Measurement for Contact Angle of Iron Ore Particles and Water

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Contact angle, as a key index for the wettability of iron ore particles by water, is of very important for the iron ore processing like beneficiation, sintering and pelletizing. Methods developed for measuring the contact angles generally can be divided into direct and indirect methods, which were summarized in present study and their advantages and disadvantages are all compared. Capillary rise method may be the most applicable approach for porous particles. Most of the contact angles between iron ore particles with water reported in the literatures were collected and the influence of the physical and chemical properties of iron ore particles were analyzed. The result shows that iron ore particles are hydrophilic and its water contact angles are influenced by the complicate interaction of chemical compositions, especially the content of oxy-hydroxides and the surface morphology. Generally, the water contact angle of goethite is the smallest. Complicate surface morphology suggest a better wettability. Furthermore, the penetration behavior of natural iron ore particles and synthetic iron ore particles are obviously different during the contact angle measurement. Compared with sessile drop method, capillary rise methods are more suitable for the measurement of natural iron oxides. Some empirical equations to predict the contact angle were collected and compared. The wettability can be improved by increasing the surface morphology of particles, coating of iron ore particles, and high-temperature treatment.

KEY WORDS: wettability; contact angle; chemical composition; surface morphology; iron ore particles.

1. Introduction

Granulation1–4) process is a typical method getting iron ore particles together to form pellets/granules using water as the binder in steel making industry. A good granulation result can make a better permeability of the bed of granules in the sintering strand.5,6) With the decreasing of high grade iron ore, sinter preparation in the iron ore industry is routinely performed using a blend of different ores with low iron content which usually called low grade iron ores. However, there is little regard for how this may be affect the total Fe content which is first expressed by Young7) discovereding the granulation performance. Maeda et al.8) discovered that the use of some low grade iron ores in granulation may cause the fracture of sintered ores, which suggests the sintered ore has a low strength. Due to the above uncertain situation, this is particularly important for iron ore samples where significant differences in surface chemistry may be expected to be altered substantially granulation process. It is believed that the granule strength is largely determined by the wettability of iron ore particles, the surface characteristics and properties of binders.9)

Wettability9) is always characterized by contact angle which is a three phases angle (solid, liquid and gas) and was further studied by many authors. Not only in granulation process, but also in mineral processing fields such as wet grinding, flotation, etc.,11–17) contact angles of iron ore particles and water, as a classical parameter, is widely studied. Generally, it is believed that smaller contact angle suggests better wettability and easier to agglomerate. The reason is that water droplet spread smoothly on material surface with good wettability, and moderate water in granulation can increase the strength of the liquid bridges between particles.18–20) Agglomeration21–23) is a process of wetting particles and making them coalesced together. As the schematic illustration of agglomerate during granulation process shown in Fig. 1, first, water droplet is dripped on the surface of powder bed and begin to disperse. At the same time, penetration occurs and water contact inner particles through void of inter-particle. According to the distribution situations of water, it can be classified into pendular, funicular, capillary and droplet.24,25) When penetration time increases, water gradually filled into the space of inter-particles, while the states are transferred from pendular to droplet. Rumpf26) and Kapur et al.24) found that the strength of granules depends on the porosity of particles and connecting forces between particles. Among these forces, capillary force is conservative that act to pull particles together.27) Willet et al.28) numerically solved the full Laplace–Young
equation and then fitted empirical expressions to the results, as Eq. (1) shows.

\[
F = \frac{2\pi \alpha \gamma_{LV} \cos\theta}{1.0 + 2.1 \left( \frac{h^2a}{V} \right)^2 + 10.0 \left( \frac{h^2a}{V} \right)} \tag{1}
\]

Where \( \gamma_{LV} \) is the liquid surface tension, \( a \) is the radius of particle, \( h \) is the half distance between two vertical slices of particle surface, \( V \) is the bridge volume, \( \theta \) is contact angle and \( r \) is the curvature of the bridge surface, which can be calculated from the two principal radii of curvature of the surface, as shown in Fig. 2. It can be seen that the force turns out to be directly proportional to the contact angle of the system. Through this equation, the effect of water contact angle on granulation can be indirectly characterized.

However, for porous particles like natural iron ore particles, the liquid soaked into intra-granular pores influences its amount used in granulation process. It is helpful to improve granulation by optimizing proportioning of iron ore under the guidance of contact angle. Therefore, it is a vital issue that how to obtain accurate contact angle of iron ore particle.

According to various determinations for the contact angle of particles, the measurement methods for contact angle can be divided into two categories: the direct method and the indirect one. The direct measurement can be easily used for the contact angle of solid, but with a requirement of a rigid homogeneous smooth surface. And compared with the direct measurements, the latter methods are more generally used in contact angle measurements for particles, due to the great small size of particles cannot be convenient to measure with the direct one. As shown in Fig. 3, there are many measurement methods that have been developed for particles: sessile drop method, captive bubble technique, Wilhelmy plate, capillary rise method, and some other new measurements, all of the above are briefly described below.

Many previous works have been done to determine the contact angle of particles or powders, but there still has relatively few studies on the contact angle of iron ore particles. Most papers are based on synthetic iron ore particles and did not go deep into the relation between contact angles and properties of iron ore particles. Iveson et al. have done a series work on the contact angle of iron ore fines, include measure the value of advancing contact angle of 17 different iron ores. Huang et al. tested contact angles of 7 kinds of iron ore particles with water and proposed a new model for contact angle. Results of contact angles of natural porous iron ore particles and water is more significant to be evaluated for wettability of most iron ore particles and understanding granulation process. It should be understood that strict scientific contact angle is not suitable to get the overall knowledge of wettability for natural iron ore particles because some vital messages are not include, such as porosity, surface roughness and heterogeneity. In capillary rise methods, particle groups used are always porous and without uniform size, which properties is familiar with the materials used in granulators. Therefore, contact angles measured with these methods contain some surface properties of particles and can be used to improve granulation. In the paper of Mao et al., they have proved contact angles obtained by capillary rise methods are appropriate to evaluate granulation results and gave a binary linear regression equation.

The present review covers the various measurements of contact angle for particles, and some important basic theories were explained in detail. Materials and results of contact angle measurement for iron ore particles and water were collected and summarized. Also, influencing factors were discussed carefully and some useful suggestions were proposed.
2. Contact Angle

2.1. Equilibrium Contact Angle

Contact angles can be defined as equilibrium and dynamic contact angle. Droplet is always spherical as it is free from the effect of force field and only forced by the surface tension. But when it contacts with solid surface, the final shape of the droplet depends on the cohesion inside and the adhesive force between solid and liquid. In addition, droplet can spread out on solid surface and form an angle on the contact line between three phases: solid, liquid and gas, which is defined as the equilibrium contact angle. As shown in Fig. 4, the droplet on solid surface bears three forces, and an equilibrium contact angle emerged when the forces balance.

In 1805, Young\(^\text{10}\) proposed the famous equation to describe this situation, which is known as the Young’s equation:

\[
\gamma_{SG} \cos \theta_f = \gamma_{SL} - \gamma_{LS} \tag{2}
\]

Where \(\gamma_{SG} \) (N/m) is the solid-gas interfacial energy, \(\gamma_{LG} \) (N/m) is the liquid-gas interfacial energy, and \(\gamma_{LS} \) (N/m) is the liquid-solid interfacial energy, where interfacial energy has unit \( \text{mJ m}^{-2} \). But this equation is valid only when the solid surface is an ideal one which is rigid smooth, homogenous, inert, planar and non-deformable.\(^5\)

2.2. Dynamic Contact Angle

The surface of real solid is not as smooth and uniform as the ideal, so the interfacial energy of the surface in different position is inconstant. Hence, the contact angle isn’t a settled value suggest by the Young’s equation, but is a dynamic value between two relatively stable angles, which is called the contact angle hysteresis. The contact angle hysteresis is the embodiment of surface roughness and heterogeneity. As shown in Fig. 5, the advancing contact angle is a special angle formed when the gas-solid interface is replaced by the liquid-solid interface as the droplet is going to run at a gradient plate. While, on the other side of the droplet, the liquid-solid interface is replaced by the gas-solid interface. And the angle formed on the gas-liquid-solid contact line is the receding contact angle. The contact angle hysteresis can be calculated by the following equation:

\[
\Delta \theta = \theta_A - \theta_R \tag{3}
\]

Where \(\Delta \theta \) (degree) is the contact angle hysteresis, \(\theta_A\) (degree) is the advancing contact angle and \(\theta_R\) (degree) is the receding contact angle.

