Intra–Particle Water Migration Dynamics during Iron Ore Granulation Process

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The influence of iron ore properties, such as ore type, mineralogical texture, and particle size, on the intra-particle water migration dynamics were evaluated using immersion method. When immersed, ores reached 68–78% of their final saturation in first 60 s and then approached final saturation slowly. It typically took up to $1 \times 10^5$ s to reach final saturation. Compared with the initial and final saturation water contents of 2.8–4.0 mass% in the case of Brazilian ores, Australian ores showed higher water contents of 5–6.4 mass% due to more porous structure. While the final saturation water content was partially explained by the porosity and total pore volume of ores, the kinetics of water migration should be considered to explain the saturation curve of different ores. In terms of mineralogical texture, porous texture showed higher final saturation water contents than dense texture. Finer particles showed higher final saturation water contents than coarser particles.

A revised migration model was introduced to explain the effect of pore size distribution and trapped air. It was revealed that water migration proceeds more readily in the finer pores due to the larger capillary force, which is needed to overcome the trapped air. The water migration in the coarser pores is restrained due to the weak capillary force against trapped air, resulting in lower degree of saturation at equilibrium. Compared with Australian ores, Brazilian ores showed a lower degree of saturation due to their higher proportion of coarse pores.

KEY WORDS: intra-particle water migration; degree of saturation; absorption; iron ore; capillary force; pore size distribution; trapped air.

1. Introduction

The quality of iron ore has changed considerably in recent years. Hence understanding of iron ore characteristics turns to be an urgent matter for steel makers worldwide to maintain their stable and highly productive operations. Changes in quality, such as rising gangues and fine particles in iron ore, can not only directly influence the sintering performance, but also lead to an increase in reducing agent ratio in blast furnace operations. In the sintering process, iron ore fines are first granulated with addition of water to make ideal quasi-particles for securing the permeability of the sintering bed. Water, as a binder, is needed for effective granulation, however excess water does not favor the energy consumption as additional energy is required to drive it off during sintering. The amount of water required for effective granulation strongly depends on the iron ore properties, such as porosity, specific surface area, and wettability. Therefore, change in ore quality should be evaluated in order to decide an appropriate amount of water for effective granulation.

Khosa et al.1) developed a prediction model for the optimum granulation moisture from the ore chemical composition, such as LOI (loss on ignition), $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, and size distribution, which are practically measured in actual operations. The LOI and size distribution of ores are good indicators of pore volume and particle surface area potentially available for water during granulation. Meanwhile, Matsumura et al.2) studied the effect of open pore volume on the amount of saturation moisture which is believed to affect the optimum granulation moisture. They concluded that the difference between the optimum and saturation moisture contents increased as the open pore volume of ores increased because more pores remained unsaturation due to relatively slow intra-particle water migration. It could take up to 100 min for some ores to reach saturation, indicating that water migration kinetics should be considered. The above studies have clearly shown that the optimum granulation water content was strongly influenced by the water migration kinetics. However, most of the past researches focused mainly on the estimation of the optimum granulation water content based on the physical and chemical characteristics of ores.

During iron ore granulation, water first infiltrates through
ore particles under the influence of capillary force to reach the surface and then migrates further into ore particles. Therefore water transportation should be evaluated separately in two dynamical phases, namely inter-particle infiltration and intra-particle migration. As water gradually migrates into ore particles, more water is needed to ensure sufficient moisture available on the surface to adhere fine particles. The migration behavior of water through porous particles has been studied by various methods, such as absorption method, centrifugal method, and so on. Iveson et al. further developed a closed pore model to represent the migration phenomena of water into iron ore particles qualitatively. In their model, Iveson et al. considered an average pore diameter to simplify pore structure and assumed one side absorption. In addition, they have used large ore particles of around 30 mm in diameter, which are considerably larger than the sinter feed. The aim of this paper is hence to explain the intra-particle water migration behavior with considering the porosity, pore size distribution and mineralogical characteristics of typical ores used in sintering. In addition, the dynamics of water migration into particles was discussed in detail.

2. Experimental Method

2.1. Raw Materials

Four iron ores were studied, covering from porous Australian sinter fines (Ores A and B) to micro-porous to dense Brazilian sinter fines (Ores C and D). Table 1 and Fig. 1 show the chemical composition and representative photomicrograph of ores in the present study, respectively.

