Effect of Iron Oxide Mineral Structure on Agglomeration Behaviour and Agglomerate Properties

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Abstract
Presence of different iron oxides (e.g., goethite, hematite and magnetite) may not only affect the leaching behaviour and acid consumption rate of laterite ores, but can also influence its agglomeration behaviour and agglomerate properties which impact on heap geotechnical structure and performance. In this study, the effect of iron oxide mineral type (goethite, hematite and magnetite) on the agglomeration behaviour and product properties (e.g., compressive strength, re-wetting stability and microstructure) was investigated. Batch, drum agglomeration tests performed with 30 %w/w H$_2$SO$_4$ solution binder showed distinct mineral structure-dependent particles’ wetting nucleation and agglomeration growth behaviour. For effective agglomeration to produce 5 – 40 mm size agglomerates in <14 min, goethite markedly required lesser binder dosage than hematite and magnetite. Goethite agglomerate growth rate was slightly slower than that of magnetite and hematite due to its lower binder dosage, but all the three samples displayed coalescence growth behaviour. Microstructure analysis revealed that the pore volume of both wet and dry agglomerates of hematite is greater than those of magnetite and goethite. Comparatively, the dry agglomerate compressive strength of goethitic Ni laterite was greater than magnetite and hematite but lower than goethite. The wet agglomerate strength decreased in order of goethite ≈ magnetite > hematite ≈ goethitic Ni laterite. The re-wetting stabilities of the agglomerates markedly decreased in the order of goethite > magnetite > hematite. The findings foster our understanding on how mineralogically different iron oxide phases may impact on ore agglomeration and product attributes which are pivotal in laterite ore heap leaching performance.

Keywords; Iron oxide; Agglomeration; Compressive strength; Re-wetting stability

I. INTRODUCTION

Iron (Fe) oxides (e.g., goethite, magnetite and hematite) are key mineral phases present in complex low grade limonitic laterite ores [1, 2]. In goethitic nickel (Ni) laterite ores, majority of the Ni and cobalt (Co) exist in association with Fe in these mineral phases as amorphous or poorly crystalline structures [2-12]. The Ni extraction rate is strongly linked with the leaching behaviour of the type and nature of the host Fe oxides.

Heap leaching (HL) is an attractive, low cost promising technology for processing low-grade Ni laterites (e.g., limonitic) [13]. However, HL processing lateritic ores is limited due to certain geotechnical and hydrological problems linked to complex mineralogy/chemistry. For example, Moroney et al. [14] reported that leaching of goethite and magnetite from lateritic ore during heap leaching led to heap instability and poor permeability. Thus resulted in low metal recovery, rendered the operation economically non-viable. Agglomeration of the fine lateritic ore feed particles into coarser, robust but porous products prior to heap leaching eliminates some of the geotechnical problems and enhances the efficiency of the heap leaching, as exemplified in gold and copper processing [15]. The marked variation and remarkable complexity of the laterite ores make it very difficult to produce agglomerates with desirable characteristics necessary for successful heap leaching [2, 3, 16-19]. For instance, a comparative leaching behaviour studies of Fe oxides (magnetite and goethite) and limonitic laterites in sulphuric (H$_2$SO$_4$) acid showed that under similar processing conditions structurally different Fe oxides behave differently [1]. Cornell et al. [20] also indicated that magnetite in most conditions dissolves faster than hematite and goethite due to its spinel nature. A study to understand the processing behaviour (e.g., agglomeration) of individual mineral phases is therefore, crucial for improved efficacy of lateritic ores processing [4].

The present study investigates batch, drum agglomeration behaviour and product properties of magnetite, goethite and hematite minerals using 30 %w/w H$_2$SO$_4$ solution as a binder. Particular interest is devoted to the influence of mineralogical structure on binder dosage requirement, agglomeration
mechanisms and kinetics, and agglomerate structure (size, microstructure, rewetting stability and strength). The agglomerate structure results obtained in this study were also compared with reported data on typical Fe oxide rich-Ni laterite ores (goethitic).

