1}]$      |
| 19 | Thermal conductivity               | $κ$    | Wm$^{-1}$K$^{-1}$ | $[M^1L^{-1}T^{-1}θ^0]$      |
| 20 | Equilibrium pressure of limestone  | $P_C$  | Pa            | $[M^1L^{-1}T^2θ^0]$        |

Equation (1) was determined using the computed Buckingham's Pi Theorem with Gauss-Jordan elimination MatLab syntax \textit{rref}. This equation involving 20 variables with 4 primary or fundamental dimensions, which are mass, length, time, and temperature. Thus, it can be rewritten in terms of a set of 16 dimensionless \( \Pi \) parameters constructed from the original variables.

The final form of Process Parameter (X) is written as in equation (2) and the detailed calculations are listed in Appendix A.

\[
X = \left[ \frac{T_R^8 κ^8 T t L_T D_T V W_M ρ_M d_M ρ_O ρ_C W_C D_C S_C C_P P_C}{S_M^{22} η^{35}} \right]
\]  \hspace{1cm} (2)

The equation (2) is determined using constant values of parameters, as listed in table B.1.

The final form of the Dimensionless Degree of Oxidation Prediction Model (DDOPM) is then given as in equation (3). This model depicts the degree of oxidation (O) governed by the process parameters. There are two dimensionless constants of the model that emerged, i.e., $ϕ$ and $A$, known as characteristic
constant. These constants can be obtained by conducting an experiment. To solving equation (3), it was carried out by varying the time and keeping other parameters (as listed in table B1) constant.

\[ O = \Phi(X)^A \] (3)

Taking the logarithmic of equation (3) on both sides:

\[ \log O = \log \Phi + A \log X \] (4)

This is similar with the general of linear equation of \( y = c + mx \).

3. Experimental Procedures

3.1. Material preparation

The mill scale was mechanically grinded into a fine powder and sieved into 400 mesh that provided by PT Krakatau Steel Tbk., Indonesia. It was then heated at the temperature of 200 °C for 1 hour as pretreatment to reduce dirt and lubricant. Chemical analysis was conducted by using XRF Analyzer (S2 Puma, Bruker, Germany).

Limestone (CAS:1317-65-3) technical grade was grounded into a fine powder then sieved into 325 mesh. Limestone powder was prepared as a pellet by pressing 2 grams of powder using Hydraulic Lab Press CMG 100H-15 (Carver, America) at the pressure of 200 MPa for 5 minutes. The pellet diameter is about 2 cm with a density of 0.5127 g cm\(^{-3}\). The conductivity and specific heat capacity of limestone are measured using TCi Thermal Conductivity Analyzer (C-Therm, Canada).

3.2. Mill Scale Oxidation Processes

The applied ceramic boat in this work has the dimension of half-cylinder shape with length of 9.3 cm, width of 3 cm, and height of 1.5 cm, as shown in figure 1. The 6 limestone tablets with each weight of 2 grams placed on the bottom (figure 1(a) and top of mill scale powder (figure 1(c)), and the 20 grams of mill scale powder (figure 1(b) were loaded into the boat for each heating process. The crucible was then placed inside the center of heating zone that covered with the glass tube with length of 1 m and diameter of 5.5 cm (figure 2). The tubular furnace (figure 2) used in this present study was made by the Research Center for Physics, Indonesian Institute of Sciences (LIPI, Indonesia). There was no pure oxygen supply used in this process, and the oxidant used in the calcination process was solely ambient air. Therefore, both end of the glass tube was free exposed into the air. The calcination process was carried out at holding temperature of 900 °C, heating rate of 5 °C/min, at a varying holding time of 1, 2, and 4 hours. The corresponding samples are then abbreviated as HEM1, HEM2, and HEM4; the same approach was also carried out for CON1, CON2, and CON4, as listed in table 2, to showing with and without limestone addition respectively.

![Figure 1](image.png)

**Figure 1.** (a) Schematic diagram of limestone pellets on the bottom of the crucible, (b) mill scale powder was placed on top of limestone pellets, and (c) the three limestone pellets were placed on top of mill scale powder.
Figure 2. (a) Schematic of furnace used for oxidation of mill scale, (b) side view of furnace showing the crucible inside the tube and (c) explode view of the tube showing the placement of the crucible.

