Negative impact of humidity on the flowability of steel powders

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ABSTRACT
Atmospheric humidity is introduced into powders during handling, transportation, and storage. High moisture content can increase cohesive forces between particles and make it difficult to spread a powder into thin layers in powder bed processes or to fill a mold in processes such as press-and-sinter. Furthermore, water can cause porosity and uptake of oxygen in the final component, damaging its mechanical properties. In this study, a Freeman FT4 powder rheometer was placed inside a climate chamber. Both flowability and shear tests were performed on four steel powders under a range of humidity and temperatures. Basic flowability energy and specific energy were both found to increase significantly with humidity (typically increase by 50% for 80% of relative humidity compared to dry conditions) and were insensitive to temperature change (10–30°C). Conversely, the behavior of the powders under shear was neither sensitive to relative humidity nor temperature. Measurements of moisture content revealed that finer powders contained more moisture than coarser ones, but the moisture content was not correlated with humidity, probably due to shortcomings with the measurement method. This knowledge can be used to optimize powder processing conditions.

KEYWORDS
Flowability; steel powders; moisture; humidity; powder rheometer

1. Introduction
Powder bed additive manufacturing techniques are often used for demanding applications, such as in the biomedical and aerospace sectors, where component failure is greatly expensive or dangerous. For this reason, it is considered important that there is demanding quality control on the finished component. Defects are often generated in additive manufacturing for various reasons and when this happens, defective components must be rejected. This raises unit costs and damages the economic case for additive manufacturing (Baumers and Holweg 2019). Such problems also reduce the environmental sustainability of additive manufacturing.

1.1. Cohesion in powders
One problem that can lead to defects in powder bed additive manufacturing using a metal powder feedstock is the poor spreading of the powder on the build plate. This can be caused by large cohesive forces in the powder that prevents rearrangement of the particles. One potential origin of such forces is liquid bridging (Finn 1999). When powders are exposed to the environment, they can easily pick up moisture: water bonds or sorbs to the surface of the particles to reduce the surface energy of the system (Brunauer, Emmett, and Teller 1938). This effect is especially significant since powders have a very high specific surface area (Hausner 1978). For example, 1 kg of spherical particles of iron powder with a bulk density of 7800 kg m⁻³ and a diameter of 100 μm has a surface area of 3.8 m², which is equivalent to a cube of side length 0.8 m, which would have a mass of 4 tons. Water can progressively cover the particle surface, increasing the cohesive forces between particles (Coelho and Harnby 1978). This adversely affects the flow behavior and processability of powders (Stanford and DellaCorte 2006; Weingarten et al. 2015; Bauer et al. 2017; Lefebvre, Dai, et al. 2019). For powder bed additive manufacturing, which typically requires powders with median particle diameter, \( d_{50} \): 25 ≤ \( d_{50} \)/μm ≤ 45 for selective laser melting and 40 ≤ \( d_{50} \)/μm ≤ 105 for electron beam melting (Vock et al. 2019), powders may become too cohesive to be spread into thin layers, which is a necessary step in both techniques (Bauer et al. 2017). Furthermore, moisture, combined with the high heat around the melt pool in laser powder bed fusion processes, can lead to the formation of oxygen and hydrogen gases during printing operations (Weingarten et al. 2015; Cordova, Campos, and Tinga 2017b). The presence of gases can contribute to undesired porosity in the built component (Weingarten et al. 2015; Li, O’Donnell, and Sercombe 2016; Szemkus et al. 2017).

1.2. Quantifying the effect of moisture on powder cohesion
It is not easy to predict the humidity to which these materials will be exposed, as the amount of moisture in the environment is not easy to predict. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
atmosphere can vary consistently during the day, season, and location (Du, Cooper, and Fueglistaler 2012; Räisänen and Ruosteenoja 2013). Furthermore, the temperature has a large effect on the total amount of moisture that can be accommodated in air. When the water vapor partial pressure, $p$, is lower than the saturation water pressure, $p_s$, then water is dissolved in its gaseous state in the air. The amount of water relative to its saturation level can also be expressed through the relative humidity, RH (Equation (1), where RH is expressed in percent). If $p > p_s$, water condenses out of the air. The Arden-Buck equation can model how the water saturation pressure depends on temperature (Equation (2), where $T$ is the temperature expressed in $^\circ$C) (Buck 1981).

$$\text{RH} = 100 \frac{p}{p_s}$$

(1)

$$p_s(T) = 6.1121 \exp \left[ \frac{18.678 - \frac{T}{234.5}}{\ln \frac{T}{257.14 + T}} \right]$$

(2)

To shield metal powder from humidity, the use of sealed containers is common, although different containers offer different degrees of protection against moist environments (Szemkus et al. 2017). Along with the containers, the use of desiccants or inert gases such as nitrogen can further protect powders from moisture during storing or transportation. Inert gas can also be introduced in the printing chamber during printing operations in powder bed fusion processes. However, powders can be exposed to the atmosphere when containers are opened, if they are sealed improperly or when only a portion of the powder batch is used at any one time, exposing the remaining material to the atmosphere. If a powder adsorbs humidity, drying it in a static oven can help reduce its water content (Bauer et al. 2017). While this is beneficial, it adds step and expense to the manufacturing process.

