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ROLE OF FLOCCULATION AND DISPERSION IN PELLETIZATION OF IRON
ORE

By

Victor Claremboux

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Chemical Engineering

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2020

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Chemical Engineering.

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Abstract

Traditional modeling of iron ore pellet strength utilizes micromechanical models such as Rumpf's equation, which correlate attractive forces and pellet properties into an average expected pellet strength. These models combine with repulsive forces within pellets to predict that pellet strength decreases with the introduction of these forces. However, naïvely applying Rumpf's equation readily leads to incorrect predictions about the resulting behavior. Pellets created with strong repulsive forces arising from dispersion conditions are observed to be significantly stronger overall than pellets formed in the absence of dispersants. A new model is required to understand and predict the effects of these additives within the iron ore pelletization process. This model can be developed by expanding on the coordination number term within Rumpf's equation utilizing information from the repulsive forces of dispersants. In particular, pellet strength roughly doubles under dispersion, which is most strongly promoted by anionic polymers.

1 Introduction

The strength of iron ore pellets has been a critical parameter of interest essentially since pelletization was developed. There is much literature discussing the theoretical and practical aspects of controlling iron ore pellet strength (Rumpf, 1962; Capes, 1972; Meyer, 1980; Seville et al., 1997, 2000; Iveson et al., 2001; Bika et al., 2001; Ripke and Kawatra, 2003; Eisele and Kawatra, 2003; Casey, 2016; Halt and Kawatra, 2017). The most heavily cited model of pellet strength is Rumpf's (1962) equation, which provided significant insight into many of the parameters involved in making strong pellets. However, recent experimental work has uncovered a situation where the intuition of Rumpf's equation is catastrophically incorrect: dispersion and flocculation.

Dispersion and flocculation are phenomena associated with the surface charge of particles in liquid solution (Halt and Kawatra, 2017; Zhang et al., 2019). Essentially no model of pelletization takes this surface charge into account, but the experimental work of Halt and Kawatra (2017) shows that it has a drastic effect on the final pellet strength. It had previously been considered that electrostatic interactions were of little interest to pellet strength (Seville et al., 1997, 2000), but these considerations were primarily based on potential electrostatic attractions within the pellet. The role of electrostatic repulsion has essentially never been considered prior, but according to Rumpf's equation should only serve to decrease the strength of a pellet overall. Instead, exactly the opposite phenomena occurs – pellets made with dispersants, that is to say pellets formed with strong repulsive forces, are much stronger than pellets made with flocculants (Halt and Kawatra, 2017).

Existing models of pellet strength have no treatment of dispersion or flocculation, and completely fail to explain why the introduction of a repulsive force during pelletization leads to the formation of stronger pellets in the end. The magnitude of the effect is also quite large, with the strongest pellets Halt and Kawatra (2017) reported being over twice as strong as the weakest using otherwise the same materials and binders, differing only by the nature of the dispersing or flocculating additive used.

For example, to highlight one of the key results of Halt (2017), the dustiness can be directly influenced by the nature of the flocculating or dispersing conditions achieved during pelletization. It was found that dispersing conditions lead to the formation of much less dusty pellets, while flocculating conditions result in the formation of pellets which were easily subjected to abrasion.

This is actually a very counterintuitive result when compared with other studies investigating dust suppression. Copeland and Kawatra (2005) and Copeland, Eisele and Kawatra (2009) found that the addition of calcium chloride suppressed the formation of airborne dust when added to finely crushed hematite. This effect was attributed to the hygroscopic nature of calcium chloride (Copeland et al., 2009), but calcium chloride is also known to have coagulating properties in flotation processes (Halt, 2017). In short, calcium chloride suppresses dust formation from the finely ground particulate stream, but

causes pelletization to form dustier pellets. Understanding why these two phenomena occur should clarify some of the more mysterious physics of pelletization.

The goal of this work is intended to critically analyze the failings of Rumpf's equation in this scenario, and provide a novel model for predicting the conditions and magnitude of the strength changes caused by dispersants and flocculants.

1.1 Background on Iron Ore Pelletization

Much of the iron ore mined today must be upgraded before it can be reduced into metallic iron. Blast furnaces require, at the barest minimum, an iron grade of 58% (Halt and Kawatra, 2013). Often, iron ores are upgraded well beyond that, as this significantly reduces the slag volume during blast furnace processing. Direct reduction processes also require higher iron grades.

Thus, most iron ore which is mined undergoes a concentration process of some variety. This typically involves crushing the iron ore to its liberation size, separating it via either surface selective flotation or magnetic separation, and then filtering it to remove excess water (Eisele and Kawatra, 2003; Zhang et al., 2019).

In all of these cases, the concentrate has had its size reduced to a fine dust, which presents many challenges for both transportation and utilization (Copeland et al., 2019). Fine dusts can be easily caught in the air, resulting in product losses to the wind and atmosphere while presenting considerable worker health risks due to exposure to fine airborne particles. Furthermore, the tight packing that fine dusts would produce in the blast furnace would completely obstruct air flow within the furnace. To avoid these problems, the finely ground concentrated iron ore is agglomerated into a larger, more manageable form.

In current practice, the most popular agglomeration technique is pelletization (Meyer, 1980). The pelletization process consists of rolling a slightly wetted granule over finer particles of material, which then layer onto the granule forming a larger granule. Iron ore pellets are typically controlled to a fairly tight size range around 9-12mm in diameter, and properly formed pellets are approximately spherical (Halt, 2017). After an induration step these pellets have considerable compressive strength, exceeding 1780N (400lbf), allowing them to be stacked tall in the blast furnace without being crushed (Halt, 2017). The spherical nature of the pellets limits the maximum packing which can be achieved, allowing for air flow within the blast furnace to be maintained through the void space between the pellets. Additionally, these pellets are significantly easier to transport between facilities, and do not give rise to nearly as much airborne dust.

1.1.1 Goals of Pelletization

The iron ore pelletization process has several goals. The primary intent of pelletizing the fine iron ore concentrate is to make it easier to handle and easier to effectively reduce to

metallic iron. To provide appropriate context, the aspects leading to these properties will be discussed individually.

With regards to shipping and handling, the final pellet product has several advantages over the fine concentrate. The most ubiquitous of these is that it is easier to transport the larger 9-12mm pellets than it is to handle piles of dust. Less dust is kicked up by gusts of wind or unexpected air currents, leading to less product loss and a safer and more manageable working environment. Hardened pellets can be effectively loaded and unloaded into containers without excessive loss of material to impact, abrasion, or an inability to recollect it. The fine concentrate however, while resilient to impact and abrasion as its size is not readily reduced further without grinding, can be quite challenging to handle in comparison.

Before hardening, however, pellets are rather weak. The goal when making green pellets is to make a green pellet with a good composition, good microstructure, and which is able to survive the hardening process. The hardening process involves sintering the pellets at upwards of 1200°C, and the period of pre-heating where the green pellets lose their moisture is when the pellets are at their absolute weakest. The green pellets must be able to withstand the thermal stress of the rapid heating as they enter the sintering kilns, or they will shatter. The pellets which do survive the sintering process are much stronger than the green pellets, with compressive strengths typically exceeding 1760N (400lbf).

One key property to handling before sintering is the ability for the green pellet to survive mild drops, such as those between sections of conveyor belts. This is often tested via the wet drop number, which measures the average number of drops the pellet can withstand before fracturing. The wet drop number depends not only on the compressive strength but also the plasticity of the green pellet. Green pellets can become highly plastic under some conditions, which can impart a significant amount of durability to the pellet but can also allow for an excessive amount of deformation during handling.

To summarize thus far, for the sake of creating a pellet which can be handled easily, it is important that the pellet become strong enough to survive the sintering process. Once that has been achieved, the pellets will often be physically strong enough for all transportation purposes and will be strong enough to survive being stacked in the blast furnace. The other aspect which matters for handling is material loss, particularly to abrasion, impacts, and dustiness.

Note that a high compressive strength does not necessarily mean that the pellet is resistant to material losses – very strong bonding can be achieved in a pellet after sintering, as the sintering physically fuses the iron ore concentrate together using the silica remaining after pelletization, but if the microstructure is poor then the stresses on any particular section may be very high. If sufficiently small section points out sufficiently far, then as the pellet rolls over that section, that section must support the entire weight of the pellet. Even though each pellet weighs only a handful of grams, these sections may be very small themselves on rougher pellets. As a very rough back-of-the-

envelope example, 1mN divided over an area of $1\mu\text{m}^2$ is almost 100000atm worth of pressure. One could never reasonably expect pellets to have load bearing areas that fine, precisely because the amount of pressure the pellet's weight can exert on the offending area is so extreme. Thus, the abrasion resistance and dustiness depend significantly on the precise structure of the pellet's exterior, while the compressive strength of the pellet depends largely on the bonding forces available in the pellets interior. While there is a weak correlation via the bonding strength, as loose of a term as that is, these properties can vary considerably with respect to each other.

The blast furnace is another major contributor to prescribing the required pellet properties. In the blast furnace, pellets are stacked on top of each other and a very hot reducing gas (typically from burning a carbon source, such as coke) is passed upwards through them to melt the iron oxides and reduce them to metallic iron. While strength is important to ensure that the pellets can survive being stacked on top of each other, it is also important that the pellets allow for this upward blast of reducing gas to proceed smoothly through the pellet layer (Eisele and Kawatra, 2003). This is to help ensure that reduction takes place in a relatively uniform, smooth, and complete fashion.

This airflow requirement is met, primarily, by the narrow uniform size distribution and consistent shape achieved during pelletization. Pellets are roughly spherical, and the size distribution of 9-12mm helps guarantee that the packing of the pellets is not too much tighter than the packing of similarly sized uniform spheres (Eisele and Kawatra, 2003). The tightest packing of equal spheres is known to have a void fraction of 0.25952, which was proved by Gauss in 1831. The addition of size and shape variations will more often than not decrease the void fraction that the blast furnace uses for airflow, so the number for equal spheres should be taken as a very rough estimate for what might be achieved within the blast furnace.

Instead this number should be compared to the nearly 0 void fraction most fine powders will achieve, owing to the very wide size distributions available in a typical powder. While in truth even fine powders will not pack perfectly the space remaining in such a powder will still be too small to allow for effective air flow. Additionally, even if the fine powder did not pack so tightly as to completely obstruct air flow then the upward blast in the blast furnace would tend to blow the powder out of the furnace regardless (Eisele and Kawatra, 2003).

Again, to summarize, the requirements for pellet size and shape are defined by the necessity to maintain airflow within the blast furnace. Without these size and shape requirements being met, the difficulty of reducing the pellets in the blast furnace varies from highly impractical to completely impossible. These size and shape requirements are also the reason why a pellet shattering during the sintering process is undesirable. Once the pellet has shattered it has broken into smaller, irregular pieces which can block the airflow within the blast furnace.

However, the macroscopic flow of air within the furnace is only one aspect of pellet reduction. It is also important that the reducing gases be able to penetrate into the pellet, so that the iron oxides trapped inside of the pellet can be reduced. This requires maintaining moderately low silica content, so that the sintering process does not simply coat the entire pellet in a resilient layer of glass. The silica within the iron ore requires significantly harsher conditions to reduce. While the blast furnace will eventually melt the silica into the slag phase, because of this same slag phase one cannot rely on this melting process to actually expose the remaining iron oxide to the reducing gas phase. This is one aspect which leads to the iron grade requirements of pellets, though there are others which are typically more pressing overall which will be discussed a bit later.

The microscopic air flow also requires maintaining reasonably high pellet porosity. If the pellet porosity drops too low, then the flow of reducing gases within the pellet can be greatly slowed. 0.3 to 0.35 can be considered to be a fairly typical range of pellet porosities (Halt, 2017). Higher porosities tend to indicate better pellet reducibility, because of the increased ability of the reducing gases to penetrate into the pellet, but are also correlated with a drastic decrease in pellet strength. Thus, pellet reducibility and pellet strength represent a tradeoff to be made in the pelletization process. Different reduction processes have different performances and tolerances, so which of the two is more important and whether or not either can be sacrificed depends heavily on the ultimate destination of the pellet.

The nature of the blast furnace process contributes another major factor to the pellet's requirements: the minimization of slag volume. This is almost wholly a requirement on the silica content of the pellet. When the silica is melted into the slag phase, its density is drastically lower than the molten iron metal phase. Thus, an equal mass of silica and iron oxide will form hugely varying volumes of slag and molten iron, respectively. Due to the limited volume of the blast furnace before it overfills and the necessity to use the volume efficiently, the silica content of the pellet must be minimized. At the barest minimum a 58% iron grade is required to process iron ore in the blast furnace, but a more common industry requirement is at least 62% (Halt and Kawatra, 2013). The direct reduction process, which is the major competitor to the blast furnace process, also imposes a strict silica requirement on the pellet (Halt, 2017).

These silica requirements are typically going to be stricter than the requirement presented by reducibility. With regards to reducibility, the silica must simply be prevented from coating the reducible portions of the pellet during the sintering process, which can be achieved in other manners (such as reducing the sintering time or temperature at the cost of overall pellet strength). It is largely the reduction process's slag characteristics that require low silica contents.

These pellet qualities can all be measured quantitatively as prescribed in Table 1. Table 1 describes the measures which are in common industrial use, the standards defining them (if any), acceptable ranges for industrial pellets (if any), and the methods by which to evaluate them.