Table 2. Process condition for oxidation of mill scale.

| Sample | $W_M$ (g) | $W_C$ (g) | $T$ ($^\circ$C) | $t$ (h) |
|--------|-----------|-----------|----------------|--------|
| HEM1   | 20        | 12        | 900            | 1      |
| HEM2   | 20        | 12        | 900            | 2      |
| HEM4   | 20        | 12        | 900            | 4      |
| CON1   | 20        | 0         | 900            | 1      |
| CON2   | 20        | 0         | 900            | 2      |
| CON4   | 20        | 0         | 900            | 4      |

The resulting powder was then ball milled at 300 rpm for 2 hours. The ball to powder weight ratio was set at 20:1 wt.% with large to medium to small weight ratio of the ceramic ball used are 4:2:4 wt.%

4. Results and Discussion
The XRF results of used mill scale in this work mainly consist of wustite and magnetite, as shown in table 3. The oxidation of wustite into magnetite and magnetite into hematite occurs according to the following reaction:

$$6 \text{FeO} + \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3$$  \hfill (5)

$$\Delta H_{900^\circ C} = -641.36 \text{kJ/mol, } \Delta G_{900^\circ C} = -316.59 \text{kJ/mol}$$

$$\Delta H_{25^\circ C} = -604.56 \text{kJ/mol, } \Delta G_{25^\circ C} = -522.02 \text{kJ/mol}$$

$$4 \text{Fe}_2\text{O}_4 + \text{O}_2 \rightarrow 6 \text{Fe}_3\text{O}_4$$  \hfill (6)

$$\Delta H_{900^\circ C} = -454.08 \text{kJ/mol, } \Delta G_{900^\circ C} = -141.62 \text{kJ/mol}$$

$$\Delta H_{900^\circ C} = -471.60 \text{kJ/mol, } \Delta G_{900^\circ C} = -392.19 \text{kJ/mol}$$

This reaction was set-up in two-step processes. First step, the wustite converted into magnetite and then the next oxidation step is converted the magnetite into hematite. This means that there are two solid phases can coexist during the reaction either with pure oxygen or oxygen from ambient air, i.e., wustite and magnetite phase or magnetite and hematite phase [19].

Both of the reaction are exothermic, and thermodynamically possible to occur at room temperature; however, the kinetic rate of the oxidation process is extremely slow at low temperature. A study by Monazam et al. [20] shows that oxidation of magnetite into hematite starts to occur at a decent rate at
750 °C. It takes 10 to 60 minutes for the oxidation process of wustite to magnetite to occur, and 30 to 240 minutes to convert magnetite into hematite. Both depend on the oxygen supply flow rate.

Table 3. XRF results of mill scale as raw material.

| Components   | Weight (%) |
|--------------|------------|
| Fe           | 98.744     |
| FeO          | 54.070     |
| Fe₃O₄        | 44.829     |
| MnO₂         | 0.756      |
| SiO₂         | 0.171      |
| Cr₂O₃        | 0.083      |
| TiO₂         | 0.025      |
| V₂O₅         | 0.023      |
| CaO          | 0.021      |
| Others       | 0.023      |

The black-colored powder was obtained after the calcination process for both HEM and CON samples. When the sample is held close to a hard magnet (NdFeB), all HEM samples show weak attraction on it, while all CON samples show paramagnetic behavior, as shown in figure 3. HEM and CON turn into bright, red-colored powder and brown powder, respectively, after dry milling processes. This due to some extra oxidations happen during the milling as a consequence of ball impact and speed. The complete XRF results for all samples after the oxidation processes at 900 °C and dry milling for 2 hours are listed in table 4.