Individual metal particles can adsorb water molecules on their surface by physical or chemical adsorption (Rouquerol et al. 2013). In both cases, the capacity of a powder to retain water is affected by its surface texture and the presence of open micro-pores (Rouquerol et al. 2013, A Manaf et al. 2019). In physical adsorption, water molecules bond to a thin and stable metal oxide surface thanks to weak van der Waals forces (Rouquerol et al. 2013; Cordova, Campos, and Tinga 2017b). With a reactive powder material, chemical adsorption is also possible. In this case, water molecules chemically bond to the powder, permanently modifying its chemistry (Rouquerol et al. 2013). When an increasing amount of water is adsorbed on the particle surface, more layers can stack on top of each other. When two particles are close to each other, Coelho and Harnby modeled how the adsorbed layers can form stable liquid bridges across particles of iron oxides (Coelho and Harnby 1978). It is also possible to calculate the attractive water bridging force, $F_{\text{WB}}$, between a pair of spherical particles of equal radius, $r_p$, at equilibrium conditions (Equation (3), where $\sigma$ is the surface tension of the water, taken to be 0.076$J$ m$^{-2}$, $R_0$, the azimuthal curvature radius at the meniscus neck (Figure 1) and $P_c$ is the capillary pressure acting in the neck) (Kralchevsky and Nagayama 2001). $R_0$ can be derived from geometrical considerations using an expression derived by Kelvin (Equation (4), where $V_m = 18ml$ mol$^{-1}$ is the molar volume of liquid water under standard conditions, $R_s$ and $R_m$ are the azimuthal and meridian radius of curvature of the liquid bridge (Figure 1), respectively, $R$ is the universal gas constant and $T$ is the absolute temperature) and the approximation that for capillary bridges with small length but relatively high volume, then $R_s \gg R_m$, which is known as the Derjaguin approximation (Thomson 1871; Derjaguin 1934; Rabinovich, Esayanur, and Moudgil 2005; Lian and Seville 2016). A more complete derivation is provided in Appendix A. $P_c$ may be derived using an expression published by Laplace and Young (Equation (5)) (marquis de Laplace 1805). $F_{\text{WB}}$ decreases significantly with an increase in relative humidity, mostly due to the drop in capillary pressure (Figure 2).

$$F_{\text{WB}} = -\pi(2R_0\sigma - R_0^2P_c)$$

(3)

$$\ln \left( \frac{P}{P_c} \right) = \ln \left( \frac{\text{RH}}{100} \right) = \frac{\sigma V_m}{RT} \left( \frac{1}{R_s} + \frac{1}{R_m} \right)$$

(4)

$$P_c = \sigma \left( \frac{1}{R_s} + \frac{1}{R_m} \right)$$

(5)

It is equally possible to approximate the strength of the attractive van der Waals forces between the same two spheres, $F_{\text{vdW}}$, (Equation (6), where $A$ is the Hamaker constant and is $3.87 \times 10^{-19}$ $J$ for iron (Tolias 2020) and $L$ is the separation between the particles) (Israelachvili 2011). The gravitational force acting on an individual particle, $F_g$, may be calculated as a function of the particle diameter, $d_p$ and density, $\rho_p$, using the well-known equation: $F_g = \pi d_p^3 \rho_p g/6$. For particles with an inter-particle distance, $L = 5\AA$, the water bridging force is comparable to van der Waals forces for fine powders, while it dominates for coarse ones. It should be noted that at higher humidity, the inter-particle distance in a bulk solid can be higher due to moisture adsorption, lowering the van der Waals forces.

![Figure 1. The liquid bridge between two particles of radius $r_p$. $R_m$ and $R_s$ are the water bridge meridional and azimuthal curvature radii, respectively. $R_0$ is the azimuthal bridge radius at the water bridge neck and $L$ is the distance between particles.](image-url)
can have seven contact points (German 1989; 2014); however, a single sphere in a loose random packing arrangement there is a large number of individual bodies that can interact. A single sphere in a loose random packing arrangement (German 2014) and as a condensed layer in the liquid bridge (Equation (8), where $d$ is the half-filling angle of the bridge and depends on humidity, particle size and inter-particle distance as shown in Appendix A) (Weigert and Ripperger 1999) (Figure 3). The water volume in the liquid bridge, $V_b$, which is two orders of magnitude larger than the water bridge volume in the adsorbed layers, $V_{ads}$, has been found to correlate with the energy needed to break a liquid bridge, $W$ (Equation (9), where $k$ is a constant). Hence, the energy required for breaking a liquid bridge is predicted to increase with the relative humidity.

$$V_{ads} = A_p \left[ 0.691 + \frac{0.014 \cdot 11.5 \cdot \frac{RH}{100}}{1 - \left( \frac{RH}{100} \right) \left[ 1 + (11.5 - 1) \frac{RH}{100} \right]} \right]$$  \hspace{1cm} (7)

$$V_b = \frac{\pi}{4} d_p^3 \sin^2(\beta) (1 - \cos(\beta)) - \frac{\pi}{12} d_p^3 (1 - \cos(\beta))^2 [2 + \cos(\beta)]$$  \hspace{1cm} (8)

$$W = k \sigma \sqrt{2d} V_b$$  \hspace{1cm} (9)

When considering a defined volume of fine particles, there is a large number of individual bodies that can interact. A single sphere in a loose random packing arrangement can have seven contact points (German 1989; 2014); however, it is common for particles to have fewer contact points, as cohesive forces prevent the formation of a loose random packing arrangement (German 2014). In the presence of humidity, this implies a very high number of interactions, which develop an interconnected network of attractive forces across the sample, which will increase the cohesive strength of the powder. Models such as the adapted Rumpf tensile strength model (Rumpf 1962; Capece et al. 2015), or the application of the Warren Spring model (García-Triñanes, Luding, and Shi 2019) aim at explaining bulk behavior based on the interaction of forces between particles. The Rumpf model includes both adsorption and liquid bridging as separate mechanisms (Turner and Balasubramanian 1974). However, such models are generally limited to the study of the tensile strength of bulk solids or a compacted powder sample, not for powder undergoing flow or spreading.

