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Le mottage du lactose : Compréhension des mécanismes et prévention

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**Le mottage du lactose :
compréhension des mécanismes
et prévention**

***Lactose caking: Understanding
the mechanisms as a route
to prevention***

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Lactose caking:

Understanding the mechanisms as a route to prevention

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Preface

This PhD thesis is the result of a collaboration between a company, Arla Foods Ingredients (AFI, Viby, Denmark), and two research units, namely National Institute for Agricultural Research (INRA) - Agrocampus Ouest (AO) Science and Technology of Milk and Eggs (STLO, Rennes, France) and the department of Food Science at the University of Copenhagen (UCPH, Frederiksberg, Denmark). The project is an industrial PhD funded by Innovation Fund Denmark.

Because I have had three different workplaces during the project, it has been a fantastic opportunity to meet so many highly skilled people. I would like to thank them all for being willing to share their knowledge with me.

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Thesis Outputs

Publications

Carpin M., Bertelsen H., Dalberg A., Roiland C., Risbo J., Schuck P., & Jeantet R. (2017). Impurities enhance caking in lactose powder. *Journal of Food Engineering*, 198, 91–97. <https://doi.org/10.1016/j.jfoodeng.2016.11.013>

Carpin M., Bertelsen H., Dalberg A., Bech J. K., Risbo J., Schuck P., & Jeantet R. (2017). How does particle size influence caking in lactose powder? *Journal of Food Engineering*, 209, 61–67. <https://doi.org/10.1016/j.jfoodeng.2017.04.006>

Review

Carpin M., Bertelsen H., Bech J. K., Jeantet R., Risbo J., & Schuck P. (2016). Caking of lactose: A critical review. *Trends in Food Science & Technology*, 53, 1–12. <https://doi.org/10.1016/j.tifs.2016.04.002>

Oral communication

Carpin M., Bertelsen H., Bech J. K., Jeantet R., Risbo J., & Schuck P. Combination of methods to understand the lactose caking mechanisms. IDF Dairy products concentration and drying, 11-13 April 2016, Dublin, Ireland. Elsevier sponsored prize Best Oral Presentation - Powder category.

Poster

Carpin M., Bertelsen H., Bech J. K., Jeantet R., Risbo J., & Schuck P. Combination of methods to understand the lactose caking mechanisms. Partec, 19-21 April 2016, Nuremberg, Germany.

International workshop

Carpin M., Bertelsen H., Dalberg A., Bech J. K., Risbo J., Schuck P., & Jeantet R. Influence of the process on the product parameters – Example of lactose caking. Seydlitz Engineering Course Powder Formulation: Design principles, Characterisation and Processes, 12 October 2017, Copenhagen, Denmark.

Abstract

Lactose caking: understanding the mechanisms as a route to prevention

Driven by the growth in the infant formula market, lactose production is increasing worldwide, and at the same time the requirements for the product quality are becoming stricter. Caking, or the unwanted agglomeration of lactose powder particles, is synonym of poor quality for the customers and should therefore be prevented to avoid significant economic loss. This PhD project aimed at understanding the caking mechanisms in lactose powder in order to establish means to limit caking. The process – product relationship has been in focus in order to find and control the parameters that determine the caking tendency of the product. Samples from pilot production were analyzed for different physicochemical characteristics (impurity content, moisture sorption, particle size) and caking behavior. Impurities (i.e. non-lactose components) were shown to increase moisture sorption and caking. The particle size distribution of the powder also exhibited a large effect on caking. Indeed, smaller particles were characterized by enhanced moisture sorption and stronger caking, which were explained by a larger impurity content and surface area. In addition, for a similar mean particle size, a broader distribution span led to stronger caking because of the multiplication of contact points. Analyses on the commercial powder confirmed these results and revealed the instability of the water activity during storage of the powder after drying, which was linked to caking in the lactose bags. This PhD project also addressed an essential need in the dairy industry, i.e. the development of an accelerated caking test. Samples from different production sites were discriminated in terms of caking in less than a day, using appropriate test conditions (50°C and 60% RH). A similar test implemented at all sites would highlight batches with a high caking tendency before shipment to the customers. The better understanding of the caking mechanisms provided by this PhD work enables industrials to target the critical processing steps requiring optimization to avoid caking in the finished product.

Keywords: Lactose powder, caking, production process, moisture.

Résumé

Le mottage du lactose: compréhension des mécanismes et prévention

L'augmentation de la demande en lait infantile génère une forte croissance de la production mondiale de lactose. Les exigences sur la qualité du produit s'accroissent également. La prise en masse spontanée de la poudre de lactose, appelée mottage, est donc une non-conformité pouvant s'avérer très coûteuse. Ce projet vise ainsi à comprendre les mécanismes de mottage du lactose, pour donner les moyens aux industriels de prévenir le mottage. Pour ce faire, une approche procédé – produit a été mise en œuvre, permettant d'identifier les paramètres qui déterminent la tendance au mottage de la poudre de lactose et de proposer des leviers d'action. Des poudres produites à l'échelle pilote ont été analysées pour leurs caractéristiques physico-chimiques (teneur en impuretés, isotherme de sorption et granulométrie) et soumises à des tests de mottage. Les résultats obtenus montrent le rôle déterminant des impuretés (i.e. composés autres que le lactose) et de la granulométrie dans le mottage. En effet, l'hygroscopicité et le mottage augmentent avec la teneur en impuretés. De plus, une diminution de la taille des particules et un élargissement de la distribution de tailles renforcent le mottage. Cet effet s'explique par une teneur en impuretés et une surface spécifique plus importantes pour les petites particules, ainsi qu'une multiplication des points de contact. L'analyse des poudres commerciales a confirmé ces résultats mais aussi mis en lumière un comportement inhabituel de la poudre: l'activité d'eau peut augmenter jusqu'à des valeurs extrêmes pendant le stockage après séchage de la poudre sur lit fluidisé. Une forte activité d'eau entraîne du mottage dans la majorité des lots concernés. Un autre résultat marquant de ce travail est le développement d'un test de mottage accéléré. La tendance au mottage de poudres de lactose issues de différents sites de production a pu être obtenue en moins d'une journée, après un stockage à 50°C et 60% RH. L'implémentation d'un test similaire sur chaque site de production permettrait l'identification rapide des lots à forte tendance au mottage avant expédition. Grâce à la meilleure compréhension des mécanismes de mottage fournie par ce travail, les industriels peuvent cibler les étapes critiques du procédé à optimiser pour prévenir le mottage du lactose.

Mots-clés: Poudre de lactose, mottage, procédé de fabrication, humidité.

Sammendrag

Sammenklumpning af laktose: Forstå nøglemekanismerne til forebyggelse

Laktoseproduktionen vokser verden over, drevet af væksten på markedet for modermælkserstatning og dette sker samtidig med at kravene til produktkvaliteten bliver strengere. Sammenklumpning, eller uønsket agglomering af laktosepulverpartikler, opleves af kunderne som dårlig kvalitet, og klumpning skal derfor forebygges for at undgå betydelige økonomiske tab. Målet med dette PhD projekt er at forstå sammenklumpningsmekanismerne i laktosepulver for dermed at fastlægge metoder til begrænsning af sammenklumpning. Sammenhængen mellem procesforhold og produktkvalitet har været i fokus for at detektere og kontrollere de parametre, der bestemmer tendensen til sammenklumpning i produktet. Prøver fra pilotproduktionen blev analyseret med hensyn til diverse fysisk-kemiske karakteristika (indhold af urenheder, fugtsorption og partikelstørrelse) og sammenklumpningsadfærd. Urenheder (ikke-laktose komponenter) viste sig at øge fugtsorption og sammenklumpning. Partikelstørrelsesfordelingen i pulveret udviste også en stor effekt på sammenklumpningen. Især tilstedeværelsen af mindre partikler var kendetegnet ved forøget fugtsorption og give stærkere sammenklumpning, hvilket kan forklares med et højere indhold af urenheder og et større overfladeområde. Derudover førte en bredere størrelsesfordeling med en lignende gennemsnitlig partikelstørrelse til stærkere sammenklumpning pga. forøgelse af kontaktpunkter mellem partiklerne. Disse resultater blev bekræftet i det kommercielle pulver. Ydermere blev en ustabilitet i vandaktiviteten under lagring af pulveret efter tørring identificeret og kædet sammen med sammenklumpning i laktosesækkene. Dette PhD projekt omhandler også et vigtigt behov i mejeriindustrien, i.e. udviklingen af en accelereret sammenklumpningstest. Der kunne skelnes mellem prøver fra forskellige produktionssteder med hensyn til sammenklumpning efter mindre end én dag ved brug af relevante testforhold (50°C og 60% RH). En sådan test burde blive indført på alle produktionssites for dermed at identificere partier med høj tendens til sammenklumpning før afsendelse. Den bedre forståelse af sammenklumpningsmekanismer, som formidles i denne PhD-afhandling, gør det muligt for industrien at optimere kritiske procestrin for at forebygge sammenklumpning i slutproduktet.

Nøgleord: Laktosepulver, sammenklumpning, produktionsproces, fugt.

Table of Contents

Preface	i
Thesis Outputs	iii
Abstract	iv
Résumé	v
Sammendrag	vi
Table of Contents	vii
List of Symbols and Abbreviations	x
General Introduction	1
Part 1 Economic and Scientific Contexts	3
Chapter 1 – Dairy market and focus on lactose powder processing and caking	4
1.1. Economic context	5
1.2. Lactose powder	10
1.3. Caking	17
1.4. Conclusion	33
Chapter 2 – Aim and research question	35
2.1. Context and research question	36
2.2. Objectives and strategy	37
Part 2 Understanding the Main Caking Mechanisms in Lactose Powder	39
Chapter 3 – Materials and methods	40
3.1. Introduction	41
3.2. Materials - Production and sampling	41
3.3. Post processing of samples	42
3.4. Characterization of the powder intrinsic properties	45
3.5. Caking measurement	48
Chapter 4 – Impurities increase caking	51
4.1. Introduction	52
4.2. How do impurities increase caking?	53
4.3. Conclusions	61
4.4. Take-home messages	61
	vii

Chapter 5 – The size target to obtain a non-caking powder: a narrow size distribution with large particles	62
5.1. Introduction	63
5.2. Why do smaller particles cake more?	64
5.3. A narrow size distribution to prevent caking	70
5.4. Conclusions	72
5.5. Take-home messages	72
Part 3 Industrial Development	74
Chapter 6 – On the process line: how to control the impurity content and the PSD in the final product in order to avoid caking?	75
6.1. Introduction	76
6.2. Amorphous lactose in commercial powders	77
6.3. How to control the impurity content on the process line?	84
6.4. How to control the PSD on the process line?	91
6.5. Conclusions	93
6.6. Take-home messages	94
Chapter 7 – Monitoring the powder water activity as a mean to prevent caking	96
7.1. Introduction	97
7.2. Evolution of water activity in factory samples	98
7.3. Controlling the powder water activity	105
7.4. Conclusions	112
7.5. Take-home messages	113
Chapter 8 – Development of an accelerated test to quantify the caking tendency	114
8.1. Introduction	115
8.2. Development of the method	115
8.3. Screening of production samples	123
8.4. Assessing the effect of aeration	126
8.5. Conclusions	129
8.6. Take-home messages	130
General Conclusion	131

Table of Contents

Recommendations for Future Work	136
References	140
Table of Figures	155
Table of Tables	159
Résumé de la Thèse en Version Longue	160

List of Symbols and Abbreviations

AFI: Arla Foods Ingredients

AFM: Atomic Force Microscopy

a_w : water activity

BOD: Biological Oxygen Demand

Ca: Calcium

CAGR: Compound Annual Growth Rate

Cl: Chloride

CP/MAS NMR: Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance

D_{50} : median of a volume-based particle size distribution

DRH: Deliquescence Relative Humidity

DSC: Differential Scanning Calorimetry

DVS: Dynamic Vapor Sorption

DWP: Demineralized Whey Powder

ERH: Efflorescence Relative Humidity

ESEM: Environmental Scanning Electron Microscopy

ffc : flow function coefficient (ratio of σ_1 to σ_c)

GAB: Guggenheim–Anderson–De Boer (equation)

GOS: Galacto-oligosaccharides

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry

INRA-AO STLO: French National Institute for Agricultural Research - Agrocampus Ovest Science and Technology of Milk and Eggs

K: Potassium

Mg: Magnesium

MT: Metric Ton

MTDSC: Modulated Temperature Differential Scanning Calorimetry

Na: Sodium

NMR: Nuclear Magnetic Resonance

P: Phosphorus

PSD: Particle Size Distribution

RH: Relative Humidity

SEM: Scanning Electron Microscopy

σ_c : unconfined yield strength

σ_1 : consolidation stress

σ_{pre} : normal stress at preshear

T_g : glass transition temperature

TMS: Trimethylsilane

UCPH: University of Copenhagen

UCT: Uniaxial Compression Test

UF: Ultrafiltered

USD: US dollar

WLF: Williams–Landel–Ferry (equation)

WPC: Whey Protein Concentrate

WPH: Whey Protein Hydrolysate

WPI: Whey Protein Isolate

XPS: X-ray Photoelectron Spectroscopy

General Introduction

Driven by the growing demand in infant formula worldwide, the production of lactose powder is currently increasing, with a mean growth rate of 5% per year between 2011 and 2015. At the same time, new applications are emerging and the quality requirements on the microbiological, chemical and physical characteristics of the product are becoming more and more strict. The product stability is also a critical focus point of the lactose producers and their customers. Indeed, the powder is increasingly transported to customers located all over the world, where it can be subjected to large variations in temperature and humidity.

In this context, powder caking or the unwanted agglomeration of powder particles, is a well-known and recurrent issue in various industries, including dairy. Caking can be described as the formation of lumps of varying size and hardness in the powder bag. It is associated with an increase in production time and cost as powder handling becomes more difficult. Thus, customer complaints are frequent at reception of bags of caked powder and substantial economic loss are involved for the producer.

For this reason, caking has been the subject of extensive research, focusing on the following points: caking mechanisms, characterization of caking at the bulk level and particle scale, modeling of caking, anti-caking means. However, given the complexity of the caking mechanisms, which also depend on the powder under consideration, powder caking remains a recurrent issue for many products.