![Figure 3. Magnetic interaction of (a) CON1 and (b) HEM1.](image)
Table 4. XRF analysis of oxidized mill scale at 900 °C.

| Sample | Fe₂O₃  | Fe₃O₄  | CaO   | SiO₂  | MnO₂  | Others |
|--------|--------|--------|-------|-------|-------|--------|
| HEM1   | 93.382 | 5.866  | 0.093 | 0.110 | 0.476 | 0.072  |
| HEM2   | 95.487 | 3.440  | 0.260 | 0.147 | 0.545 | 0.117  |
| HEM4   | 96.769 | 1.871  | 0.400 | 0.108 | 0.482 | 0.370  |
| CON1   | 37.053 | 61.905 | 0.018 | 0.120 | 0.403 | 0.502  |
| CON2   | 43.062 | 56.097 | 0.011 | 0.113 | 0.395 | 0.321  |
| CON4   | 49.737 | 49.944 | 0.000 | 0.153 | 0.166 | 0.000  |

The number of Fe₂O₃ content in table 4 shows significant different number between with and without of limestone pellets. This can be explained due to the effect as a heating storage media of limestone during the calcination (roasting). Therefore, it will extend the effect of heat distribution into the mill scale powder during the calcination, as illustrated in figure 4. Then, resulting into better oxidation process and significant effect into the number of resulted hematite. Figure 4 shows that HEM4 undergo a longer time at a temperature region above the minimum limit for the oxidation process to occur than CON4. The same phenomenon occurs between HEM2 & CON2 and HEM1 & CON1. It should be noted that the values given on this graph are rough estimation from the temperature measurements made every 30 minutes during the oxidation process. For the first 3 hours, all HEM and CON samples undergo the temperature rise step from 30 to 900 °C. Oxidation of wustite in mill scale to magnetite starts to occur at this step. The second step is the holding time which varied as shown in table 2. Then it was the temperature drop step, where all CON samples undergo a drop of 2 to 5 Kmin⁻¹, whereas all HEM samples undergo a slower temperature drop. This phenomenon happens due to the presence of limestone pellet as heat storage media. The placement of the pellets was arranged in such a way that heat was trapped around the sample. Conductivity and specific heat capacity measurement results are 0.086 Wm⁻¹K⁻¹ and 238.564 Jkg⁻¹K⁻¹, respectively. Limestone's low thermal conductivity plays a huge role in maintaining temperature drop as slow as possible. Limestone's excessive specific heat capacity and low thermal conductivity allow it to absorb a high amount of heat during the temperature rise step and release it at a slower rate during the cooling temperature drop step [18].
Figure 4. Estimated changes of temperature of CON4 and HEM4 inside the furnace during the oxidation processes.

The forgoing analysis highlights the individual effect of the holding time (t) on the purity of hematite in the resulting powder or the degree of oxidation (O). As given by equation (3), the dimensionless mathematical model has been formulated to establish a logical relationship. A summary of the experimental degree of oxidation (O_E), predicted degree of oxidation (O_P) from DDOPM calculation, % relative error, and logarithmic value of (X) for HEM1, HEM2, and HEM 4 are given in table 5.

From equation 4, a graph of log X vs. log O_E was fitted using Fit Linear Regression Model from MatLab, fitlm. It was found that the linear correlation coefficient of adjustment is 0.959. Conforming to the linearization shown in figure 5, The values of the characteristic constant of A and \( \phi \) are found to be 0.0257 and 0.0128, respectively. Therefore, the DDOPM equation is:

\[
O = 0.0128(X)^{0.0257}
\]

which gives the value of the predicted degree of oxidation (O_P) as listed in table 5. An infinitesimal relative error shows that the DDOPM calculation successfully predicted the hematite purity in the resulting powder. It should be emphasized that this DDOPM equation, shown in equation (7), can only be used to predict hematite purity based on the variation of time. Further experiment with the more varied variable is required to obtain the individual characteristic constant if other variable relationships will be further measured.

Table 5. Process condition for oxidation of mill scale.

| Sample | log (X)  | O_P   | O_E   | % Relative Error |
|--------|---------|-------|-------|------------------|
| HEM1   | 150.3283| 93.4646| 93.382| 0.088%           |
| HEM2   | 150.6293| 95.1445| 95.487| -0.360%          |
| HEM4   | 150.9303| 96.8545| 96.769| -0.088%          |
Figure 5. Linear relationship of the logarithmic value of dimensionless degree of oxidation log[O] vs. log[X] to obtain characteristic constant.