It is reported that the advancing contact angle is always larger than the receding contact angle. The swelling behavior and surface roughness make contribution to this phenomenon.\(^3\)

3. Contact Angle Measurement Methods for Particles

Contact angle measurement methods can be divided into two categories according to various methods proposed by literatures. One is called the direct methods and the other is the indirect methods.\(^3\)

3.1. Direct Methods

Generally, sessile drop method,\(^36,54,55\) captive bubble method,\(^38,56,57\) environmental scanning electron microscopy (ESEM) method\(^44,52,58,59\) and gel trapping method\(^45,47\) are direct methods. These methods obtain contact angles by observing the forming angles directly based on the theory of Young. The use of high speed CCD camera, scanning electron microscope (SEM), or Environment Scanning Electron Microscope (ESEM) makes it possible to observe contact angles from macroscopic to microscopic. Obviously, the direct methods have advantages of convenient operation and apparent results compared to indirect methods.

Sessile drop method is one of the most widely used direct techniques to measure the contact angle. Usually, the surface of materials is highly required smooth planar and non-porous so that it can obtain reliable results. For solid particles, the sessile drop method still can be applied when particles are compressed into compacts or tablets to form flat surface. In this way a high speed CCD camera is used to capture pictures of the compressed particle substrate and droplet on the compact/table. The schematic of the apparatus is shown in Fig. 6. The dynamic contact angle is produced by increasing/decreasing the volume of droplet by using a syringe. Pictures of equilibrium states or dynamic states are analyzed by image analysis software and then the static contact angle is obtained. There are some drawbacks exist in the traditional sessile drop method, and some measures have been proposed to improve this method.\(^33-35,53,60-63\) also, it was modified for finely particles.\(^32,44\)

3.2. Indirect Methods

For indirect methods, the core theories are the famous Washburn equation or some other mechanical equilibrium formulas (such as Wihelmy plate method\(^41\)), and contact...
angles can be obtained by calculating these equations. Compared with direct methods, indirect methods seem to more popular in contact angle measurements for particles. Among these indirect methods, capillary rise methods are broadly used for contact angle measurement of particles due to its appropriate for porous particles. The classical capillary rise method is the Washburn method proposed by Washburn in 1921. Based on the traditional one, varieties of alternative capillary rise methods have been developed to apply in particle contact angle measurements. Wei et al. have classified the capillary rise method as the height method, the pressure method, mass method, and other methods such as thin-layer wicking method and equilibrium height method. To apply the Washburn equation, the properties of liquid and flow are restricted as follows:

\[ h^2 = \frac{\gamma \cos \theta}{2 \mu} \frac{t}{r_{\text{eff}}} \]  

(1) Newtonian fluid (i.e., constant viscosity) acting as a continuum, (2) incompressible (i.e., constant density) laminar flow, (3) steady-flow situation (4) fully developed flow, and (5) no-slip (i.e., zero velocity of fluid at the fluid/capillary wall interface). (6) no external pressure and (7) negligible gravitational.

As the Washburn equation shows:

\[ h^2 = \frac{\gamma \cos \theta}{2 \eta} t \]  

Where \( h \) (m) is the height of liquid front, \( t \) (s) is the penetrating time, \( \gamma \) (N/m) is the surface tension of penetrating liquid, \( r_{\text{eff}} \) (m) is the effective capillary radius, \( \eta \) (Pa.s) is the viscosity of the wetting liquid. The contact angle can be calculated by curves of square of penetration height \( h^2 \) verses time \( t \).

As it’s shown in Fig. 7, the test particles are compressed in a tube which bottom is always covered by a film to bare the particles and allow the liquid penetrate. The liquid start penetrating when the tube bottom contacts liquid. The height of the liquid front is recorded and the relation of the square height and time obtained to calculate the contact angle using Eq. (4).

3.3. Summary of the Various Methods

Contact angle measurement methods were proposed and modified by many authors. In chronological order, Wilhelmy plate method appeared to be the earliest way to measure contact angle among these methods. The famous Washburn method was developed in 1921 for contact angle measurement of powders, and after that the pressure method was delivered. Both sessile drop method and captive bubble method were developed in 1930s, and extended by Zisman and co-workers in 1946. Diggins, Delker and Lago modified capillary rise methods based on equilibrium capillary height. Moreover, thin layer wicking method, the ESEM method, weight method and gel trapping technique were developed in recent years. The overview of the development time of each measurement method is shown in Fig. 8.

The advantages and disadvantages of these methods were summarized from literature and were shown in Table 1, including some modified ways.

4. Measurements of Contact Angle for Iron Ore Particles

Iron ore particles are natural particles that most are irregular and porous. It may be difficult to determine contact angles of natural iron ore particles due to the complicated surface morphology and pores inside particles. Various methods were used to determine contact angles between iron ore particles and some common reagents, but among these methods, capillary rise method and sessile drop method are widely used methods.

4.1. Sessile Drop Method

4.1.1. Materials

In this method, the test iron ore particles are most made in laboratory and some come from industrial raw materials. The main physical properties of iron ore particles that authors used are listed in Table 2.

Magnetite nanoparticles were synthesized by co-precipitation of Fe(II) and Fe(III). Hematite particles obtained by the mixture of FeCl₃ solution and NaOH solution are monosized cuboid, and Plaza R C et al. synthesized hematite particles by hydrolysis of Fe(III)-chloride solutions. Goethite and hematite that J Shang experimented were got following the way Schwertmann and Cornell proposed.

![Fig. 7. Left: The schematic diagram of Washburn method. Right: A typical curve of h² versus time.](image-url)

![Fig. 8. Research overview of the development time of measurement methods for contact angle.](image-url)
Table 1. Advantages and disadvantages of methods commonly used in particles.

| Method               | Sample          | Advantages                                | Disadvantages                                                                 | Modified ways                           |
|----------------------|-----------------|-------------------------------------------|-------------------------------------------------------------------------------|-----------------------------------------|
| Direct methods       |                 |                                           |                                                                               |                                         |
| Sessile drop         | compact/tablet  | Easy to conduct, apparent                 | Influenced by liquid diffusion, compacting ways                               | Use adhesive to prepare sample          |
| Single particle      | Precise for finely particles                  | Not suitable for porous non-spherical particles                                   | –                                           |
| Captive bubble       | Substrate made of particles                     | Convenient, and apparent                | Not suitable for water swelling particles, and influenced by distortion       | Accurately adjust the bubble size by pressure |
| ESEM                 | Single particle | No damage to materials and can be used in established temperature or humidity   | Not suitable for low contact angle and wettability                            | –                                           |
| Gel trapping         | Single particle | apparent                                  | Not suitable for porous non-spherical particles                                | –                                           |
| Indirect methods     |                 |                                           |                                                                               |                                         |
| Wilhelmy plate       | Plate           | a wide range of wettability               | Not suitable for water swelling particles, and influenced by compacting ways   | Use adhesive to prepare sample          |
| Washburn method      |                 | reproducible                               | The true liquid front is uncertain                                             | Use laboratory centrifuge to prepare particle bed |
| Weight method        | Column          | reproducible and good sensitivity         | Influenced by packing ways                                                    |                                         |
| Capillary rise method|                 |                                           |                                                                               |                                         |
| Wicking method       | Thin layer      | can be used for non spherical particles, and avoids the packing influence       | The true liquid front is uncertain and not usable for contact angles larger than 90° | –                                           |

Table 2. Main physical properties of particles.

| Author         | Particles         | Source   | Particle shape  | Size            |
|----------------|-------------------|----------|-----------------|-----------------|
| Potapova⁷⁹)   | Magnetite nanocrystals | Synthetic | Spherical           | 5–15 nm         |
| Costanzo⁸⁰)   | Monosized hematite | Synthetic | Cuboid           | About 2/3 in 1 μm |
| Plaza⁸¹)      | Hematite          | Synthetic | Approximately spherical | 60 ± 7; 520 ± 30 nm |
| Shang⁵¹)      | Goethite          | Synthetic | Acicular   | 1 814 ± 38 nm  |
|                | Hematite          |          | Spherical       | 146±1 nm        |
| Susana 1, 2⁵²) | Fe⁺              | Ores     | –               | 42.24 μm        |
|                | Fe²              |          | –               | 129.36 μm       |
| Javanbakht⁵³)  | Bare SPIONs      | –        | –               | 10.9 ± 0.2 nm   |
|                | Bare SPIONs (treated) | –         | –               | 12.5 ± 0.4 nm   |
|                | Negatively charged SPIONs | –         | –               | 11.8 ± 0.3 nm   |
|                | Negatively charged SPIONs (treated) | Synthetic | –               | 12.3 ± 0.3 nm   |
|                | Positively charged SPIONs | –         | –               | 12.2 ± 0.2 nm   |
|                | Positively charged SPIONs (treated) | –         | –               | 13.6 ± 0.2 nm   |
| Kulal⁵⁴)       | Fe₂O₃ (thin film) | Synthetic | –               | ≤1.2 μm (thickness) |
| Ratha⁸⁵)       | Hematite          | –        | –               | –               |
|                | Magnetite         | Ores     | –               | –               |
|                | Goethite          |          | –               | –               |
| Neto⁸⁶)        | S1                | Synthetic | Spherical       | 10.9 ± 3.5 nm   |
|                | S2                |          | –               | –               |
|                | S3                |          | –               | –               |
|                | S4                |          | –               | –               |
|                | S5                |          | –               | –               |
| MAEDA⁵)        | Reagent hematite  | –        | –               | –               |
|                | A                 |          | –               | –               |
|                | B                 |          | –               | –               |
|                | F                 |          | –               | –               |
|                | K                 |          | –               | –               |