Commercial lactose powder is generally considered to present a good stability, with a shelf life up to two years. However, reports on the occurrence of lactose caking are not rare in the dairy industry. Because of the severe consequences that caking can have, AFI is willing to acquire more knowledge on this subject. Indeed, AFI is one the major lactose producer. In the highly competitive dairy market, product quality is a crucial differentiation factor and caking has to be prevented.

In order to address this issue, a collaboration between AFI and the two research units, INRA-AO STLO and the department of Food Science at UCPH was initiated. The project time has been divided between the three workplaces. Thus, this PhD project has benefited from the combination of expertise in different areas and access to various equipment on laboratory and pilot scale. Moreover, data from experiments on the production scale and from real production at AFI have been utilized.

The present PhD thesis first introduces the economic and scientific context of the project. The overview of the dairy market, the lactose physicochemical characteristics and the caking mechanisms together with the methods used to characterize caking (chapter 1) lead to the research question and strategy implemented in the project (chapter 2).

The overall goal of the project was to understand the mechanisms leading to caking in lactose powder, in order to find means to prevent it. To achieve this goal, work performed on a pilot scale was complemented with direct sampling on the production line. The powders were analyzed for their chemical and physical characteristics including caking tendency (chapter 3). In the first part of the work, on a pilot scale, lactose powders were produced with a controlled variation of critical product parameters, namely the impurity content (chapter 4) and the particle size distribution (chapter 5). Focus was then shifted to the production line in order to investigate how these two product parameters could be controlled (chapter 6). Moreover, measurements on the finished product highlighted that water activity was another parameter which should be monitored in order to prevent caking. Different means to achieve this objective on the process line were presented (chapter 7). In addition, a crucial need of the lactose producer was addressed, namely the development of an accelerated caking method (chapter 8).

Part 1

Economic and Scientific Contexts

Chapter 1 – Dairy market and focus on lactose powder processing and caking

Summary

This chapter aims first at highlighting the increasing importance in the dairy market of whey ingredients in general and lactose powder more specifically. In order to acquire a better understanding of the caking issue, the most important characteristics of the different lactose forms in relation to caking are given. A critical review of the caking mechanisms and of the methods used to characterize caking is included. Caking appears as a complex scientific question with several parameters that can contribute to the different caking mechanisms. These sections were published as a review paper in *Trends in Food Science and Technology* (Paper¹). They constitute the basis of this chapter, which is completed with additional information about the dairy market, most recently published research on caking, and a description of the lactose production process. Indeed, the process parameters are essential to control in order to obtain the right product properties, including a low caking tendency. Depending on the complexity of the process, lactose powder with various levels of purity and physical properties can be obtained, which may impact on the caking of the final product.

The objectives of this chapter were to:

- Give an overview of the dairy market with a focus on dry products and whey ingredients
- Introduce the most important properties of the lactose molecule in relation to caking
- Familiarize the reader with the lactose production process
- Present the caking mechanisms and the parameters which can influence them
- Describe the methods to characterize caking reported in the literature

¹ Published as Carpin, M., Bertelsen, H., Bech, J. K., Jeantet, R., Risbo, J., & Schuck, P. (2016). Caking of lactose: A critical review. *Trends in Food Science & Technology*, 53, 1–12. <https://doi.org/10.1016/j.tifs.2016.04.002>

1.1. Economic context

1.1.1. Fresh dairy market

Milk, the first food of mankind as mammals, has been consumed for millions of years. The domestication of milk producing species of animals is very ancient and these species are still used today to produce the milk we consume on a daily basis. Cow's milk represents the vast majority of the world's production (82%) followed by buffalo's milk (13%), goat's milk (2%) and sheep's milk (1%) (International Dairy Federation, 2016). The milk composition varies according to species (Table 1) but also intra species depending among others on the breed, age, diet and stage of lactation.

Table 1: Typical composition of human milk and milk of the major producer domesticated mammals (Holsinger, 1988).

Mammal	Fat (%)	Protein (%)	Lactose (%)	Total solids (%)
Man	3.8	1.0	7.0	12.4
Cow	3.7	3.4	4.8	12.7
Water buffalo	7.4	3.8	4.8	17.2
Goat	4.5	2.9	4.1	13.2
Sheep	7.4	5.5	4.8	19.3

Milk derived products such as cheese, cream, butter and yoghurts have also existed for several millenniums. Historically, the production of dairy products was very local with each product having its own sensory characteristics. The progressive trade globalization has led to a great variety of products available for the consumers. The consumption of dairy products varies between regions of the world. Average annual per capita consumption ranged from about 50 kg in Africa to over 270 kg in Europe in 2015. An increase of 22% in total dairy consumption is forecasted between 2015 and 2025. Developing and least developed countries will have the most significant growth with almost 3% growth per year (International Dairy Federation, 2016).

The largest producer of fresh cow milk and cheese is the EU, where raw milk is used primarily for the production of cheese. USA is the second leading country in the production of cheese, accounting for 27% of the global production against 45% for the EU. Considering liquid milk output, a growth of 5% between 2014 and 2015 was observed in the production from India and China, the second largest producer while production decreased in the developed countries as the EU and USA. The dairy fat market is largely dominated by India which accounts for nearly half of the world's production, followed by the EU producing half the amount of India.

These figures show that production of dairy products is spread worldwide. Moreover, 9% of global milk output was traded across borders in 2015 with an average annual growth rate of 5.9%

between 2010 and 2014. The two largest dairy exporting regions of the globe are New Zealand and the EU, accounting for 28% and 27% of the global trade respectively. USA is the third one with a share of 14% (International Dairy Federation, 2016).

1.1.2. Focus on dry products

Along with this increase in global trade, dry products are taking more and more importance in the dairy market. USA export growth from 2009 to 2016 across dairy sub-categories (Figure 1) and dairy investments in the EU between 2012 and 2014 (Figure 2) illustrate the interest of the main dairy producing regions in the world for dry products.

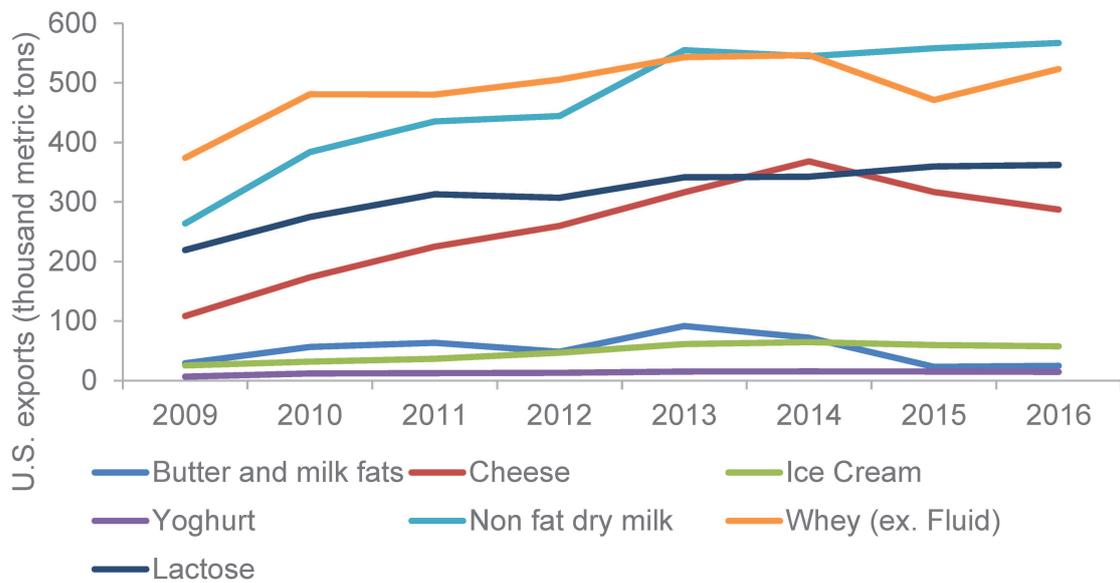


Figure 1: USA export growth from 2009 to 2016 for several dairy products (data from (U.S. Dairy Export Council, 2017)).

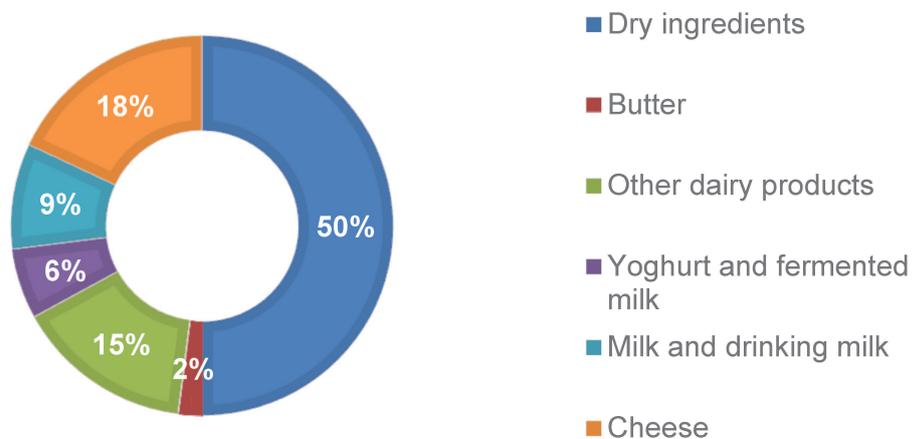


Figure 2: Share of announced finalized investments between 2012 and 2014 in the EU ((European Dairy Association, 2016).

Dry products are attracting considerable interest due to ease of handling, storage and transport. As an increasing part of the dairy production is indeed exported nowadays, the stability of a product over time is crucial. Dry products are commonly considered to have a better stability and a longer shelf life than their liquid counterparts. Moreover, transporting ingredients in powder form sharply decreases transportation costs.

Drying of dairy products started on an industrial scale at the beginning of the twentieth century. Roller drying, a process developed by Just and Hatmaker and patented in 1902, was the main drying process until the Second World War. However, the harsh heat treatment, poor solubility and cooked flavor of the dried product together with high maintenance costs and low capacity associated with roller driers led to the development of spray driers after the Second World War. Dehydration of dairy products is nowadays most frequently done by spray-drying which is a gentle drying technique (Knipschildt & Andersen, 1994).

The milk powder industry includes various products: regular or agglomerated skim milk powder and whole milk powder, instant milk powder, modified milk powders with high free fat content and fat filled milk powder. Dried milk based products are also largely available on the market. They can be used either as household consumer products such as cocoa-milk-sugar powder, flavored milk drinks, coffee whitener or as raw material for the food industry such as caseinate powder, cheese powder and butter powder (Pisecky, 2012). Over the past 20 years, the dairy industry has been increasing the share of valuable milk protein fractions by means of milk fractionation. Following this trend and beyond commodities, more elaborated and specific dried products such as high protein powders have been developed with various functional and nutritional properties. In the meantime, the market of infant formula has shown a continuous increase, supported by the growth in the world population and the rise in the standard of living in emerging countries. Indeed, the use of high protein powders represented up to 150 000 metric tons (MT) of equivalent pure protein a year in the EU in 2012 (FranceAgriMer, 2012), whereas the global infant formula production reached 2 million MT a year in 2014, out of the 12 million MT of dairy powders produced a year (Bonke, 2016). These production indicators emphasize how the segment of these specialized products now represent essential market opportunities for the dairy sector, both in volume and added value.

1.1.3. Whey ingredients

From the seventies, whey related products have been taking a growing importance on the market. Whey is a by-product of cheese manufacturing. Cheese production has been increasing worldwide leading to larger amounts of whey to be disposed of. In 2015, approximately 19.7 million MT cheese were produced worldwide, yielding 178 million MT liquid whey or 11 million MT of whey solids (Affertsholt & Pedersen, 2016). Whey was traditionally a waste product used as pig feed, for irrigation or disposed of by sewage treatment (Lifran, Hourigan, Sleight, & Johnson, 2000).

However, whey has a high biological oxygen demand (BOD), which presents environmental problems. The high BOD is essentially due to lactose, the major solid component of whey, accounting for 70 to 80%. Minerals and proteins constitute the remaining part (Hobman, 1984). Because of environmental but also commercial concerns, dairy companies were therefore forced to find new ways of valorizing whey.

The first option was to spray dry the whole whey. Whey powder can be used as an ingredient in various food and feed applications. Depending on the application, demineralized whey powder can be preferred. Nowadays, whey powder is the largest whey ingredient in volume, with 3 million MT produced in 2015 (Affertsholt & Pedersen, 2016). The other option for whey processing, which leads to higher value products, is to apply membrane filtration to the whey to separate it into its different constituents. At the beginning of the eighties, ultrafiltration of whey to extract proteins was already a well-established process. However, utilizing the permeate from ultrafiltration of whey to produce crystalline lactose was not straightforward especially because of the high calcium content (Hobman, 1984). Advances in dairy technology over the years have rendered this last process the most used to produce crystalline lactose (Durham, 2009). Alternatively, manufacture of crystalline lactose directly from whey can be done.

Nowadays a great variety of whey based dry products can be found on the market (Figure 3), with an added-value level depending on the product purity and process complexity. Given the high versatility of the world dairy product prices since 2002, dairy companies are increasingly investing in the high value products (International Dairy Federation, 2016). Applications of whey based ingredients are numerous (Figure 4) and dictate the purity level required from the product. Sports nutrition and infant formula are nowadays the two sectors driving growth (Affertsholt & Pedersen, 2016). As the two major cheese-producing regions, EU and USA dominate the whey business (International Dairy Federation, 2016). European and American exports of all whey ingredients are both significant and increasing, with Asia being the dominant market (Affertsholt & Pedersen, 2016).