The Fe$_2$O$_3$ purity shows a power-law relationship with time, as indicated in figure 6. This graph is computed by MatLab curve fit of the 'power order-1'. It shows that the increase rate of Fe$_2$O$_3$ purity tends to decelerate after 4 hours of holding time as the gradient of the graph tend to flatten. This imply that the roasting process with holding time above 4 hours is unnecessary and not effectively convert into targeted Fe$_2$O$_3$ phase. Other consideration is the discharge energy and time wasted for the furnace to run up to 14 hours.

Figure 6. Power-law relationship of Fe$_2$O$_3$ purity based on DDOPM calculation vs. time.

5. Conclusion

The Dimensionless Degree of Oxidation Prediction Model (DDOPM) has been obtained using the Buckingham Pi theorem. The characteristic constant derived from this model can be used to predict
Fe$_2$O$_3$ purity relationship with time as selected parameters. The dimensionless model for analyzing the degree of oxidation has been established with $R^2 = 0.959$ and characteristic constant of $\phi = 0.0128$ and $A = 0.0257$. $O$ configures the degree of oxidation, and the influencing parameters process are configured by $X$. A relationship between the experimental degree of oxidation ($O_e$) and predicted degree of oxidation ($O_p$) is in close agreement with % relative error less than 0.36%. The XRF analysis results show that the addition of limestone pellets as heat storage media in the proposed experimental design significantly increases the Fe$_2$O$_3$ purity in the resulting powder.

References

[1] Legodi M A and de Waal D 2007 Dyes Pigm. 74 161–8
[2] Bagatini M C, Zymla V, Osorio E and Vilela A C F 2011 ISIJ Int. 51 1072–9
[3] Nurjaman F, Prilitasari N M, Prasetyo A E and Nugroho E 2019 Maj. Metall. 34 37–48
[4] Zulhan Z 2013 Maj. Metall. 28 105–20
[5] Cornell R and Schwertmann U 2003 The Iron Oxides: Structures, Properties, Reaction, Occurences and Uses (John Wiley & Sons, Ltd)
[6] Zheng X and Li J 2014 Ion. 20 1651–63
[7] Teja A S and Koh P Y 2009 Prog. Cryst. Growth Charact. Mater. 55 22–45
[8] Ismail H, Zaki M, Hussein G and Magar M 1990 Powder Technol. 63 87–96
[9] Ismail H M, Cadenhead D and Zaki M I 1996 J. Colloid Interface Sci. 183 320–8
[10] Bailey J K, Brinker C and Mecartney M L 1993 J. Colloid Interface Sci. 157 1–13
[11] Itoh H and Sugimoto T 2003 J. Colloid Interface Sci. 265 283–95
[12] Jikar P, Sabban R, Tadwalkar C and Dhokey N 2020 Mater. Today : Proc. 44 4013–19
[13] Dhokey N and Jikar P 2020 J. Sustain. Metall. 6 622–30
[14] Wu T and Lei C 2016 Energy Build. 116 198–208
[15] Khare S, Dell’Amico M, Knight C and McGarry S 2013 Sol. Energy Mater. Sol. Cells 115 114-22
[16] Dinker A, Agarwal M and Agarwal G 2017 J. Energy Inst. 90 1–11
[17] Harold W 1953 Thermodynamic Properties of Molecular Oxygen (National Bureau of Standards Report)
[18] Khosa A A, Xu T, Xia B, Yan J and Zhao C 2019 Sol. Energy 193 618–36
[19] Mori K, Okada T, Takagi Y, Takada Y and Mizoguchi T 1999 Jpn. J. Appl. Phys. 38 189–91
[20] Monazam E R, Breault R W and Siriwardane R V 2014 Ind. Eng. Chem. Res. 53 13320–8

Acknowledgments

This work was supported by the Lembaga Ilmu Pengetahuan Indonesia (LIPI), Indonesia. The authors would also like to thank the Research Center for Physics of LIPI for allowing the use of their excellent testing equipment.