<table>
<thead>
<tr>
<th>Ore Samples</th>
<th>T. Fe</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>LOI</th>
<th>MPS (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore A</td>
<td>57.6</td>
<td>5.7</td>
<td>1.5</td>
<td>10.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Ore B</td>
<td>61.5</td>
<td>3.7</td>
<td>2.3</td>
<td>5.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Ore C</td>
<td>62.5</td>
<td>6.5</td>
<td>1.3</td>
<td>1.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Ore D</td>
<td>64.0</td>
<td>3.4</td>
<td>1.9</td>
<td>1.9</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Ore A displayed typical characteristics of a pisolithic Channel Iron Deposit Ore type dominated with earthy and vitreous goethite (vG), followed by small amounts of hydrohematite, quartz and goethitic shale. It contained a high LOI content and hence less Fe grade. Ore B was a blended ore consisting of mixed Marra Mamba and Brockman Banded Iron Formation Ore types. Therefore it had a moderate LOI content and consequently a moderate Fe grade. As it was a blended ore, this Ore was texturally quite complicated and variable with notable proportions of many different ore groups, including moderately dense to dense hematite/martite particles, combined hematite/martite (more often martite dominated) particles with goethite infill, and goethite dominated particles. Compared with Ores A and B, Brazilian ores (Ores C and D) consisted predominantly of dense to moderately dense hematite particles. Hence Ores C and D had measured a lower LOI value and consequently a better Fe grade. Hematite particles in Ore C (specular hematite) were dense and present as interlocking anhedral crystals or as coarse aligned tabular plates. Relic kenomagnetite was also observed in Ore C within some dense hematite particles or as small discrete grains. In contrast, hematite particles in Ore D (microplaty hematite) were more micro-porous and present as fine, interlocking microplates. Similar to Australian ores, martite particles were also observed in both Brazilian sinter fines but in less proportion.

Typical textural groups according to the classification suggested in past research were identified, collected and quantified from the −4.75+2.8 mm size fraction of Ores A and C. The washed ore particles were classified into proper textural groups manually with a petrological microscope and based on their appearance, hardness, magnetic and other physical properties. The particles of the same textural groups were subjected to further characterisation to evaluate the effect of ore texture on intra-particle water migration.

2.2. Measurement of Intra–particle Water Migration Behavior

The ore samples were screened to five size fractions, +4.75, −4.75+2.8, −2.8+2.0, −2.0+1.0 and −1 mm. During the granulation process, the ore particles of over 1 mm are generally believed to act as nucleus particles. For this reason, the three size fractions of over 1 mm were selected in the present paper. The sized particles were then washed thoroughly to remove the adhering fines that will potentially interfere the measurement of intra-particle water migration. The washed particles of −4.75+2.8, −2.8+2.0 and −2.0+1.0 mm were dried at 105°C for 24 hours and sealed in plastic bags for subsequent tests.

An immersion test was performed by soaking the oven dried, washed particles into a water bath at a depth of 20 mm. The immersion time was changed from 10 to 6×10⁵ seconds. After being immersed for a specific time t, the soaked particles were removed from the water bath and gently wiped using towel papers to remove free dripping water present on the surface until the shiny appearance almost diminished. The wiped sample was then weighed prior to and after being dried at 105°C for 24 hours. The sample’s capacity to absorb and hold water at time t, w(t), is defined in Eq. (1).
2.3. Characterisation of Pore Structure

Intra-particle water migration is considered to occur in pores due to the capillary force. Therefore the pore structure of the nucleus particles is expected to affect the water migration dynamics while the porosity or pore volume of the nucleus particles determines the final water holding capacity. Helium displacement test was performed on a test portion of 12 to 15 g ore particles of −4.75 +2.8 mm by a gas pycnometer (Micromeritics, AccuPycII 1340) to measure the envelope density, \( \rho_e \). The measured skeletal density still includes the closed pores present in the substance and is therefore expected to be slightly smaller than the true density. The same sample was later subjected to a powder displacement test in a geo-pycnometer (Micromeritics, GeoPyc 1360) to measure the envelope density (\( \rho_g \)). As the dryflo\textsuperscript{o} powder used is very fine and readily flows, it is possible to evaluate the particle volume accurately. The total porosity, \( \varepsilon \), can therefore be calculated by Eq. (2).

\[
\varepsilon = 1 - \frac{\rho_g}{\rho_s} \quad \text{.................................. (2)}
\]

Where \( \varepsilon \), \( \rho_g \), and \( \rho_s \) are the total porosity (−), envelope density (kg/m\(^3\)), and skeletal density (kg/m\(^3\)), respectively.

Duplicate measurements with a fresh set of test portion were carried out and the average value was used for the analysis. In order to evaluate the pore size, mercury intrusion test was also carried out on a test portion of 2 to 3 g ore particles of −4.75 +2.8 mm by a mercury porosimeter (Micromeritics AutoPore IV 9500). The size distribution and total volume of open and partially closed pores were hence derived. Table 2 shows the measurement results of the pore structure. The median pore diameter was defined as the pore size which corresponds to a cumulative pore volume of 50%.

