2017

# Controlling Properties of Agglomerates for Chemical Processes

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## Recommended Citation

Halt, Joseph A., "Controlling Properties of Agglomerates for Chemical Processes", Open Access Dissertation, Michigan Technological University, 2017.
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# CONTROLLING PROPERTIES OF AGGLOMERATES FOR CHEMICAL PROCESSES

By

Joseph A. Halt

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

In Chemical Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2017

This dissertation has been approved in partial fulfillment of the requirements for the Degree of DOCTOR OF PHILOSOPHY in Chemical Engineering.

Department of Chemical Engineering

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Committee Member: *Stephen Kampe*

Committee Member: *Tony Rogers*

Committee Member: *Timothy Eisele*

Department Chair: *Pradeep K. Agrawal*

To GEF (July 1928 - Dec. 2015) and RMF (May 1929 - Aug. 2016). I stayed for you.

The poem below is for SEH

A robin sings the rain away
-----------------------------------------------
Blocked-stone drips, aseptic, grey.
Mossy-mottled cherubs lay
nearby. You cry, implore – oh just one more!
one hour! one day! one chance! to say
unspoken words! to love! to cherish! –
while one-lone bird and parish
mourners warbles, pray, sing.
Just-parted clouds reveal, unshrouds for
you, for them, a beaming ray,
a touch, a kiss of warmth-hope-joy.
Oh! Auguring eternal spring.

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# Table of Contents

# List of Figures

# Preface

This dissertation summarizes my published papers and manuscripts submitted for review. All figures herein were modified from their published form.

1. Halt, JA and Kawatra, SK, 2017. ‘Development of low-silica binders for iron ore pelletization’. [TO BE SUBMITTED]
2. Halt, JA and Kawatra, SK, 2017. ‘Binder mixtures and green ball surface coatings to reduce the friability of starch-bonded pellets’. [TO BE SUBMITTED]
3. Halt, JA and Kawatra, SK, 2017. ‘Does the zeta potential of an iron ore concentrate affect the strength and dustiness of unfired and fired pellets?’ *Mineral Processing and Extractive Metallurgy Review,* Available Online, DOI: 10.1080/08827508.2017.1288114.
4. Halt, JA and Kawatra, SK, 2016. ‘Can modified starch be used as a binder for iron ore pellets?’ *Mineral Processing and Extractive Metallurgy Review*, Available Online, DOI: 10.1080/08827508.2016.1262857.
5. Halt, JA, Zhou, Y, and Kawatra, SK, 2016. ‘A comparative analysis of binders for iron ore pelletization’, XXVIII International Mineral Processing Conference, Paper No. 171, Quebec City, Canada.
6. Halt, JA and Kawatra, SK, 2016. ‘Engineering iron ore pellets to reduce their dustiness’, *Minerals & Metallurgical Processing*, 33(3): 156-156.
7. Halt, JA, Silva, B, and Kawatra, SK, 2015. ‘A new on-line method for predicting iron ore pellet quality’, *Mineral Processing and Extractive Metallurgy Review*, 36(6):377-384.
8. Halt, JA and Kawatra, SK, 2015. ‘Iron ore pellet dustiness Part II: Effects of firing route and abrasion resistance on fines and dust generation.’ *Mineral Processing and Extractive Metallurgy Review*, 36(5):340-347.
9. Halt, JA, Nitz, MC, Kawatra, SK, and Dubé, M, 2015. ‘Iron ore pellet dustiness Part I: Factors affecting dust generation.’ *Mineral Processing and Extractive Metallurgy Review*, 36(4):258-266.
10. Halt, JA and Kawatra, SK, 2015. ‘Cold bonding of iron ore concentrate pellets’, *Mineral Processing and Extractive Metallurgy Review*, 36(3):192-197.

11. Halt, JA and Kawatra, SK, 2014. ‘Understanding the bonding mechanisms in iron ore pellet binders,’ XXVII International Minerals Processing Congress, Paper No. 421, Santiago, Chile.
12. Halt, JA and Kawatra, SK, 2014. ‘Review of organic binders for iron ore concentrate agglomeration.’ *Minerals & Metallurgical Processing,* 31(2):73-94.
13. Halt, JA, 2014. ‘Increasing the preheat strength of cornstarch-bonded pellets’, *Minerals & Metallurgical Processing,* 31(3):179-179.
14. Kawatra, SK and Halt, JA, 2011. ‘Binding effects in hematite and magnetite concentrates.’ *International Journal of Mineral Processing*, 99(1-4):39-42.

The following outlines the author contributions to the above papers: I designed my experiments and collected laboratory experimental data with help from undergraduates* in Chemical Engineering at Michigan Technological University. Youlian Zhou (paper # 5 above) prepared the Modified Humic Acid binder that was tested in that paper. MHA binder research is not part of this dissertation. Benito Silva (paper # 7 above) provided the industrial stack emissions and abrasion index data from the Brazilian pelletization plant. Matthew Nitz (paper # 9 above) characterized the dust tower airflow parameters, collected dustiness data and helped predict the dust tower performance. Mathieu Dubé (paper # 9 above) provided pellet samples and their characterization from the COREM research laboratory and from Canadian pellet plants. Following data collection, I analyzed all of the data and wrote the papers. I performed all research/writing under the supervision and funding of Dr. S Komar Kawatra.

*Undergraduates were Jeff Kiel, Mark Preston, Lauren Bodeis, Matthew Nitz, Aaron Steeg, Ben Updike, Valerie Clevenger, David VanBergen, Brooke Basto, and Spencer Ketola.

# Acknowledgements

Thank you, Dr. Kawatra, for the opportunity to study mineral and particulate processing.

Thank you, Dr. Tim Eisele, Dr. Tony Rogers, and Dr. Stephen Kampe, for volunteering your time and energy whilst serving on my dissertation committee.

Thank you Alexis, Taana, Sue, Jerry, Steve, and Tim for your help with departmental forms/procedures and equipment-related problems.

Thank you, Dr. Tim Eisele (Michigan Tech), Mathieu Dubé (COREM), Tom Anderson (Bentonite Performance Minerals), Black Hills Bentonite, Jason St. Onge (Minerals Technologies), Michael Hyland (Headwaters Resources), Grain Processing Corporation, Manildra Millling, Gilles Zakosek (SNF Floerger), Akzo Nobel, Josh Carlson (Cliffs Natural Resources), and Michael Ketola (Cliffs Natural Resources) for arranging/supplying us with the raw materials needed for pelletizing research.

Thank you, ASISC members, for your support of mineral processing research at MTU.

Thank you, Mr. and Mrs. Michael Halt, for your support.

Thank you, Kristen, for your patience.

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# Abstract

Iron ore pellets are hard spheres made from powdered ore and binders. Pellets are used to make iron, mainly in blast furnaces. Around the time that the pelletizing process was developed, starch was proposed as a binder because it's viscous, adheres well to iron oxides, does not contaminate pellets and is relatively cheap. In practice, however, starch leads to weak pellets with rough surfaces – these increase the amount of dust generated within process equipment and during pellet shipping and handling. Thus, even though the usual binder (bentonite clay) contaminates pellets, pelletizers prefer it to starch or other organics.

This dissertation describes three ways to make good starch-based binders for pellets. Importantly, they solve the usual problems of weak rough pellets and lots of dust. The three approaches are:

(1) Addition of clay to starch. This is not a novel idea. In fact, it is the standard method used for their improvement. However, it has not been tested extensively with starch. This approach was expected to be – and indeed was – successful.

(2) Addition of a clay-rich layer to green ball surfaces. This approach is a novel idea. The coating's purpose was to mimic the good surface properties of standard bentonite-clay bonded pellets; as a benefit, clay consumption was significantly reduced. This approach was successful.

(3) Addition of dispersants to starch. This approach was a novel idea. The intent of the dispersants was to enable pelletization to occur at lower moisture contents, thus leading to denser particle packing and lower porosity. The dispersants resulted in significantly stronger, smoother pellets without contaminating them with silica.

Using approaches 1 and 3, starch can be used directly in traditional pelletizing operations, and importantly, in new pelletizing processes for new iron making operations. For approach 2, new application methods must be developed.

Future engineering work is suggested as follows: design better dispersants for magnetic magnetite ores; incorporate the dispersing agent and starch into bead form for easy use; design a simple way to add coatings in existing drum-based pelletizing circuits; and optimize the coating composition to decrease both abrasion losses and pellet clustering (for new Direct Reduction pellets).

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# Chapter 1 Introduction

Many raw and processed materials contain large quantities – or entirely consist – of small particles. Often, they are agglomerated into larger pellets, tablets, granules, etc. in order to minimize dust, improve handling, and tailor their properties for their intended use. Table 1 lists several commonly agglomerated materials. Although it lists only inorganic powders, agglomeration is widely used to process foodstuffs and pharmaceuticals.

Binders and coatings are frequently applied during and after agglomeration to control agglomerate properties. Consider two examples. One, fertilizer manufacturers use water-soluble polymers as binders when pelletizing limestone powders. The polymers make pellets strong and reduce dust as they are spread onto fields, yet still enable the pellets to disintegrate and revert to fine particles when the fields are irrigated. Two, proppant[1] manufacturers coat porous proppants with resin in order to lower their density in hydraulic fracturing fluids and to encapsulate fine fragments if the proppants happen to break during use. The coating makes proppants easier to pump underground into the hydraulic fractures where they are used, and prevents fines from plugging up fissures and reducing oil or natural gas recovery.

Iron ore pellets are a special type of agglomerate used in iron and steel production. They typically contain a binder to hold them together. Starch was proposed long ago as a chemically pure binder; it was never successful because it made weak, rough, dusty pellets. As non-blast furnace ironmaking methods become more common and iron ore producers try to diversify their product portfolio, new types of binders – such as low-silica binders from starch – will be needed. This dissertation reviews starch binders (Chapter 2), describes three ways to solve the starch-related problems (Chapter 3), and compares the three approaches through laboratory and pilot scale tests (Chapter 4). Our work shows that starch-based binders may now be viable for pelletizing.

The following sections of this chapter describe the iron ore pelletizing process, and briefly review pellet dustiness, binders, and coatings for iron ore pellets.

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[1] Proppants, short for propping agents, are special products used in certain methods of oil recovery. Per their name, they prop open fissures in the ground so oil or natural gas can flow.

*Table 1. Commonly agglomerated materials and their products (Anon, 2013)*

| Starting material | Final Product | Starting material | Final Product |
|---|---|---|---|
| Sulfur stack emissions | Fertilizer | Diatomaceous earth | Filter aids |
| Calcium chloride | Ice melt granulates | Calcium carbonate | Fertilizer |
| Clay | Absorbents, proppants | Coal dust | Briquettes, pellets |
| Cu, Ni, Au ore fines | Heap leaching feed | Bone ash, phosphates | Fertilizer |
| Foundry, EAF* dusts | Briquettes, pellets | Titanium dioxide | Pigment pellets |
| Iron ore fines | BF* and DR* pellets | Limestone | Fertilizer |
| Talc ore | Baby powder | Ammonium sulfate | Fertilizer |
| Potassium chloride | Fertilizer pellets | Flue dusts and sludge | Briquettes, pellets |
| Sulfur dust | Non-explosive pellets | Ceramic oxides | Refractory |
| Gypsum | Fertilizer | Zn, W oxides | Metal Recovery pellets |

* EAF-electric arc furnace. BF-blast furnace. DR-direct reduction.

## 1.1 **Iron ore pelletizing**

Iron ores are mined and beneficiated to make “concentrates”. Concentrates mainly contain the iron-rich minerals hematite and magnetite, and small amounts of impurity minerals such as quartz, silicates, carbonates, and clays. In some cases, concentrate particles are too small[2] to be used directly in most ironmaking furnaces, so they are pelletized with binders and additives to form hard, spherical agglomerates, approximately ½ inch (12.7 mm) in diameter. Additives can include fluxstone (e.g. calcium and magnesium carbonates) and solid fuel (e.g. powdered coke), while the binder is usually bentonite clay.

Figure 1 diagrams the pelletizing process. The two main steps are ball formation (balling) and induration (heat hardening or firing). During balling, wet balls (green balls) form as the moist powder tumbles inside of rotating drums or discs. Green balls then travel through furnaces where they are dried, indurated and cooled to form pellets. The ultimate goal of the pelletizing process is to form a mechanically strong, uniformly shaped, iron-rich product that can easily be turned into iron and subsequently steel.

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[2] Concentrate particles are often smaller than 350 mesh, or 44 µm. For comparison, typical human hair diameters are around 17-181 µm (Ley, 1999).

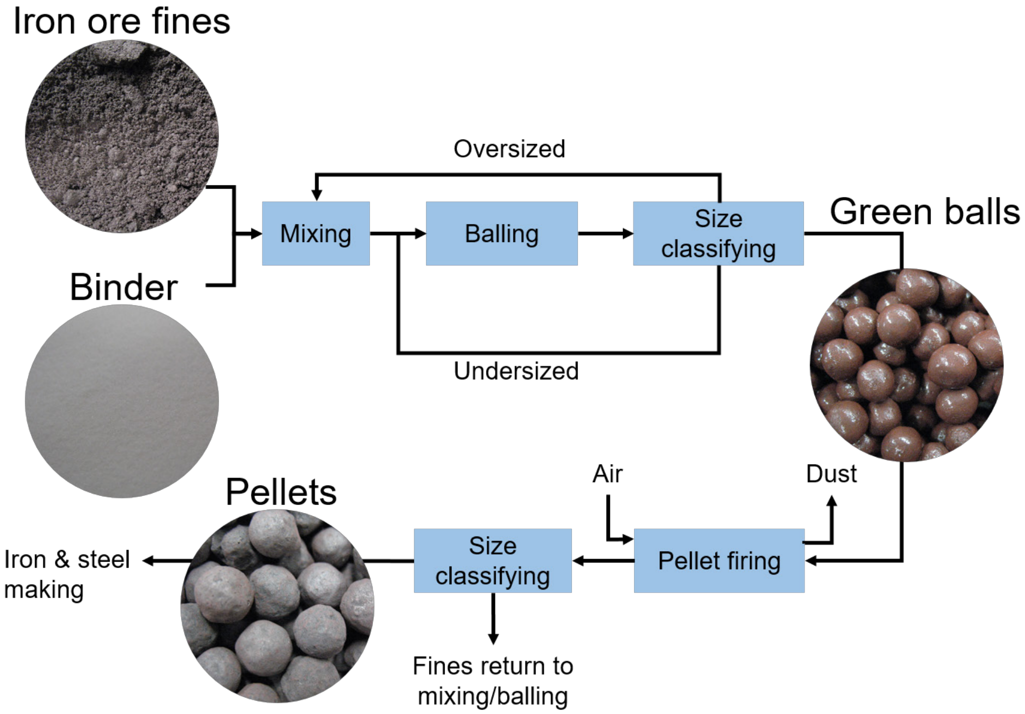

*Figure 1 Iron ore pelletizing process diagram. During iron ore pelletizing, moist iron ore concentrate and binder are turned into green balls and then heat-hardened to form pellets. Pellets are an intermediate ironmaking product used in blast and direct reduction furnaces.*

### *1.1.1 Iron ore pellet prevalence*

Blast furnaces and other ironmaking processes recover iron from lump ore[3], sinter[4] or pellets. In the USA and Scandinavia, pellets are the most common iron burden (Figure 2). Sinter still prevails over pellets in other countries; however, worldwide pellet production is increasing[5] with the decreased occurrence of high-grade ores; the increased beneficiation of finely disseminated ores; the occurrence of direct reduction shaft furnaces and mini-mill steel production; and preference for pellets instead of sinter and lump ore. Pellets generally have superior mechanical and metallurgical properties compared to sinter and lump, as well as uniform size and shape; these positively affect the ironmaking process.

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[3] Lump is the coarse portion (>6 mm) recovered by crushing and screening very high Fe containing ores (Geerdes et al., 2009)

[4] Sinter is a lumpy, irregular agglomerate made from medium-sized particles (around 1 mm) and flux. (Geerdes et al., 2009)

[5] Pellet production increased from 264 to 442 million metric tons from 1990 to 2010, a 67% increase. Kirk (1991; 1996, 2001, 2006, 2011).

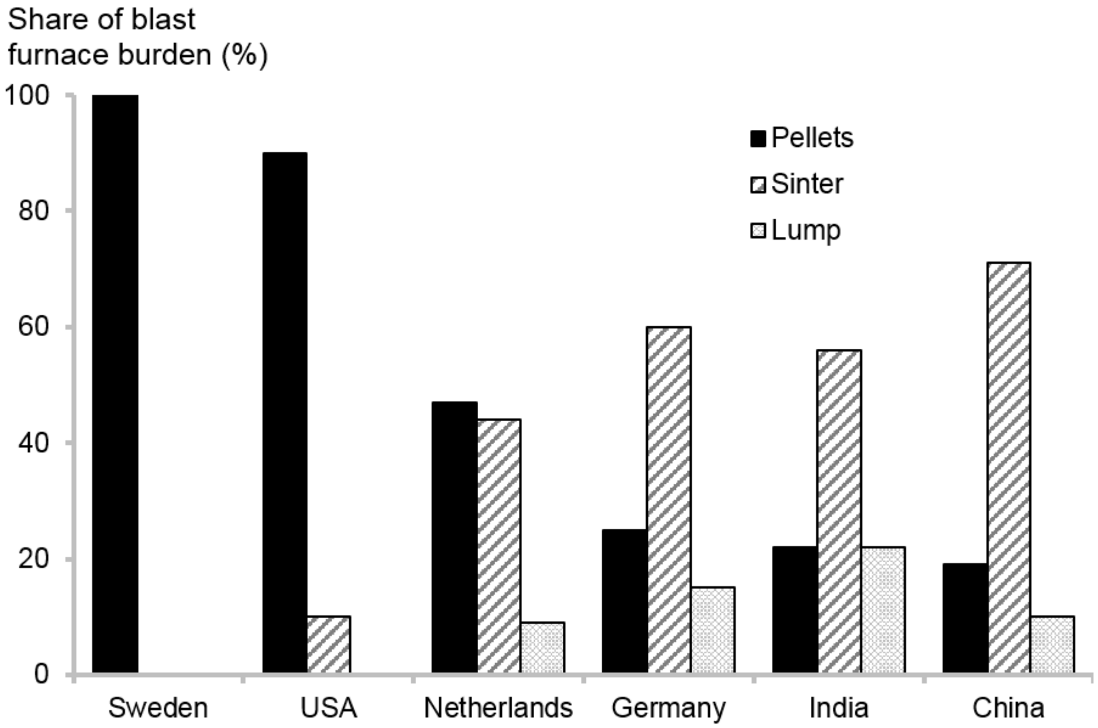

*Figure 2 Typical blast furnace burden proportions. Pellets dominate the burden in the USA and Sweden, but sinter is more common worldwide (Data collected from Mehl, 2011).*

### *1.1.2 Iron ore quality characteristics*

Table 2 lists commonly tested characteristics of pellets, their relevant test procedures and typically desired values (Halt and Kawatra, 2014). Pellet dustiness (not listed) is not commonly determined, but should be considering that "dust emissions are a high profile issue for the [mineral processing] industry…" (U.S. D.O.E., 2000).

#### 1.1.2.1 Pellet Dustiness

Pellets abrade during induration and as they are shipped and handled. Abrasion generates small particles that, depending on their size, can become airborne. Dust typically has aerodynamic diameters[6] less than ten micrometers ($PM_{10}$). For iron ore concentrates, this means the Stoke's diameters (or equivalent spherical diameters, which is close to the actual particle dimensions) are five micrometers and smaller (CEC, 1975).

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[6] The aerodynamic diameter of a dust particle is the diameter of an imaginary spherical particle, of unit density (1000 kg/$m^3$), that settles at the same velocity as the dust particle.

*Table 2 Desirable properties of iron ore pellets (After Halt and Kawatra, 2014). For conversion to Imperial units: 1 lbf = 4.448 N, 1 in = 25.4 mm, and °F = °C·9/5 +32.*

| **Pellet property** | **Test procedure** | **Desired values** |
|---|---|---|
| Compression Strength | Green, dry or fired pellets are crushed until they break. The maximum load before failure is recorded. ISO 4700 | >22 N/pellet, dry<br>>1780 N/pellet, fired |
| Size distribution | Pellets are sieved on screens of size 6.3-15 mm. ISO 4701 | >90% 9-12 mm |
| Drop number | Green balls are dropped 18 inches (45 cm) onto a steel plate repeatedly until they break. | >4-5 drops to break |
| Thermal shock | Green balls heated in a preheated furnace at various temperatures (100-1000 °C) for 10 min. Pellets removed and checked for cracks. Temperature where 90% of pellets survive without cracking is the shock temperature. | >350 °C |
| Tumble and abrasion indices | Tumble pellets in a drum of standard size. Then sieve pellets on 500 mesh and 6.3 mm screens. ISO 3271. TI is tumble index. AI is abrasion index. | >90% pellets +6.3 mm after tumble (TI)<br><5% minus 500 mesh after tumble (AI) |
| Reducibility | Record the weight loss of pellets as they are heated in the presence of a reducing gas. Gas composition and temperature are standardized. ISO 4695 | >0.5% $\text{min}^{-1}$ $(dR/dt)_{40}$ |
| Low-temperature Breakdown | Size distribution of pellets are measured after a static reduction test and dynamic tumble test. ISO 4696 | >80% pellets +6.3 mm |

Dust can be emitted from various points in the induration process as well as from fugitive sources such as pellet stockpiles, conveyor transfer points and ship or rail loading operations. Dust negatively affects process equipment (Jonsson et al., 2013); is a health nuisance and surrogate for hazardous air pollutants (NESHAP, 2003); and is regulated by environmental/pollution agencies.

How dusty is pelletization relative to other unit operations? Table 3 lists average uncontrolled emission factors measured during various iron ore beneficiation plant activities. Based on assumptions for the relative tonnages of materials handled in each activity, the rotary kiln portion of pelletizing was nearly as dusty as fine crushing. This intuitively makes sense, since pellets are still relatively weak when they first enter the kiln and abrade as they tumble. Relative dustiness levels of each activity are shown in Figure 3; the steps in between crushing and induration are wet processes and so aren't dusty.

*Table 3 Uncontrolled emission factors for various pelletizing activities (After EFIG, 1997). I calculated the normalized emission factors and relative magnitudes using the listed normalizing factors.*

| **Sampling Location** | **# of tests** | **Uncontrolled Emission factors, kg/t (lb/ton)** | **Normalizing factor** | **Normalized Emission factors** | **Relative Mag. %** |
|---|---|---|---|---|---|
| Crude ore dumps | 2 | 0.022 (0.044)[a] | 1.0 | 0.022 (0.044) | 0.33 |
| Coarse crushing | 16 | 0.029 (0.058)[a] | 1.0 | 0.029 (0.058) | 0.44 |
| Ore transfer | 32 | 0.43 (0.86)[a] | 1.0 | 0.43 (0.86) | 6.5 |
| Fine crushing | 22 | 6.6 (13)[a] | 1.0 | 6.6 (13) | 100 |
| Bentonite transfer | 2 | 1.6 (3.2)[b] | 0.0033[d] | 0.0053 (0.011) | 0.08 |
| Bentonite blending | 4 | 9.6 (19)[b] | 0.0033[d] | 0.032 (0.063) | 0.48 |
| Grate feed | 2 | 0.32 (0.63)[c] | 0.33[e] | 0.11 (0.21) | 1.7 |
| Grate Discharge | 2 | 0.69 (1.4)[c] | 0.33[e] | 0.23 (0.46) | 3.5 |
| Kiln | 61 | 18 (36)[c] | 0.33[e] | 5.9 (12) | 89 |
| Pellet handling | 7 | 0.52 (1.0)[c] | 0.33[e] | 0.17 (0.33) | 2.6 |

Notes: a-based on ore tonnage; b-based on bentonite tonnage; c-based on pellet tonnage; d-assuming a bentonite dose of 1% in pellets, and see note 'e'; e-assuming 33% of crude ore is recovered as pellets.

Note that Table 3 does not list the controlled emission factors. The controlled emission factors would be around 1-10% of the uncontrolled values based on typical capture efficiencies for control equipment (EFIG, 1997b; MRI, 1997), as well as the controlled values given in the report (EFIG, 1997a).

Two additional points to note are i) the emission factors from ore transfer and pellet handling are similar in magnitude and ii) the kiln is the dustiest part of pelletizing. Regarding the first point, pellets are handled in ports, often near densely populated areas, so uncontrolled pellet dust could have a wider social impact than ore dust.

Regarding the second point, plant operators are more concerned with effects of binders on dust loads in furnaces than on dust generated from handling pellets (confidential personal correspondence, October 29, 2014). Higher dust loads could lead to more furnace maintenance and downtime, thus negatively affecting furnace and pellet plant productivity. Furthermore, it is easy to spray pellets with water and dust suppressants to reduce dust emissions during shipping and handling (although, more fines will require greater consumption of dust suppressants).

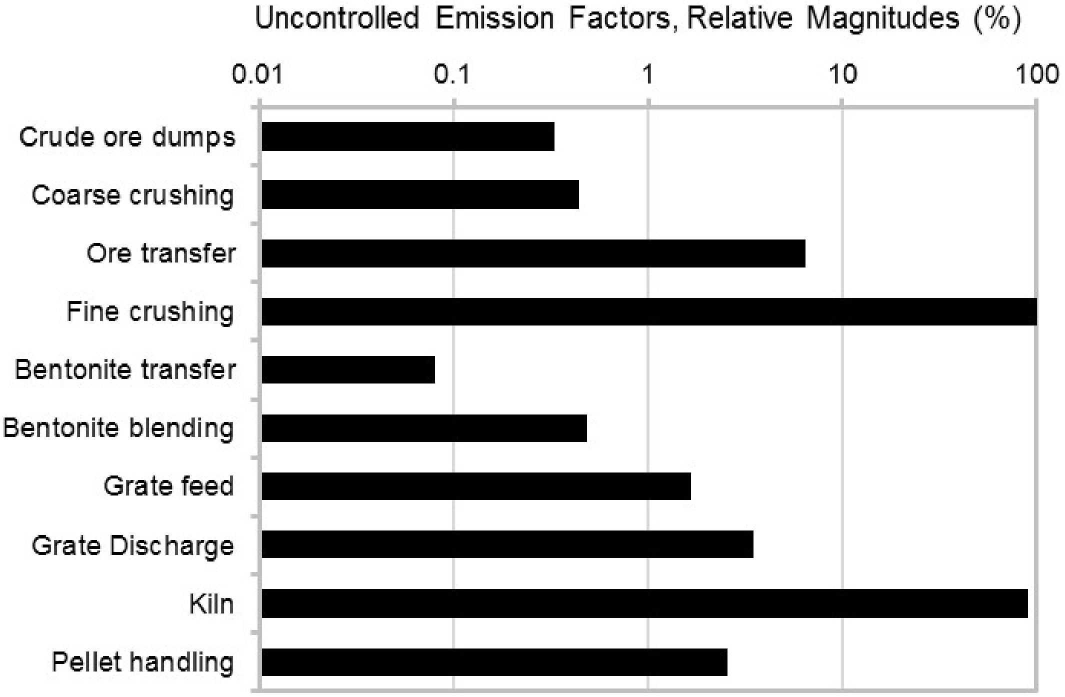


*Figure 3 Magnitudes of uncontrolled emission factors relative to fine crushing. For reference, fine crushing emissions were 6.6 kg dust per ton of crushed ore. I calculated the values from a summary of field tests reported in EFIG (1997), and give my calculation assumptions in Table 3.*

How can we control dustiness? Reactively, such as with suppressants, or proactively, by limiting fine particle generation. Not all generated fine particles are dust-sized, but the dustiness of pellets generally follows their abrasion resistance (Halt and Kawatra, 2015b; Halt et al., 2015a,b). You can see this in Figures 4-7, which show four correlations between fine particle generation and pellet dustiness. Three curves were obtained by laboratory experimentation with sieve shakers, rotary drums, and laboratory- and industrial-made pellets; the fourth contains several years of pelletizing stack emissions data from an operating pellet plant in Brazil. Altogether, they illustrate that to reduce pellet dustiness, we can increase the abrasion resistance of pellets (which is easier to test and better understood than dustiness). Unlike suppressants, this approach reduces dustiness both inside equipment and during shipping/handling.

What factors affect the abrasion resistance of pellets? Firing temperature, flux, binder, the concentrate's particle size distribution, porosity, furnace type and the quantity of oversized pellets influence the abrasion resistance and dustiness of pellets. The furnace type and large-pellet effects could be fundamentally related to firing temperature/intensity, as the pellet bed in straight-grate may not be uniformly fired (Gudenau et al., 1985; Oja, 2013) and large pellets are often underfired compared to small pellets (Gudenau et al., 1985). Furthermore, pellets fired in Grate-Kiln furnaces tumble as they travel through the kiln, which can smoothen their surfaces.

Considering the aforementioned factors, pellet abrasion resistance can be increased by increasing firing temperature, adding small quantities of flux (to acid pellets), increasing bentonite dose, making the concentrate finer, decreasing porosity, using grate-kilns instead of traveling grates, and screening out all oversized pellets before shipment. Of these factors, firing temperature, pellet screening and binder contents may be the most important and easiest to control and adjust at existing pellet plant. For preheated and under-fired pellets, such as inside of furnaces, the absence or presence of binders may be especially important.