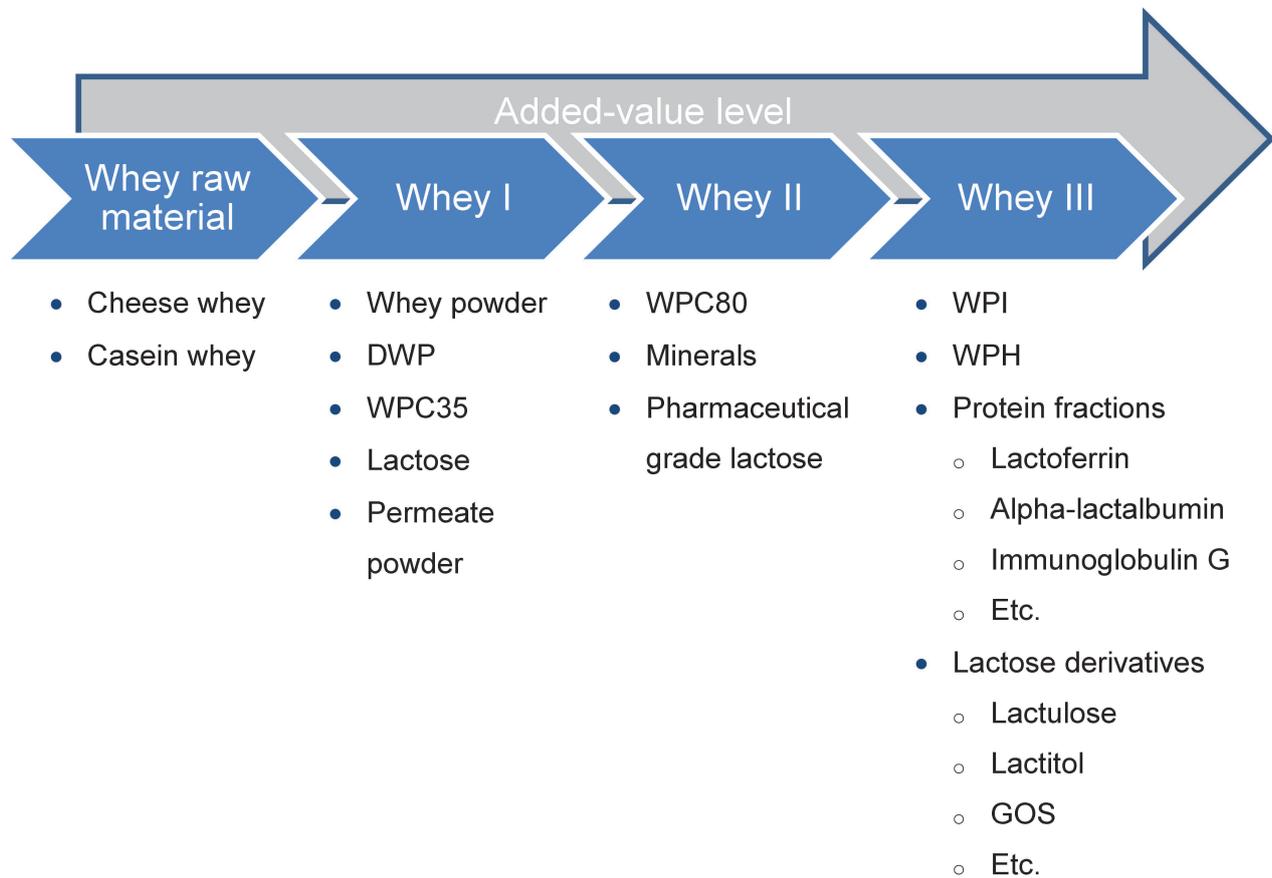


Figure 3: Range of whey based products according to the added-value level (modified from (Affertsholt & Pedersen, 2016)).



Figure 4: The different applications of whey based ingredients (European Whey Products Association, 2016).

1.2. Lactose powder

1.2.1. Lactose powder market

Among the whey derived ingredients, lactose powder is important both in terms of production and revenue. Lactose production increased by 5% between 2011 and 2015 and amounted 1.384 million MT in 2015. The expected lactose production volume for 2020 is 1.654 million MT. Lactose is the second whey ingredient in terms of volume after whey powder. However, regional differences can be observed in production growth (Table 2). The EU and the US are the two main production regions, together accounting for 80% of the global lactose production (Affertsholt & Pedersen, 2016).

Table 2: Production of lactose (in thousand MT) by region between 2011 and 2015 together with the Compound Annual Growth Rate (CAGR) and forecast for 2020 (Affertsholt & Pedersen, 2016). CIS: Russia, Belarus, and Ukraine. MEA: Middle East and Africa.

Lactose	2011	2012	2013	2014	2015	CAGR 11-15	F2020
EU-area	432	467	498	531	603	9%	800
CIS-area	10	15	20	25	30	32%	40
North America	459	471	478	525	489	2%	525
Oceania	170	170	170	173	170	-	175
Latin America	6	10	14	16	18	32%	24
Asia	14	22	25	30	30	21%	40
MEA	32	36	40	42	44	8%	50
GLOBAL	1,123	1,189	1,245	1,342	1,384	5%	1,654

The global market value of lactose (including pharmaceutical grade) was approximately USD 1.2 billion in 2015 and is expected to reach about USD 1.5 billion in 2020. The two main end-use sectors for lactose in the EU and the USA are food and infant formula, which together account for 76 to 79% of the demand. The remaining lactose is used in the pharmaceutical industry and as animal feed. Main uses for lactose in food are in baked goods, milk chocolate and other confectionery, processed meat, as a carrier base for dry mixes and for milk powder protein standardization (Affertsholt & Pedersen, 2016). Applications of lactose powder in food are various due to its broad range of properties: low glycemic index, prebiotic function, low cariogenicity, low sweetness, reducing sugar properties, emulsifying properties, stable protective functions. In the pharmaceutical industry, lactose is used as tableting excipient and dry powder inhaler (Durham, 2009).

1.2.2. The different lactose forms (Paper¹)

Lactose is a disaccharide composed of a D-galactose and a D-glucose unit bonded through a β -1,4-glycosidic linkage. Lactose (4-O- β -D-galactopyranosyl-D-glucopyranose, C₁₂H₂₂O₁₁) can occur in α and β forms. As can be seen in Figure 5, the two forms are stereoisomers, which differ

by the spatial arrangement of the hydroxyl group at carbon number 1 of the hemiacetal group. The α -form has the greater optical rotation in the dextro direction (Holsinger, 1988). In solution, the rate of the transformation between the α - and β -anomers, called mutarotation, is temperature- and pH-dependent. On the other hand, the ratio at equilibrium depends only slightly on temperature and is not affected by pH (Holsinger, 1997).

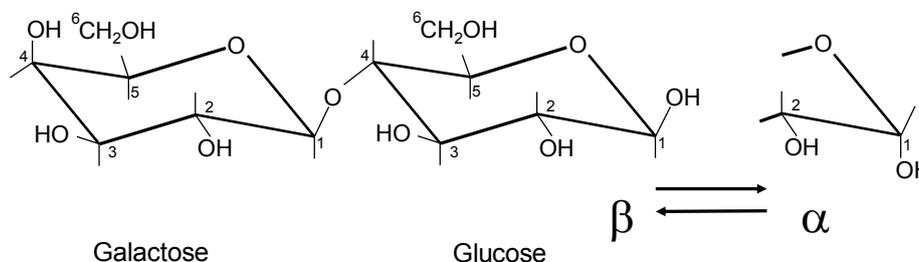


Figure 5: Lactose structure in α and β forms (Schuck, 2011).

As a powder, lactose can be found in a crystalline state, an amorphous state or a mixture of both. By definition, crystalline lactose presents a very ordered structure, with the exact morphology of the crystal depending on the crystallization conditions. In amorphous lactose, the lactose molecules are not organized according to a regular lattice. Moreover, lactose is polymorphic, meaning that it can crystallize into different forms. The six currently known forms of lactose are presented in Table 3. The crystalline form α -lactose monohydrate has a different chemical composition due to the inclusion of water in the crystal structure. It is however often presented as a lactose polymorph in the literature (Kirk, Dann, & Blatchford, 2007).

Table 3: Currently known forms of lactose (from Listiohadi et al. (2005b)).

	Monohydrate	α -lactose
Crystalline		Unstable α -lactose
	Anhydrous	Stable α -lactose
		β -lactose
		Compound β/α lactose ¹
Amorphous	Mixture of α -lactose and β -lactose	

¹ Can be obtained at different molar ratios but there is no consensus to date on the actual existence of this form of lactose (Hourigan, Lifran, Vu, Listiohadi, & Sleigh, 2013).

The properties of each lactose form have been summarized by Listiohadi et al. (2005b). The most important of these properties in relation to the caking phenomenon are given below.

1.2.2.1. α -lactose monohydrate

α -lactose monohydrate is the most common and stable form of lactose under normal temperature and humidity conditions. The crystal structure includes one molecule of water of crystallization for

each lactose molecule. This water molecule is crucial to the structure and stabilization of the crystal lattice as it links together oxygens of four lactose molecules (Clydesdale, Roberts, Telfer, & Grant, 1997). It also explains the relative non-hygroscopicity (ability to attract moisture from the atmosphere) of α -lactose monohydrate. At 25°C this form of lactose is stable below 95% relative humidity (RH) (Salameh, Mauer, & Taylor, 2006). The most common crystal shapes for α -lactose monohydrate are tomahawk and prism shapes (Holsinger, 1988) as seen in Figure 6. The process commonly used in the dairy industry to obtain the tomahawk crystal shape consists of slow cooling of whey permeate concentrate in a crystallizer (Hourigan et al., 2013).

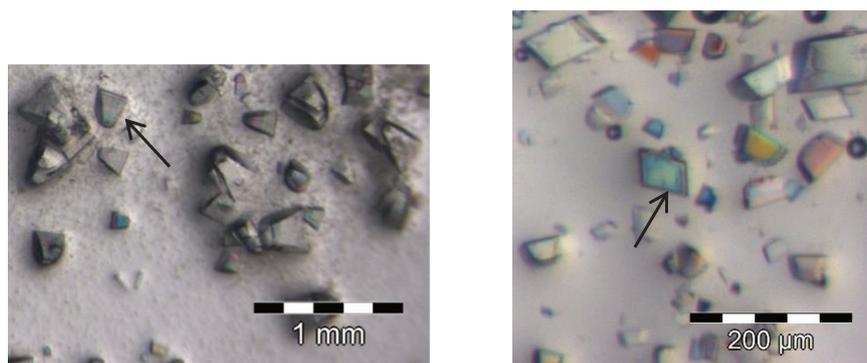


Figure 6: Typical tomahawk (left image) and prism (right image) shapes of α -lactose monohydrate.

1.2.2.2. Stable and unstable anhydrous α -lactose

Stable and unstable forms of anhydrous α -lactose are derived from the previous form upon release of the water of crystallization from the crystal lattice. In unstable anhydrous α -lactose, the arrangement of the lattice is left unchanged, giving a highly porous and unstable structure. This lactose form is therefore extremely hygroscopic (4% water sorption at 10% RH and 20°C (Figura & Epple, 1995)) and reforms α -lactose monohydrate upon moisture sorption. In contrast, stable anhydrous α -lactose presents a different crystal structure to that of α -lactose monohydrate. This form is stable at room temperature and relative humidity below 50% (Figura & Epple, 1995).

Both forms can be produced from α -lactose monohydrate by heating at temperatures between 100°C and 190°C, preferably under vacuum. It has been shown that unstable anhydrous α -lactose is a precursor of the stable form during thermal dehydration of the monohydrate lactose form (Figura & Epple, 1995). Stable anhydrous α -lactose can also be produced by different techniques using an organic solvent not miscible with water.

1.2.2.3. Anhydrous β -lactose

Anhydrous β -lactose is the only form of the β anomer of crystalline lactose. This lactose form is stable below 95% RH at 25°C and therefore less hygroscopic than anhydrous α -lactose (Salameh et al., 2006). The crystal shapes differ from those of the α anomer. Crystallization of anhydrous β -

lactose from water yields uneven-sided diamonds (Figure 7) while crystallization from alcohol leads to curved needle-like prisms (Holsinger, 1988).



Figure 7: Typical uneven-sided diamond shape of anhydrous β -lactose crystallized from water (personal authorization from Dr T.D. Dincer, Curtin University, Western Australia).

Different ways of producing anhydrous β -lactose have been reported in the literature, either from a saturated lactose solution or from α -lactose monohydrate. Most of these methods involve heating the saturated solution at high temperature, as lactose preferentially crystallizes in the β form at temperatures higher than 93.5°C (Hudson, 1904). Independently of the method used, obtaining a powder of one anomer completely free of the other appears to be particularly difficult. Commercial anhydrous lactose contains up to 80% β -lactose and is usually produced by roller drying (Hourigan et al., 2013).

1.2.2.4. Compound crystals of anhydrous α - and β -lactose

The compound crystals of anhydrous α - and β -lactose are characterized by the occurrence of both anomers in the same crystal lattice. Several methods of obtaining compound crystals of anhydrous α - and β -lactose at different molar ratios have been published in the literature. There is however no consensus to date on the actual existence of this form of lactose (Hourigan et al., 2013).

1.2.2.5. Amorphous lactose

Amorphous lactose can be seen as a concentrated low moisture syrup in a glassy state. This lactose form is a mixture of α - and β -lactose molecules. The molecules are not organized in a regular lattice but amorphous lactose appears to be solid due to its high viscosity. Amorphous lactose has a higher energy state than crystalline lactose and is therefore thermodynamically unstable. It is also very hygroscopic. Amorphous lactose is formed during drying of a lactose solution when a rapid increase in viscosity occurs and prevents crystallization (Holsinger, 1997). Spray-drying and freeze-drying are typically used to produce amorphous material. Amorphous lactose can also be formed during mechanical processes such as milling (Newell, Buckton, Butler, Thielmann, & Williams, 2001b).

The glass transition temperature (T_g) characterizes amorphous lactose. Above this temperature, the solid which was in a hard and glassy state turns into a rubber-like state. The T_g of anhydrous lactose glass is 101°C (Roos & Karel, 1990), but it decreases when the moisture content of the material increases (Roos & Karel, 1991). As can be seen in Figure 8, the T_g drops to 24°C at a water activity level of 0.37, corresponding to a water content of 6.8% w/w (Jouppila & Roos, 1994).

The water activity-temperature state diagram of amorphous lactose can be used to predict the storage conditions which ensure the stability of amorphous lactose-based dry products (Thomsen, Jespersen, Sjøstrøm, Risbo, & Skibsted, 2005). When amorphous lactose absorbs moisture, the mobility of the lactose molecules increases. At a certain point, a collapse in the structure leads to the rubber-like state. Subsequently, crystallization takes place, accompanied by a release of absorbed water (Buckton & Darcy, 1999). The resulting crystalline lactose is a mixture of anhydrous and hydrous forms in proportions depending on the ambient conditions. Amorphous lactose crystallizes as α -lactose monohydrate when the moisture content reaches about 8% w/w (Holsinger, 1997).