Two theoretical water holding capacity values, \( w_{15} \) and \( w_{25} \) (mass%), were calculated to confirm which pore structure parameters are related better to the water immersion test results. \( w_{15} \) was calculated from helium and envelope pycnometers by Eq. (3) while \( w_{25} \) was calculated from the mercury intrusion method by Eq. (4).

\[
w_{15} = \frac{V_{unit} \cdot \varepsilon \cdot \rho_w}{V_{unit} \cdot \rho_u + V_{unit} \cdot \varepsilon \cdot \rho_e} \cdot 100 = \frac{\varepsilon \cdot \rho_w}{\rho_u + \varepsilon \cdot \rho_e} \cdot 100 \quad \text{........................ (3)}
\]

\[
w_{25} = \frac{\rho_u \sum_i v_{tpi}}{W_{unit} + \rho_u \sum_i v_{tpi}} \cdot 100 \quad \text{........................ (4)}
\]

Where \( \rho_u \) is the density of water (kg/m\(^3\)), \( V_{tpi} \) is the incremental volume per unit kilogram of sample intruded by mercury at step \( i \) (m\(^3\)/kg), \( V_{unit} \) is the unit volume; 1 (m\(^3\)), \( W_{unit} \) is the unit weight; 1 (kg).

3. Results

3.1. Influence of Ore Type on Intra-particle Water Migration

Figure 2 shows the time dependence of water content retained by the −4.75 +2.8 mm particles of four ores. All the ores appeared to show similar behavior but achieve different water contents of final saturation approximately at 1×10\(^5\) seconds. Figure 2(b) was plotted in the time range of 600 seconds to show in detail the early stage dynamics. As soon as the particles were immersed, they started to absorb water rapidly and reached about 68 to 78% of final saturation in less than 60 seconds (Phase I), as shown in Fig. 2(b). The water content then increased gradually in Phase II. Finally the water content leveled off at approximately 1×10\(^5\) seconds (Phase III), indicating that the ores might reach their final saturation points, as shown in Fig. 2(a). Two characteristic water contents can therefore be defined.

![Fig. 2. Change in the water content of ores with immersion time. (a) immersion time up to 10\(^5\) s, (b) immersion time up to 600 s (particle size: −4.75 +2.8 mm).](image)

<table>
<thead>
<tr>
<th>Ore samples</th>
<th>Helium/powder displacement methods</th>
<th>Mercury porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Skeletal Density (kg/m(^3))</td>
<td>Envelope Density (kg/m(^3))</td>
</tr>
<tr>
<td>A</td>
<td>−4.75 +2.8</td>
<td>3 790</td>
</tr>
<tr>
<td>B</td>
<td>−4.75 +2.8</td>
<td>4 300</td>
</tr>
<tr>
<td>C</td>
<td>−4.75 +2.8</td>
<td>4 620</td>
</tr>
<tr>
<td>D</td>
<td>−4.75 +2.8</td>
<td>4 910</td>
</tr>
</tbody>
</table>

\[
w_i = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100 \quad \text{.................................. (1)}
\]

Where \( w_i \) is the water content absorbed and held by the sample at time \( t \) (mass%), \( t \) is the immersion time (s), \( W_{wet} \) is the weight of the wiped sample after being immersed in the water for time \( t \) (g), \( W_{dry} \) is the weight of the sample after being oven dried (g).

Duplicate measurements, each involving a test portion of 50 g, were performed to ensure the repeatability. The average values of the duplicate tests are discussed in the paper.
in Fig. 2, initial (60 seconds) and final saturation ($1 \times 10^5$ seconds). Ores took longer than expected time to achieve final saturation. Therefore they are likely only partially saturated at the end of granulation given the residence time of a sinter mixture in the granulation drum.

Clearly, ores from the same origin showed similar characteristic water contents. As shown in Table 2, Australian ores were generally more porous than Brazilian ores as evidenced by the total pore volume measured by mercury porosimetry. The pores in Australian ores were also finer than Brazilian ores as evidenced by the median pore diameter. This generally agrees with the mineralogical abundance of texture groups observed in Fig. 1. Therefore Australian ores can absorb and hold more water than Brazilian ores, which also agrees well with industrial experience.

As shown in Fig. 2, the initial and final saturation water contents of Australian ores were approximately 5.0 and 6.4 mass%, respectively, considerably higher compared to 2.8 and 4.0 mass% for the Brazilian ores. As the final saturation water content measures the amount of water present in the pores, it is reasonable to assume that the final saturation water content is related to the total accessible pore volume. Therefore the final saturation water content was plotted against the water holding capacity values calculated based on Eqs. (3) and (4) in Fig. 3. Overall the experimentally measured final saturation water content showed a good agreement with the calculated water holding capacity values except for Ore C. While Ore C had a total pore volume and porosity similar to Ore A, and was considerably more porous than Ore D, it measured a final saturation water content lower than Ores A and D. This implies that the final saturation water content is affected not only by the total pore volume but also the pore structure and mineralogical characteristics.

While overall good agreement was observed, the final saturation water contents were generally lower than those calculated, suggesting that the ore particles have unfilled pores even at the immersion time of $1 \times 10^5$ seconds. Therefore the intra-particle water migration dynamics needs to be considered.