## 1.2 Iron ore pellet binders

Binders influence pelletizing dynamics as well as the durability and strength of balls and pellets. Thus, they influence the operating behaviors and productivities of balling circuits, induration furnaces and entire pellet plants. In laboratory-scale pelletizing experiments, binders aren't always needed; in industrial pelletizing plants, they are necessary.

Bentonite clay is the most common binder, and it has been since the pelletizing process was developed around World War II. The main alternatives to bentonite are organic binders and slaked lime. Slaked lime can also be considered a flux, so we won't discuss it further.

### *1.2.1 Bentonite clay*

Bentonite contains mainly montmorillonite, an alumino-silicate mineral, and lesser amounts of other clay minerals and impurities. Montmorillonite has a laminated, or layered, structure with hydrated cations ($Ca^{+2}$, $Mg^{+2}$, $Na^{+}$) and water adsorbed on the inter-layer surfaces, which gives it unique properties (Murray, 2007; Odom, 1984).

Bentonite clay properties depend upon the interlayer cations present and their ratios. Iron ore pelletizers prefer sodium bentonite because it has higher viscosity, swelling, cation exchange capacity and water absorption than calcium/magnesium bentonites. Typical sodium bentonite doses in pellet plants in the USA are 18-20 lb/lt (8-9 kg/t) (Oja, 2013). With low-quality bentonite elsewhere in the world, doses can be as high as 40-60 lb/lt (18-27 kg/t), even after the clays are processed to improve their binding properties (Yang et al., 2007).

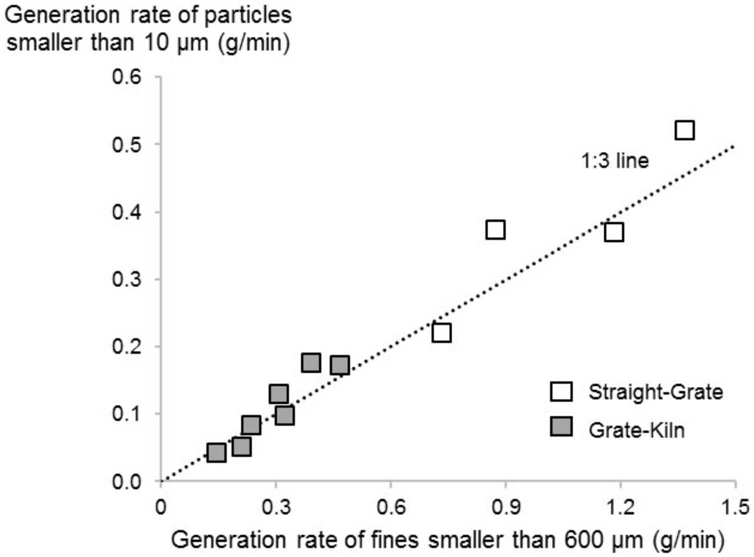


*Figure 4 Effects of furnace type on dust generation. Approximately 1/3 of the fines collected during sieve-shaker abrasion tests were smaller than 10 µm. Interestingly, the pellets fired in straight-grate furnaces (with a static pellet bed) were dustier than pellets fired in grate-kiln furnaces (containing a dynamic rotary kiln). After Halt and Kawatra (2015b).*

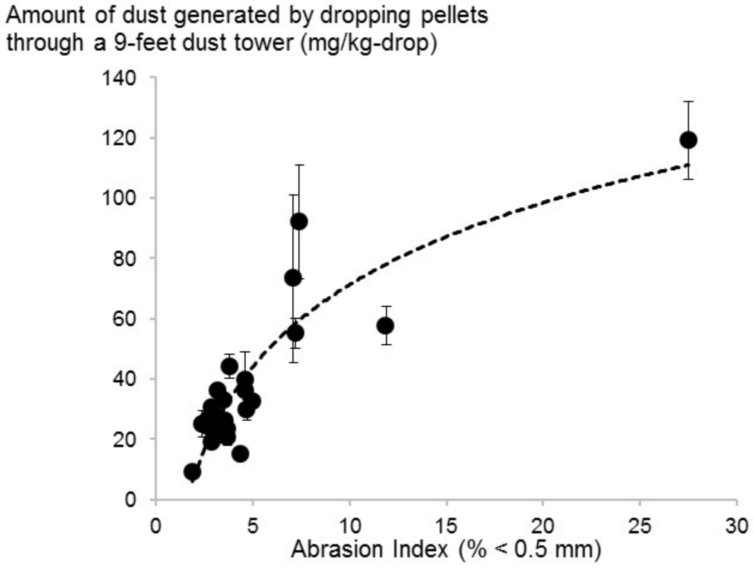


*Figure 5 Effects of Abrasion Index on dust generation. The Abrasion Index correlated to the amount of fresh dust generated by dropping pellets through a 9-feet dust tower. Importantly, firing temperature significantly affected the abrasion index and dustiness results. After Halt et al. (2015a).*

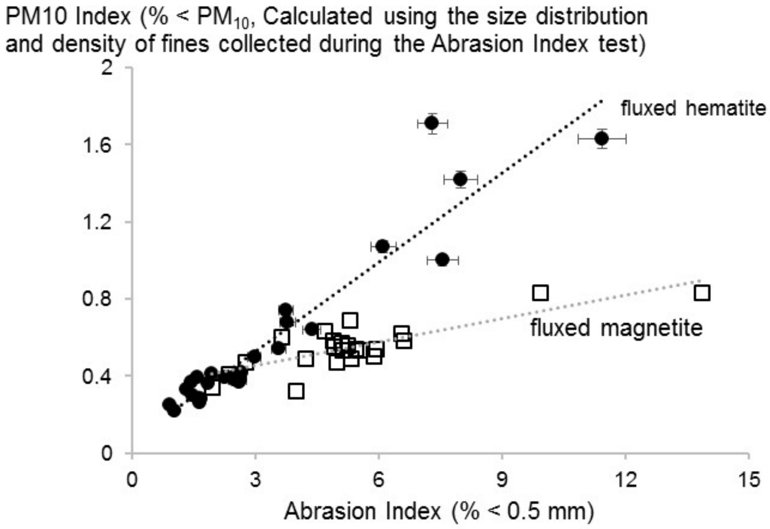


*Figure 6 Correlations between Abrasion Index and pellet dustiness, or the proportion of fines generated during an abrasion test that had aerodynamic diameters of 10 micrometers and smaller (called PM10). Importantly, firing temperature, binder and iron ore concentrate significantly affected the dustiness of pellets. After Halt and Kawatra (2015b) and Halt et al. (2015b).*

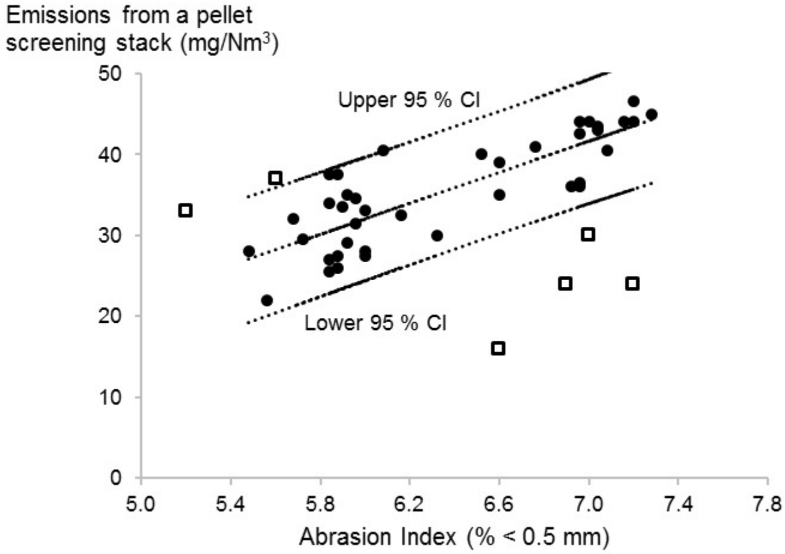


*Figure 7 Influence of the Abrasion Index on particulate emissions from a gas stack serving the pellet screening facility at a pelletizing plant in Brazil. The data spans a period of four years, and each point represents a monthly average. The hollow data points are those outside of the 95% confidence intervals (CI). After Halt et al. (2015b)*

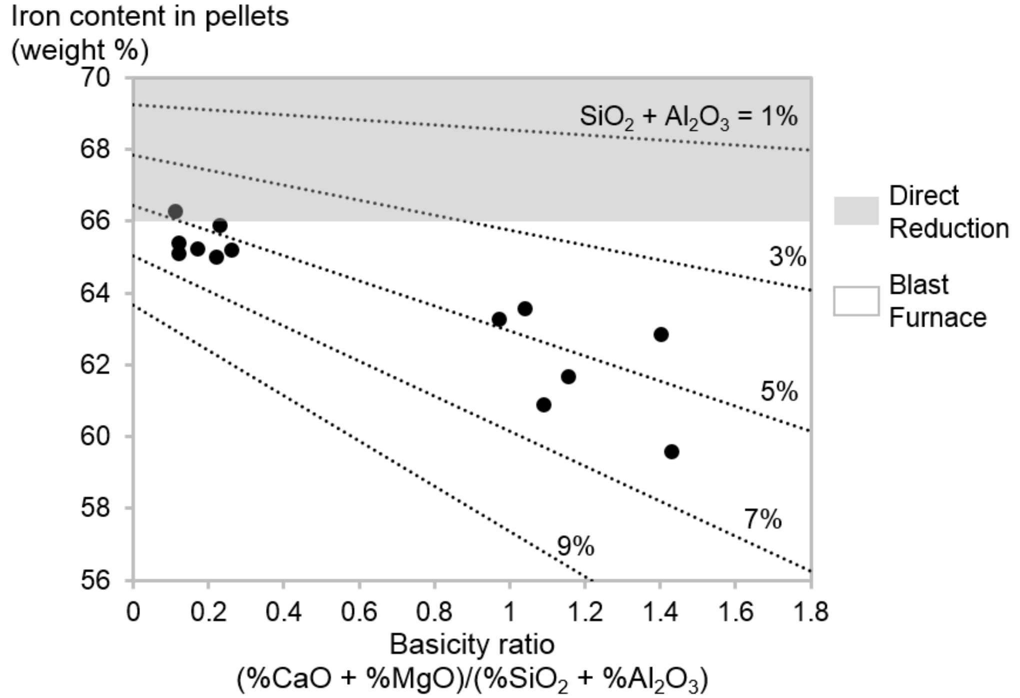


*Figure 8 Influence of basicity ratio and gangue content on iron ore pellet purity. The black circles show compositions of USA pellets from 1997 (compiled from Poveromo, 1999). The concentrate grade and the flux and binder contents affect pellet composition. Organic binders are of interest especially when making low-silica pellets for direction reduction furnaces and mini-mills. After Halt and Kawatra (2014a).*

Bentonite clay is a good binder: it retards green-ball growth, giving balls time to densify and strengthen before they reach the desired size; it increases the inter-particle moisture's viscosity which increases balls resistance to impact breakage and spalling; and it forms films between particles that bond green-balls as they dry. Then during firing, pellets strengthen at lower temperatures with bentonite than they do without.

Despite its many benefits, it is ironic that bentonite is the most common binder – unwanted minerals such as quartz, silicates and clays are separated from the iron-rich minerals and discarded during the process stages preceding pelletization, only to be mixed back into the concentrate to make pellets! This affects pellet grade (although not as significantly as the concentrate grade received from the beneficiation plant) which ultimately influences whether pellets can be used in blast furnace or direct reduction processes (Figure 8).

*Table 4 List of organic binders for iron ore pellets. Tabulated from Halt and Kawatra (2014a)*

| | | | | |
|---|---|---|---|---|
| Guar gum | Sulfonated Bitumen | Bitumen | Fuel oil | Wheat starch |
| Corn starch | Dextrin | Dextrose | Carboxymethyl Starch | Peat moss |
| Humates | Causticized Leonardite | Polyacrylamide | Whey & lactose | Papermill sludge |
| Alginates | Lignosulfonates | Molasses | Carboxymethyl Cellulose | Hydroxyethyl Cellulose |

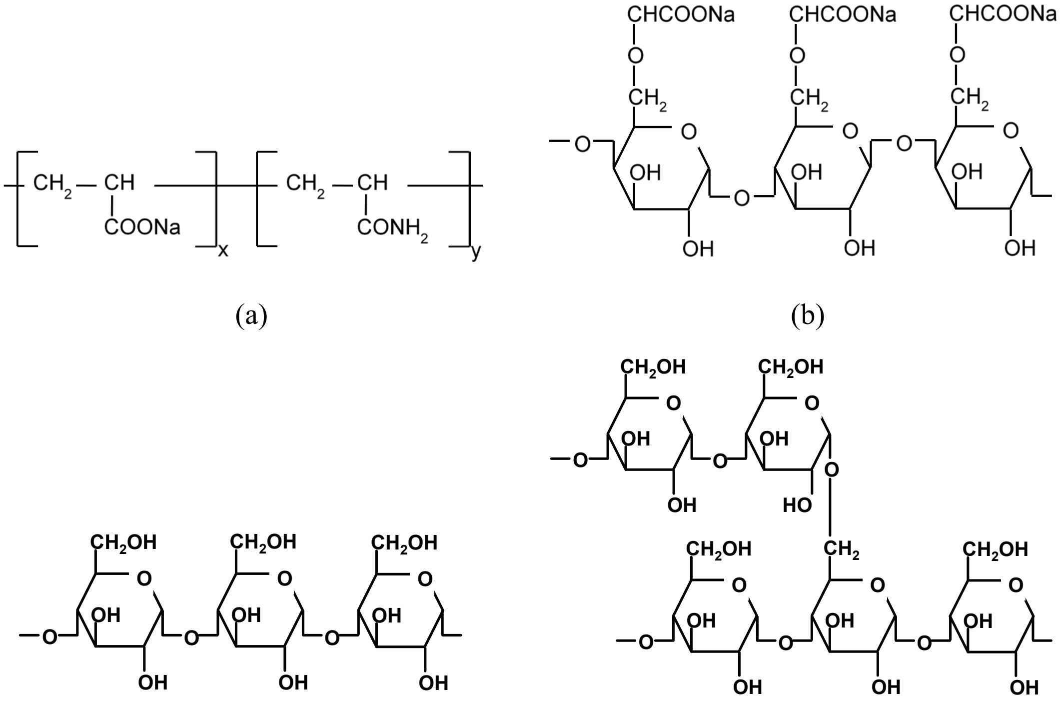
Bentonite also decreases pellet reducibility, especially at low reduction temperatures, by impeding gas transport into the pellets (Erickson and Stone, 1987; Haas et al., 1989; Yang et al., 1983). Reducing the formation of glassy slags (such as from bentonite) is usually the first step taken to improve reducibility (Tokutake, 1989). Because bentonite contaminates pellets and decreases reducibility, researchers continue to try to increase its quality and find suitable alternative binders.

### *1.2.2 Organic binders*

Many types of organic materials have been proposed, patented and evaluated as binders for iron ore pellets. They have ranged from natural materials such as peat moss and animal manure (!), to waste products from paper mills and dairies, to synthetic polymers including anionic polyacrylamides and cellulose ethers. Table 4 lists several examples. Pelletizers can add them in the form of aqueous solutions or dry powders, but dry powders are preferred for wet concentrates.

Organic binders all combust to some degree during the high temperature pellet firing process – this is why they are so attractive compared to bentonite, and purportedly why they are so problematic compared to bentonite. Let us understand why.

Organic binders combust at around 200-300 °C, while pellet strength doesn't begin to increase significantly until around 900 °C. On one hand, binder combustion increases pellet purity and purportedly porosity, which leads to higher reducibility. On the other hand, the long interval without binder and resultant lower solid volume fractions can weaken pellets, which makes them more friable. Weaker pellets can lead to more fragments, chips, and dust when making, shipping, and handling pellets as well as when making iron in blast furnaces and direct reduction furnaces.



(a) (b)

(c) (d)

*Figure 9 Molecular structures of organic binders. Shown are anionic polyacrylamide (a), sodium carboxymethyl cellulose (b), and the main starch components amylose (c) and amylopectin (d). After Halt and Kawatra (2014a).*

The most successful organic binders have been anionic polyacrylamides (aPAM), the cellulose derivative carboxymethylcellulose (Na-CMC), and to a very limited degree, modified starch (Figure 9). These contain the hydrophilic and polar groups $–COO^-$, -OH, and $-CONH_2$ that are important for ore wettability and adhesion (Qiu et al., 2003).

Figure 10 shows the quality of green and dry balls made with aPAM, Na-CMC and starch binders. The aPAM (samples b through g) and Na-CMC (samples h-j) binders spanned a range of molecular weights and ionic contents, and the two starch samples (samples k and l) spanned a range of cold-water-solubility values. This shows us that it is possible to control pellet quality by varying the molecular structure and processing history of the binders, and hence their properties.

It is also important to note that the organic binder dose was 0.1% (dry weight to weight) while the bentonite dose was 1.0% (dry weight to weight). Those are typical order-of-magnitude doses for each. It is commonly stated that 10 times more bentonite binder is required than organic binder. If the concentrate needs a lot of organic binder to make good pellets, the binder can become too expensive to use (especially if the binder is a manufactured polymer).

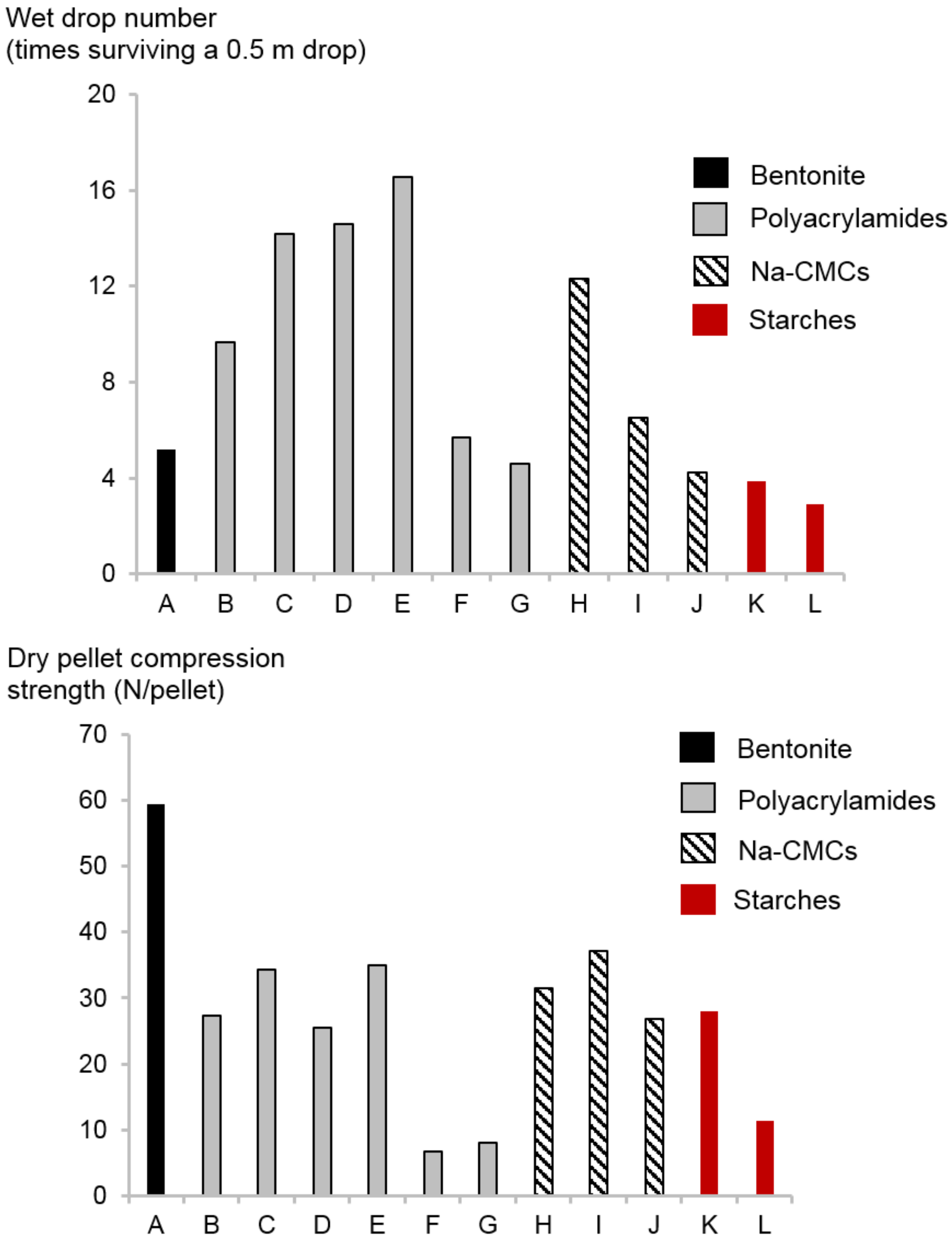


*Figure 10 Green and dry ball quality with organic binders. Effects of bentonite, polyacrylamides, sodium carboxymethyl celluloses and starches on the wet drop number (top) and dry compression strength (bottom) of fluxed magnetite pellets. Bentonite dose was 1.0%. Organic binder dose was 0.1%. Green ball moisture content was 9.4 ± 0.6% (mean ± 1 standard deviation). Plant D magnetite. (JA Halt, unpublished data, collected during MS Thesis research).*

## 1.3 Coatings for iron ore pellets

Pelletizers or furnace operators may coat certain types of iron ore pellets for a variety of reasons. It could be to minimize abrasion, reduce the potential for stickiness, or improve induration. To reduce abrasion and stickiness, they add coatings to fired pellets; to improve induration, they add coatings to green balls.

Bitumen and polymer coatings have been added to fired pellets to reduce friability and abrasion losses (Bales et al., 1986; Hey et al., 2008; Alves et al., 2014; Araujo et al, 2016). They help smoothen surfaces by covering surface asperities, and make surfaces hygroscopic which helps to retain water (meaning less water is required for suppression purposes).

Cement, limestone, dolomite, alumina, and bentonite coatings have been added to direct reduction (DR) pellets to stop pellets from sticking together and forming large clusters in the DR furnace (Basdag and Arol, 2002; Hayashi, et al., 1993; Hooey, et al., 2004; Poveromo, 2006; Yi et al., 2014; Wong et al., 1999). The clusters develop as iron forms near the pellet surfaces, which then sinters and bonds separate pellets together into clumps. The siliceous minerals reduce sticking, but are not always as effective as the basic minerals. Sterneland and Jönnson (2003) unexpectedly found that coatings reduced dust formation inside of an experimental blast furnace.

Solid fuel coatings have been added onto hematite pellets to improve the induration process (Lellep, 1956; Apuli, 1957; Godin & Wilhelmy, 2008). Adding the fuel as a coating allows easy adjustment of the fuel ratio, increases furnace capacity, and minimizes sintering of pellet cores. As we've already seen, under firing pellets is the main factor causing fines and dust generation.

## 1.4 Organization of dissertation

The rest of this dissertation is organized as follows. Chapter 2 contains a review of starch and its use as a binder. This includes results from my own early experiments, since there was so few published results surrounding starch. Chapter 3 presents our three approaches to improving starch-based binders. This includes published literature supporting their development and our experimental results with sand, and hematite and magnetite concentrates. Chapter 4 presents laboratory and pot-grate results (a type of pilot scale test) comparing the three approaches. Finally, the dissertation concludes in Chapter 5. Experimental materials, procedures, and typical test statistics are described in Appendices 1, 2 and 3.

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# Chapter 2 Starch Binder Review

Around the time that the pelletizing process was developed, DeVaney (1952) proposed starch as a binder. In the year 2014, my advisor charged me to use starch as the binder for iron ore pellets. Starch is relatively cheap, doesn't contaminate pellets, and its gels are viscous and adhesive; these are all good binder characteristics. In practice however, starch leads to weak pellets with rough surfaces (Figure 11). Weak, rough pellets are friable, meaning they increase the amount of fine particles and dust generated within process equipment (increasing furnace downtime and reducing productivity) as well as during pellet shipping and handling (requiring more dust suppressants).

## 2.1 Starch

Starch is made up of two types of carbohydrate polymers, amylose and amylopectin, that are bound up within water insoluble granules. The major sources of starch are corn, potato and wheat; hence, it's easy to get and cheap. Amylose is a linear, low molecular weight molecule, and amylopectin is a bulky, branched molecule with high molecular weight. Starch granules also contain small quantities of fats, proteins, and ash-forming inorganic materials. Table 5 lists typical native starch granule compositions.

Starch is physically modified by extrusion, drum drying, and jet milling processes, or by cooking them in water-alcohol solutions. The modification process weakens and eventually breaks the granules so they swell, become more soluble and form gels. Caustic soda addition decreases the temperature required to gelatinize the starch. Starch can also be chemically modified, with acids, oxidizers, cross-linkers and enzymes, to form starch derivatives with many types of properties. For example, researchers made graft copolymers of starch and polyacrylic acid, and carboxyethyl starch to increase starch water absorption and water solubility (Haas et al., 1989; Qiu et al., 2003; Zhou et al., 2010). For thorough reviews of starch and its processing and properties, see Ashogbon and Akintayo (2013), Whistler (1973), Rutenberg (1980) and Swinkels (1985).

Figure 12 shows pregelatinized starch granules in glycerol (top). Their angular, coarse structure resulted from the extrusion and subsequent milling process. When we added distilled water to the imaging solution (bottom), the starches swelled and formed a viscous mass. We'd like to point out that physically modified starches (such as found in Figure 12) and chemically modified starches are all commonly called modified starches – this can be confusing since the side groups

*Table 5 Typical starch granule compositions. After Swinkels (1985)*

| **Granule properties** | **Potato starch** | **Maize starch** | **Wheat starch** | **Tapioca starch** | **Waxy maize starch** |
|---|---|---|---|---|---|
| Amylose content (%) | 21 | 28 | 28 | 17 | 0 |
| Amylopectin content (%) | 79 | 72 | 72 | 83 | 100 |
| Amylose, (Degree of polymerization, DP) | 3,000 | 800 | 800 | 3,000 | --- |
| Amylopectin (DP) | 2,000,000 | 2,000,000 | 2,000,000 | 2,000,000 | 2,000,000 |
| Lipids (%, dry basis) | 0.05 | 0.7 | 0.8 | 0.1 | 0.15 |
| Proteins (%, dry basis) | 0.06 | 0.35 | 0.4 | 0.1 | 0.25 |
| Ash (%, dry basis) | 0.4 | 0.1 | 0.2 | 0.2 | 0.1 |
| Phosphorus (%, dry basis) | 0.08 | 0.02 | 0.06 | 0.01 | 0.01 |

Ash content derives from mineral matter. It mainly contains Ca, K, Mg, Na and P.

Phosphate content significantly influences properties of potato starch solutions.

on amylose and amylopectin molecular structures are not significantly altered during physical processing (Weissenborn et al., 1995).

Modified starch preferentially adsorbs to hematite surfaces over hematite-associated gangue minerals. Researchers still debate the fundamental mechanisms, but generally consider it irreversible (Weisenborn et al., 1995). Thus, starch is used as a hematite flocculant in reverse hematite flotation and dispersion-selective-flocculation processes (Carlson & Kawatra, 2013; Haselhuhn and Kawatra, 2015; Ma, 2011; 2012). Perhaps beneficial for fluxed pellets, dextrin, a low molecular weight starch derivative, has similar adsorbabilities onto hematite and calcite (Khosla et al., 1984; Liu et al., 1994).

## 2.2 Starch as binder

Raw or unmodified starch is insoluble, which makes it a bad binder (Ball et al, 1973; Haas et al, 1989; Srivastava et al, 2013). If the drying conditions are appropriate, however, you may be able to gelatinize the starch as balls dry. Capes (1971; 1980) showed that starch gels stopped soluble salt-based pellet binders from wicking to the ball surfaces. The gel eliminated salt crust formation and homogenized salt distribution, so ball strength increased (more from salt homogenization than starch addition).

Haas et al. (1989) tested many modified potato, corn and wheat starches as pellet binders, perhaps expecting that their differing amylose-amylopectin ratios and molecular weights would influence balling behavior and ball quality. However, the variation between corn, potato and wheat starches was less than the variation that existed within a single starch type (Figure 13). Interestingly, most of their starches were first cooked and dried and then added as a dry powder to the dry concentrate. Starch can recrystallize as it dries, making rehydration difficult and affecting its solubility – we believe that this may have caused the wide variability in the compression strengths that they observed. Unfortunately, Haas et al (1998) did not describe any of their binder preparation details.

Based on that hypothesis, and the simple observation that uncooked starch gives 'bad' results while modified starch gives relatively 'good' results, McDonald and Kawatra (2016) tested pregelatinized starches of varying cold-water-solubility. They found that dry compression strength linearly correlated to the solubility value, regardless of starch type (Figure 14), and that high soluble starches formed extensive films within unfired pellets (Figure 15). Their pellets were also significantly stronger than those made by Haas et al., (1989), either due to the starch preparation or to the ore types tested. McDonald and Kawatra (2017) also found that pellet quality was unaffected as the particle size of approximately 50% cws starches decreased from 200 to 75 μm.

As seen in Figure 14, modified starch gives high dry compression strengths, or strong unfired pellets. However, that is a transient benefit as starch burns away, roughly around 300 °C. After it burns, pellets are as weak as when binder isn't used. Because of the low ash content, preheated pellet compression strengths and abrasions resistances are lower than they would be with bentonite (Figure 16). Pellets bonded with starch also have low drop numbers and rough surfaces.

