A feasibility study to investigate caking in washing powder formulations using a Freeman FT4 powder rheometer

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Abstract – Because of legislation and environmental concerns, washing powder manufacturers have phased out phosphate builders in favour of substitutes such as sodium carbonate. This has meant that the new formulations have a greater tendency towards unwanted agglomeration (caking), based on moisture uptake and migration. This study examines the feasibility of using a Freeman FT4 powder rheometer to examine the effect of moisture migration, using the Basic Flow Energy (BFE) value to compare formulations of sodium carbonate content 27-37% and sodium sulphate content 10-20% by mass after 7 days exposure to 80% relative humidity at 20°C. The results showed that 31% and 33% sodium carbonate formulations were the most resistant to caking, with 27% and 37% being the most susceptible under the test conditions. Using the method of Brockbank et al. (2015), the FT4 was also used to detect the presence of a hard crust; under the test conditions, no hard crust was found. However, the presence of soft caking was detected in the force-height profile, showing a less abrupt transition.

1.   Introduction

Eutrophication, where algal blooms de-oxygenate waterways and lakes, is caused by high levels of phosphates, with detergent powders being a major source. In order to reduce this, recent European legislation has banned any significant use of phosphates in these formulations (EU, 2004 and 2012; De Madariaga et al., 2009). This has led to a dramatic change in washing powder formulations, with sodium carbonate being the cheapest and most abundant alternative, performing the function known as a *builder*, which reduces the effect of magnesium and calcium ions in hard water. However, sodium carbonate is present in an amorphous form which has a higher affinity for moisture compared to crystalline material, and cakes very easily. This means that existing powder processing systems that were

designed to handle phosphate-based systems may need modifying to prevent powder caking and that more rigorous testing systems are required to achieve this.

The testing methods for bulk powder strength are well-established and are based on initial designs by Jenike (Schwedes, 2003). However, many of these are used for the design of silos and require a skilful operator to obtain reliable data, making them less suitable for use in industry. In measuring caking there is also the issue of replicating the interaction between the powder and the moisture in the air to produce a relevant result. The uniaxial tester is usually chosen as it is relatively easy to replicate results, particularly for comparative studies, and there is scope for using a porous system to allow a flow of humid air through the powder (Röck et al., 2006; Wegl et al, 2006; Calvert et al, 2013; Thakur et al., 2014). With these systems, caking is quantified as the strength of the resulting agglomerate formed. However, where caking is present only as a crust or as a weak cake, this approach may not be appropriate.

Another approach is to examine how individual particles bond to each other under humid conditions, with an emphasis on mechanisms rather than quantifying cake strength. This can be done either using macroscopic systems where large particles are contacted under conditions that favour caking, and then pulled apart (Wahl et al., 2008), or by using Atomic Force Microscopy (AFM) to examine changes in particle properties (Prime et al., 2011a&b; Murieta-Pazos et al., 2012; Leaper and Prime, 2013) or particle-particle contact points (Leaper et al., 2012). Clearly this approach needs to be combined with bulk measurements to take account of statistical variation.

Often caking occurs in larger containers, where the poor heat transfer properties of the system can create significant temperature gradients. This provides complex moisture concentration gradients both within the powder and the interstitial air which can drive moisture migration caking, as the surface temperature of the container is cycled throughout the day and night and causes the formation of interparticle liquid bridges, which then solidify. With crucial parameters obtained experimentally, predictive models can be formulated to determine zones within the container where caking is likely to occur (Christakis et al., 2004, 2006; Leaper et al., 2002, 2004). These have shown that caking is initiated in a relatively thin zone close to the surface of a bulk solid, even when it is sealed in a container, with the central portion usually unaffected; this is consistent with experimental studies (Leaper et al., 2002).

The powder examined in this study is usually packed into boxes of 0.5-1.5 litre, so it is unlikely to experience a significant load and therefore surface caking due to interaction with moisture is the most likely mechanism. Previous studies showed that the contact of amorphous sodium carbonate with moisture rapidly caused hard caking (Leaper et al., 2012). This study examined the feasibility of using a Freeman FT4 rheometer to examine crusting caking in systems with a low consolidation.