1, 2: iron ores but they differ in terms of particle size distribution.
besides, particles used in the experimental work of Susana L are the raw materials used in the production of welding wires,87) and handpicked hematite, magnetite, and goethite samples used in the test of Ratha88) were obtained from different iron ore mines of Odisha, which iron oxide content varies between 97.5 and 99%. Nanoparticles were obtained by heating the mixture of FeCl2·4H2O and FeCl3·6H2O in diethylene glycol. Among the process, negatively charged SPIONs and positively charged SPIONs were obtained by a series of treatments. The treated SPIONs were taken directly from photo-initiated chemical vapor deposition (PICVD).89) The Fe2O3 thin films were prepared by Kulal,90) which were obtained by immersing a glass/stainless steel substrate in a FeSO4 solution and a NaOH solution, in turn. In the experiment of Neto,91) sample S1 is magnetic iron oxide, S2 is magnetic iron oxide coated with PDMS at 250°C for 8 cycles in soxhlet, S3 is magnetic iron oxide coated with PDMS at 250°C, 17 cycles in soxhlet, S4 is magnetic iron oxide coated with PDMS at 50°C for 8 cycles in soxhlet, S5 is magnetic iron oxide coated with PDMS at 50°C 17 cycles in soxhlet. Ores A, B and F are hematite iron ores, and ores J and K are limonite iron ores.7)

Surface morphology of iron ore particles are shown in Fig. 9, which were captured by SEM or TEM. It indicates that the particles synthesized in laboratory were granular and regular. The synthetic particles were always pre-processed before contact angle measurements, since sessile drop method required a continuous flat sample. The test iron ore particles were made into suspension and the suspension were withdrawn and equally distributed on a glass microscope slides which were held strictly horizontal. The slides covered with a suspension of particles were dry in air or a vacuum. This preparation method is mentioned at the second part, and it’s an alternative way to prepare samples for no harm to samples and can make uniform plats. But the natural ore particles used in the work of Susana L have not undergone any preparation or surface cleaning and were used ‘as received’.

4.1.2. Contact Angles

By use of a Gaertner (Chicago, IL) telemicroscope with an eyepiece goniometer, the advancing contact angles of monosized hematite were directly measured by Costanzo.84) Due to the particles are cuboid, the film made of particles are flat and shiny, as shown in Fig. 10. Contact angles were read within only a second or so after depositing the drops,
and for a-bromonaphthalene, diiodomethane, water, glycerol, formamide, ethylene glycol are $13.8 \pm 0.4^\circ$, $19.4 \pm 0.5^\circ$, $22.5 \pm 0.5^\circ$, $26.4 \pm 0.5^\circ$, $17.3 \pm 0.5^\circ$, $14.0 \pm 0.5^\circ$, respectively.

In the experiment of Shang, contact angles of goethite with diiodomethane, water and formamide are $19.4 \pm 0.4^\circ$, $22.8 \pm 1.8^\circ$ and $24.1 \pm 1.0^\circ$, respectively; for goethite, they are $25.0 \pm 0.8^\circ$, $46.9 \pm 2.3^\circ$ and $18.5 \pm 1.7^\circ$. As shown in Fig. 11, during the measurement, contact angles stay constant for hematite sample, which indicates that hematite particles formed a nonporous film with a periodical surface roughness. The different behavior of typical slip/stick patterns of the three liquid that in dynamic method can be explained by their different Bond numbers. Based on the result, they developed three types of mechanisms during contact angle measurements, which are swelling, non-swelling and porous and non-swelling, non-porous. Swelling films seal itself when in contact with polar liquid, but acid–base interactions can cause the drop shape to change with time. The non-swelling, porous films, as goethite, both acid-base interactions and imbibition can cause the drop shape changes. The hematite sample is a non-swelling, non- porous film (The hematite are non-porous because it was manmade), so the drop shape remains stable during the measurement.

Potapova et al. found an interesting phenomenon that contact angles are changed a lot after the treatment of calcium ions and it seems that calcium ions have a great influence on the contact angle of iron ore particles and water. Contact angles of water with magnetite of different treatments are slightly above $20^\circ$. It is reported that calcium ions can react with hydroxyls and release protons and adding positive charge to the surface. Interactions of metal–water are stronger than hydrogen bonding between the surface hydroxyls and water. The Gibbs energy increased as hydroxyl groups is substituted with calcium and the surface hydrophilicity increased with the result of the decreasing of contact angle. The silicate species could increase the amount of hydroxyl groups which caused the decrease of contact angle. The contact angle of water and the magnetite treated with maleic acid ester reached $44 \pm 3^\circ$ may be due to the formation of hemimicelles on the surface.

Javanbakht investigate the charge effect of bare, positively and negatively charged SPIONs (superparamagnetic iron oxide nanoparticles) on surface functionalization of the particles following treatment by PICVD (photo-initiated chemical vapour deposition). Contact angles of samples and deionized water are obtained as shown in Table 3. It can be concluded that both positively and negatively charged SPIONs take on a hydrophobic behaviour post-treatment.

Kulal observed that the $\text{Fe}_2\text{O}_3$ thin films are superhydrophilic. Figure 12 shows contact angle measurement of $\text{Fe}_2\text{O}_3$ thin films and the SEM micrographs of thin films, and through SEM picture, smooth, irregular shaped particles gather on the thin film surface can be observed. Results show that water contact angle is less than $10^\circ$. This may be due to the strong cohesive force between the water droplet and hydroxide present in the iron oxide compound.

Contact angle of the three minerals with sodium oleate solutions of different concentrations were measured by Rath and are shown in Table 4. Contact angles of magnetite are larger than others at any concentrations of oleate which indicates a worse wettability. According to their results, contact angles increased by increasing the concent-

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**Table 3.** Contact angle of deionized water and samples.

| Samples               | Untreated | Treated  |
|-----------------------|-----------|----------|
| Bare SPIONs           | $40^\circ \pm 9^\circ$ | $77^\circ \pm 14^\circ$ |
| Positively charged SPIONs | $58^\circ \pm 12^\circ$ | $100^\circ \pm 23^\circ$ |
| Negatively charged SPIONs | $47^\circ \pm 13^\circ$ | $97^\circ \pm 15^\circ$ |

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Fig. 10. Photograph of a microscope glass slide coated with a layer of hematite (arrow).

Fig. 11. Contact angles and drop diameters of test liquids as a function of time. Left: static method; right: dynamic method.

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The particles of magnetic iron oxide were synthesized by the coprecipitation method. The functionalization of the iron oxides was performed by coating surface with PDMS oil. S1 is magnetic iron oxide, S2 is magnetic iron oxide coated with PDMS at 250°C for 8 cycles in soxhlet, S3 is magnetic iron oxide coated with PDMS at 250°C for 17 cycles in soxhlet, S4 is magnetic iron oxide coated with PDMS at 50°C for 8 cycles in soxhlet and S5 is magnetic iron oxide coated with PDMS at 50°C 17 cycles in soxhlet.

Sample S1 showed hydrophilic behavior as the water droplet on the surface of sample S1 spreaded completely. However, the samples coated with PDMS showed hydrophobic behavior. Contact angles of each sample with water are measured by sessile drop method as shown in Fig. 13.

MAEDA discussed the effect of porosity on iron ores and concluded the relationship between surface roughness and contact angle of iron ore in detail in their paper. Contact angle of pure hematite with different porosity and surface roughness are shown in Table 5. The surface roughness of each sample was measured by the laser microscope. From the result, it indicates that the contact angles of the reagent hematite samples become small in the order of samples with 10%, 5%, 15% and 20% porosity. For the reason, they think it due to that the sample surface becomes impossible to hold droplet on the sample surface as the porosity becomes over 15%. Figures 14 and 15 show the relationships between contact angle and surface roughness of pure hematite and iron oxides. Both the result shows that contact angle became large as the surface roughens became large.

Susana not only measured contact angles but also obtained the experimental mean drop penetration time and the standard error of the mean for each powder varying liquid binder. As shown in Fig. 16, 85.7 wt.% potassium silicate solution penetrated in to particle bed. They think the infiltration of the fluids into powders interferes with the measurement of contact angle, because it is an unstable condition and not meet the thermodynamic definition of contact angle according to the theory of Young. There is not a general trend between the fluid rate penetration and the contact angle values for the powder–liquid systems they examined, but only for iron (Fe^2+), the larger the penetration velocity, the lower the contact angle.