Starch contents in unfired pellets are higher on the surfaces than in the core (Figure 17). The enrichment occurs during balling, and not the drying process (Halt and Kawatra, 2016a). Contrary to popular belief, the starch content on pellet surfaces did not correlate to the friability of the pellets. Qualitatively, friability seemed to follow surface roughness: we previously observed that the fineness of indurated pellet abrasion products increased with tumble time (ie larger asperities worn away first, then smaller and smaller, etc.) (Halt and Kawatra, 2015b). So, reducing pellet roughness should reduce dustiness.

Pelletizers can add starch binders as dry powders or as aqueous solutions. The dry form may not be as effective because the amylose retrogrades (recrystallizes) as the gels are dried and powdered (Rutenberg, 1980), but the decrease in effectiveness may be outweighed by the ease of application and other benefits. Aqueous solutions will be easy to homogenize into the concentrate, but may add too much water to the concentrate and require an additional concentrate drying stage prior to balling. Alternatively, using starch slurries will require lower filter cake moisture levels than usual, which could decrease plant throughput (lowering filter cake moisture to appropriate levels for pelletizing can be a process bottleneck [Carlson et al, 2008]).

*Figure 11 Magnetite pellets prepared with modified starch binder (top) and the standard binder bentonite (bottom). Starch-bonded pellets are visually much rougher than bentonite bonded pellets. Plant A magnetite. 60% cold water solubility corn starch. Sodium bentonite (SB1). Refer to Appendix 1 beginning on page 89 for material descriptions.*

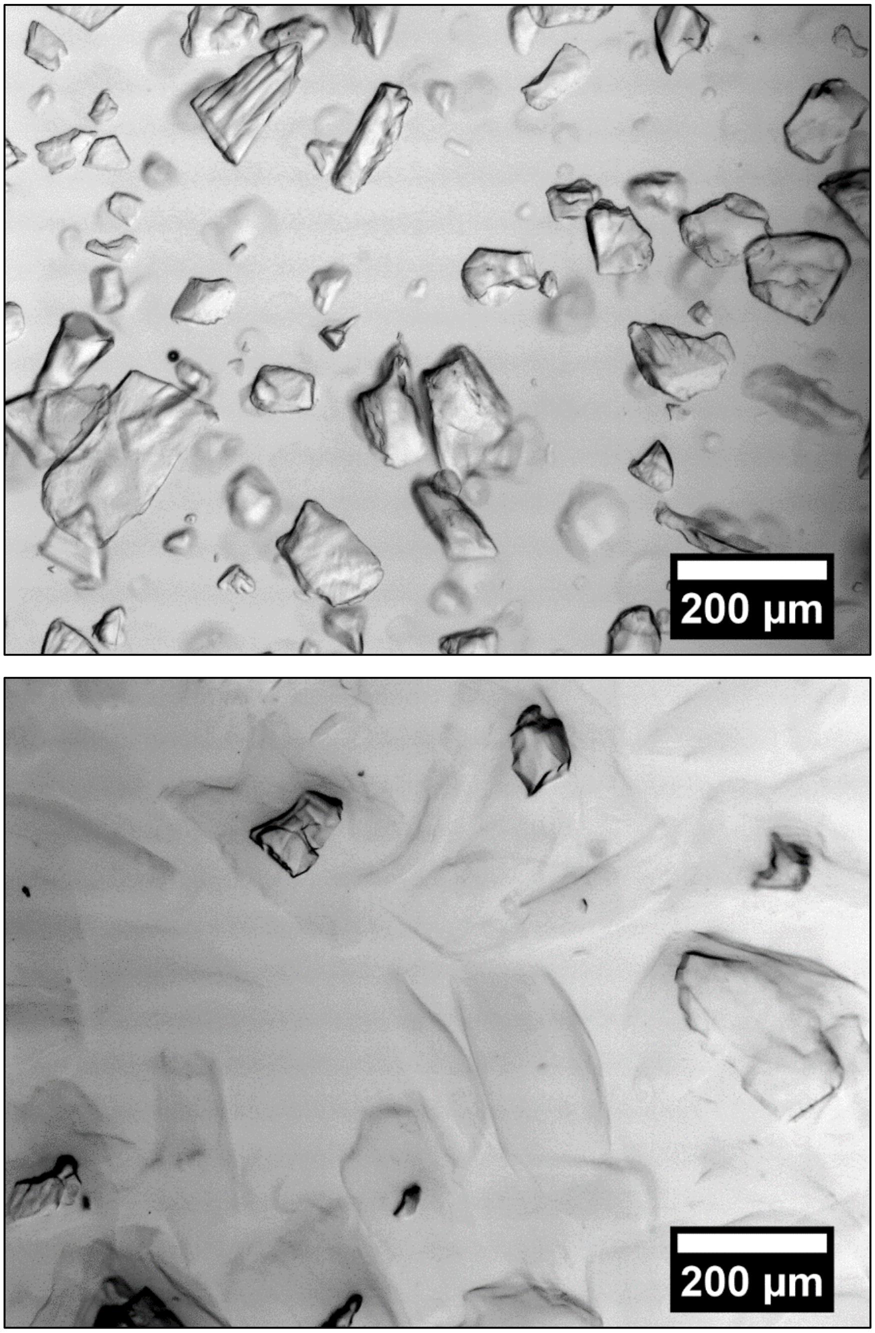


*Figure 12 Photomicrographs of modified starch granules.*

*Photomicrographs of pregelatinized starch granules in glycerol (top) and in an approximately 50/50 mixture of distilled water and glycerol (bottom). Starch cold-water-solubility was 60%. The granules, initially angular from the milling process, swelled as they absorbed water from the imaging solution.*

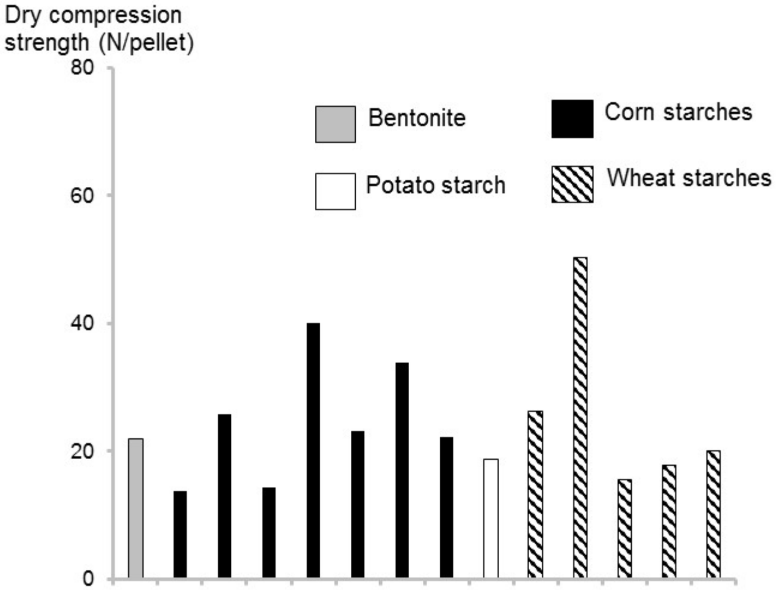


*Figure 13 Effects of many starches on dry compression strength. Adapted from Haas et al (1989). Average green-ball moisture content for these conditions was 7.9±0.7 % (± 1 standard deviation). Bentonite dose was 0.5%. Starch dose was 0.1%. The starches were gelled before pelletizing and then added as a dry powder to dry concentrate. Variations within starch type were greater than the variation between starch types.*

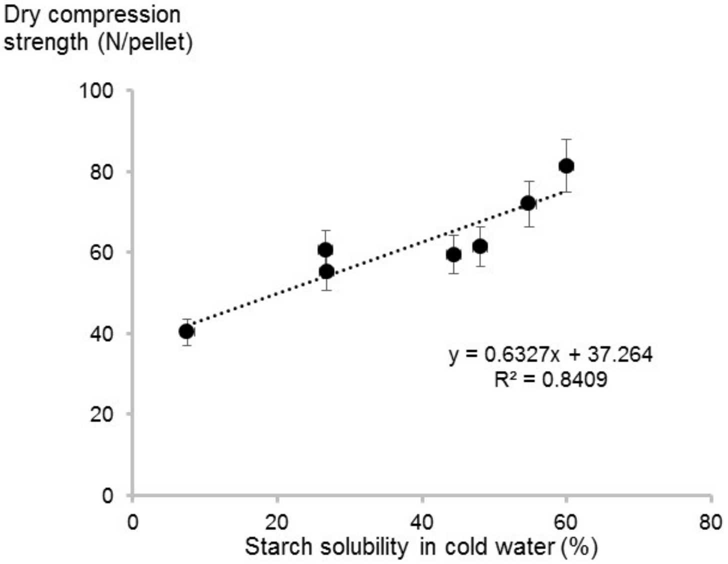


*Figure 14 Effect of starch cold-water solubility on dry compression strength of unfired pellets. Both corn and wheat starches included in the curve. After McDonald and Kawatra (2016; 2017). Error bars are reportedly 95% confidence intervals*

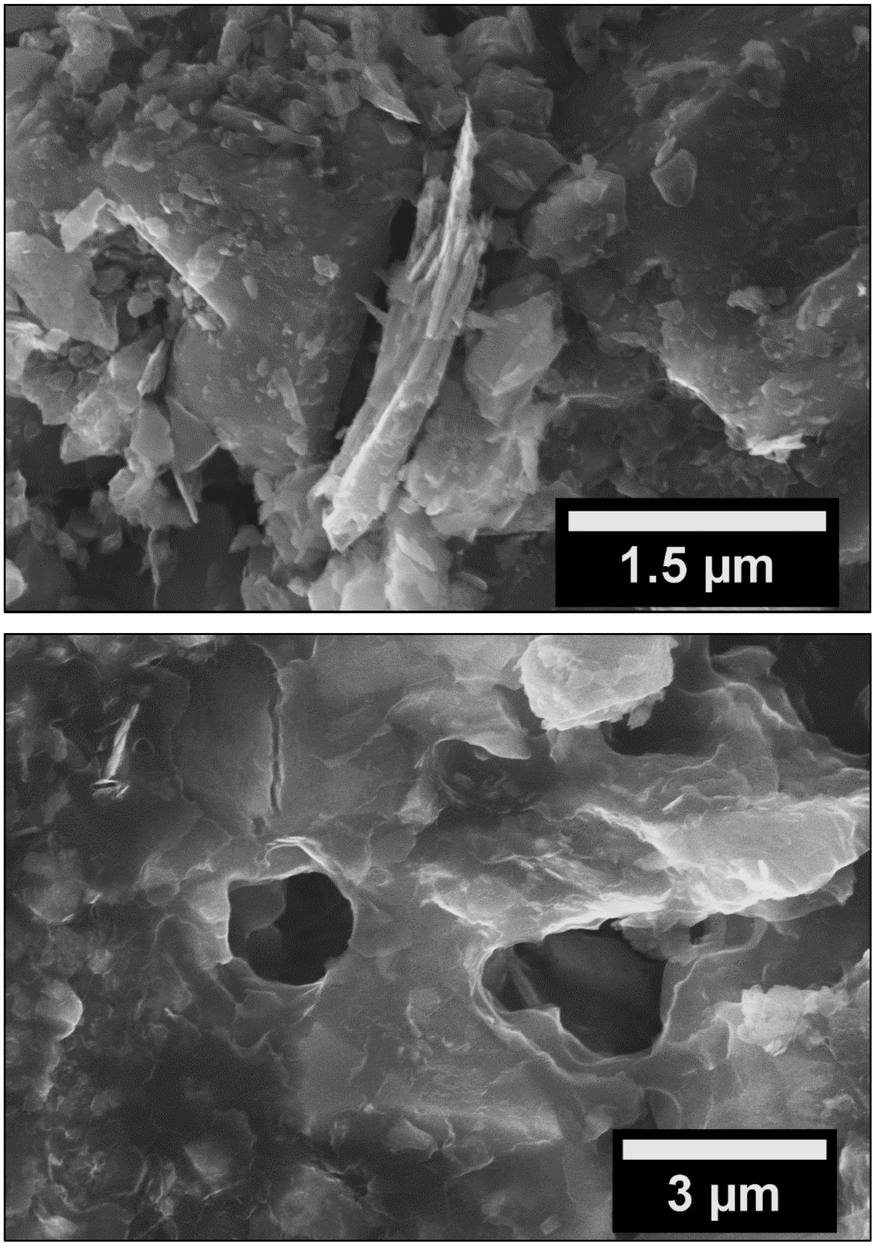
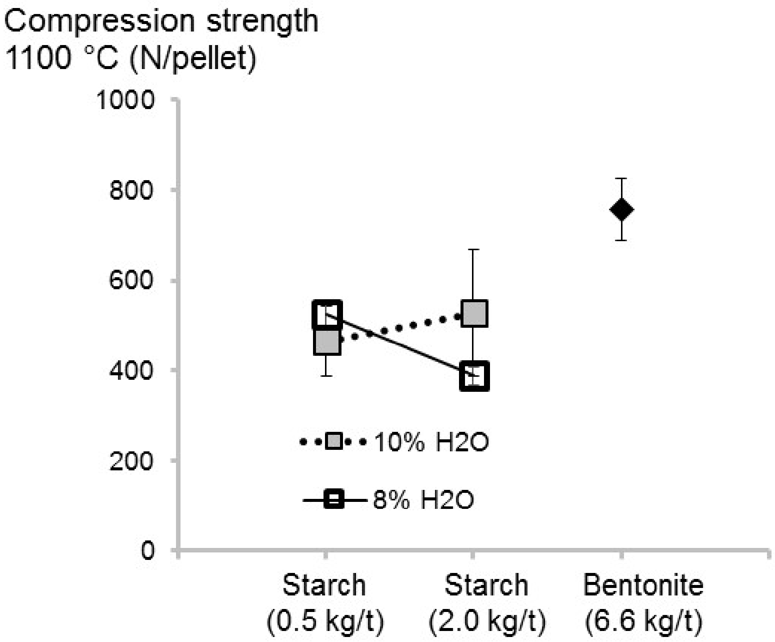


*Figure 15 Presence of starch films in unfired pellets. Unfired pellet without starch (top), showing discrete particles from the concentrate (Plant F). Unfired pellet with starch (bottom), showing an extensive film covering and bonding particles together. Photomicrographs first published in XXVII International Minerals Processing Congress, Santiago, Chile (Halt and Kawatra, 2014). See Appendix 4, Figure 46, for permission.*



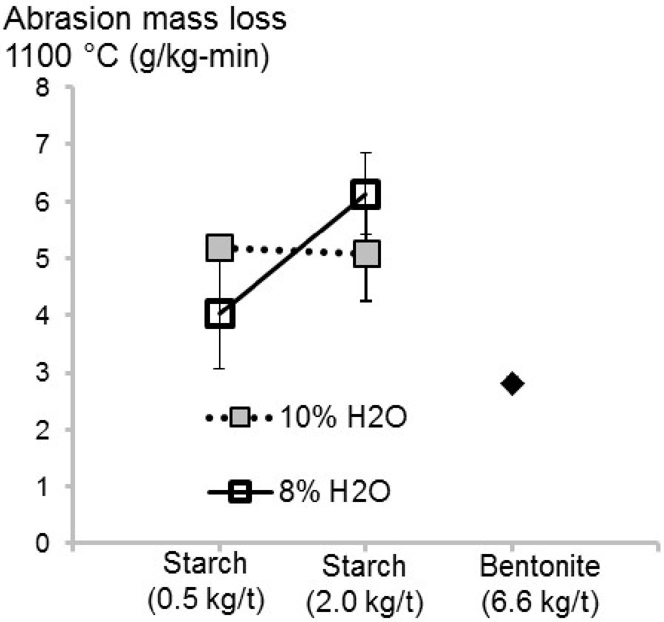
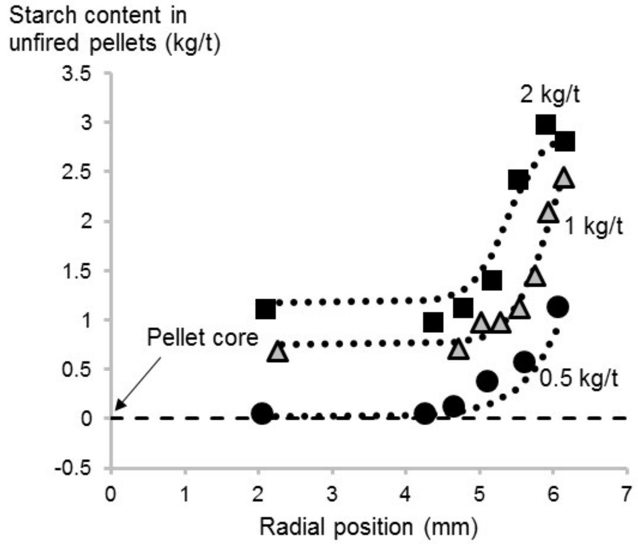


*Figure 16 Starch effects on fired pellet quality. Effects of modified starch and sodium bentonite on the compression strength (top) and abrasion mass loss (bottom) of preheated hematite pellets. Similar results seen with pellets fired at 1250 °C, though the moisture effects were less. After Halt and Kawatra (2016a). Plant F hematite. 60% cws corn starch. Sodium bentonite SB1. Refer to Appendix 1 beginning on page 89 for material descriptions.*



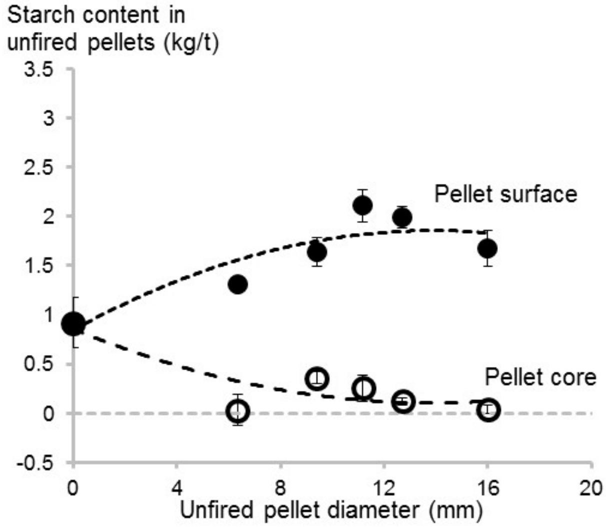


*Figure 17 Starch distribution in unfired pellets. Effects of modified starch dose on its distribution in unfired pellets (top), and the effects of unfired pellet diameter on the starch content in unfired pellet cores and surfaces (bottom). Starch content found by tumbling unfired pellets in a drum, periodically collecting the powder that abraded from the surfaces, and analyzing their weight loss profiles in a TGA. After Halt and Kawatra (2016a). Plant F hematite. 60% cws starch. Refer to Appendix 1 beginning on page 89 for material descriptions.*

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# Chapter 3 Engineering Binders to Reduce Dustiness

So far, we know that modified starch is a poor binder that leads to rough pellets and high levels of fine particles and dust. How can we build better low-silica binders using modified starch as the base material? Here, we'll show three approaches, with silica content in the binders decreasing from approach 1 to 3. The three approaches are

(1) Addition of clay to starch. The addition of clay to organic binders is not a novel idea. In fact, it is the standard method used for their improvement. However, it has not been tested extensively for starch. This approach was expected to be successful.
(2) Addition of a clay-rich layer to green ball surfaces. The coating's purpose was to mimic the good surface properties of standard bentonite-clay bonded pellets; beneficially, clay consumption will decrease as the coating layer becomes thinner. This approach is a novel idea.
(3) Addition of dispersants to starch. The intent of the dispersants was to enable pelletization to occur at lower moisture contents, thus leading to denser particle packing and lower porosity. The dispersants resulted in significantly stronger, smoother pellets without contaminating them with silica. This approach is a novel idea.

To develop these approaches, we pelletized acid magnetite concentrate (Plant A), fluxed hematite concentrate (Plant F) and pure silica sand, with binders made from starch, clays, clay substitutes, and many chemical reagents commonly found in mineral processing plants. See Appendices 1-3 for material descriptions, experimental procedures, and typical pelletizing test statistics.

## 3.1 Approach 1: Addition of clay to starch

The first approach to decrease pellet friability is to add bentonite clay to starch. This is a simple way to solve organic binder problems. Examples of this approach include bentonite plus Alcotac FE4 (Eisele and Kawatra, 2003), bentonite plus Peridur XC-3 (Steeghs, 1989), and bentonite plus paper mill sludge (Haas et al., 1988). Haas et al's pot-grate testing showed that the sludge-bentonite mixture led to higher wet drop number, dry compression strength, and fired compression strength, and lower Abrasion Index and R40 value than sludge; the only drawback in their study was the lower R40 reducibility value (Haas et al., 1988). We acknowledge that McDonald and Kawatra (2017) recently added bentonite to starch to improve its performance;

however, they only tested fired compression strength, which is an insignificant or insensitive test when evaluating binders.

Generally, bentonite improves pellet mechanical properties, decreases pellet reducibility, and aids balling. Since starch will help with balling, we may not need high quality bentonite clay in the mixture. In other words, lower quality clays may work. Haas et al (1987) showed that, at a dosage of 1%, many low-quality clays from the Midwestern United States gave sufficient strengths to fired pellets. We tried to use lower quality clays and silica-containing wastes instead of high quality bentonite clay in order to reduce total binder cost. Although this clay-starch mixture approach is not a unique idea, it was effective.

### *3.1.1 Approach 1 – Laboratory results using fluxed hematite concentrate*

We prepared pellets using Plant F hematite and 60% solubility corn starch. See hematite XRD in Figure 41, particle size distribution in Figure 42, and chemical composition in Table 7. Pelletization procedures are described in Appendix 2.

After preliminary comparison tests with a variety of sodium and calcium bentonites and silica-rich waste materials, we chose to study binder mixtures composed of starch plus Class F fly ash, starch plus sodium bentonite and starch plus calcium bentonite. See Table 9 (in Appendix 1) for their compositions, 80% passing size by laser diffraction ($P_{80}$), and plate water absorbance values (PWA). The alumina content and particle size of the Class F fly ash were relatively high, and its water absorption very low, compared to the bentonite samples.

Figures 18-19 shows that sodium bentonite improved green and dry ball quality more than calcium bentonite and Class F fly ash, but all balls were of good quality; the dry compression strength results clearly confirmed that starch is more adhesive than clays. They also show that sodium bentonite gave the best overall abrasion resistance to pellets, but at moderate dosages, calcium bentonite and sodium bentonite performed equally well.

The poor results with the Class F fly ash were unexpected, considering its composition was similar to the clay materials. We had hypothesized that, because of the similar chemical compositions, they would react equally with the concentrate and give similar abrasion resistances. That did not occur.

Using SEM-EDS and optical microscopy, we easily found spherical fly ash particles dispersed throughout the pellet matrix. In Figure 20, of a pellet fired at 1250 °C, the fly ash particle ‘A’ clearly reacted with and wetted the surrounding grains, as seen in the inset labeled ‘Region A’. In the inset, the dark gray phase is fly ash and the light phase is iron oxide. However, the fly ash still presented as spherical particles. Thus, despite bond formation between the iron oxide and Class f fly ash, the potential bonding material provided by the fly ash was in effect insufficiently dispersed throughout the pellet – if it’s locked within large spherical particles, it can’t be used for bond formation. Bentonite, which gave good results, has a flaky structure, very small particle size, and high surface area.

In attempts to improve fly ash’s performance, we wet screened the as-received ash and retained only the ultrafine fraction (-500 mesh fraction); milled the ash in an attritor for one hour with sodium polyphosphate dispersant until its size distribution approximated the clay’s size distribution; and leached the ash in boiling sulfuric acid for forty minutes to attempt to lower the alumina content (Matjie et al., 2005). Lowering the alumina content could potentially improve its fluidity and thus increase its ability to wet the ore particles.

Figure 20 shows that only the milling process improved the Class F fly ash's performance, presumably by reducing the ash’s sphericity (Jeong, 2016) in addition to particle size. The quantity of material passing 8 µm increased from 37% to 94% during milling.

In summary, adding clay or clay substitutes to starch binders can, and did, improve the quality of preheated and fired pellets. Sodium bentonite gave the best overall performance, but calcium bentonite and sodium bentonite gave similar results at intermediate dosages. There is potential to manufacture good binders from Class F fly ash, but we did not investigate this approach any further.

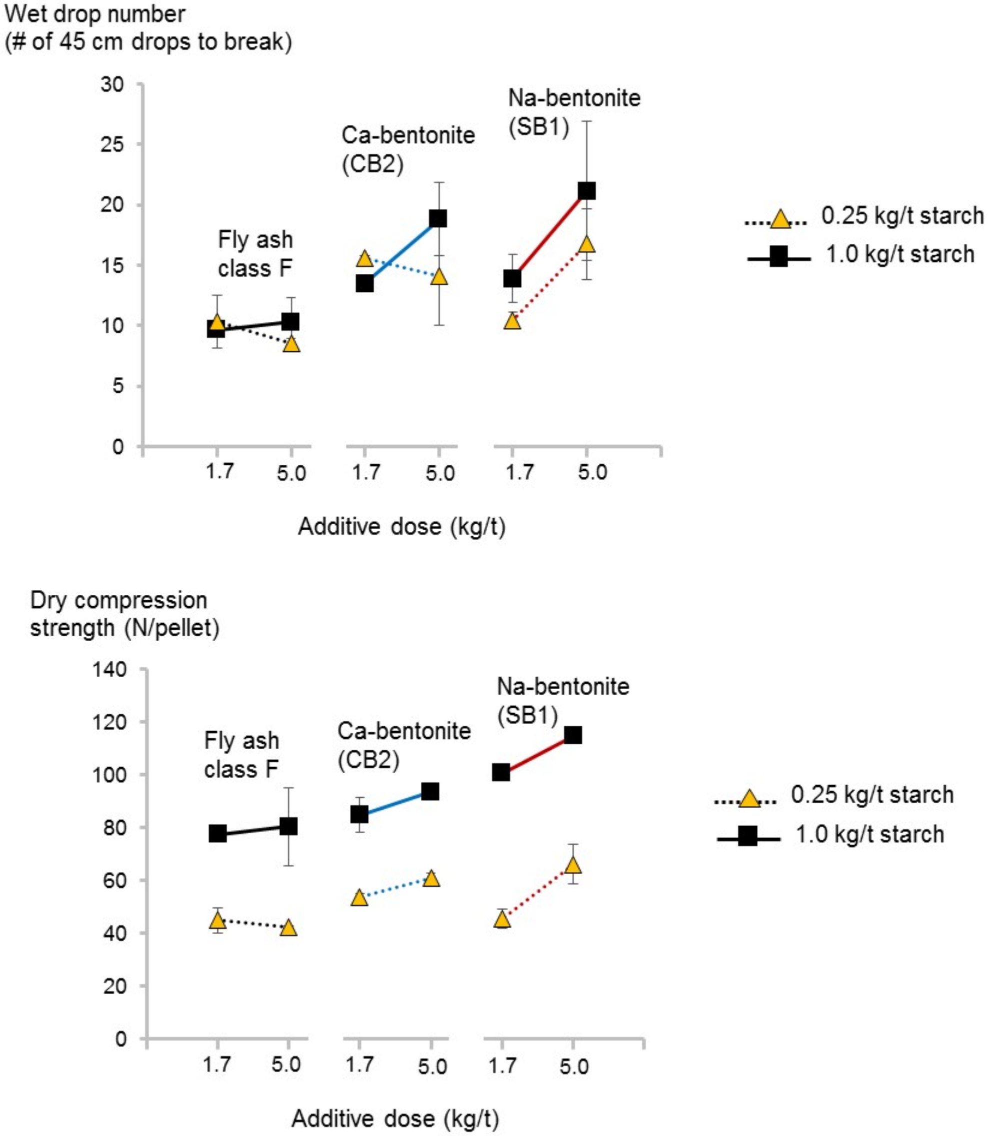
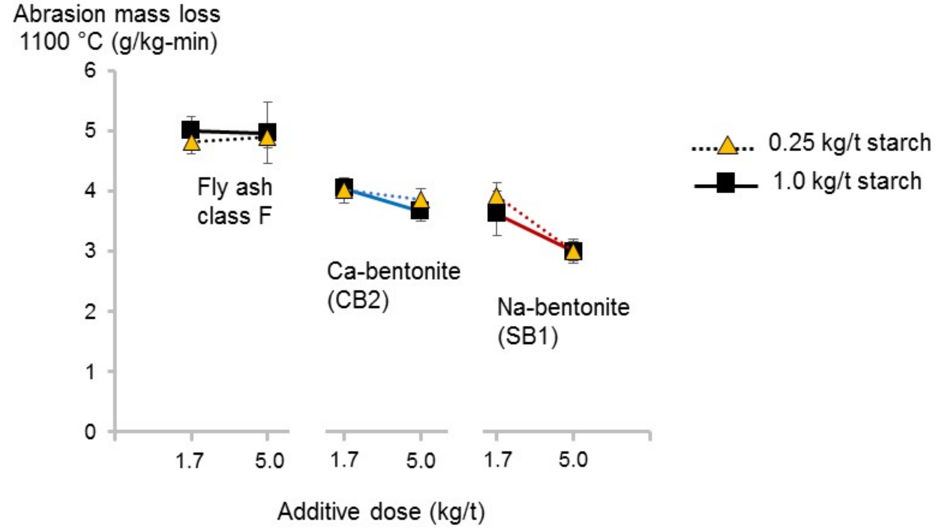