Authorship contribution statement

M T Aldiramadan: Methodology, Formal analysis, Investigation, Validation, Visualization, Writing - original draft. J Nabilah: Formal analysis, Investigation, Validation, Writing - original draft. M Ridwan: Validation, Supervision. D S Khaerudini: Conceptualization, Methodology, Formal analysis, Investigation, Supervision, Writing - review & editing, Funding acquisition.
Appendix A. Derivation of Process Parameter (X) with Buckingham Pi Theorem

Total Number of Variable: 20
Total number of Fundamental Dimensions: 4
Π Terms Required: 20 – 4 = 16

\[ X = f(\Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5, \Pi_6, \Pi_7, \Pi_8, \Pi_9, \Pi_{10}, \Pi_{11}, \Pi_{12}, \Pi_{13}, \Pi_{14}, \Pi_{15}, \Pi_{16}) \]  

(A.1)

Repeating Variables
1] Heating Rate (T_R) [M^0L^0T^{-1}θ^1]
2] Specific Surface Area of Mill Scale Powder (S_M) [M^{-1}L^2T^0θ^0]
3] Viscosity of Oxygen (η) [M^{-1}L^1T^{-1}θ^0]
4] Thermal Conductivity of Calcite (κ) [M^{-1}L^{-3}T^{-1}θ^1]

1. Π_1 Term Calculation
Non-repeating variable: holding temperature (T) [M^0L^0T^0θ^1]

\[ \Pi_1 = T_R^a S_M^b η^c κ^d T \]

\[ [M^0L^0T^0θ^0] = [M^0L^0T^{-1}θ^1]^a[M^{-1}L^2T^0θ^0]^b[M^{-1}L^1T^{-1}θ^0]^c[M^{-1}L^1T^{-3}θ^{-1}]^d[M^0L^0T^0θ^0] \]

For M : - b + c + d = 0
For L : 2b – c + d = 0
For T : - a – c – 3d + 1 = 0
For θ : a – d = 0

a = 0; b = -2; c = -3; d = 1

\[ \Pi_1 = \frac{κ T}{S_M^2 η^2} \]  

(A.2)

2. Π_2 Term Calculation
Non-repeating variable: holding time (t) [M^0L^0T^1θ^0]

\[ \Pi_2 = T_R^a S_M^b η^c κ^d t \]

\[ [M^0L^0T^0θ^0] = [M^0L^1T^1θ^0]^a[M^{-1}L^2T^0θ^0]^b[M^{-1}L^1T^{-1}θ^0]^c[M^{-1}L^{-3}T^3θ^{-1}]^d[M^0L^0T^0θ^0] \]

For M : - b + c + d = 0
For L : 2b – c + d = 0
For T : - a – c – 3d + 1 = 0
For θ : a – d = 0

a = 1; b = -2; c = -3; d = 1

\[ \Pi_2 = \frac{T_R κ t}{S_M^2 η^3} \]  

(A.3)

3. Π_3 Term Calculation
Non-repeating variable: Length of the tube (L_T) [M^0L^1T^0θ^0]

\[ \Pi_3 = T_R^a S_M^b η^c κ^d L_T \]

\[ [M^0L^0T^0θ^0] = [M^0L^1T^1θ^0]^a[M^{-1}L^2T^0θ^0]^b[M^{-1}L^1T^{-1}θ^0]^c[M^{-1}L^{-3}T^3θ^{-1}]^d[M^0L^0T^0θ^0] \]

For M : - b + c + d = 0
For L : 2b – c + d + 1 = 0
For T : - a – c – 3d = 0
For θ : a – d = 0

a = 1; b = -3; c = -4; d = 1

\[ \Pi_3 = \frac{T_R κ L_T}{S_M^3 η^4} \]  

(A.4)
4. Π₄ Term Calculation

Non-repeating variable: Diameter of the tube (D_t) \([M^0L^1T^0θ^0]\)
\[ Π₄ = T_r^k S_m^b η^c D_t \]
\[ [M^0L^1T^0θ^0] = [M^0L^1T^1θ^1][M^1L^1T^0θ^0][M^1L^1T^1θ^1][M^1L^1T^1θ^0][M^1L^0T^0θ^0] \]

