A comparison of compacting and caking behaviour of carbonate-based washing powders

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Abstract – Two types of sodium carbonate powder produced by spray drying (SD) and dry neutralisation (DN) were studied for their compaction properties using a uniaxial compression tester. A comparison was also made with Persil washing powder. Dry neutralised sodium carbonate showed a greater resistance to compression and also produced a weaker compact when compressed to 100kPa. Spray dried sodium carbonate had an absence of fine particles, but compacted easily. Differential Scanning Calorimetry (DSC) showed that both types of powder were predominantly amorphous in nature. Moisture sorption measurements showed that both powders behaved in a similar way below 50% RH. However, dry neutralised sodium carbonate had a high moisture affinity above this RH. Particle structures were also examined using Scanning Electron Microscopy (SEM), showing the heterogeneous interior of the spray-dried particles.

Introduction

The global laundry cleaning market is very important and was estimated to be worth $56.4bn in 2007. Laundry powders make up a significant proportion of this, particularly in developing markets such as the Far East. However, many powder formulations are still based on the use of phosphates which have a large environmental impact when discharged in wastewater. One major consequence of a large concentration of phosphates in the environment is to encourage algal growth which depletes oxygen levels in lakes and rivers. Many countries now legislate against the use of phosphates, with the EU aiming for an outright ban by 2015 [1-2]. The major producers of laundry powder are now examining using zeolites as an alternative. However, a stumbling block to the complete phasing out of phosphates is the limited supplies of zeolite feedstocks in some areas of the world and the residue left behind in clothes.

An alternative approach is to use sodium carbonate based powders. Although spray-dried sodium carbonate detergents already exist in some markets, they display different behaviour to conventional detergent powders and generally have a greater tendency to cake, even at moderate temperatures and relative humidities and this limits their applicability. This is particularly problematic as a typical storage time from production to consumer use for washing powders can, in some cases, be in excess of twelve months. Previous studies by the authors have demonstrated the ease with which spray-dried sodium carbonate can cake, either through the formation of inter-particle bridges [3] or by interactions with atmospheric moisture to form a sticky particle surface [4-5]. The behaviour of spray-dried particles is linked to process parameters, particularly the amorphous nature [4-8].

However, an alternative method of producing sodium carbonate powders is to use a process known as *dry neutralisation*. The exact nature of the process is detailed in a number of patents which vary according to manufacturer and application [9], but the main principle is that mobile particles of sodium carbonate are sprayed with a fine layer of surfactant acid and the neutralisation product causes particle agglomeration. The acid is typically linear alkylbenzene sulphonate. The use of a shear granulator provides control over particle size,

as well as the rate and quantity of acid. The aim is to provide a process that does not heat the product in the same way as wet granulation or spray drying.

The aim of this study is to compare the compaction and load-induced caking characteristics of sodium carbonate produced by each method. Clearly the spray-dried method allows flexibility with nozzle dimensions, feed flowrate and drying air temperature, flowrate and relative humidity. Dry neutralisation offers an option of using less water, with low energy requirements. This study will demonstrate how these different processing methods influence the characteristics of the powder. A comparison is also made with a commercial brand (Persil), bought at a supermarket.

Materials and Method

The spray-dried sodium carbonate (SD) was manufactured from a pilot scale spray drier 3m in diameter. A solution of 30% sodium carbonate was delivered to the atomiser, consisting of a twin-filled atomiser that used compressed air as the atomising gas. The solution was spray-dried using inlet and outlet temperatures of 350°C and 105°C respectively; no further ingredients were added. A generic formulation of dry-neutralised sodium carbonate (DN) was also manufactured using linear alkylbenzene sulphonate. The Persil consisted of 15% - 30% zeolite, 5% - 15% oxygen-based bleaching agents, anionic surfactants, non-ionic surfactants, and 5% of soap, polycarboxylates, phosphonates, perfume, and optical brighteners. The powders were analysed using sieves and the results are shown in Figure 1 and Table 1.