*Figure 18 Effects of starch-clay mixtures on wet drop (top) and dry strength (bottom). Hematite concentrate from Plant F. 60% cold water solubility starch. This figure shows that sodium and calcium bentonite gave equally good wet drop numbers, and sodium bentonite induced the highest dry strengths. Class F fly ash was relatively ineffective at all doses. To be submitted as Halt and Kawatra (2017a). See Appendix 1 (page 89) for material characterizations.*



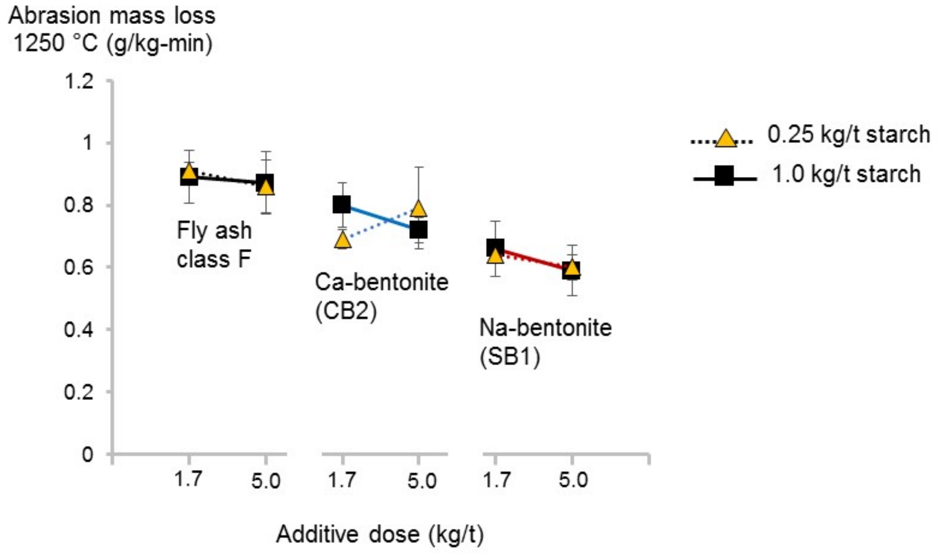


*Figure 19 Effects of starch-clay mixtures on pellet friability: preheated pellets (top) and fired pellets (bottom). Hematite concentrate from Plant F. 60% cold water solubility corn starch. This figure shows that sodium bentonite induced the lowest friability, though calcium bentonite performed similarly at lower doses. Class F fly ash was relatively ineffective at all doses. To be submitted as Halt and Kawatra (2017a). See Appendix 1 beginning on page 89 for material characterizations.*

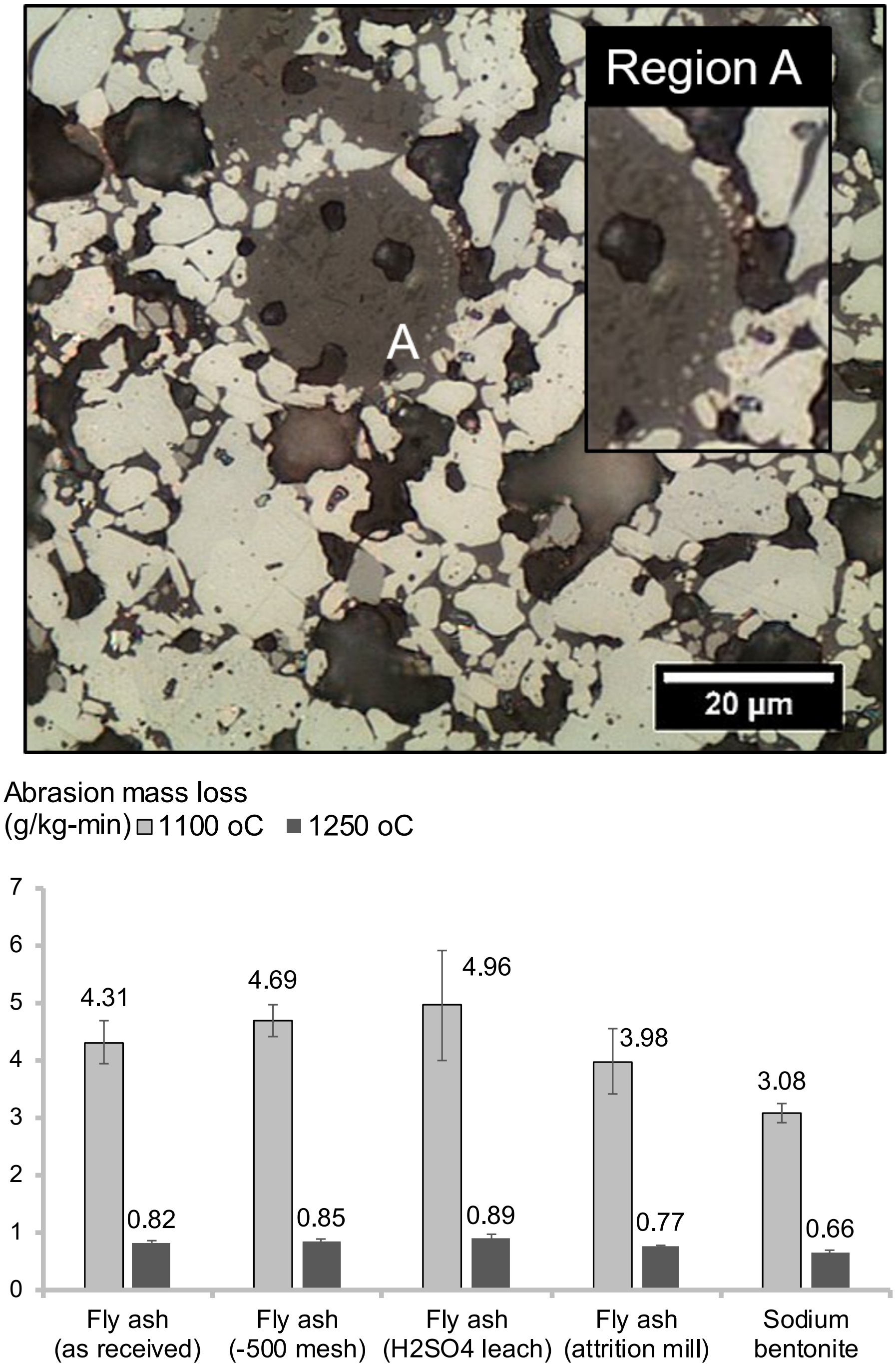


*Figure 20 Enhancing Class F fly ash binder performance. Photomicrograph of Class F fly ash particles in an indurated pellet (top): Fly ash is dark gray phase and iron oxide the light gray phase in the inset. The inset illustrates that ash wets nearby iron oxide grains. Effects of ash preprocessing techniques on pellet abrasion resistances with starch-fly ash mixtures (bottom): attrition milling fly ash to reduce its particle size and sphericity improved its performance. To be submitted as Halt and Kawatra (2017a). See Appendix 1 beginning on page 89 for material characterizations.*

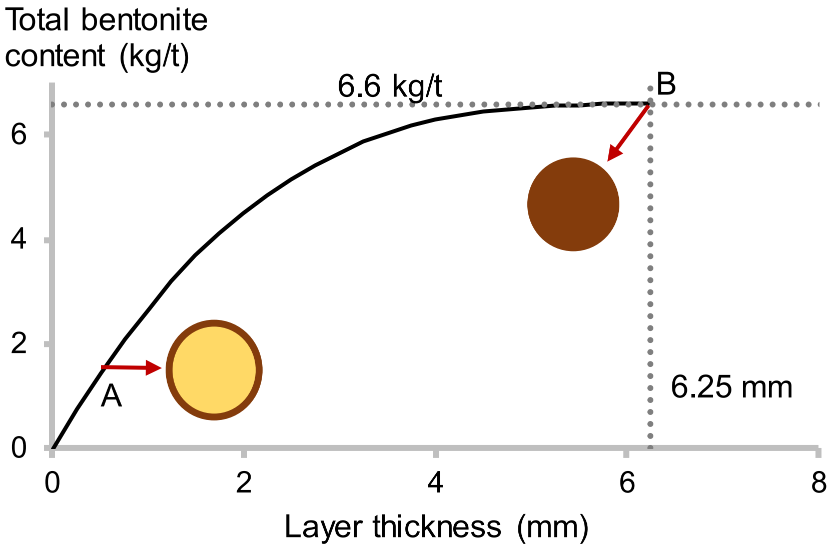


*Figure 21 Bentonite content vs layer thickness. Total bentonite content in pellets vs the thickness of the bentonite-containing layer. Calculation assumptions: 6.6 kg/t bentonite in the layer, 3.4 g/cm$^3$ density, 12.5 mm pellet diameter. Dark brown/grey is bentonite-containing layer, and light brown/grey is bentonite-free layer. To be submitted as Halt and Kawatra (2017a).*

## 3.2 **Approach 2: Addition of a clay-rich layer to green ball surfaces**

Abrasion, which produces the fine particles making up dust, is a surface phenomenon. Thus, if we induce starch-bonded pellets to have similar surface characteristics as standard bentonite-bonded pellets, we can reduce fines generation and dust. We believed we could decrease friability by adding a bentonite-rich coating, or layer, to the outside of green balls made with starch binders.

The quantity of bentonite will be much lower in pellets if bentonite is applied as a surface coating rather than a homogeneous dispersion throughout the whole pellet. Figure 21 shows the potential reduction in total bentonite dose, based on the thickness of the bentonite-containing layer. For example, with a thickness of 0.5 mm (point A), total bentonite dose is approximately 1.5 kg/t – a 77% decrease from the standard dose in iron ore pellets (point B). I calculated the curve by assuming the following: 6.6 kg/t of bentonite in the layer, 3.4 g/cm$^3$ pellet density, and 12.5 mm diameter pellets.

This approach is novel – nobody has studied or patented green ball coatings aiming to lower bentonite dose, or to lower the abrasion index for pellets made with organic binders. This approach is not absurd since coatings of cement, alumina, and bentonite (and/or basic minerals) are already added to direct reduction (DR) pellets; the coatings stop pellets from sticking together and forming large clusters in the DR furnace (See section 1.3). The major difference between those practices and ours is that we propose adding the coatings before firing, while those listed above are sprayed as aqueous slurries onto fired pellets. Again, Sterneland and Jönnson (2003) unexpectedly found that coatings, designed to minimize clustering, reduced dust formation inside of an experimental blast furnace. Perhaps researchers could design coatings to solve both abrasion/dust and pellet clustering problems.

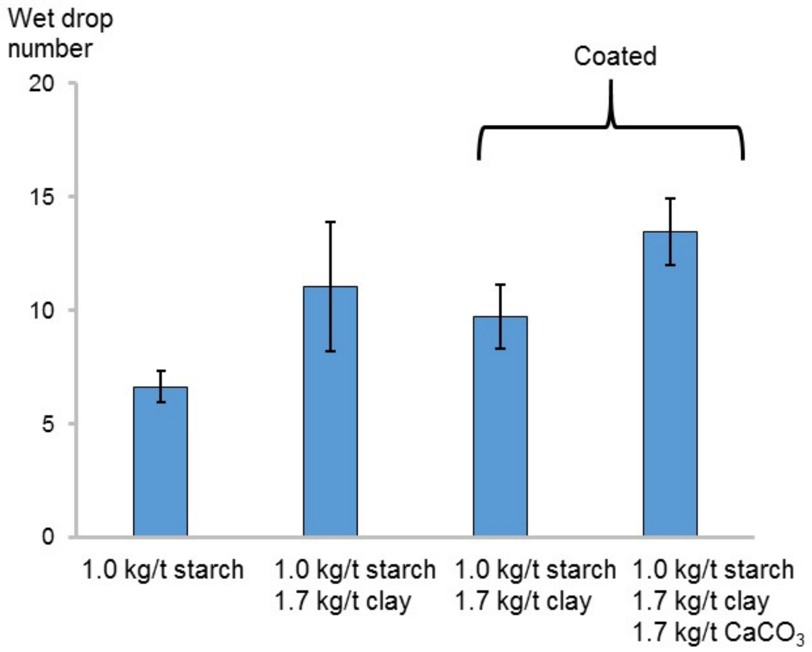
### *3.2.1 Approach 2 – Laboratory results with acid magnetite concentrate*

We prepared coated green balls using an acid magnetite concentrate from Plant A, sodium bentonite (SB1), and reagent grade calcium carbonate (Sigma Aldrich, ACS grade). The concentrate's XRD is in Figure 41, particle size distribution in Figure 42, and composition in Table 7. Our green balling and coating procedure is in Appendix 2, especially in Figure 43 and the associated description.

We added two types of coating layers to the acid magnetite balls. One type of coating contained sodium bentonite (SB1). The other type contained sodium bentonite (SB1) and calcium carbonate. Based on our coating procedure, balls with 5.0 kg/t clay in the coating globally contained 1.7 kg/t clay. Similarly, balls with 5.0 kg/t calcium carbonate in the coating globally contained 1.7 kg/t calcium carbonate. All green balls contained 1.0 kg/t starch (60% cold water solubility). To determine if coatings were effective, we prepared green balls containing 1.7 kg/t evenly mixed into the concentrate (the typical way to make pellets).

Figures 22-23 shows that the coatings improved the wet drop number, did not affect the dry compression strength, and decreased pellet friability. So, concentrating the bentonite near the pellet surface significantly improved the pellets abrasion resistance compared to homogenously dispersed bentonite. In this simple test case, the coating was more effective because it had a higher surface concentration of bentonite than the reference case. The bentonite-only layer led to a 30% decrease in friability at 1100 °C and a 26% decrease at 1250 °C., while the bentonite-carbonate layer led to a 20% decrease at 1100 °C and an 8% decrease at 1250 °C.

In summary, when we added a bentonite-concentrate mixture in thin layers near green ball surfaces, pellet abrasion resistance was significantly higher than when we added the bentonite homogeneously throughout the pellet. In these comparison tests, the global bentonite concentrations were the same.



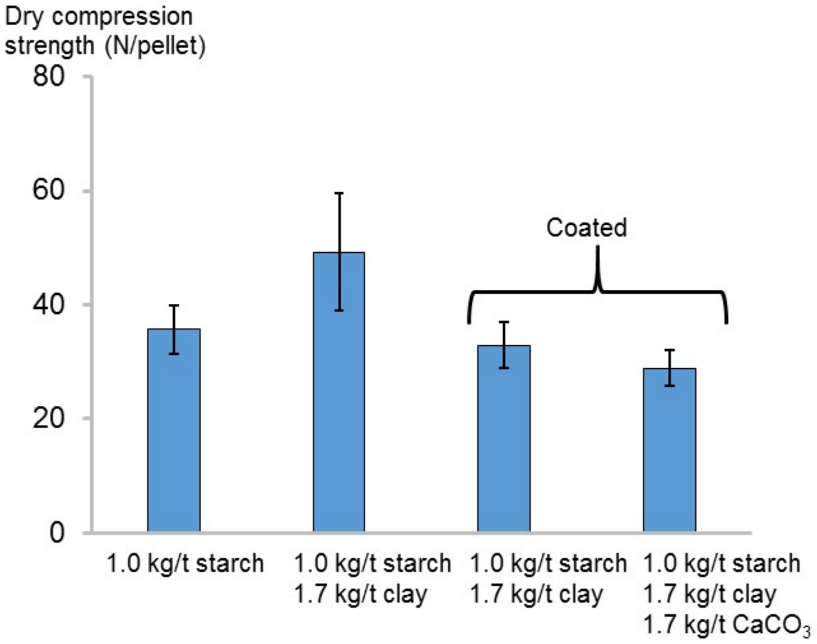


*Figure 22 Effects of coatings on green and dry balls. Coating effects on wet drop number (top) and dry compression strength (bottom). Plant A concentrate. 60% cold water solubility corn starch. Sodium bentonite clay (SB1) and calcium carbonate (Sigma Aldrich, ACS grade) contents were 1.7 kg/t. See Appendix 2 for coating procedure. See Appendix 1 for material characterizations. To be submitted as Halt and Kawatra (2017a).*

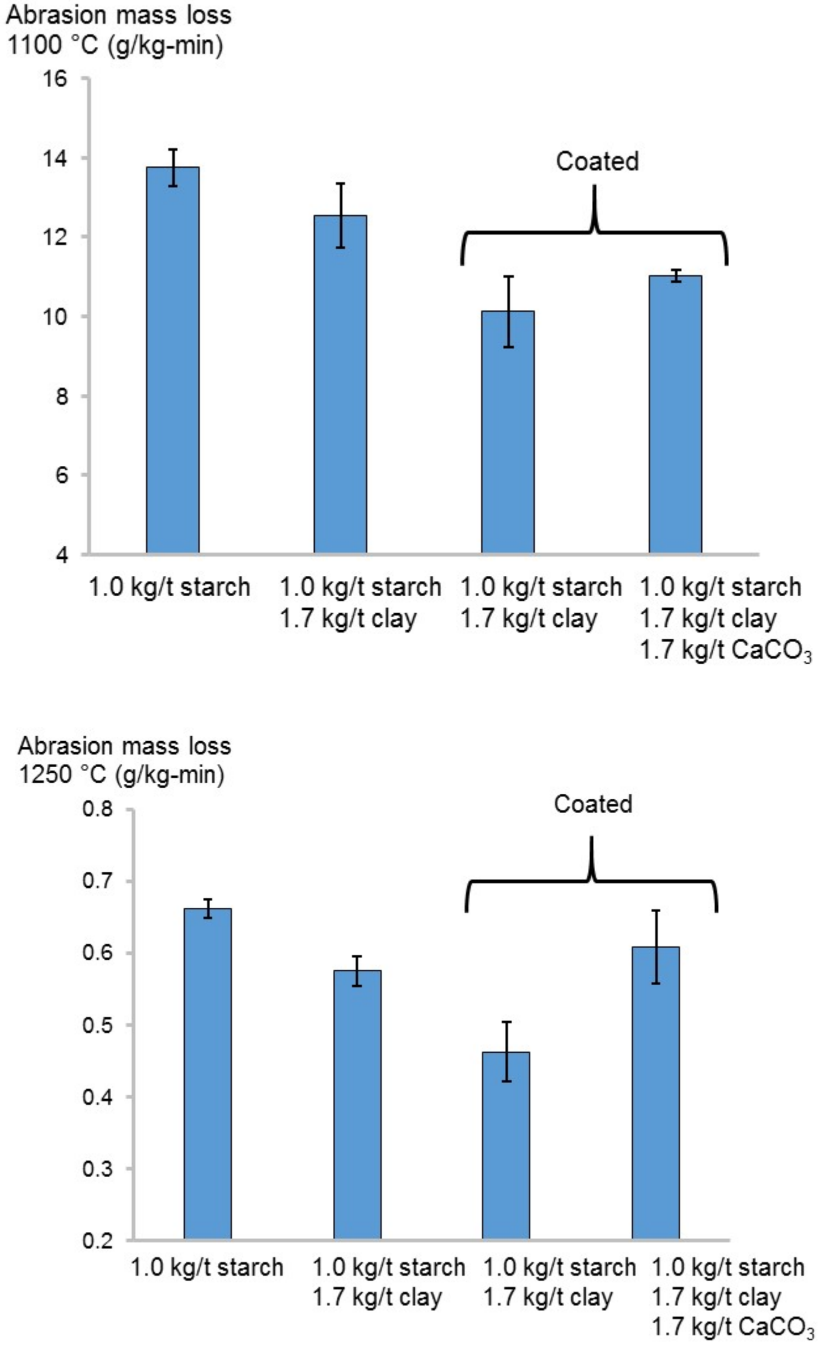


*Figure 23 Effects of coatings on fired pellets. Effects of coatings on abrasion mass losses of preheated (top) and indurated pellets (bottom). Plant A concentrate. 60% cold water solubility starch. Sodium bentonite clay (SB1) and calcium carbonate (Sigma Aldrich, ACS grade) contents were 1.7 kg/t. See Appendix 2 for green ball coating procedure. See Appendix 1 beginning on page 89 for material characterizations. To be submitted as Halt and Kawatra (2017a).*

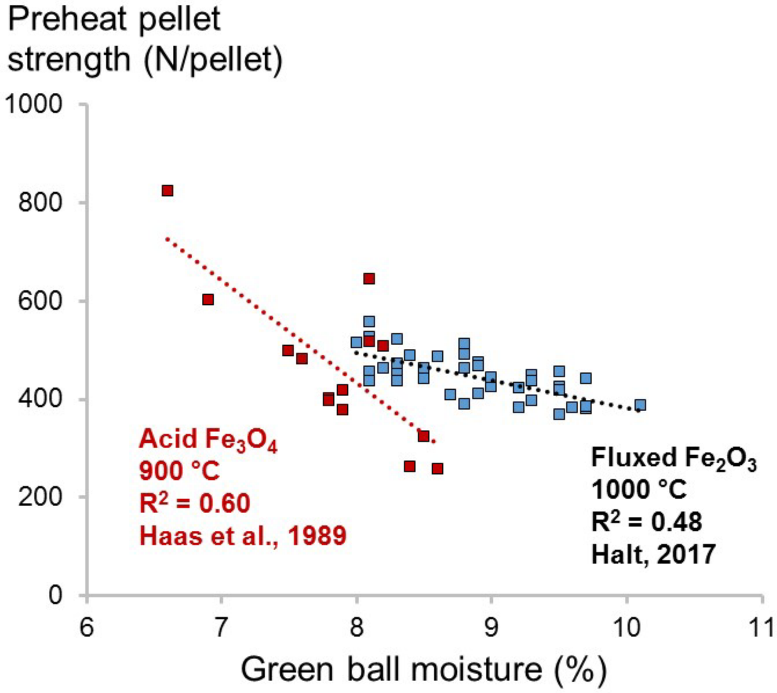


*Figure 24 Effects of green ball moisture on preheat pellet strength. Left – acid magnetite concentrate, balled with 0.1-0.15% starch binder, fired at 900 °C; I plotted this curve from data tabulated in Haas et al., (1989). Right – fluxed hematite concentrate (Plant F), balled with 0.05-0.2% starch, or 0.1% starch plus one of several additives, all fired at 1000 °C. I generated this curve during my preliminary starch binder investigation. See Appendix 1 beginning on page 89 for Plant F concentrate characterization To be submitted as Halt and Kawatra (2017b).*

## 3.3 Approach 3: Addition of dispersants to starch

Our reasoning for approach 3 is lengthier than for approaches 1-2. We will discuss porosity and how it affects pellet quality, then how to control porosity, and finally give results with silica sand, hematite concentrate, and magnetite concentrate.

### *3.3.1 Relationship between porosity and pellet quality*

Theoretically, pellet porosity is related to pellet compression strength through the following equation (Equation 1)

$$\sigma = A\cdot(1/\varepsilon-1)^{B}\cdot d^{-C} \qquad [1]$$

where σ is the pellet's strength, ε is the pellet's porosity or void fraction, d is the diameter of the 'primary' particles (those that make up the agglomerate), and A, B and C are constants (Capes, 1972). Per Rumpf (1962) the bracketed term in Equation 1 describes the coordination number (the number of neighboring particles or bonds surrounding an individual particle) and volume fraction of solids. Equation 1 predicts that pellet strength will increase as porosity decreases; it also predicts that strength will increase with coordination number and decreasing particle size.

Many researchers have attributed porosity levels in pellets to organic binder burnout. For large quantities of binder, this may be a factor. For small binder dosages, which are typical for modern organic binders, this assumption is not valid. In preheated and indurated pellets, porosity mainly arises from the loss of green ball moisture and the decomposition of flux/carbonate particles (Yang, 1990). Again, porosity significantly affects the mechanical and metallurgical properties of pellets. Figure 24 shows that green ball moisture content inversely correlates to the strength of preheated pellets – the relationship held for an acid magnetite concentrate (no/low carbonate decomposition) and for a highly fluxed hematite concentrate (with significant amount of carbonate decomposition).

The curves in Figure 24 are interesting; we have not seen similar curves in the pelletizing literature. As aforementioned, pelletizers may hesitate to use starch instead of bentonite because they are concerned what will happen in their furnaces. Will dust loads significantly increase? Will furnace downtime increase and productivity decrease? Unfortunately (or fortunately depending on your viewpoint), organic binders don't add additional solid bonds to compensate for the voids remaining in pellets as moisture is removed during drying. These curves suggest that one way to control pellet quality (such as the preheat strength) with a purely organic binder is to control the moisture content, and thus porosity, of green balls entering the furnace.

How do we control moisture content and porosity? One way to control moisture content, and eventually porosity, is to control the size distributions of the balling feed, either using the binder or independently. Pellets contain a wide range of particle sizes that follow some size distribution. The size distribution will affect the packing of the particles, plus the balling behavior and ball/pellet quality. Effects of size distribution are completely unaccounted for in Equation 1 but we believe they are as, or more, important than particle size. Effects of size distribution are illustrated in Figures 25-26, where span indicates the size distribution width. In the span definition given in the figures, Dv90 is the 90% particle passing size, Dv50 is the 50% particle passing size (mean particle size), and Dv10 is the 10% particle passing size.

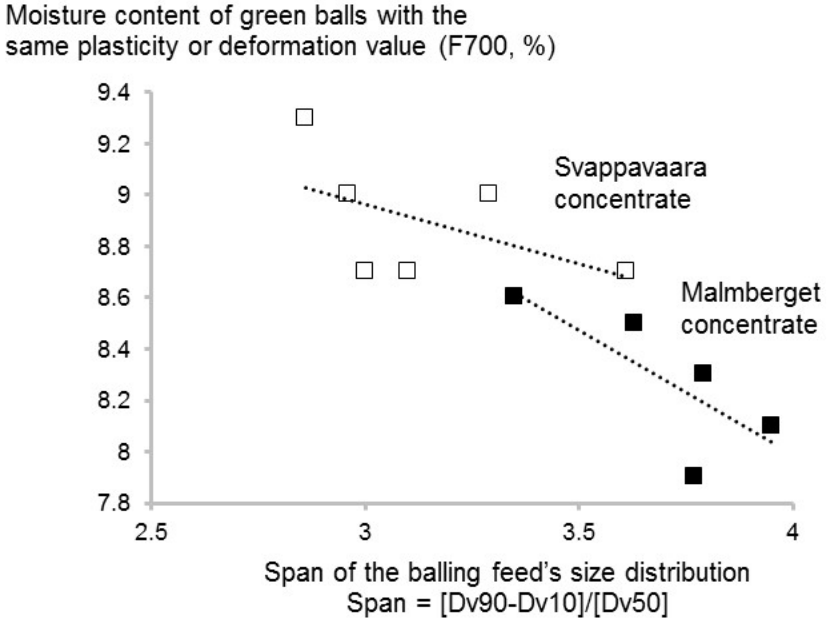
Figures 25-26 shows how the span of a balling feed's size distribution affects its balling behavior and ball quality. By definition, as span increases, the width of the size distribution increases. The curves show that as span increased, the moisture content required for balling decreased. This may be because the particles packed more tightly together as span increased and the specific surface area decreased as span increased. As moisture decreased, porosity decreased because of better packing. As porosity decreased, the 'Bonding Factor' or the bracketed term in Equation 1 increased. Finally, as span increased, pellet strength increased.

In fact, strength increased despite the fact that the mean particle size (Dv50) actually increased as span increased! From Equation 1, strength should have decreased as particle size increased. Forsmo et al., (2006) missed the point about span in their analysis and could not explain why pellet strengths did not vary as they had expected. Our curves here suggest that span, or the size distribution's width, significantly affects pellet strength.

### *3.3.2 Controlling porosity or particle packing*

So far, we've seen that porosity can be decreased, and pellets strengthened, by widening the size distributions of balling feeds. This presents an interesting opportunity since immediately before agglomeration, pelletizers destabilize balling feeds by coagulation/flocculation, in order to narrow their size distributions and increase filtration rates. From our packing theory, this should weaken pellets and inadvertently force pelletizers to use more binder during pelletization.

We hypothesized that by stabilizing particles, for example with electrostatic stabilization, the 'effective' particle size distributions of balling feeds would be wider. This would lead to better particle packing during agglomeration and denser, stronger pellets. More specifically, we were interested in using chemical reagents called dispersants (or water-reducers or plasticizers in other industries) to strengthen pellets, and believed we could use zeta potential measurement techniques (which approximates the surface charge) to predict dispersant effectiveness and pellet quality. We believed that increasing the balling feed's zeta potential would lead to denser, stronger pellets (Figure 27).