### 1.3. Experimental evidence

There is no consensus in the literature on the effect of moisture on powder flow. Some evidence shows that the flow behavior of various metal powders for additive manufacturing is largely insensitive to moisture, except for an aluminum powder (Cordova, Campos, and Tinga 2017a). Similar studies have found that the flow behavior of metal powders does depend on relative humidity above 65% (Stanford and DellaCorte 2006) and in the case of titanium powders (Lefebvre, Dai, et al. 2019). Lefebvre et al. also found that relative humidity does affect powder flow, but different tests provided different sensitivities. Hall and Carney flowmeters and Hegman gauge tests all showed high sensitivity, powder rheometry showed sensitivity only when low stresses were applied (unconfined flow) and rotating powder analysis showed low sensitivity. However, other studies have shown that moisture has a measurable negative impact on flowability measured by rotating powder analysis on lactose powders (Lumay et al. 2016) and an aluminum-silicon alloy (Bauer et al. 2017). One study used a powder rheometer to measure the flow of steel powders and found that some stored at (moist) ambient conditions flowed better than the ones that were dry (Dattani et al. 2019). The variety of effects could be due to the range of mechanisms by which water can affect interparticle forces. For example, the formation of a monolayer of moisture on all surfaces could improve flowability by lubricating the particles, which would show as an
increase in flowability with humidity. At higher humidity, liquid bridges could form and flowability would fall. Such effects have been demonstrated in excipients and starch, measured by the Haunser ratio, static angle of repose and rotating powder analysis (Crouter and Briens 2014). Similarly, a minimum in the inter-particle forces was identified for a relative humidity interval between 45% and 60% (Karde and Ghoroi 2015). The nature of the powder also plays a key role: an increase in relative humidity has been shown to lead to an increase in specific surface energy and a decrease in flowability for a hydrophilic pharmaceutical powder, but not for a hydrophobic one (Karde and Ghoroi 2015).

1.4. Powder flowability measurement techniques

Multiple methods to characterize the flowability of powder exist. Each test subject powders to a different condition of flow, sometimes using different metrics to describe flow behavior (Prescott and Barnum 2000). Some tests measure the flow rate of powders flowing through a funnel, such as the Hall, Carney, or Gustavsson flow rate tests (International Standard Organisation 2013; ASTM International 2017b, 2013). Others measure the static angle of repose of a powder (International Standard Organisation 1976) or the ratio between tapped density and an apparent density (Santomaso, Lazzaro, and Canu 2003; ASTM International 2017a, 2015b). While standards suggest using flow rate tests for additive manufacturing metal powders (ASTM International 2014), these tests may not be suited for cohesive powders (Leturia et al. 2014; Spierings et al. 2016). Other testing equipment, such as the rotating drum (Krantz, Zhang, and Zhu 2009) or the powder rheometer (Leturia et al. 2014), allow more flexibility on the materials tested and can test powders in different conditions.

In this study, the effect of humidity on the flowability of four steel powders will be assessed systematically. The powder samples will be moisturized over a range of relative humidity (0–80%), temperature (10–30°C), and allowing different times for the powder to equilibrate with the atmosphere in a climate chamber (up to 650 h). This will allow conditions typical of powder storage to be emulated. Powder rheometry will be used to measure the flowability of the power within the climate chamber and the moisture content of selected samples will be analyzed.

2. Materials and methods

An overview of the test procedure is given in Figure 4. Four different powders were separately placed inside a climate chamber that also contained a powder rheometer (Freeman FT4, Freeman Technology, Tewkesbury, Gloucestershire, U.K.). Before testing, both the powder and rheometer were left in the climate chamber for a significant period to allow the moisture content to approach equilibrium. The amount of time required for the moisture content to equilibrate was investigated in an initial set of trials. Flowability and shear cell tests were conducted under controlled temperature and relative humidity. The water content of selected samples was estimated via Karl Fischer titration (Karl Fischer 740 sample processor, including an oven and an 831 coulometer, Metrohm AG, Herisau, Switzerland).

2.1. Materials

Four different steel powders from two producers were tested (Tables 1 and 2). Powder A is a gas atomized 17-4 PH stainless steel powder, sieved to a nominal size fraction of particle diameter, \( d : 10 \leq d / \mu m \leq 53 \), which is typical for laser powder bed fusion additive manufacturing. Powder B is the same alloy but sieved to a finer fraction (Table 2). Powder C is also the same alloy with a similar size distribution to Powder A but produced by water atomization, which will result in different particle morphology. Powder D is a gas atomized tool steel. This choice of samples makes it possible to investigate if the effect of humidity on flowability depends on particle size, production technique, and/or chemistry.
2.2. Particle size and morphology

Particle size and aspect ratio were measured under the relevant standard, ISO 33221-2:2006 (Bruno and Hancock 2008) using dynamic image analysis with a Camsizer XT (Retsch Technology, Haan, Germany). Additional properties of the powder that are relevant to its flow behavior were also measured: the conditioned bulk density, which is measured as part of other tests in powder rheometer, and the number of contact points per unit volume, which is estimated from the Camsizer data. The average number of contact points per volume \( N_v \) is derived using Equation (10), where \( N_C \) is the estimated average number of contact points per particle and \( n_V \) is the expected number of particles per unit volume. The number of contact points per particle, \( N_C \), can be estimated from a model which offers best fit between spherical powder particles with a fractional density, \( f : 0.5 < f < 0.8 \) (Equation (11)) (German 2014). The number of particles per unit volume, \( n_V \), was derived from the measured size distribution statistics (Equation (12), where \( V_P \) is the average particle volume).

\[
N_C = 15.1f - 2.8 \quad (11)
\]

\[
n_V = \frac{f}{V_P} \quad (12)
\]

All powders were sampled by the relevant standard (ASTM International 2015a), using a spinning riffler to obtain two samples of approximately 30 ml each. Some samples were then dried at 105 °C for 30 min in an electric oven to remove excess moisture while others were used in the as-stored condition (Table 3). Immediately after drying, each specimen was moved into the appropriate sample vessel for the FT4 powder rheometer. These vessels are open-ended glass tubes, which allow moisture to pass between the powder and the atmosphere. A pre-set mixing sequence (‘conditioning cycle’) was performed using the rheometer to improve the homogeneity of the powder in the vessel, reducing possible segregation, excesses of trapped air, or caking effects that may arise when handling and pouring the powders (Freeman 2007). After the conditioning cycle, one sample was reduced to 25 ml following standard operating procedures for the FT4 powder rheometer and used for a ‘stability and variable flow rate test’ (Freeman 2007). The powder in the other vessel was conditioned and compacted under normal compressive stress of 9 kPa in preparation for a shear cell test. After compaction, this second sample was reduced to a volume of 10 ml (with a height of 20 mm).