II. MATERIALS AND EXPERIMENTAL METHODS

A. Materials

Three polydispersed (1-130 µm) samples of magnetite, goethite, and hematite (Unimin, Australia) were used. The feed particle characteristics, chemical and mineralogical compositions are presented in Fig. 1 and, Tables 1 and 2. The feed particle size distribution (Fig. 1) measured using laser diffraction (Malvern Mastersizer X, Malvern UK) showed that the magnetite feed particles was coarser than goethite and hematite particles. The BET specific surface areas of the particles determined via a 5 point N2 BET [21] analysis (Coulter Omnisorp 100, Hialeah FL, USA), bulk densities, bed pore volume also appeared different for each sample. The mineralogical composition of the samples (Tables 2) determined via quantitative, powder X-ray diffraction (XRD) using Scintag ARL X'tra diffractometer and Cu Kα radiation where the samples were scanned between 2° and 90° 2θ at 0.02° intervals at rate of 1.2° per min. Prior to the analyses, each sample was “spiked” with about 10 wt.% of ZnO to enable the amorphous content calculation. XPowder and SIROQUANT V3 software were then used for mineral phases’ identification and quantification, respectively. The differences in the feed properties are expected to lead to differences in solubility, binder saturation, agglomeration behaviour and product properties.

Notably, the mineralogical composition of goethitic Ni laterite ore which comprises goethite, magnetite, kaolinite, hematite and Mg-bearing silicate as dominant minerals with nontronite, gibbsite, quartz, Cr-bearing minerals, Asbolane and Co-Lithiophorite as minor mineral phases [22] is shown in Table 2 are for comparison purposes.

![Fig. 1: Particle size distribution of magnetite, goethite and hematite mineral samples.](image)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Specific surface area (m²/g)</th>
<th>Bulk density (g/cm³)</th>
<th>Bed porosity (vol.%)</th>
<th>Binder dosage (wt.%)</th>
<th>Initial bed porosity (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>1.6</td>
<td>2.6</td>
<td>22</td>
<td>14</td>
<td>28.9</td>
</tr>
<tr>
<td>Goethite</td>
<td>2.2</td>
<td>2.8</td>
<td>18</td>
<td>18</td>
<td>30.3</td>
</tr>
<tr>
<td>Hematite</td>
<td>3.1</td>
<td>3.0</td>
<td>23</td>
<td>15</td>
<td>33.0</td>
</tr>
</tbody>
</table>

*Table 1: Characteristics of magnetite, goethite and hematite samples and amount of binder used

Table 2: Quantitative XRD mineralogical composition of magnetite, goethite, hematite, and goethitic laterite ore

<table>
<thead>
<tr>
<th>Mineral phases</th>
<th>Magnetite (wt.%)</th>
<th>Goethite (wt.%)</th>
<th>Hematite (wt.%)</th>
<th>Goethitic Laterite (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Goethite</td>
<td>1.50</td>
<td>86.18</td>
<td>-</td>
<td>73.70</td>
</tr>
<tr>
<td>Magnetite</td>
<td>42.70</td>
<td>-</td>
<td>-</td>
<td>4.70</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-</td>
<td>7.00</td>
<td>-</td>
<td>7.00</td>
</tr>
<tr>
<td>Mg-bearing silicates (e.g., Chabasite)</td>
<td>-</td>
<td>1.59</td>
<td>-</td>
<td>2.60</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>-</td>
<td>-</td>
<td>3.90</td>
<td>1.30</td>
</tr>
<tr>
<td>Asbolane</td>
<td>-</td>
<td>-</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>Co-Lithiophorite</td>
<td>-</td>
<td>0.79</td>
<td>-</td>
<td>1.10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>-</td>
<td>3.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alumina</td>
<td>-</td>
<td>-</td>
<td>1.40</td>
<td>-</td>
</tr>
<tr>
<td>Nontronite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
</tr>
<tr>
<td>Cr-bearing minerals</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.70</td>
</tr>
<tr>
<td>Asbolane</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.48</td>
</tr>
<tr>
<td>Co-Lithiophorite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.05</td>
</tr>
<tr>
<td>Amorphous</td>
<td>55.80</td>
<td>3.42</td>
<td>4.00</td>
<td>-</td>
</tr>
</tbody>
</table>

*n.d – not detected, suggesting very little (if any)