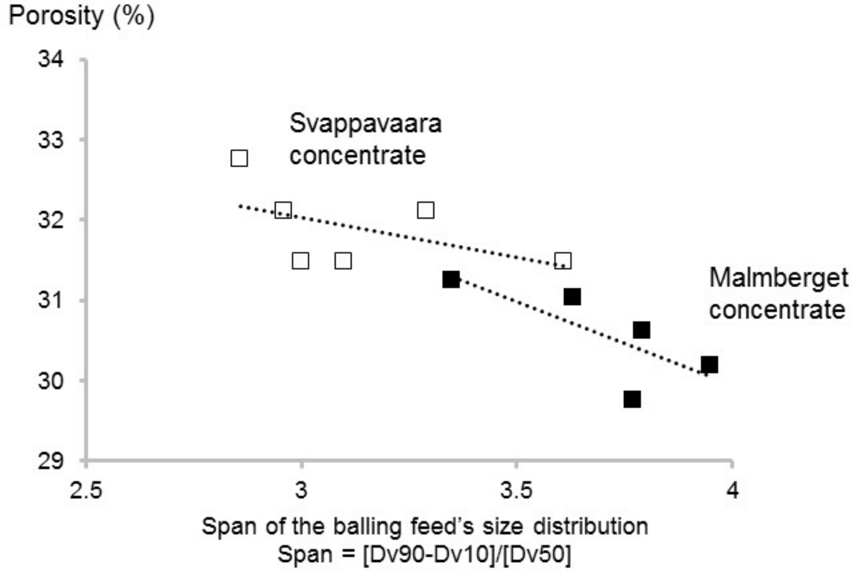


*Figure 25 Effects of size distribution width on green and dry ball quality. Effect of a balling feed's span (the width of its size distribution) on its balling behavior (top), and dry ball porosity (bottom). Forsmo et al., (2006) gave the F700 values for several iron ores. I calculated the porosity values using the moisture vs porosity relationship they observed during balling, and I calculated the Dv90, Dv50 and Dv10 values by fitting their size distribution data to log-normal distributions.*

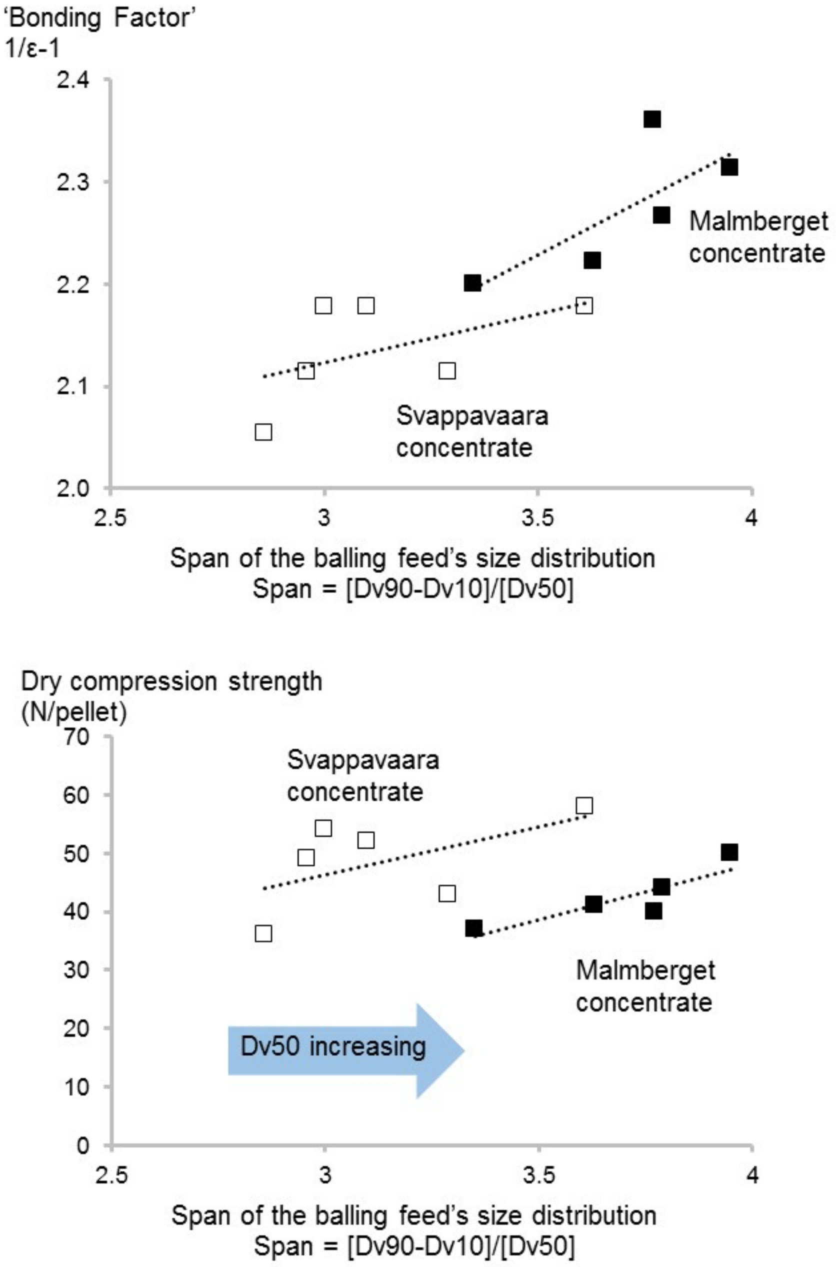


*Figure 26 Effects of size distribution width on green and dry ball quality. Effect of a balling feed's span (the width of its size distribution) on pellets 'Bonding Factor' (top), and dry compression strength (bottom). I calculated the 'Bonding Factor' values from the porosity values in Figure 25, and I calculated the Dv90, Dv50 and Dv10 values by fitting Forsmo et al's (2006) size distribution data to log-normal distributions. Compression strength data was given in Forsmo et al (2006).*

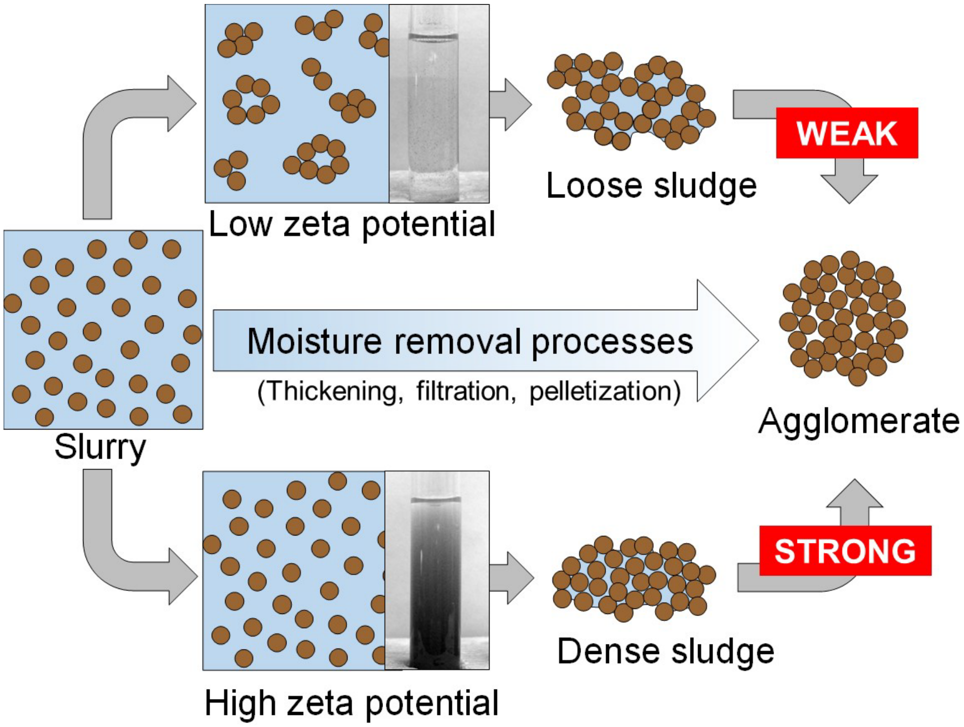


*Figure 27 Influence of particle zeta potential on structures of slurry, sludge and agglomerates. Upper path: particles coagulate at low zeta potential, rapidly settle, and form loose sludge and weak pellets. Lower path: particles disperse at high zeta potential, slowly settle, and form dense sludge and strong pellets. To be submitted in Halt & Kawatra, (2017b). Traditionally, pelletizing operations follow the upper route, adding bentonite particles to compensate for the 'loss' of fines in the feed. With fine ores, dispersants can be added to the loose sludge following filtration, liberating the fines and making enhanced pellets.*

### *3.3.3 Explanation of the Key Dissertation Figure, Figure 27*

Figure 27 illustrates the crux of our approach 3. Instead of considering pelletization in the usual manner, as a size enlargement method, we considered it a moisture removal method. In effect, thickening, filtration and pelletization turn slurries into compacted, shaped forms by removing water and forcing particles to come together. Following the upper path, slurry is destabilized in order to quickly dewater the ore. Without binder, ball growth is hard to control and pellets are weak. Pelletizers thus add fine bentonite clay particles, which help absorb moisture, fill voids in the agglomerate and bind pellets.

Following the lower path, particles are stabilized, which increases settling time and sludge compaction. Pellets would be stronger even without binder. We don't suggest this approach due to poor filtration. However, following filtration along the upper path, balling feed particles could be re-stabilized with certain reagents, liberating the ultra-fines and making enhanced pellets.

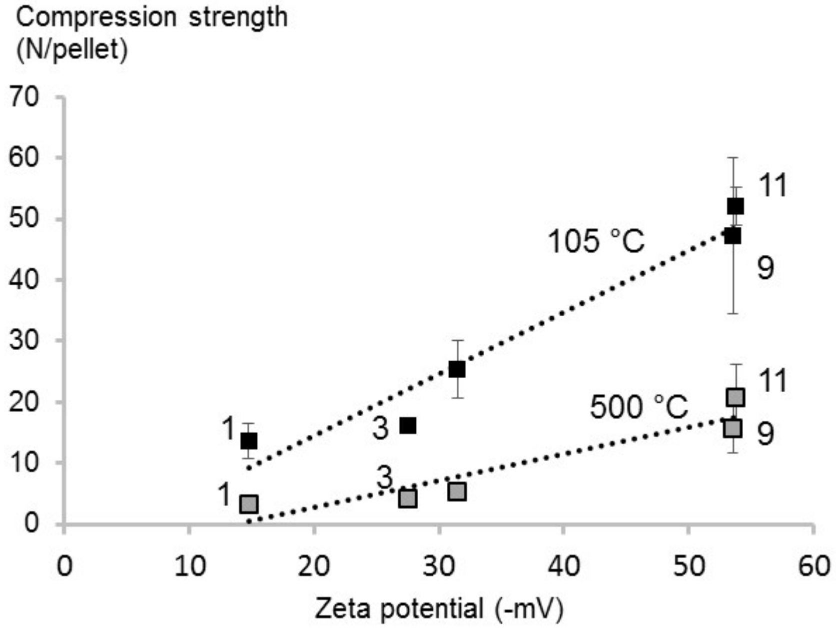


*Figure 28 Zeta potential effects on sand ball strength. Ball strength after drying (105 °C) and after starch combustion (500 °C) correlated to the sand's zeta potential. All pellets contained 1 kg/t corn starch of 60% solubility. Each ID number represents a separate additive, dosed at 1.75 kg/t. 1=aluminum sulfate, 3=magnesium sulfate, 9=polyacrylic acid, 11=sodium tripolyphosphate. Unpublished data. See Appendix 1 beginning on page 89 for material characterizations and Appendix 2 beginning on page 94 for test procedures.*

### *3.3.4 Approach 3 – Laboratory results with sand, hematite and magnetite concentrates*

#### 3.3.4.1 Sand agglomeration

Iron ore concentrates are complex mixtures of many minerals, so we first tested approach 3 with a pure mineral system: silica sand. The sand's XRD is seen in Figure 41. We dry ground the sand in a ball mill to an 80% passing size of approximately 60 µm (Figure 42).That's coarser than iron ore concentrates in the United States, but still fine enough for pelletizing. We modified the zeta potential with two coagulants (aluminum and magnesium sulfates) and two dispersants (sodium tripolyphosphate and polyacrylic acid). See Appendix 2 for experimental procedures.

During balling, moisture content was approximately 13.5% by weight, which is significantly higher than used for iron ore pelletizing. However, the water-to-solid volume ratios were equivalent in both systems, and thus the drum-filling degrees were similar. In addition, binders contained 1.0 kg/t starch (60% cold-water-solubility) and 1.75 kg/t additive (higher than required for iron ore), because of how weak and fragile sand pellets can be and as well as to keep the additive-to-calcium/magnesium ratios the same in the sand and iron oxide systems. The composition of the water used to make sand pellets is given in Table 11.

Figures 28-29 show the strength and appearance of sand balls prepared with coagulants and dispersants. With coagulants, balls were rough and weak. With dispersants, balls were strong and very smooth. After drying, balls made with dispersants had some discrete rough patches: some balls bonded together as they sat in the drying oven and those bonds broke, often tearing away portions of the actual ball, as we handled the dry balls. However, the regions around the inter-pellets bonds were still smoother than the balls containing coagulants. Inter-pellet bonds can be seen in the lower right portion of Figure 29,

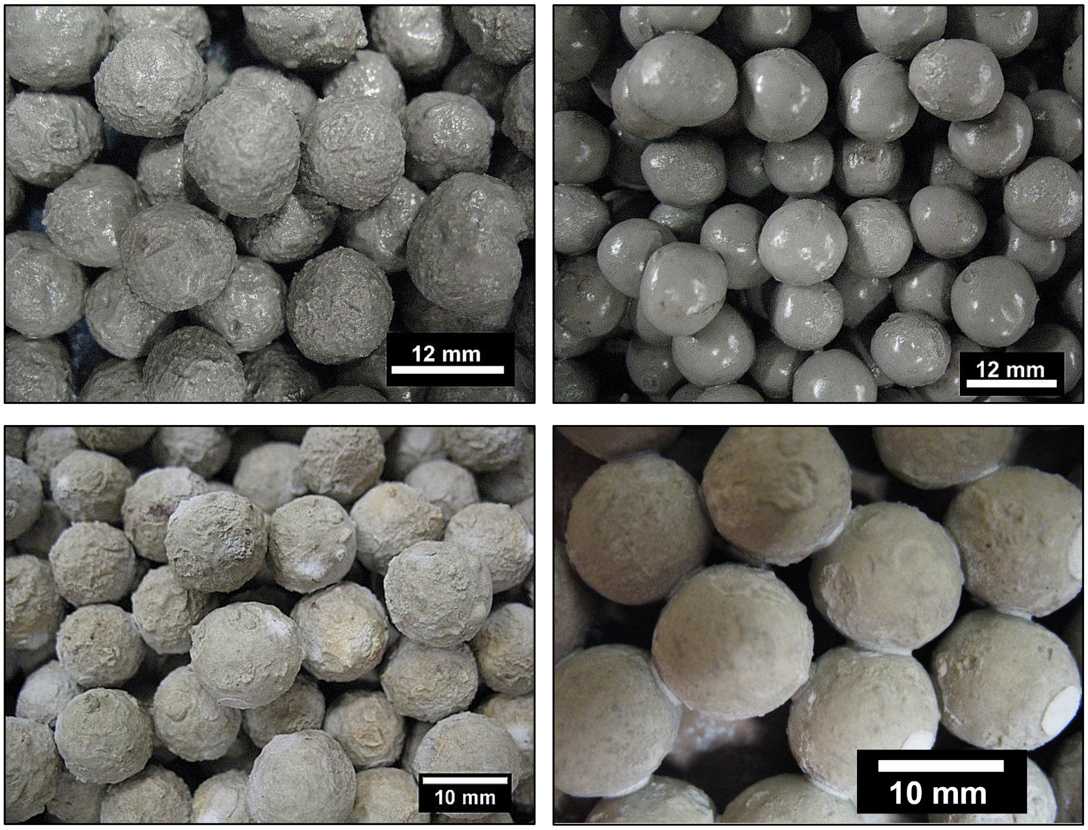


*Figure 29 Appearance of green sand balls (top) and dry sand balls (bottom). Balls made with 1.75 kg/t coagulant magnesium sulfate (left) and 1.75 kg/t dispersant sodium tripolyphosphate (right), plus 1 kg/t starch (60% cold water solubility). Wet balls were rough with coagulants and smooth with dispersants. Dry balls were also rough with coagulants and smooth with dispersant, although the dry dispersant-containing balls had small rough patches where balls had bonded together while drying.*

The positive correlation between strength and zeta potential remained after the 500 °C thermal treatment. We attribute this to better particle packing as void fraction, determined following a wax-coating method (see Table 12 in Appendix 2), was 0.29 with coagulants and 0.28 with dispersants. These porosity values are similar to typical porosity values in iron ore pellets, due the similar solid-to-liquid volume fractions in both systems. In addition, balls prepared with the organic polyacrylic acid dispersant retained strength (similar to inorganic sodium tripolyphosphate dispersant), even though the organic dispersant significantly combusted by 500 °C. Following conventional thought, the polyacrylic acid additive should have resulted in significantly weaker pellets.

Abrasion and TGA tests showed starch migrated to sand ball surfaces, similar to hematite ball surfaces. This confirms the radial starch distributions presented in section 2.2, but we did not study starch distributions any further.

#### 3.3.4.2 Hematite agglomeration

We prepared hematite pellets from Plant F concentrate. The concentrate's XRD is seen in Figure 41, particle size distribution in Figure 42, and chemical composition in Table 9. We modified its zeta potential using many types of coagulants, pH modifiers, and dispersants commonly found in mineral processing plants. All but one additive were purchased from chemical companies; the remaining, a sodium polyphosphate based dispersant, was supplied by the Plant F beneficiation plant. A full list of the additives is given in Table 10 (Appendix 1).

Binders were composed of a low level of starch (0.25 kg/t corn starch of 60% cold water solubility, or 0.25 kg/t wheat starch of 54.8% cold water solubility) and 1.0 kg/t coagulant, pH modifier, or dispersant (See Table 10). In three cases, the additive was also dosed at 0.25 kg/t. Balling, zeta potential measurements and balling feed settling behavior tests are described in Appendix 2.

Figure 30 shows that the additives affected the hematite balling feed’s stability, and thus its settling behavior and sludge structure. Coagulants destabilized the balling feed, causing rapid settling, clear supernatants (test tube at left, containing aluminum sulfate) and voluminous sludge. Dispersants led to very turbid suspensions, even after lengthy settling times (test tube at right, containing sodium tripolyphosphate), and dense sludge. Sludge height and void fraction generally correlated to zeta potential.

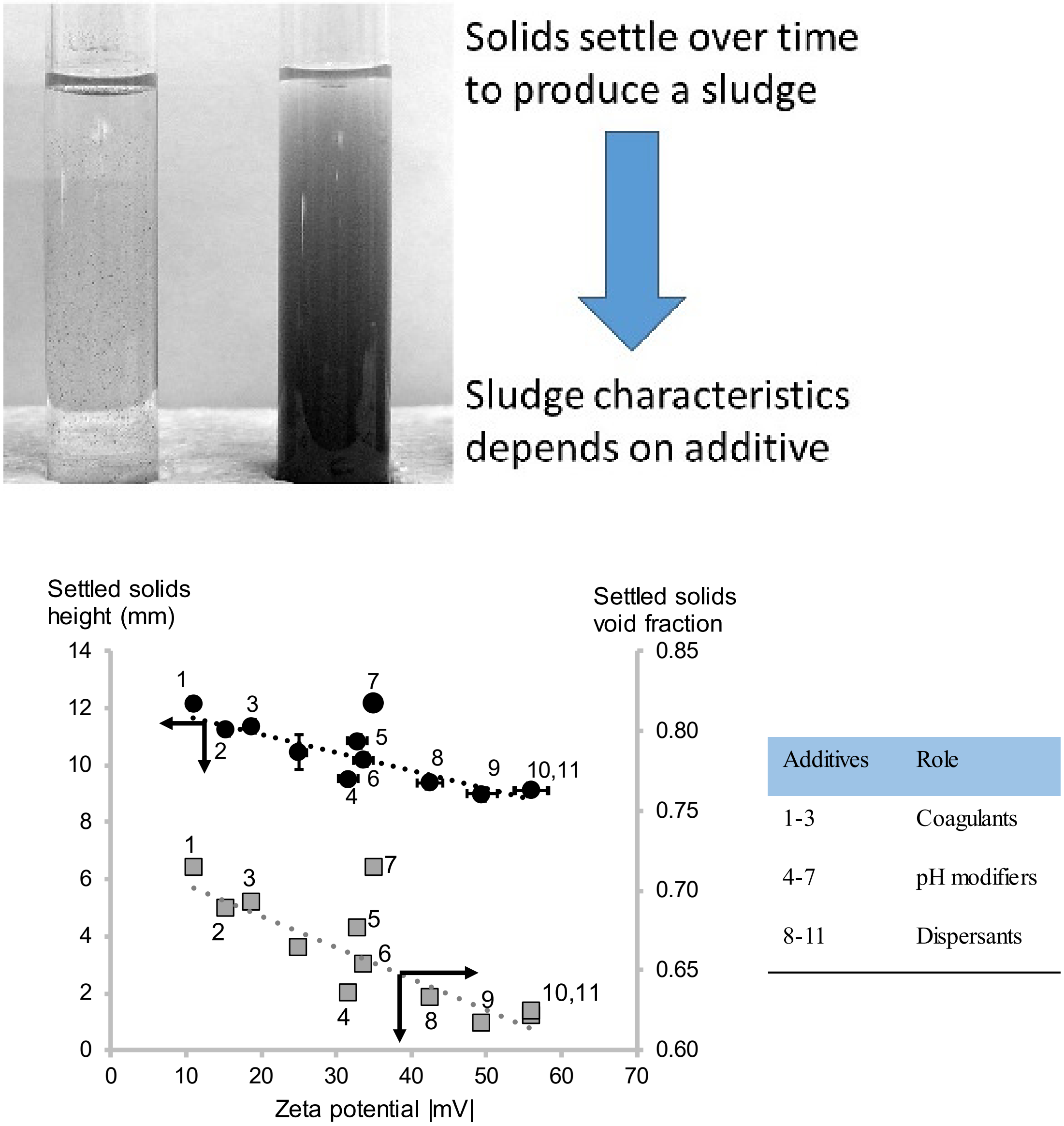
It’s interesting that balling feeds are flocculated or destabilized prior to filtration in order to increase the filtration rates and increase plant productivity (Carlson and Kawatra, 2011). Thus, balling feeds arrive at agglomeration circuits with larger ‘effective’ particle size distributions and narrower spans than they might otherwise have. Based on our particle packing theory, destabilized feeds will produce weaker green balls and pellets. We showed this was true for a simple sand system. Will hematite ball and pellet quality follow zeta potential?

Binders were composed of starch plus the same coagulants, pH modifiers, and dispersants used to develop Figure 30. Again, binders contained either corn or wheat starch (0.25 kg/t), plus either 0.25 kg/t or 1.0 kg/t additive. For a detailed additive list, see Table 9 in Appendix 1.

Figure 31 shows that dry ball strength linearly correlated to the balling feed’s zeta potential. Pellets were heated at 500 °C to burn away starch (some organic additives combusted as well). After the heating process, strength also linearly correlated to zeta potential. The high-zeta potential pellets retained their high strength because dry ball porosity decreased as zeta potential increased. Green ball porosity also decreased as zeta potential increased (supporting our particle packing theory, Halt and Kawatra, 2017c).

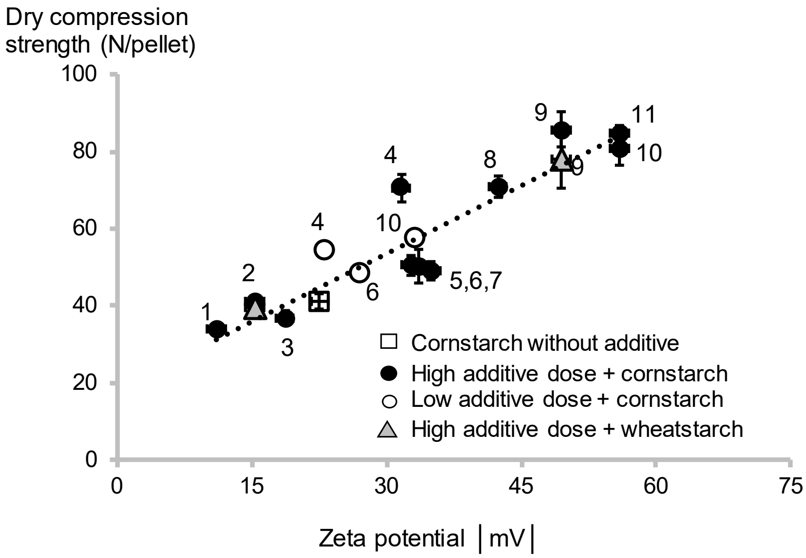
The additive benefits were carried through the firing process, as the abrasion resistances of pellets made with dispersants were higher, and dustiness lower, than those made with pH modifiers and coagulants (Figure 32). Decreased friability came from the better packing, lower porosity, and lower surface roughness (pellets were smooth at high ZP and rough at low ZP) – not from the additives' chemical compositions. For example, additive # 7 (sodium hydroxide) had much higher sodium content than additive #11 (sodium tripolyphosphate) but its abrasion results were much worse. Some might argue that the good abrasion results were obtained because sodium is a good fluxing aid, but our results suggest smoother surfaces and lower porosity were the reasons.

Photographs of unfired pellets are shown in Figure 32. They illustrate the typical surface characteristics resulting from the different additives. Similar to the sand system, coagulants produced rough pellets, as did the pH modifiers. Also similar to the sand system, dispersants led to very smooth pellets. We believe the very low surface roughness is the main reason why the abrasion resistances are higher with dispersants than with the other additives. The smoothness results from the smaller effective size distributions which can pack together more tightly.