Table 1: Pellet properties and testing procedures. (Halt, 2017)

Pellet Property	Test Procedure	Desired Values
Compression strength	Green (wet), dry, or fired pellets are crushed with a compression rate of 40mm/min. The maximum load before pellet failure is recorded. The testing procedure is standardized in ISO 4700.	>22 N/pellet, green or dry >1780 N/pellet, fired
Size distribution	Pellets are sieved with screens between 6.3mm and 15mm. The testing procedure is standardized in ISO 4701.	>90% 9-12mm
Drop number	Green balls are dropped 18in (45cm) onto a steel plate repeatedly until they break. The number of drops required is recorded.	>4-5 drops (But also usually <10 drops.)
Thermal shock	Green balls heated in a preheated furnace at various temperatures between (100-1000°C) for 10min. Pellets are then removed and checked for cracks. The temperature where 90% of the pellets survive without cracking is the shock temperature recorded.	>350°C
Tumble and abrasion indices	Tumble pellets in a standard pelletization drum. Sieve on 500 mesh and 6.3mm screens. Tumble Index is the percent of pellets retained at 6.3mm. Abrasion Index is the percent of mass passing 500 mesh. Procedure is standardized in ISO 3271.	>90% pellets +6.3mm (Tumble) <5% pellets -500mesh (Abrasion)
Reducibility	Record weight loss of pellets as they are heated in the presence of a standardized temperature and reducing gas according to ISO 4695.	$>0.5\% \text{ min}^{-1} (\text{dR}/\text{dt})_{40}$
Low-temperature breakdown	Size distribution of pellets is measured after a static reduction test and dynamic tumble test. Procedure is standardized in ISO 4696.	>80% pellets +6.3mm
Porosity	Can be measured in a porosimeter. (Forsmo, 2005)	Ore dependent, always <33%.

1.1.2 Understanding Pellet Strength

While there are many aspects to pellet quality, this discussion will focus largely on the details of the wet and dry compressive strengths. The reason for the narrow scope of

discussion is to focus on the precise aspects which lead to strong pellets and to provide more precise insight into the physics at work. However, observations from the other quality measures provided in Table 1 will be taken into account, as the fundamental physics backing the quantitative assessment of compressive strength are also at play in many aspects of the pellet's overall quality.

The mathematical analysis of pellet strength usually begins with an analysis of tensile strength, however, rather than compressive strength (Rumpf, 1962; Iveson, 2001). The tensile strength is the strength of the pellet as it is ripped apart, whereas the compressive strength is the strength of the pellet when compressed under unidirectional load. The reason for the choice of modeling tensile strength is fairly straightforward: the tensile strength has fewer frictional contributions. When a pellet is ripped apart, its constituent particles do not typically end up in highly constricted, interlocking structures where friction plays a major role. In compression, however, this is perhaps the usual case. However, the tensile strength is what ultimately controls how the pellet fractures, so the compressive and tensile strength are very much related.

The simplest way to approach tensile strength is to assume that there is some average force required to split a unit area and that there is a cross-sectional area which is to be split (Rumpf, 1962). Then, this average force per unit area multiplied by the cross-sectional area of the fracture yields the total force of required quite directly.

The details then are in the assumptions required to mathematically evaluate these two terms: average tensile breaking force per unit area, and the cross-sectional area of the fracture. The latter is a matter of geometry more than forces, while the former is a matter of forces more than geometry. However, both forces and geometry can play a role in both terms.

Following one of the earliest detailed derivations (Rumpf, 1962) the fracture geometry can be assumed to be a smooth plane across which the force experienced is uniform. While in reality the fracture will deviate from this, for pellets made with very monosized, reasonably packed, and somewhat coarse size distributions it has been found to be reasonably accurate (Iveson et al., 2001). However, in cases with poor packing, uneven size distributions, or very fine size distributions, this assumption can break down. In reality, in most pellets the weakest areas inside the pellet break first, increasing the stress on the remainder of the fracture area proportionally. Once the fracture starts the stress experienced by a unit area increases, so it is as though only the weakest portion of the pellet matters. Even though in reality pellets can be very complicated, it will be assumed that the fracture geometry is relatively simple based on this minimum force for as long as possible.

The forces, on the other hand, cannot be so readily simplified. There are five major contributing factors to pellet tensile strength according to Rumpf (1962), of which four are primarily forces:

1. The strength of any solid bridges which are present within the particle. In iron ore pelletization specifically, this is the primary force applicable within sintered pellets. Sintering causes the silica, magnetite, and hematite to re-fuse, and this change in crystallization allows the formation of solid bridges. However before sintering these forces are largely absent in iron ore pelletization. There are no commonly used iron ore pellet binders which form solid bridges between grains at low temperatures, though such “cold-bonding” has been investigated (Capes, 1972; Eisele and Kawatra, 2003).
2. The strength of the interfacial forces between the liquid and solid phases within the pellets, along with the corresponding capillary forces arising from those interactions. Because iron ore is somewhat hydrophilic, the aqueous phase which is present in green pellets can contribute to the overall binding of the pellet at lower moisture contents. At higher moisture contents (typically above 11%), the pellet becomes saturated with water and the water surface fully extends beyond the pellet’s boundaries. Above this saturation point, the interfacial forces within the pellet quickly vanish, and the pellet essentially collapses into a muddy puddle. Below it, however, the aqueous phase’s comparative aversion to forming liquid-gas surfaces contributes significantly to the binding of the pellet. There are limitations to the overall strength of these bonds, as they do not immobilize the constituent particles with respect to each other as much as it constrains the entirety of the pellet to within the liquid volume.
3. The adhesional and cohesional forces arising in fixed liquid bridges between particles within the pellet. These are the largest contributor to the strength within green pellets, and correspond to the forces that arise as particles of the pellet are being pulled apart and the liquid layer begins to stretch and narrow between the particles. These bridges end up representing a major contribution to the tensile strength because of their extended reach and considerable strength. However, they contribute to compressive strength as well, because the fracture that occurs under compressive stress is still ultimately a tensile fracture.
4. Attractive forces arising from the electrostatic conditions within the particle. This can refer to the attractive forces resulting from a high concentration of ions within the aqueous phase, or to the van der Waals forces arising from extremely close surface contacts. The van der Waals can be a major contributing force at extremely fine size distributions or where extremely close contacts can be expected, but have an active range on the order of 100 Angstroms (Rumpf, 1962). The electrostatic forces arising from ionic matrices in aqueous solutions are typically negligible on their own (Rumpf, 1962). However, keep these forces in mind going forwards through this discussion, as the intent of this work as a whole is to explain that the role these forces play within the pellet is perhaps far more significant than previously thought.

5. Lastly, geometric interlocking of particles within the pellet. Rumpf (1962) acknowledges these forces and promptly assumes them away (by assuming that pellets are composed of uniform spheres, which under tension essentially cannot interlock), but they can be a considerable factor when explaining the activity of certain binders. For example, sodium bentonite, which is very commonly used in the U.S. as an iron ore pellet binder, is known to expand significantly as it absorbs water, and it achieves very good contact within the pellet (Eisele and Kawatra, 2003). Between a combination of geometric interlocking and electrostatic interactions, sodium bentonite has been found to be a very reliable pellet binder, especially as it can persist in the pellet up to sintering temperatures and continue to contribute to the pellet strength in the very crucial regime of the pre-heating step (Eisele and Kawatra, 2003; Casey, 2016; Halt, 2017).

Between these five effects, the one which has received the most overall attention is the effect of the fixed liquid bridges. These are a major contributor to the strength especially of green pellets. The strength of dried pellets is typically lower, due to the absence of an aqueous phase, but also often follows the strength of the green pellets fairly directly. Perhaps this should be attributed to the shape of the pellet. If a pellet is dried under relatively mild conditions, e.g. in a laboratory drying oven at 105°C over the course of 8-24 hours, then the structure of the pellet is not given much opportunity to change drastically. Thus, the location and quantity of bonding sites is largely the same, even if the actual force behind each bond has been decreased. Under the more extreme conditions such as the relatively rapid sintering pre-heat step in a plant, it is likely that considerable internal stresses can be evolved from the evaporation of the water.

Again it should be emphasized that the major difference between compressive and tensile strengths is largely the effect of friction (Iveson et al., 2001). Thus, it should be expected that compressive strength should be higher, in general, than the tensile strength. Additionally, it should be expected that for finer size distributions, unusual shape distributions among the individual particles, or extremely large quantities of particles (whether from larger granules or finer feeds) that the impact of frictional forces may cause the compressive strength to increase disproportionately compared to the tensile strength (Iveson et al., 2001).

There is perhaps considerable analysis which could be performed on determining the evolution of the critical weak points under compression to fully compare these two types of strengths, but again it would go beyond the scope of the investigation this particular work sought to undertake. Instead, it will be assumed that factors which increase the tensile strength should generally correspondingly increase the compressive strength, and vice versa. The frictional effects are assumed to be largely additive to the strength of the pellet, and largely consistent among pellets of reasonably similar geometries and microstructures.

One further assumption is that the pellets do not exhibit much plasticity. Large amounts of plastic deformation can render any amount of fracture strength analysis largely

irrelevant, as for the most part highly plastic pellets simply do not fracture. Instead, they deform from relatively small forces and can be broken apart by repeated interactions over a large period of time as opposed to instantaneously fracturing.

Returning to the mathematics of the issue, the original expression determined by Rumpf (1962) for the tensile strength from a liquid bridge between two equal spheres is Equation 1:

$$\sigma_t = 6 \left(\frac{1 - \epsilon}{\epsilon} \right) \frac{\gamma_{LV}}{d} \cos \theta \quad (1)$$

Where σ_t is the tensile strength of the pellet, ϵ is the porosity of the pellet, γ_{LV} is the surface tension between the liquid phase of the pellet and the surround vapor phase (the air), d is the diameter of the particles making up the pellet (which is assumed to be monosized), and θ is the contact angle between the liquid phase and the solid surface.

The term $\gamma_{LV} \cos \theta$ is also sometimes referred to as the adhesion term, and it is directly proportional to the resulting tensile strength of the pellet. In short, if the liquid phase can be made to bind strongly to the pellet, the pellet itself will be strong under tension.

The particle diameter d is inversely proportional to tensile strength in Rumpf's (1962) equation. Finer particles result in stronger pellets. This is directly caused by the increasing number of individual bonds per unit area at finer and finer particle sizes. This is also the reason that decreasing porosity ϵ results in stronger pellets.

While there have been advances since Rumpf's (1962) equation, it has provided key insights into the behavior of pellet strength under varying conditions and it still forms the basis of pellet strength modeling to this day. This work seeks to expand on those insights by highlighting and investigating key areas where Rumpf's (1962) equation is contradicted by experimental results and physical observations, both from past investigations and new work. These criticisms and the limitations of Rumpf's equation in general are discussed further in a later chapter.

1.1.3 Electrical Double Layer Theory

The key point of this work will rely on a far greater understanding of the electrical forces at play in the aqueous phase during pelletization. The electric double layer theory provides a method to understand how these forces arise, and the impact of these forces elsewhere in the iron ore concentration process has been recognized in many locations (Uwadiale, 1992; Haselhuhn, 2015).

The electric double layer is a phenomenon arising when a material surface is placed in a liquid. Especially in the case of a highly polar liquid like water and in the case of the surface of an ionic solid such as hematite, magnetite, or silica, it should be clear that the electrical potential at the point these phases meet is almost certainly not neutral. In simple

terms, the solid surface carries a charge which will influence the behavior of the fluid around it.

For example, if a negatively charged surface is placed into water, the polar water molecules will align in a fashion which minimizes the influence of the negatively charged surface. This means that the water molecules will orient themselves with the partially positively charged hydrogen atoms pointing towards the negatively charged surface. Solubilized ions will also be displaced, with negative ions being moved away from the surface and positive ions being moved towards the surface. These effects lead to the shielding of the surface charge from the solution as a whole.

The closest of these water molecules, ions, or other species will tend to follow the surface as it moves, whereas the ones which are further away will tend to move with the bulk liquid. The boundary between these two regions is called the shear plane, and represents the “surface” where the electrical potential governs the movement of the particle as opposed to the liquid. It is almost never the actual physical surface of the particle, but instead extends a very short distance past the particle’s surface into the liquid phase. The electrical potential at the shear plane is known as the zeta potential. The zeta potential largely determines the motion of the particle through an electrical field propagating through the liquid phase.

This theory applies to essentially every aspect of the iron ore concentration process. The major application of electrical double layer theory in iron ore processing is in the flotation step. Reagents are added in flotation to modify the surface chemistry of the iron ore and silica particles. These reagents include flocculants, dispersants, collectors, depressants, and frothers. Flocculants and dispersants alter the zeta potential of the surface, collectors attach to the surface to modify the interfacial tension, depressants are used to influence the effects of other reagents on specific surfaces or to modify the interfacial tension directly, and frothers stabilize the formation of bubbles in the liquid (Zhang et al., 2019).

In the desliming step that often precedes iron ore flotation, dispersion plays the same role again. However, selective flocculation has also been used in that process to selectively sink the valuable minerals to improve separation rate. In that process, known as selective flocculation and dispersion desliming, starch is added to the dispersed solution and it flocculates the iron-bearing minerals specifically (Colombo, 1980; Ma, 2012). Thus, the gangue minerals (typically silica) are allowed to remain largely suspended while the iron ore agglomerates at the bottom of the deslime thickener unit.

In filtration, the strongly dispersing conditions maintained through flotation suddenly become undesirable. Highly dispersed solutions filter very slowly, as the finest material is free to maneuver and block the filters. If the solution is flocculated, such as by neutralizing the dispersant, then the filtration rates can be increased significantly (Kawatra and Claremboux, 2019). Very often the dispersant in these conditions is simply

a pH modifier, such as sodium hydroxide, which can be neutralized with an acidic compound such as carbon dioxide (Kawatra and Claremboux, 2019).