2.3. Moisturization and conditioning

Before this study, the powders had been stored for approximately three months in commercial containers, which were not sealed against moisture. For testing, powder samples
and the rheometer were sealed in a Weiss C1000-40 climate chamber located in Swerim AB (Kista, Sweden) under known conditions of temperature and relative humidity (Figure 5). The relative humidity and temperature were set in the climate chamber. An initial series of trials were conducted on dried powders immediately after drying to establish the properties of the powders in the absence of moisture. The second set of trials was performed to test how long powders needed to be left in the climate chamber for the effects of environmental moisture on the powder behavior to stop changing. A final set of trials was performed using this ‘moisturization time’ to test the effect of temperature and relative humidity on the powder properties (Table 3).

The rheometer was sealed in the climate chamber to avoid the need to remove the powders for testing, which could allow them to lose moisture during the test, which has been identified as a potential problem in a previous study (Lefebvre, Bernier, et al. 2019). The temperature was controlled through two Pt100 thermometers and the moisture was controlled by a dry and wet-bulb sensor. The temperature was set at 10°C to 30°C, while relative humidity was set at 40%, 60%, or 80%.

Immediately before testing, the 25 ml samples for the stability and variable flow rate test were agitated thoroughly by running 10 conditioning cycles. The impeller on the rheometer was moved through the powder in the test vessel, each time moving at a different speed and helix angle. The agitation took approximately 10 min. This step intends to homogenize the powder and, especially, minimize possible differences in the powder humidity between the top and the bottom of the vessel. However, the compacted 10 ml shear cell testing samples were not homogenized after moisturization, as the shear test requires the powder to be compacted and occupy a volume of precisely 10 ml, which is not possible if the powder is agitated after compaction. Also, the shear test depends on the behavior of the top surface of the powder, where it is likely that the powder will be equilibrated with the atmosphere without any additional homogenization.

During the experimental trials, the rheometer was controlled from a computer situated outside the climate chamber. To move the vessels filled with powders to and from the rheometer, the climate chamber had to be accessed from a small lateral port with a diameter of 10 cm. During this process, air circulating in the climate chamber was flushed over the equipment, to minimize any interaction between the sample and the external atmosphere. During testing, air flushing was paused to avoid interference with the load cell readings on the FT4 rheometer, during which time the climate chamber was sealed.

### 2.4. Stability and variable flow rate tests

For all the powders, a 25 ml powder sample was tested using the ‘stability and variable flow rate’ test program of the Freeman FT4 powder rheometer (Hare et al. 2015; Radjai et al. 2017). A cylindrical borosilicate glass vessel with a

| Table 2. Powder properties relevant to their flow behavior: bulk density, shape (aspect ratio), the estimated number of contact points per unit volume and size distribution statistics. |
| Powder | Conditioned bulk density (g ml⁻¹) | Aspect ratio | Contact points per volume (10⁶ x 1 ml⁻¹) | D₁₀ (µm) | D₅₀ (Mm) | D₉₀ (µm) |
|--------|----------------------------------|-------------|----------------------------------------|--------|----------|--------|
| A      | 4.2                              | 0.88        | 370                                    | 5.7    | 17.0     | 37.2   |
| B      | 3.9                              | 0.91        | 1928                                   | 7.5    | 10.7     | 15.4   |
| C      | 3.7                              | 0.78        | 150                                    | 7.4    | 19.9     | 44.6   |
| D      | 4.5                              | 0.89        | 81                                     | 18.4   | 30.9     | 55.7   |

| Table 3. Overview of the experimental trials and their climatic chamber parameters. |
| Trial | Material | Time (h) | Temperature (°C) | RH (%) | SH (mass%) | Vials |
|-------|----------|---------|-----------------|-------|------------|-------|
| 1.1   | A, B, C, D | /       | Room temp.      | 0°    | 0°         | –     |
| Moisturized samples |
| 2.1   | A, B     | 24      | 30              | 80    | 2.2        | –     |
| 2.2   | A, B     | 24      | 40              | 60    | 0.61       | –     |
| 2.3   | A, B     | 72      | 30              | 40    | 1.2        | –     |
| 2.4   | A, B     | 650     | 30              | 60    | 1.1        | –     |
| 3.1   | A, B     | 72      | 10              | 40    | 0.31       | Yes   |
| 3.2   | A, B     | 24      | 30              | 60    | 0.61       | –     |
| 3.3   | A, B     | 30      | 40              | 80    | 0.58       | –     |
| 3.4   | A, B     | 72      | 30              | 40    | 1.2        | –     |
| 3.5   | A, B     | 650     | 30              | 60    | 1.1        | –     |
| 3.6   | A, B     | 80      | 40              | 80    | 2.2        | Yes   |
| 3.7   | C, D     | 72      | 40              | 80    | 0.58       | –     |
| 3.8   | C, D     | 72      | 40              | 80    | 1.2        | –     |
| 3.9   | C, D     | 80      | 40              | 80    | 2.2        | –     |