The Freeman FT4 dynamic test system consists of a twisted blade that rotates first downwards and then upwards through a column of powder, with the resistance over the distance covered used to calculate the energy required to deform the powder, as shown in Figure 1; this is called the Basic Flow Energy (BFE) and can be used to compare a new powder against the behaviour of a standard powder (Freeman, 2007; Leturia et al, 2014); it is usually within the range of 500-5000mJ. The test has often been performed in combination with a shear cell test using the same equipment. Conventionally a full dynamic test consists of 11 cycles where the blade tip rotates at 100 mm/s for 8 cycles and then decreases to 70, 40 and 10 mm/s for the final three cycles.


Direction of
movement downwards
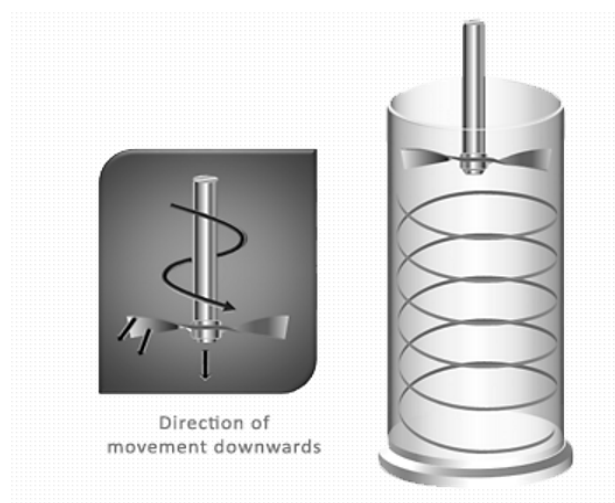
Figure 1: **The basic principle of the Freeman FT4 powder rheometer (Freeman, 2007)**

Powders which show a strong tendency to de-agglomerate show a decrease in BFE with successive cycles, along with a reduction in the rate of decrease, with the reverse behaviour shown by powders that tend to agglomerate or segregate; the ratio of the BFE in cycle 1 to cycle 7 is defined as the *stability* of the powder. This is shown as a schematic plot in Figure 2.
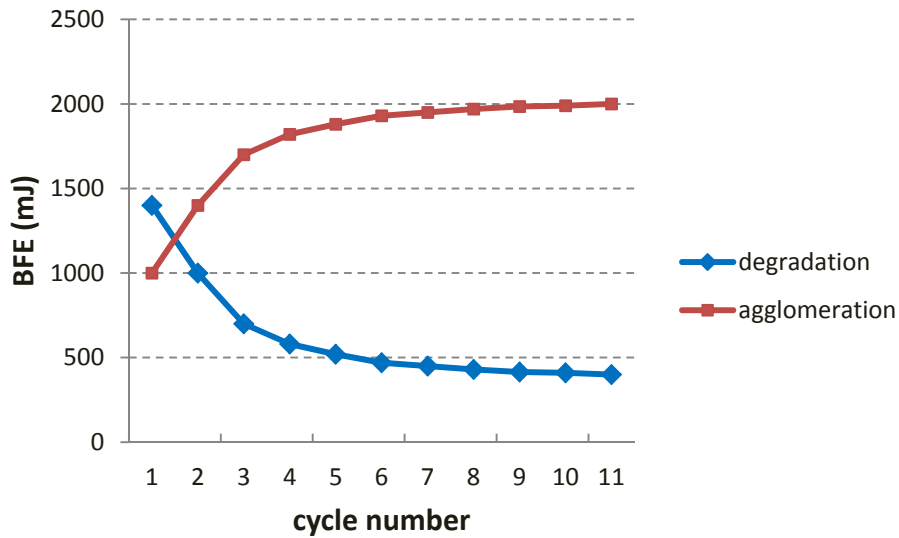
Figure 2: **Repeated Basic Flowability Energy (BFE) tests on powders that degrade and agglomerate with successive cycles.**