The effects of flocculation and dispersion appear even as early as the crushing and grinding stage, where dispersants are added to decrease the grinding energy requirement (Fuerstenau, 1995). This energy decrease is primarily attributed to a reduction in slime coating during grinding, which can absorb a tremendous amount of energy while preventing the coarser particles from being crushed.

It should not be surprising then that it may also play a critical role in the pelletization process, but this has not previously been investigated.

To understand how flocculants and dispersants influence the zeta potential is a bit more involved. Dispersants largely involve accumulating a large set of similarly signed charges at the particle surface. Maintaining a very high or very low pH is often sufficient for oxide minerals, as the oxides become hydrated over time and these hydrated sites can dissociate and lose their hydrogen or acquire hydrogen cations from solution (Uwadia, 1992; Haselhuhn, 2015). In either case, the surface gains a large quantity of similarly signed charges. For iron ore specifically, the acidic case is of considerably less interest, as iron oxides can become soluble at such conditions which presents its own considerable processing difficulties. Otherwise, dispersants can also include reagents which specifically adsorb to the particle surface but have tailing functional groups with considerable charge.

Flocculants behave largely similarly, and again flocculation can be induced by changing the pH. Flocculants can act via a variety of mechanisms, such as by directly bridging similar particles together or inducing capillary effects between particles even within the liquid phase, but the ones of greatest interest for this project are those which lower the absolute value of the zeta potential. These reagents are usually specifically adsorbed ions which have opposing charges to the existing surface charge.

In both cases, these reagents typically depend on specifically adsorbed ions. These are ions which attach to the surface for reasons that extend beyond simple charge negation within the solution. Specifically-adsorbed ions are dependent on the material in question, but for both iron ore minerals and silica polyvalent metallic cations (especially Ca^{2+} and Mg^{2+}) are typical examples. These ions penetrate through the shear plane to bind directly to the surface of the silica or iron ore. Conversely, non-specifically adsorbed ions may or may not penetrate through the shear plane, but largely only contribute to the dissipation of the surface charge. Thus, a sufficiently high concentration of specifically adsorbed ions in solution may continue to attach even past the point of flipping the sign on the zeta potential, but non-specifically adsorbed ions will never result in a sign change.

As previously mentioned, the zeta potential is strongly correlated with the movement of the particle under an electrical field in the liquid phase. Large zeta potentials of the same

sign are considered dispersing conditions for this reason – similarly signed charges repel each other, and thus result in the dispersion of the elements of the solution.

Small absolute zeta potentials are considered flocculating conditions and have exactly the opposite effect. Small zeta potentials imply small repulsive forces, limiting the extent to which particles can be separated. The vast majority of the inter-particle interactions besides zeta potential are found to be attractive, after all. These forces include primarily electrostatic effects such as van der Waals forces and capillary effects based on surface energy.

Large zeta potentials of opposing signs are an uncommon situation, but lead to extreme flocculating conditions. These potentials actively pull the oppositely charged surfaces together, a phenomenon referred to as heteroflocculation or heterocoagulation (Fuerstenau et al., 1958; Iwasaki et al., 1962; Usui, 1972; Uwadiae, 1992). Note that all surfaces of the same chemistry are likely to have very similar charges in the same liquid system, and thus heteroflocculation predominantly occurs between different species.

In iron ore flotation, heteroflocculation is one of the major reasons why silica slimes prevent the successful flotation of iron ores or silica under mildly acidic conditions. Under these conditions, the silica slimes and the iron ore surfaces have oppositely charged surfaces, which lead to the ultrafine slime particles coating the iron ore. Thus, the surface chemistry of the whole agglomerate behaves like silica, making the surface-selective flotation process essentially useless. This issue is avoided by proper desliming (Zhang et al., 2019), which is a common step taken during the concentration process.

1.2 Limitations of the Rumpf Equation

The properties of pellets can vary significantly based on the exact conditions under which they are pelletized. Several of the most important variables include the size distribution of the solid materials, the interfacial forces between the solids and the liquids present, and the saturation of liquid within the pellet (Rumpf, 1962; Iveson et al., 2001; Benali et al., 2009). The manner in which the liquid binder is added and the forces experienced by the pellets during the pelletization process play a significant role in determining how the pellets can form, influencing their size and bulk density (Iveson et al., 2001).

Iveson et al. (2001) said that granulation processes were often considered an “empirical art”, to mean that the industrial operation and design of these processes were largely based on prior experience. While almost every aspect of pelletization has been studied to great detail the connections between these separate fragments of knowledge remain somewhat more difficult to process. Pelletization takes place with relative particle velocities on the order of 1 m/s (Iveson et al., 2001), which presents notable difficulties for systematic and rigorous data gathering for the dynamic parameters of interest. While it is certainly possible to use existing knowledge and data to model pelletization procedures in a rigorous fashion (Litster, 2003), there are several aspects where predictive power is still lacking.

Rumpf's equation has been previously shown in this work, but is repeated here for clarity as Equation 2 (Rumpf, 1962; Iveson et al., 2001).

$$\sigma_t = SC \frac{1 - \varepsilon \gamma_{LV} \cos \theta}{\varepsilon d_p} \quad (2)$$

Where σ_t is the tensile strength of the granule, S is volume fraction of pores saturated by liquid, C is a material constant which depends on the geometry and is 6 for the uniform sphere geometry that Rumpf assumes, ε is the pellet porosity, γ_{LV} is the surface tension between the liquid binder the vapor phase present (typically air), θ is the contact angle between the liquid binder and the solid materials being bound (assuming a single solid species is present), and d_p is the diameter of the particles making up the pellet (Iveson et al., 2001).

This equation is derived by a theoretical analysis which considers a fracture plane formed within a pellet composed entirely of uniform, mono-sized spheres. Rumpf's (1962) approach essentially totals the force required to break every bond which occurs along this fracture plane. The bonds found to be most important in this analysis are those based on capillary forces evolved due to the liquid bridges being broken as the pellet is torn apart.

Rumpf's equation provides insight into the importance of porosity and pellet structure in pellet strength, along with the role of the liquid binder. The ability to identify its limitations has improved the understanding of the physics involved.

There are several known weaknesses of the Rumpf equation (Iveson et al., 2001), primarily stemming from the unrealistic nature of its assumptions for most pelletizing processes and from neglecting forces on both the extremely small and large scales of particle sizes. However, the Rumpf equation has been successful in guiding thought on developing pelletization processes and understanding the forces involved in pelletization since its origination in the literature. Rumpf's equation is also limited in its ability to handle variations in binder systems beyond simple surface tension changes – so binder systems with added complexity, such as solid binders (as in Eisele and Kawatra, 2003), precipitating solids (as in Delenne et al., 2011), or significant surface charges (as in Halt and Kawatra, 2017) are all beyond its ability to explain in its original form.

For the sake of completeness, it should be acknowledged that there have been several improvements made to Rumpf's original model, which has been found to very often over-predict the strength of many agglomerate systems (Bika et al., 2001; Iveson et al., 2001). Kendall's model is conceptually very similar, but separates out the terms involved slightly differently, using a porosity term which is quartic instead of semi-linear and based on interfacial energy instead of interfacial forces (Bika et al., 2001). This model represents a substantial improvement in quantitative accuracy over Rumpf's original

equation (Bika et al., 2001), but the similarity of the analysis and assumptions means that the points reviewed in this chapter are still rather applicable.

The value of improving on the modeling of pellet strength stems from the ability to create stronger or more consistent pellets from fewer or less expensive materials, the development of more reliable or controllable pelletization processes, or potentially an increase in pelletization throughput or efficiency. Rumpf's (1962) equation fails to predict the effects of dispersants or flocculants, and thus is missing some fundamental aspect of the physics from its formulation.

1.2.1 Applicability of the Rumpf Equation

The assumptions of the Rumpf equation are rather stringent, and cannot be said to closely resemble the reality of most pelletization situations. Despite this, the trends predicted by the Rumpf equation have been verified for most scenarios in sign, if not precisely in magnitude (Iveson et al., 2001).

1.2.1.1 Uniformly Spherical, Mono-Sized Particles

One of the major assumptions at the core of Rumpf's (1962) analysis is the assumption that granules were uniformly distributed, mono-sized spheres. This assumption is greatly at odds with the reality of most pelletization processes. It is very often that the powders being granulated are those which have been crushed or ground and thus often have very wide size distributions and decidedly non-spherical shape distributions.

Never-the-less, there are some situations wherein the assumption is accurate. In tests where the materials are screened to a nearly mono-size distribution, tests where the materials are nearly mono-sized to begin with, or processes in which the feed material is formed by a relatively consistent and controlled physical process it is possible to acquire a pelletization feed which meets at least the size requirements of the assumption. In these situations it has been found that, except for very large or very small particle sizes, Rumpf's equation holds rather well (Iveson et al., 2001). The failings at very large or very small particle sizes are likely attributable to the limitations of other inherent assumptions with Rumpf's equation, particularly that the dominant force at work in holding the pellet together are capillary forces.

However, even for size distributions which grossly violate this mono-size assumption, the trends of Rumpf's equation still typically hold. Rumpf's (1962) analysis specifically addresses the reasoning as to why the assumption is allowed as a mathematical convenience rather than necessarily discarded for its unrealistic nature. In particular, Rumpf (1962) refers to an earlier work wherein it is hypothesized that the largest particles in the granule end up being coated in smaller particles which contribute the majority of the binding forces. Thus, it is not so-to-speak the strict average particle size which contributes to the granule strength, but the particle size which contributes the

majority of the bonds – that is, the smallest populous particle size. Effectively, Rumpf (1962) asserts that the larger particles contribute nothing to the binding of the pellet.

The effects of the particle shape distribution however remain more complex. It should be obvious that generically classifying particle shapes is a difficult endeavor at best, but the effects of particle shapes cannot be completely disregarded either. There have been some studies addressing the impact of shape on granulation kinetics, such as Cavinato et al.'s (2010) work, but it remains a relatively obscure issue. It seems likely that highly aspherical shape distributions would tend to lead to greater amounts of particle interlocking and frictional interactions. It is unlikely that the issue of particle shape can be generally unwrapped into a short and simple expression, and instead may need to be investigated using far more complex modeling techniques such as discrete element methods.

It is also important to note that the shape distribution of particles can have a significant and unintuitive effect on particle motion in aggregate. An example known primarily from mathematical simulations is that stacks of perfect spheres do not have an angle of repose (Matuttis and Chen, 2014). Thus, the fact that most materials do have an angle of repose is direct evidence of the inaccuracy of the uniform spheres assumption for those materials. The angle of repose arises from the inability of particles to roll over each other, and this is likely to have considerable impact on the frictional effects experienced by such particles during pelletization.

It is important to note that the porosity term, $(1 - \varepsilon)/\varepsilon$, is dependent on the uniform mono-sized spherical geometry and a certain type of disrupted spherical packing. The direct predecessor to this term in the derivation is $k(1 - \varepsilon)/\pi$, where k is the coordination number and π is the constant (Rumpf, 1962). The π is then replaced with $k \cdot \varepsilon$ based on an empirical correlation for the coordination number of displaced spheres to form the more commonly used term (Rumpf, 1962). However, changing the shape distribution means that the coordination number's dependence on the porosity can change more drastically than the current correlation, which should be kept in mind. It is also worth noting that in general this simplification is a significant assumption about the packing of the spheres which need not hold in general for any given porosity value (Bika et al., 2001).

Perhaps the most direct method handling cases besides mono-sized spheres is to directly include the geometry in the problem solving. Discrete element methods and other analytic techniques have been applied for quite some time to these systems (Bika et al., 2001), but require much more computation overall.

Efforts in discrete element modeling have highlighted one of the most important quirks of modeling with perfect spheres – perfect spheres can always roll over each other. A pile of perfect spheres experiences no angle of repose for realistic frictional forces, as there is no way for the force at the top of a pile to be counterbalanced by the spheres on the bottom without something rolling out of place. Thus, it is sufficient in many cases to say that

because some material has an angle of repose, meaning that it can be stacked into a pile of granules with some angle maintained between the ground and the surface of the pile, then the granules are not perfect spheres.

This would also imply that during pelletization, the kinds of frictional effects observed between small, smooth, and spherical particles are completely different than the frictional effects which would be observed between small, smooth, but rough particles. Particles with flat surfaces can interfere with each other's rotation, and particles with rough surfaces can become interlocked with each other. While spheres are always free to roll over each other, real particles are not.

1.2.1.2 Uniform Distribution of Liquid

Rumpf's (1982) analysis assumes that the liquid distribution can be modeled with a single term (S), which is linearly correlated to the tensile strength. This is found to be relatively accurate at low saturation values and for coarse particle size distributions, but there is a distinct point for finer size distributions where increasing the liquid saturation begins to sharply decrease the pellet strength (Iveson et al., 2001). Above this critical saturation value, the strength decrease is attributed to lubrication effects (Iveson et al., 2001).

It is also important to note that somewhat uneven liquid distributions can form during pelletization, especially if water is added during the process. These effects can have a distinctive impact on the kinetics of the pelletization process overall (Iveson et al., 2001), but likely even out by the point where static strength testing is being performed.

Rumpf's (1962) analysis also assumed the presence of a liquid phase in general, and is not directly applicable to the determination of dry pellet strength. Dry pellet strength can be derived from a variety of factors, including solid bridging by cementation with the dissolved solids (Delenne et al., 2011), the addition of solid binders which may operate via a variety of mechanisms (Eisele and Kawatra, 2003), or by short range interactions such as van der Waals forces even in the absence of any additional binders.

1.2.1.3 Simultaneous Breakage along Fracture Plane

Rumpf's (1962) analysis is based on the assumption that all of the bonds on the fracture plane are stressed uniformly during tension, and thus that all of them must simultaneously be broken to result in fracture. In reality, some bonds will be stressed more than others and break first, concentrating the force among the remaining bonds. Thus, the simultaneous breakage assumption would be expected to tend to lead to over-estimates of the tensile strength.