![Fig. 12. Water contact angle of Fe_2O_3 thin films and SEM micrographs of Fe_2O_3 thin films at two different magnifications (a) x 5000 and (b) x 10000.](image)

![Fig. 13. Superficial wetness of samples S1 (A); S5 (B); S4 (C); S3 (D) and S2 (E).](image)

![Fig. 14. Relationship between contact angle at 0 min of retention time and surface roughness of pure hematite.](image)

![Fig. 15. Relationship between contact angles at 0 min of retention time and surface roughness of iron ores.](image)

![Table 4. Contact angle of hematite, magnetite and goethite with water.](table)

| Sample     | Oleate concentration (g/t) | 0  | 50  | 100 | 150 | 200 | 300 |
|------------|----------------------------|----|-----|-----|-----|-----|-----|
| Hematite   |                            |    |     |     |     |     |     |
|            | 32.67°                     | 60.89° | 70.79° | 80.69° | 83.66° | 87.13° |
| Magnetite  |                            |    |     |     |     |     |     |
|            | 34.16°                     | 62.38° | 75.74° | 83.66° | 90.10° | 91.58° |
| Goethite   |                            |    |     |     |     |     |     |
|            | 19.31°                     | 21.29° | 27.72° | 34.65° | 37.62° | 40.59° |

![Table 5. Contact angle at 0 min of retention time for pure hematite with different.](table)

| Porosity (%) | Surface roughness (µm) |
|--------------|------------------------|
| 3.2–3.5      | 3.6–5.5                |
| 3.3–4.7      | 2.6–3.9                |
| 1.4–1.7      |                        |
| 5            | 67.08° 74.58° 76.67° 72.92° 58.33° |
| 10           | 75.42° 83.75° 81.67° 80.42° 75.83° |
| 15           | 48.33° 71.25° 82.08° 68.75° 45.00° |
| 20           | 35.42° 65.58° 60.42° 68.75° 33.75° |
Fig. 16. Penetration of 85.7 wt.% potassium silicate solution on iron. The picture are taken at (a) after the impact on powder compact, (b) 0.02 s, (c) 0.10 s, (b) 0.20 s and (d) 0.30 s after the impact.87)

Table 6. The test liquid, iron ore particles and contact angles (°).

| Authors       | Materials          | A    | B    | C    | D    | E    | F    | G    | H    |
|---------------|--------------------|------|------|------|------|------|------|------|------|
| Costanzo      | Hematite           | 13.8±0.4 | 14.0±0.5 | 19.4±0.5 | 17.3±0.5 | –    | –    | 26.4±0.5 | 22.5±0.5 |
| Potapova      | Magnetite¹         | –    | –    | –    | –    | –    | –    | –    | 22±3  |
|               | Magnetite²         | –    | –    | –    | –    | –    | –    | –    | 19±2  |
|               | Magnetite³         | –    | –    | –    | –    | –    | –    | –    | ≤10   |
|               | Magnetite⁴         | –    | –    | –    | –    | –    | –    | –    | 44±3  |
| Plaza         | Hematite           | –    | –    | 17.1±0.5 | 30.7±1.0 | –    | –    | –    | 21.5±0.5 |
| Susana        | Fe⁷                | –    | –    | –    | –    | 87.50±0.77 | 83.00±1.13 | –    | –    |
|               | Fe⁶                | –    | –    | –    | –    | 85.15±1.62 | 80.70±2.89 | –    | –    |
| Shang         | Goethite           | –    | –    | 19.4±0.4 | 24.1±1.0 | –    | –    | –    | 22.8±1.8 |
|               | Hematite           | –    | –    | 25.0±0.8 | 18.5±1.7 | –    | –    | –    | 46.9±2.3 |
| Javanbakht    | Bare SPIONS        | –    | –    | –    | –    | –    | –    | –    | 40±9  |
|               | Positively charged SPIONS | –    | –    | –    | –    | –    | –    | –    | 58±12 |
|               | Negatively charged SPIONS | –    | –    | –    | –    | –    | –    | –    | 47±13 |
|               | Bare SPIONS*       | –    | –    | –    | –    | –    | –    | –    | 77±14 |
|               | Positively charged SPIONS* | –    | –    | –    | –    | –    | –    | –    | 100±23 |
|               | Negatively charged SPIONS* | –    | –    | –    | –    | –    | –    | –    | 97±15 |
| Kulal         | Fe₂O₃ thin films   | –    | –    | –    | –    | –    | –    | –    | <10   |
| Rath          | Hematite           | –    | –    | –    | –    | –    | –    | –    | 32.67 |
|               | Magnetite          | –    | –    | –    | –    | –    | –    | –    | 34.16 |
|               | Goethite           | –    | –    | –    | –    | –    | –    | –    | 19.31 |
| Neto          | S1                 | –    | –    | –    | –    | –    | –    | –    | 0     |
|               | S2                 | –    | –    | –    | –    | –    | –    | –    | 120.4 |
|               | S3                 | –    | –    | –    | –    | –    | –    | –    | 107.9 |
|               | S4                 | –    | –    | –    | –    | –    | –    | –    | 83.8  |
|               | S5                 | –    | –    | –    | –    | –    | –    | –    | 45.9  |
| MAEDA         | Pure hematite      | –    | –    | –    | –    | –    | –    | –    | 33.75–83.75 |
|               | A                  | –    | –    | –    | –    | –    | –    | –    | 80–93.89 |
|               | F                  | –    | –    | –    | –    | –    | –    | –    | 51.61–72.95 |
|               | K                  | –    | –    | –    | –    | –    | –    | –    | 61.35–71.30 |

A: a-bromonaphthalene
B: ethylene glycol
C: diiodomethane
D: formamide
E: 85.7 wt.% sodium silicate
F: 85.7 wt.% potassium silicate
G: glycerol
H: water
1: synthetic magnetite
2: synthetic magnetite after consequent conditioning with 4 mM CaCl₂
3: synthetic magnetite after consequent conditioning with 0.4 mM Na₂SiO₃
4: synthetic magnetite after consequent conditioning with 25 mg L⁻¹ maleic acid ester
5: Iron ore powders with a size of 42.24 μm.
6: Iron ore powders with a size of 129.36 μm.
*: they are particles following treatment by PICVD
4.2.1. Materials

Iron ore particles used in these methods are most commonly obtained from natural mines. The chemical composition and physical properties of used iron ore particles are shown in Table 6, and the properties of test liquids are given in Table 7.

4.2.2. Contact Angles

Contact angles of iron ore particles measured by sessile drop method that above-mentioned are shown in Table 6, and the properties of test liquids are given in Table 7.

Figure 17 shows contact angles of synthetic particles, ores and treated particles. From Table 6 and Fig. 17 it can be concluded that for a kind of iron ore particle the contact angle is not a fix value but varies in some influencing factors. Contact angles of synthetic hematite are less than 46.9°, and for synthetic magnetite and synthetic goethite which are less than 40° and about 22.8°. What’s more, there is not great difference in contact angles between synthetic particles and ore particles. But the contact angles of treated particles vary in a large interval relates to the treated method.

4.2. Capillary Rise Methods

Capillary rise methods, including Washburn method, the weight method, equilibrium height method, the pressure method and thin-layer wicking method, are fully developed and commonly used in the contact angle determination of particles. But in contact angle measurements, only Washburn method, the pressure method and thin-layer wicking method were used by some authors, wherein Iveson and Huang classified iron ores into two types which are partly due to the measuring technique and physical properties of natural particles.

Adsorption of flotation reagents makes effect on the wettability of magnetite concentrate. In their previous research, it can be concluded that sodium metasilicate could suppress the adsorption of the model collector on magnetite with the absence of calcium ions. Table 10 shows contact angle of magnetite concentrate upon modification of the surface with 1 mg g⁻¹ water glass and Atrac 1 563 in 10 mM NaCl and 4 mM CaCl₂ solution. It indicates that calcium ions contribute to the increasing of contact angle of magnetite concentrate by collector adsorption.

As Table 11 shows, water contact angle of the magnetite concentrate after flotated is decreased by increasing the concentration of water glass, and similar effect appeared in the addition of sodium polycrylate with the presence of calcium, as shown in Table 12. But, the wettability didn’t improved by increasing the concentration of sodium polycrylate at a constant level of calcium. Wettability of the flotated magnetite concentrate could be improved observably by prolonged treatment with water glass or rather short conditioning with sodium polycrylate.