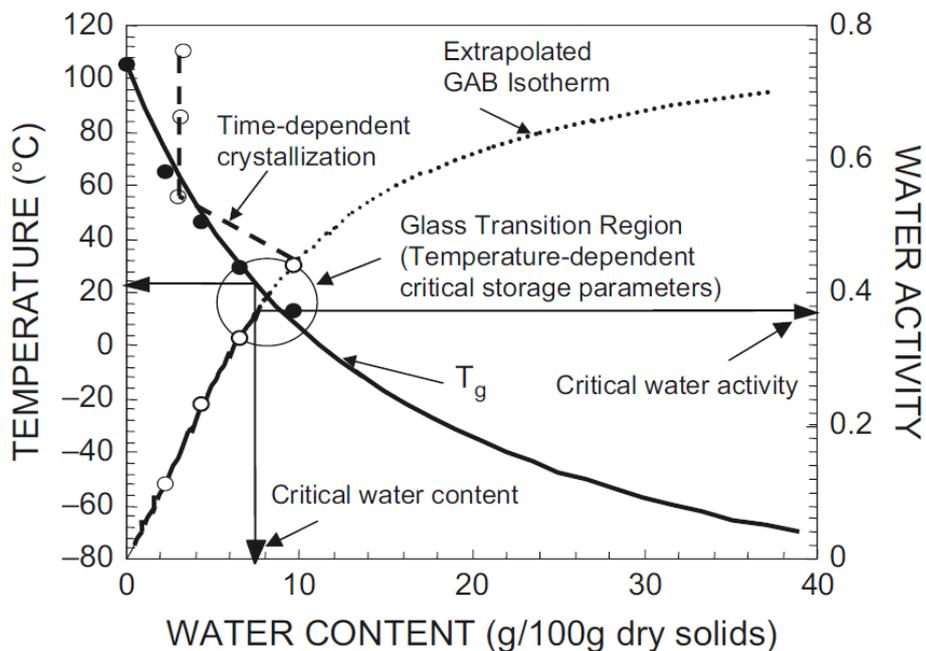


Figure 8: Relationships between glass transition temperature (T_g), water content and water activity for amorphous lactose (Roos, 2009).

As reported by others (Hourigan et al., 2013), control of the different lactose forms is critical for the dairy industry in order to avoid quality issues. For example, given its high hygroscopicity, the presence of amorphous lactose will damage the storage stability of dairy powders by promoting caking. It can also trigger changes in the texture of any product in which lactose is incorporated. A summary of the inter-relationships between the types of lactose was first published by King in 1965 (King, 1965). It has been updated several times and most recently by Hourigan et al. (2013).

1.2.3. Lactose production process

When referring to lactose production in the dairy industry, it is usually meant α -lactose monohydrate. As mentioned above, this form is the most stable at normal ambient conditions.

Lactose powder can be produced directly from whey. However, whey proteins have become extremely valuable and for this reason, whey is nowadays usually ultrafiltered (UF) to separate the protein stream (retentate) from the lactose and soluble mineral stream (permeate). The UF permeate is then further processed according to the process presented in Figure 9 to produce edible grade lactose. The first steps, calcium phosphate removal and nanofiltration, are optional but increase the runtime and efficiency of the process. If not removed upstream, calcium phosphate indeed precipitates in the evaporators due to elevated temperatures, fouling the heating surfaces. The nanofiltration step aims at concentrating and demineralizing the whey permeate, which reduces the lactose solids lost in the separation step and increases the yield (Durham, 2009). Reverse osmosis is also often used to concentrate the permeate before evaporation. Concentration by falling film evaporators increases the dry matter content to about 60% (Hourigan et al., 2013). The concentrated whey permeate is then pumped into a crystallizer where it is subjected to a slow batch cooling for 20 to 24 hours. The lactose crystals formed should be big enough (200-300 μm) with a narrow size distribution to be easily separated from the mother liquor and washed afterwards. Thus, the crystal size distribution highly impacts the lactose yield (Paterson, 2017). The mother liquor contains minerals, peptides, organic acids and some dissolved lactose. The separation and washing steps will therefore determine the final level of impurities in the product. Too many fines in the lactose crystals can clog the separator leading to a poorer separation of the mother liquor and higher levels of impurities and moisture. Recirculation of wash water can be done to increase the yield of the process. However, depending on the chemical composition (lactose and impurities) of the wash water and at which step this water returns into the process, recirculation can negatively impact the purity of the final product. After the washing step, the crystals usually have a 88-90% dry matter content and must be dried further. Drying takes place in a fluidized bed dryer with dehumidified air. The final water content of the crystals is 4.5 – 5.5%. Drying temperature and time should be controlled to avoid the formation of amorphous glass and lactose polymorphs other than α -lactose monohydrate (Durham, 2009). Finally, lactose should be cooled prior to packaging to avoid caking due to moisture migration from the hot to the cold regions in the bag during storage (Bronlund & Paterson, 2008). Additionally, lactose crystals can be milled and sieved to obtain the desired size specifications.

Pharmaceutical grade lactose, the most pure lactose available on the market (Hourigan et al., 2013), is recrystallized from edible grade lactose and crystals undergo the separation and washing steps once more. The redissolved edible lactose is usually pretreated with activated carbon, which adsorbs riboflavin and to a lower extent peptides and gives its white color to pharmaceutical lactose (Durham, 2009). This activated carbon treatment can also be an additional step in the process of high-value edible grade lactose.

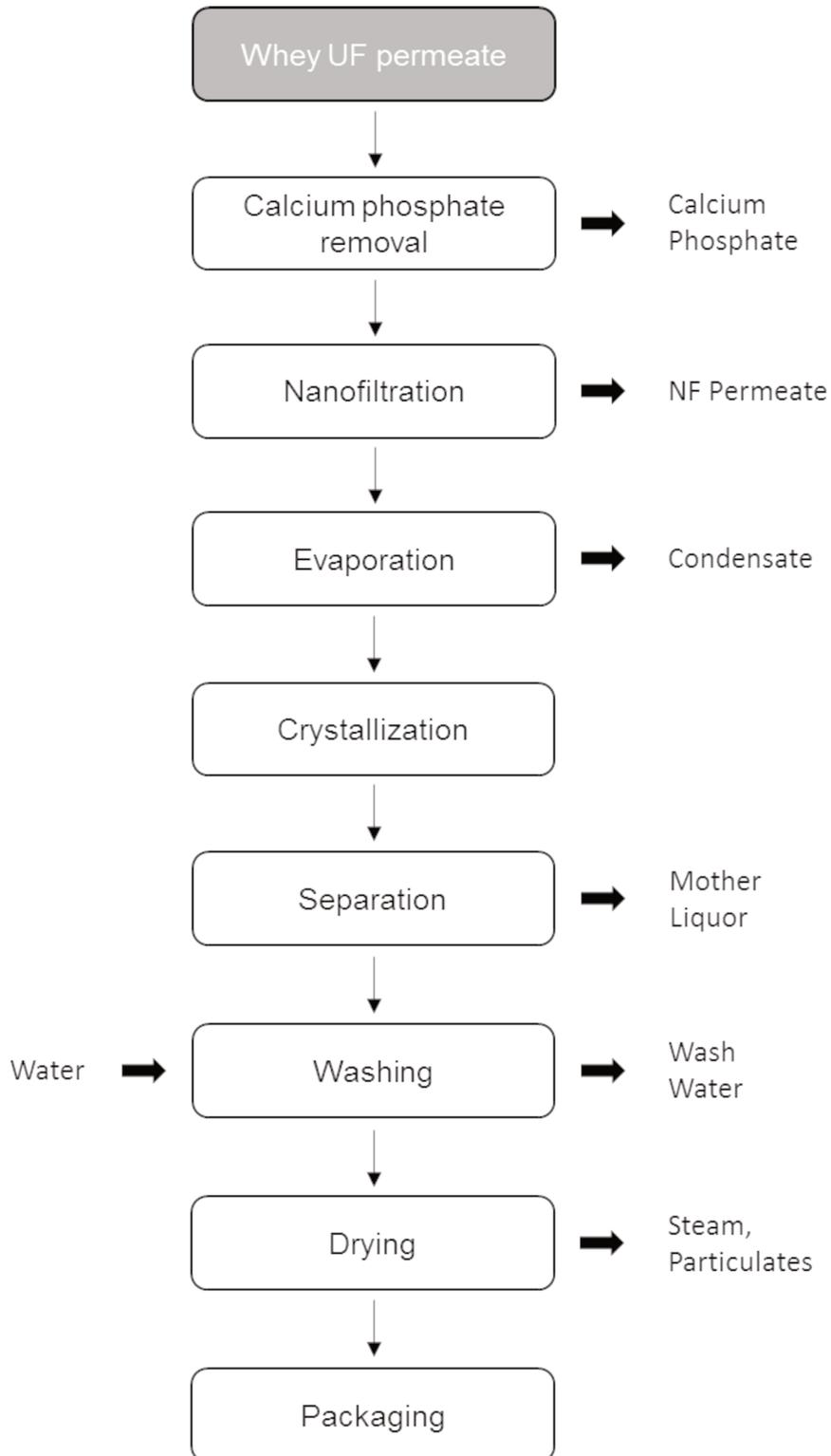


Figure 9: Process chart for the manufacture of edible grade lactose (modified from (Durham, 2009)).

1.2.4. Specifications for lactose powder

Lactose powder can be found in different grades on the market: feed, edible, wet or dry blend for infant, and pharmaceutical. The microbiological quality and chemical purity are specific for each grade and depend on the degree of hygiene and purification steps in the lactose process. The

chemical purity is lowest for the feed grade and highest for the pharmaceutical grade. Product specifications for edible grade lactose and for pharmaceutical grade lactose (Table 4) are given in the Codex Standard for sugars (Codex Alimentarius, 2001) and in the Pharmacopoeia (British Pharmacopoeia, 2001; US Pharmacopoeia, 1995), respectively.

Table 4: Specifications for the composition of pharmaceutical and edible grade lactose.

Analysis	US (1995) and British (2001) Pharmacopoeia	Codex Alimentarius (2001)
Lactose content (on a dry basis)	99.8%	> 99.0%
Sulfated ash (on a dry basis)	≤ 0.1%	≤ 0.3%
Moisture content <ul style="list-style-type: none"> • Loss on drying (120°C for 16 hours) • Loss on drying (80°C for 2 hours) 	≤ 0.5%	≤ 6.0%
Total water (Karl Fischer)	4.5 – 5.5%	
pH (for a 10% solution)		4.5 – 7.0

Beyond the regulatory matter, product specifications are important to lead the customers in their choice for an ingredient. As an illustration, AFI chemical and physical specifications for edible grade lactose are given in Table 5.

Table 5: AFI chemical and physical specifications for edible grade lactose powder.

Chemical specifications		Physical specifications	
Protein (Nx6.38) as is	Max. 0.2%	pH (10% solution – ambient temp.)	5.0-7.0
Lactose monohydrate as is	Min. 99.0%	Bulk density	
Sulphated ash	Max. 0.3%	- Unmilled	0.8-1.0g/cm ³
Moisture at 87°C	Max. 0.2%	- 100 mesh	0.8-1.0g/cm ³
Total water	Max. 5.2%	- 200 mesh	0.7-0.9g/cm ³
Riboflavin	Max. 0.2mg/100g	Solubility (10% solution – ambient temp.)	Clear
		Scorched particles	Equal to A
		Colour	White/Cream
		Flavour/Odour	Free from foreign odour and flavours
		Taste	Free from foreign taste
		Appearance	Free flowing powder

1.3. Caking

1.3.1. Definition and industrial consequences

Specifications for lactose powder also mention a free flowing powder. However, this characteristic is not always easy to obtain due to a well-known issue in the food industry: powder caking. Caking can occur at different steps in the process and storage and take various aspects. It is therefore difficult to define in general terms but involves the agglomeration of powder particles in all cases. It can lead to the formation of a hard crust of powder on a spiral conveyor during production or

loose and hard lumps of different sizes in a bag of powder after storage (Figure 10). Financial consequences can be severe for the lactose manufacturers. Caking indeed increases production time and costs as it can block equipment and induce additional processing steps to obtain a free flowing powder again. Moreover, customers associate caking with poor quality and complaints are frequent at reception of bags of caked powder. The loss of trust from the customers financially impacts the supplier in the long term. Caking should therefore be avoided. The food industry would consequently greatly benefit from a better understanding of the caking mechanisms and means to prevent them.

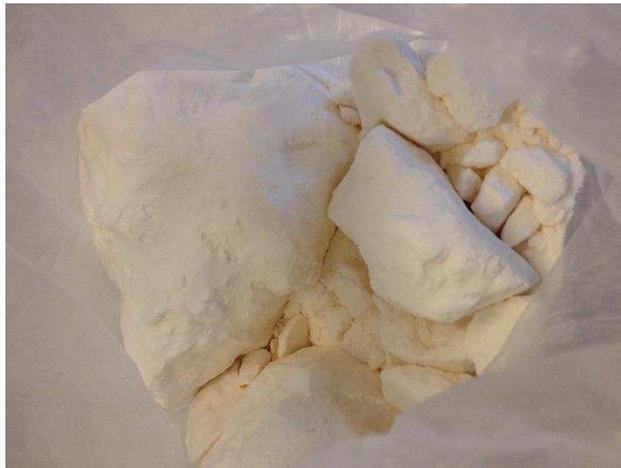


Figure 10: Lactose powder caked in a bag.

1.3.2. Caking mechanisms (Paper¹)

Caking of dairy powder has been an issue in the dairy industry for many years. As early as 1930, Troy and Sharp (1930) proposed a simple and general mechanism for caking in dried milk consisting of three steps: (1) absorption of moisture by lactose, (2) agglomeration of the particles, and (3) crystallization and solidification of some of the lactose. More precisely, three mechanisms have to be considered to understand caking and these are especially relevant for lactose powder. The first involves crystallization of amorphous material, and the second the deliquescence of crystalline particles. Moisture has a crucial role in both mechanisms, as explained in greater detail below. In contrast, the third mechanism does not involve moisture but is influenced by the balance of forces existing between particles.