B. Drum agglomeration procedure and product characterisation

Agglomeration tests were conducted at ambient temperature 24 ± 1 °C in a batch, laboratory-scale, 316 stainless steel drum (0.3 m diameter and 0.2 m in length) granulator powered by a variable speed motor (Fig. 2A) operating at 60 rpm drum speed in the manner described by [23]. For all agglomeration tests, ore feed and binder (30% w/w H₂SO₄) charge consisting of 500 g of powder and a known amount of binder (depending on binder dosage requirement) were used. The feed and binder mass loading corresponded to ~4% of drum volume. The ore and binder were first pre-mixed in a tray by quickly hand spraying the binder (Fig. 2B) and subsequently transferred the mixture into the drum to commence agglomeration. During the agglomeration process, where necessary, the drum was periodically stopped for 30 s to scrape the particles that were adhering to the drum walls using a spatula. Three replicates experiments were performed for each agglomeration tests for a maximum batch time of 14 min.
Evolution of agglomerate size distribution with time on mass basis was determined via a conventional sieving technique and the cumulative mass fractions undersize were then plotted against mean granule size (defined as mesh size of retaining sieve).

The stability of agglomerate in solution was estimated via acid soak tests, where the disintegration time gives an indication of the re-wetting strength of agglomerates [24]. The procedure involved submerging of agglomerates in pH 1 H$_2$SO$_4$ solution and recording the time prior to the complete disintegration. The compressive strength measurements were conducted by determining the agglomerate fracture stress under compressive load. A bench top compressive/tensile strength testing machine (Hounsfieid, UK), which enables both tensile and compressive force-distance measurements to be performed, was used (Fig. 3). Compression consisted of applying a load to agglomerate held between two parallel flat surfaces, one of which was held stationary while the other was attached to a constant velocity drive. The resultant force was measured using a load cell (of known compliance) attached to the upper drive surface. Based on the agglomerate diameter and the measured maximum applied uniaxial force ($P_{\text{max}}$) at which breakage or fracture occurred, the fracture stress was calculated from (1) [25]

$$\sigma_f = \frac{2.8 P_{\text{max}}}{\pi d^2}$$

where $\sigma_f$ is stress to failure/fracture and $d$ is the diameter of the test agglomerate. Notably, two sets of agglomerates were used for these stability and strength measurements, one set air-dried at ambient temperature $\sim 24 \pm 1$ °C and the other kept wet in air-tight plastic for 24 h. For each strength and rewetting stability tests, ten spherical and uniform size agglomerates of 10-20 mm were used.

The internal microstructure analysis was conducted on 10 mm agglomerates using an Xradia microXCT-400 tomography machine (Xradia, USA). Agglomerates were scanned at 100 kV accelerating voltage and 10 W power in the 0 – 180 ° interval rotation using a 0.225 ° scan rotation step (2.5 s exposure time for each projection) and images with 18.6 μm pixel size were produced. During the rotation of the specimen stage, a total of 800 images were acquired. The collected projections were reconstructed, using the Xradia XMReconstructor software. It is worth mentioning that, for each case of agglomeration conditions, the same granule was used for both wet and dry micro-structure analysis.

### III. RESULTS AND DISCUSSION

#### A. Agglomeration behaviour

Figs. 4A, B and C show the evolution of agglomerate size with time for magnetite, goethite and hematite at 14, 10 and 15 wt.% binder dosages, respectively. Within 2 min of agglomeration the fine fractions of all the three samples disappeared rapidly. The nucleation and initial growth rate (within 2 min of agglomeration) decreased in the order of hematite > magnetite > goethite. Subsequent agglomerate growth in the course of 12 min for all the three samples was controlled by coalescence mechanism. After 14 min of agglomeration, the mean sizes ($D_{25}$, $D_{32}$) of magnetite agglomerates were larger than those of hematite and goethite (Table 3). This suggests that the overall agglomerate growth rate of magnetite is faster than that of hematite and goethite.

The differences in the agglomerate growth behaviours of are linked to the variations in their primary feed particles’ properties (e.g., specific surface areas, bulk densities and initial bed pore volume), leaching behaviour (solubility) and binder saturation (binder dosage) (Tables 1 and 2) [18, 26]. The faster initial growth (nucleation) displayed by hematite compared with goethite and magnetite is largely due to its greater initial binder dosage used for wetting. The relative fast growth rate displayed by magnetite can also be linked to its lower pore volume relative to the binder dosage used, leading to ~ 80% saturation, which according to Iveson et al. [26] facilitates faster agglomerate growth rate. Studies of these samples conducted by Quaicoe et al. [27] showed that magnetite has greater solubility than goethite and hematite which is expected to result in higher binder saturation [28] and ultimately leading to faster growth rate [26] as observed.
Notably, an unexpected trend was also observed where goethite with the greatest particles’ specific surface area required lower amount of binder to initiate nucleation and subsequent agglomerate growth. This suggests that the wetting/nucleation behaviour is not only influenced by particles’ wetted perimeter but also by other factors. Hence further studies to deconvolute the other relevant factors that may have contributed to the observed trend are required.