Iveson et al. classified iron ores into two types which are oxides and oxy-hydroxides. In a sense, hematite is oxide for...
its main composition is Fe₂O₃ and goethite oxy-hydroxide for its primary is FeO(OH). Natural ores are consisted of complex mixtures of those oxides and oxy-hydroxides. Both Iveson and Zhang found there is a linear relationship between the density and percent hematite, as Fig. 19 shows, the ore density increased with the increasing of the content of hematite. The large uncertainties in their results are to be expected the follows: (1) the materials are with significant variation in both composition and morphology between individual particles in the batch; (2) There is also a difficulty in achieving uniform packing of the powders in the columns. These uncertainties may cause the results not accurate. But despite the large uncertainty in the contact angle data, the content of oxides and oxy-hydroxides has a

Table 8. Chemical composition and physical properties of iron ore particles.

| Author        | Sample | Chemical composition (mass%) | Size | \(S_{\text{BET}}\) (10³ m²/kg) | True density (10³ kg/m³) |
|---------------|--------|------------------------------|------|-------------------------------|--------------------------|
| Huang⁴⁸       |        | TFe  Fe₂O₃  CaO  SiO₂  Al₂O₃  MgO |      |                              |                          |
| S1            |       | 61.53  0.29  0.02  3.05  2.06  0.16 |      | 9.098                         | 4.32                     |
| S2            |       | 63.34  0.71  0.05  5.74  1.12  0.05 |      | 2.888                         | 4.9                      |
| S3            |       | 64.51  0.45  0.02  4.3   0.68  0.05 |      | 1.602                         | 4.96                     |
| S4            |       | 58.27  0.22  0.04  5.55  1.37  0.08 | ≤200 μm | 24.544                        | 3.93                     |
| S5            |       | 59.14  0.21  0.05  4.38  1.5   0.08 |      | 23.462                        | 4.08                     |
| S6            |       | 61.26  0.32  0.03  3.69  2.25  0.06 |      | 7.788                         | 4.58                     |
| S7            |       | 65.29  0.16  0.02  1.36  1.49  0.09 |      | 6.836                         | 4.49                     |
| Qiu⁹⁷         |        | Magnetite | 68.11  21.25  0.98  1.65  0.42  2.21 | ≤74 μm | 0.182                         | –                        |
| Akdemir⁹⁸     |        | Hematite | 67.82  –  –  –  –  –  –  –  –  –  – | 10–38 μm | –                             | –                        |
| Iveson⁴⁷      | A      | – – 3.2 – – – – – – – – – – – – – – – – | 134 μm | 4.06                          |                          |
|                 | B      | – – 3.4 – – – – – – – – – – – – – – – | 77 μm  | 4.58                          |                          |
|                 | C      | – – 0.6 – – – – – – – – – – – – – – – | 87 μm  | 5.29                          |                          |
| Shang⁵¹       | Goethite | – – – – – – – – – – – – – – – – – | 1814±38 nm | –                             | –                        |
| Susana⁸²      | Fe¹    | – – – – – – – – – – – – – – – – – | 42.24 μm | 7.684                         |                          |
|                 | Fe²    | – – – – – – – – – – – – – – – – – | 129.36 μm | 7.812                         |                          |
| Long⁹⁹⁰       | Vanadium–Titanium magnetite concentrate | 53.97  20.89  1.13  3.38  4.18  2.73 | ≤400 μm | –                             | –                        |
| Potapoya⁸⁸⁵   | Magnetite concentrate | – – – – – – – – – – – – – – – – – | 0.5 | –                             |                          |
| Liu⁹⁶³        | LIMS iron ore concentrates | 56.17  23.81  1.54  7.64  1.98  4.33 | 25–150 μm | 8.12                         | –                        |
| Kirchberg⁶⁷⁷   | Magnetite | 71.04  –  0.3  0.6  0.1  0.4 | ≤146 μm | –                             | –                        |

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vital influence on contact angles which as Fig. 20 shows. Contact angles increased by increasing hematite content or decreasing goethite content.\cite{48,49} They developed a fit function from the data:

\[
\theta = 45x + 8 
\]

Where \( \theta \) is the contact angle and \( x \) is the volume fraction of hematite.\cite{49}

From the results they obtained, there has a strong correlation between the hematite/goethite composition ratio and the contact angle. They think particle porosity and surface roughness are not the main strong influence on contact angle measurement, but no powerful evidence was provided.

Zhang et al.\cite{105} obtained a liner relationship between \( \text{LOI} \)
Fig. 21. Relationship between loss on ignition and weight loss ratio. 

\[
\text{Table 9. Reference liquids used in literature.}
\]

| Author     | Liquid            | Surface tension (mN/m) | Viscosity (mPa.s) |
|------------|-------------------|------------------------|-------------------|
| Huang      | Cyclohexane       | 25.0                   | 0.908             |
| Iveson     | N-heptane         | 21.0                   | 0.400             |
| Zhang      | Water             | 72.1                   | 1.002             |
| Long       | Hexane            | 17.9                   | 0.300             |
| Mao        | n-Hexane          | 18.43                  | 0.308             |

*: They determined the constant C used quartz powder and water for which contact angle is 0.

Table 10. Water contact angle of magnetite concentrate upon modification of the surface with 1 mg g\(^{-1}\) water glass and Atrac 1 563 in 10 mM NaCl and 4 mM CaCl\(_2\) solution at pH 9.

| Collector concentration (mg g\(^{-1}\)) | 0      | 0.04   | 0.08   |
|---------------------------------------|--------|--------|--------|
| 10 mM NaCl                            | 34 \(\pm\) 1\(^\circ\) | 28 \(\pm\) 4\(^\circ\) | 32 \(\pm\) 5\(^\circ\) |
| 4 mM CaCl\(_2\)                       | 40 \(\pm\) 3\(^\circ\) | 44 \(\pm\) 5\(^\circ\) | 58 \(\pm\) 1\(^\circ\) |

Table 11. Water contact angle of the magnetite concentrate upon modification of the surface with water glass in 10 mM NaCl at pH 9 for 9 h.

| Water glass concentration (mg g\(^{-1}\)) | 0      | 0.5    | 1      | 3      |
|-----------------------------------------|--------|--------|--------|--------|
| Contact angle (\(^\circ\))              | 57 \(\pm\) 5\(^\circ\) | 41 \(\pm\) 2\(^\circ\) | 35 \(\pm\) 1\(^\circ\) | 28 \(\pm\) 3\(^\circ\) |

Table 12. Water contact angle of the magnetite concentrate upon modification of the surface with 0.04 mg g\(^{-1}\) sodium polyacrylate at pH 9 for 1 h.

| CaCl\(_2\) concentration (mg g\(^{-1}\)) | 0      | 0.04   | 0.08   |
|----------------------------------------|--------|--------|--------|
| Contact angle (\(^\circ\))             | 55 \(\pm\) 1\(^\circ\) | 41 \(\pm\) 8\(^\circ\) | 25 \(\pm\) 11\(^\circ\) |

Fig. 20. Contact angle versus ore hematite content. Error bars show 95% confidence intervals.

\[
\theta = 0.24x - 1.9445y + 65.40 
\]

Where x (vol.\%) is the content of hematite and y is the LOI (vol.\%) of iron ores.

They also didn’t give a clear explanation of how surface morphology influences the contact angle.

Huang et al.\(^{[60]}\) used the difference between the two surface areas to describe the surface morphology index (SMI) and defined \(SMI = S_{BET}/S_{LPSA}\). \(S_{LPSA}\) is the external surface area from laser diffraction method.

They introduced \(LOI\) and gave formulas to calculate compositions of each oxide (Fe\(_2\)O\(_3\).H\(_2\)O\(_x\), Fe\(_2\)O\(_3\)M, Fe\(_3\)O\(_4\)T and Fe\(_2\)O\(_3\)fH represents the mass fraction of goethite, magnetite, total hematite and free hematite, respectively.):

\[
Fe_2O_3 \cdot H_2O = \left(LOI - LOI^0\right) \times \frac{77.72}{18.02} \left(LOI^0 = 0.1 \times LOI\right) 
\]

\[
Fe_2O_3M = FeO \times \frac{231.55}{71.85} 
\]
With the calculated composition of each oxide, they also found a relationship between measured density and calculated goethite content which is show in Fig. 22.

Then the volume% of goethite ($\varphi_G$) in an iron ore can be calculated as:

$$\varphi_G = \frac{Fe_2O_3\cdot H_2O_G}{3.83} \times \rho_{ore} \quad \quad \quad \text{(11)}$$

Where, $\rho_{ore}$ is the true density of iron ore particles. Using the Young-Dupre equation\(^\text{107}\) and similar to the calculation of viscous Gibbs free energy for mixing, by using the rule for average adhesion energy of heterogonous surfaces,\(^\text{108,109}\) the adhesion energy between water and the iron ore surfaces can be estimated as:

$$W = W_O \times (1 - \varphi_G) + W_G \times \varphi_G \quad \quad \quad \text{(12)}$$

Where, $W_O$ represents all adhesion energy between water and all non-hydroxide oxides (J/m\(^2\)); $W_G$ is the adhesion energy between water and goethite (J/m\(^2\)).

Thus, a mathematical model for contact angle with the volume% of goethite ($\varphi_G$) can be built as follows.

$$\sigma_{\text{l-v}} \times (1 + \cos(\theta)) = W_O + (W_G - W_O) \times \varphi_G \quad \quad \quad \text{(13)}$$

Where, $\sigma_{\text{l-v}}$ is the surface tension of water (0.072 J/m\(^2\)).