This effect has been credited for the overestimation of pellet strengths for large mono-sized particles (Iveson et al., 2001). In pellets made from large particles, the forces applied tend to be relatively more concentrated, leading to fracture growth through the

pellet rather than the instantaneous failure of the whole fracture plane. This can be accounted for by using a quartic porosity term instead of a linear one (Iveson et al., 2001), but this represents a significant departure from the original analysis. Kendall's model includes such a porosity term, and additionally a term for maximum flaw size within the crystal structure (Bika et al., 2001), and tends to show greater accuracy in such cases.

Naturally, this assumption also fails for pellets which are capable of undergoing plastic deformation. Plastic deformation allows the pellet to change shape under force without fracturing, and the analysis of Rumpf's equation will tend to underestimate the forces subsequently required as it does not account for the energy loss from the deformation. In the plastic deformation case as well it would seem probable that the correlation between tensile and compressive strength could change significantly, as plastic deformation implicates significant viscous and frictional effects from the liquid binder phase.

1.2.1.4 Primary Binding Force is Capillary Bridging

Rumpf's (1962) analysis assumes that the majority of pellet strength stems from the effect of the interfacial forces within capillary bridges. For moderately sized and wetted particles this is a reasonable assumption, since the capillary bridges can be retained for longer than most other influences under tensile strain. In this case, moderate size would be taken to mean particles significantly larger than the typical length scales of van der Waals interactions of approximately 100 nm (Rumpf, 1962) and small enough to avoid the large scale length effects stated in the prior assumption.

For extremely small particles, however, van der Waals forces may become more important (Rumpf, 1962). Frictional forces also begin to play a major role in very fine size distributions, and in these cases Rumpf's analysis typically underestimates pellet strength (Iveson et al., 2001).

For very large particles, the effects of capillary pressures become less relevant than more macroscopically familiar forces, especially gravity. Combined with a decreasing number of bonds per unit surface area, it is unsurprising that pelletizing with very coarse material is comparatively ineffective.

Frictional forces and viscous forces require a dynamic strength approach to handle appropriately rather than a static strength analysis. This requires a different approach entirely, and no longer describes static tensile strength. Iveson et al. (2001) reviews the matter in detail, but a quick summary of the matter is that in situations involving very fine particles especially, the dynamic strength of pellets can be orders of magnitude larger than the static strengths.

The choice of capillary bridging effects alone is also perhaps incomplete. It has been found that surface charge effects, such as those caused by flocculants or dispersants, can have a significant impact on pellet strength (Halt and Kawatra, 2017). These effects

would occur in tandem with the capillary bridging forces, not as a replacement of it, and are most often repulsive in nature. Despite the implications of repulsive forces within Rumpf's model, experimental results found that the binder systems with the largest surface charge repulsion were also the ones which produced the strongest pellets (Halt and Kawatra, 2017). The theoretical explanation provided is relatively limited, suggesting that the pellets were stronger due to kinetic processes which occurred during the pelletization process. However, the experimental differences exceed what could plausibly be allowed by porosity differences alone.

It is certainly possible to use a portion of Rumpf's analysis to substitute alternative static binding forces in. Equation 3 shows the force term separately, using the same variable names as Equation 2 with the addition of the binding force term F (Rumpf, 1970; Wollborn, 2017):

$$\sigma_t = \frac{1 - \varepsilon}{\varepsilon} \frac{1}{d_p^2} F \quad (3)$$

This arrangement allows the substitution of any static adhesion force as necessary, such as van der Waals interactions. This can also be used to implement refinements of the modeling of capillary bridging forces which have been developed over the years, such as the numerical fits reported by Willet et al. (2000).

1.2.1.5 Tensile Strength vs. Compressive Strength

Rumpf's (1962) analysis primarily focuses on tensile strength due to the comparative mathematical simplicity and the necessity that any fracture must at least meet the tensile strength to cause the breakage. However, compressive strength is an important measure for many applications as well, as pellets are often stacked on top of each other or expected to resist moderate to extreme loads. Because the formation of a fracture requires exceeding the tensile strength in at least one direction, the two strengths share a considerable correlation with each other (Rumpf, 1962; Iveson, 2001; Wollborn et al., 2017).

However, the compressive strength's correlation with tensile strength is not cut and dry, as it depends heavily on the brittleness of the pellet, the capacity of the material to deform, and the evolution of frictional forces as the pellet is compressed. Under tension, especially in brittle pellets, the particles are not being forced into each other but in compression this is instead precisely what occurs.

Common correlations between compressive and tensile strength have compressive strength as between 40% to 700% higher than the tensile strength, depending on the specifics of the material and geometries involved (Bika et al., 2001; Wollborn et al., 2017). However, the correlating factors remain largely empirical derivations, aside from the theoretical 700% for ideally elastic and brittle materials (Bika et al., 2001). However, it does appear that the correlation factor remains relatively constant for similar materials under similar testing conditions, leading to a roughly linear correlation between the

tensile strength predicted by Rumpf's equation and the measured compressive strength for small differences in input conditions.

There is also a critique by Darvell (1990) that posits that the tests used for both compressive or tensile strength are perhaps not measuring the theoretical tensile strength of agglomerates. Instead, it is suggested that common tensile and compressive strength tests are both subjecting the pellets to failure modes that implicate shear failure. However, in this case then it can be stated that despite the comparatively unexplained nature of the true failure mode, then the empirical strengths in question are both related to the same fundamental property of the pellets and thus could be expected to be correlated. Further, this criticism does not diminish the fact that Rumpf's model and modifications have been effectively used to model many agglomerate processes. Even in shear failure it remains the case that the pellet can only be broken by breaking the bonds along the fracture plane, so Rumpf's equation would be expected to provide insight if not necessarily precision into the process regardless.

1.2.1.6 Wet vs. Dry Compressive Strength

Rumpf's (1962) analysis is largely dependent on the presence of liquid bridging and the resulting interfacial forces. Thus, it is not directly applicable to the compressive strength of dried pellets. However, pellets do tend to dry over time, and there are industries which intentionally dry pellets for further processing. Since wetted pellets are held together by the capillary forces of the liquid binder phase, the drying process can often lead to weakening of the pellets, and often it is when these pellets are at their weakest that they are most likely to be subjected to considerable stress.

It is possible to account for the strength changes during drying in terms of cementation processes where dissolved solids precipitate as the water evaporates. Delenne et al. (2011) provides a crystallization law and a simple method of accounting for the resulting solid bonding in terms of particle pair interactions, which could potentially be applied within the modification presented in Equation 2.

1.2.2 Developments from Rumpf's Equation

Rumpf's equation has led to the theoretical identification and understanding of several critical factors for controlling pellet strength. While there are significant accuracy issues with Rumpf's equation when it comes to precisely predicting pellet strengths (Iveson et al., 2001), it does serve to very effectively highlight several trends within the pelletization process.

In particular, it highlights the importance of pellet porosity and coordination number, the impact of the liquid binder's surface tension on tensile strength, and the impact of the particle diameter. More than merely identifying these critical variables, it explains in detail why each of these variables is important.

Perhaps more illuminating than its explanations are the places where it is insufficient. As highlighted, many of the assumptions in Rumpf's equations are only vaguely applicable to real pelletization situations. Highlighting where they have failed and what has been done to manage that has led to further insight into the nature of the process.

Perhaps the key failure to highlight is the behavior of very fine and non-uniform particle size distributions. Rumpf's equation often underestimates the strengths of pellets formed from such distributions (Iveson et al., 2001), but these sorts of powders are not at all uncommon in industrial practice. The very fine powders present a complex physical situation wherein viscous and frictional forces play a major role and where van der Waals interactions can become dominant as surfaces come into close contact. The geometries of these fine powders are rarely truly spherical, and the geometries of the granules formed can become intractably complex.

Another interesting point which has recently arisen is the influence of surface charge on pellet strength. Many inorganic compounds will attain surface charges in water, which presents an additional force which does not appear to have previously been investigated in the context of pelletization. Halt and Kawatra (2017) reported pellet strengths of iron ore pellets formed with the addition of surface charge modifiers. While it is likely that these forces are more directly implicated in the kinetics of pelletization rather than in their static strength at the end, the reported differences in strengths and porosities appear to exceed what would be predicted by the Rumpf equation. The feed material in question had an 80% passing size of 35 μ m. Using either of the common porosity terms provided by Rumpf's or Kendall's models, however, is insufficient to explain the variation in strength observed. Over porosities ranging from approximately 0.31 to 0.33, dry compressive strengths varied from approximately 30 N to 85 N. The porosity difference only allows a 9% change in compressive strength under Rumpf's model or 12% under Kendall's model, while the observed difference in strength is roughly 3 times. Even assuming an extremely drastic change in coordination number would seem to fall short, as at these porosities coordination number would be expected to be between roughly 6 and at most 12 (Bika et al., 2001). It is likely that these effects can only be described by some combination of the above.

To add to the surprise, the lower porosities and higher strengths were observed among the surface charge modifiers which were expected to increase the repulsive forces between the particle surfaces (i.e. the dispersants) (Halt and Kawatra, 2017). An increase in repulsive force during formation, which would be expected from Rumpf's equation to directly decrease compressive strength, resulted in increased dry compressive strengths. Prior to this work, the precise mechanism behind these results remains largely unexplained.

1.2.3 Summarizing Rumpf's Equation

Rumpf's equation has provided considerable insight into the pelletization process as whole. In both its successes and failures it has highlighted much of the physics at work

within pellets and within pelletization. While approaches to modeling pellet qualities and pellet strength in particular continue to advance, many of them have clearly benefited from the initial forays made by Rumpf's analysis.

However useful the equation has been however, it is important to continue to emphasize work on deciphering the reasoning behind where it fails. While many failure cases can be attributed to simply stretching its stringent assumptions too far, the modeling of fine particles in general seems to present an ongoing challenge.

Additionally, it appears that there are forces which can play a major role in pelletization which have previously been left unexplained, such as surface charge. Understanding these effects requires revising Rumpf's model with careful attention paid to the behavior of the real particles forming the pellet. By accounting for the methods in which particles can move within pellets, an understanding can be gained about how pellets grow and their overall resulting strength.

As it currently stands, Rumpf's equation fails to explain dispersion and flocculation phenomena. This work seeks to rectify that issue, providing a novel method of determining the conditions of dispersion and flocculation, and identifying the corrections required to predict the strength of pellets formed under those conditions.

2 Goals and Hypotheses

The basic intuition from the electric double layer theory and the role of forces in the tensile strength as described by Rumpf (1962) should lead one to believe that the use of flocculants will lead to the formation of higher strength pellets. This is because the flocculants increase the total force pulling the particles together and as a result increase the effort required to pull them back apart. Correspondingly, dispersants should do exactly the opposite.

However, experimentally, the opposite behavior is observed. Dispersants result in stronger pellets, while flocculants result in weaker pellets (Halt, 2017; Halt and Kawatra, 2017). These differences cannot be immediately explained in the context of Rumpf's (1962) equation, though it provides a mechanism by which to understand the issues.

The goal of this work is to provide a framework in which these differences can be understood. There are two primary hypotheses which could explain the difference between these conditions and the resulting pellets.

2.1 Hypothesis A

The first hypothesis is as follows: pellets under flocculating conditions come together too rapidly, and end up locking into loose and porous structures. Conversely, pellets under dispersing conditions come together much less hastily, and the dispersion keeps the individual particles far enough away from each other that mobility is retained for long enough for the pellet to appropriately compact. This is a rephrasing and expansion of the proposed mechanism in Halt (2017). Figure 1 presents this hypothesis graphically.

There are two key predictions which can be made from this hypothesis.

The first prediction is why flocculated pellets are rougher and dispersant pellets are smoother: the pellets formed with dispersants retain their mobility longer and compact effectively, so less material is allowed to remain jutting out on the exterior. Flocculating conditions effectively lock each newly added particle in place, however, which limits the rate at which this compaction can occur. Even if the particles are not completely locked in place, the larger flocs may form in configurations which sterically prevent them from being able to fully compact. While these results have been qualitatively observed, it is unclear from prior work that these qualitative explanations fully coincide with this particular proposed mechanism.

Figure 1: Potential reasoning for strength difference observed between flocculating and dispersing conditions. By counting the number of bonds that need to be broken to fracture the pellet, and thus determining the effective coordination number of the pellet, the difference in strength can be determined. In most cases, it would be expected to be a factor of somewhere on the order of 2 for the 2D case, and similar in magnitude for the 3D case.

The second prediction stems from the decreased mobility of flocculated pellets: this decreased mobility manifests itself as closer surface packings in various locations which should lead to highly restricted liquid flow. When these flocculated pellets are heated for drying, additional stress is placed upon the pellet internals than in a corresponding dispersed pellet. Thus, the ratio of dry compressive strength to wet compressive strength in the flocculated pellet would be expected to be lower overall than in a correspondingly dispersed pellet. This is because some stress has already been applied to the pellet, potentially weakening or breaking internal bonds and making it easier to fracture later.

2.2 Hypothesis B

The second hypothesis is that the presence of coagulants leads to the evolution of comparatively strong, very short-range, and very immobile binding during pelletization. The immobility of the binding sites combined with the relatively high binding strength leads to a rapid and nearly random utilization of binding sites. Since many binding sites are going to be very close to each other and the particles which will be attaching relatively large, several of these sites will be rendered unusable due to geometry.

This hypothesis essentially suggests that the coordination number of flocculated systems will be lower than otherwise anticipated, due to the relative immobility of the bonds making it more difficult to increase the coordination number.