The powders tested in trials 3.1 and 3.6 were also tested using Karl-Fisher titration to determine the moisture content. RH means relative humidity and SH means specific humidity.
25 mm diameter and 25 ml testing capacity was used. In this program, an impeller with a diameter of 23.5 mm moves through the powder sample following a pre-determined path, while two load cells record the torque and normal force which must be applied to the impeller to achieve the path and speed set in the program. The load cell data are used together with measurements of the position of the impeller to calculate the total work done. Eleven test cycles are performed during this test: in the first eight cycles, the impeller moves at a constant tip speed of \( \frac{100 \text{ mm s}^{-1}}{1} \). This allows any effect of repetitive motion on the powder behavior to be detected. In the remaining three cycles the impeller moves downwards at a progressively slower speed, while the upwards movement remains unchanged. This shows any changes in powder behavior as a function of movement speed. When the impeller blade moves downwards, the powder is compressed against the (sealed) base of the test vessel, which results in a flow condition known as ‘confined flow’. The basic flowability energy (\( E_{BF} \)) represents the energy needed from the impeller to move through the powder in this ‘confined’ flow state, and it is calculated from the forces recorded during the seventh test cycle. By contrast, ‘unconfined flow’ occurs when the impeller moves upwards through the powder, as the top of the vessel is open, and the powder is free to move upwards as the impeller rises. The specific energy (\( E_S \)) is the energy needed from the impeller to move the powders when moving upwards divided by the total sample mass. In this work, a modified basic flowability energy (\( E_{BF}^m \)) and specific energy (\( E_S^m \)) were calculated as an average of the energies required for moving the powder for the first eight cycles, all of which used the same impeller tip speed. This was possible as the behavior of the steel powders was very stable, and the operating conditions of the climate chamber were kept constant. Both \( E_{BF}^m \) and \( E_S^m \) are measured for a constant volume of powders, but liquid bridging is expected to act at the contact points between individual particles. The estimated total number of contact points per volume changes greatly for the samples studied (Table 2). Hence, it is possible to calculate the increment of the dissipated energy per contact point during upwards, \( \Delta E_{cp,u} \), and downwards, \( \Delta E_{cp,d} \), testing due to the relative humidity (Equations (13) and (14)).

\[
\Delta E_{cp,d} = \frac{1}{N_V} \left( E_{BF}^m_{RH=0} - E_{BF}^m_{RH=x} \right)
\]

\[
\Delta E_{cp,u} = \frac{m_{sample}}{N_V} \left( E_S^m_{RH=0} - E_S^m_{RH=x} \right)
\]

2.5. Shear cell tests

The powder vessel containing the 10 ml samples was subjected to a shear test using the Freeman FT4 shear cell according to the relevant standard: ASTM D7891-15 (ASTM International 2015c). A round flange with small fins on the lower surface applies force to the top surface of the powder sample. A compressive force and a shear are applied at the top of the powder column. Before measuring the main data, the powder is sheared under a compressive stress of 9 kPa while the flange rotates at a constant speed. The shear stress gradually increases until steady shear stress is reached, at which point the rotation of the flange is stopped, and the normal stress is lowered to the test value before shear stress is gradually applied until the flow is initiated. This process is repeated for a range of normal stresses below 9 kPa (in this case, 7 kPa, 6 kPa, 5 kPa, 4 kPa, and 3 kPa). After plotting the shear stress required to cause flow against normal stress in a Mohr’s circle, metrics can be derived from the graph. The metrics used in this study are unconfined yield stress, \( \sigma_{UYS} \), and the major principal stress, \( \sigma_{MPS} \) (Schwedes 2003; Schulze 2007).

The major principal stress is obtained when the powder is sheared at a constant speed under the pre-compaction load of 9 kPa. The stress state under which flow begins is
plotted on the Mohr’s circle, together with the five results at lower normal stresses. A yield locus is drawn that goes through the pre-compaction shear point and is tangential to the best fit line. The major principal stress is the larger of the two normal equivalent stresses to that yield locus. Unconfined yield strength is a similar metric that is derived by plotting a yield locus that is tangential to the best fit line through the five data points at lower normal stresses and passes through the origin of the Mohr’s circle plot. It is taken as the non-zero equivalent normal stress of the yield locus. The unconfined yield strength is the equivalent normal stress required to fracture a powder column after it has been compacted to the major principal stress.

2.6. Karl Fischer titration

In experimental trials 3.1 and 3.6 (Table 3), 5 vials of powder were added to the climate chamber in addition to the samples required for other tests. Three of these vials were left empty and the remaining two were filled with approximately 10 g of powder. This sample mass was consistent with that found to be suitable to analyze the content of water in metallic powders in a previous study (Mellin et al. 2020). In the same study, it was suggested that five samples are needed to guarantee repeatability in the data. However, in our study, it was only possible to obtain two samples, due to limitations on the amount of powder available. All vials were equilibrated and sealed in the climate chamber immediately before powder testing to preserve the moisture content at the time of testing the powder.

There are no accepted standards for measuring the water content of metallic powders. However, Karl Fischer titration is appropriate to analyze water content in several media. A test solution containing iodine is used and the iodine is consumed by any water present. The amount of iodine in the solution is monitored with a double-platinum electrode, which enables the total water content of the test solution to be deduced. From this, the water content of the sample can be determined with high precision (ASTM International 2016). Karl Fischer titration is also fast and sensitive to very small water contents. Gravimetric measurements may not be precise enough to detect water contents that are as small as can be absorbed by metallic powders from the atmosphere, but Karl Fischer titration has already been used to analyze the water content in metallic powders (Lefebvre et al. 2020).

Usually, in Karl Fischer titration, the water-bearing medium is dissolved in the test solution. However, most metal powders will not dissolve in common Karl Fischer test reagents. If the powder were simply immersed in the solution, some water may be retained on the powder surfaces. Therefore, each vial was placed inside a small electric oven at 250°C. The oven was flushed with nitrogen. The nitrogen was then bubbled through the titration cell, where any water vapor collected in it is exposed to the reagent (Lefebvre et al. 2020; Mellin et al. 2020).

Any water found during our experimental trials can have three sources: it could be adsorbed or condensed within the powder, adsorbed on the vial’s borosilicate glass surface, or be contained in the air in the vial. To measure the amount of water present on vial surfaces and in the air, three empty vials per powder were exposed to the conditions in the climate chamber and were subsequently tested. The amount of water present in the empty vials can be subtracted from the amount measured in the vials containing powder (Mellin et al. 2020).