**Figure 23.** Adhesion energy as function of volume% of goethite for iron ores used.\(^\text{50}\)

The results indicate that goethite content influenced strongly on contact angles. But, opposite opinions hold on the issue whether surface roughness and the particle porosity between the samples can make strong influence on measured contact angles. With a correlation coefficient $R^2 = 0.9$ and $SMI \geq 1$, an equation was obtained to describe the influence of physical properties on relative contact angles, shown as Fig. 24.

$$\theta_{RCA} = 90 / SMI^{0.1} \quad \quad \quad \text{(14)}$$

By using multilinear regression method, the volume% of goethite ($\varphi_G$) can be expressed as a function of $SMI$ and (pore volume) $V_{pore}$ with a regression correlation $R^2 = 0.927$.

$$\varphi_G = 0.266 \cdot SMI + 0.769 \cdot V_{pore} \quad \quad \quad \text{(15)}$$

They also compare with the literature from Iveson.\(^\text{48,49}\)

The measured $\theta_{RCA}$ versus the calculated $\theta_{cal}$ based on
Iveson’s data is shown in Fig. 25. It shows that the relative contact angles have a linear relation with the calculated contact angle with a fitting coefficient equals 0.515. But some differences exist due to the error in measurements.

Long et al.\textsuperscript{102) }have studied the influence of surface morphology on contact angles of water and iron ore particles. They controlled the size distribution by grinding particles, surface roughness of particles after 60 min increased obviously and a relationship between contact angles and grinding times was obtained as shown in Table 13.

From Table 13, we can see that contact angles decreased with the increasing of grinding time. This may be due to the surface roughness has changed after grinding, and they thought this phenomenon agrees well with the finding that the contact angle decreases when the roughness factor is increased.\textsuperscript{110) }

Qiu G\textsuperscript{101) }concluded that the physical properties of binders influence the wettability of iron concentrate (magnetite). Two binders were used in their experiment, and the chemical compositions were shown in Table 14.

Contact angle for magnetite is about 46° from Fig. 26, and Funa has a stronger influence on the contact of iron concentrate than bentonite. The effects of binders on the wetting heat of the concentrate were obtained and shown in Fig. 27. It can be seen that both Funa and bentonite can increase the wetting heat of the concentrate. However, the increase of the wetting heat caused by Funa is much greater than that by bentonite. It suggests that Funa can greatly change the wettability of the magnetite and make the surface much more hydrophilic.

Shang\textsuperscript{53) }has determined contact angles of three different liquids with goethite by using thin-layer wicking method and Washburn method, which are shown in Figs. 28 and 29, respectively. Through the thin-layer wicking method, contact angles for goethite with water, formamide, diiodomethane are 34.1° ± 3.4°, 20.9° ± 1.8° and 46.7° ± 2.9°, respectively. But for Washburn method, they didn’t calculate contact angles because there distinct stage 2 of column wicking wasn’t find. This may due to pore structure of the packed soil colloids changed as the fluid was imbibed during measurement. Surface tension and viscosity of the three liquids can be seen in Table 9. They concluded that Thin-layer wicking was better suited for contact angle measurements because the colloids on the plates formed a more rigid porous structure, and did not easily disperse.\textsuperscript{111) }

Because tested liquid wets the powder bed better than the reference liquids they choose, Susana L et al.\textsuperscript{87) }try to choose better reference liquid by employed the lipophilic to hydrophilic ratio (\textit{LHR}).\textsuperscript{112) }But all these results suggest that the \textit{LHR} can give only limited information on the affinity of the wetting medium with the powder and cannot be used as a general guide for the selection of the proper wetting fluid, which confirm that Washburn’s method is extremely sensitive to the choice of the reference liquid used. They used three surfactant solutions to be the reference liquids in the Washburn method according to literature\textsuperscript{113) }and obtained curves of \textit{w} versus time as shown in Fig. 30. Contact angles of two iron ore particles can be calculate by using Washburn equation.\textsuperscript{64) }The result is bigger than the contact angle of water and iron ore particles.

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Grinding time (min) & 0 & 3 & 6 & 9 & 12 & 30 & 60 \\
\hline
Contact angle (°) & 71 & 65 & 64 & 62 & 55 & 43 & 34 \\
\hline
\end{tabular}
\caption{Contact Angle for Different Grinding Times.\textsuperscript{102)}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
Binder & \textit{O}_{org} & SiO$_2$ & Al$_2$O$_3$ & CaO & MgO & Fe$_2$O$_3$ & P & S & C$_F$ \\
\hline
Funa & 46.50 & 13.81 & 6.16 & 4.72 & 0.21 & 4.04 & 0.03 & 0.04 & 28.14 \\
Bentonite & 0 & 72.91 & 13.59 & 1.7 & 2.48 & 1.40 & 0.025 & 0.01 & 0 \\
\hline
\end{tabular}
\caption{Chemical compositions of Funa and Bentonite.\textsuperscript{101)}
\end{table}
Liu\textsuperscript{100} used the Washburn method to determine contact angles of iron ore concentrate particles of different fractions. They found that contact angle decreased with the increase of particle size, and this opinion has been confirmed in literature. The contact angle values of four size grades were given in Table 15. There is a great difference between the contact angle measured by WCR and contact angle measured by sessile drop which is nearly 37.7° in the research result. The packing and tapping operations and the great roughness and surface properties of particles are the two aspects caused the great difference in their idea. The contact angle of LIMS iron ore concentrate particles versus CTAB (cetyl trimethyl ammonium bromide, which as an absorbate to improve the interfacial behaviors of iron ore particles) concentration were also studied in this paper. The Table 16 shows that the wettability of sample particles would get better if increasing CTAB concentration continuously.

Mao\textsuperscript{51} obtained contact angles of natural iron ore particles with water. The chemical composition and surface properties of iron ores are shown in Table 17. Ore A and ore C are hematite, ore B and ore D are limonite, respectively. The particle size is less than 0.125 mm.

The effects of the particle shape, size and size distribution on the wetting behavior of soft magnetic micropowders are investigated in the experiment of Kirchberg.\textsuperscript{71} Calculated contact angles of different particle sizes of Fe$_3$O$_4$ powders with different test liquids are summarized in Tables 18, and 19 shows the properties of test liquid. From the test

---

**Table 15.** The advancing contact angle of iron ore concentrate particles of different fractions by WCR (Washburn Capillary Rise).

| Particle size (µm) | 25–45 | 45–62 | 62–96 | 96–150 |
|-------------------|--------|--------|--------|--------|
| Contact angle (*)  | 73.93±7.26 | 69.35±4.03 | 67.01±3.48 | 64.92±2.35 |

**Table 16.** Contact angle of LIMS iron ore concentrate particles versus CTAB concentration.

| Concentration of CTAB solutions (mg/L) | 0 | 40 | 80 | 120 | 160 |
|----------------------------------------|---|----|----|-----|-----|
| Contact angle (*)                      | 69.37 | 74.15 | 80.83 | 85.02 | 78.04 |

**Table 17.** Chemical composition and surface properties of iron ores.\textsuperscript{51}

| Materials | Chemical composition | Surface properties |
|-----------|----------------------|--------------------|
| TFe | SiO$_2$ | CaO | Al$_2$O$_3$ | MgO | LOI | SLS | BET (m$^2$/g) | Contact angle (*) |
| Ore A | 65.29 | 1.36 | 0.02 | 1.49 | 0.09 | 2.18 | 0.51 | 6.84 | 53.84 |
| Ore B | 58.27 | 5.55 | 0.04 | 1.37 | 0.08 | 10.13 | 0.21 | 24.54 | 76.30 |
| Ore C | 64.51 | 4.3 | 0.02 | 0.68 | 0.05 | 2.04 | 0.18 | 1.60 | 69.58 |
| Ore D | 59.14 | 4.38 | 0.05 | 1.5 | 0.08 | 9.52 | 0.40 | 23.97 | 79.47 |

**Table 18.** Contact angle of Fe$_3$O$_4$ micropowders.

| Powder (µm) | Powder contact angle (*) |
|-------------|--------------------------|
| H$_2$O$_{dist.}$ | EG/H$_2$O(50/50) | FADEE |
| Fe$_3$O$_4$ (0–20) | 75.38 | 62.16 | 54.1 |
| Fe$_3$O$_4$ (20–40) | 75.10 | 60.10 | 52.63 |
| Fe$_3$O$_4$ (40–63) | 74.01 | 58.71 | 50.53 |
| Fe$_3$O$_4$ (63–80) | 73.50 | 54.80 | 47.46 |
| Fe$_3$O$_4$ (80–100) | 72.44 | 50.95 | 45.59 |
| Fe$_3$O$_4$ (unsieved) | 73.65 | 57.60 | 49.81 |

**Table 19.** Properties of test liquids at 25°C.

| Test liquid | Density [g/cm$^3$] | Viscosity [mPa s] | Surface tension [mN/m] |
|-------------|--------------------|-------------------|------------------------|
| Fumeric acid diethyl ester | 1.045 | 2.85 | 31.40 |
| Ethylene glycol-water (50/50) | 1.064 | 3.81 | 57.89 |
| Dist. water | 0.998 | 1.00 | 72.30 |
result, they concluded that contact angles decreased with the increasing of particle size and increased with the increasing of particle porosity, which is agree with the conclusion of literature.114) Finally it was found that higher liquid surface tension results in higher contact angle and worse wetting of the different powder beds.