To provide a very rough sketch of the extent to which this could matter macroscopically, the optimal packing of equal circles onto a 2D plane is known to be $\pi\sqrt{3}/6 \approx 0.9069$

(this result was proven by Gauss in 1831). However, if the circles are to be considered immobile once placed, the distribution of the covering fraction is significantly different.

By randomly choosing several locations to put equal circles into a fixed region of a 2D plane, it is possible to determine roughly what the resulting coverings will average out to. After 10,000 iterations of this procedure, it was found that the mean of this distribution was roughly 0.35 with a standard deviation of approximately 0.06. Thus, the average covering achieved was only about 38% of the optimal covering. While 2D planes and 3D spheres are very different, the former should provide a reasonable order of magnitude estimate of the behavior on the latter.

In particular, if the issue is on a microscopic scale, then the assumption of a 2D plane is not even necessarily an ill-conceived one. If the microscopic presence of flocculant molecules or atoms is blocking some portion of the binding surface that could otherwise have been used, then perhaps this strength reduction could be attributed to that effect.

Testing the microscopic variation of this hypothesis thankfully is somewhat easier. Magnesium and calcium are known to both be specifically adsorbed ions on hematite, but the effect of magnesium is expected to be more extreme than that of calcium in most situations involving adsorbed ions. This is due to the diameter of the magnesium and calcium cations, which are 274pm and 342pm respectively (Pyykkö and Atsumi, 2009; Haselhuhn, 2015), which are on different sides of the hematite hydroxyl spacing at 285pm (Pradip, 1994; Haselhuhn, 2015). Magnesium is small enough to attach at every available hydroxyl site but calcium can only at most at every other hydroxyl site. This provides a convenient method to investigate the impact of greater degrees of surface saturation.

The comparatively less microscopic variation of this hypothesis, as it pertains to micron scale particles instead nanometer scale, is also directly testable. Pellets are known to decrease in porosity as they roll, due in part to the abrasion of loosely attached material and in part to the compaction of the material which is already present. A comparison of the rates of compaction achieved by flocculating and dispersing conditions would allow for the potential falsification of the claim that flocculants lead to highly immobile and uncompactable pellets. An analysis of the diffusion of water through the pellets during the pelletization process would correspondingly allow for the potential elimination of effects from Hypothesis A. Since Hypothesis A does not have the framework to justify the quality differences between pellets at differing degrees of flocculating conditions, the evaluation of these conditions still requires some explanation.

3 Methods

The primary experimental methods used here are similar to those used by Halt (2017), with a focus on understanding pellet strength via dry and wet compressive strengths. Pellets were formed using a laboratory balling drum and then subjected to a variety of tests, and the pellet feed material was characterized in a variety of conditions using zeta potential measurements.

Pellets were formed in a laboratory balling drum utilizing a fine hematite pellet feed collected from an operating plant facility. This material has an 80% passing size of less than 35 μ m. The material was balled at a variety of moisture contents (in the range of 8.5wt% to 9wt%), binders (bentonite, starch), and additives (various dispersants and coagulants). The additives were chosen based on their expected flocculating or dispersing characteristics, while the binders were chosen based on typical industry usage. Thus, among the binders the primary choices were sodium bentonites and from the data collected by Halt (2017) which utilized cornstarch and wheatstarch. Binder dosages were based on typical dosages for the material in question. For bentonite, a 6.6g per kg feed dosage was used. For the prior work with starches, 0.2 or 1.0 g/kg were used instead (Halt, 2017).

The additives were more complex – the data from Halt (2017) is highly relevant to this work, and it would be remiss to omit it. The additives used there include aluminum sulfate, calcium chloride, magnesium sulfate, sodium hydroxide, sodium carbonate, EDTA, sodium metasilicate, sodium citrate, sodium polyacrylate, sodium polyphosphate, and sodium tripolyphosphate. These materials are flocculants and dispersants, see Table 2 on page 28 for details on these additives. One of the primary additional additives tested in this work is magnesium chloride, to allow for the direct comparison of calcium and magnesium compounds without variation due to differing anions.

In each case, the additives were added before the binder. During pelletization, the pellets were occasionally removed from the pelletizing drum and sieved to maintain a narrow size distribution between mesh sizes, with a final size range target of 7/16x1/2 inches in diameter. Water was added during the pelletization process using a spray bottle to maintain a balling sheen, a fine layer of water on the surface of the pellet which allows it pick up new material effectively.

The moisture content of the pellet feed was adjusted at the same time of additive addition. The target moisture content for all tests was within the range of 8.5-9wt%, and the prior data was collected at 9wt% (Halt, 2017). Additional moisture was added as necessary during pelletization to maintain a balling sheen to promote agglomeration (Halt, 2017).

Various tests were run on the pellets following Table 1 on page 6. The procedures outlined in that table were followed for all tests utilized in this work. The particular tests which were most relevant were the wet compressive strength, dry compressive strength, moisture content, and zeta potential. Porosity was also investigated briefly.

The strength of the pellet was determined by crushing a number of pellets at constant linear velocity utilizing a Mark-10 M5-50 force sensor. Wet compressive strength was tested immediately after pelletization, and dry compressive strength was tested after drying in an oven at 105°C for 24 hours.

Porosity measurements were carried out in accordance with ASTM C914-09(2015). Pellets for porosity measurements were allowed additional rolling time to compact.

Zeta potential was recorded as a primary characteristic of the pellet feed material under some of the conditions for which coagulants were added. The zeta potential for a given additive was determined by mixing a slurry of the same solid, binder, and additive dosage into a 1000mg/L suspension and utilizing a Zetasizer Nano ZS (Malvern) unit to perform the measurement.

4 Results

4.1 Dispersion vs. Flocculation

Figure 2: Dry compressive strength of hematite pellets formed under the conditions specified by Table 2 (Halt, 2017). Note that flocculants (F1-F3) decreased pellet strength compared to the baseline, pH modifiers very moderately increased strength (pH1-pH3), and dispersants (D1-D5) greatly increased strength. The strongest pellets were created with sodium polyacrylate (D3) as an additive.

Table 2: Identity and approximate zeta potential of additives used by Halt and Kawatra (2017).

Label	Additive	Observed zeta potential (-mV)
Baseline	None	23
F1	Aluminum sulfate tetradecahydrate	10
F2	Calcium chloride dihydrate	15
F3	Magnesium sulfate heptahydrate	18
pH1	50:50 ratio of sodium hydroxide and EDTA by weight	33
pH2	Sodium carbonate	33
pH3	Sodium hydroxide	33
D1	Sodium metasilicate	31
D2	Sodium citrate dihydrate	42
D3	Sodium polyacrylate	49
D4	Sodium polyphosphate	55
D5	Sodium tripolyphosphate	55

All of the pelletization experiments in Table 2 and Figure 2 took place under alkaline conditions. The porosity measurements under the same conditions are also available (Halt and Kawatra, 2017). The most flocculated conditions had a porosity of approximately 0.335, while the most dispersed conditions had a porosity of approximately 0.315 (Halt and Kawatra, 2017).

Also available was data on the water content of these pellets after pelletization (Halt and Kawatra, 2017). The moisture contents of the coagulant pellets were consistently higher, averaging around 9wt% (Halt and Kawatra, 2017). The moisture contents of the dispersant pellets were consistently lower, averaging around 8.6wt% (Halt and Kawatra, 2017). The error bars on both measurements are on the order of about 0.4wt%.

Furthermore, Halt (2017) found that the pellets created with dispersants were far smoother and produced less dust during handling than pellets created under flocculating conditions such as the starch baseline. This result in particular is interesting because there has been comparatively little insight into how to control the dustiness of pellets prior to Halt's work.

The key point to take away from this figure is that dispersants appear to promote the formation of stronger pellets in all cases, and in all cases flocculants led to the formation of weaker pellets.

4.2 Calcium vs. Magnesium

Figure 3: Impact of calcium and magnesium cations from calcium chloride dihydrate and magnesium chloride hexahydrate on the dry strength of pellets formed using bentonite as a binder. The dry strength of pellets decreases roughly linearly as the cation concentration increases. Note the unusually high strength magnesium data point at the far end of the graph.

Figure 4: Impact of calcium and magnesium cations from calcium chloride dihydrate and magnesium chloride hexahydrate on the wet strength of pellets formed using bentonite as a binder. The strength of pellets decreases significantly as the concentration of cations increase, up to a certain point. Above about 5 moles/mt solid, the pellet strength appears to level out. Note the unusually high strength of the first calcium data point.

Figure 5: Zeta potential versus wet compressive strength in pellets created with calcium chloride dihydrate and magnesium chloride hexahydrate. Note that the concentration of the cations increases from right to left, as the additives were coagulants and thus decreased the surface zeta potential of the hematite. Though the right most data points were expected to be of essentially identical composition, as neither contained any additive, they were measured to be different – potentially indicating a significant variability of the natural zeta potential of the ore.

The tests were performed utilizing calcium chloride dihydrate and magnesium chloride hexahydrate. These pellets were also generally troublesome to form, as they did not compact well while rolling and remained lumpy and rough.

4.3 Evolution of Pellet Porosity with Rolling

Figure 6: The impact of additional rolling time on the measured porosity of pellets created with bentonite binder plus additives. Note that in general the porosity experiments were subject to a lot of variability. The low Na-metasilicate point at 3 minutes may be a legitimate outlier point, or perhaps simply due to a coincidental choice of pellets to sample for that instance.

These pellet porosities were higher than expected.

4.4 Pellet Strength with Varying Dispersant Dosages

Figure 7: Pellet strengths with error bars for varying dosages of sodium metasilicate between multiple tests. The upper set of points is distinguished by having slightly lower pellet moisture during pelletization. The addition of up to 1kg/t of dispersant clearly improves pellet strength, but increases pellet strength variation. The addition of more dispersant may have a detrimental effect. Error bars are 1 standard deviation, with 40-80 pellets per test.

Figure 8: Histogram of pellet strength distributions for various dosages of sodium metasilicate dispersant. Note that the addition of any amount of dispersant allows for the formation of significantly stronger pellets, which become moderately more common once additional dispersant is added. However, adding more dispersant beyond a certain point does not further improve pellet strength.

5 Discussion

5.1 Insufficiency of Rumpf's Equation

Once again, the goal of this work is to examine how Rumpf's equation fails, and demonstrate that the shortcomings this work highlights can be overcome with a new approach. In the discussion section, we will highlight the approaches that provide an explanation for both the conditions which are established by dispersants and expected results of these conditions on pellet strength overall.

Revisiting the original reason for this research with Figure 2, we find that the strength of pellets formed with dispersants are significantly stronger than would be predicted by Rumpf's equation. If Equation 1 or 2 are to be used to explain the strength differences between the dispersant and flocculant cases, then at one of the following must be true:

- The porosity decreased by a significant amount. Changing porosity from 0.36 to 0.29 would result in a roughly 38% increase in pellet strength, according to Rumpf's equation. In actuality, the porosity difference is much smaller, from 0.335 to 0.315.
- The liquid adhesion term $\gamma_{LV} \cos \theta$ increased significantly. However, θ in water is already very small for hydrophilic surfaces in water, and hematite is close to being such a surface. Additionally, the addition of dispersants is generally expected to decrease surface tension rather than increase it. Flocculants, on the other hand, can lead to moderate increases in surface tension in some situations.
- In the dry pellet case, the strength of the salt bridges would need to have increased drastically. There is no particular reason to believe such an effect would be unique to dispersants and not pH modifiers or flocculants, aside from the polymeric nature of some of them potentially allowing for inter-particle bridging. However, even the non-polymeric dispersants led to increased pellet strength.
- The effective particle diameter decreased by a factor of up to 2. However, it is hard to justify as to why the effective particle size in the presence of dispersants was so much smaller when compared to the baseline pellets. Even if one was to assume that the particles in the baseline pellets were somewhat flocculated (perhaps due to the presence of the starch binder), it somewhat undermines the result that the flocculants performed worse than the starch did. After all, starch itself is a flocculating compound, though not strictly one which acts via surface charge.

If option 1 and 4 together fully accounted for the difference in pellet strength, then the resulting effective particle diameter was approximately 70% of that of the baseline

pellets. Even if that is the case, Rumpf's equation provides no insight into how to determine that number from the conditions provided.

The diameter dependence of Rumpf's equation is dependent on an increase in diameter decreasing the total number of bonds available to the particles (Rumpf, 1962) – so even if the flocculating conditions created flocs of higher average diameter, unless these flocs were so irregularly shaped that they could not bind with each other at their individual particle sites, that cannot explain the difference either. If that were the case, it would also be expected that there would be a wider variation between pellets with flocculants and the baseline or pH modifier pellets, simply based on the various sizes of flocs which might be formed under those conditions. This is not to say that flocs do not form during pelletization under coagulating conditions, but that they do not impact the bonding characteristics in the manner required for them to impact Rumpf's equation's diameter parameter.

It turns out that the results for the porosity under the same conditions are also available. The most flocculated conditions had a porosity of approximately 0.335, while the most dispersed conditions had a porosity of approximately 0.315 (Halt and Kawatra, 2017). That porosity difference accounts for an approximately 5% increase in pellet strength, which is clearly deficient in explaining the considerable difference in compressive strength observed.

From these observations, it is concluded that Rumpf's equation does not provide sufficient insight to be useful in explaining the effects of these reagents.

Instead, there appears to be a stepwise difference between flocculating and dispersing conditions, which is further impacted by slight differences in inter-particle bond strength between the particles. It is also worth noting that in dried pellets, capillary bridges are not present – instead, the bonds are due to precipitated solids, particle interlocking, and the presence of any solid binders (Rumpf, 1962; Capes, 1972; Bika et al., 2001; Delenne et al., 2011). These can be treated using the same framework, but it should be noted that the strength of these bonds cannot depend on the properties of a liquid environment. It should be relatively safe to assume that there is not a tremendous amount of variation between the strength of these bonds, even in the presence of the additives.