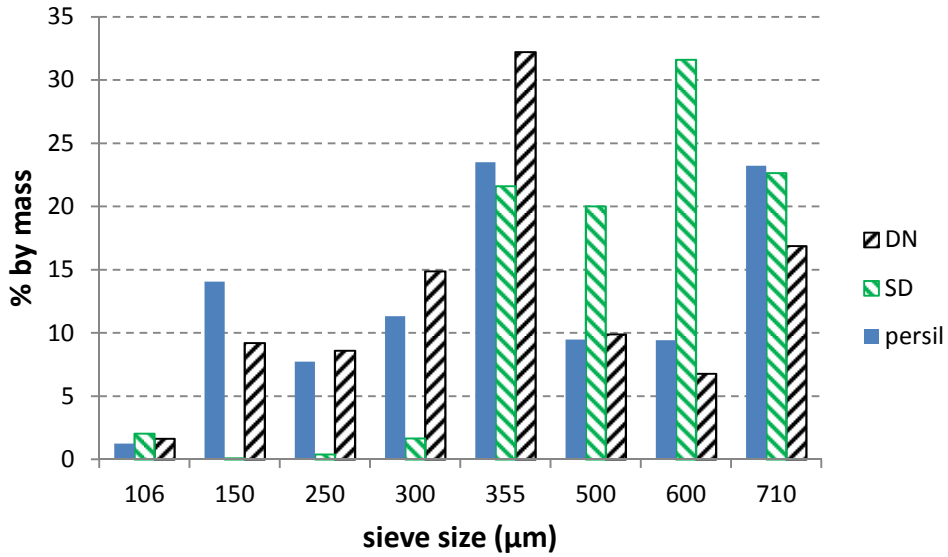


Figure 1: Sieve analysis of DN, SD and Persil powders.

	SD	DN	Persil
d_{50}	567µm	371µm	420 µm
d_{10}	357µm	190µm	210 µm
d_{90}	705µm	695µm	700 µm

Table 1: Particle sizes of spray-dried (SD), dry-neutralised (DN) sodium carbonate and Persil particles analysed by sieving.

This showed the absence of independent fine particles below 355µm in the spray dried material, suggesting the prevalence of agglomeration.

A uniaxial compression tester of diameter 100mm and height 150mm with a split die was used to examine both the compaction properties of the test powders and the tensile strength of the compacts produced. A schematic diagram of the uniaxial tester is shown in Figure 2. Initially the die is completely filled with powder and compressed at a rate of 20mm/min using a stainless steel platen. The platen is connected to an Instron 3366 testing machine which allows a careful monitoring of the platen position, rate of compression and maximum load. Once the powder is compacted to the desired load, σ, the split die is removed and the resulting compact is compressed at 20mm/min and the maximum load recorded. This equivalent to the vertical tensile strength σ_T .The uniaxial compression tester has been used effectively by a number of researchers [10-11] for comparing the flow and storage properties of different powder formulations. It has the advantage of requiring a less-skilled operator than a shear cell and is also used in industry. The test material was kept at 25℃ and 30% relative humidity overnight prior to testing.