Contact angles of iron ore particles and test liquid by using capillary rise method are shown in Table 20. By analyzing the data of contact angles, some important information can be obtained:

From the results of authors, contact angles vary from 0 to 87.25 with chemical compositions. Most samples are complex of hematite, goethite and magnetite. There's a strong relation between water contact angle and the ratio of goethite and hematite from the results of Huang and Iveson.48–50) Unfortunately, content of these chemical compositions didn’t be obtained by other authors to support this opinion.

For capillary rise methods, totally wetting liquid is of great important for contact angle measurements. The constant $C$ can be counteracted by citing a prefect wetting liquid which contact angle is assumed to be zero, and then the contact angle of test liquid is obtained. The pivotal thing to choose the totally wetting liquid is that the reference liquid should not have a lower wettability than the test water, or contact angles can’t be calculated. For different reference liquid, the contact angle is different. As reported, values of

| Author | Method | Sample | Hematite (Vol.%) | Goethite (Vol.%) | Contact angle (degree) |
|--------|--------|--------|-----------------|-----------------|-----------------------|
| Potapoya88) | Washburn method | Magnetite | – | – | 50–60 |
| Huang48) | The pressure method | S1 | 63.47 | 24.87 | 71 |
| | | S2 | 92.27 | 23.45 | 57 |
| | | S3 | 90.02 | 62.41 | 66 |
| Qiu97) | Washburn method | Magnetite | – | – | 46 |
| Akdemir 98) | The height method | Hematite | – | – | 47 |
| | | A | 8.6 | 87.2 | 0 |
| | | B | 15.6 | 78.6 | 12 |
| Iveson47) | The pressure method | C | 55.6 | 42.0 | 23 |
| | | D | 19.2 | 79.2 | 27 |
| | | E | 22.4 | 77.4 | 30 |
| | | F | 71.6 | 28.0 | 32 |
| Iveson48) | The pressure method | G | 53.2 | 41.0 | 37+5 |
| | | H | 77.6 | 22.4 | 37 |
| | | J | 93.4 | 5.0 | 40±13 |
| | | K | 97.2 | 1.4 | 43±10 |
| | | L | 94.0 | 1.0 | 46 |
| | | M | 92.2 | 2.8 | 48±3 |
| | | N | 88.2 | 7.0 | 49±4 |
| | | O | 98.6 | 0.6 | 49±10 |
| | | P | 85.0 | 12.4 | 54 |
| | | Q | 20.0 | – | 29 |
| | | R | 86.0 | 6.0 | 56±10 |
| Shang51) | Thin–layer wicking method | Goethite | – | – | 34.1±3.4 |
| Susana20 | Washburn method | Fe$^3$ | – | – | 67.35$^a$ |
| | | Fe$^2$ | – | – | 71.03$^a$ |
| Zhang99) | The pressure method | A | – | – | 57.70 |
| | | B | – | – | 62.83 |
| | | C | – | – | 67.17 |
| | | D | – | – | 73.19 |
| | | E | – | – | 66.79 |
| | | F | – | – | 79.19 |
| | | G | – | – | 77.86 |
| | | H | – | – | 80.30 |
| | | I | – | – | 83.00 |
| | | J | – | – | 87.25 |
| Long100) | The pressure method | Vanadium–Titanium magnetite concentrate | – | – | 73.93±7.26$^c$ |
| Liu96) | Washburn method | LIMS iron ore concentrate | – | – | 69.35±4.03$^c$ |

1: Iron ore powders with a size of 42.24 μm.
2: Iron ore powders with a size of 129.36 μm.
3: LIMS iron ore concentrate with a size of 25–45 μm.
4: LIMS iron ore concentrate with a size of 45–62 μm.
5: LIMS iron ore concentrate with a size of 62–96 μm.
6: LIMS iron ore concentrate with a size of 96–150 μm.
7: Fe$_3$O$_4$ micropowders with a size of 0–20 μm.
8: Fe$_3$O$_4$ micropowders with a size of 20–40 μm.
9: Fe$_3$O$_4$ micropowders with a size of 40–63 μm.
10: Fe$_3$O$_4$ micropowders with a size of 63–80 μm.
11: Fe$_3$O$_4$ micropowders with a size of 80–100 μm.
12: unsieved Fe$_3$O$_4$ micropowders.

$^a$: The test liquid is 85.7 wt.% sodium silicate.
$^b$: The test liquid is 85.7 wt.% potassium silicate.
$^c$: The test liquid is fumeric acid diethyl ester.

$^1$ Fe$_3$O$_4$ $^{7}$, $^2$ Fe$_3$O$_4$ $^{8}$, $^3$ Fe$_3$O$_4$ $^{9}$, $^4$ Fe$_3$O$_4$ $^{10}$, $^5$ Fe$_3$O$_4$ $^{11}$, $^6$ Fe$_3$O$_4$ $^{12}$
cosθ exceed unity when using n-heptane as the reference liquid, and in addition, the situation improves little as the water is the reference liquid. It is because n-heptane is an apolar fluid and water is a polar fluid, as polarity of these liquids is a limitation for them to determine contact angles of powders which are lipophilic or hydrophilic. Surface tensions of surfactant solutions are extremely low and it’s great for the calculation of contact angles.

4.3. Captive Bubble and Wihelmy Plate Method

The test particles are natural and synthesized in laboratory in the paper of Copeland C R et al., and Shang J et al., respectively. The content of Taconite is 67% hematite (Fe₂O₃), 10% magnetite (Fe₃O₄), few silica and other gangue minerals. Hematite and goethite were pure.

Contact angle of taconite and water is 18° ± 3° by captive bubble method, and for Wihelmy plate method contact angles of hematite and goethite are 71.7° ± 2.0° and 14.2° ± 2.4°, respectively. As the same result of calcium chloride, adding acetylenic glycol lowered the contact angle of taconite and water. The Wilhelmy plate method generally leads to an underestimation of the advancing contact angle when the plate surface is rough, because the effective plate perimeter is larger than that determined by a caliper.

5. Influencing Factors

Various methods have used to determine contact angles of iron ore particles and liquids. According to the results obtained in these methods, it can be observed that there exist some differences between contact angles measured by the two typical approaches: direct method and indirect method. The reason may be settled in the chemical compositions and physical properties of particles.

According to Yong’s equation, contact angle is related to solid-gas interfacial energy, liquid-solid interfacial energy and liquid-gas interfacial.

\[
\cos \theta_f = \frac{\gamma_{SG} - \gamma_{LS}}{\gamma_{LG}} \quad \text{..................(16)}
\]

The liquid-gas interfacial and solid-gas interfacial energy are constant values which only vary with different liquid and materials. In other words, different kinds of liquid and materials indicates different chemical compositions or phase constitution possess discrepant free enthalpy. The liquid-solid interfacial is related to the whole interfacial energy of the contact surface. For an ideal material, which surface is flat and homogeneous, the liquid-solid interfacial energy is a fix value and only varies with chemical composition or phase constitution. But in an actual surface, the surface roughness increases the specific surface area thus changes the surface free enthalpy of solid materials making the variation of contact angle.

Wenzel defined roughness factor r as the ratio of the area of the actual surface to that of a smooth surface having the same geometric shape and dimensions, It is assumed that roughness makes hydrophilic surface a better wettability, but for hydrophobic a worse wettability. By developing the theory of Wenzel, Cassie proposed that a rough surface of low interface energy possesses super-hydrophobicity. The iron ore particles are hydrophilic materials so based on the above theory that roughness will make it more hydrophilic.

Contact angle is influenced by the two significant factors: surface chemical compositions and surface morphology. The effect on contact angle of both factors will be described in the coming sections.

5.1. Chemical Compositions

Iron oxides are hydrophilic materials. Due to the fact that in the atmosphere, surface hydroxyl groups exist at the surfaces of most metal oxides, these metallic oxides have different effect on wettability. For pure hematite, magnetite and goethite, the major ingredient are Fe₂O₃ (α-Fe₂O₃), Fe₃O₄ and FeO(OH) (α-FeOOH). The schematic diagrams of crystal structures of the three iron oxides are shown in Fig. 31. Both α-Fe₂O₃ and α-FeOOH has an octahedral structure that each iron atom is bonded to six oxygen atoms or three oxygen atoms and three hydroxyls. In the case of magnetite, the crystal structure is complicated inverse spinel structure, where each unit cell contained 32 O²⁻ and 24 iron atoms, 8 Fe³⁺ and 8 Fe²⁺ with 8 Fe²⁺ are filled into the interspace of
tetrahedrons and octahedrons, respectively. It can be found both tetrahedral structure and octahedral structure in a unit cell of Fe₃O₄. Tetsuo Morimoto[117] figured out the mechanism of formation of surface hydroxyl groups on the surface of metal oxides. Firstly, water is adsorbed on the surface of metal oxide to form adsorption complex, and then, it transfer to surface hydroxyl groups. The two neighboring surface hydroxyl groups adsorb water through hydrogen bonding.