For M : \(-b + c + d = 0\)
For L : \(2b - c + d + 1 = 0\)
For T : \(-a - c - 3d = 0\)
For θ : \(a - d = 0\)
a = 1; b = -3; c = -4; d = 1
\[ Π₄ = \frac{T_r k D_t}{S_m^3 η^4} \] (A.5)

5. Π₅ Term Calculation

Non-repeating variable: Crucible Volume (V) \([M^0L^3T^0θ^0]\)
\[ Π₅ = T_r^k S_m^b η^c d V \]
\[ [M^0L^3T^0θ^0] = [M^0L^1T^0θ^0][M^1L^2T^0θ^0][M^1L^1T^1θ^0][M^1L^1T^3θ^0][M^0L^1T^0θ^0] \]

For M : \(-b + c + d = 0\)
For L : \(2b - c + d + 3 = 0\)
For T : \(-a - c - 3d = 0\)
For θ : \(a - d = 0\)
a = 3; b = -9; c = -12; d = 3
\[ Π₅ = \frac{T_r^2 k^3 V}{S_m^5 η^{12}} \] (A.6)

6. Π₆ Term Calculation

Non-repeating variable: weight of mill scale (W_M) \([M^1L^0T^0θ^0]\)
\[ Π₆ = T_r^k S_m^b η^c d W_M \]
\[ [M^1L^0T^0θ^0] = [M^0L^0T^0θ^0][M^1L^1T^0θ^0][M^1L^1T^1θ^0][M^1L^1T^3θ^0][M^1L^0T^0θ^0] \]

For M : \(-b + c + d + 1 = 0\)
For L : \(2b - c + d = 0\)
For T : \(-a - c - 3d = 0\)
For θ : \(a - d = 0\)
a = 2; b = -5; c = -8; d = 2
\[ Π₆ = \frac{T_r^2 k^2 W_M}{S_m^5 η^8} \] (A.7)

7. Π₇ Term Calculation

Non-repeating variable: apparent density of mill scale (ρ_M) \([M^1L^{-3}T^0θ^0]\)
\[ Π₇ = T_r^k S_m^b η^c d ρ_M \]
\[ [M^1L^0T^0θ^0] = [M^0L^0T^1θ^1][M^1L^2T^0θ^0][M^1L^1T^1θ^0][M^1L^1T^3θ^0][M^1L^3T^0θ^0] \]

For M : \(-b + c + d + 1 = 0\)
For L : \(2b - c + d - 3 = 0\)
For T : \(-a - c - 3d = 0\)
For θ : \(a - d = 0\)
a = -1; b = 4; c = 4; d = -1
\[ Π₇ = \frac{S_m^4 η^4 ρ_M}{T_r k} \] (A.8)
8. $\Pi_8$ Term Calculation
Non-repeating variable: Mill Scale Particle Size ($d_m$) [$M^0L^1T^0$]
$$\Pi_8 = T_R^6S_M^5\eta^4\kappa^4d_M$$
$$[M^0L^0T^0] = [M^0L^1T^0]^0[M^1L^2T^1]^{a}[M^1L^3T^1]^{b}[M^1L^3T^{-1}]^{c}[M^0L^1T^0]$$
For $M$ : 
- $b + c + d = 0$
- $2b - c + d + 1 = 0$
For $L$ : 
- $a - c - 3d = 0$
For $\theta$ : 
- $a - d = 0$
- $a = 1; b = -3; c = -4; d = 1$
$$\Pi_8 = \frac{T_R^6\kappa d_M}{S_M^3\eta^4} \tag{A.9}$$

9. $\Pi_9$ Term Calculation
Non-repeating variable: Oxygen purity ($P_O$) [$M^0L^0T^0$]
$$\Pi_9 = T_R^6S_M^5\eta^4\kappa^4P_O$$
$$[M^0L^0T^0] = [M^0L^1T^0]^0[M^1L^2T^1]^{a}[M^1L^3T^1]^{b}[M^1L^3T^{-1}]^{c}[M^0L^0T^0]$$
For $M$ : 
- $b + c + d = 0$
- $2b - c + d = 0$
For $L$ : 
- $a - c - 3d = 0$
For $\theta$ : 
- $a - d = 0$
- $a = 0; b = 0; c = 0; d = 0$
$$\Pi_9 = P_O \tag{A.10}$$