3. Results and discussion

3.1. Moisturization time and memory effect

The results trials 2.1, 2.2, and 2.4 (Table 3) clearly show that both the modified basic flowability energy and the modified specific energy are higher for powder B than for powder A (Figure 6). This implies that the reduction in particle size leads to higher total cohesive forces for all moisturization times, as may be expected, possibly due to the higher sensitivity of finer powders to surface interactions (Lefebvre, Dai et al. 2019). In trial 2 the powders were moisturized for
650 h before testing, which can be expected to give the highest possible moisture content. In trials 2.1 and 2.2 powders were moisturized for 24 h and then tested. Two sets of tests were conducted using these identical conditions to examine the repeatability of the measurements. However, these repeats gave very different results for both powders A and B. This suggests that 24 h is not sufficient to be confident that the moisture has permeated the powder. Both samples show a similar flow behavior between trials 2.2, 2.3 (in which powders were moisturized for 72 h) and 2.4, so 72 h was taken to be sufficient time to achieve thorough moisturization while still being practicable.

Powder history seems to have a strong effect on its flowability, in partial agreement with the literature, where the flow of titanium powders was found to vary with the relative humidity of the laboratory in Hall and Carney flowmeter tests, but not in the FT4 powder rheometer (Lefebvre, Dai, et al. 2019). However, in that case, powders used in the rheometry tests were moisturized in a bottle and then placed in the rheometer vessel, so the density of the test samples was not controlled. It is known that bulk density can affect powder flowability measurements (Marchetti and Hulme-Smith 2019).

The effect of drying powder before moisturization can be observed comparing trials 2.3 and 3.1 (Figure 6). In both trials, powders were moisturized for 72 h. In trial 3.1, the samples were first dried, while in trial 2.3, the powders were taken directly from storage and moisturized. For powder B there is no significant effect on the basic flowability energy and specific energy, but for powder A there is an effect on the basic flowability energy, which is 8% higher with powders dried beforehand. This was attributed to an increase in density in the dried sample, which is 7% higher than the undried sample (Table 4). If a greater powder mass needs to be moved by the impeller, this will require higher forces and do more work. This will result in higher basic flowability energy during testing. However, the specific energy is divided by the sample mass, so this effect is removed, as is seen in the current case. This suggests that the cohesive forces between the powders with and without drying before moisturization are similar and only the powder mass (or, since the powder volume is constant between tests, density) affects the work done by the impeller.

Powder B shows a change in density due to prior drying that is (slightly) greater than the standard deviation of the measurements performed in this study. This is likely to be due to the finer particle size in Powder B, which will lead to more contact points within the sample (Equation (10)) and therefore greater total cohesion. This will inhibit particle rearrangement and result in a bulk material with a lower density. While powder A (coarser particles, Table 2) does change density if dried, removing the moisture does not have a strong enough effect on the inter-particle forces for powder B to overcome cohesion and change density. This agrees with published findings, where relative humidity has been shown to influence the apparent density, but less so for finer powder (Lefebvre, Dai, et al. 2019). Further experiments involving more powders and drying regimes would enable this theory to be tested, especially if accurate measurements of the moisture contents could be taken at each stage.

3.2. Effect of relative humidity on flowability

Trials 3.5–3.10 were conducted after drying and moisturizing the samples for 72 h in the climate chamber to remove any effect of sample history and ensure even moisturization throughout the samples. These results can be compared with those from trial 1.1, where powders were tested immediately after drying (Figure 7). Both the basic flowability energy and the specific energy increase significantly with relative humidity, while the effect of temperature is negligible in the range investigated.

When powders particles adsorb moisture on their surface, the contact points are favorable locations for the condensation of liquid bridges. Previous studies have identified such liquid bridges as critical to the behavior of moisturized powders (Coelho and Harnby 1978) and speculate that liquid bridges affect the flow properties of metallic powders (Stanford and DellaCorte 2006). When relative humidity increases, a higher volume of water is present in the powder, either adsorbed on the surface of the particles or condensed at the liquid bridges (Equations (7) and (8)). The increase in the energy necessary to break these liquid bridges can be seen as an increase in the work done when moving the powder, in this case, both the basic flowability energy and the specific energy (Figure 7). This is consistent with published literature (Stanford and DellaCorte 2006; Crouter and Briens...
2014; Lu et al. 2017; Cordova, Campos, and Tinga 2017b; Lefebvre et al. 2020).

However, some studies that use the FT4 powder rheometer show no variation in the basic flowability energy with humidity (Lefebvre, Dai, et al. 2019) and others show that the basic flowability energy decreases with increasing humidity (Lu et al. 2017). This may be explained by differences in the experimental procedure. In the current study, powders were placed inside the test vessel at ambient humidity, which means that all samples of a particular powder have very similar bulk densities when they are first loaded into the test vessel (Table 4, trials from 3.1 to 3.4). In other studies, the powders were moisturized and then placed into the vessel. In that case, the density of the powders will be sensitive to the humidity being tested, as wet powders have a lower apparent density (Table 4).

3.3. Effect of powder characteristics on flowability in humid conditions

All powders show a significant increase in both basic flowability energy and specific energy as relative humidity increases (Figure 8). For powders A and B, this trend is linear across the entire range studied, up to 80% relative humidity. Powder C also shows a strong increase in both metrics when increasing relative humidity from 0% to 40%, but no increase between 40% and 80%. Powder D shows a linear increase in the basic flowability energy, but a non-linear trend in the specific energy, with little difference between 0% and 40% relative humidity, before a large increase to 80%. Compared to dry conditions, the increase in the recorded energies for a relative humidity of 80% is very high for all powders (Figure 9).

Powder B, which has the finest particle size and therefore the higher number of contact points per unit volume shows an increment of energy per contact point smaller than any other powder (Figure 10). As the particle size of the powders increases, there is a higher increase in dissipated energy per contact point. The downward energy increment measured for powder C, which is water atomized, deviates from this trend showing a higher increase than powder D, which has the coarsest particle size fraction of all the powders studied (Figure 10(a)). Another deviation is observed in the increase in downwards energy per contact point in powder D, which at a relative humidity of 40% records an energy increment lower than powder B and C (Figure 10(b)).

The energy necessary to break a liquid bridge between two particles, $W$, depends on the liquid bridge volume (Equation (9)). For a pair of particles, this volume increases with the relative humidity and particle size (Equations (7) and (8)), which is reflected in the measured data (Figure 10). The fact that powder C was water atomized may explain the unexpectedly high increase in work done per contact point due to humidity. It is well known that water atomized powders are less regular in shape than gas atomized powders and are more prone to mechanical interlocking. Interlocking is most significant when the powder flows in a confined state and particles are forced together (downwards impeller motion).