More surface hydroxyl groups means more water molecules absorbed on the oxide surface by hydrogen bonding, partly, which suggests a lower contact angle or a better wettability.

Generally, natural ores contain most iron oxides and some other metallic oxides such as silicon oxide, calcium oxide, alumina and magnesium oxide. In the theory of Iveson,[49] natural iron oxides are complex mixture of different iron oxides, and these oxides can be divided into oxides and oxy–hydroxides. Considering the hydration in oxy–hydroxides, there are more surface hydroxyl groups generated in the surface of oxy–hydroxides than hydroxides. For goethite after highly weathered and roughed will wet better than magnetite. So, in the surface of goethite, an oxy–hydroxide, density of surface hydroxyl groups would be expected to be probably higher than that in hematite and magnetite. It agrees with the results of authors that goethite has the lowest water contact angle among these iron oxides. However, other oxy-hydroxides, such as Al₂Si₂O₅(OH)₄Si an Ca(OH)₂, which constituted by element Ca, Mg, Si and Al in iron ore particles are too little to contribute to the density of surface hydroxyl groups. From the statistical analysis of contact angles with different chemical compositions, it shows that SiO₂, CaO, MgO and Al₂O₃ have not significant effect on contact angles.

As Fig. 32 shows, there is a clear trend that contact angles decreased with the decreasing of the volume fraction of goethite. It confirms that the increasing amount of goethite decreased contact angles,[50] performing a better wettability.

5.2. Surface Morphology

Surface morphology is a general designation of surface feature of material, such as particle size, surface roughness and porosity. On account of multiple thermodynamic equilibrium states exist, these surface features make different wetting behaviors on material surface when contacted water.

Pores, whether in sessile drop method or capillary rise methods, are exist in test samples for individual particles were generally made into a closely united tablet or a lump in column to measure contact angle. Actually, according to the testing principle of sessile drop method, it is not suitable for contact angle measurement of natural iron ore particles with water. In sessile drop method, natural iron ore particles show a different behavior in contact angle measurements compared to synthetic particles. The above-mentioned two typical behaviors of droplet in contact angle measurements are shown in Fig. 33. As shown in picture, for synthetic particles, contact angles stay constant in the measurement period which suggests that the shape of droplets doesn’t change. But for natural particles, the droplet shape changes with time, which indicates that water is absorbed into bed. These phenomenon due to the differences in surface morphology of synthetic particle and natural particle. The synthetic particles are always smooth in a certain shape. However, natural iron ore particles has a more complicated surface morphology due to its irregular, rough and porous. It is said that irregular shape and uneven size fractions contribute more space between particles due to its worse anastomosis,[121] and thus, the space of inter-particle can function as pores in contact angle measurements, which means a higher porosity. So, for packed bed of natural particles, penetration happens as the time the droplet spread on the surface of bed when it contacts particle bed. The thermodynamic equilibrium of three phases doesn’t exist in this situation and it ends with the complete suction of droplet. Only at a thermodynamic equilibrium situation, contact angle is meaningful according to the definition of contact angle. Thus, sessile drop method is not recommended as contact angle measurement of natural iron ore particles.

Unlike the sessile drop method, advancing contact angle is determined in capillary rise methods by penetration. There is no need to create a thermodynamic equilibrium and according to the Washburn equation, contact angle seems to only relate to liquid physical properties (viscosity and surface tension) and effective capillary radius.
In order to avoid calculating $r_{\text{eff}}$ directly, a reference liquid which contact angle for iron ore particles equals to zero is used. The assumption is based on the fact that reference liquid can wet perfectly on the surface of iron ores. This assumption may not be strict as natural iron ore particles may contain several different kinds of iron oxides. Thus, the measured contact angle should be called relative contact angle, preferably. The second assumption of this method is that the density and porosity of packing beds stay constant in each measurement. In fact, it’s harsh to meet these requirements and the best way is to do repeated trials to reduce errors.

**Figure 34** shows the relationship between water contact angle and particle size in using capillary rise methods. Different color means of results were obtained by different angle and particle size in using capillary rise methods. Different color means of results were obtained by different angle and particle size in using capillary rise methods.  

In capillary rise methods, Iveson, 49) Zhang et al. 105) and Huang 50) got an agreement that contact angle depends on ore compositions, and they have concluded equations about contact angle with the volume fraction of hematite or goethite. Furthermore, Zhang et al. 105) obtained a liner relationship between LOI and WLR, and Huang 50) combined SMI to characterize the relation between contact angles and physical properties. The conclusion contains more details about contact angle varies with the volume fraction of goethite and surface morphology compared with results of Iveson. 49) It accords with the opinion which both chemical composition and surface morphology lead to the variation of contact angle. As things stand, the preferable approach for the measurement of water contact angle of natural iron ore particles is the capillary rise method, which is always used in the determination of contact angles between water and porous iron ore particles. This method takes into account the characteristics of natural ore particles, porous and rough. The measured relative contact angle is more reliable than it measured by direct methods. In the study of Mao et al., 101) they defined the granulation...
property \((k)\) of ores, which is a parameter relevant contact angle and increased with the decreasing of it. The results show that bed permeability can be exactly estimated by granulation property and mass fraction, namely, contact angle measured by capillary rise methods are appropriate for granulation process evaluation.

With the decreasing of high quality hematite, the dosage of limonite becomes larger and it makes a better wettability of iron ore particles as well as a better balling behavior. However, an extremely good wettability may be not a good behavior in granulation as there is excess moisture in granules in the same stacking volume. It should be noted here that excess moisture makes particles crust on the inner wall of mixer, which blocking the granulation process. Another aspect is that excessive moisture increases the thickness of overdamp layer, reduces sintering temperature, makes a worse permeability and deteriorates the sinter bed. Thus, a novel and practical technology adopting low moisture should be developed based on the research on wettability of different iron ores.

In order to alter the wettability of iron ores and make a better granulation behavior, the following methods can be taken into consideration. According to the above mentioned literature, it can be realized by changing the surface tension of water by adding some reagents, and varying the surface free energy of iron ore particles by increasing the \(SMI\) of particles. Moreover, coating of iron ore particles, high-temperature treatment, such as oxidation roasting and magnetization rotating, are useful approaches to improve the wettability.

7. Summary

Contact angle is a vital parameter in many fields to present the wettability of materials and many methods were developed for the measurement of contact angle. The contact angle measurement methods for particles can be divided into two types, direct methods and indirect methods, all these methods have their features and are summarized. Natural iron ore particles are almost rough, porous and irregular and with a wide range of size fraction. It’s difficult to obtain accurate contact angles for natural particles.

Among these methods, sessile drop method and capillary rise method are commonly used, because their easy conduct and clear result. For capillary rise methods, totally wetting liquid is of great important for contact angle measurements. Anyway, it’s still the most applicable way for porous particles like natural iron ore particles. To obtain accurate results, centrifuge and vibration technique have been used to get uniform packing beds. So in future, developments of preferable techniques to get uniform packing beds for capillary methods will be a significant research content.

Many authors have obtained contact angles of iron ore particles and liquid, and their results show some important information about contact angle measurement and wettability of iron ore particles.

(1) Iron ore oxides (magnetite, goethite and hematite) are hydrophilic and the contact angles of iron ores varies with chemical composition (phase constitute). Oxy-hydroxides play a key role in the improvement of wettability of iron ores, as these species contribute surface hydroxyl groups. There has an agreement that goethite has the smallest contact angle among hematite and magnetite.

(2) Complicate surface morphology (the specific surface area, pore volume) makes iron ore particles better wettability, which a surface of higher \(SMI\) is verified to have a lower contact angle. But the mechanism of it influenced on contact angle is still unclear. In reality, contact angle is influenced by the complicate interaction of chemical compositions and surface morphology.

(3) For pure synthetic iron oxides, contact angle is similar in both direct and indirect method. Capillary rise methods are relatively better for the measurement of natural iron oxides due to penetration takes place on the surface of packed lump by sessile drop method.

(4) Surface treatment can alter the wettability of iron ore particles by varying the surface free energy. The wettability can be improved by increasing the \(SMI\) of particles, coating of iron ore particles, high-temperature treatment.

(5) With growing use of limonite, excess moisture in granulation process makes particles crust easily on the inner wall of mixer, causes a bad permeability and deteriorates the sinter bed. A novel and practical technology adopting low moisture should be developed based on the research on wettability of different iron ores.

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