Furthermore, Halt (2017) found that the pellets created with dispersants were far smoother and produced less dust during handling than pellets created under flocculating conditions such as the starch baseline. This result in particular is interesting because there has been comparatively little insight into how to control the dustiness of pellets prior to this work. Traditionally, organic binders such as starch have been considered too dusty to use industrially, but Halt's work provided insight into how to eliminate that problem. However, it did not provide a strong mathematical justification as to why these phenomena were observed. It does provide strong qualitative evidence that there is a fundamental distinction between how dispersing and flocculating conditions impact pelletizing kinetics.

Aside from Halt (2017), there has been essentially no previous work connecting the effects of the electrical double layer to the quality of iron ore pellets. It is clear that the effect of dispersants extends beyond the bounds of prior understanding, and the goal of this work is to help provide insight into these effects.

5.2 Explaining Dispersion vs. Flocculation

As mentioned in the preceding section, it has been found by Halt (2017) that pellets formed with dispersants are approximately twice as strong under compression as the baseline pellets, which are in turn modestly stronger (roughly 10-20%) than pellets formed with coagulants. The focus is to explain the forces which lead up to this effect – that is, to identify consistently the conditions which can be considered dispersion or flocculation. The resulting conditions are then combined with the corrections proposed in Hypotheses A and B and compared with the experimental results to show where the proposed model describes existing data points, and which data points remain unexplained.

Rumpf's equation in its widely reported form is incapable of explaining this effect, but perhaps by returning to the original derivation a more appropriate expression can be found. One particularly general expression of Rumpf's equation, reproduced as Equation 4 here using the notation presented by Bika et al. (2001), is perhaps the most widely cited of the micromechanical models for predicting pellet strength.

$$\sigma_t = \frac{1 - \varepsilon}{\pi} \left(\frac{QF}{d^2} \right) \quad (4)$$

Where σ_t is the tensile strength of the pellet, ε is the porosity of the pellet, Q is the average coordination number within the pellet, d is the characteristic diameter of the particles composing the pellet (assumed to be uniform spheres), and F is the strength of a singular bond holding the particles within the pellet together.

Many other forms are often quoted, including substitutions of F for capillary bridging presented as Equation 5 or using an empirical correlation for the coordination number Q presented as Equation 6 (Rumpf, 1962).

$$F_{cap} = SC\gamma d \cos \theta \quad (5)$$

Where F_{cap} is the bonding force due to a capillary bridge between two particles, S is the extent of liquid saturation within the pellet as a volume fraction, C is a geometric constant which for uniform mono-sized spheres is 6 (Rumpf, 1962), γ is the surface tension of the liquid, d is the characteristic particle diameter again, and θ is the contact angle of the liquid with the solid phase.

$$\varepsilon Q \approx \pi \quad (6)$$

The correlation presented in Equation 6 is based on an empirical correlation available for ragged sphere packings during Rumpf's original derivation. It is often used to eliminate the coordination number dependence from Equation 1. Combining Equations 4-6 recovers perhaps the most often cited version of Rumpf's equation, presented again as Equation 7:

$$\sigma_t = SC \frac{1 - \varepsilon \gamma \cos \theta}{\varepsilon d} \quad (7)$$

The variables are the same as used previously in Equations 4 through 6.

Most of the predictions of Equations 4 and 7 have been experimentally verified to be qualitatively true, if somewhat quantitatively lacking (Iveson et al., 2001; Bika et al., 2001). These predictions include, for example, the behavior of decreasing particle size resulting in increased pellet strength, the effects of increasing or decreasing the surface tension of the liquid binder, the impact of contact angle on capillary bridging effectiveness, and the effects of increasing or decreasing porosity. Significant work has been put forth to improve the quantitative accuracy of Rumpf's equation, often by changing the treatment of the coordination number Q (Bika et al., 2001).

Despite this effort, Rumpf's equation catastrophically fails at explaining dispersion and flocculation. Dispersion and flocculation are conditions where, primarily due to the surface charges of the particles in the liquid phase, particles may spontaneously separate or aggregate. Chemical additives, such as dispersants and coagulants, can change these surface charges to promote one behavior over the other. Coagulants promote the rapid binding of particles together by decreasing the repulsion between particles, while dispersants prevent the spontaneous agglomeration of particles by increasing the repulsion between particles.

Contrary to traditional intuition, it is dispersants which result in the formation of stronger pellets (Halt and Kawatra, 2017). In the context of Rumpf's equation, especially as listed in Equation 7, this result is completely inexplicable. It would appear that a decrease in inter-particle binding force leads to an increase in pellet strength, in direct and significant contradiction to the equation.

The differences between these pellets are not adequately explained by a single factor. If the pellet strength is compared to the zeta potential, it is clearly found that aside from sodium metasilicate (D1), higher zeta potentials indicate higher pellet strength (Halt, 2017). However, sodium metasilicate has a zeta potential comparable to all of the pH modifiers, and yet creates far stronger pellets. If stronger pellets are associated with dispersion, then it is clear that sodium metasilicate is the more effective dispersant – but why? Another question is, will adding more dispersant make pellets even stronger?

Another interesting set of strength differences to explain are the differences between F1, F2, and F3. While all of those pellets are at flocculating conditions, what could be the reason for the difference in observed strengths between them?

The last major outlier is D3, which displays unexpected strength even beyond the other dispersants.

The key failing of Rumpf's equation to predict the effects of dispersants can be traced back to two of its main assumptions. The first problematic assumption, formally stated in Equation 6, is its choice of coordination number. This is demonstrably inaccurate: If one returns to Equation 1, extracts the coordination number Q by dividing out everything else for each of the reported pellet conditions, normalizing it against the baseline pellet for the given conditions, then one finds Figure 9.

Figure 9: Coordination number from Rumpf's equation, normalized versus the baseline pellet (near x-value 24), versus zeta potential. The key result here is that the high point at zeta potential 31 (sodium metasilicate) is not an outlier, but rather simply on a different curve than the lower trend-line. There is a distinct jump between the lower and upper lines, which supports different behaviors between dispersion and flocculation.

The second problematic assumption is its choice of uniform sphere geometry. Uniform spheres do not experience the same frictional effects as real particles with rough surfaces. Surfaces which are rough cannot readily roll over each other, and may get stuck on each other as they come together. Thus, if this high frictional contribution from direct contact can be overcome, it would not be surprising to see that particle strengths can increase considerably. Dispersion prevents the particles from coming into direct contact, thus reducing the frictional forces involved.

5.2.1 Modeling Zeta Potential for Dispersion

To explain the effect of dispersants, it should be helpful to understand exactly what qualifies as dispersion. In a general sense, this would be when the zeta potential's repulsive force exceeds the attractive forces available in the system. The goal of this section is to construct a force balance between the capillary bridging's attractive force and the repulsive force exerted by the zeta potential at small separation distances. By considering the balances of these forces, we can determine whether the zeta potential can achieve dispersion in the pelletizing environment and improve particle mobility.

The primary attractive force in pelletization is the capillary bridging effect, plus van der Waals interactions at extremely short ranges (Rumpf, 1962). To the best of the author's knowledge, repulsive forces have not been traditionally considered in the context of pelletization.

However, it is clear from Figure 2 that the impact of dispersants on pelletization behavior is very real. Traditionally, dispersion and flocculation has been presented in terms of a parameter known as the zeta potential. The zeta potential is a measure from electrical double layer theory which is the effective surface potential of a particle submerged in a liquid.

The surface charge for relatively large particles can be approximated by Equation 8 (Sze et al., 2003; Makino and Ohshima, 2010).

$$\sigma = \frac{\epsilon}{\lambda_D} \zeta \quad (8)$$

Where σ is the surface charge density, ϵ is the permittivity of the fluid, λ_D is the Debye length (see Equation 9), and ζ is the zeta potential.

$$\lambda_D = \sqrt{\frac{k_b T \epsilon}{\sum_i (n_i (z_i e)^2)}} \quad (9)$$

Where λ_D is the Debye length, k_b is Boltzmann's constant, T is the temperature, ϵ is the permittivity of the fluid again, n_i is the number density of the i -th ionic species present in solution, z_i is the charge of a single unit of the i -th ionic species, and e is the elementary charge (Sze et al., 2003; Makino and Ohshima, 2010). This sum of the concentration times by the charge squared should be reminiscent of the concept of ionic strength, and for convenience that term will be separated out into Equation 10:

$$I = \sum_i (n_i (z_i e)^2) \quad (10)$$

Given these, an approximation of the force between two particles due to zeta potential can be achieved by integrating Coulomb's law over the surfaces involved. Assuming mono-sized uniform spheres for the sake of simplicity, the expression can be broken down into two major parts in Equations 11 and 12:

$$F_{\zeta} = \left(\sqrt{\frac{\epsilon I}{k_b T}} \zeta \right)^2 \left(\frac{1}{4\pi\epsilon} \right) F_{\zeta}^* \quad (11)$$

$$F_{\zeta}^* = \iint_{S_1, S_2} \frac{(\vec{p}_2 - \vec{p}_1) \cdot \hat{i}}{||\vec{p}_2 - \vec{p}_1||^3} dS_1 dS_2 \quad (12)$$

In Equation 11, F_{ζ} is the repulsive force between particles 1 and 2 evolved due to the zeta potential, ϵ is the permittivity again, k_B is Boltzmann's constant, I is as defined in Equation 7, T is the temperature, ζ is the zeta potential, and F_{ζ}^* is as defined in Equation 12.

In Equation 12, F_{ζ}^* is the distance-dependent factor for Equation 8, which involves integrating over the surfaces S_1 and S_2 of the two interacting spheres point-wise, $\vec{p}_1$ and $\vec{p}_2$ being points on the spheres, and $\hat{i}$ being the unit-vector in the direction of the line connecting sphere 1 to sphere 2. This geometry is shown in Figure 10. Note that depending on how dS_1 and dS_2 are integrated, additional geometric factors may appear. In particular, for spherical coordinates, the radius to the fourth and the sines of the zenith angles should appear.

The restrictions on Equations 11 and 12 should be noted. Most notably, the effects of the counter-ions in the liquid phase which balance out the overall charge of the system have been neglected. This means that the expression is only going to be meaningful at extremely short ranges. Using a dipole force law in place of a pure inverse-square law may be a viable alternative for longer ranges, but considering the capillary bridges act on very short separation distances to begin with, this restriction is not considered to be too extreme. The other approach would be to apply a charge distribution to the liquid volume (bounded by the Laplace-Young equation) and directly integrate in its contribution. However, while such distributions are available for single spheres completely submerged in fluid, they have not been derived in the context of dual spheres within capillary bridges. It is worth noting that the interaction of the first shell of counter-ions on one sphere with the first shell of counter-ions on the second sphere will be very similar to the interaction between the sphere surfaces themselves, and the attractive forces between the spheres and the shells should be largely cancelled out by the same.

Figure 10: The two-sphere geometry used in Equation 12. The interactions are being calculated for an inverse-square force law between the dark shaded regions of the spheres. These regions are defined by the angle β , and the spheres have a radius of a and a separation distance of $2h$. $\hat{i}$ points from the center of the left sphere to the center of the right sphere. $\vec{p}_1$ indicates a point within S_1 , and $\vec{p}_2$ indicates a point within S_2 .

Also note that for the same reason this zeta potential force is not expected to progress beyond the boundary of the capillary bridge phase. The charges within the bridge as a whole are neutral, and at all but the shortest distances very quickly vanish in reality. The assumed force relation in Equation 12 is expected to vanish less rapidly at long distances than reality, but should be quite reasonable at shorter distances.

Additionally, the uniform spherical particle geometry has been assumed for the actual computational work, though this is not strictly speaking necessary from the formulation of Equation 12. The goal of this work is to identify the critical point between dispersion and flocculation and why it occurs, and for that purpose these two assumptions are not expected to cause issues.

The geometry chosen within Figure 3 is chosen to align with the geometry of common capillary bridge models, such as the model reported by Willet et al. (2001). The model used in this work is the more complex model reported by Willet et al. (2001), but the simpler model is presented as Equations 13, as it has overall very similar character.

$$\frac{F_{cap}}{2\pi a\gamma} = \frac{2a\pi\beta^2 \cos \theta}{2\pi a\beta^2 + 2.1(\sqrt{2\pi ah\beta^2}) + 10.0h} \quad (13)$$

Where F_{cap} is the attractive force of the capillary bridge; a , h , and β are the geometric parameters shown in Figure 3, θ is the contact angle of the liquid and the solid; and γ is the surface tension. This formulation assumes that β is relatively small.

For any combination of geometric parameters in which a capillary bridge can still form, there is a zeta potential which will allow for the equilibrium $F_{cap} = F_{\zeta}$ to be achieved.

Let us call that zeta potential at the shortest possible separation distance the critical zeta potential. The first component of the proposed modification to micromechanical modeling is as follows:

- If the zeta potential of the system is above the critical zeta potential, then the system is dispersive, and particles can break away from direct contact without debonding.
- If the zeta potential of the system is below the critical zeta potential, then the system is flocculating, and particles are in direct contact if they are bonded.

This critical zeta potential is a bit tricky to calculate directly, as Equation 10 presents a singularity if the two spheres are actually directly touching. However, by assuming a fairly small separation distance, e.g. $h/a = 1/100$, it becomes simple to calculate a relatively close to critical zeta potential. As Halt and Kawatra (2017) do not report many of the values required to be precise with this modeling, a consistent set of reasonable conditions will be assumed.