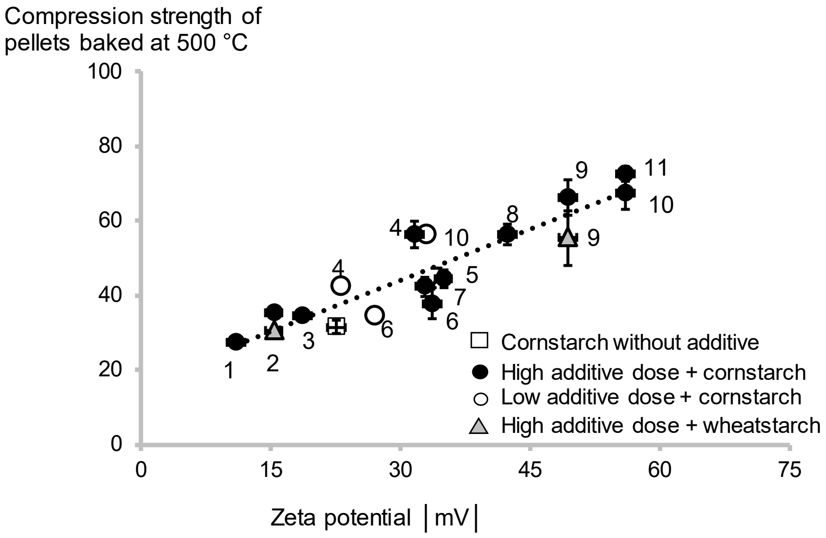


| Additives | Role |
|---|---|
| 1-3 | Coagulants |
| 4-7 | pH modifiers |
| 8-11 | Dispersants |

*Figure 30 Effects of zeta potential on hematite settling behavior. Suspensions were clear with coagulants (top left, hematite plus aluminum sulfate) and turbid with dispersants (top right, hematite plus sodium tripolyphosphate). Sludge height and void fraction decreased when the balling feed's zeta potential increased (bottom). Plant F hematite concentrate. After Halt and Kawatra (2017c). See Table 10 in Appendix 1 to identify the numbered additives, and Table 7, Figure 41 and Figure 42 for iron ore characteristics. See Appendix 2 for experimental procedures.*



| Additives | Role |
|---|---|
| 1-3 | Coagulants |
| 4-7 | pH modifiers |
| 8-11 | Dispersants |



| Additives | Role |
|---|---|
| 1-3 | Coagulants |
| 4-7 | pH modifiers |
| 8-11 | Dispersants |

*Figure 31 Effects of zeta potential on ball and pellet quality. Effects of Plant F balling feed stability, measured by zeta potential, on the compression strength of balls after drying (top) and low-temperature firing (bottom). Figures adapted from Halt and Kawatra (2017c). Binders contained 0.025% starch plus 0.025% or 0.1% additive. Corn starch of 60% cold water solubility. Wheat starch of 54.8% solubility. See Table 10 in Appendix 1 to identify the numbered additives, and Table 7, Figure 41 and Figure 42 for iron ore characteristics. See Appendix 2 for experimental procedures.*

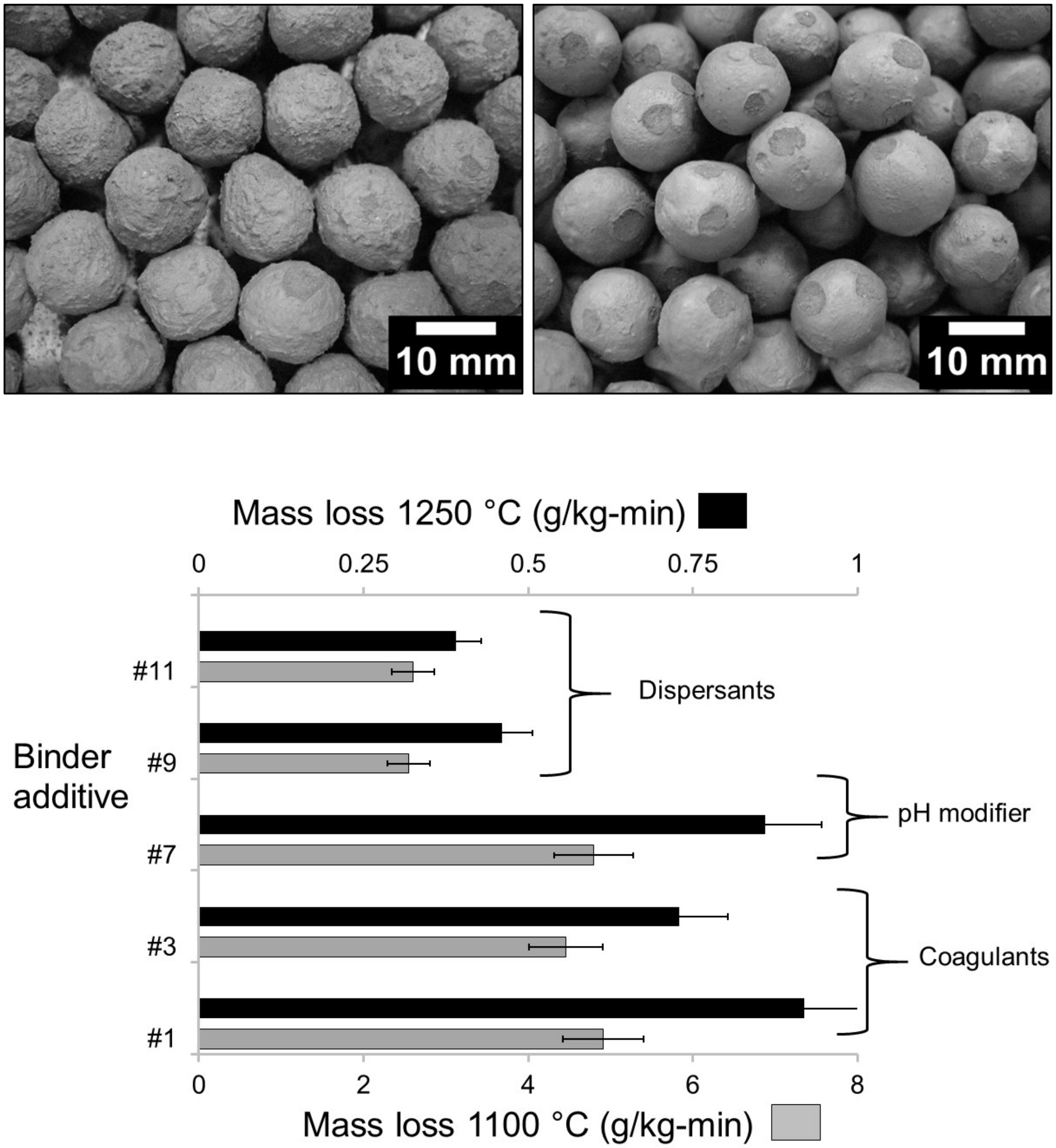


*Figure 32 Surface roughness (top) and dustiness of preheated and fired pellets (bottom). Coagulants and pH modifiers induced rough surfaces and high dust generation (top left); dispersants induced very smooth surfaces with low dust generation (top right). Plant F concentrate. 60% cold water soluble starch (0.25 kg/t). After Halt and Kawatra (2017c). See Table 10 in Appendix 1 to identify the numbered additives, which were added to these pellets at 1 kg/t. See Table 7, Figure 41 and Figure 42 for iron ore characteristics. See Appendix 2 for experimental procedures.*

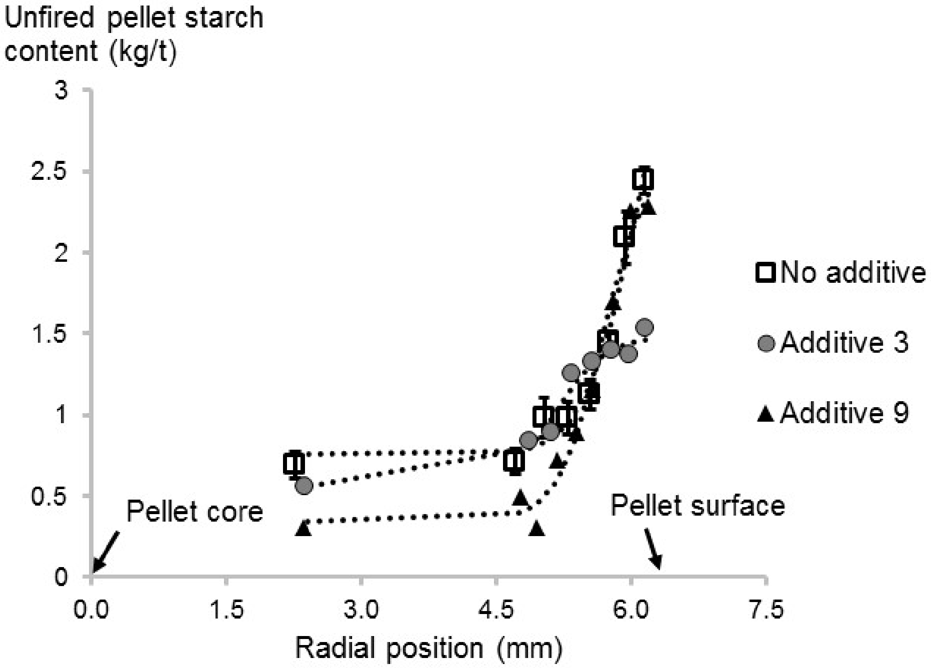


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*Figure 33 Radial starch contents in unfired hematite pellets prepared with starch alone (no additive), starch plus a magnesium sulfate coagulant (additive 3) and starch plus polyacrylic acid dispersant (additive 9). The pellets prepared with polyacrylic acid had high surface starch concentrations, even though they were very smooth. After Halt and Kawatra (2017c). See Table 7, Figure 41 and Figure 42 for iron ore characteristics. See Appendix 2 for experimental procedures.*

Figure 33 shows that despite the significant differences in roughness, all pellets still had high starch contents near the surfaces – thus, the common belief that starch causes rough pellets is wrong. We believe rough pellets arise because the particles are inefficiently arranged and 'locked' ultrafine particles cannot efficiently fill the gaps between larger particles in the mix.

A final interesting observation in the hematite study was the proportional correlation between the settled sludge void fraction and the dry ball void fraction ($\text{Void}_{\text{pellet}}=0.13*\text{Void}_{\text{sludge}}+0.23$, $R^2=0.67$). This suggests that simple settling tests could be used to quickly screen additives for pelletization. Further work should be completed using more ore types andmwider experimental conditions to improve and understand the correlation.

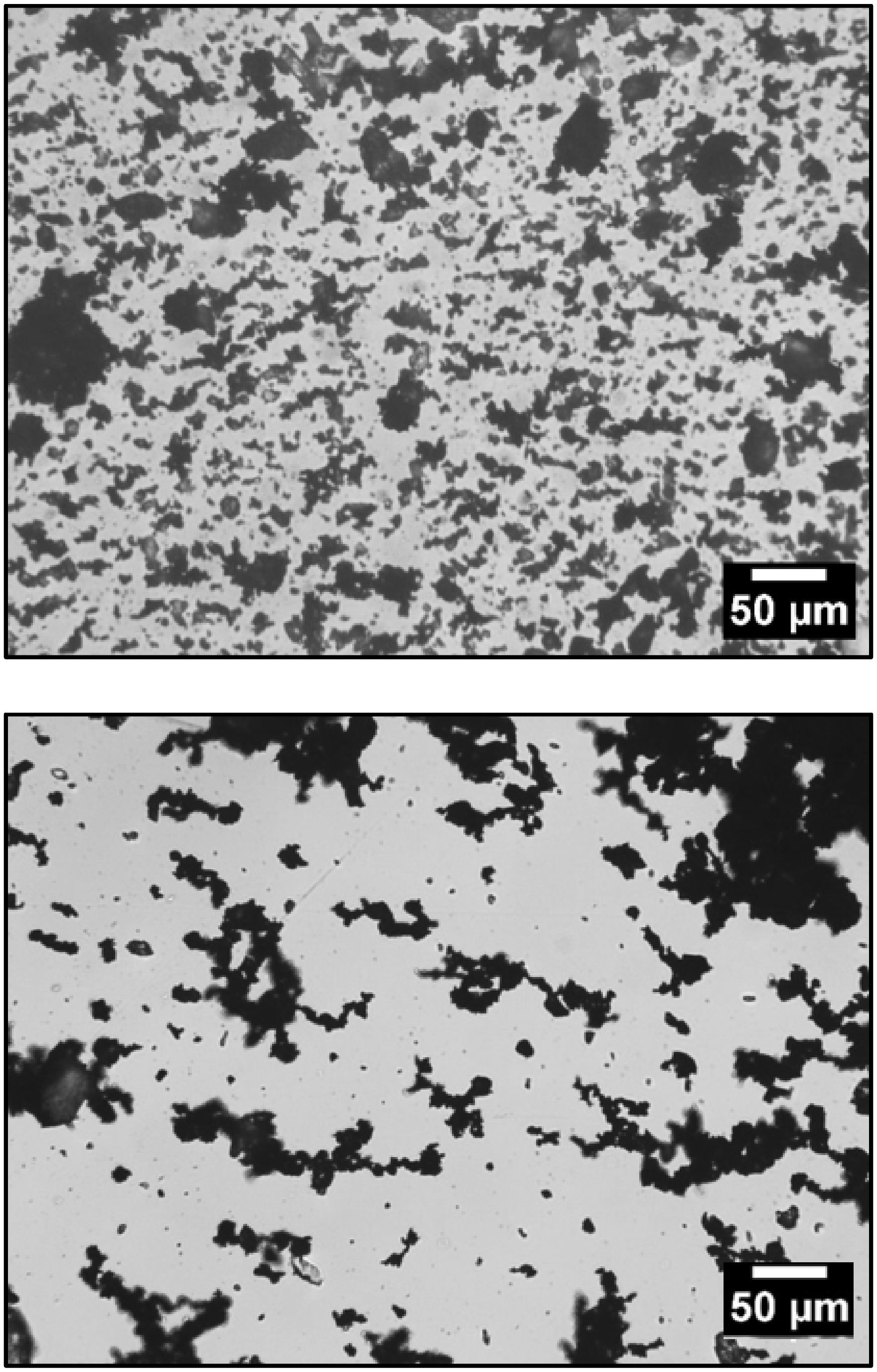

*Figure 34 Dispersion of hematite and magnetite fines in water. Hematite fines from Plant F dispersed in a petri dish filled with distilled water by gentle hand mixing (left). Magnetite fines from Plant A dispersed in a petri dish filled with distilled water by gentle hand mixing (right). Magnetite fines present as long trains due to magnetic flocculation.*

#### 3.3.4.3 Magnetite agglomeration

Low-grade magnetite concentrates are more prevalent around the world, and are especially common in the United States. In terms of their agglomeration and dispersion potential, magnetites are more complicated than sand and hematite because the particles magnetically flocculate together (Figure 34). However, major pellet producers are using low-grade magnetite ores to diversify their products and meet demand for alternative ironmaking processes (Burnes, 2017). Will the zeta potential vs strength relationship hold with an acid magnetite concentrate? Can starch-dispersant mixtures be used for magnetite pelletization?

We prepared pellets using an acid magnetite concentrate from Plant A. See Table 7 for its chemical composition, Figure 41 for its XRD pattern, and Figure 42 for its particle size distribution (All found in Appendix 1). Binders contained 60% cold water solubility starch and various additives. See Table 10 in Appendix 1 for additive identification. See Appendix 2 for the pelletization and zeta potential test procedures.

Figure 35 shows that dispersants stabilized the acid magnetite concentrates, which strengthened pellets, and the single coagulant destabilized the concentrate. The pH modifiers, which are the usual additives suggested for organic binders, increased the concentrate's zeta potential and slightly increased dry compression strength. However, unlike with the sand and fluxed hematite systems, the pellet strength plot segregated into two regions – those prepared with organic additives and those prepared with inorganic additives. We believe the organic additives sterically stabilized the concentrate, which is another way to achieve better fines dispersion.

Since the two organic dispersants, citric acid and polyacrylic acid led to the strongest and qualitatively smoothest pellets, we evaluated their effects on pellet dustiness. The reference binder condition was 1 kg/t starch (60% cold water solubility). The starch-dispersant binders were composed of 0.5 kg/t starch (60% cold water solubility) plus 0.5 kg/t dispersant. The starch-dispersant binders reduced pellet dustiness by 47% at 1100 °C and 22% at 1250 °C. These dispersants reduced dustiness, but there was no specific reason why these would have to be used industrially; a wider variety of available dispersants could be exploited or new ones designed.

In summary, approach 3 – the addition of dispersants to starch – leads to strong, smooth pellets with low fines and dust generation. Binders composed of starch and dispersants are good candidates for pellets requiring low-silica binders. More generally, balling feed zeta potential correlated well to green, dry and fired pellet quality.

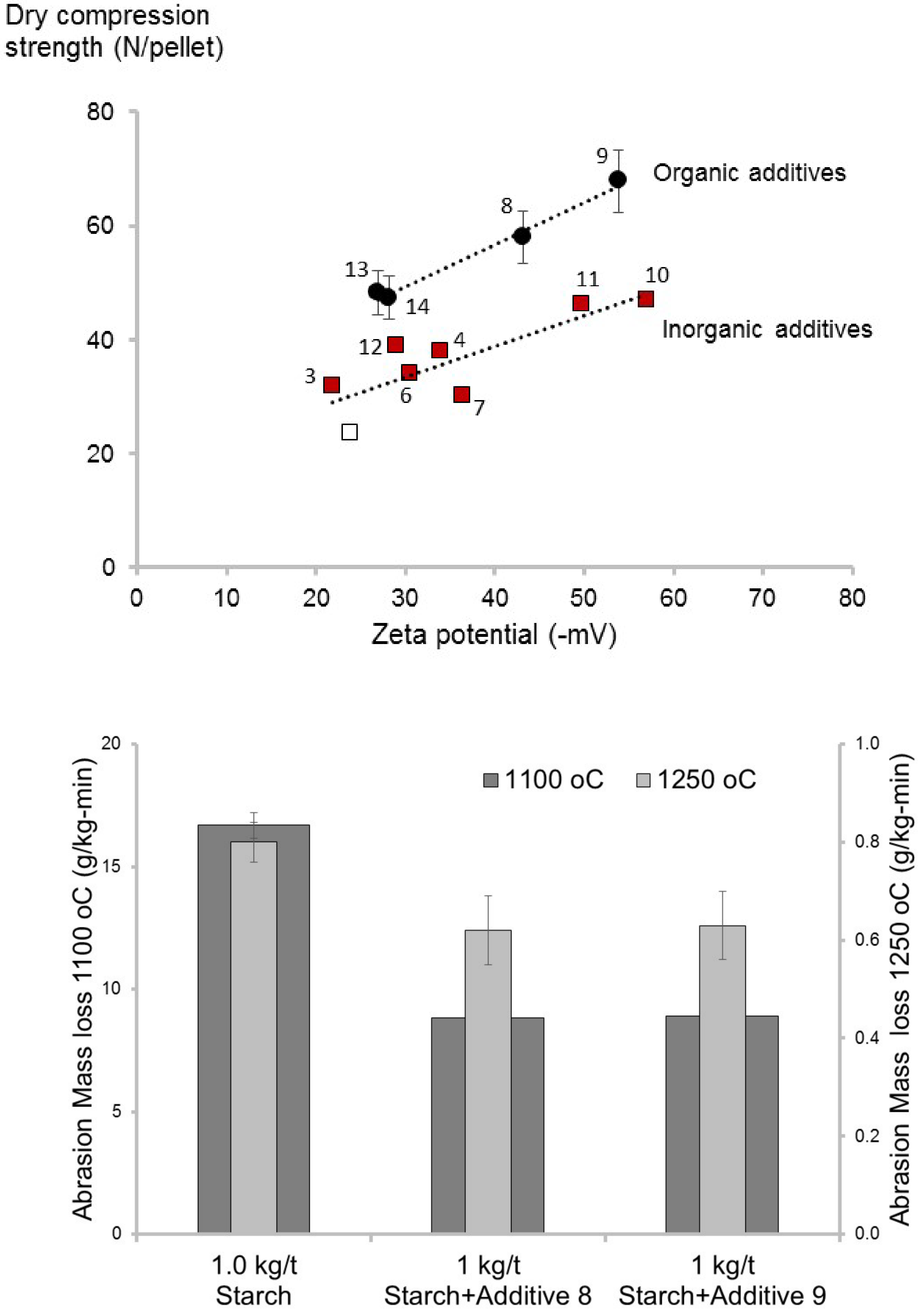

*Figure 35 Zeta potential effects with a magnetite concentrate. Effects of 1.0 kg/t additives on pellet compression strength (top), and effects of 0.5 kg/t additives on mass loss by abrasion (bottom). Plant A concentrate. 60% cold water solubility corn starch (0.5 kg/t). See Table 10 in Appendix 1 for additive identification. Additive 8 (citric acid) and Additive 9 (polyacrylic acid) gave the highest dry strengths and qualitatively smoothest pellets (determined by eye) so were tested to see how well they reduced dustiness. To be submitted as Halt and Kawatra (2017b).*

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# Chapter 4 Starch plus clay, starch plus clay-layer, or starch plus dispersant – which is the most effective?

In Chapter 3, we showed that we could reduce fines and dust generation following three approaches: (1) adding clay to starch; (2) adding a clay-rich layer to green ball surfaces; and (3) adding dispersants to starch. Total silica content in the binder, and thus in the pellets, decreases in the order of approach 1, 2, and 3. Which gives the best physical and metallurgical quality?

## 4.1 Laboratory results with fluxed hematite concentrate

We compared the three approaches with a fluxed, hematite concentrate from Plant F. The concentrate's XRD is seen in Figure 41, particle size distribution in Figure 42, and chemical composition in Table 9. The modified starch was a dry powder with 60% cold water solubility. The bentonite was a sodium bentonite (SB1); see Table 9 for its composition. The polymer dispersant, a low molecular weight polyacrylic acid (Additive 9, Table 10), is frequently used in mineral processing plants, boiler process water treatment plants, etc. We selected this dispersant over the phosphate-based dispersants, since phosphorus is a major contaminant for pellets.

The designed pellet binders contained high (1.0 kg/t) and low (0.25 kg/t) levels of starch, and high and low levels of the clay or dispersant. For clay, the levels were 5.0 kg/t and 1.7 kg/t; for dispersant, the levels were 1.0 kg/t and 0.25 kg/t. For reference, we prepared pellets with just starch binder (containing no clay or additives). Laboratory test procedures are thoroughly described in Appendix 2.

Figures 36-37 show the three-method comparison, focusing on dry compression strength, preheated pellet compression strength, and the abrasion mass losses of preheated and fired pellets. All three approaches were beneficial, as each increased preheat compression strength and decreased friability or dustiness. With the polymer dispersant – following our approach # 3 – the results were the best overall. Comparing the dispersant to bentonite, pellets had similar friability levels while consuming twenty times less additive.

We previously established that the dispersants densify pellets. Since porosity has opposing effects on pellet strength and reducibility, we found the reducibility of four different pellet samples (Figure 38). The four samples were: (1) starch – the reference pellet, made with 1 kg/t starch, (2) bentonite – made with 1 kg/t starch and 5 kg/t bentonite, (3) dispersant – made with 0.25 kg/t starch and 0.25 kg/t polymer dispersant, (4) bentonite layer – made with 1 kg/t starch and 1.7 kg/t total bentonite. We chose these conditions since they gave similar performance in the physical quality tests. Under the reduction test conditions, the four pellet types had similar reducibility values. Thus, the addition of dispersant to starch (approach # 3) gave the highest strength, lowest dust, lowest silica contamination, and equal reduction potential to pellets. This novel approach was the best among all three in the laboratory pellet testing.

## 4.2 Mini pot-grate test results with acid magnetite concentrate

We wanted to test our approaches in independent, pilot-scale tests because of the successful laboratory trials. The Natural Resources Research Institute (NRRI) in Coleraine, Minnesota balled an acid magnetite concentrate using our binders and fired pellets in mini-pot-grate furnaces; they selected the furnace-firing profile to represent a typical plant-firing profile. To save costs, we only tested approach 1 (starch-bentonite mixture) and approach 3 (starch-dispersants mixture). Reference binders were bentonite alone and starch alone. We tested a coagulant and pH modifier in addition to two dispersants, in order to induce a wide range of zeta potentials and confirm (or disprove) our laboratory results. See Table 6 for the binder compositions.

Figures 39-40 show the main mini pot-grate test results. Included are the green ball size distributions, the unfired or dry pellet compression strengths, the fired pellet Tumble Index (the quantity of pellets larger than ¼ inch, or 6.4 mm) and the fired pellet Abrasion Index and pellet chips (the quantity of undesired fines). The starch-bentonite mixture gave a size distribution that most closely followed bentonite. The mean green ball size increased in order from coagulant, pH modifier, and dispersant – this confirms that balls form faster as zeta potential increases, which we observed in the laboratory. However, it's been believed that fast ball formation makes weaker pellets (Dingeman and Skagerberg, 1992; 1994), which our data disproves.

*Table 6 Binder compositions for mini pot-grate tests conducted at the Natural Resources Research Institute (Coleraine, Minnesota, USA). Plant A concentrate. Sodium bentonite (808 PWA, 80% passing 16.1 μm). Corn starch (60% cold water solubility).*

| Component 1 | Dose (kg/t) | Component 2 | Dose (kg/t) – Role |
|---|---|---|---|
| Bentonite | 6.6 | --- | --- |
| Starch | 1.0 | --- | --- |
| Starch | 0.25 | Calcium chloride | 1.0 – Coagulant |
| Starch | 0.25 | Soda ash | 1.0 – pH modifier |
| Starch | 0.25 | Citric acid | 1.0 – Dispersant |
| Starch | 0.25 | Polyacrylic acid | 1.0 – Dispersant |
| Starch | 1.0 | Bentonite | 3.3 – Binder |

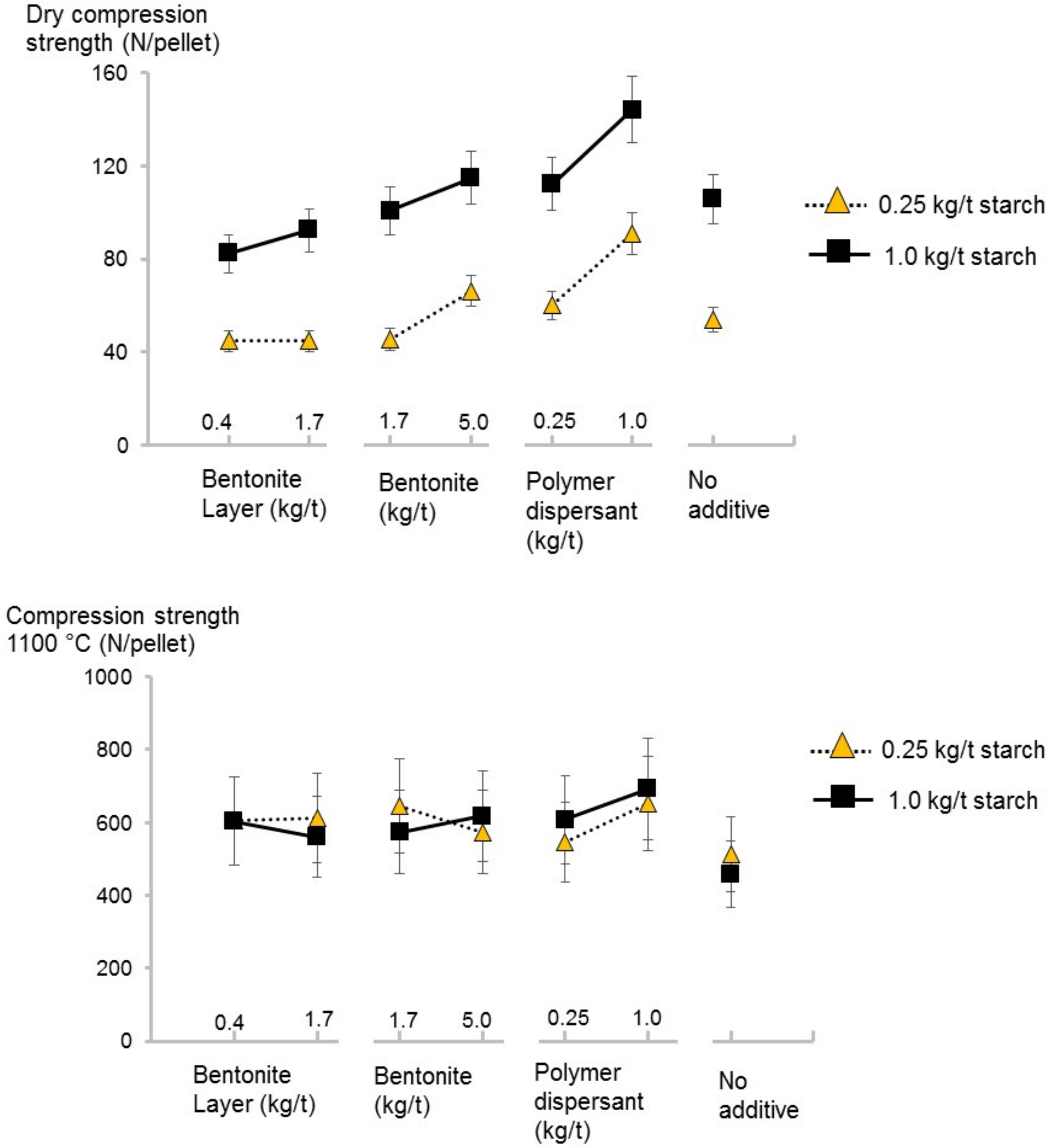


*Figure 36 Effectiveness of the three approaches on hematite pellet strengths: dry compression strength (top) and preheated compression strength (bottom). The dosages given above the bentonite layer are the dosages on a per-pellet-basis. I estimate the actual surface concentrations to be close to 1.7 and 5.0 kg/t, respectively, based on the balling procedure used (See Appendix 2). Pellets made from Plant F concentrate. Sodium bentonite SB1. Polyacrylic acid dispersant. See Tables 7,9,10 and Figures 41-42 for material characteristics. To be submitted as Halt and Kawatra (2017b).*

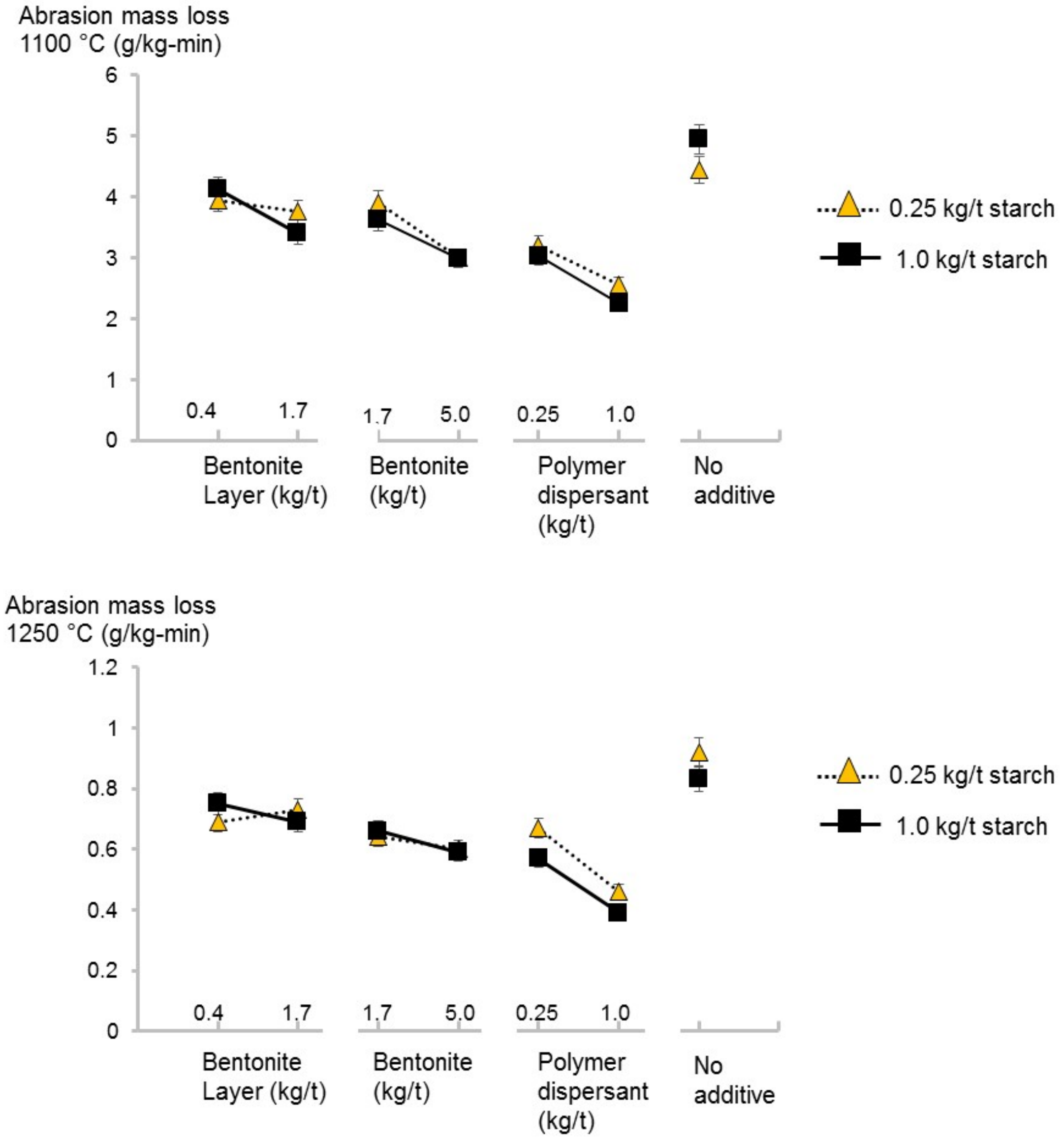


*Figure 37 Effectiveness of three approaches to reduce hematite pellet dustiness: abrasion mass losses of preheated (top) and fired pellets (bottom). The dosages given above the bentonite layer are the dosages on a per-pellet-basis. I estimate the actual surface concentrations to be close to 1.7 and 5.0 kg/t, respectively, based on the balling procedure used (See Appendix 2). Pellets made with fluxed, hematite concentrate (Plant F). Sodium bentonite SB1. Polyacrylic acid dispersant. See Tables 7,9,10 and Figures 41-42 for material characteristics. To be submitted as Halt and Kawatra (2017b).*