The volume ratio of pore occupied by water to the total pore volume measured by mercury porosimetry was further defined as the degree of saturation, $X (%)$, in Eq. (5).

$$ X = \frac{W_{net} - W_{dry}}{\rho_w W_{dry} \sum V_i} \times 100 \quad \text{............... (5)} $$

**Figure 4(a)** shows the degree of saturation for different ores ($-4.75+2.8$ mm) as a function of immersion time. Figure 4(b) was plotted in the time range of 600 seconds. Ores showed a similar degree of saturation versus time profile which shifted vertically depending on the ore type. For example, Ores A, B, C and D achieved 75, 66, 41 and 64% saturation, respectively, at 60 seconds and 99, 86, 61 and 88% saturation, respectively, at $1 \times 10^5$ seconds. Ore C showed a quite lower degree of saturation. At the final saturation point, most of the pores in Ore A are filled with water, while about 12, 14 and 39% of the pores are still unfilled in case of Ores D, B and C, respectively.

The difference in the degree of saturation in Fig. 4 was believed to be due to the nature of ore types. **Figure 5** shows the cumulative curve of pore volume and diameter (0.003–100 μm) acquired by mercury porosimetry. Ore A showed a large proportion of pores with their diameter under 0.1 μm. Ore B had less portion of pores in the size range of under 0.1 μm compared to Ore A. In contrast, Ore C showed coarse pore size distribution among ores, a majority portion of pores over 10 μm. Ore D showed the pore distribution which was slightly coarser than Ore B and finer than Ore C.

### 3.2. Influence of Mineralogical Texture on Intra-particle Water Migration

**Table 3** shows the dominance and measured porosity
of typical texture groups present in Ores A and C. Ore A contained mainly porous vG dominated particles, followed by dense vG, and G+HH (goethite with hydrohematite) particles. In the conventional classification,7) the particles dominant with hydrohematite were often classified as - the dense hematite or martite or hydrohematite group. In this study, however, hydrohematite typically co-existed with goethite. Therefore, the goethite particles containing 10 vol% or more hydrohematite were classified as an independent group - G+HH. In contrast, Ore C contained mainly microplaty hematite or martite (mH/M), followed by martite infilled with goethite (M+G), goethite with hydrohematite (G+HH), porous vG, goethite infilled with martite (G+M) and dense vG. The skeletal densities were 5 214, 4 837 and 3 925–3 949 kg/m3, for mH/M, M+G and dense to porous vG, with their particle porosities approximately at 6, 18 and 8–19%, respectively. The measurements agree well with the values reported in the past research8) showing the density and porosity were 4.7–4.9 g/cm3 and 5–7% for martite-microplaty hematite, 4.0–4.3 g/cm3 and 21–27% for martite-goethite, 3.3–3.8 g/cm3 and 13–30% for vG. It is expected that the skeletal density of G+M was smaller than M+G because the G+M group is more goethitic and therefore porous compared with the M+G group. Therefore, it can be said that the present classification scheme is capable of differentiating textural groups with distinct physical properties. 

Figure 6(a) shows the final saturation water content measured for the −4.75+2.8 mm particles of different texture groups. Porous vG showed the highest water content of 6.9 mass%, considerably greater than dense vG. The final saturation water content of mH/M was the lowest at 1.6 mass%. As expected, G+M, G+HH and M+G showed an intermediate final saturation water content between 6.4–4.9 mass%. G+M and G+HH showed a higher final saturation water content than M+G. Figure 6(b) compares the final saturation water contents measured and calculated from individual textural groups. The calculated final saturation water content was consistent with and slightly lower than the measured one for both ores. This difference between the measured and calculated values can be explained by the contribution of minor texture groups uncounted. 

Figure 7 shows the contribution of individual textural groups to the final saturation water content measured. for Ore A, followed by dense vG and goethite with hydrohematite. In the case of Ore C, on the other hand, each texture group seemed to contribute to the final saturation water content evenly. 

Figure 8 shows the relationship between the final saturation water content and porosity. Goethite dominated textural groups appeared to show a higher final saturation water content than hematite groups even at similar porosity. This may be explained by the difference in pore structure and hydrophilic properties between the goethite and hematite dominant texture groups.9,10) The difference in the final saturation water content between Australian and Brazilian ores in spite of similar porosity may be originated from their unique pore structure and texture dominance.

| Table 3. Dominance and measured porosity of typical texture groups present in Ores A and C. |
|-------|-------|-------|-------|-------|-------|
| No.  | Type  | Ore A | Ore C | Skeletal Envelope | Porosity | Final saturation water content |
| 2    | mH/M  | –     | 33.6  | 5 214 | 4 880 | 0.06 | 1.6 |
| 3    | M+G   | –     | 22.3  | 4 837 | 3 979 | 0.18 | 4.9 |
| 4    | G+M   | –     | 8.4   | 4 468 | 3 355 | 0.25 | 6.4 |
| 5    | G+HH  | 13.3  | 11.2  | 4 098 | 3 413 | 0.17 | 5.4 |
| 10a  | vG (dense) | 22.3  | 4.8   | 3 925 | 3 594 | 0.08 | 3.9 |
| 10b  | vG (porous) | 59.1  | 9.3   | 3 949 | 3 182 | 0.19 | 6.9 |

mH: microplaty hematite, M: Martite, G: Goethite, HH: Hydrohematite
vG: vitreous goethite
3.3. Influence of Particle Size on Intra-particle Water Migration