Table 3: Agglomerates properties of magnetite, goethite and hematite after 14 min of agglomeration

<table>
<thead>
<tr>
<th>Agglomerate</th>
<th>Surface weighted mean $D_{50}$ (mm)</th>
<th>Volume weighted mean $D_{40}$ (mm)</th>
<th>*Residual moisture content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>41.50</td>
<td>42.00</td>
<td>10.60</td>
</tr>
<tr>
<td>Goethite</td>
<td>32.90</td>
<td>34.90</td>
<td>6.30</td>
</tr>
<tr>
<td>Hematite</td>
<td>39.10</td>
<td>39.80</td>
<td>8.30</td>
</tr>
</tbody>
</table>

*Amount of binder remained in granules after 24 h air-dried in ambient temperature ~ 24 ± 1 °C and humidity of ~ 31 ± 1

B. Agglomerate micro-structure

Fig. 5 shows 2D micro-XCT images of the internal micro-structure of magnetite, goethite and hematite (wet and dry) agglomerates produced after 14 min, where the pores/cracks within the agglomerates are denoted by the dark regions. The concentration of pores/cracks within the core of the agglomerates is as a result of compaction and deformation-mediated stresses/strains that occurred during agglomeration which led to internal particles separation [29]. In general, the pores/cracks within dry agglomerates (A2, B2 and C2) appear greater than the wet (A1, B1 and C1) ones at fixed mineral-type. This is due to stresses/strains and cracks propagation resulting from particle shrinkage after moisture (water) loss upon drying [29]. The difference in the agglomerates’ porosities is expected to influence their compressive strength and re-wetting stability.

The hematite (wet and dry) agglomerates showed greater pore/crack volume than those of goethite and magnetite. The observed pore/crack volume difference can partly be linked to the initial powder properties (e.g., bulk density and bed pore volume) (Table 1). The agglomerates are subjected to consolidation/compaction during growth which reduces their porosities [26]. The reduction in final agglomerate porosity is higher as the initial particle’s bulk density increases. Therefore, the lower magnetite agglomerate porosity may be partly linked to its greater initial particle bulk density and lower bed pore volume (Table 1). Also, the difference in the porosities can be associated with the leaching behaviour that occurs during agglomeration [18, 19, 29, 30]. As shown by Senanayake and Das [1], using H$_2$SO$_4$ solution as a binder does not only dissolve some acid soluble minerals, but also reacts with metals to form metal sulphate compounds. The dissolved species in the wet agglomerates may solidify to fill the particle–particle gaps upon drying and therefore reduce the pore volume [19]. This phenomenon is expected to be greater in magnetite due to its higher extent of leaching propensity (solubility).
C. Agglomerate strength and re-wetting stability

Figs. 6 and 7 show the compressive strength and re-wetting stability of magnetite, goethite, hematite and goethitic Ni laterite agglomerates, respectively. Notably, binder (30 %w/w H$_2$SO$_4$) dosage of 18 wt.% was used for producing the goethitic Ni laterite agglomerates which had 7% residual moisture content after air-dried, under similar conditions reported herein [22].

In the wet state (Fig. 6), the compressive strength of hematite was lower than those of magnetite and goethite contrary to expectation that agglomerates with higher initial binder content would display greater wet strength. However, the observed difference can partly be linked to the extent of leaching of the initial feed particles upon contact with the acid. It has been shown that both magnetite and goethite samples leach faster in contact with the acid [27], hence their greater extent of leaching may increase the viscous and capillary forces (liquid bridges) that control the wet agglomerate compressive strength as a result of increase in binder’s viscosity and surface tension [18].