One, the characteristic particle diameter will be assumed to be the 50% passing size, $14.38\mu\text{m}$ (Halt and Kawatra, 2017). This passing size balances the consideration of the majority of the mass of the system having larger diameters with Rumpf's observation that the smallest particles have a disproportionately large effect on the bonding overall. Increasing the particle size increases the critical zeta potential slightly sub-linearly – that is, a doubling of particle size increases the critical zeta potential by slightly less than double.

Two, a contact angle θ is assumed to be about 35° in all cases, though it is worth noting that some of the additives should modify that. This is based on a comparison of the hematite in question with the results reported by (Tang et al., 2018), combined with a consideration of the maximum contact angle for which Willet et al.'s (2000) formula for the capillary bridge force is valid. A decrease in contact angle increases the critical zeta potential, because the capillary force becomes stronger. The effect here is considerably smaller, and a 2-fold change in contact angle leads to an approximately 10% change in the critical zeta potential. It is worth noting that high solution zeta potentials tend to decrease contact angles with water, as the large electrical potentials to an extent attract the water phase because they require the counter-ions present in the water to balance out. However, the comparatively small impact observed on the critical zeta potential means that this effect is unlikely to greatly change whether dispersion or flocculation occurs.

Three, β is assumed to be about 5° in all cases, to allow for the consideration of a constant volume liquid bridge between all cases. This will naturally vary based on water content, but by choosing a consistent value the overall trends can be established under their own consideration. Increasing β angle decreases critical zeta potential almost linearly. Assuming constant capillary bridge volume relative to particle radius, this means that the zeta potential effects are likely to become drastically less important as particle

sizes increase. Thus, dispersion would be an effect primarily seen with small particles, and large particles are correspondingly harder to disperse – which fits with common intuition regarding the subject.

Four, the ion concentrations are assumed to be only those added intentionally to the water by Halt and Kawatra (2017), and those present from the addition of the additive dissolving into the pellet moisture. This is probably inaccurate, as hematite concentrates tend to contain significant quantities of adsorbed ions of their own (Ripke and Kawatra, 2003). Increasing the ion concentration would result in decreasing the critical zeta potentials.

Please note that the first 3 assumptions would be required to use any reasonable capillary bridge model on this data as well, and should not be taken as extraordinary. While it is possible to choose parameters to cherry pick the results, the numbers chosen were chosen with the intention of hopefully being representative of the sort of behavior one might expect from the hematite pelletization system and that through their consistency may help to highlight overall trends and tendencies.

5.2.2 Applying Dispersion or Flocculation to Data

Table 2 presents the calculated critical zeta potentials, reported actual zeta potentials, and approximate pellet strengths normalized against the baseline pellets produced by Halt (2017). Unfortunately, as mentioned prior, it is impossible to precisely know the exact parameters for Equation 8 as they should be applied here. However, the hope is that the chosen parameters will highlight the key trends of this force balance and provide insight into the different behaviors observed.

The key trends identified by this analysis are as follows:

1. In general, the lowest critical zeta potentials are from anionic polymers, which influence the I term in Equations 10 and 11 extremely. These polymers are likely to be the most effective dispersants available, as they tremendously decrease the critical zeta potential while increasing the system's actual zeta potential.
2. The majority of conditions without these polymers are flocculating, except in the presence of extremely strongly ionic compounds (that is, sodium tripolyphosphate or sodium citrate) which also contain strong negative charges to emphasize the negative charge on the hematite's surface.
3. The molar mass of these compounds has a significant impact on how effective it would be. The ideal dispersant would be a highly charged ionic compound with comparatively low molar mass for its charge.

4. Ions are necessary in the solution for effective dispersion to occur. Otherwise, surface charges do not evolve to sufficient strength for the zeta potential to have a strong impact. This is the primary reason why the baseline case is flocculating.
5. The absolute amount by which the actual zeta potential and the critical zeta potential differ has apparently very little effect on dry strength compared to whether the actual zeta potential is higher or lower.

This last point can be understood by investigating why exactly this difference in strength should be expected to occur. Recall that the zeta potential is not active in the final dry strengths, as there is no liquid phase to be had. Also recall that the actual strength of the bonds formed during drying are expected to be relatively constant, though potentially weakening or strengthening a small amount based on composition. Thus, the primary difference should be the number of bonds.

Table 3: Critical zeta potential calculated via Equation 11 versus actual reported zeta potential and dry pellet strength for constant additive dosages.

Additive	Critical ζ (mV)	Reported ζ (mV)	Approx. Dry Pellet Strength (N)
Baseline	1700	23	40
F1: Aluminum sulfate	46.9	10	33
F2: Calcium chloride	52.1	15	38
F3: Magnesium sulfate	58.5	18	35
pH1: NaOH + EDTA	207.1	33	44
pH2: Sodium carbonate	44.3	33	44
pH3: Sodium hydroxide	47.1	33	43
D1: Sodium metasilicate	*25.9	31	70
D2: Sodium citrate ¹	52.2	42	68
D3: Sodium polyacrylate	*45.3	49	88
D4: Sodium polyphosphate	*59.7	55	79
D5: Sodium tripolyphosphate	36.9	55	81

*: These additives have polymeric anions, which were treated as having a degree of polymerization of 50. Increasing degree of polymerization increases the charge on the anionic compound, greatly decreasing the critical zeta potential in each case, explaining why sodium metasilicate achieved dispersion results at such a low reported zeta potential. The degree of polymerization may for D1, D2, and especially D4 may be underestimated here.

¹: Sodium citrate is the odd one out among the dispersants. The strength results and zeta potential results suggest that it should be considered a dispersant, so it failing to be selected by the critical zeta potential might be indicative that the choice of parameters for the whole system was not completely accurate.

The most probable reason for this difference is straightforward: above the critical zeta potential, the particles need not be in direct contact while bonded via capillary bridge. In the commonly assumed uniform mono-sized spherical geometry, this would not make a huge difference. But in reality, particles are rough, rigid, and non-smooth. Flat faces can be in contact with flat faces, and these real particles cannot readily roll over each other as a result. Concavities can become interlocked, and particles can be stuck together geometrically.

Under dispersing conditions, the particles do not necessarily maintain direct contact with each other. They are free to roll in space, bound only by the viscosity of the fluid itself, without being so immediately restricted by any geometry they may be in contact with.

For this reason, the character of the coordination number would be expected to change drastically. At the conditions observed in Halt and Kawatra (2017)'s pellets, the normalized coordination number fluctuated between about 0.9 and about 2.0. Comparing these to the possible spherical packings reviewed in Bika et al. (2001) for the porosity values of 0.31 to 0.33, this is fairly close to being plausible even with uniform mono-sized spheres, with the lowest coordination number being around 6.2 and the highest coordination number being around 11.5. Thus, assuming that dispersed particles pack fully while assuming that flocculated pellets simply pack randomly would explain the majority of the variation between the two cases. This would also agree with the simplified geometries discussed in Hypotheses A and B, and largely this figure supports either explanation. It is likely that both factors play their own role in increasing pellet strength by increasing the effective coordination number.

More accurate determinations of the coordination number from this model could be evolved by finding an efficient closed form approximation for Equation 11 and by implementing the resulting Equation 12 into an appropriate computational framework, such as discrete element method. While Equation 12 can be quickly calculated for one value at a time from its integral formulation, it still takes upwards of a quarter of a second to calculate for a single interaction, and thus is poorly suited for direct implementation.

The coordination number differences can be applied to other micromechanical models as well, as all micromechanical strength models are correlated to the coordination number (though the coordination number itself may be hidden away within other elements of the model). While the specifics of the derivation should be inspected for each model in question, the approximately 1.8 times strength increase shown for these hematite pellets would be expected to apply to any model which does not otherwise handle the effects of flocculants and dispersants. This also is in line with the sort of expectation provided by the macroscopic view of Hypothesis B and the geometry of Hypothesis A.

This examination provides little insight into the strength differences observed between the flocculants F1-F3, or between D3 and the remaining dispersants, however.

The high strength of dispersant D3 may be best considered to be a result of the strength of any inter-particle bridges it may form by contacting multiple hematite particles. While the other polymers are likely to do that as well, acrylic plastics are commonly considered, but polyphosphate solids are rarely heard of. In similar argument metasilicate might be transformed into glass, but clearly only under much more extreme thermodynamic conditions. However, this is largely guesswork.

Between F1-F3, the likely reasoning is the strength and volume of the solid bridges that form when the water is removed. The weakest additives have the largest unit crystal volumes. That particular correlation may be coincidence but the difference in strengths between these three reagents can likely be explained without resorting to modifications of Equation 11.

5.2.3 In the Context of Dustiness

While this work does not focus extensively on pellet dustiness, it is worth noting how this approach explains Halt (2017)'s finding that dispersants reduce dustiness. This framework supports both Hypotheses A and B for explaining why pellet strength increases, which is to say: A) avoiding the formation of tightly bound flocs prevents the formation of loosely bound formations of tightly bound groups and B) that the decrease in frictional interactions allows for better pellet compaction.

Based on Halt (2017)'s findings, however, both Hypotheses A and B can be independently supported here. In particular, in Halt's (2017) work calcium chloride decreased pellet dustiness, but did not decrease mass loss during abrasion testing. Instead, calcium chloride promoted the formation of chips instead of fine dusts with little impact on the total amount of material lost. This result suggests that for calcium chloride, Hypothesis A is likely a more accurate view of the reality of the situation.

The other flocculants did not show this behavior, having little overall impact on the ratio of chips to fines during abrasion testing (Halt, 2017). In this case, it may be that Hypothesis B was more indicative of the interactions within the pellet.

Unfortunately, Hypothesis A and Hypothesis B both make very similar predictions about their impact on pellet strength, suggesting that in both cases the coordination number should roughly double and thus that the pellet strength should roughly double. Dry strength measurements between dispersing and flocculating conditions alone cannot be expected to identify a difference between the two ideas.

5.3 Revisiting Microscopic Hypothesis B

In the beginning with Hypothesis B, it was suggested that the locking of particle movement may even be relevant down to a microscopic scale, suggesting that the presence of surface cations may be causing difficulties in hematite surfaces moving past each other. This was tested by creating pellets with varying dosages of calcium chloride

and magnesium chloride. Somewhat unfortunately, these were not directly available in equivalent hydration states – the calcium chloride was a dihydrate salt, while the magnesium chloride was a hexahydrate salt.

This did not make a huge amount of difference in the dry pellet strength, as the points in Figure 3 definitely appear to form a consistent trend-line between the ion species. The particularly interesting point is the very last magnesium point, which is inexplicably higher than the points before it. While this outlier may seem to be problematic, it can be explained in the context of the section 5.2.

The suggested explanation is that the extremely high ion concentration of the final magnesium point, approximately 10 moles of magnesium cations per ton of solid feed dissolved in the 8.5% pellet moisture is actually concentrated enough to cause the critical zeta potential to dip below the actual zeta potential. In that fashion, dispersion could be achieved. While the zeta potentials were reported in Figure 5 (the highest magnesium concentration in Figure 3 corresponds to the leftmost magnesium point in Figure 5), the solution tested would naturally have been much more dilute than within the pellet moisture itself. Since magnesium is a specifically-adsorbed ion for hematite, it is expected to continue adsorbing even if the surface has already begun to carry a positive charge. Thus, at some point, magnesium should begin to lead towards the dispersion of hematite.

The lack of difference in dry strengths between the two ions suggests that either or both of the microscopic view of Hypothesis B or the supposition that magnesium adsorbs to twice as many surface sites as calcium are incorrect.

At first glance, the distinct negative correlation between cation concentration and dry or wet pellet strength may be interpreted as a contradiction of the discussion from section 5.2. However, it is actually known that calcium and magnesium interfere with the activity of bentonite binders (Eisele and Kawatra, 2003). To head off concerns that alternative binders should have been tested in that case, calcium and magnesium also play critical roles in starch adsorption (Zhang et al., 2019). With the pellet feed in question it is possible to form weak pellets without binder, but such pellets tend to have wide variations due to both balling kinetics and overall relatively low strengths to begin with. If flocculants decreased binder-less pellet strength further, it may become impossible to form decent quality pellets at all. In this case, a comparatively known and understood interaction is favorable to a completely unknown one, which alternative binders would have run into.

5.4 Understanding Wet Strength of Calcium Chloride

With regards to the wet strength as shown in Figure 4, much greater variation is seen between the magnesium and calcium compounds. The calcium chloride additive initially caused a slight increase in wet strength, while magnesium chloride only decreased the pellet strength overall.

It may be that the wet strength variations are due more to the impact calcium chloride has on the water content of the pellet than anything to do with flocculation, however. Calcium chloride dihydrate is hygroscopic, and can pick up additional water from the solution, perhaps acting as a water control and helping to maintain a water rich environment within the pellet. That is an effect which would typically be linked to stronger pellets. Other works on dust management of iron ore have often attributed the hygroscopic activity of calcium chloride to a portion of its dust suppression abilities (Copeland and Kawatra, 2009).

Halt (2017) observed that calcium chloride did have an effect on how pellets abraded – in that they lost the same amount of material, but typically lost it as larger chips instead of fine material. This would align with the process suggested in Figure 1 in Hypothesis A, which was the idea that flocculating pellets would form loosely-bound agglomerates of tightly-bound clusters.

Hypothesis A suggests that differences in dry and wet strength would be correlated to the extent of flocculation observed, as the greater flocculation would lead to greater stresses evolving during drying. If Figure 3 and Figure 4 are combined to show wet compression strength versus dry compression strength, then we get Figure 11.

Figure 11: Wet compressive strength versus dry compressive strength for pellets created with calcium chloride dihydrate and magnesium chloride hexahydrate. As dry strength increases, so does wet strength. Little distinction can be made between calcium and magnesium cations in this configuration, except for the same outlier point previously mentioned at low calcium dosage.