If the stability value is below 0.9, this indicates a significant tendency for the powder to de-agglomerate. The presence of surface crusting could also cause this result as the caked material initially presents significant resistance to the blade and then disperses throughout the powder with repeated cycles, reducing resistance each time, as shown in Figure 3.
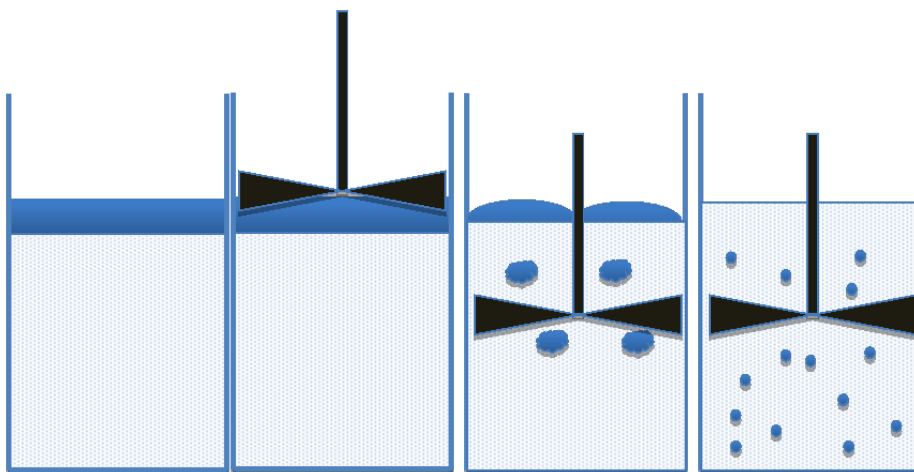
Figure 3: Schematic diagram illustrating how repeated testing disperses the crusting, reducing the overall BFE of the powder sample.

Using this methodology, this study aimed to measure the de-agglomeration of caked material that had been exposed to 80% relative humidity at 20°C, with the expectation that only the top layer had been caked. The number of cycles was increased to 25 with a constant tip speed of 100 mm/s, enabling any subsequent degradation of the primary particles to be detected. In addition, the Specific Energy (SE) was also measured; this has been shown to be closely related to powder behaviour in low stress environments such as filling operations and will give a good indication of the increase in cohesiveness. The value is obtained from the average of the resistance to the upward motion of the rotor on cycles 6 and 7. Graphs of torque against bed depth were also examined for characteristics that would indicate the formation of any hard cake.

2   Materials and Method

2.1   Test Materials

The test materials were ideal detergent granular formulations where 47% by mass of the powder consisted of a combination of sodium carbonate (particle density 2540 kgm^{-3}) and sodium sulphate (particle density 2660 kgm^{-3}). The remaining ingredients were mostly surfactants and sodium silicate. Table 1 summarises the combinations used in the study.

% Sodium Carbonate by mass	% Sodium Sulphate by mass
27	20.52
31	16.52
33	14.52
37	10.52

Table 1:   Formulation of test samples by mass.