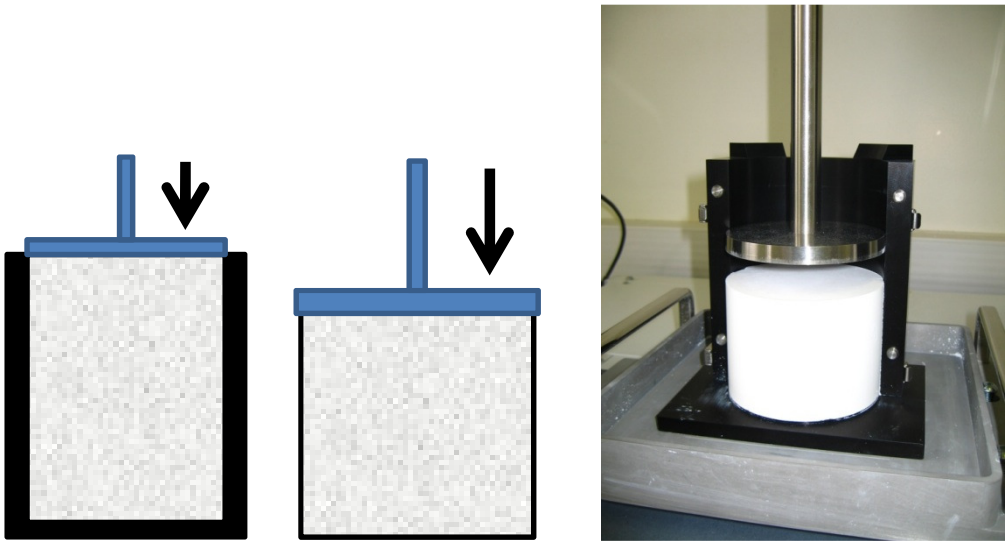


Figure 2: Uniaxial compression tester

The compaction curves are represented as scatter plots of the height ratio ε against the compressive stress, σ. The height ratio can be represented by the equation:

$$\varepsilon = \frac{h_0 - h}{h_0} \qquad (1)$$

where h_0 is the initial powder height (a constant 150mm) and h the height of the top of the compact.

The powders were compacted within the die to a range of controlled final stresses. The die was then removed each time and then the compact was then compressed until it collapsed. The resulting stress-displacement plot gave a peak stress before reducing dramatically. The peak stress was recorded as the uniaxial tensile strength σ_T.

Results and Discussion

The three main mechanisms for powder compaction are:

i) Particle re-arrangement, where gaps between particles are reduced, air leaves the structure and particles orientate themselves to minimize voidage and maximise bulk density. This usually happens in the initial stages of compaction.

ii) Plastic deformation, where the energy of compression is dissipated by particle surfaces softening and deforming irreversibly at contact points. This may lead to bonds being formed.
iii) Particle breakage, where the energy of compression causes particles to break and reduce in bulk density as in (i). This is prevalent when particles are hollow.

It is rare that a single mechanism acts in isolation. Particle hardness, elasticity and strength, influenced by temperature, relative humidity and crystallinity all contribute to the proportion of each mechanism in the compression process. This can be complicated further if the powder is a mixture.

Figure 3 shows the compaction characteristics of the powder, duplicated as a logarithmic plot in Figure 4.

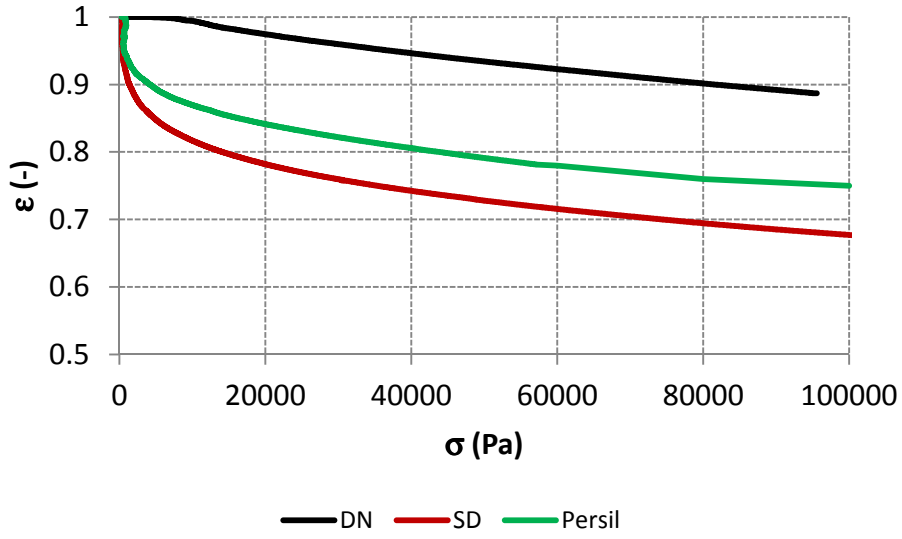


Figure 3: Compaction characteristics for DN, SD sodium carbonate and Persil powders at 20 mm/min.