1.3.2.1. Amorphous Caking

By allowing solid material from powder particles to diffuse to contact points, an increase in temperature can lead to caking. The creation of viscous bridges by viscous flow due to heat and/or pressure is called sintering (Palzer, 2005). This caking mechanism has been widely studied in amorphous powders and is commonly referred to as “amorphous caking” (Aguilera, Valle, & Karel, 1995; Bronlund, 1997; Listiohadi et al., 2005b). As explained in section 1.2.2.5, amorphous

material changes from a glassy to a rubbery state in the T_g range. A decrease in viscosity thus occurs, allowing the flow of material to contact points. If the temperature is increased further, solid bridges are formed between particles as a result of the crystallization of amorphous elements.

a. Influence of T_g

The difference between the process or storage temperature T and the onset T_g of the material, $T - T_g$, governs the rate of crystallization and the extent of caking (Foster, Bronlund, & Paterson, 2006; Lloyd, Chen, & Hargreaves, 1996; Roos & Karel, 1992, 1993). For example, the viscosity of maltodextrin DE21 decreases by a factor of 20 for every 4°C temperature increase above T_g , allowing more rapid sintering (Descamps, Palzer, Roos, & Fitzpatrick, 2013). As storage above 101°C (corresponding to the T_g of anhydrous lactose (Roos & Karel, 1990)) is unlikely to occur, it might be considered that this mechanism does not need to be taken into account to control the caking of lactose. However, the plasticizing effect of water is widely acknowledged (Roos & Karel, 1991). As already described, T_g decreases when an amorphous material absorbs moisture. At 33% RH, the T_g of freeze-dried amorphous lactose already decreases to 30°C, while at 43% RH crystallization is possible at room temperature (Roos & Karel, 1991).

Crystallization of amorphous lactose due to the plasticizing effect of water was followed under a microscope at 57% RH and 25°C by Listiohadi et al. (2005c). The highly hygroscopic amorphous material readily absorbed moisture and became liquefied. Liquid bridges then appeared between adjacent particles. The onset of crystallization was observed after 20 minutes of moisture sorption and complete crystallization took up to two hours. Moreover, the moisture sorption and desorption processes during crystallization appeared on the moisture sorption curves whatever the RH in the range studied (33 to 75%). Higher levels of relative humidity promoted more rapid crystallization (Listiohadi et al., 2005c).

b. Mathematical modelling and control of T_g

Several authors have focused on the agglomeration process between individual particles using equations from sintering technology and the theory of viscoelasticity (Haider et al., 2014; Palzer, 2005), and two caking mechanisms have been identified in amorphous powders i.e. flattening and sintering. At low positive $T - T_g$ values, the particles enter the rubbery state and surface flattening creates larger contact zones, thereby enhancing Van der Waals forces. If the temperature or the compressive force acting on the particles increases further, viscous flow sintering can be triggered (Haider et al., 2014). When sintering is the relevant process for caking, the contact time between amorphous particles required to develop sufficient adhesion force to lead to caking can be calculated using the following equation (Palzer, 2005):

$$t = \left(\frac{5a^2\pi}{4\gamma a\pi + 2F_t} \right) \left(\frac{X}{a} \right)^2 \eta(T) \quad (1)$$

X being the diameter of the sinter bridge (m), a the diameter of the particle (m), γ the surface tension ($\text{N}\cdot\text{m}^{-1}$) and F_t the force applied. It is assumed that $\left(\frac{X}{a} \right) = 0.1$ for sufficient inter-particle adhesion force. The viscosity of the material at temperature T , i.e. $\eta(T)$ ($\text{Pa}\cdot\text{s}$), is derived from the Williams–Landel–Ferry (WLF) equation (Williams, Landel, & Ferry, 1955):

$$\eta(T) = \eta_g 10^{[C(T-T_g)]/[B+(T-T_g)]} \quad (2)$$

where B and C are the constants of the WLF equation and η_g represents the viscosity in the glassy state.

Eq. (1) allows prediction of the time, temperature and moisture conditions leading to caking in amorphous food powders. The result of this calculation is concordant with published findings from various caking tests (Palzer, 2005). It should be noted that crystallisation of the amorphous material is not a prerequisite for caking. Sinter bridges which are predominantly amorphous can lead to strong inter-particle adhesion forces if they grow sufficiently. Eq. (1) also shows that, in the case of viscous flow sintering, low positive $T-T_g$ values can lead to significant caking if the amorphous material is given time to flow.

It has been reported that control of T_g through humidity and temperature conditions can prevent amorphous caking during storage (Aguilera et al., 1995; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Listiohadi et al., 2005b). However, the pressure applied to the particles, for example at the bottom of a bag, should also be taken into account, as in Eq. (1). Moreover, several aspects should be borne in mind when referring to the glass transition temperature of a material. First, T_g is often determined by differential scanning calorimetry (DSC) and the heating rate influences the value measured (Figura, 1993; Haider et al., 2014). In addition, glass transition actually takes place over a range of temperatures (e.g. ten degrees for skimmed milk powder). It is thus preferable to distinguish onset, inflexion and endset T_g values (Schuck, Dolivet, & Jeantet, 2012a). Finally, the measurement of T_g should be performed under relevant humidity conditions as the moisture content of the material influences T_g .

c. Influence of amorphous content on the caking of crystalline lactose

The findings presented above are valid for amorphous powders, and do not apply for crystalline lactose. As commercial crystalline lactose is obtained after slow crystallization and washing, the level of the remaining amorphous lactose is in principle extremely low. However, it has been suggested that amorphous material could be formed on the surface of the crystals during the rapid drying of the wet lactose crystals (J. Bronlund & Paterson, 2004). Moreover, certain mechanical

processes such as milling and grinding have been shown to produce amorphous material up to 1% of total lactose (Listiohadi, Hourigan, Sleigh, & Steele, 2005a; Murrieta-Pazos et al., 2012; Newell, Buckton, Butler, Thielmann, & Williams, 2001a; Newell et al., 2001b).

Only a few studies have addressed the role of amorphous lactose in the caking of predominantly α -lactose monohydrate powders (Bronlund, 1997; Darcy & Buckton, 1998; Listiohadi et al., 2005c). Listiohadi et al. (2005c) measured moisture sorption characteristics, amorphous content and hardness of the powder plugs during storage of physical mixes for three months at 25°C at RH ranging from 33 to 75%. The results showed that the higher the amorphous lactose content, the higher the moisture sorption and subsequent desorption. No amorphous lactose was detected after storage in the samples initially containing more than 10% amorphous material, regardless of the RH. On the other hand, crystallization was not complete in samples with up to 10% amorphous lactose. The authors suggested that in this case the amorphous material might be isolated in “micro cells”, thereby hampering nucleation, or widely distributed in the matrix and delaying crystallization. Compaction of the plugs before storage resulted in an initial hardness which was greater with a higher amorphous lactose content. However, the hardness of the samples containing less than 50% amorphous material did not increase after storage. The samples composed mainly of amorphous lactose (>50%) did not show a steady increase in hardness with time. In contrast it peaked after 20 days of storage when the inner part of the plug became sticky and then decreased when crystallization progressed from the perimeter to the center of the plug (Listiohadi et al., 2005c).

Most studies dealing with low amorphous lactose content in predominantly crystalline lactose have been performed with physical mixtures of 100% amorphous and 100% crystalline lactose (e.g. Hogan & Buckton, 2001; Katainen, Niemelä, Harjunen, Suhonen, & Järvinen, 2005; Listiohadi et al., 2005c; Royall et al., 2005). However, the amorphous content in a commercial crystalline powder has been found mostly on the surface of the particles (Buckton & Darcy, 1999; Newell et al., 2001b). An experimental design using physical mixes might therefore not be representative of reality, and might provide unreliable or even misleading results. Another limitation of such physical mixes is the difficulty of taking low levels of amorphous lactose into account. The lowest amorphous content included in the experiments is usually 5% (Katainen et al., 2005; Listiohadi et al., 2005c), which is far from the 1% produced by grinding (Newell et al., 2001b).

Sintering is not the only process whereby amorphous material can lead to caking in a mostly crystalline lactose powder. Even when the amorphous lactose content in a bag of powder is too low for formation of viscous bridges, the much higher hygroscopicity of this form can destabilize the whole bag (Bronlund, 1997). Moisture can be absorbed by amorphous material, which will crystallize once the T_g has been lowered enough. Water released upon crystallization will then be able to interact with α -lactose monohydrate crystals by the mechanism presented below.

1.3.2.2. Humidity Caking

Many food powders are hygroscopic, though to varying degrees depending on the temperature and humidity conditions (Mauer & Taylor, 2010). Crystalline sugars for example have lower hygroscopicity than their amorphous counterparts (Bronlund & Paterson, 2004; Rogé & Mathlouthi, 2003). At low relative humidity, water molecules are adsorbed on the surface of the particles (Dupas-Langlet, 2013). When RH increases, capillary condensation is triggered by surface tension effects at contact points between particles. Using the Kelvin equation, it is possible to predict the range of water activity where the critical capillary radius increases dramatically, leading to significant liquid bridging (Billings, Bronlund, & Paterson, 2006): capillary condensation can occur in lactose at relative humidity levels above 80% (Bronlund & Paterson, 2004). For soluble materials, capillary condensation leads to surface dissolution, which can be seen as the onset of deliquescence.

a. Deliquescence

Deliquescence is a special kind of dissolution which occurs when a crystalline solid takes up water vapor and turns into an aqueous solution (Martin, 2000). It is a first order phase transition taking place at a well-defined relative humidity characteristic of the crystalline solid (Martin, 2000). This relative humidity is called deliquescence relative humidity (DRH or RH_0). The reverse phase transition (i.e. from the liquid to the crystalline state) is called efflorescence and also takes place at a characteristic RH known as efflorescence relative humidity (ERH). The DRH value is dependent on the temperature and the properties of the solid (Mauer & Taylor, 2010). Below the DRH the crystalline solid surrounded by water vapor is the thermodynamically stable phase, whereas above the DRH the aqueous solution is the most stable phase (Martin, 2000). The deliquescence phenomenon has recently been reviewed by Mauer and Taylor (2010).

A DRH value of 95% at 25°C has been reported for both α -lactose monohydrate and β -lactose. The a_w values of a saturated solution of these ingredients at 25°C are 0.99 and 0.97 for α -lactose monohydrate and β -lactose, respectively (Salameh et al., 2006). These values are so high that complete deliquescence is rarely the relevant mechanism for lactose caking. However, the variations in DRH with temperature follow changes in solubility (Mauer & Taylor, 2010). In general the solubility of a compound increases with increasing temperature, leading to a decrease in DRH (Beyer, Schroeder, & Kissinger, 2014; Braban, Carroll, Styler, & Abbatt, 2003).

b. Significance of deliquescence to caking

When partial deliquescence occurs, the resulting aqueous solution at the surface of the particles can form liquid bridges if the ambient relative humidity is maintained above the DRH (Mauer & Taylor, 2010; Rogé & Mathlouthi, 2003). This is the first stage in the humidity caking process (Billings et al., 2006; Dupas-Langlet, Benali, Pezron, Saleh, & Metlas-Komunjer, 2013). The

second stage is triggered by efflorescence, which takes place if the ambient relative humidity is reduced below the ERH: crystallization then occurs from the highly concentrated aqueous solution accompanied by expulsion of water from the crystallized material. Typically hysteresis is observed between deliquescence and efflorescence, meaning that the ERH is lower than the DRH (Martin, 2000).

Nevertheless, DRH does not need to be reached before significant liquid and subsequent solid bridging occurs. For example, caking induced by liquid bridges in sucrose was found to become significant at a water activity level of 0.8 (Billings et al., 2006) whereas the DRH of sucrose is 85% (Salameh et al., 2006). Caking was probably triggered by capillary condensation and surface dissolution. When drying occurred, the caking strength was two to three times greater due to the formation of solid bridges (Billings et al., 2006). Longer storage periods (up to 20 weeks) produced significant caking in glucose monohydrate (DRH=91%) already at 53% RH (Scholl & Schmidt, 2014a). Moreover, it has been suggested that bridges could solidify even without a decrease in relative humidity due to mass transfer from particles to bridges over time (Kirsch, Williams, Bröckel, Hammond, & Jia, 2011; Scholl & Schmidt, 2014b).

c. Deliquescence lowering

Mixes of different ingredients are very often used in the food industry. When mixing several deliquescent substances one should be aware of the phenomenon of “deliquescence lowering” whereby the DRH of the mix (DRH_{mix}) is lower than the DRH of each single component. Wexler and Seinfeld (1991) have described the theory behind deliquescence lowering of mixtures of inorganic salts based on thermodynamic principles. This behavior has also been observed experimentally in atmospheric aerosols containing organic compounds and sulfates (Brooks, 2002), food and pharmaceutical ingredient mixtures of crystalline sugars, inorganic salts, and organic acids (Dupas-Langlet et al., 2013; Kwok, Mauer, & Taylor, 2010; Salameh et al., 2006). The deliquescence lowering phenomenon requires the different deliquescent ingredients to be in contact (Mauer & Taylor, 2010). Thus, with more ingredients in a blend, the decrease in DRH is limited (Salameh et al., 2006). It is also interesting to note that DRH_{mix} is independent of the composition of the mixture (Dupas-Langlet, 2013; Salameh et al., 2006), though it can be reduced significantly by increasing the temperature (Salameh et al., 2006).

Deliquescence lowering has been reported to cause caking in hygroscopic powders (Dupas-Langlet et al., 2013; Dupas-Langlet, Benali, Pezron, Saleh, & Metlas-Komunjier, 2015). Commercial lactose powder contains small quantities of impurities (no more than 0.3% sulfated ash (Codex Alimentarius 1999)). Deliquescence lowering becomes relevant to the caking issue in commercial lactose if some of the crystalline impurities are deliquescent. Guerrieri et al. (2007) showed in a polymorphic salt model that 1.5% impurities both enhanced moisture sorption below the DRH and decreased the DRH value, regardless of the polymorphic form. If all the impurities

are highly water-soluble, the moisture sorption profile is shaped by the total level of impurities but not affected by varying the individual amounts of impurities (Guerrieri et al., 2007).

d. Influence of amorphous material and polymorphism

Understanding the influence of a small amount of amorphous material on the sorption characteristics of a crystalline powder is critical in order to predict and prevent humidity caking in commercial lactose powder. Using an additive isotherm approach, Bronlund and Paterson (2004) showed that the shape of the sorption isotherm of α -lactose monohydrate was considerably modified by a level of amorphous lactose as low as 0.5% w/w. This prediction was only valid at low water activity levels where crystallization did not occur. Moreover, blends of amorphous compounds and crystalline salts or sugars were reported to present enhanced hygroscopicity compared to the individual compounds. More precisely, synergistic moisture sorption was seen in the blends already at 35% RH below the DRH of NaCl, and deliquescence lowering was also evidenced. Finally, the T_g of the blends was lower than that of the individual amorphous products after equilibration at the same RH and temperature (Ghorab, Marrs, Taylor, & Mauer, 2014; Ghorab, Toth, Simpson, Mauer, & Taylor, 2014).