The higher specific energy of powder B compared to powder A (Figure 8) is attributable to different particle size distributions. The lower energy increments per contact point expected in the (finer) powder B (Equations (8) and (9), Figure 10) are compensated for by the fact that it can hold more water: in a finer powder, more water can be stored in the adsorbed film or form liquid bridges due to a higher specific surface area (Lefebvre, Dai, et al. 2019) and in liquid bridges due to the higher number of contact points per unit volume (Equations (10–12), Table 2).

Conversely, the fact that the coarser powders (C and D) give much higher increases in energy in both upwards and downwards impeller directions than finer powders (A and B) implies that liquid bridging is more significant in coarser powders. This suggests that the greater volume of each liquid bridge, which increases the work required to break each one is more significant than the decrease in the
number of contact points found in the coarser powders. It is plausible that the large surface area in the finer powders consumes water by the formation of thin films, such that there is less water available to form liquid bridges (Lefebvre, Dai, et al. 2019). This makes liquid bridges less common than expected in fine powders and reduces the total work required to overcome them. When comparing powders A and B, this consumption of water as thin films was not significant enough to alter the trend between particle size and overall cohesion, so the coarser powder flowed better. However, changing the particle size even more (i.e., considering powders C and D) did enable a significantly greater proportion of water to form liquid bridges and strengthen cohesion.

Powder C exhibits higher energies (Figure 8), despite having a lower bulk density (Table 2). The water atomized particles have a more irregular shape and a rougher surface texture (Pinkerton and Li 2005; Tobar et al. 2016), which promotes particle interlocking. This seems to be clear from the basic flowability energy, which is significantly higher for this powder than for the other (gas atomized) samples (Figure 8). Powder C is also very sensitive to moisture, especially at lower humidity (Figure 10). As moisture is expected to enhance the adhesion between neighboring particles, this can consolidate their bonding at their contact points and might enhance interlocking. This could explain the strong effect on work done by the impeller at 40% humidity. However, since irregular powders have fewer contact points per unit volume than spherical ones, the number of sites for liquid bridging is lower in powder C. This can also explain the lack of any effect above 40% humidity if the contact points are already saturated by liquid bridges at 40% humidity. Any further increases in humidity would only form slightly larger liquid bridges, not form new ones.

Powder D is the least sensitive to humidity when considering the basic flowability energy (Figure 8). This could be due to the larger particle size, which leads to a lower specific surface area and a smaller number of contact points per unit volume (Tables 1 and 2). This means that adding moisture has less effect on the powder ensemble, but the spherical shape means that there is still a large coordination number. This has the result that the effect of adding moisture does not saturate as it does in powder C. Gravitational forces are also more relevant with powder D, due to the
larger particle size. This may also lead to cohesive forces being partially overcome by gravity, reducing the work required to cause rearrangement during the flowability tests.

### 3.4. Shear cell tests

The results from the shear cell test do not show any clear trend, such as those observed in the data from the flowability tests (Figure 11 cf. Figures 8–10). All powders show some increase in the unconfined yield strength, but only powder A has a change that seems to be significant. None of the increases is monotonic. The major principal stress is approximately constant for all powders and shows no overall trend in any case. The shear cell test is performed on static powder and the point at which movement starts is the end of the test. Furthermore, the powders are subject to significant compressive load, which can increase the number of contact points per unit volume (Equation (11)). This contrasts with the results of the stability and variable flow rate test (Figure 8), where powders are tested in the dynamic condition. It is conceivable that these differences affect the relationship between powder behavior and humidity. For example, friction may play a much more significant role in the shear cell test and could dominate the effect of humidity. Another possible explanation is that dynamic rearrangement of powder, such as in the stability and variable flow rate test, allows the continuous formation of liquid bridges during testing, the coordinated sharing of powder layers may not. However, this effect must be investigated further using experiments and suitable modeling to understand the nature of the behavior.

The current findings are not in full agreement with published findings, where for hydrophilic pharmaceutical powders an increase of relative humidity causes a significantly higher unconfined yield strength at RH = 60%, but hydrophobic powders showed no dependence (Karde and Ghoroi 2015). Metal powders are hydrophilic, but their behavior did not show any dependence on humidity. Similarly, aluminum powders show a moderate increase in the unconfined yield strength between RH = 20%, and RH = 50%, while an increase of the major consolidation stress is shown between RH = 50%, and RH = 80%, (Stevens et al. 2009). However, a direct comparison between these two articles and the current study is not necessarily fair or useful, as all use different materials that may react differently to moisture. The powder considered in the current study may show similar behavior to those in Stevens et al. at RH > 80%. This is suggested by the predicted change in the liquid bridge water volume, which, is very significant above RH = 80% (Figure 3). However, testing was not possible above RH = 80%, as the electronic components of the rheometer are not designed for such conditions.

### 3.5. Powder water content analysis

Karl Fischer titration results of powders A and B indicate that all the powder samples contained water, confirming that metal powders adsorb a detectable amount of moisture from the air (Table 5). Powder B adsorbed more moisture than powder A, which is consistent with its higher specific surface area, similar chemistry, particle shape, and surface condition.