Fig. 6 also shows that the compressive strength of dry agglomerates for all the samples was greater than the wet ones. This is due to the formation of interparticle solid bridges within the dry agglomerates [19, 29]. The compressive strength of wet and dry agglomerates decreased in the order of goethite ≈ magnetite > hematite and goethite > magnetite > hematite, respectively. The greater dry agglomerate strength of goethite compared with magnetite and hematite may due to (i) the amount of residual moisture/binder (liquid) within the agglomerates after drying (Table 3), (ii) the presence of structure-building mineral phases (such as calcite, dolomite, chlorite and kaolinite) in the goethite feed (Table 2). Thus, the leaching/dissolution of these mineral phases and their precipitates are expected to produce strong binding calcium compounds such as calcium sulphate (e.g., gypsum) and calcium silicates, which may tend to bind the particles strongly upon drying [31]. The dry agglomerate compressive strength results, therefore, suggest that high proportion of goethite in ores impart greater strength to the agglomerates. This is consistent with reported studies where the hardening of the laterite ores during inundation was attributed the dehydration, further oxidation of high iron content and precipitation of the oxides/hydroxides, as cementing materials [32-36]. In comparison, the dry compressive strength of goethitic Ni laterite agglomerate was greater than those of hematite and magnetite but lower than that of goethite. The influence of goethite mineral phase in the observed trend is consistent with studies of Fe oxide reported by Xu et al. [22] where dry agglomerate strength decreased significantly with decreasing goethite mineral phase content of the ore in the order of goethitic > siliceous goethitic > saprolitic Ni laterite.

The re-wetting stability data (Fig. 7) also showed that all the wet agglomerates of the samples were more stable in pH 1 solution than their dry ones. This may be linked to the fact that (i) the liquid binder-mediated capillary and viscous forces within the wet granules can resist rapid fresh acid influx and attack, delaying granule disintegration and/or (ii) the decrease in liquid/solid mass ratio within dry agglomerates leads to greater osmotic flow and hence, faster influx of fresh acid solution which facilitates disintegration [19, 29]. This is consistent with the micro-structure data (Fig. 5) where hematite agglomerates (wet and dry) with greater porosity disintegrated faster than those of magnetite and goethite. The rewetting stability for both wet and dry agglomerates also decreased statistically in the order of goethite > magnetite > hematite > goethitic Ni laterite and goethite > magnetite > goethitic Ni laterite > hematite, respectively. The greater stability of goethitic Ni laterite wet agglomerates may be linked to its initial higher binder content (18 wt.%) whilst the least re-wetting stability of dry agglomerate of hematite may also be due to its greater pore volume (microstructure).
Overall, the results suggest that feed mineralogical / chemical structure has considerable influence on binder-particle interaction, binder requirement, agglomeration process and agglomerate structure (strength and re-wetting stability). For example, it is expected that laterite ores rich in goethite would require lesser amount of binder dosage for effective nucleation and subsequent agglomeration and the cured agglomerate product is also expected to be stronger and fairly porous. Evidently, such expectation can partly explain the lower binder dosage and greater dry compressive strength of goethitic Ni laterite ore compared with siliceous goethitic and saprolitic Ni laterite ores reported by Xu et al. [22].

CONCLUSIONS

The influence of Fe oxide mineral structure on agglomeration behaviour and products’ characteristics was investigated. The results revealed that:

- Goethite required lower amount of binder dosage (10 wt.%) to produce 5–40 mm size agglomerates within 14 min compared with hematite (15 wt.%) and magnetite (14 wt.%).
- All the three Fe oxide particles displayed coalescence growth behaviour. The agglomerate growth rate/size decreased in the order magnetite > hematite > goethite.
- Both wet and dry agglomerates of hematite have greater pore volume compared with those of goethite and magnetite. The pore volume of all the three agglomerates markedly increased upon drying.
- The dry compressive strength of goethitic Ni laterite is appreciably greater than those of magnetite and hematite but lower than that of goethite. The wet compressive strength also decreased in order of magnetite ≈ goethite > hematite ≈ goethitic Ni laterite.
- The re-wetting stabilities of both wet and dry agglomerates decreased in the order of goethitic Ni laterite > goethite > magnetite > hematite and goethite ≈ magnetite > hematite ≈ goethitic Ni laterite, respectively.
- The presence of different iron mineral phases in laterite ores will lead to different agglomeration and product characteristics which will impact on the Ni laterite heap stability and Ni/Co extraction rates.

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