Figure 9 shows the changes in water content of different sizes from Ores A and C. The water content appeared to increase as the particle size decreased. As a result, the initial and final saturation water contents tended to increase as the ore particles became finer. However the effect of particle size was likely more profound on the initial saturation. The difference in the final saturation water content between different size fractions of the same ore type was considerably smaller than those observed for the initial saturation. This may suggest that the coarse ore particles experienced quicker water migration kinetics during the later stage of saturation. The effect of particle size also depended on the ore type of interest.

4. Intra-particle Water Migration Modelling

4.1. Conventional Intra-particle Water Migration Models

The intra-particle water migration kinetics is believed to be driven by capillary force and therefore will depend on the contact angle and capillary radius according to Lucas-Washburn (LW) equation.\(^{11,12}\) In the conventional migration model, a single capillary tube dipped in the water with an open end was used to describe intra-particle water migration, the water level is expected to rise or decrease along the tube. The speed at which water travels in the capillary tube, migration kinetics, can be expressed in Eqs. (6) and (7).

\[
\frac{dV}{dt} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \eta L} \quad \text{.................. (6)}
\]

\[
\Delta P = \frac{2 \gamma \cos \theta}{R} - \rho g L \quad \text{.................. (7)}
\]

Where

- \(V\): Flow volume (m³),
- \(L\): Capillary rise (m),
- \(R\): Capillary radius (m),
- \(\Delta P\): Pressure difference across the meniscus (Pa),
- \(\gamma\): Surface tension of liquid (N/m),
- \(\eta\): Viscosity of liquid (Pa·s),
- \(\theta\): Contact angle (°),
- \(g\): Acceleration of gravity (m/s²)

According to the conventional model, water migration speed (\(dV/dt\)) is a function of \(\Delta P\), \(L\) and \(R\) resulting from the capillary force and gravity. \(\Delta P\) decreases as \(L\) increases. Furthermore, \(dV/dt\) is in an inverse proportion to \(L\). Consequently, water migration becomes slower as capillary rises. This explains the trend shown in Fig. 2(a). In terms of the effect of \(R\), \(\Delta P\) is in an inverse proportion to \(R\), indicating that \(\Delta P\) is higher when pores are finer. However, \(dV/dt\) is a function of \(R^4\). Overall, water migration proceeds quickly in coarse pores, however does slowly in fine pores.\(^{13}\) The effect of pore radius on water migration is evidenced in the simplified LW equation below in Eq. (8) where capillary rise shows a positive relationship with capillary radius.\(^{13}\)

\[
L = \sqrt{\frac{R \gamma \cos \theta}{2 \eta} t} \quad \text{.................. (8)}
\]

As to contact angle, \(\theta\) is included in the \(\Delta P\) equation, indicating that water migration proceeds quickly in the case of good wetting materials. Assuming that ores of the same origin have a similar contact angle, Ores A and D are hence expected to show slower migration kinetics than their counterparts of the same origin according to LW equation due to their relatively smaller median pore size of 37 and 498
nm. However, no remarkable difference in migration speed and degree of saturation could be observed in Figs. 2 and 4(b). Therefore, it is not sufficient to use the median pore diameter to represent the pore structure of different size distributions. The pore size distribution should be appropriately considered to reflect the actual ore properties.

As discussed earlier, conventional model failed to address the pore size distribution and back pressure resulting from the trapped air. Obuchi et al.\(^{14}\) found that liquid migration was deterred due to the cancellation of capillary force by the back pressure from the trapped gas. Iveson et al.\(^{15}\) suggested that the intra-particle water migration kinetics could be explained by a closed pore model which includes trapped air counteracting the capillary force. According to this model, water migration proceeded rapidly until the pressure balance was established. Iveson’s model. However, their work involved a packed layer of iron ore fines, which is quite different from intra-particle migration. In addition, the previous researchers have not yet considered the actual pore size distribution of the ore particles. Consequently, new models are needed to consider both the pore size distribution and the effect of trapped air.