This is not an unexpected result: the error bars for the wet compressive strength data are rather considerable and make detailed analysis of these circumstances more difficult. While it is good to see that wet and dry compression strengths are correlated with each other, it is not possible to identify a difference in behavior between calcium and magnesium in this method.

5.5 Understanding Pellet Porosity

Figure 6 is unfortunately too variable to make strong claims about the relative impacts of various additives on rate of compaction. It seems possible that there is a slight tendency for pellets made with sodium metasilicate to compact faster than pellets made with calcium chloride, but such a claim should be taken skeptically at the data provided in that figure.

Perhaps the more interesting result is to consider that overall pellet porosity is likely a statistical phenomenon. Under the correct conditions, the pellet will manage to randomly rearrange itself to a denser state, but otherwise it may be stuck in poor configurations for quite some time. In this view, only one of the measured porosity groups (which were done in groups of 10 pellets at a time) happened to be in a more condensed form. While this should not be taken as quantitatively indicative of much of anything, qualitatively it would support the thought of particles becoming interlocked with each other and being unable to be compacted effectively.

It is worth noting that the porosity and liquid content results reported by Halt and Kawatra (2017) are highly correlated, and potential causative of each other. Due to the higher compaction achieved in dispersant pellets, it would make sense that more water would be forced out. Simultaneously, however, it could be interpreted that the higher water mobility allowed for greater compaction. The direction of causation is not clear on this regard.

5.6 Correcting Rumpf's Equation

Between Figure 9, Figure 1, the geometry discussed in Hypothesis B, and the observed strength results in general, the primary correction to Rumpf's equation would be to modify the coordination number. The simplest correction would be to double the coordination number in dispersion, which is supported by the available arguments and evidence. Dispersion is determined in turn by comparing the real and critical zeta potential of the system in question – if the real zeta potential is larger, dispersion occurs; otherwise, the system is flocculating. Equation 4 is shown again here, and it should be noted that tensile strength is directly proportional to the coordination number (Q).

$$\sigma_t = \frac{1 - \varepsilon}{\pi} \left(\frac{QF}{d^2} \right) \quad (4)$$

The factor of 2 is empirically justified for the porosity range tested of approximately 0.32 with particle sizes on the order of 10 μ m. For larger porosity values, it is likely that slight variations may be seen. There are models which assume different coordination correlations than Rumpf's equation, and it is likely that each of them is correct in some isolated condition. If a wider variety of materials can be tested, it may be possible to elucidate a more precise correlation between these different coordination models.

In particular, Figure 7 and Figure 8 support this correction particularly: the addition of dispersant directly improves pellet strength, but in a stepwise fashion. The intermediate average strengths experienced at low dosages of dispersants are likely a result of limitations in mixing. The utilized dosages on the order of 1kg/t are difficult to ensure complete mixing in, as there is significantly more feed material than there is dispersant being added.

6 Future Work

6.1 Investigate Polymeric Anion Dispersants Further

In this work, 3 polymeric anionic dispersants were referenced and used, both from historical data and in new experimental work. These three dispersants were sodium metasilicate, sodium polyacrylate, and sodium polyphosphate. The degree of dissociation of these dispersants was a critical factor within the analysis for explaining the likely cause of their effectiveness, but the precise degree of dissociation was simply guesswork.

This degree of dissociation, however, is not something that is readily available on the labeling and packaging of the substances, nor does it need to correlate to the degree of polymerization (also not available on the packaging). To be clear, the degree of dissociation is the degree to which the polymer dissociates in water – how many cations it loses, and the anionic charge it develops as a result.

It is likely that very effective dispersants could be identified by carefully investigating this effect quantitatively in the future.

6.2 Verify Substitution of Dispersants with Salts

Dispersants are relatively complicated compounds and typically have a fairly hefty expense associated with any bulk usage. According to the results of the discussion in section 5.2, it seems very probable that many dispersant dosages could be at least partially substituted by common salts without a major sacrifice in overall pellet strength.

Most pellets formed in plants are already close to strength requirements, and the decreased dustiness of pellets formed under dispersing conditions is likely desirable for the sake of minimizing material losses if nothing else. A minor decrease in individual bond strength should be made up for in spades by the increase in coordination number predicted and observed in Figure 1 and Figure 9 respectively.

To minimize the cost of implementing such a shift, however, utilizing common ionic compounds may be important.

Two particularly important categories of compounds would also be calcium oxides and magnesium oxides, often used as flux materials in iron ore pellets. While this work does not directly investigate their impact, it is likely important to consider what role these flux materials may play on pellet strength and dustiness in the context of surface charges. The divalent cations combined with the relatively high dosages of typical flux materials means that they may have a significant impact on dispersion effects, after all.

6.3 Investigate Coordination Number Distributions

Coordination number is ultimately a geometric problem. However, there are no concise geometric solutions to coordination number problems as they exist in mineral processing. While Bika et al. (2001) reports a comparison curve of potential coordination numbers for a given porosity, there is little intuition provided as to what may cause the changes between different coordination states.

While this work claims that the coordination number change is largely due to the presence of the repulsive zeta potential dispersion force, this has not been investigated rigorously.

Large scale computer simulations present an opportunity to proceed in this direction, but are complicated by the problem of implementing Equation 12 efficiently in a computational sense and by a lack of solid knowledge about the real geometry of the particles involved in iron ore pelletization.

While tedious, it is likely that any exhaustive attempt to correlate coordination number to various styles of pair interaction, mixing, and time evolution conditions would provide insight into much of the phenomena present in at least the realm of dispersion and flocculation within pelletization. Likely, it would shed light on far more information about pellet formation in general.

7 Conclusions

Dispersion and flocculation clearly play a major role in how pellets form over time. Traditional pellet strength models, such as Rumpf's equation, provide no insight into this phenomenon. The primary flaw of the Rumpf's equation is that it assumed a consistent coordination number distribution based on the porosity. The conditions of dispersion and flocculation, however, lead to distinct differences in the coordination numbers achieved during pelletization.

Instead, the conditions of dispersion are identified to be a stepwise difference in the kinetics of pellet formation, which leads directly into a large variation of the frictional effects within the pellet. In dispersion conditions, the coordination number approximately doubles for the pellets shown in this work. This is supported by geometric arguments in both Figure 1 and Hypothesis B, and experimentally by Figure 7, Figure 8, and Figure 9.

The suggested reasoning for this is that above a certain critical zeta potential, the repulsive force of the surface charge is large enough that particles cease to be in direct frictional contact. Because real particles are rough and non-smooth, this difference is tremendous – in particular, because particles which were previously interlocked and prevented from rolling over each other are now able to move relatively freely past each other's surfaces.

The difference between flocculation and dispersion is investigated by creating a force balance within the capillary bridge between particles. This is primarily discussed in section 5.2, and finds that the zeta repulsion force is very strongly dependent on the ionic nature of the solution. This balance was applied with best guess parameters to the available data, and provided insight into what factors lead to a highly dispersed solution. The force balance also predicts that dispersion is much more effective with very small particle sizes, and that for coarser materials the amount of dispersant required to achieve these increases is likely to be significantly larger.

Due to the stepwise nature of the increase in strength observed from the addition of dispersants under this model, it is expected that further addition of dispersants will not result in similarly large increases in pellet strength. While pellet strength may improve if the dispersant can otherwise act as a binder, the coordination number could not be reasonably expected to improve further.

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A On the Calculation of F_ζ

During the initial discussion of Equations 11 and 12, the direct computation was somewhat glossed over. The equations in question are reproduced here for clarity:

$$F_\zeta = \left(\sqrt{\frac{\epsilon I}{k_b T}} \zeta \right)^2 \left(\frac{1}{4\pi\epsilon} \right) F_\zeta^* \quad (11)$$

$$F_\zeta^* = \iint_{S_1, S_2} \frac{(\vec{p}_2 - \vec{p}_1) \cdot \hat{i}}{||\vec{p}_2 - \vec{p}_1||^3} dS_1 dS_2 \quad (A2)$$

These equations are based off of the geometry demonstrated in Figure 1Figure 10, also reproduced here for clarity:

Figure A.1. The geometry used in Equation A2. The interactions are being calculated for an inverse-square force law between the dark shaded regions of the spheres. These regions are defined by the angle β , and the spheres have a radius of a and a separation distance of $2h$. $\hat{i}$ points from the center of the left sphere to the center of the right sphere. $\vec{p}_1$ indicates a point within S_1 , and $\vec{p}_2$ indicates a point within S_2 .

To clarify how the calculations were performed, however, this appendix will provide a full expansion and associated *Mathematica* code for calculating the values of F_ζ and F_ζ^* . F_ζ^* is the trickier part, and will be addressed first.

To start with, the variables of integration are the surfaces S_1 and S_2 , which are the shaded regions in Figure 3. The differential surface areas can be interpreted using two spherical geometries, each centered at the center of one of the spheres. Using radius a , azimuthal angle ϕ , and zenith angle θ , with the zenith axis pointing from the center of the sphere towards the other sphere, the differential angles expand out as below:

$$\begin{aligned}dS_1 &= a^2 \sin \theta_1 d\phi_1 d\theta_1 \\dS_2 &= a^2 \sin \theta_2 d\phi_2 d\theta_2\end{aligned}$$

The coordinates for $\vec{p}_1$ and $\vec{p}_2$ can be expanded in terms of the same coordinates:

$$\begin{aligned}\vec{p}_{i,r} &= a \\ \vec{p}_{i,\phi} &= \phi_i \\ \vec{p}_{i,\theta} &= \theta_i\end{aligned}$$

To convert these to rectilinear coordinates requires defining the separation distance between the two spheres. For simplicity, using a half-separation distance h allows avoiding extraneous factors of 2 during further computations. Note that the zenith axis of sphere 2 is assumed to point in the opposite direction of the zenith axis of sphere 1. Also note that the first sphere is assumed to be on the negative-x side of the origin.

$$\begin{aligned}\vec{p}_{1,x} &= -h - a + a \cos \theta_1 \\ \vec{p}_{1,y} &= a \sin \theta_1 \cos \phi_1 \\ \vec{p}_{1,z} &= a \sin \theta_1 \sin \phi_1 \\ \vec{p}_{2,x} &= h + a - a \cos \theta_2 \\ \vec{p}_{2,y} &= a \sin \theta_2 \cos \phi_2 \\ \vec{p}_{2,z} &= a \sin \theta_2 \sin \phi_2\end{aligned}$$

From these, the interior term of Equation 10 can be determined to have the following numerator:

$$N = a^4(-2a - 2h + a \cos \theta_1 + a \cos \theta_2) \sin \theta_1 \sin \theta_2$$

While the denominator is as follows:

$$\begin{aligned}D &= (4(a + h)^2 \\ &\quad + 2a(a - 2(a + h) \cos \theta_2 + \cos \theta_1 (-2(a + h) + a \cos \theta_2) \\ &\quad - a \cos(\phi_1 - \phi_2) \sin \theta_1 \sin \theta_2))^{3/2}\end{aligned}$$

These two terms together as a fraction form the interior of Equation 10.

The limits of integration are those which correspond to the surfaces in Figure 3. Explicitly, θ_1 and θ_2 are integrated from 0 to β , and ϕ_1 and ϕ_2 are integrated from 0 to 2π .

Thus, Equation 10 can be re-written as:

$$F_{\zeta}^* = \int_0^{\beta} \int_0^{\beta} \int_0^{2\pi} \int_0^{2\pi} \frac{N}{D} d\phi_1 d\phi_2 d\theta_1 d\theta_2$$

And it should be clear that F_{ζ}^* depends only on β , a , and h .

A *Mathematica* formula implementing this same result is provided below:

```
ffactor[a_,h_,β_]:=a^4 NIntegrate[(((2 (a+h)-a (Cos[φ1]+Cos[φ2]))
Sin[φ1] Sin[φ2]))/(4 (a+h)^2+2 a (a-2 (a+h) Cos[φ2]+Cos[φ1] (-2 (a+h)+a
Cos[φ2]))-a Cos[θ1-θ2] Sin[φ1] Sin[φ2]))^(3/2),
{φ1,0,β},{φ2,0,β},{θ1,0,2π},{θ2,0,2π}];
```

At large h values, this can be integrated relatively quickly, but at small h values the numerical stability decreases. This is a primary reason for not using this expression in the extremely small h -value limiting case, though that would be most appropriate for determining the critical zeta potentials.

For calculation efficiency and any future fitting endeavors, it is very worthwhile to note that this formulation can be written in terms of a , h/a , and β . So long as h/a and β remain constant, the value of F_{ζ}^* depends on a precisely quadratically. Thus, it may be best to fit this term for a single constant a value but with varying h/a and β and simply correlate other a values onto the 2-dimensional fit function using this relation.

In *Mathematica*, this can be written as something like:

```
fstar[a_,h_,β_]:=a^2 ffactor[1,h/a,β];
```

At this point, the “ffactor” term on the right-hand side can be replaced with any relevant 2D fit of the original function.

The formula in Equation 9 can then be directly implemented in terms of “fstar”, e.g. via:

```
fζ[i_,kbt_,ζ_,a_,h_,β_]:=((Sqrt[2 ε i]ζ)/Sqrt[kbt])^2(1/(4 π
ε))fstar[a,h,β];
```

Where “ i ” is the ionic concentration factor from Equation 8, “ kbt ” is Boltzmann’s constant multiplied by temperature, “ ζ ” is the Zeta potential, “ a ” is as shown in Figure 3, “ h ” is as shown in Figure 3, “ β ” is as shown in Figure 3, and “ ϵ ” is the combined permittivity of the fluid phase.

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