Figure 4 shows the particle size distributions of formulations containing 27% and 37% sodium carbonate prior to the investigation, obtained by sieving. Sodium sulphate is a *filler* within the formulation, reducing the costs and enabling better flow properties. The granules were prepared according to the dry neutralisation method (Chapple, 2011; Leaper et al., 2013), where the components were combined to form granules that were non-homogeneous in nature and composed individually of varying amounts of sodium carbonate and sulphate. There is also evidence that the process produces the combined sodium carbonate-sulphate crystal, known as *Burkeite*; an SEM image of a typical granule is shown in Figure 5.
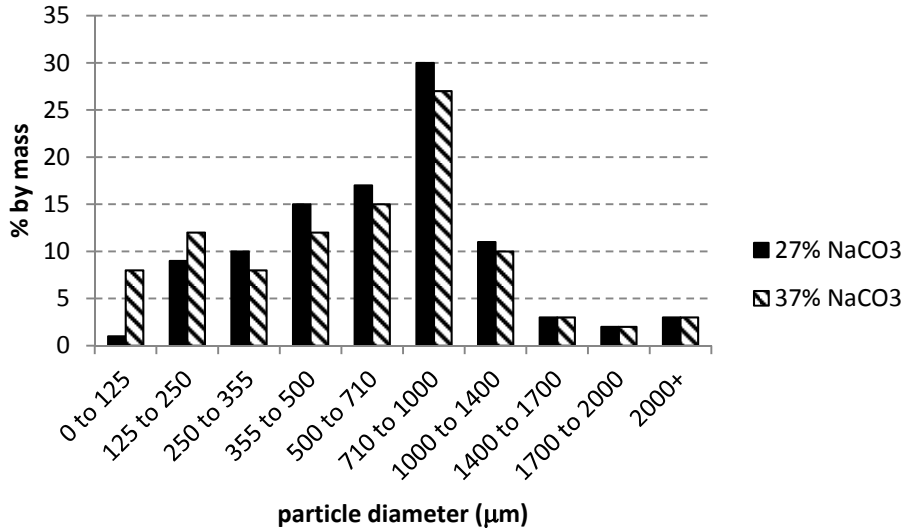
Figure 4: Particle size distributions of test formulations containing 27% sodium carbonate and 37% sodium carbonate respectively, obtained using sieves.
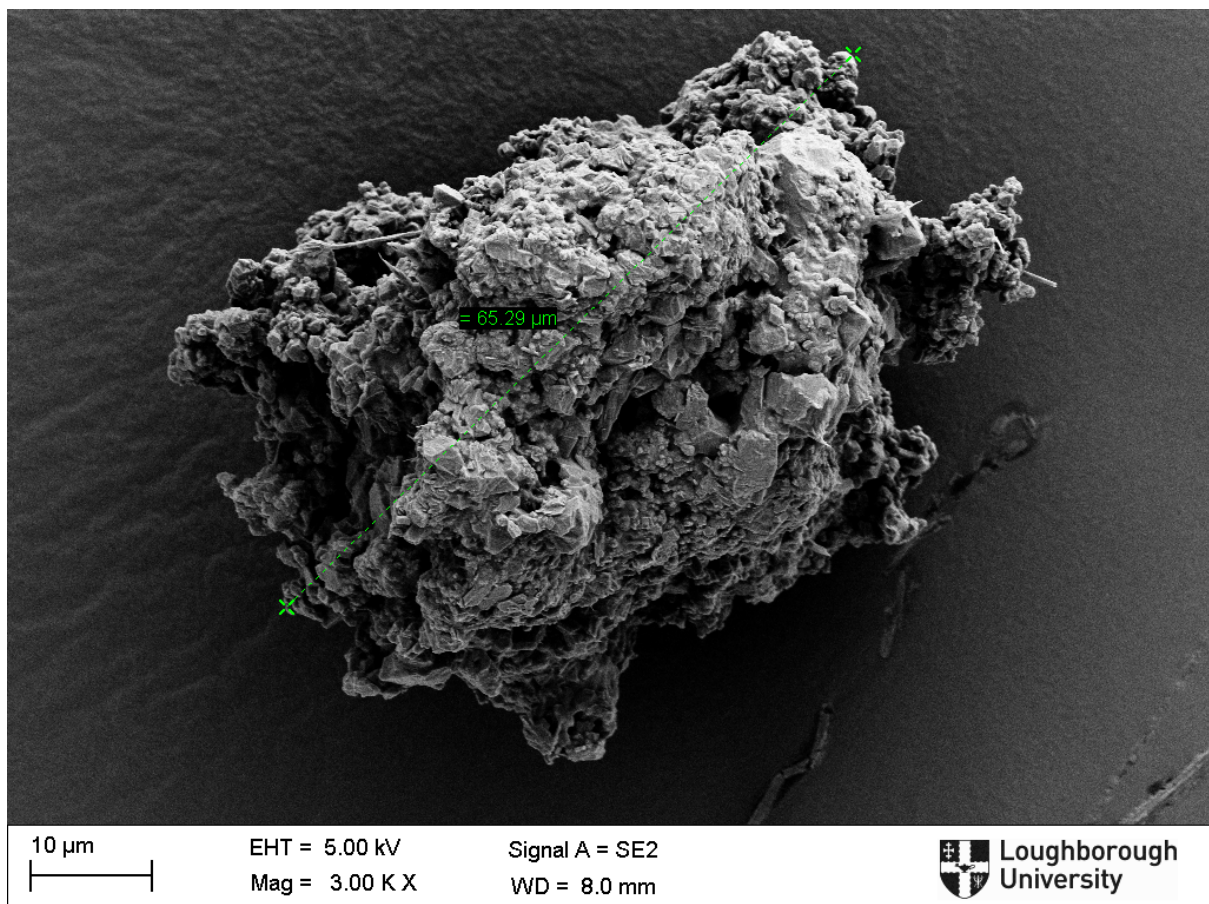
Figure 5: Scanning Electron Microscopy (SEM) image of test material of approximate diameter 70μm, showing the complex morphology.