10. $\Pi_{10}$ Term Calculation
Non-repeating variable: Density of oxygen ($\rho_O$) [$M^1L^{-3}T^0$]
$$\Pi_{10} = T_R^6S_M^5\eta^4\kappa^4\rho_O$$
$$[M^0L^0T^0] = [M^0L^1T^0]^0[M^1L^2T^1]^{a}[M^1L^3T^1]^{b}[M^1L^3T^{-1}]^{c}[M^1L^3T^0]$$
For $M$ : 
- $b + c + d + 1 = 0$
- $2b - c + d - 3 = 0$
For $L$ : 
- $a - c - 3d = 0$
For $\theta$ : 
- $a - d = 0$
- $a = -1; b = 4; c = 4; d = -1$
$$\Pi_{10} = \frac{S_M^4\eta^4\rho_O}{T_R^6\kappa} \tag{A.11}$$

11. $\Pi_{11}$ Term Calculation
Non-repeating variable: Weight of Calcite ($W_C$) [$M^1L^0T^0$]
$$\Pi_{11} = T_R^6S_M^5\eta^4\kappa^4W_C$$
$$[M^0L^0T^0] = [M^0L^1T^0]^0[M^1L^2T^1]^{a}[M^1L^3T^1]^{b}[M^1L^3T^{-1}]^{c}[M^1L^3T^0]$$
For $M$ : 
- $b + c + d + 1 = 0$
- $2b - c + d = 0$
For $L$ : 
- $a - c - 3d = 0$
For $\theta$ : 
- $a - d = 0$
- $a = 2; b = -5; c = -8; d = 2$
$$\Pi_{11} = \frac{T_R^6\kappa^2W_C}{S_M^5\eta^8} \tag{A.12}$$
12. **Π₁₂ Term Calculation**

Non-repeating variable: Calcite Pellet Diameter (Dc) \([M^0L^1T^0θ^0]\)

\[
Π_{12} = \frac{T_RκD_c}{S_M^3θ^4}
\]

13. **Π₁₃ Term Calculation**

Non-repeating variable: Surface Area of Calcite Pellet (S_C) \([M^1L^2T^0θ^0]\)

\[
Π_{13} = \frac{S_C}{S_M}
\]

14. **Π₁₄ Term Calculation**

Non-repeating variable: apparent density of calcite (ρ_C) \([M^1L^3T^0θ^0]\)

\[
Π_{14} = \frac{S_M^3θ^4ρ_C}{T_Rκ}
\]

15. **Π₁₅ Term Calculation**

Non-repeating variable: Specific Heat Capacity of Calcite (C_P) \([M^0L^2T^2θ^{-1}]\)

\[
Π_{15} = \frac{θ^C_P}{κ}
\]
16. $\Pi_{16}$ Term Calculation

Non-repeating variable: Equilibrium Pressure of Calcite Decomposition ($P_C$) [$M^1L^{-1}T^{-2}\theta^0$]

$$\Pi_{16} = T_R^a S_M^b \eta^c \kappa^d P_C$$

$$[M^1L^{0}T^{0}\theta^0] = [M^1L^{-1}T^{-1}\theta^0]^a [M^1L^2T^0\theta^0]^b [M^1L^{-1}T^{-1}\theta^0]^c [M^1L^1T^{-3}\theta^{-1}]^d [M^1L^{-1}T^{-2}\theta^0]$$

For $M$ : \(-b + c + d + 1 = 0\)
For $L$ : \(2b - c + d - 1 = 0\)
For $T$ : \(-a - c - 3d - 2 = 0\)
For $\theta$ : \(a - d = 0\)

$$a = -1; b = 2; c = 2; d = -1$$

$$X = \frac{\kappa T}{S_M^2 \eta^3} \times \frac{T_R \kappa t}{S_M^3 \eta^4} \times \frac{T_R \kappa L_T}{S_M^3 \eta^4} \times \frac{T_R \kappa D_T}{S_M^3 \eta^4} \times \frac{T_R^2 \kappa^2 V}{S_M^3 \eta^5} \times \frac{T_R^2 \kappa^2 W_M}{S_M^3 \eta^8} \times \frac{S_M^4 \eta^3 \rho_M}{T_R \kappa} \times \frac{T_R \kappa d_M}{S_M^3 \eta^4} \times P_D$$