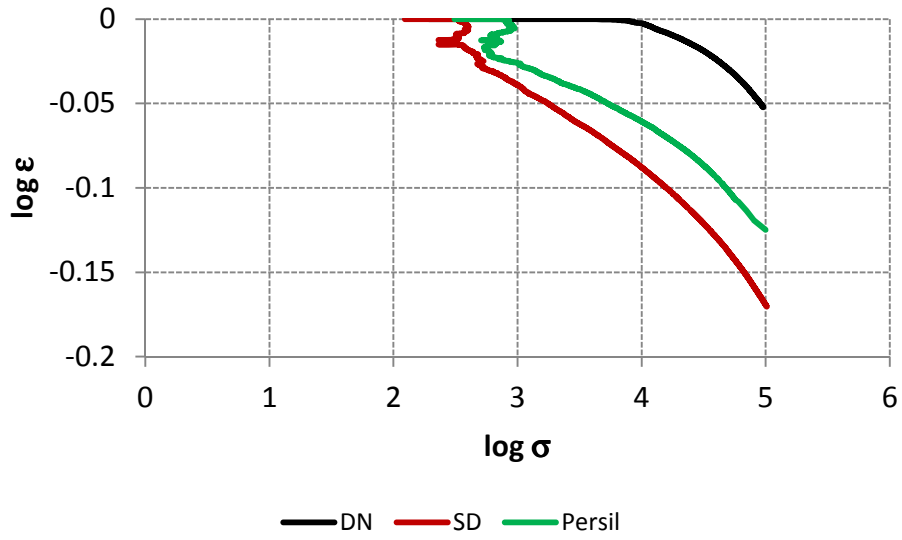


Figure 4: Compaction characteristics for DN, SD sodium carbonate and Persil powders at 20 mm/min expressed as logarithms.

Although both powders compacted by a combination of mechanisms, as shown by the non-linear nature of the logarithmic plots in Figure 4, the data show very different behaviour between the same material produced by the different methods. There is a significant reduction of bed height of over 20% for the spray-dried powder with a load of 20kPa, whereas the dry-neutralised powder has reduced by only a few percent. The two plots also show that the spray dried material follows a similar trend to the Persil, although it shows a greater tendency to compact under load. The discrepancy in behaviour between the powders is also found when comparing the uniaxial strength of compacts, as shown in Figure 5.

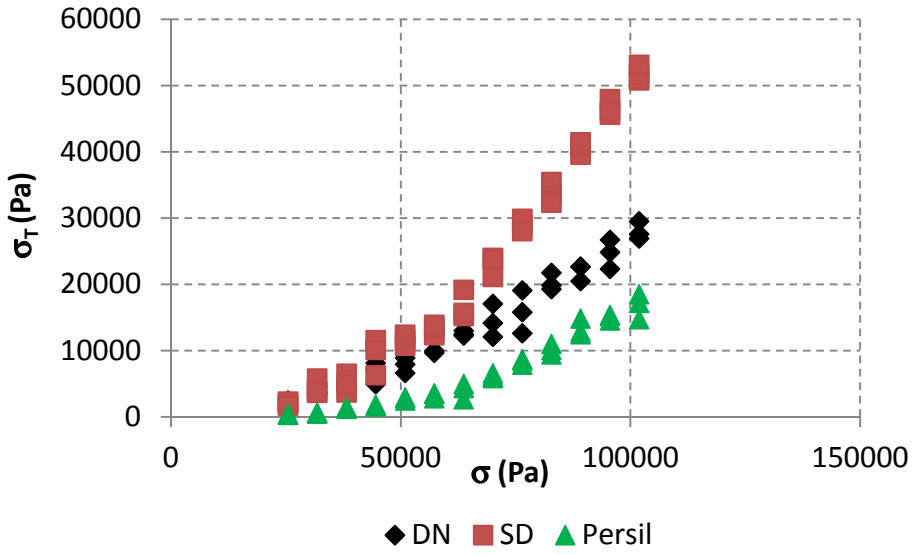


Figure 5: Comparing the uniaxial compression strength σ_T of DN and SD compacts formed over a range of compaction stresses σ.