2.2   Test Method

The BFE for the test materials was obtained using the FT4 dynamic rheometer method described by Leturia et al. (2014). This involved filling a 50mm split cell with the test powder, as shown in Figure 6. The powder was then brought to a consistent initial packing configuration by exposing it to one cycle of the rotating blade. After this, the top part of the powder was removed by sliding the top portion of the split cell as shown in Figure 6.
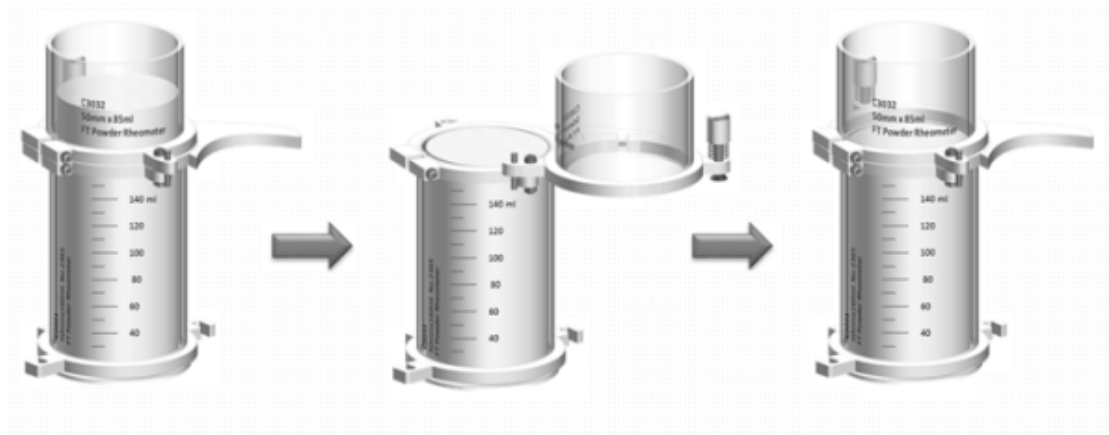
Figure 6:   How the sample is prepared using the split cell (Leturia et al, 2014).

At this point, the BFE test could be performed immediately in the case of an "initial state" test or the sample could be placed in controlled environment to assess the effect of humidity. For this study, the samples were placed in an 80% RH environment at 20°C, with the maximum exposure time being 7 days. This approach also enabled multiple samples to be exposed simultaneously. The samples were then exposed to repeated cycles with the rotating blade, with the BFE measured for each successive cycle.

In order to examine the caking profile, further experiments were conducted where the first cycle was analysed to detect a variation in the force-height profile, using the method described by Brockbank et al. (2015); a crust of hard-caked material would give a peak as shown in Figure 7, whereas a weaker cake would give a less-pronounced deviation in the plot.
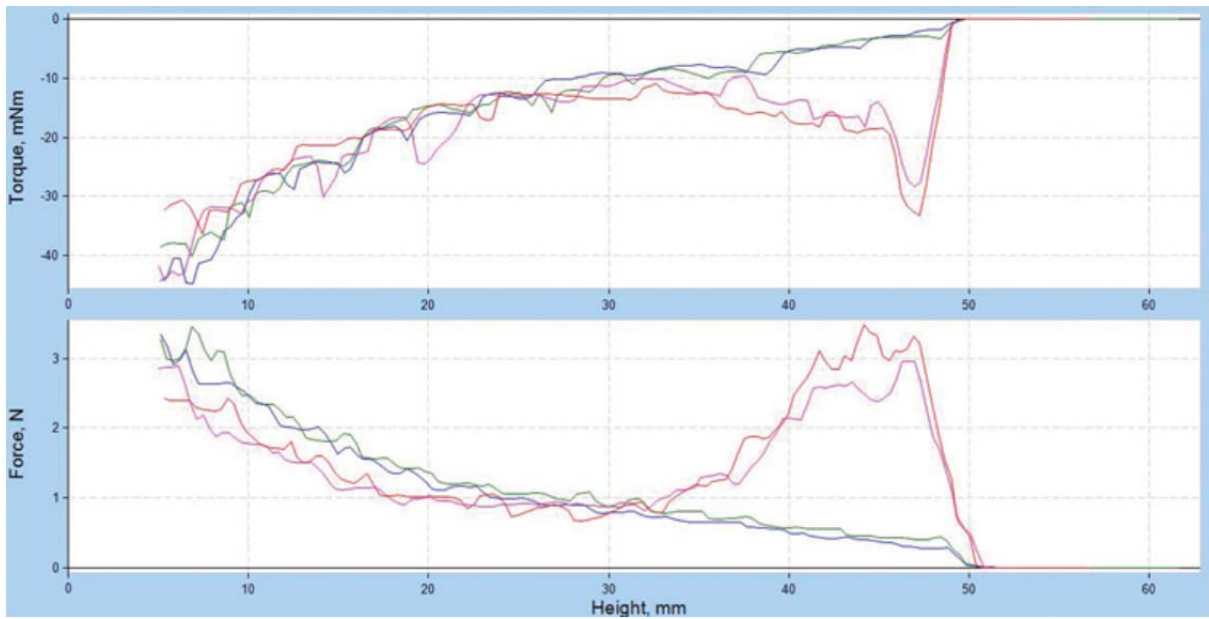
Figure 7: Profiles of materials with a hard crust, obtained by Brockbank et al. (2015). The two plots that show peaks have a crust, compared to plots without caking that have a smooth transition of force with height.