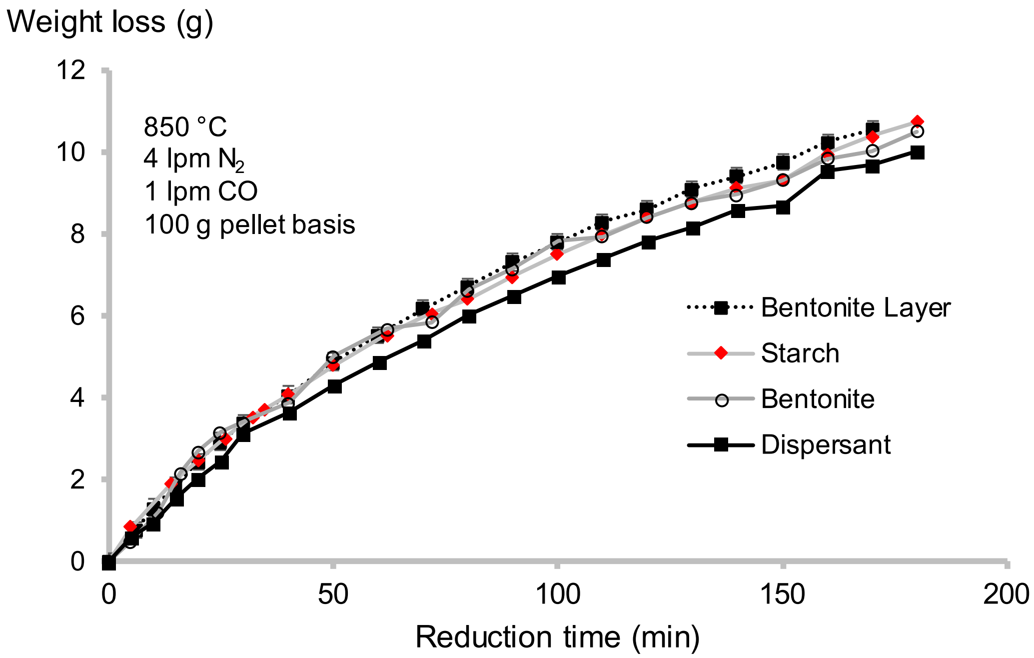
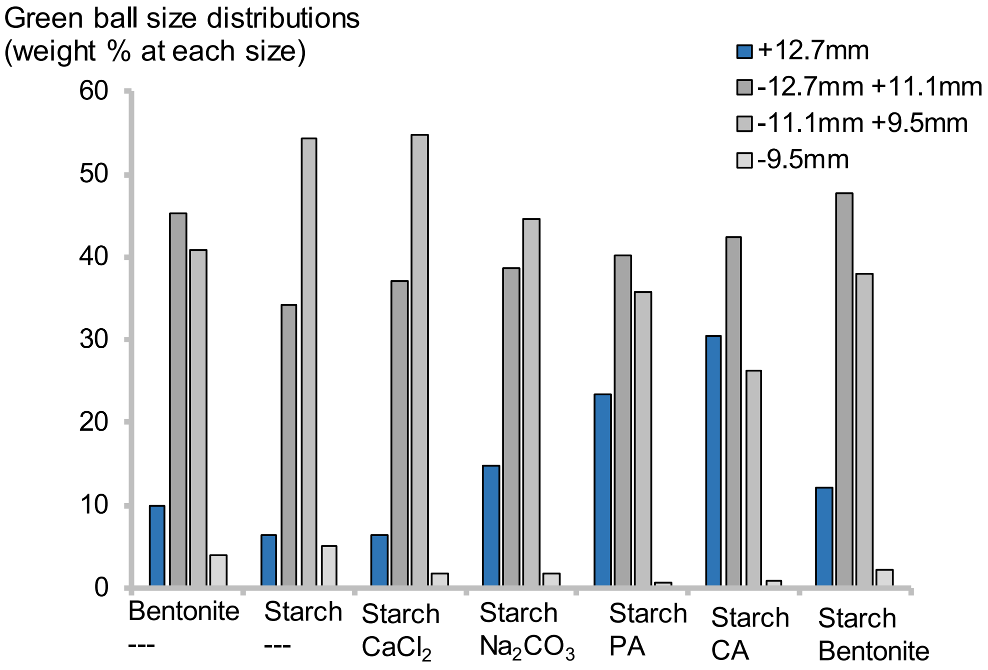


*Figure 38 Isothermal reduction of pellets made with various binders: bentonite layer (1 kg/t starch +1.7 kg/t), starch (reference condition, 1 kg/t starch), bentonite (1 kg/t starch + 5 kg/t bentonite SB1), dispersant (0.25 kg/t starch + 0.25 kg/t dispersant). No significant differences in pellet reducibility were observed under the reduction test conditions. See Appendix 2 for coated pellet preparation. Sodium bentonite SB1. Polyacrylic acid dispersant. 60% cold water solubility starch. Plant A acid concentrate. To be submitted as Halt and Kawatra (2017b).*



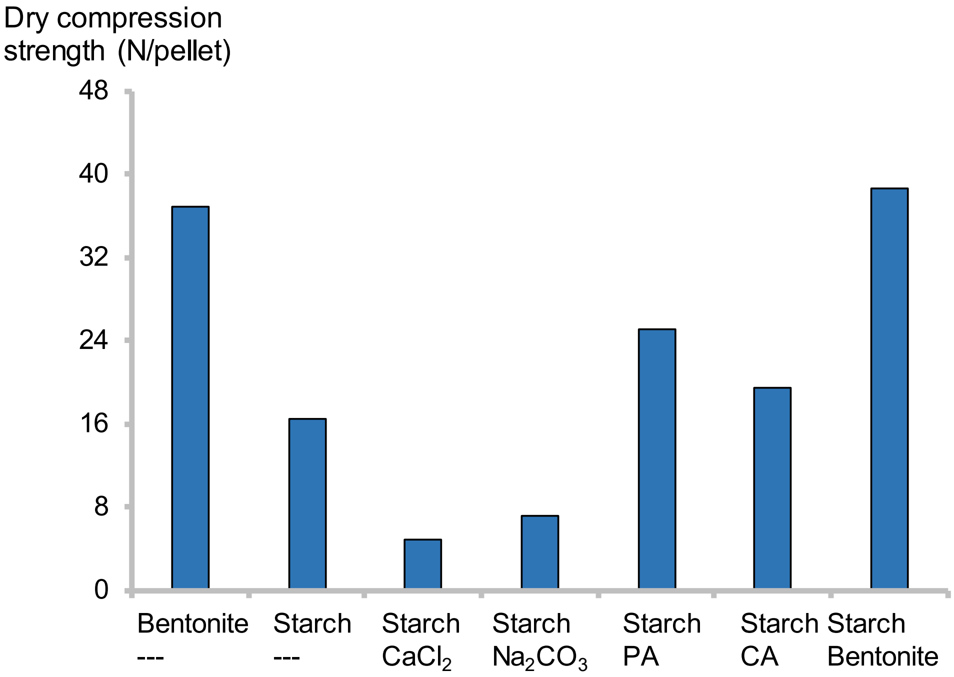


*Figure 39 Pot-grate test results of new starch binders: Green ball size distributions (top) and Dry compression strength (bottom). Starch plus dispersants citric acid (CA) and polyacrylic acid (PA) increased ball growth rate and ball strength compared to just starch. Plant A concentrate. 60% cold water solubility starch. Pellets fired at the Natural Resources Research Institute (Coleraine, Minnesota). See Table 6 for detailed binder compositions. To be submitted as Halt and Kawatra (2017b).*

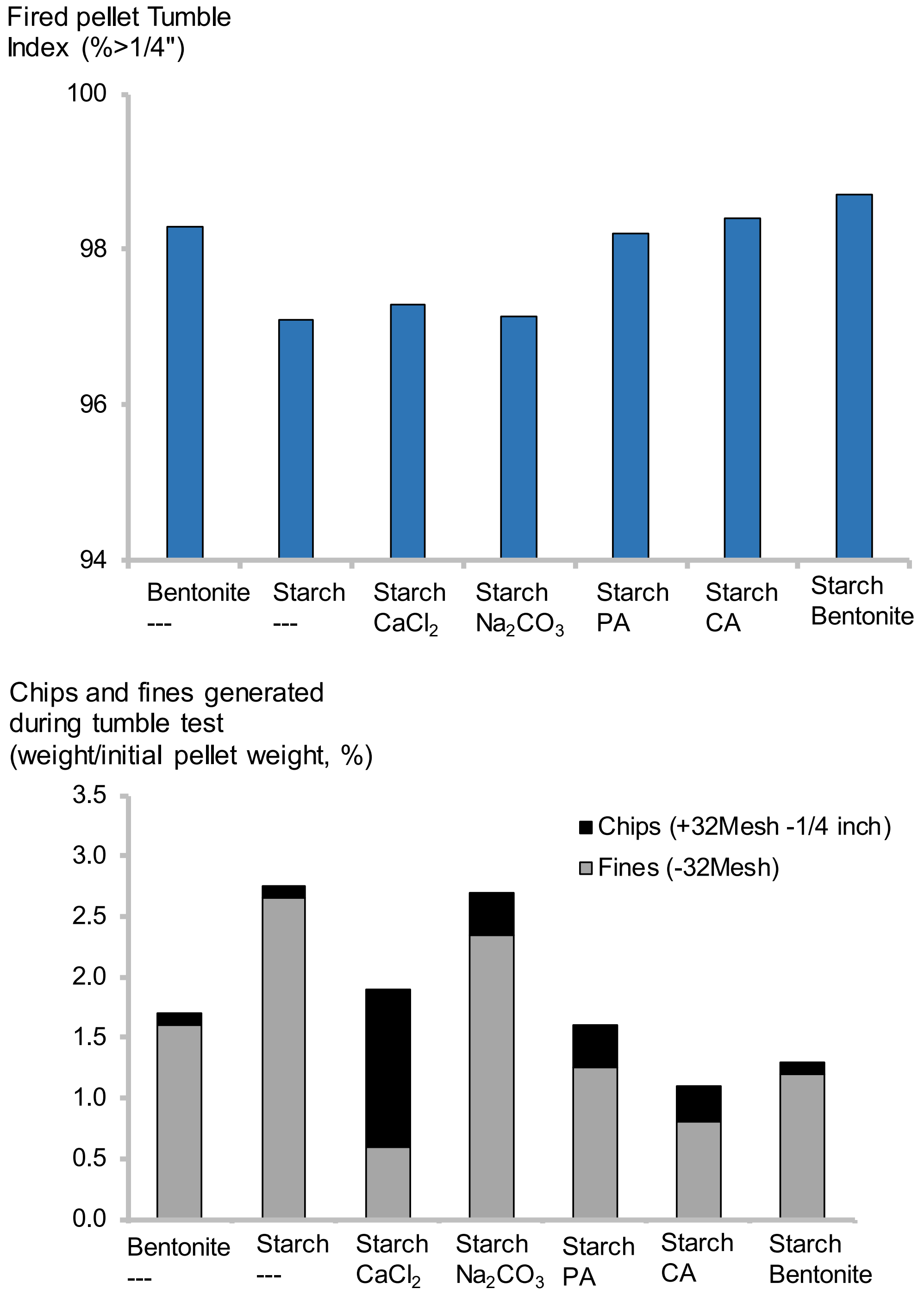


*Figure 40 Pot-grate test results of new starch binders: Tumble Index (top) and the Abrasion Index and pellet chips (bottom). Starch plus dispersants citric acid (CA) and polyacrylic acid (PA) increased the tumble index and decreased the abrasion index and chips formation compared to just starch. Plant A concentrate. 60% cold water solubility starch. Pellet prepared at the Natural Resources Research Institute (Coleraine, Minneseota). See Table 6 for detailed binder compositions. To be submitted as Halt and Kawatra (2017b).*

The tumble, abrasion and chips indices confirm what we saw in the lab: (i) starch binders make pellets much more friable than bentonite; (ii) dispersants give better results than coagulants and pH modifiers, (iii) strength and abrasion resistance generally follows zeta potential; and (iv) adding bentonite to starch significantly reduces friability and dustiness. Thus, we can solve starch binder problems with appropriately selected dispersants, or bentonite, and potentially use the low-silica binders in new ironmaking processes.

Again, the only complicating factor we found in the pot-grate study was finding the best dispersant for magnetite concentrates. Magnetite concentrates are magnetic, so the particles magnetically flocculate together. Magnetic flocculation can inhibit the dispersion of the very fine particles in the pellet, counteracting the functionality and performance of our selected dispersants. Our zeta potential curve for the acid magnetite concentrate (Figure 35) showed the additives separated into two distinct regions – an inorganic additive region and an organic additive region. This suggests we need to consider factors besides zeta potentials – perhaps we should look at steric and electrosteric stabilization, and thus more complicated polymers – to identify the best dispersants for magnetite. An example of this approach is in magnetic nanofluids, where magnetite nanoparticles are stabilized using high concentrations of oleic acid (Papell, 1965).

# Chapter 5 Conclusions & Future Works

New types of pellets, made with new types of low-silica binders, will be needed for non-blast furnace ironmaking processes. In this work, we showed three approaches to making low-silica binders for iron ore pellets. All three approaches used starch as the base material, which has historically led to weak, dusty pellets. The three approaches were:

(1) Addition of bentonite clay to starch. This is the traditional approach for organic binder improvement. This approach worked, but it contaminated pellets with silica.
(2) Addition of a clay-rich layer to the surfaces of green balls. This is a novel idea. The intent of the coating was to mimic the good surface properties of standard bentonite-bonded pellets. Beneficially, clay contamination decreases significantly as the layer becomes thinner, which is an improvement over traditional methods of clay application.
(3) Addition of dispersants to starch. This is a novel idea. Dispersants resulted in significantly smoother and less friable pellets in laboratory and pot-grate studies.

In order to develop this work further, researchers could:

(1) Identify or design better dispersants for magnetite concentrates;
(2) Optimize the coating composition to reduce both pellet abrasion and clustering in Direct Reduction furnaces;
(3) Design a simple way to add coatings in existing drum-based circuits (re-roll rings can be added to discs, but discs are not common in the US);
(4) Incorporate the starch and dispersant into bead form so it’s easy to use and the binder itselft doesn’t generate dust at the plant.

Furthermore, researchers could study the fundamentals of water chemistry, surface forces, and magnetic forces to better show how binders, concentrates and balling water interact to affect ball and pellet formation. This knowledge will be more important as balling feeds become finer, and process water chemistry more complex, in the future.

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# Appendix 1 Materials[7]

### Iron ore concentrates and sand

I made pellets from fluxed hematite (Plant F) and unfluxed magnetite (Plant A), and in a few cases, sand (Series F). See Table 7 and Figures 41-42 for their chemical compositions, x-ray diffractograms, and particle size distributions. We dry ground the sand to obtain a particle size distribution similar to the iron ore concentrates, but did not analyze its chemical composition.

### Clays and clay-substitutes

We used six clays and clay-alternatives as binders: two sodium bentonites (SB1, SB2), two calcium bentonites (CB1, CB2), nepheline syenite (NS) and Class F fly ash (FA). The nepheline syenite fines were waste materials from a roofing granule manufacturer, and the fly ash was waste from a coal-fired power plant. See Table 8 and Table 9 for their descriptions, and chemical and physical characteristics.

### Modified starch

We used three modified starches as binders: two corn starches from Grain Processing Corporation (Muscatine, Iowa) and one wheat starch from Manildra Milling Corporation (Mission, Kansas). Their reported cold-water-solubility values were 7.5%, 60%, and 54.8%.

### Additives for zeta potential adjustments

We used eleven additives during the hematite zeta potential adjustment study. See Table 10 for the additives and their common roles in mineral processing. All were purchased commercially except for sodium polyphosphate, which was received from an iron ore beneficiation plant (Plant F). Three additional additives were used in the magnetite study, they are listed as 12, 13, and 14 in the table.

### Salt-water

We prepared a salt-water stock solution (for zeta potential, sedimentation and balling tests) from laboratory distilled water and reagent grade $CaCl_2$-$2H_2O$ (Fisher-Scientific, ACS grade), $MgSO_4$-$7H_2O$ (Fisher-Scientific, ACS grade), and $NaHCO_3$ (Sigma-Aldrich, ACS grade). See Table 11 for its composition.

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[7] Material descriptions were published in *Minerals Processing & Extractive Metallurgy Review* in the articles Halt and Kawatra (2016a, 2017c). See appendix 4, Figure 47, for permission to reuse the material.

Why did I choose this composition? I assumed that the composition of the pore water in green balls (Plant F concentrate) was identical to Plant F's filtrate water. The approximate water chemistry of the filtrate water from Plant F is shown in Table 11 (Haselhuhn *et al* 2012: Haselhuhn and Kawatra, 2015).

With that assumption, for an additive dose in the pelletizing tests of 1 kg/t (0.1%), the additive-to-($Ca^{++}$ plus $Mg^{++}$) ratio in the green-ball moisture is approximately equal to 100:1. Thus, the salt-water stock solution kept the additive-to-($Ca^{++}$ plus $Mg^{++}$) ratios in the zeta potential and sedimentation tests similar to those in the pelletizing tests.

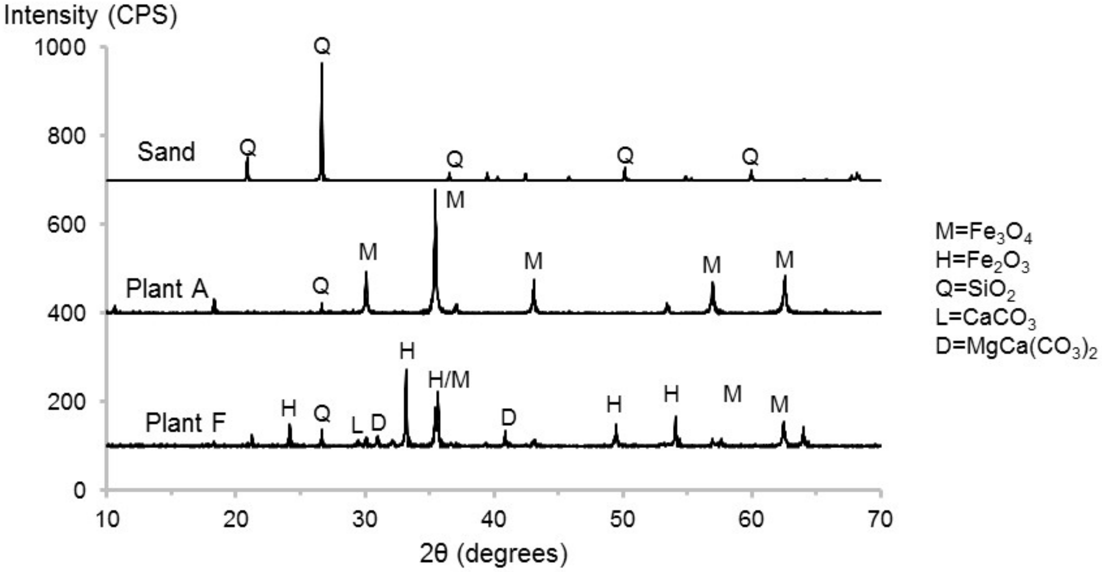

*Figure 41 X-ray diffraction patterns of the iron ore concentrates and sand.*

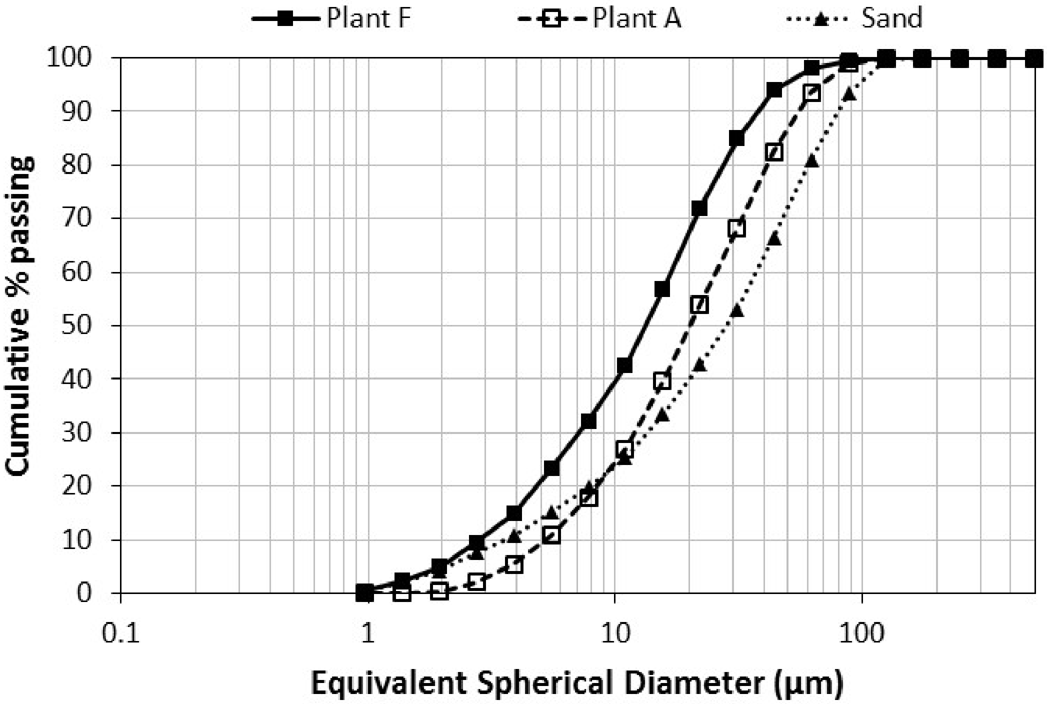

*Figure 42 Particle size distributions of pelletizing raw materials: Plant F hematite concentrate, Plant A magnetite concentrate and dry-ground sand.*

*Table 7 Chemical compositions of iron ore concentrates. XRF analysis from SGS Minerals Services (Lakefield, Canada).*

| **Sample type** | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **MgO** | **CaO** | **$Na_2O$** | **$K_2O$** | **$TiO_2$** | **$P_2O_5$** | **MnO** | **LOI** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant F Concentrate(1) | 4.42 | 0.44 | 82.10 | 1.88 | 4.24 | 0.04 | 0.02 | 0.09 | 0.09 | 0.40 | 6.31 |
| Plant A Concentrate | 4.37 | 0.27 | 96.20 | 0.56 | 0.92 | 0.04 | 0.02 | 0.08 | 0.04 | 0.24 | -2.71(2) |

Notes:
(1) Average of two separate filter cake samples
(2) LOI value is negative because the sample oxidizes and gains weight

*Table 8 Identification of clay samples and clay alternatives evaluated as binders*

| ID | Company | Location |
|---|---|---|
| SB1 | Bentonite Performance Minerals, LLC | Lovell, Wyoming |
| SB2 | Black Hills Bentonite | Casper, Wyoming |
| CB1 | Minerals Technologies, Inc. | Hoffman Estates, Illinois |
| CB2 | Minerals Technologies, Inc. | Hoffman Estates, Illinois |
| FA | Headwaters Resources | Somerset, Massachusetts |
| NS | 3M | Wausau, Wisconsin |

*Table 9 Chemical compositions, 80 % passing sizes ($P_{80}$) and plate water absorbance (PWA) values of the clays and clay-substitutes. Chemical compositions obtained via a fusion/ICP method (SGS Minerals Services, Burnaby, Canada; reported results are weight percentages. $P_{80}$ measured with a Microtrac particle size analyzer. PWA measured following ASTM E946-83.*

| **Sample**<br>(ID) | **Sodium bentonite**<br>**1**<br>(SB1) | <br>**2**<br>(SB2) | **Calcium bentonite**<br>**1**<br>(CB1) | <br>**2**<br>(CB2) | **Fly ash**<br>**Class F**<br>(FA) | **Nepheline**<br>**Syenite**<br>(NS) |
|---|---|---|---|---|---|---|
| $SiO_2$ | 53.9 | 63.3 | 58.4 | 57.5 | 57.8 | 56.7 |
| $Al_2O_3$ | 18.2 | 15.6 | 13.9 | 18.4 | 26.6 | 17.7 |
| $Fe_2O_3$ | 3.8 | 3.0 | 3.2 | 3.4 | 5.1 | 7.1 |
| MgO | 2.2 | 1.9 | 3.5 | 2.1 | 1.1 | 1.0 |
| CaO | 1.1 | 1.8 | 2.3 | 1.9 | 1.2 | 2.2 |
| $K_2O$ | 0.6 | 0.5 | 0.7 | 0.6 | 2.3 | 5.5 |
| $Na_2O$ | 2.0 | 2.3 | 0.3 | 1.4 | 0.7 | 5.6 |
| LOI | 5.8 | 5.0 | 7.1 | 5.9 | 2.5 | 1.0 |
| $P_{80}$ (um) | 17.7 | 22.7 | 60.9 | 26.4 | 38.0 | 51.0 |
| PWA | 938 | 731 | 172 | 336 | 38 | 36 |

*Table 10 Additives used for zeta potential adjustments and to make binders.*

| ID | Additive | Formula | Purpose | Details |
|---|---|---|---|---|
| 1 | Aluminum sulfate | $Al_2(SO_4)_3 \cdot 14H_2O$ | Coagulant | FisherScientific, TG |
| 2 | Calcium chloride | $CaCl_2 \cdot 2H_2O$ | Coagulant | FisherScientific, >98%, ACS |
| 3 | Magnesium sulfate | $MgSO_4 \cdot 7H_2O$ | Coagulant | FisherScientific, >98%, ACS |
| 4 | Sodium metasilicate | $Na_2SiO_3$ | pH modifier/ dispersant | AlfaAesar, TG |
| 5 | Sodium hydroxide: EDTA (50:50 by weight) | NaOH: $C_{10}H_{16}N_2O_8$ | pH modifier/ dispersant | SigmaAldrich, TG/ FisherScientific, |
| 6 | Sodium carbonate | $Na_2CO_3$ | pH modifier | SigmaAldrich, 99.5% ACS |
| 7 | Sodium hydroxide | NaOH | pH modifier | SigmaAldrich, 95% TG |
| 8 | Sodium citrate dihydrate | $Na_3C_6H_5O_7 \cdot 2H_2O$ | Dispersant | SigmaAldrich, 99% FG |
| 9 | Sodium polyacrylate | $C_3H_3NaO_2$ | Dispersant | SigmaAldrich, 5100 $M_w$ |
| 10 | Sodium polyphosphate | $(NaPO_3)_x$ | Dispersant | Plant F supplied |
| 11 | Sodium tripolyphosphate | $Na_5P_3O_{10}$ | Dispersant | SigmaAldrich, 85% TG |
| 12 | Sodium metasilicate | $Na_2SiO_3 \cdot 5H_2O$ | pH modifier/ Dispersant | FlukaAnalytical, 95%, TG |
| 13 | Sodium lignosulfonate | $C_{20}H_{24}Na_2O_{10}S_2$ | Dispersant | SpectrumChemical, TG |
| 14 | Sodium acetate | $CH_3COONa \cdot 3H_2O$ | Dispersant | Mallinckrodt, 99%, ACS |

*Table 11 Ionic content of Plant F filtrate water (used as an estimate of the composition of the pellet feed moisture) and the stock solution for sedimentation and zeta potential measurements. Filtrate water chemistry compiled from Haselhuhn et al (2012) and Haselhuhn and Kawatra (2015).*

| Analyte | | Filtrate water mg/L | Salt-water stock solution mg/L |
|---|---|---|---|
| Calcium | $Ca^{++}$ | 71 | 1.55 |
| Sodium | $Na^{+}$ | 495 | 6.27 |
| Chloride | $Cl^{-}$ | 100 | 2.75 |
| Sulfate | $SO_4^{--}$ | 100 | 3.12 |
| Magnesium | $Mg^{++}$ | 58 | 0.79 |
| Bicarbonate | $HCO_3^{-}$ | 1295 | 16.63 |

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# Appendix 2 Methods[8]

## Balling

*Iron ore balling*

We received 55 gallons of wet concentrate from the iron ore pellet plant. The concentrate was split into 2.5 kg batches by coning, quartering and riffling methods (rotary riffle splitting was not used due to the high moisture content). We mixed batches of iron ore concentrate (2 kg, 9% moisture) with the desired binder quantity for 5 minutes (250 W Kitchen Aid mixer) on speed setting 2, then forced the batches through an 8 mesh screen to remove lumps. Balling immediately preceded mixing.