In addition to this, it is possible to compare the measured water content with the maximum theoretical water content in powders A and B at a relative humidity of 80% (Table 3, trials 3.1, 3.6). This can be obtained by adapting the

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**Table 5.** The water content of powder measured using Karl Fischer titration, expressed in units of milliliters of water per kilogram of powder; maximum estimated water content calculated using Equation (15).

| Trial T/°C | RH (%) | Powder A | Powder B | Powder A | Powder B |
|-----------|--------|----------|----------|----------|----------|
| 3.1       | 10     | 0.13     | 0.16     | 93       | 132      |
| 3.6       | 30     | 0.10     | 0.13     | 96       | 137      |

**Figure 11.** (a) Unconfined yield strength and (b) major principal stress in the function of relative humidity for all powders. All data were recorded at a temperature of 30 °C.
equations for the adsorbed water volume on the surface of the particles (Equation (7)) and the condensed volume for each water bridge (Equation (8)), as shown in Equation (15).

\[ V = n_V V_{\text{ads}} + N_V V_{\text{bridge}} \]  

(15)

The measured water content is significantly lower than the maximum theoretical water content (Table 5). This implies that liquid bridges were not present at each contact point, which is an assumption of Equation (15). If this is the reason for the discrepancy, liquid bridges are present at approximately 0.1% of the contact points. Another possible reason may be that the method did not measure all the water from the powder. While all the water was driven off the powder when it was heated to 250°C, not all of the water may have been carried to the test solution by the carrier gas. Also, some of the water may have remained within the gas as it bubbled through the test solution and did not react with the reagent. Other authors suggest that the Karl Fischer method contains inherent sources of error (Lefebvre et al. 2020; Mellin et al. 2020). Mellin et al. suggest that at least five vials of powder are used for each measurement (Mellin et al. 2020). However, as the Karl Fischer titration is a destructive analysis, this was not possible in our study due to the limited size of our samples and the limited availability of the climate chamber and the titration equipment. Indeed, only powders A and B could be tested within the limits of the current study.

When comparing the different trials, both powder A and powder B showed a lower moisture content for the higher relative humidity (Table 5). This is contradictory to expectations and the flowability data for those trials: both powder A and B worsen significantly their flowability with higher relative humidity (Figure 8). It is believed that this is an artifact in the measurement, but no specific source error was identified. However, all vials needed to be exposed to the laboratory atmosphere, outside the climate chamber, for a short time to be sealed. If the empty vials from trial 3.1 picked up moisture, or if the vials from trial 3.6 containing powder lost moisture, it could lead to the results in Table 5. Further investigation is required to measure the moisture content in the powders accurately, possibly identifying or developing a new test method.

4. Conclusions

The flow behavior of four steel powders at precise conditions of relative humidity and temperature. To reduce the interference of the external atmosphere, a powder rheometer was inserted in a climate chamber and operated remotely. Powders were also dried and equilibrated for sufficient time to avoid memory effects. Moisture content was measured for two powders using Karl Fischer titration.

- Water was detected in both powders tested at low relative humidity (40%). Finer powders seemed to pick up more moisture.
- The measurement of moisture in the powder is not consistent with the exposure to the various conditions. Additional investigations should be conducted to understand the effect of relative humidity on the powder moisture adsorption, as well as which measurements technique is more indicated to determine the water content in metallic powders.
- Different temperatures did not influence the powder flow in the range investigated (10–30°C).
- In stability and variable flow rate tests, relative humidity impacts on both basic flowability energy and specific energy. The basic flowability energy was shown to increase between 20 and 60%, while the specific energy was between 40 and 80% at a relative humidity of 80%, compared to powders that were dried and tested immediately.
- In the shear cell tests, relative humidity was not found to be significant in the range investigated (40-80% RH). The unconfined yield strength does not show a clear dependence when increasing the relative humidity and the major principal stress shows no dependence at all. This is because the shear cell is performed on static powders, which is different from the stability and variable flow rate test which is conducted on dynamic powders. Shearing does not promote the continuous formation of liquid bridging through powder mixing.

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Figure 12. Liquid bridge geometry.

### Appendix A

The radius $R_0$ can be derived from geometrical considerations in Figure 12, which represent a simplified scheme of the liquid bridge between two particles, where $x$ represents the angle between the liquid bridge meridional curvature radius $R_m$ and the segment CD, $\beta$ indicates the half-filling angle between the segment AB and AE, and $\theta$ the contact angle. First, it can be helpful to express the angles $x$ and $\beta$ in the function of more meaningful parameters, such as $r_p$, $R_m$, $L$ and $\theta$ (Equation (16)). The terms of the system in Equation (16) can be rearranged as shown in Equation (17). The second term of Equation (17) can be expressed as a quadratic expression for the $\cos(\beta)$ (Equation (18)) and solved (Equation (19)), in which only the physically meaningful expression for $\beta$ is used. $x$ can be obtained by substituting the solution of Equation (19) into Equation (17).

$R_0$ can ultimately be obtained by substituting $x$ and $\beta$ obtained in Equations (19) and (17) into Equation (20). The final equation is (21), where $a$, $b$ and $c$ were previously obtained in (18).

$$\begin{align*}
x + \beta + \theta &= \frac{\pi}{2} \\
AB &= r_p + \frac{L}{2} = r_p \cos(\beta) + R_m \sin(x)
\end{align*}$$

$$\begin{align*}
x &= \frac{\pi}{2} - \theta - \beta \\
r_p + \frac{L}{2} + \cos(\beta)[R_m \cos(\theta) + r_p] &= R_m \sin(\theta) \sqrt{1 - [\cos(\beta)]^2}
\end{align*}$$

$$\begin{align*}
a[\cos(\beta)]^2 + b \cos(\beta) + c &= 0 \\
&= [R_m \cos(\theta) + r_p]^2 + [R_m \sin(\theta)]^2 \\
b &= 2r_p^2 + 2r_p R_m \cos(\theta) + r_p L + R_m L \cos(\theta) \\
c &= r_p^2 + r_p L + \frac{1}{4} L^2 - [R_m \sin(\theta)]^2
\end{align*}$$

$$\begin{align*}
\beta &= \cos^{-1}\left(\frac{b + \sqrt{b^2 - 4ac}}{2a}\right) \\
R_0 &= r_p \sin(\beta) - R_m [1 - \cos(x)]
\end{align*}$$

$$R_0 = r_p \sin\left[\cos^{-1}\left(\frac{b + \sqrt{b^2 - 4ac}}{2a}\right)\right] - R_m \left[1 - \cos\left(\frac{\pi}{2} - \theta - \cos^{-1}\left(\frac{b + \sqrt{b^2 - 4ac}}{2a}\right)\right)\right]$$