These results show that the spray dried sodium carbonate forms significantly stronger compacts when placed under load than the dry neutralised material, showing a greater tendency to cake. Unsurprisingly, the anti-caking agents present in the commercial Persil formulation ensure that the ability to form strong compacts under load is reduced, allowing easier processing and packing. A correlation of the form:

$$\sigma_T = \alpha\sigma^{\beta} \qquad (2)$$

was obtained by plotting the data in Figure 5 on a logarithmic scale and obtaining a linear regression plot:

$$log(\sigma_T) = log\alpha + \beta log\sigma \qquad (3)$$

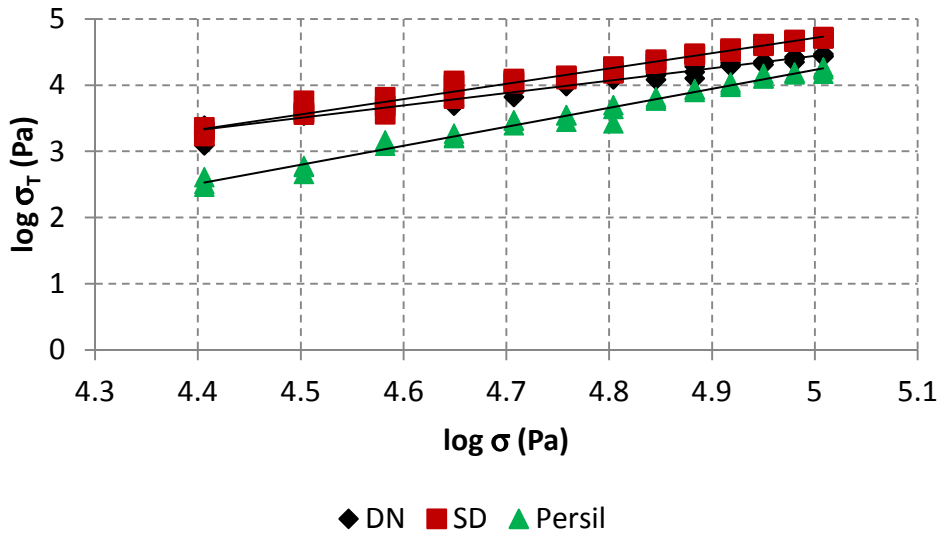


Figure 6: Comparing the uniaxial compression strength σ_T of DN and SD compacts formed over a range of compaction stresses σ (logarithmic scale).

This is shown in Figure 6 and also confirms that there is no "dog-leg" in the spray-dried data. The parameters obtained are shown in Table 2:

	DN	SD	Persil
Gradient β	1.871	2.311	2.873
Intercept logα	-4.911	-6.844	-10.132
α	1.227×10^{-5}	1.432×10^{-7}	7.379×10^{-11}
R^2	0.9664	0.976	0.9842

Table 2: Parameters obtained from Figure 9 for use in Equation (2)

An idealised system where the powder strength was only influenced by contact points between regularly arranged mono-sized spheres would have a value β=2, as the area of contact between particles has a direct effect on agglomerate strength [12] and this is reflected in the real values of β being close to 2.