### 4.2. Revised Intra-particle Water Migration Model

Figure 10 shows a schematic diagram of the revised water migration model, which considers the pore size distribution, trapped air and surface location of pore openings. However, pores were treated as being isolated and closed at one end, with different radii. \(A_U\) and \(A_B\) are the top and bottom surfaces of ore particles where the total pressures act on. The position where the total pressure acts on the pores located on the side surfaces is not shown in this diagram, but varies with the immersion depth of the pores of interest. Assuming that the ore particles are cubic, the pressure difference across the meniscus \(\Delta P_y\) for the pores located on the upper, side and bottom surfaces are defined in Eq. (9).

\[
\Delta P_y = \frac{2\gamma \cos \theta}{R_y} + \rho \cdot g \cdot L_y - P_{\text{inside,}i,U} + P_{w,i,U} + P_{\text{air}} \quad \text{... (9)}
\]

Where \(P_{\text{inside,}i,j}\): Inner pressure of trapped air in Pore \(i\) located on Surface \(j\) (Pa), \(P_{\text{air}}\): Atmospheric pressure (Pa), \(P_{w,i,j}\): Hydraulic pressure in Pore \(i\) located on Surface \(j\) (Pa)

The suffix of \(i\) denotes any individual pore of a particular size (\(i = 1, 2... n\)) while \(j\) refers to the surface location of an individual pore (\(j = \text{Upper, Side, Bottom}\)).

Clearly the capillary force acts as the driving force of water migration together with the hydraulic pressure and atmospheric pressure irrespective of the pore location while the inner pressure of trapped air acts as a counter force. However the gravity force can act as either the driving or counter force depending on the pore location. For any individual pore \(i\), the inner pressure of trapped air, \(P_{\text{inside,}i}\), can be expressed by the water volume migrated \(V_{i,j}\) (m\(^3\)) and initial pore volume \(V_{p(i,j)}\) (m\(^3\)) in Eq. (10), assuming that there is negligible change in the temperature of trapped gas during the process.

\[
P_{\text{inside,}i,j} = P_{\text{air}} \frac{V_{p(i,j)} - V_{i,j}}{V_{p(i,j)}} \quad \text{... (10)}
\]

Assuming an even distribution of pores across the surfaces of the cubic ore particle, the volume of Pore \(i\) at each surface \(j\), \(V_{(p)i,j}\), is defined by Eq. (11).

\[
V_{(p)i} = V_{\text{particle}} \rho \cdot V_{(p)i,j} \quad V_{(p)i} = V_{(p)i,U} = \frac{1}{6} V_{(p)i} \quad \text{... (11)}
\]

Where \(V_{\text{particle}}\) is the average envelope volume of the ore particles (m\(^3\)). The total pore volume of Pore \(i\), \(V_{(p)i}\), was calculated from \(V_{(p)i}\) measured by mercury intrusion.

At this point, the effect of trapped air was assumed to act only on the pores located at the bottom and on the side surfaces because the trapped air is thought to escape easily upwards due to the buoyancy force for the pores opened on the upper surface. Considering a case where contact angle is 60° and capillary radius is 50 μm, the maximum capillary rise was calculated to be around 15 cm, considerably larger than the average particle diameter used in this study, indicating that the gravity force can be ignored. On the other hand, assuming a capillary rise at the average particle radius and a contact angle of 60°, the critical capillary radius, above which ore particles cannot hold the water against gravity, was calculated to be around 4 mm, which is larger than the average diameter of ore particles used in this study. Therefore it is reasonable to ignore the gravity effect. Moreover, the hydraulic pressure of water, \(P_{w,i,j}\), was set around 200 Pa in this study, which is approximately
0.2% of the atmospheric pressure (100 kPa). Hence it was not considered in the calculation. Therefore, Eq. (9) can be rewritten into Eq. (12).

\[
\Delta P_{li} = \frac{2\gamma \cos \theta}{R_{li}} + P_{air}
\]

\[
\Delta P_{ij} = \frac{2\gamma \cos \theta}{R_{ij}} - P_{air} \frac{V_{(p)j}}{V_{(p)j} - V_{ij}} + P_{air}, \ (j = \text{Side, Bottom})
\]

\[\text{(12)}\]

The degree of saturation, \(X_{ij}\) for Pore \(i\), \(j\), is defined in Eq. (13).

\[X_{ij} = \frac{V_{ij}}{V_{(p)j}} \\\n\text{(13)}\]

The degree of saturation, \(X\), is then calculated by summing \(X_{ij}\) across the size range of pores located on different surfaces.

\[X = \frac{\sum (V_{(p)i} X_{i} / 100)}{\sum V_{(p)i}} \times 100 \text{ (14a)}
\]

\[X = \frac{\sum V_{(p)i} X_{i} / 100}{\sum V_{(p)i}} \times 100 \text{ (14b)}
\]

\[\text{(14)}\]

Compared to the conventional model shown in Eqs. (6) and (7), the revised model considered the inner pressure of trapped air, pore size distribution and surface location. Intra-particle water migration can start at any accessible pores on any surfaces. Pores located on the upper surface showed a constant driving force during migration, likely leading to a final saturation. However, for the pores located on the side and bottom surfaces, \(\Delta P_{ij}\) decreased as the water volume migrated \((V_{ij})\) increased due to the increasing effect of trapped air, consequently, leading to a lower water migration speed \((dV/dt)\). In term of the effect of contact angle, the new model predicted the same trend as the conventional model because the terms newly introduced in the revised model does not affect the parameters relating to contact angle. Similarly the revised model predicts the same trend as the conventional model when it comes to capillary radius.