3.   Results and Discussion

Figure 8 shows the Basic Flow Energy plots of the formulations which had not been exposed to high humidity. The plots show little difference between the different formulations 31-37%, although there is evidence of some initial weak agglomeration of the powder at room conditions. The values shown are the average of three experiments for clarity. It also shows that 27% sodium carbonate/20.52% sodium sulphate shows slightly more resistance than the other formulations. It also indicates that after 25 cycles there is no degradation present.
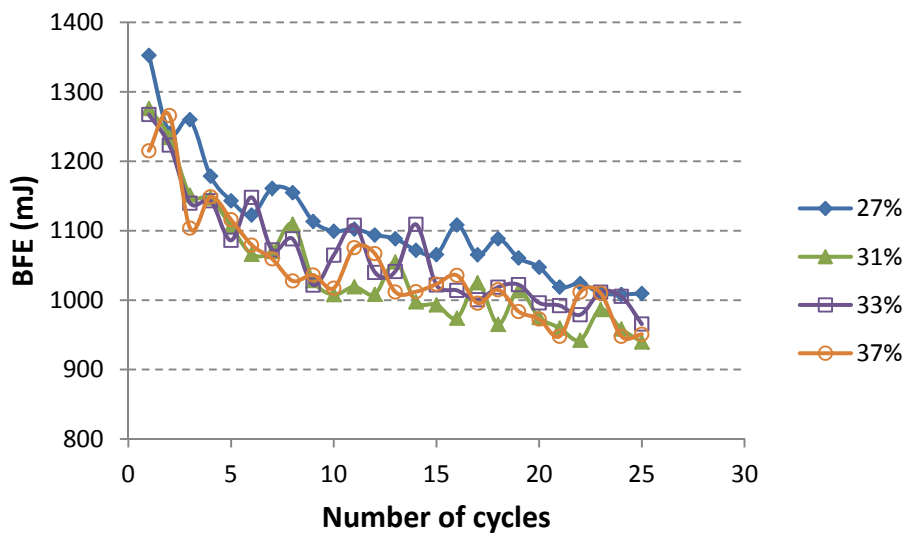

Figure 8:   BFE values for formulations containing different concentrations of sodium carbonate by mass.

In order to check how the particle size distribution was affected by the tester itself, comparisons of the particle size distributions before and after testing were made. The results for the 37% sodium carbonate/10.52% sodium sulphate formulation are shown in Figure 9, and suggest that a small proportion of particles above 1000μm are degraded, but there is some agglomeration of fine particles, particularly under 500μm. These effects should not exaggerate the effect of inter-particle bonds formed during caking.
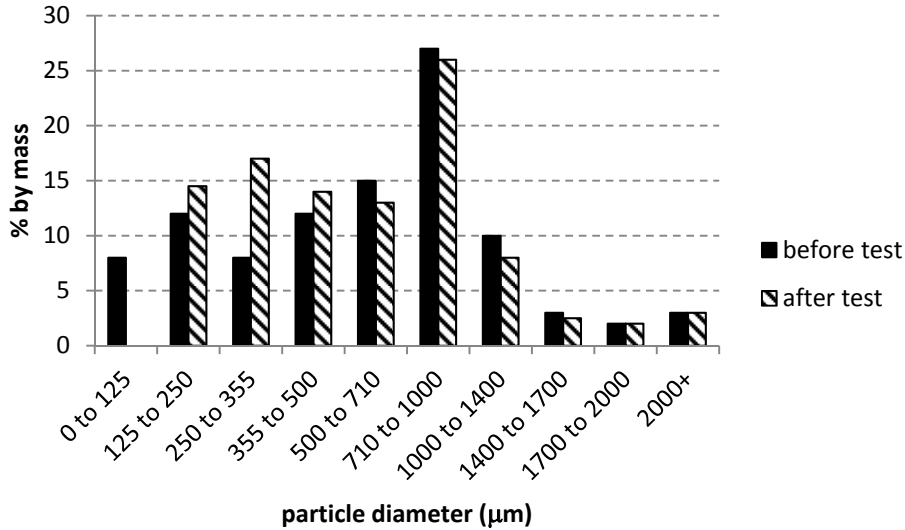
Figure 9: **Particle size distributions of test formulations containing as received 37% sodium carbonate before and after the FT4 test.**