There are also some differences in the force-distance curves when the unconfined compacts fail uniaxially. Figure 7 compares the unconfined stress-strain plots of compacts formed by compressing the three powders to 250N, which corresponds to a stress of 28.9kPa. Persil produces a weak compact that fails at around 500Pa, consistent with Figures 5 and 6. The dry neutralised compact immediately distorts on compaction, with a rapid increase in resistance after about 25% of its maximum strain. The spray dried compact distorts at a much smaller rate for the same increase in stress, the rate gradually increasing towards the failure value. However, both systems fail at similar values. The DN system bulk distorts considerably in all planes without the constraints of the die when a load is applied before it fails, suggesting some mobility of particles within the structure. This is not so prevalent in the SD system, where the fine particles are absent as free entities.

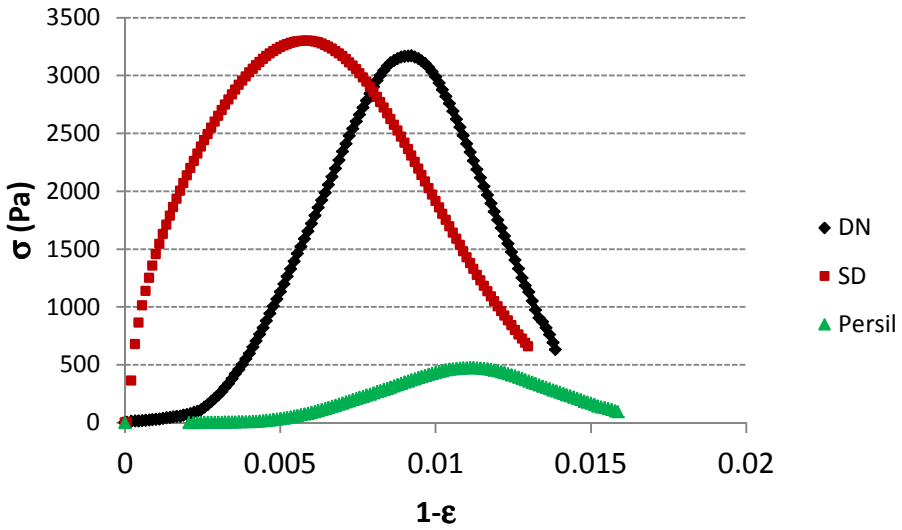
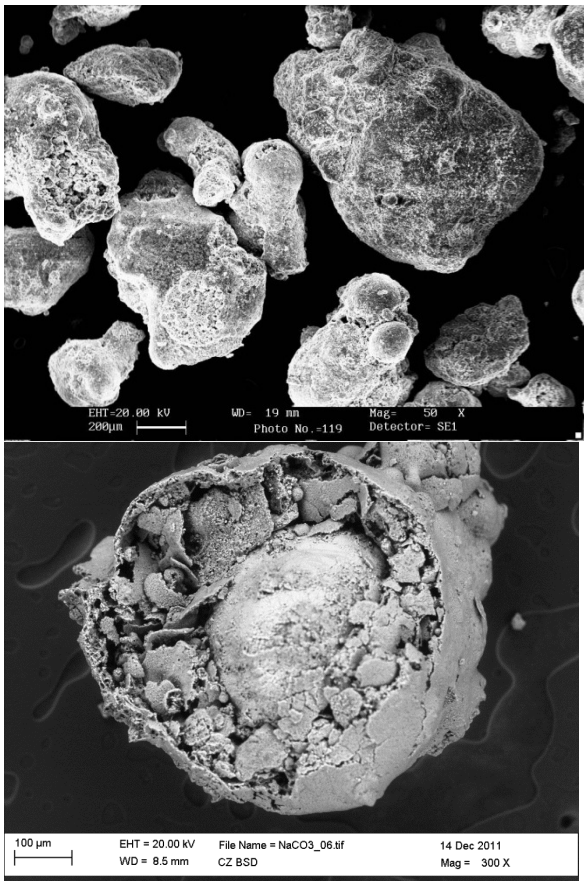


Figure 7: The unconfined uniaxial failure of samples initially compacted to 250N (28.9kPa).

Scanning Electron Micrographs of all the particles are shown in Figure 8, with DN at the top, SD in the centre and Persil at the bottom. The SD particles clearly show a heterogeneous interior and a greater fragility. DN particle are less spherical and have a wider range of particle size. The multiple ingredients of Persil are clearly shown in the complex surface profile of the particles.