When the inner pressure \((P_{\text{inside},i})\) reaches the sum of capillary force \((2\gamma \cos \theta / R)\) and atmospheric pressure \((P_{air})\), \(\Delta P_{ij}\) become zero, suggesting that the water migration reaches equilibrium. \(\text{Lv et al.}^{[9]}\) mentioned that the steady state was achieved after actual flow velocity became zero. In order to explain the difference in migration kinetics in Phase I between the ores as shown in Fig. 4(b), the degree of saturation at equilibrium was calculated from Eqs. (12) and (13). In the case of the pores located at the upper side, it is assumed that water completely fills these pores, and achieves a 100% saturation. In terms of the pores located at the side and bottom surfaces, zero value was given to \(\Delta P_{S}\) and \(\Delta P_{B}\) in Eq. (12). The degrees of saturation at equilibrium were shown in Eq. (15).

\[X_{i} = \begin{cases} 1 & (j = S) \\ \frac{2\gamma \cos \theta}{R_{ij}} + 2\gamma \cos \theta & (j = B) \end{cases} \]

\[\text{(15)}\]

**Figure 11** shows the calculated degree of equilibrium saturation for different size pores present in the ores based on Eqs. 14(a) and 15. Contact angles of 45° and 60°, reported in previous work,\(^{[9,10]}\) were used for Australian and Brazilian ores, respectively. The pore size distribution of the Ores shown in Fig. 5 was used in the calculation. Finer pores showed higher degrees of saturation at equilibrium due to their stronger capillary force. For the pores of over 20 \(\mu m\), they reached only 20% saturation. The influence of contact angle on the degree of saturation at equilibrium does not seem to be as severe as that of the pore size distribution. However, good wetting likely contributes to a slightly higher degree of equilibrium saturation.

**Figure 12** shows the comparison of the pore volume intruded by mercury and water at equilibrium calculated based on the pore size distribution in Figs. 5 and 11 for Ore C. The calculated water intrusion volume at equilibrium was very close to the pore volume when the pore diameter is below 0.1 \(\mu m\) as finer pores displayed a higher degree of saturation at equilibrium. However, the difference between the pore volume and water intrusion volume increased with the pore diameter when the pore diameter is over 1 \(\mu m\). The degree of saturation at equilibrium was calculated by the area ratio of water intrusion volume (shown as gray color) to pore volume. Ore A had the highest calculated degree of saturation at equilibrium, 80%, as it contained the largest proportion of finer pores, especially less than
0.1 μm, followed by 72 and 65% in the case of Ores B and D, respectively. Ore C showed a lowest value of 49% due to large amount of coarse pores around 10 μm.

Overall compared with the conventional migration model, the revised model predicted a higher degree of saturation at equilibrium for finer pores and a lower degree of saturation for coarse pores due to the effect of trapped air. In contrast, as mentioned earlier, the coarse pores showed a quicker migration speed \( \frac{dV}{dt} \) and higher flow volume \( V \) than the finer pores based on the conventional model. Therefore the new model gave an opposite trend for the equilibrium flow volume. Figure 13 shows a schematic illustration of time dependence of flow volume based on the new migration model. Two curves represent the cases of coarse and fine pores, respectively. While \( \frac{dV}{dt} \) is higher for coarser pores compared with finer pores, the coarse pores show a lower \( V \) at equilibrium. Therefore, the coarse pores achieve equilibrium at time \( t_c \) earlier than \( t_f \) for the fine pores.

Figure 14 shows the comparison of the experimental degrees of saturation at the immersion time of 60, 3 000 and \( 1 \times 10^5 \) seconds and calculated degree of saturation at equilibrium based on Eq. 14(b). The revised model is well capable of predicting the degree of saturation at 3 000 seconds in Phase II.

4.3. Intra-particle Water Migration Mechanism

Based on abovementioned discussion, the intra-particle water migration behavior observed in Figs. 2 and 4 was summarized below:

(i) From 0 to 60 seconds in Phase I, water starts to migrate into all the pores, coarse and fine, opened on the surface. As the coarse pores gives a quicker migration speed, the inner pressure of trapped air in the coarse pores increases rapidly as water migration proceeds, resulting in an earlier local equilibrium with a lower degree of saturation. As a result, this time regime includes \( t_c \), the time when the coarse pores reach equilibrium in Fig. 13. Fine pores, on the other hand, continue to take water under the influence of the capillary force and inner pressure of trapped air, indicating that the degree of saturation increased steadily. Therefore, Ores A and D showed higher degrees of saturation than Ores B and C within 60 seconds in Fig. 4(b). However, Ores A and D had less pore volume than their counterparts even though they showed higher degrees of saturation. Overall, they achieved similar flow volumes to their counterparts as shown in Fig. 2(b).