Figure 10 compares the initial values in Figure 8 with the equivalent systems after 7 days of the split cell being exposed to 80% RH. Figure 10 shows that the formulations at 27% and 37% sodium carbonate were affected the most by exposure to high humidity, although all formulations showed a higher BFE after 7 days.
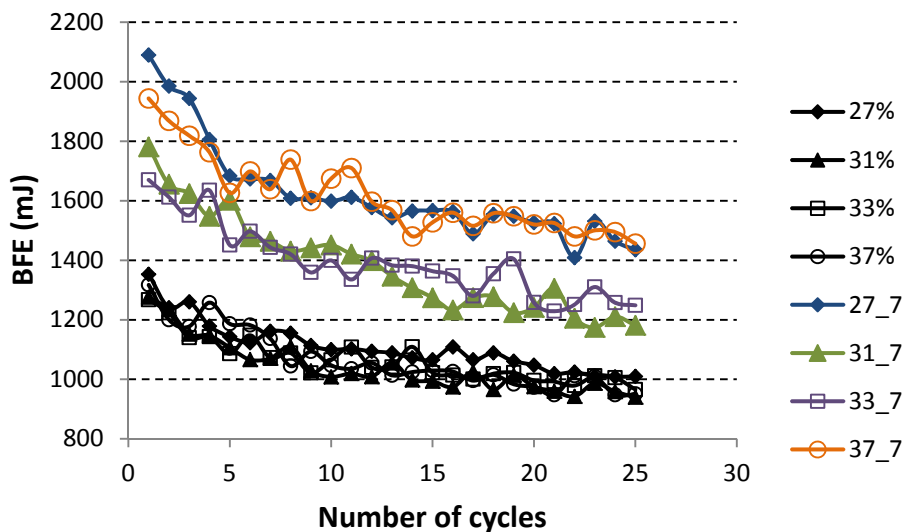

Figure 10: **A comparison of BFE values for the test formulations after 0 days and 7 days at 80% RH. The 7 day results are denoted by _7.**

Table 2 shows the value of Specific Energy before and after storage under the test conditions. Before storage at high humidity, all powders showed a SE of 3.5 to 4, which indicated a low cohesion. However, 27% and 37% sodium carbonate formulations showed a value of over 6, which is clearly associated with more cohesive behaviour; these findings are consistent with other behaviour.

% sodium carbonate by mass	Initial SE		SE after 7 days 80% RH 20°C	
	mean	s.d.	mean	s.d.
27	3.74	0.119	6.17	0.078
31	3.91	0.272	5.17	0.586
33	3.82	0.163	5.20	0.198
37	3.71	0.006	6.10	0.074

Table 2: **A summary of the Specific Energy (SE) values obtained for the test formulations after 0 days and 7 days at 80% RH and 20°C**

Having identified the formulations most vulnerable to caking under these conditions, the force-height profiles of the initial cycle were examined as described in Brockbank et al. (2015) and are shown in Figures 11 and 12 for four samples each of 27% and 37% sodium carbonate respectively.
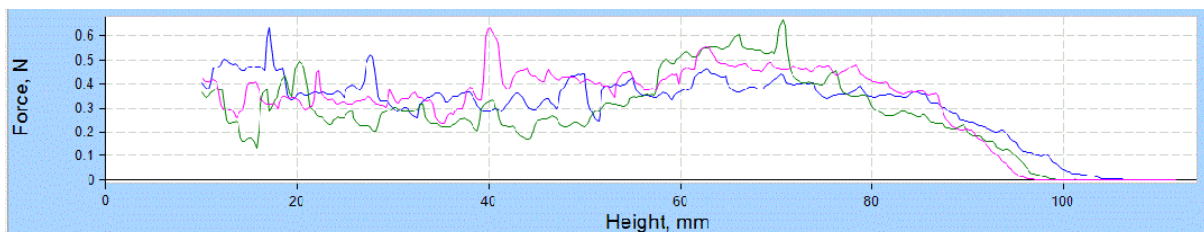
**Figure 11:** **Force-height profile of initial cycle of three samples of 27% sodium carbonate exposed to 80% RH for 7 days.**
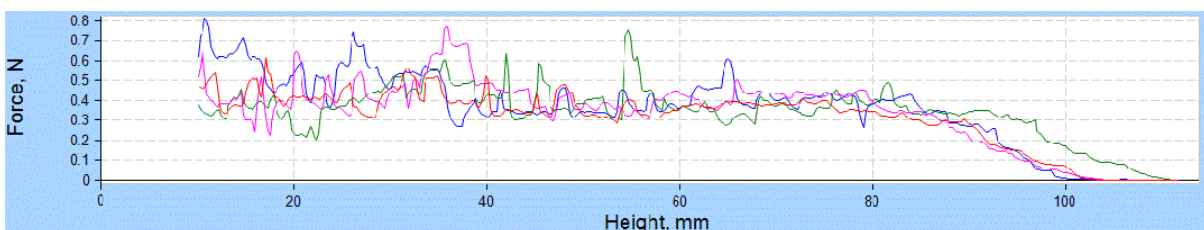
Figure 12: **Force-height profile of initial cycle of three samples of 37% sodium carbonate exposed to 80% RH for 7 days.**