We made green balls by continually adding fresh feed into a rotating steel drum (46 cm dia., 25 rpm) and spritzing water as needed, which was determined by eye by watching for the presence of a surface sheen (from a surface layer of moisture) on the green balls. Periodically, the entire drum contents were removed and screened to ensure only a narrow size range of balls was in the drum. Screen sizes used were 8 mesh, 6 mesh, 4 mesh, 3 mesh, 1/4 inch, 3/8 inch, 7/16 inch, and 1/2 inch. Typically, we made 3 to 4 batches of green balls of size 7/16" x 1/2" in diameter (11.2 x 12.7 mm) to ensure enough pellets were available for the abrasion tests.

*Sand balling*

When we balled sand instead of iron ore concentrate, we adjusted the solids weight and water weight because sand is less dense than iron ore. 1040 g. of sand was required instead of 2 kg, and the moisture content was 13.5% by weight instead of 9%. Performing the experiments this way ensured that the solids and liquid volume percentages were approximately equivalent in the iron ore and sand experiments.

*Balling procedure for layered pellets*

The layered pellet preparation procedure is diagrammed in Figure 43 and a description of the procedure follows. We first mixed the desired quantity of starch into the concentrate and then split the mixture into four parts by coning and quartering – three were removed from the mixture and used to make green ball cores, while bentonite was added to the fourth and used to make the outer layer. After mixing the bentonite and one fourth of the feed mixture together for 5 minutes

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[8] Experimental procedures have been published in *Minerals Processing & Extractive Metallurgy Review* in the articles Halt and Kawatra (2016a, 2017c). See appendix 4, Figure 47, for permission to reuse the text.

(see Iron Ore Balling description above), we stored this 'coating' material in a sealed plastic bag so it would not dry out. The green ball cores were then prepared in the usual manner (see Iron Ore Balling description above) using the three portions containing only starch. When all of the core material was consumed (green-balls reached approximately 3/8 x 7/16 inches (9.5 x 11.2 mm) in diameter by this point), the coating material was added to enlarge green-balls to the correct size of 11.2 x 12.7 mm in diameter.

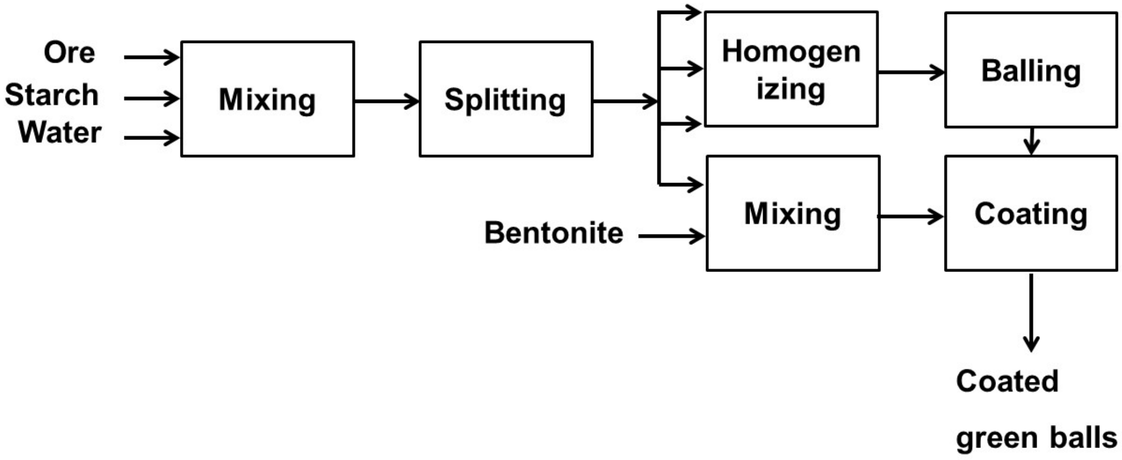

*Figure 43 Procedure for the preparation of coated green balls*

Based on this procedure, pellets prepared with 5.0 kg/t bentonite in the coating contained 1.7 kg/t bentonite on a whole pellet basis. Similarly, pellets prepared with 1.7 kg/t bentonite in the coating contained 0.4 kg/t bentonite on a whole pellet basis.

### Drying

We gently placed green balls in a large pan, and placed the pan in a Blue-M forced air oven at 105 °C for 3-24 hrs.

### Iron ore pellet firing

Before induration, all batches made under the same experimental conditions were mixed together by hand. Then, we evenly divided 1300g of dry pellets between two flat crucibles, gently blew them off with compressed air from the fume hood air supply to remove loose dust, and heated them from room temperature to 500, 1100 or 1250 °C at 10 °C per min. in a Sentrotech ST-1700-C box furnace. Our heating rate of s10 °C is lower than industry heating rate, but is the highest heating rate in this furnace we could obtain in the large capacity furnace need to fire large quantities of pellets. Pellets were held at the induration temperature for 10 min. (1100 and 1250 °C) or 30 min. (500 °C), then cooled to room temperature inside the furnace. Induration occurred in an air atmosphere. After induration, we remixed the batches together by hand, and determined the compression strength for 20 pellets (crosshead speed 25 mm/min.).

### Ball and pellet quality tests

We measured ball and pellet quality using several tests. See Table 12 for test descriptions; the typical or desired results are in the rightmost column. The 'Mass loss by abrasion' test was used as an indicator of pellet dustiness. Green and dry ball quality was determined for every batch of pellets; the reported values are the global mean of all tests. Preheated and fired pellet quality was determined after firing composite pellets samples prepared by mixing all dry balls together before firing.

### Zeta potential measurements of sand and iron ore concentrates

We dried powder samples at 105 °C, cooled them, and then mixed them into a salt water solution (see Table 11 in Appendix 1 for salt water composition) to prepare a 1000 mg/L suspension. The suspensions gently stirred for 2 h. We measured zeta potential with a Zetasizer Nano ZS (Malvern) as each additive was titrated into the slurry from 0 mg/L to a final concentration of 100 mg/L. The Zetasizer measures zeta potential using an electrophoretic light scattering method (laser Doppler micro electrophoresis). Each zeta potential measurement reported is the mean value from three separate titration experiments.

### Sedimentation test to determine structure of iron ore concentrate sludge

We added 15 mL of salt-water solution and 2 g of balling feed to a 16x125mm Pyrex test tube. See Appendix 1 for the salt-water composition. Then, we sonicated the suspension for 5 min. in a Bransonic 1510R-MT ultrasonic cleaner (70 W, 42 kHz) and allowed it to sit for 2 h. After 2 hours, we shook the test tube by hand, and into it, pipetted 575 μL of additive solution (1.2 g additive in 200 mL). See Appendix 1 for the list of additives used. We capped the test tubes, gently inverted them 20 times, and stored them in a vertical position. After 20 hours of undisturbed settling, we measured the heights of the settled solids using a ruler. The reported heights are the mean values of from four separate test tubes, with the height in each tube measured twice (taken after rotating the test tube 180° around the vertical axis). Following the measurement, we extracted 3 mL of supernatant from approximately 38 mm below the liquid surface, and measured their suspended solids contents via an UV-Vis absorption method (450 and 810 nm, calibrated gravimetrically). The UV-VIS spectrophotometer used was a Hach model DR5000, with cuvettes with a 10 mm light path.

*Table 12. Descriptions of ball/pellet quality tests, and desired/typical values.*

| **Test** | **Procedure** | **Typical values** |
|---|---|---|
| Wet drop number | Drop a fresh green-ball from a height of 45 cm (18 in.) onto a steel plate until it fractures. | 5 drops |
| Wet compression strength | Compress a fresh green-ball between two platens (speed 15 mm/min) until it breaks. Record the peak load before failure as the compression strength. | 10 N (2.3 lbf) |
| Deformation | Record the inverse slope of the load vs. distance curve during the wet compression test. Measure the slope using the linear portion of the curve. Alternatively, give deformation as the distance the platen travelled when force reaches 1 N. | |
| Moisture content | Record the difference between wet and dry weight of fresh pellets, as a percentage (wet basis). | 9-10 % |
| Dry/Fired compression strength | After drying or firing, compress a single pellet (speed 25 mm/min) until it fractures. Record the peak load before failure as the compression strength. | 22 N (5 lbf), dry;<br>1780 N (400 lbf), fired |
| Ball/pellet density & porosity | Dry, cool and weight balls/pellets. Then, coat them in paraffin wax, weigh them, suspend them in distilled water and weigh again. Calculate porosity after measuring powder specific gravity with specific gravity bottles. ASTM C914 | > 30 % dry<br>20-30% fired |
| Mass loss by abrasion | Abrade 500 g of fired pellets in a Tyler Rotap for 15 minutes, using 3 and 28 mesh sieves and a pan. The abrasion rate measures the generation of -28 mesh fines. | |

### Measuring starch distribution in unfired pellets

We determined the radial starch distribution in unfired pellets by abrading pellets in a rotating drum and analyzing the abrasion products in a thermogravimetric analyzer. Approximately 330 grams of pellets tumbled in a 3.3 gal Roalox grinding jar (without grinding media or lifters) for a predetermined amount of time (4 or 10 minutes). The jar had a diameter of 12 and 3/8 inches and a height of 10 inches. Following abrasion, the products passing 600 μm were collected.

We placed the remaining pellets back into the mill for further tumbling. We repeated the procedure until approximately 100 grams of pellets remained: we hand-ground this fraction using a mortar and pestle to also pass 600 μm. From each 330-gram sample, about 7 weight-fractions (or layers) were generated in total.

We determined the starch content in each layer by thermogravimetric analysis in an air atmosphere. Each layer was analyzed 4 to 6 times. We heated 1-2 g samples in a TGA (Leco 701) from 25 to 107 °C (at 10°C/min.) where they remained for 30 minutes. The temperature then increased to 550 °C (at 5°C/min.) and held for 30 minutes. We used the sample's dry and final weights to determine the mass loss for each sample. After accounting for mass losses from the fluxed concentrate, we attributed the additional losses to starch. We compared peak locations on the derivative TG curves to a starch standard curve for confirmation that the starch degradation behavior was not significantly influenced by the balling feed.

We calculated the radial positions corresponding to the layers' midpoints using Equations 1-3 and the following assumptions: (a) pellets were uniform spheres; (b) pellet density was equal to the layer density; and (c) all pellets abraded equally. We qualitatively confirmed assumption c by eye as dry pellets were removed from the mill following abrasion.

$$t_L = R_1 - R_2 \tag{2}$$

$$V_L = (4\pi/3)(R_1^3 - R_2^3) \tag{3}$$

$$\rho_L = M_L/V_L \tag{4}$$

In Equations 2-4, $t_L$ is layer thickness; $R_1$ and $R_2$ are the layer's outer and inner radii; $V_L$ is layer volume; $\rho_L$ is layer density; and $M_L$ is layer mass. We plotted starch contents at the midpoints of each of the layers.

Additionally, we hand pressed a small quantity of the premixed starch and balling feed into cylinders (4 g, 13.3 mm dia, 9.5 mm long) using a Leco pellet press. We left each cylinder in the mold, and dried the mold/cylinder at the same conditions used for pellets. After drying, we removed the cylinders from the mold using the Leco pellet press and cut them into 4 longitudinal sections using a small knife. Descriptions of the 4 sections are: i) the top, which was exposed to the drying oven, from 0 mm to 1.58 mm, ii) the middle, from 1.58 mm to 3.16 mm, iii) the bottom, from 3.16 mm to 4.75 mm, and iv) the base, from 4.75 to 9.5 mm. We analyzed the starch content in each layer following the TGA procedure described previously. This test allowed us to see whether the drying process influenced binder distribution. In other words, did the starch distribution we saw originate from moisture wicking to the surface during drying, or did it develop during agglomeration?

### Isothermal Reduction Tests

Test aims: The aim of the isothermal reduction test is to determine the reducibility of iron ore pellet samples.

Test equipment: A capped alumina tube is suspended within an electric furnace (Thermolyne Type 54500). The tube is half-filled with alumina grinding media, which preheats the nitrogen or reduction gas as it enters the tube. The sample pellets are loaded into a stainless steel basket, and suspended into the furnace using a platinum wire. The wire is connected to a sensitive balance (Mettler Toledo XS), which measures the pellet weight throughout the test.

Test Procedure: The pellet samples are dried (105 °C) to constant weight, loaded into the stainless steel basket, and suspended within the tube furnace. The tube is capped, furnace temperature set to the predetermined test temperature of 850 °C, and nitrogen gas flow rate set to 4 lpm. When furnace temperature reaches set point, pellet weight is recorded; the weight is continually recorded until pellets reach a stable weight. When weight is stable, carbon monoxide gas flow rate is set to 1 lpm, and the initial pellet weight is recorded. Pellet weight is periodically recorded (five minute intervals for first hour, ten minute intervals for hours two and three) throughout the test. After three hours, carbon monoxide gas flow is turned off, nitrogen gas flow increased to 8 lpm, and the furnace set point set to zero degrees Celsius.

# Appendix 3 Pelletizing Test Statistics

In order to establish typical error levels for our laboratory pelletizing tests, we made 10 replicate batches of hematite pellets with 1 kg/t (0.1 %) modified corn-starch (60 % cws) as binder. We determined green and dry ball metrics for all the individual batches, and then found the composite mean value of the 10 trials. We determined fired pellet metrics after firing composite samples prepared by mixing all pellet batches together (before and after firing). The reported value for the fired compression test is the mean of 50 individual pellets. The reported value for the abrasion tests is the mean from 10 abrasion tests from samples prepared by rotary splitting.

Figures 44-45 show the results, with the whiskers giving the minimum and maximum values. Dotted lines indicate the minimum recommended values for the common tests.

Relative standard deviations for the test results ranged from 3.2 to 27.8 %, with the greatest deviations in fired pellet compression strength (Table 13). In industry, operators will calculate and use the percentage of pellets weaker than 200 lbf (890 N) instead of the mean value because of the large variation in individual pellet strengths (differences between the mean values of different pellet types are often insignificant). I used the mean because few pellets were weak following our firing procedure. Relative standard deviations in our fired pellets and industry fired pellets were similar.

Another important point is that in industry pelletizing, filter cake moisture contents are tightly controlled, with a range of about 0.3-0.5 %. In our replicate balling trials, the moisture content ranged from 9.3 to 10.2 %, which significantly affected the void saturation, wet compression strength and deformation values. We tried to control moisture content by 'eye' and ‘feel’, but because of the variation we obtained, elected to mask moisture effects in fired pellets by mixing dry balls together before and after firing.

*Table 13 Typical error levels associated with replicate hematite balling experiments. The given error is the relative standard deviation (standard deviation/mean*100) between the 10 trials. For the preheated and fired compression strength tests, it is the relative standard deviation between 50 individual pellets from the composite pellet samples. Forsmo et al (2006) reported that the observed error range in pellet quality tests will be wider within a single batch than between batches; we also observed the same.*

| **Green/Dry ball test** | **Error (%)** | **Preheated/Fired Pellet test** | **Error (%)** |
|---|---|---|---|
| Moisture content | 3.2 | 1100 °C comp. strength | 21.4 |
| Wet drop | 3.6 | 1250 °C comp. strength | 27.8 |
| Saturation | 6.7 | 1100 °C mass loss by abrasion | 4.8 |
| Wet comp. strength | 17.9 | 1250 °C mass loss by abrasion | 3.7 |
| Deformation | 27.8 | | |
| Void fraction | 2.8 | | |
| Dry comp. strength | 8.4 | | |

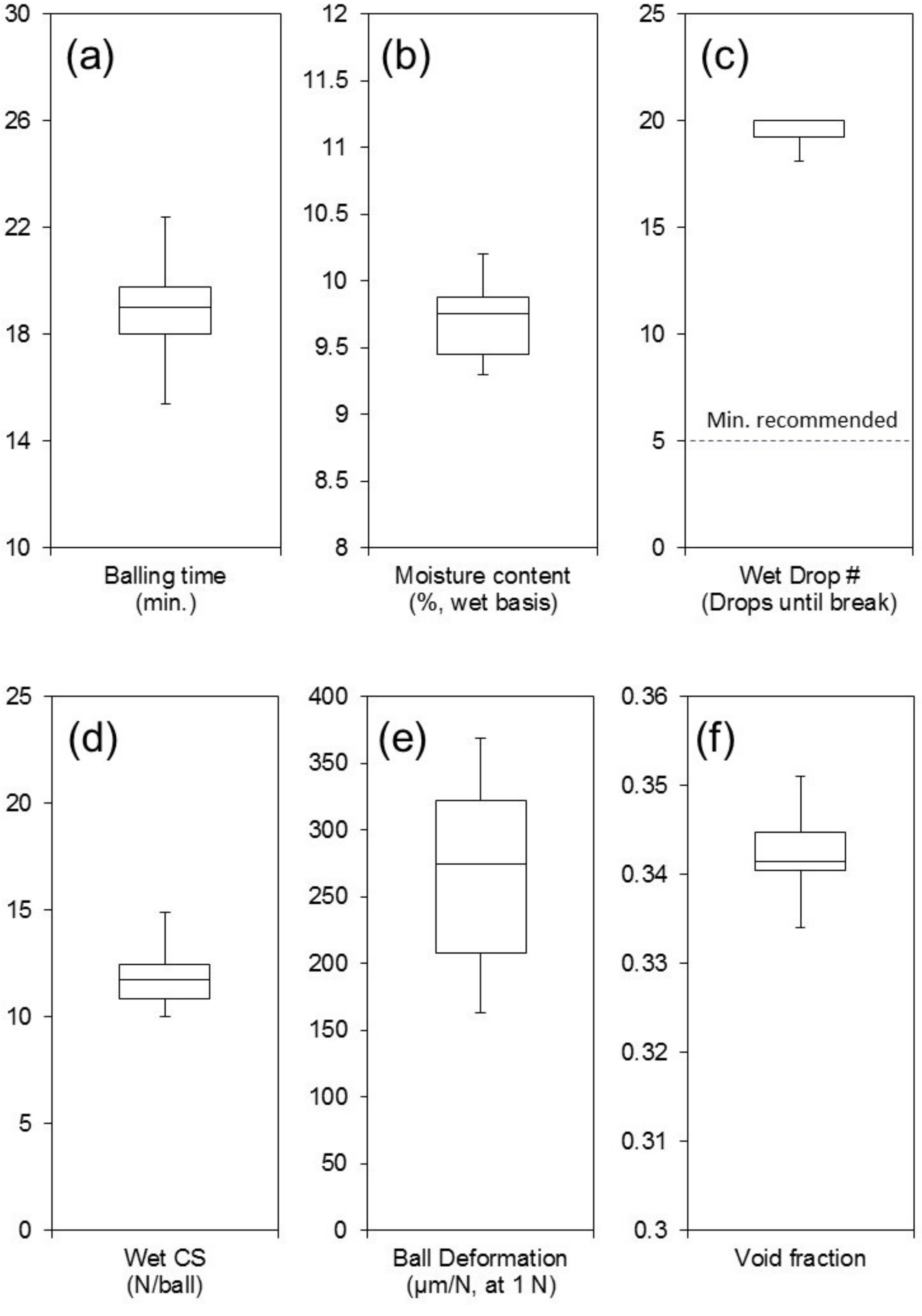

*Figure 44 Reproducibility of pelletizing tests. Balling time (a), moisture content (b), wet drop number (c), wet compression strength (d), ball deformation (e), and void fraction (f). Plant F hematite concentrate. Corn starch (60% cold-water solubility, 1 kg/t dose). N=10 for a,b,c,d,e,f.*

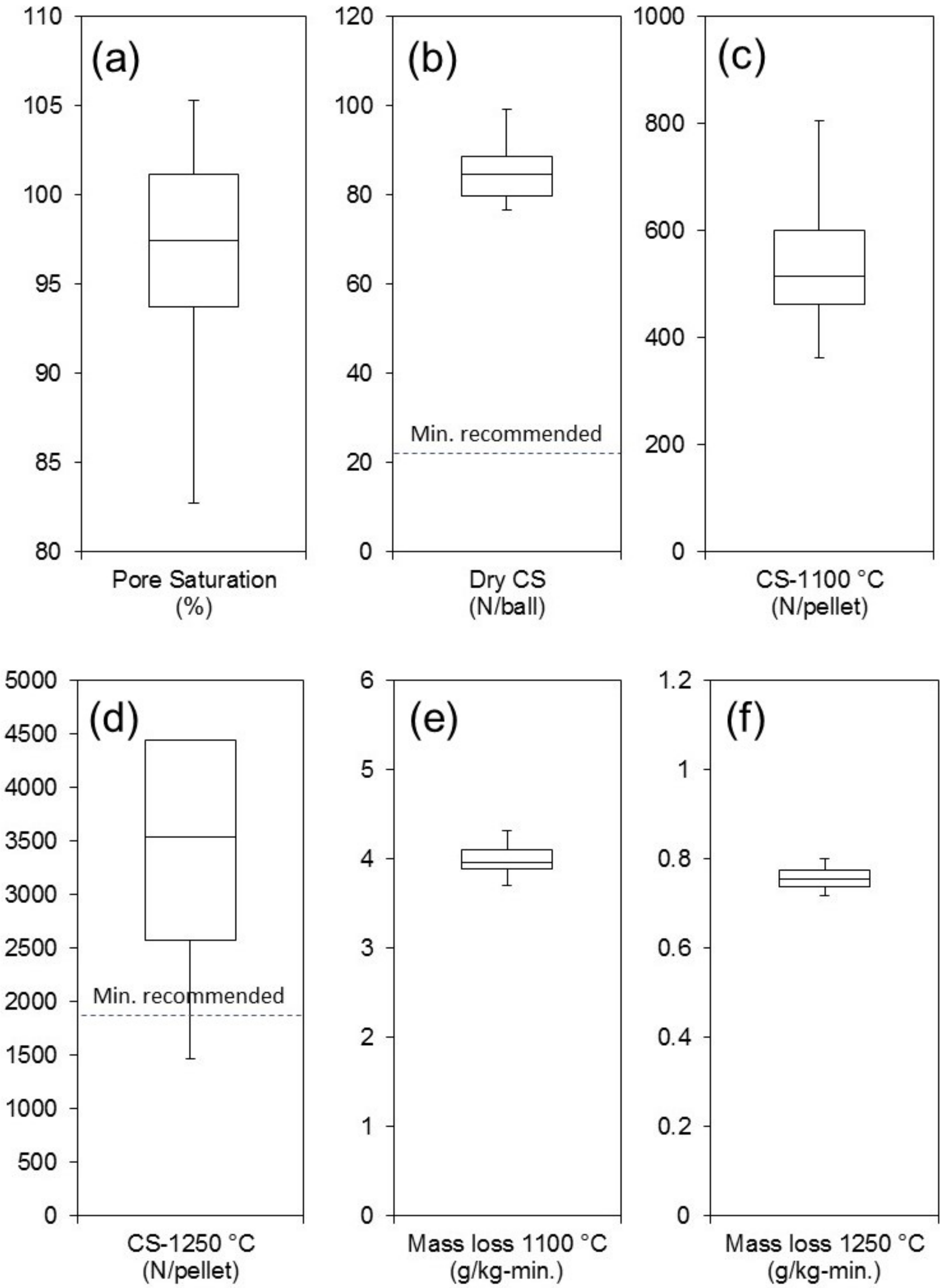

*Figure 45 Reproducibility of pelletizing tests. Pore saturation (a), dry compression strength (b), preheat compression strength (c), fired compression strength (d), preheated mass loss by abrasion (e), and fired mass loss by abrasion (f). Plant F hematite concentrate. Corn starch (60% cold-water solubility, 1 kg/t dose). N=10 for a, b, e, and f; N=50 for c and d. CS = compression strength.*

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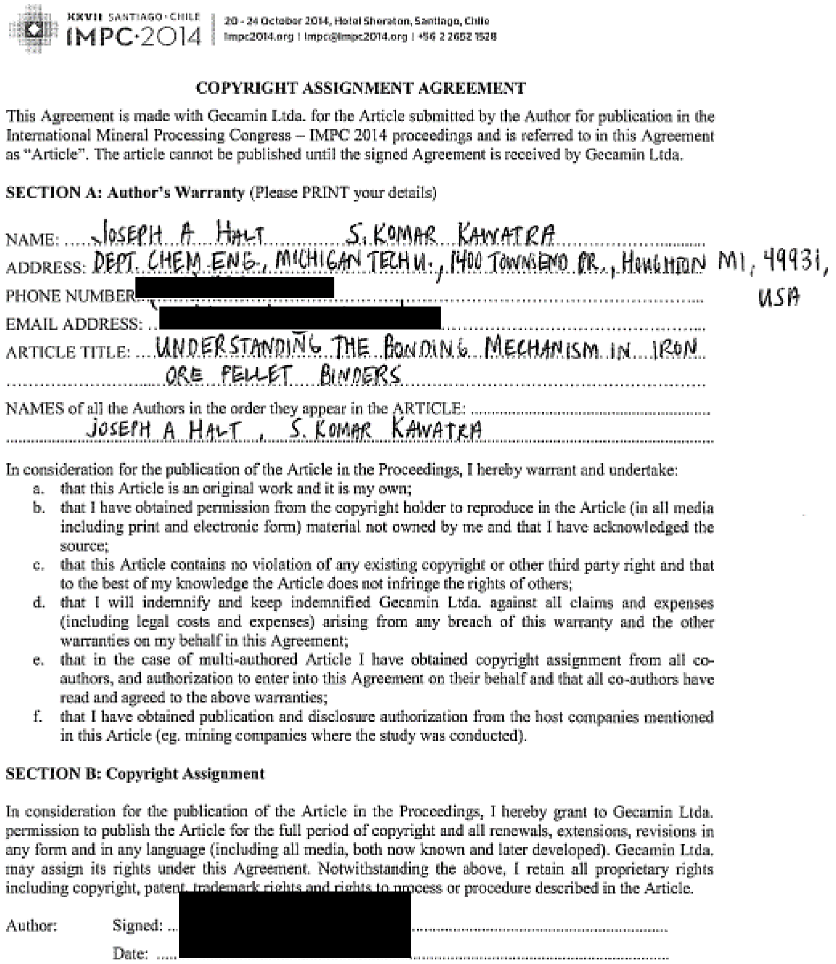

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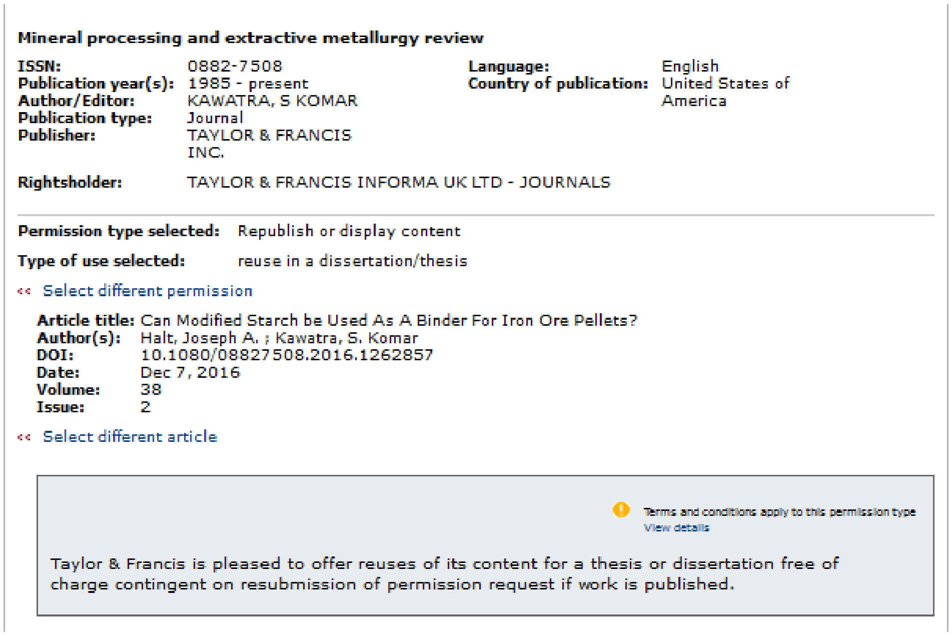

**Mineral processing and extractive metallurgy review**

**ISSN:** 0882-7508
**Publication year(s):** 1985 - present
**Author/Editor:** KAWATRA, S KOMAR
**Publication type:** Journal
**Publisher:** TAYLOR & FRANCIS INC.
**Language:** English
**Country of publication:** United States of America

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**Article title:** Can Modified Starch be Used As A Binder For Iron Ore Pellets?
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**DOI:** 10.1080/08827508.2016.1262857
**Date:** Dec 7, 2016
**Volume:** 38
**Issue:** 2

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**ISSN:** 0882-7508
**Publication year(s):** 1985 - present
**Author/Editor:** KAWATRA, S KOMAR
**Publication type:** Journal
**Publisher:** TAYLOR & FRANCIS INC.
**Language:** English
**Country of publication:** United States of America

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**Author(s):** Halt, Joseph A. ; Kawatra, S. Komar
**DOI:** 10.1080/08827508.2017.1288114
**Date:** Feb 16, 2017
**Volume:** 38
**Issue:** 2

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