(ii) At the immersion time of 60 seconds, as water migration continues with the available pores, the counter effect of trapped air increases. This explains why the water migration kinetics slowed down considerably after 60 seconds in Figs. 2(b) and 4(b).

(iii) From 60 to 3 000 seconds in Phase II, water continued to migrate moderately into the available pores in the presence of trapped air. Like Step (i), water migration kinetics observed in Figs. 2 and 4 is interpreted to be the process where local equilibrium is established gradually from coarse pores to fine pores.

(iv) At the immersion time of 3 000 seconds, all available fine pores are completely filled with water in the presence of trapped air. Water migration reaches overall equilibrium. This period is assigned to \( t_f \) in Fig. 13, the moment when the finer pores reach their equilibrium, resulting in overall equilibrium.

(v) From 3 000 to \( 1 \times 10^5 \) seconds in Phase II, water continues to migrate into the ore particles. This process cannot be explained only by LW equation. As reported in the past research,\(^6\) the trapped air gradually dissolves into the water, and then are diffused and released to air through nucleation of air bubbles. Therefore, in this time regime in Figs. 2 and 4, water migration takes place due to air dissolution and nucleation. As air dissolution speed is dependent predominantly on the concentration of dissolved air and temperature, instead of the pore structure. Therefore, water migration kinetics in this time regime showed similar trend for the ores.

(vi) After the immersion time of \( 1 \times 10^5 \) seconds in Phase III, the open pores are fully filled with water. This is the reason why water saturation levelled off afterwards in Figs. 2 and 4. The required time for fully filling into pores depends on ore types.

In conclusion, the overall water migration kinetics into coarse ore particles is explained by two competing phenomena: capillary force and trapped air. As migration proceeds, the effect of trapped increases and must be considered. This is why conventional migration model doesn’t match the experimental results.
5. Interpretation of Experimental Results for Actual Granulation Operation

In the granulation process, water absorbed and held inside the nucleus particles rarely contributes to granulation. As reported before, it is known that the optimum water content required to achieve the same granulated particle size increased when ores were pre-wet. The ore particles used in this study were initially dried to avoid any possible interference of raw material conditions. In the practical granulation process, on the other hand, almost all iron ores are wet as waters are given due to unavoidable reasons such as handling requirement, nature conditions and environmental issues for preventing dust emissions during storage and transport before granulation. Ores will almost certainly absorb and lose water during storage. Therefore, the amount of water which iron ores have already absorbed varies depending on the situation. In addition, contact angle was referred to past research in this study. Wetting behavior on the surface, however, is dependent on wetting history and hysteresis. Therefore, the influence of pre-wetting on intra-particle water migration kinetics is hence needed to be studied further.

As shown in Fig. 2, nucleus particles need prolonged time to achieve final saturation. However the residence time of ore particles inside a drum during granulation is no more than several hundred seconds, which took place within Phase II in the case of dry material. Therefore the nucleus particles are not fully saturated in the granulation drum. As mentioned above, almost all the ores are naturally wet, based on the relationship shown in Fig. 4, which will reduce the time required to reach the final saturation water content. It is hence important to optimize the residence time of ore particles inside the drum to achieve the level of saturation required.

6. Conclusion

The influence of iron ore properties on the intra-particle water migration dynamics of iron ores was investigated. All ores appeared to show similar water content and time profiles which shifted vertically depending on the ore types. As soon as the particles were immersed in the water, they started to absorb water rapidly and reached about 68 to 78% of their final saturation in less than 60 seconds (Phase I). The water content then increased gradually in Phase II. Finally the water content started to level off at approximately 1\times10^5 seconds (Phase III). Australian ores showed higher final saturation water contents (5–6.4 mass%) than Brazilian ores (2.8–4.0 mass%). Iron ores having a high porosity or pore volume showed higher final saturation water contents than those with a low porosity or pore volume. In the light of mineralogical texture, porous textures showed a higher final saturation water content than dense textures. The final saturation water contents measured and calculated from individual textural groups for Ores A and C were consistent with and only slightly lower than the measured ones for both ores. Finer particles showed higher final saturation water contents than coarser particles.

While the pore structure generally showed good agreement with the measured final saturation water content, it was revealed that pores are not completely filled, indicating that the effect of trapped air should be considered. Moreover, water migration speed cannot be explained by the conventional model which has only used the median pore diameter to represent the pore structure. In order to better evaluate the water migration kinetics, a new water migration model was developed by considering both the pore size distribution and trapped air. The new model predicted a higher degree of saturation at equilibrium for finer ores, but a lower degree of saturation for coarse pores because of a weak capillary force to overcome the increasing inner pressure of trapped air. Compared with the ores containing a higher proportion of finer pores, ores having coarser pores showed a remarkably lower degree of saturation at equilibrium. Overall the intra-particle water migration kinetics was explained by the degree of saturation at equilibrium. Finally the intra-particle water migration mechanism was discussed in detail.

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