Figures 11 and 12 clearly show that the strength of crust obtained at 20°C is too low to be reliably investigated using this method, despite visual evidence of a caked layer which did not flow when the test sample was inverted. The results also showed a wide variability in the formation of the crust. This shows that the interparticle bonds formed are likely to be based on either liquid or sticky visco-plastic contact points, rather than "hard" bonds that caused the more pronounced peaks shown in the work by Brockbank et al. (2015). Preliminary studies at 40°C gave a more pronounced maximum, as shown in Figure 13, but not of the sharp characteristics shown in Figure 7; this confirms that even in the most extreme cases, the caking is likely to consist of soft, plastic bonds rather than behaving as a "hard" agglomerate. It is likely that the increased humidity has caused a change in the glass transition characteristics of the particles and caused the outer layers to become plastic and sticky. This contrasts with the study by Brockbank et al. (2015) where chemical caking was the dominant mechanism.
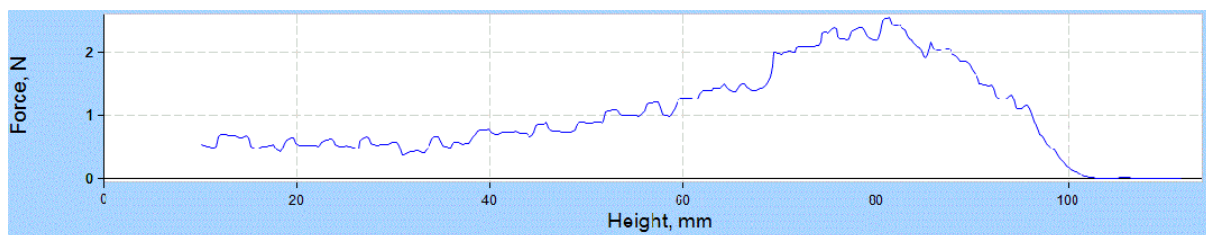
Figure 13:   **Force height profile of 33% sodium carbonate exposed to 80% RH for 7 days.**

4.   Conclusion

Washing powder formulations consisting of different proportions of sodium carbonate and sodium sulphate were assessed for resistance to caking at 20°C and 80% RH, using a Freeman FT4 powder rheometer. Basic Flow Energy (BFE) measurements showed that all formulations increased cohesiveness after 7 days, but the formulations most affected were 27% and 37% sodium carbonate; this was confirmed by visual inspection, where a caked layer allowed the test container to be inverted without loss of material, with the powder still free-flowing underneath. 31% and 33% sodium carbonate formulations showed resistance to caking and did not display this behaviour.

The method used by Brockbank et al. (2015) was used to measure the depth of caking in the affected formulations, based on the assumption that the crust was hard enough to cause a significant deflection in a force-height plot. However, this method revealed that the cake consisted of a matrix held together with sticky plastic bonds, rather than a hard agglomerate; there was an absence of a sharp peak in the force-height plot, even when a cake produced by a higher temperature was analysed.

This feasibility study has shown that the FT4 rheometer can be used for optimising complex washing powder formulations for flow and caking resistance, particularly on a comparative basis; more work needs to be done, however, to examine the effects of temperature, focussing on conditions up to 40°C and high relative humidity. The method also needs further refinement with regards to analysing the crust formation, as the "softer" cakes formed by washing powder give less-defined peaks on a force-height plot. However, this method could be an improvement on subjective soft-caking tests such as tipping the powder through sieves or penetration test, as it can also determine the depth of caking.

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