Even when a powder is 100% crystalline, different polymorphs are often present. The moisture sorption characteristics and caking profile vary from one polymorph to another, as shown for lactose (Listiohadi, Hourigan, Sleight, & Steele, 2008). The polymorphic composition can change during storage, depending on the temperature and humidity conditions. Hydrate formation in glucose was not shown to cause caking but it might influence the strength of the bridges formed between particles (Scholl & Schmidt, 2014a).

e. Influence of milling and fines

Milling and grinding, which are frequent processes in the food industry, affect the moisture sorption properties of the final product in competing ways. On the one hand, smaller particles have an enhanced specific surface area to exchange moisture with ambient air. Moreover, the milling operation has been reported to trigger formation of amorphous material known to be more hygroscopic than crystalline powder (Listiohadi et al., 2005b). On the other hand, Bronlund and Paterson (2004) measured increased moisture sorption in unmilled lactose compared to milled lactose and explained it by a broader particle size distribution, resulting in a greater packing density in unmilled lactose. More capillaries can be formed when the particles are closer, thereby enhancing capillary condensation and moisture sorption.

The presence of fine crystals in a powder bed has been shown to increase the water sorption of sugars and their ability to cake by acting as binders between crystals (Rogé & Mathlouthi, 2003; Scholl & Schmidt, 2014a). The higher caking tendency of the fines in unmilled lactose can be explained by a greater degree of amorphicity (Rogé & Mathlouthi, 2003), an extended specific

surface area available for the adsorption of moisture, and increased capillary condensation due to more contact points and smaller capillaries allowing liquid bridging at lower relative humidity (Scholl & Schmidt, 2014b).

In conclusion, a critical aspect in the prevention of humidity caking is the thorough characterization of the powder. The presence of different polymorphs, amorphous material and impurities can influence the sorption properties of a powder and thereby the storage stability against caking. The amount of fines should also be controlled as they enhance the moisture sorption of the whole powder bed. In addition, they affect the packing density of the powder, which is an important parameter in the caking process as explained below.

1.3.2.3. Mechanical Caking

Mechanical caking can be defined as powder consolidation due to mechanical pressure. As a rule, the flowability of a powder depends on the adhesive forces between the individual particles. Liquid bridges, which are usually the dominant adhesive forces in a moist powder and already described above, are not considered here.

a. Importance of Van der Waals interactions

In a dry powder the Van der Waals interactions are the strongest (Schulze, 2008b). In contrast, the electrostatic forces are often overlooked in relation to the caking issue since the particles are in continuous contact (Hartmann & Palzer, 2011). Van der Waals interactions are intense when distances between particles are short but decrease rapidly with increasing distance. Thus, when powder particles come closer to each other due to mechanical pressure (e.g. packing), cohesion increases in the powder. Moreover, this rearrangement of the particles leads to the multiplication of contact points and an extension of the contact surface. As a consequence, some particle parameters such as particle size and shape, and deformability, strongly influence mechanical caking through the number of contact points. Although smaller particles can be rearranged more effectively in terms of contact points, Van der Waals interactions decrease with decreasing particle size.

b. Calculation of the consolidation stress

To be able to investigate and predict mechanical caking, it is necessary to estimate the consolidation stress acting on the powder under the relevant process conditions. Here it should be borne in mind that calculation of the stress differs according to the system under consideration, whether the bottom of a silo or a bag. Roberts (1883) and Janssen (1895) demonstrated more than a century ago that, from a certain filling height, the stress at the bottom of a silo remains independent of height (Roberts, 1883), as the silo walls support the weight of the powder by friction (Janssen, 1895). Janssen (1895) also developed an equation which allows calculation of the

vertical stress in a silo at a given powder height. This equation, known as the “Janssen equation”, is still used today in the design of silos (Schulze, 2008b).

Mandato et al. (2012) measured the stress distribution of a laterally confined semolina bed under static conditions. Interestingly the local stress profile (measured at different positions in the cell) was found to differ from the global stress profile (over the whole horizontal surface) as measured by Janssen (1895). The authors identified a critical length (λ_c) which seems to correspond to the depth from which the force network percolates to the side walls. Deeper than λ_c , the vertical stress is not horizontally uniform, and at a short distance from the side walls it is shielded by the side walls to some extent.

The approach is different when storage of a powder in Flexible Intermediate Bulk Containers (FIBCs), also called Big Bags, is considered. As the sides of a Big Bag are flexible, they cannot support the weight of the powder as silo walls do (Schulze, 2008b). In this case the pressure inside the powder bed increases linearly with depth, and the bottom of the Big Bag is the most consolidated part. The same applies to powder stored in sacks stacked on pallets. The total height of the pile should be used to calculate the maximum pressure applied to the powder. For example, for a powder with a bulk density of $980 \text{ kg}\cdot\text{m}^{-3}$, the maximum vertical stress at the bottom of a one meter high Big Bag is $\sigma_v = 9.6 \text{ kPa}$ (Schulze, 2008b).

Caking can therefore occur in a dry environment as a consequence of mechanical pressure. However, pressure is more often an aggravating factor rather than the main cause of caking. Röck and Schwedes (2005) tested the effects of consolidation time, relative humidity and consolidation stress (3.5 to 11.5 kPa) on particle cohesion in ammonium chloride. They concluded that powder consolidation was mainly influenced by time and relative humidity. When these two parameters were kept constant, the caking tendency was influenced only in a limited fashion by consolidation stress.

In conclusion, caking cannot be avoided by controlling the mechanical pressure in the powder bed alone. The pressure threshold for caking to occur is highly dependent both on the ambient conditions and on particle properties (e.g. particle size and shape). Nevertheless, it is an important parameter to be taken into account. A common situation is strict control of the environmental conditions in a warehouse to ensure that a single Big Bag will not cake. However, in the case of unexpectedly high stocks, stacking the pallets is likely to take place. This will multiply the number of contact points between particles at the bottom of the pile and can lead to significant hardening of the powder. Understanding of common operations and worst case scenarios during storage in silos or bags is therefore essential to characterize and control the caking ability of a product.

1.3.3. Additional information

This section summarizes the most recent papers investigating various aspects of caking, and published after the publication of the review paper¹ in *Trends in Food Science and Technology* (cf. page 4).

1.3.3.1. Amorphous caking

Caking in amorphous powders has been the focus of a recent review, which explains the modeling to predict viscous sintering leading to cake formation. Analytical and numerical approaches to solve the models are also presented (Kamyabi, Sotudeh-Gharebagh, Zarghami, & Saleh, 2017). Fitzpatrick et al. (2017) combined measurement of cake strength with visual assessment of two particles to investigate the caking behavior of binary mixes of sticky and non-sticky food powders. Caking was not observed for sticky powder mass fractions below 20%. Cake strength varied depending on the type of sticky and non-sticky powder used in the mix. These differences were explained by the sticky powders ability to deform and flow to contact points. Recent studies (Fan & Roos, 2016, 2017) introduced a strength parameter, S, to measure the structural stability of lactose systems above their glass transition. The strength parameter is derived from a WLF model-based analysis of structural relaxation times. It can be applied more generally to amorphous sugar containing mixtures to control structure formation in food processing and stability of the resulting products.

1.3.3.2. Humidity caking

A recent paper focused on the role of capillary condensation in humidity caking (Afrassiabian, Leturia, Benali, Guessasma, & Saleh, 2016). The study was limited to smooth, spherical, equal-sized and non-soluble particles. The particle size, the contact angle and the particle arrangement all influenced the onset and extent of capillary condensation and the resulting adhesive forces. However, capillary condensation was shown to play a significant role only for sub-micronic powders within the frame of the study. Several aspects of the deliquescence phenomenon have also been investigated. Deliquescence kinetics of crystalline ingredients and blends were determined (Li, Taylor, & Mauer, 2016). The presence of a common ion in a blend of crystalline ingredients was demonstrated to limit deliquescence lowering (Allan, Taylor, & Mauer, 2016). A comparison of methods to determine the deliquescence point of single ingredients and blends was performed (Allan & Mauer, 2016). In addition, the influence of the drying RH on efflorescence after partial deliquescence was investigated for sucrose (Samain, Dupas-Langlet, Leturia, Benali, & Saleh, 2017). Contrary to the sorption step, drying kinetics were not linear with a faster water loss at the beginning. For RH above 60%, the closer to DRH the drying RH was, the slower the drying. On the contrary, the drying trend was the same for all RH investigated below 60%. These water uptake and loss rates measurements also provided a new method to determine DRH.

1.3.4. How to characterize caking? (Paper¹)

Caking can present as a few agglomerates of various sizes in an otherwise free-flowing powder bed through to a complete Big Bag or silo being as hard as a stone. With such a wide field of applications, developing a universal method to characterize the caking ability of any powder is a difficult task. Another constraint is time. Caking is usually a slow process which can take days or even months under common industrial conditions. On the other hand, any measurement method should be quick to apply, especially if it is to be used as quality control in an industrial setting. A long period of storage of a sample before analysis is therefore not an option.

Several methods are used nowadays to characterize caking, from simple visual qualitative ranking (e.g. Scholl & Schmidt, 2014a) to analysis of the rheological properties of the powder (e.g. Descamps et al., 2013). Listiohadi et al. (2005b) briefly reviewed and categorized the methods available in the literature in five groups: flowability measurements, crushing strength measurements, shear and tensile strength measurements, morphological examinations, and other miscellaneous methods. The most useful methods for the food and pharmaceutical industries are presented below to guide the choice of a method, together with the most important features to be taken into consideration.

1.3.4.1. Flowability measurements

Usually quick and easy to perform, flowability measurements are extensively used in industry. The methods to characterize flowability were reviewed by Juliano and Barbosa-Cánovas (2010). Among others, they include the angle of repose, funnel testers and measurement of the tap density to calculate the Hausner Ratio. However, care should be taken in the interpretation of the results. Although they are linked, caking and flowability are two different powder properties. Caking obviously leads to reduced flowability but a powder with impaired flowability will not necessarily cake (Juliano & Barbosa-Cánovas, 2010). Poor flowability indicates strong particle-particle interactions which do not always include liquid or solid bridges. The tests for flowability are of no use for a caked powder as, by definition, the powder no longer flows. Nevertheless, the onset of caking is seen as a decrease in flowability, which can justify the use of such tests to characterize caking.

1.3.4.2. Compression tests

Cake strength can be investigated using simple uniaxial compression tests (UCT) (Chávez Montes, Santamaría, Gumy, & Marchal, 2011). A hollow cylinder with frictionless walls is filled with powder. The powder sample is then stored for a defined time, under fixed temperature and humidity conditions. A weight can also be placed on the sample to generate mechanical pressure. When the storage time has elapsed, the cylinder is removed and the cake formed is crushed with a compression plate. The force required to break the cake gives an indication of the cake strength.

There are several variants of this test. The powder can be compressed at the beginning to obtain a cake which is then stored before being crushed (Listiohadi et al., 2008). This method, close to tableting, is not representative of the reality where caking is triggered by a combination of applied stress and environmental conditions. The UCT requires a cake to be formed during storage to be able to measure cake strength. If the caking ability of the powder is low under the conditions investigated, the cake is too fragile to stand by itself after removal of the cylinder (Chávez Montes et al., 2011). Extrusion of the cake from the cylinder can also disturb the weak bonds between the particles and transform a consolidated mass into a free flowing powder (Calvert et al., 2013). In such cases, it is still possible to assess the compressive strength of the powder by penetrating the powder sample inside the cylinder (J. Bronlund, 1997; Renzetti, Voogt, Oliver, & Meinders, 2012).

1.3.4.3. Shear tests: procedure, application and comparison with compression tests

To overcome the shortcomings of the UCT, time consolidation tests with shear testers can be performed. The Jenike Shear Cell, the first translational shear cell developed by Jenike in the 1960s, is nowadays an industrial standard (Carson & Wilms, 2006; Schulze, 2008b). Shear testers can be used to measure both powder flowability and caking. The shear testing procedure, described in detail by Schulze (Schulze, 2008b), is represented in Figure 11.

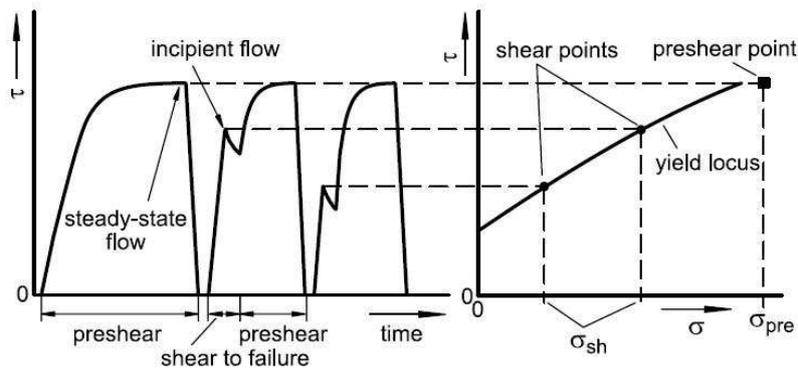


Figure 11: Measurement of a yield locus by preshear and shear to failure with a ring shear tester (Schulze, 2008b).

Briefly, the powder sample is preconsolidated under normal stress σ_{pre} and sheared until it reaches steady-state flow. This first step ensures that the stress history of the powder is erased. Then the normal stress is lowered and the sample is sheared to failure. From a shear-to-failure series at different normal stresses, a yield locus curve $\tau = f(\sigma)$ can be obtained. The next step consists of drawing Mohr stress circles which represent the stresses in all possible cutting planes within a powder element. As represented in Figure 12, it is then possible to deduce from the yield locus the consolidation stress (σ_1) and the stress leading to failure of the powder, called unconfined yield strength (σ_c). For most powders, σ_c increases with the use of higher consolidation stress (Schulze, 2008b), meaning that the powder gains in strength under increasing consolidation stress. Saw et al. showed this relationship for several lactose powders using shear testing (Saw, Davies, Jones,

Brisson, & Paterson, 2013). The ratio of σ_1 to σ_c (*ffc*) is a measure of the flowability of the powder: the higher the *ffc*, the better the powder flows (Schulze, 2008b). The consolidation stress σ_1 is proportional to σ_{pre} . Therefore σ_{pre} needs to be chosen so that σ_1 is representative of the process conditions.