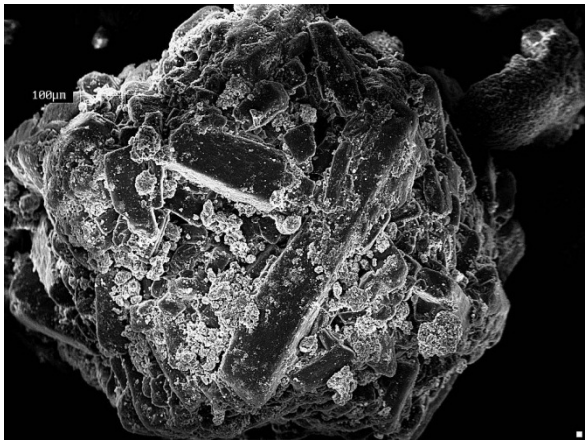


Figure 8: SEM images of Dry Neutralised (top), Spray Dread (centre) and Persil (bottom)

The crystalline nature of the two carbonate powders and their interaction with atmospheric moisture was also examined. Figure 9 shows Differential Scanning Calorimetry (DSC) plot for crystalline sodium carbonate monohydrate, anhydrous, spray dried and dry neutralised forms at a 20°C/min rise. The data clearly shows that both the SD and DN versions are predominantly amorphous, with DN showing slight crystalline tendencies.

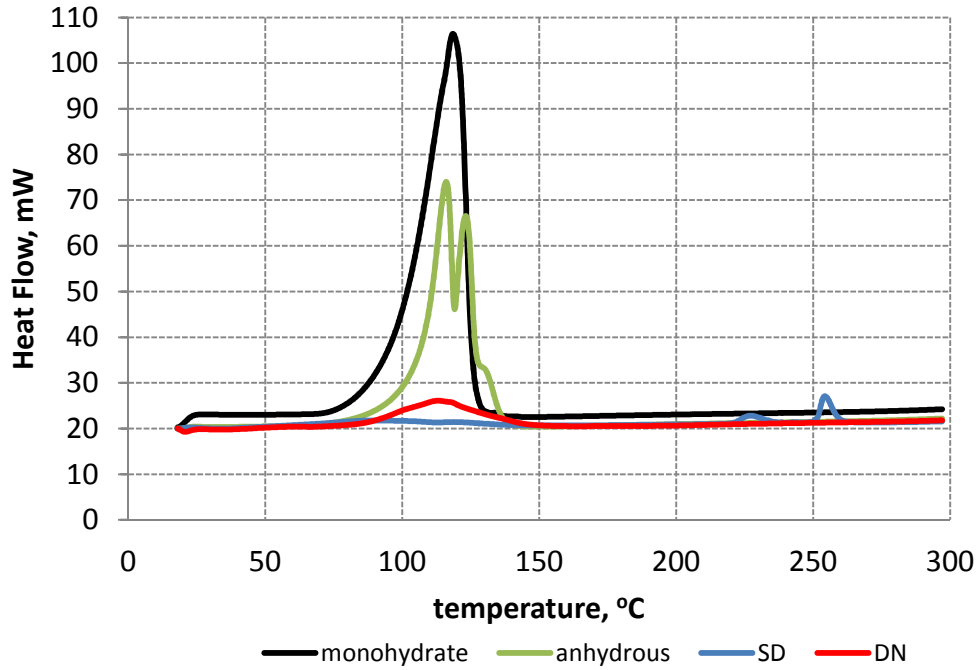


Figure 9: Differential Scanning Calorimetry (DSC) plots for sodium carbonate monohydrate, anhydrous sodium carbonate, spray-dried sodium carbonate and dry-neutralised sodium carbonate at a 20°C/min rise.