(A.17)

$$X = \left[ \frac{T_R^3 \kappa^0 T t L_T D_T V W_M P_M d_M P_D \rho_D W_C D_C S_C \rho_C C_P P_C}{S_M^{22} \eta^{35}} \right]$$

(A.18)
Appendix B. Calculation of Process Parameter

Process Parameter X is defined by,

$$X = \frac{T_R^8 k^8 T t L_T D_T V W_M \rho_M d_M P_0 \rho_0 W_C D_C S_C \rho_C C_P C_L}{S_M^3 \eta^{35}}$$  

(B.1)

This equation is solved using constant values of parameters listed in table B.1.

**Table B.1.** Experimental constant values used to solve Process Parameter (X).

| No | Variables                              | Symbol | SI Unit | Value               |
|----|----------------------------------------|--------|---------|---------------------|
| 1  | Holding Temperature                    | T      | K       | 1173                |
| 2  | Holding time                           | t      | s       | Varied              |
| 3  | Heating rate                           | T_R    | Ks⁻¹    | 0.0833              |
| 4  | Length of the tube                     | L_T    | m       | 1.0                 |
| 5  | Diameter of the tube                   | D_T    | m       | 0.055               |
| 6  | Crucible volume                        | V      | m³      | 3.287 × 10⁻⁵        |
| 7  | Weight of mill scale                   | W_M    | Kg      | 0.02                |
| 8  | Apparent density of mill scale         | ρ_M    | Kgm⁻³   | 5106.7              |
| 9  | Mill scale particle size               | d_M    | m       | 3.70 × 10⁻⁵         |
| 10 | Specific surface area of mill scale powder | S_Mistraight | m²Kg⁻¹ | 0.2                 |
| 11 | Oxygen purity                          | P_O    | Function of T [17] |
| 12 | Density of oxygen                      | ρ_O    | Kgm⁻³   | Function of T [17] |
| 13 | Viscosity of oxygen                    | η       | Kgm⁻¹s⁻¹| Function of T [17] |
| 14 | Weight of limestone                    | W_C    | Kg      | 0.012               |
| 15 | Limestone pellet diameter              | D_C    | m       | 0.02                |
| 16 | Surface area of limestone pellet       | S_C    | m²Kg⁻¹  | 0.44                |
| 17 | Apparent density of limestone          | ρ_C    | Kgm⁻³   | 2580                |
| 18 | Specific heat capacity of limestone    | C_P    | J Kg⁻¹K⁻¹| 238.564            |
| 19 | Thermal conductivity                   | κ      | Wm⁻¹K⁻¹| 0.086               |
| 20 | Equilibrium pressure of limestone decomposition | P_C    | Pa      | Function of T [18] |

Oxygen density (ρ) as a function of temperature is defined by

$$\rho(T) = 397.65 T^{-1.003}$$  

(B.2)

with R-squared value of 1. Equation (B.2) is obtained by curve fitting the data of dimensionless density of molecular Oxygen (ρ/ρ₀) at 1 atm with the range of temperature from 100 K to 2300 K [17]. The tabulated value was converted to the desired unit (Kg/m³) by multiply the dimensionless density with 1.42904.

η as a function of temperature is defined by

$$\eta(T) = 4 \times 10^{-7} T^{0.7071}$$  

(B.3)
with R-squared value of 0.9964. Equation (B.3) is obtained by curve fitting the data of dimensionless coefficient of molecular oxygen viscosity ($\eta/\eta_0$) from 100 K to 2000 K [17]. The tabulated value was converted to the desired unit (Kg/ms) by multiply the dimensionless viscosity with $1.9191944 \times 10^{-5}$.

$P_C$ as a function of temperature is defined by

$$P_C(T) = 101325 \times \exp \left(17.74 - 0.00108 T + 0.332 \ln T - \frac{22020}{T}\right)$$

(B.4)

Equation above defines as equilibrium pressure when Limestone undergo a decomposition process and it was calculated by Azhar et al [18].