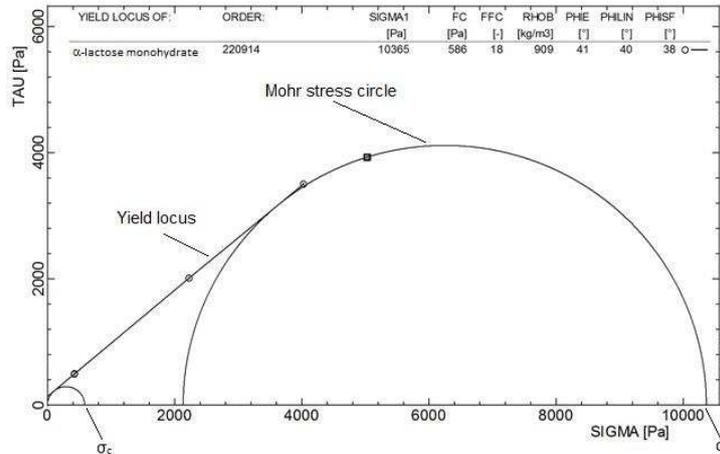


Figure 12: Output of a test for the measurement of flowability of α -lactose monohydrate with a Schulze ring shear tester.

Shear testing methods have become standard in powder flow characterization (Carson & Wilms, 2006) and several articles have been published in which a shear cell was used to measure powder flowability (Fitzpatrick et al., 2007; Rogé & Mathlouthi, 2003; Vasilenko, Koynov, Glasser, & Muzzio, 2013). For example, Saw and coworkers (Saw et al., 2013; Saw, Davies, Jones, & Paterson, 2014) investigated the influence of consolidation stress (σ_1) and particle diameter on bulk density and estimated cohesion in a wide range of lactose powders. They showed that cohesion is proportional to particle surface area per unit volume of the powder bed and dimensionless preconsolidation stress (Saw et al., 2013).

In a time consolidation experiment used to quantify caking, the first step is to measure the initial yield locus of the powder at the consolidation stress of interest, as described above. Then the sample is presheared until it reaches steady-state flow, before storage under defined conditions. During storage, the shear cell is loaded with the same consolidation stress as for preshear. Finally the sample is sheared to failure to obtain a time yield locus and the flowability value after storage, which provides a quantification of the caking ability of the powder under the storage conditions selected. For example, Descamps et al. (2013) used a ring shear tester to measure the cake strength of maltodextrin DE 21. They clearly demonstrated strong caking of the powder stored at or above its glass transition temperature for up to a week. According to Cleaver et al. (2004), shear cells are especially useful for measuring cake strength when the cake is plastic. Characterization of rigid cakes can be more challenging.

Shear tests and UCT have the advantage of providing a truly quantitative measurement of cake strength at a defined consolidation load (Descamps et al., 2013). On the other hand, both techniques are time-consuming and reproducibility can be difficult to achieve (Fitzpatrick & Descamps, 2013). A common limiting factor of time consolidation experiments including shear cells and UCT is the low exchange of moisture between the sample and the surrounding air during the consolidation phase, because cells are almost closed (Hartmann & Palzer, 2011). According to Hartmann and Palzer (2011), one strength of the ring shear cell in comparison to the UCT is being able to measure the yield locus of the powder and to consolidate the sample until steady state flow is reached. Fitzpatrick and Descamps (2013) obtained a good correlation between the two techniques of assessment of cake strength using a single scaling factor. They performed their measurements in triplicate but unfortunately did not state the standard deviation associated with the results. However, in a previous article they reported a reproducibility level of 5% associated with the uniaxial powder cake strength tester (Fitzpatrick, O'Callaghan, & O'Flynn, 2008). Others stated that ring shear cells provide a more accurate and reproducible measurement of caking (Hartmann & Palzer, 2011).

1.3.4.4. Powder rheometer

A novel instrument called a powder rheometer has been the focus of much interest in recent years, both in academia and in industry. A well-known tester in this category of equipment is the FT4 Powder Rheometer (Freeman Technology, Tewkesbury, UK) which has been used in many studies to measure flowability (Fu et al., 2012; Hare et al., 2015; Leturia, Benali, Lagarde, Ronga, & Saleh, 2014; Sandra Mandato, Ruiz, & Cuq, 2013). The main difference from the other tests presented above is that the powder rheometer operates under dynamic conditions (Freeman, 2007). A blade is rotated and moved down into the sample while the rotational and translational resistances are measured. The total flow energy can be calculated from the combination of these two values, and represents the resistance of the powder to flow while in motion. The device has many additional features such as quantification of the influence of air, consolidation and flow rate on flowability, shear testing, measurement of density, compressibility and permeability (Freeman Technology, 2015). The measurements have been found to be quick and reproducible and the results correlate well with those originating from traditional characterization techniques. On the other hand, difficulty in interpreting the data is often pointed out as they depend on many different physical properties and environmental parameters (Leturia et al., 2014).

Only a few articles have focused on characterization of caking with a powder rheometer. Chávez Montes et al. (2011) investigated caking in cocoa beverage powders with a UCT and a powder rheometer. They measured the force needed to break the cake with the UCT and the energy required to move the rotating blade down into the powder cake with the powder rheometer. Both methods were able to differentiate between the samples, but the powder rheometer was preferred

for its ability to investigate a broader range of environmental conditions (Chávez Montes et al., 2011). Brockbank et al. (2014) quantified caking from the difference in flow energy measured in the sample before and after caking. They evidenced the formation of a crust at the powder surface for some powders, showing that caking does not always occur uniformly in a powder sample. Most of the other techniques used to quantify caking provided an average value for the whole sample and thus could not identify variations in caking through the sample (Brockbank et al., 2014).

1.3.4.5. Additional methods

Other methods used to characterize caking include the caking index and measurement of the avalanche angle (Lipasek, Ortiz, Taylor, & Mauer, 2012). The caking index is defined as the weight fraction of a powder which remains on a sieve with a defined opening size allowing free-flowing powder to pass through (Aguilera et al., 1995). According to Cleaver et al. (2004), this method works well for comparison purposes and for quality control. However, a systematic analysis is needed as some erosion of the powder cakes occurs on the sieve, depending on the sieving conditions. Moreover, the caking index value indicates the extent of cake formation but does not provide any information about cake strength. The avalanche angle is the angle of a powder just before it avalanches within a rotating cylinder. This method was developed to measure the flowability of cohesive powders (Alexander et al., 2006) and it is suitable to detect small differences in agglomeration. On the other hand, it does not perform well for analysis of strongly caked powders (Lipasek et al., 2012).

Finally, microscopy was recommended by Aguilera et al. as a characterization tool for caking as early as 1995 (Aguilera et al., 1995). For example, structural changes in amorphous particles in different temperature and humidity conditions were followed in real time using videomicroscopy. A caking index could be derived from the changes in the projected area of the particles (Saragoni, Aguilera, & Bouchon, 2007). Microscopy has however mainly been used to complement the results obtained with other methods. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been the two techniques of choice. SEM enabled Cleaver et al. to observe a well formed crystal forming a bridge between two particles as a result of addition of water to the powder sample and temperature cycling (Cleaver et al., 2004). In addition, the formation of a sinter bridge between two maltodextrin particles upon exposure to high relative humidity could be followed with a light microscope (Fitzpatrick et al., 2010). Sinter bridges in caked, predominantly amorphous, food powders have also been evidenced by SEM images (Hartmann & Palzer, 2011).

Several authors have used microscopy to visualize particle surfaces (Prime et al., 2011) and especially to track changes on the surface due to water sorption (Bode et al., 2015; Leaper & Prime, 2013; Murrieta-Pazos et al., 2011). Environmental scanning electron microscopy (ESEM) is particularly suitable for this purpose as the relative humidity can be controlled inside the chamber of the microscope, allowing the observation of surface modifications in real time (Watling,

Elliott, Scruton, & Cameron, 2010). SEM micrographs have been used to show a decrease in the amount of fines on the surface of lactose particles after exposure to 75% RH for 6 months (Watling et al., 2010). The overall surface of boric acid particles on AFM images was found to become smoother after exposure to humid air for 48 hours (Cleaver et al., 2004).

1.3.4.6. Characterizing caking in powders with low caking tendency

Measurement of caking in powders which have a limited tendency to caking is challenging. The test conditions should reflect the reality of the process or storage if the results are to be used in an industrial context. However, these conditions are often too mild to make the powder cake in a reasonable time. Some researchers have therefore attempted to develop accelerated caking tests. Cleaver et al. (2004) accelerated the caking process by adding a predetermined amount of water to the sample and subjecting it to temperature cycling. The caking index showed a steady increase with time of storage. The amount of water to be added was chosen according to the moisture sorption isotherm. Calvert et al. (2013) developed a tester in which conditioning air was percolated through the powder sample for rapid equilibration of the sample with the desired environmental conditions. The powder was compacted using weights and the whole tester was placed in a temperature controlled chamber. The authors were able to differentiate between environmental conditions during consolidation from the cake strength measured after only 24 hours consolidation at realistic storage conditions. The performance of the tester was however assessed on a highly hygroscopic and deliquescent powder. It is likely that realistic storage conditions for 24 hours would not be sufficient to discriminate between the caking ability of less hygroscopic powders. If more drastic conditions are used in an accelerated caking test, it should be borne in mind that the chemical state of the powder may be modified (e.g. hydrate formation) thereby preventing the results from being applied to an industrial situation (Calvert et al., 2013). The development of an accelerated caking test for use on commercial lactose powder will be the focus of chapter 8.

1.4. Conclusion

Among the whey ingredients, lactose powder now represents a key product both in terms of revenue and volume. Driven by the growing demand for infant formula, lactose production is increasing. Lactose has also many other applications both in the food and pharmaceutical industries due to its broad range of interesting properties. Commercial lactose consists in α -lactose monohydrate which is the most stable form of the lactose molecule, characterized by a low hygroscopicity. Lactose powder is therefore considered to present a good stability. However, occurrences of caking, where the powder spontaneously agglomerates to form lumps, have been reported. Caking is a ubiquitous problem which is encountered in various powder handling industries. Yet, characterization of caking is still a challenge. Multiple caking mechanisms have been reported in the literature and can be specific to the product under consideration. An overview

of the parameters which need to be taken into account in the caking process for lactose is presented in Figure 13.

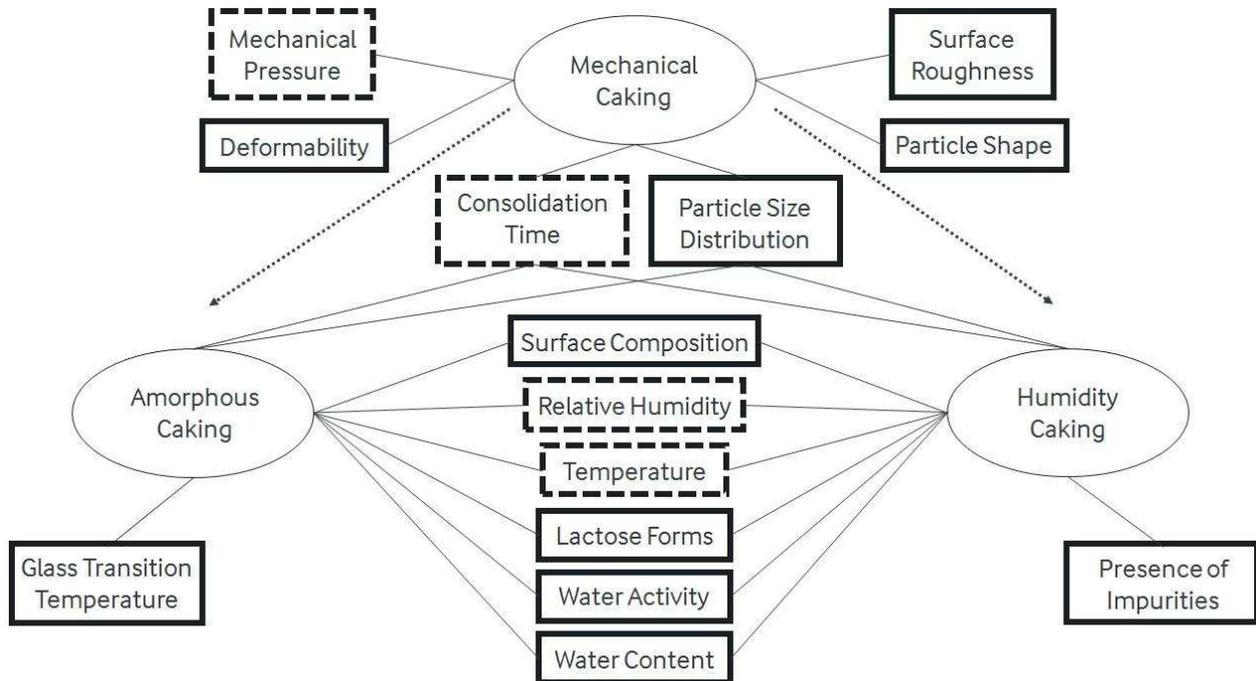


Figure 13: Overview of the three caking mechanisms (in the ovals) together with the internal (in solid line rectangles) and external (in dotted line rectangles) parameters which can influence caking in lactose. The links between the mechanisms and the parameters show which mechanisms each parameter influences significantly. The arrows show that mechanical caking is not independent but influences the other two mechanisms.

Most parameters affect more than one of the three mechanisms proposed. Mechanical caking also influences amorphous and humidity caking by bringing the particles closer to each other, which makes its influence even more complex. The presence of impurities (including amorphous material), the particle size distribution in commercial crystalline lactose and the water activity of the powder appear to be the most critical internal parameters needing to be controlled in order to prevent caking in lactose powder. This cannot be done without a thorough understanding of the production process.