Figure 10 compares the moisture sorption curves for both types of carbonate powder, showing that at 50% relative humidity and below, both types of powder absorb atmospheric moisture to the same extent. However, the dry neutralised system has a greater capacity to

absorb moisture at higher relative humidities. This may be because of the rougher surfaces of the DN particles shown in Figure 8, or the influence of the small amount of neutralisation product. Crystalline sodium carbonate has minimal absorption of moisture below 80% relative humidity [13].

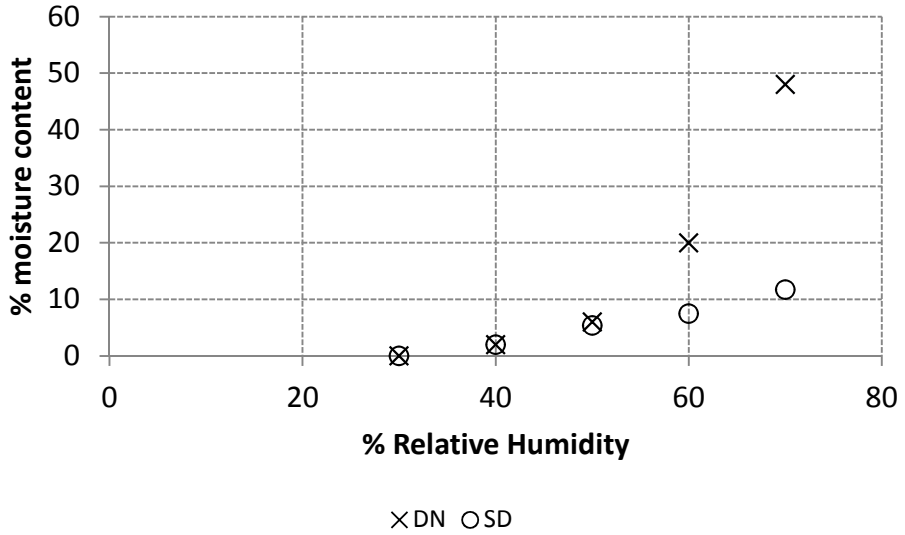


Figure 10: Moisture sorption data for spray-dried and dry-neutralised sodium carbonate at 25°C

The data shows that whilst the DN and SD powders are the same chemically, the method of producing them has a clear effect on their behaviour. Whilst using spray drying minimises the production of fine particles, the structure of each particle allows extensive compaction. As proven in previous studies [3], the surface properties of the spray-dried particles encourage particle-particle interaction, allowing the powder to have a relatively low bulk density prior to compaction. Even in the absence of high humidity, there is opportunity for consolidation and a considerable change in bulk density when the powder is compressed. However, the dry neutralised material is more difficult to compact at the test humidity. It is clear that the particle structure and strength provides a greater resistance to compaction. This is significant in terms of packaging and storage, as dry neutralised material will be less aerated and be more controllable during packaging. It will also experience less consolidation as the contents settle, reducing the risk of caking. Although dry neutralised particles were developed for use in the detergent industry, this quality may extend their application into other areas such pharmaceutical solid dosage forms.

Conclusion

The compaction characteristics of sodium carbonate particles produced by spray drying and dry neutralisation were shown to differ considerably, with DN particles being more resistant to compaction. However, at low consolidation values, the two types of carbonate powder had compacts with similar unconfined uniaxial tensile strengths. These failed in different ways, with the DN compacts showing more bulk distortion prior to failure. At low values of relative humidity, the moisture content of the two systems is virtually the same and plays no part in their different behaviour. However, a further study at high humidity would reveal to what extent the comparison changes.

High consolidation values caused the spray-dried material to form stronger compacts and this suggests that the spray-dried material should not be stored in large quantities to avoid load-induced caking. The compaction curves also suggest that dry neutralised sodium carbonate will be less aerated and be more suitable for packing systems. The moisture

sorption data indicates that precautions to eliminate moisture sorption are necessary for both powders, as they are more prone to moisture uptake than conventional crystalline sodium carbonate because of their amorphous nature.

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