Chapter 2 – Aim and research question

Summary

This chapter aims at pointing out the benefit that lactose producers would gain from a better knowledge of the caking mechanisms. Based on the review of the caking mechanisms, the complexity of the caking phenomenon in lactose production and storage is also highlighted. All the major objectives of the project are listed in this chapter. As the PhD project was funded by a company, applied objectives were defined. However, achieving the scientific objectives was a prerequisite to complete the applied ones. Finally, our research strategy is described: it consists in focusing on the process – product relationship in order to control the parameters that determine the caking tendency of the product.

The objectives of this chapter were to:

- Define the context of the study
- List the scientific and applied objectives
- Present the innovative strategy taking the production process as a starting point

2.1. Context and research question

2.1.1. Industrial context

Driven by growth in infant formula market, lactose production is increasing. In the highly competitive dairy market, the product quality is an essential differentiation factor. Product quality is a broad term which includes the microbiological load, the chemical composition and the physical properties. The product stability is another focus point of dairy manufacturers. Along with other whey ingredients, lactose powder is indeed increasingly sold to customers located all over the world, where product stability can be challenged due to variability in the environmental conditions (e.g. high RH and temperature) during transport and storage.

In this context, caking of lactose powder can lead to significant economic loss as it reflects limited stability, is associated with poor quality and leads to difficult handling in the formulation process. As one of the world's leading supplier of lactose, AFI wants to achieve a better understanding of the caking mechanisms to secure a non-caking product for its customers. Improving the product stability against caking would also allow AFI to explore new markets where environmental conditions can be challenging.

2.1.2. Scientific context

As explained in section 1.3, caking is a complex scientific problem. Several caking mechanisms have been reported in the literature and their prevalence depends on the powder under consideration. Moreover, numerous product intrinsic characteristics such as hygroscopicity, compressibility, amorphous content and many more can influence caking. In the lactose production process presented in section 1.2.3, various process parameters can be adjusted at each step and will influence the properties of the final product and its ability to cake. In addition, extrinsic factors such as humidity, temperature and mechanical pressure also largely condition the caking behavior of the powder. This explains the relative randomness associated with caking. For example, a powder which cakes when sent to Asia can remain free flowing when sent around Europe. Moreover, characterization of caking is challenging given the broad definition of the caking phenomenon and the potentially long timescale associated with the development of caking. Qualitative observations are still the method of choice in industrial settings.

Last but not least, it is interesting to mention that crystalline lactose is generally considered to be reasonably stable given its low hygroscopicity. Yet, lactose caking is not rare according to industrial reports. The reasons behind caking of this product are therefore far from obvious and this challenge naturally leads to the following research question for our study:

“What are the mechanisms leading to caking in lactose powder?”

2.2. Objectives and strategy

2.2.1. Scientific and applied objectives

The objectives for this PhD project were two-sided with some being purely scientific and others being applied in industrial settings. Achieving the scientific objectives was a prerequisite to complete the applied ones.

The scientific objectives were as follows:

1. Develop a method which can discriminate samples according to their caking tendency.
2. Highlight the most important intrinsic parameters in relation to caking in lactose powder.
3. Understand the mechanisms behind caking due to variations in the key intrinsic parameters in relation to caking, as highlighted in point 2.

The applied objectives were as follows:

4. Investigate the process steps which are key to control the main product parameters responsible for caking in lactose powder (in relation to point 2).
5. Give recommendations to the dairy industry on how to control the critical process steps in order to limit the caking tendency of the final product (in relation to points 2 and 3).
6. Develop a method to predict the caking tendency of a lactose sample before it is shipped to a customer.

2.2.2. Strategy: focus on the relationship between the production process and the product properties

The role of several parameters in lactose caking has been investigated by others: the different lactose polymorphs (Listiohadi et al., 2008), amorphous lactose (Listiohadi et al., 2005c) and the milling procedure (Listiohadi et al., 2005a). The effects of particle size and temperature on the moisture sorption characteristics of lactose powder (Bronlund & Paterson, 2004) and temperature-induced moisture migration in a lactose bag (Paterson & Bronlund, 2009) have also been examined.

However, the product properties are determined by the process parameters on the production line. The strength of the project was to originate from a collaboration between a major lactose producer and two academic research groups having complementary core competences. For this reason, an innovative approach was adopted in this PhD project, namely to focus on the link between the process and the product in order to control the caking tendency of the lactose powder. The first task was therefore a sampling of the product on the process line combined with a thorough physicochemical characterization of the samples. Typical values for the product chemical composition and physical properties were thus obtained. This work will not be included in this

thesis for confidentiality reasons. It provided however the basis for the understanding of the production process and how the different steps could influence the parameters of the final product. It should be noted that a choice was made at that point to limit the research to the unmilled lactose product.

The results of the sampling combined with the literature review led us to focus on the following two parameters as critical for the caking issue: the content of impurities and the particle size distribution. A study on a pilot scale investigated the influence of these two parameters on caking (chapters 4 and 5). A method to characterize caking was developed as part of this work.

Then the focus was shifted to the production line again to investigate how we could apply the results on the industrial scale (chapter 6). As humidity was found to play a crucial role in caking, the control of humidity in the powder along the process was investigated (chapter 7). Finally, we addressed a urgent need in the dairy industry, namely the development of an accelerated caking test to predict the caking tendency of a powder (chapter 8).

Part 2

Understanding the Main Caking Mechanisms in Lactose Powder.

Study on a Pilot Scale

Chapter 3 – Materials and methods

Summary

This chapter aims at describing the materials and the methods used in the experiments. Samples were either produced on a pilot scale or obtained directly from the process line at different steps. They were then characterized for their chemical composition in impurities (i.e. components other than crystalline lactose) and various other chemical and physical intrinsic properties. The experimental setup and procedure for the caking tests are also described. Materials and methods used to produce the results of chapters 4 and 5, that are presented here, have been published as part of Paper² and Paper³ in *Journal of Food Engineering*.

The objectives of this chapter were to:

- Explain how powders were obtained on pilot and production scales
- Present the methods used to characterize the chemical and physical intrinsic properties of the lactose powders
- Describe the experimental procedure for the caking tests developed

² Published as Carpin, M., Bertelsen, H., Dalberg, A., Roiland, C., Risbo, J., Schuck, P., & Jeantet, R. (2017). Impurities enhance caking in lactose powder. *Journal of Food Engineering*, 198, 91–97. <https://doi.org/10.1016/j.jfoodeng.2016.11.013>

³ Published as Carpin, M., Bertelsen, H., Dalberg, A., Bech, J. K., Risbo, J., Schuck, P., & Jeantet, R. (2017). How does particle size influence caking in lactose powder? *Journal of Food Engineering*, 209, 61–67. <https://doi.org/10.1016/j.jfoodeng.2017.04.006>

3.1. Introduction

As the research strategy developed in the PhD focused on the link between the process and the product, it was crucial to sample the powder directly on the production line. However, in order to gain a better understanding of the caking mechanisms, lactose powders should also be produced on a pilot scale to induce controlled variations in the critical product properties. The pilot production would allow to fulfill the scientific objectives whereas the sampling on the production line aims at achieving the applied ones.

One of the main scientific objective of the PhD project was to develop a method that can discriminate samples in terms of their caking tendency. As described in chapter 1 (section 1.3.4), various methods can be used for the purpose. In this PhD project, focus was made on ring shear testing.

3.2. Materials - Production and sampling

3.2.1. Production on a pilot scale (chapters 4 and 5)

3.2.1.1. Lactose powders with different washing grades

Decalcified and decolored ultrafiltered whey permeate was obtained from Arla Foods Ingredients (Viby J, Denmark). The solids content was raised to 60% in a Centritherm CT2 evaporator (Flavourtech, Griffith, Australia). For lactose crystallization control, the concentrate was cooled in a tank from 79°C to 11°C in about 18 hours. Then, a Lemitec MD80 laboratory decanter centrifuge (Lemitec GMBH, Berlin, Germany) was used to produce five lactose powders with different washing grades. The slurry was first run through the decanter once without water for a pre-wash (Wash 0). This prewashed slurry was then mixed with water at different water / lactose slurry w/w ratios: 1/3 (Wash 0.3), 1/2 (Wash 0.5), 1/1 (Wash 1) and 2/1 (Wash 2). The different washing grades of the prewashed slurry were run through the decanter once more, and then dried in an Anhydro SFD 47 spin flash dryer (SPX Flow Technology, Søborg, Denmark) with an inlet temperature of $105 \pm 2^\circ\text{C}$ and an outlet temperature of $85 \pm 3^\circ\text{C}$. Finally, the powders were packaged in two layers of plastic bags and a Kraft paper bag before transportation to the analysis laboratory where they were sieved and poured into airtight plastic containers of various sizes to minimize the headspace. The powders were stored at 20°C prior to analysis.

Pharmaceutical grade lactose (Lactochem® Crystals, batch number 663108) was obtained from DFE pharma (Goch, Germany) for comparison with the experimental lactose powders produced with different washing grades.

3.2.1.2. Amorphous lactose for solid-state Nuclear Magnetic Resonance (NMR) measurements

Pharmaceutical grade lactose was mixed with distilled water to make a 15% (w/w) lactose solution which was left to stand at 40°C for one hour. The solution was then cooled down to 20°C and spray dried on a pilot-scale spray dryer (GEA Niro A/S, Mobile Minor Dryer (MMD), Soeborg, Denmark) in order to obtain amorphous lactose. The inlet and outlet air temperatures were 200°C and 90°C, respectively, and the feed flow rate was 40 mL.min⁻¹.

3.2.2. Sampling on a production scale (chapters 6, 7 and 8)

Powder samples were obtained from three different production sites, named production site A, B and C in the following. Samples designated as “fluid bed samples” were taken from the powder stream falling from a 2x2 mm sieve placed after the last section of the fluid bed. Samples designated as “finished good samples” were taken from the powder stream falling from a silo to the bag at the packaging station. At both places, an autosampler allowed automatic sampling.

For some powders, the exact sampling point on the process line varied according to the experimental objectives and will therefore be specified in the relevant sections of chapters 6 and 7 where sampling was performed.

3.2.3. Amorphous lactose for mix with crystalline lactose (section 6.2.3)

A 15% lactose solution was stirred for two hours at ambient temperature. The solution was then filtered and the filtrate was divided onto three shelves within the freeze-dryer (LyoBeta, Telstar, Terrassa, Spain). The freeze-drying process involved a freezing step at -30°C, a primary drying step for 26 hours employing successively the temperatures of -10°C, 20°C and 25°C and vacuum pressure of 500 µbar, then secondary drying for 8 hours at 25°C and atmospheric pressure. The product obtained was rapidly crushed and placed in desiccators containing silica gel.

3.3. Post processing of samples

3.3.1. Sieving

The lactose powders of different washing grades were sieved through a series of standard testing sieves (80, 160, 250, 355 and 500 µm) stacked in a sieve shaker (Retsch sieve shaker AS 200, Retsch GmbH, Haan, Germany) in order to obtain different size fractions. The sieving was performed in batches of 500 g of powder for 5 minutes at a 1 mm amplitude.

To investigate the effect of the span on caking (section 5.3), two different size fractions of Wash 0.3 powder were produced by sieving; one by sieving Wash 0.3 through 100 and 355 µm sieves and another one by sieving Wash 0.3 through 160 and 250 µm sieves.

3.3.2. Aeration

Aeration was performed in a pilot fluid bed (MINI-LAB, Diosna, Osnabrück, Germany) (Figure 14) equipped with a dehumidifier (Cotes A/S, Slagelse, Denmark) which allowed to operate at a lower RH than the ambient RH. Air sent into the fluid bed was around 10% RH, with a flow rate of $20\text{m}^3\cdot\text{hour}^{-1}$. Air temperature was 20°C . Air was blown through the powder mass from the bottom of the fluid bed. At the air outlet, the fluid bed was equipped with filters which were flushed by air sent from the inside in order to remove any powder accumulated on them. Time between two air inlets through the filters to flush them was eight seconds.

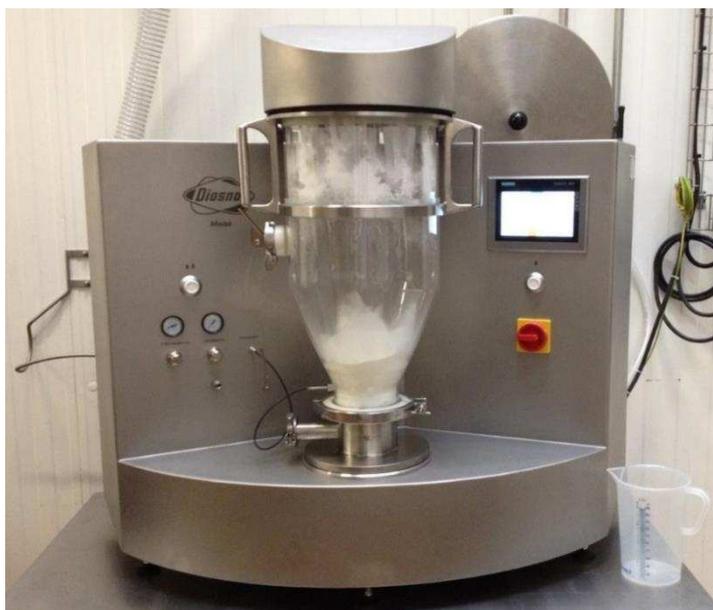


Figure 14: Aeration of lactose powder in a pilot fluid bed (MINI-LAB, Diosna, Osnabrück, Germany).

The powder used for the aeration tests was sampled at the exit of the fluid bed of production site A into plastic bags. The sample size was minimum 2.5 kilos. The powder was then stored at ambient conditions until aeration, which was performed six to seven days after sampling. For each sample, two kilos of powder were placed in the fluid bed for aeration.

After each aeration, minimum two samples were collected in polypropylene containers. Samples were stored at 20°C and 30% RH for at least four days in a climate chamber (MKF 240 (E3.1), Binder, Tuttlingen, Germany) where temperature and humidity could be controlled and programmed.

3.3.2.1. Effect of aeration time (section 7.3.3.1)

As mentioned above, the initial sample size for aeration was two kilos. At the end of the three and six-hours aeration period, the fluid bed was stopped to take two samples corresponding to a removal of approximately 500g of powder, and aeration was continued with the rest of the powder.

3.3.2.2. Effect of continuous aeration vs. discontinuous aeration (section 7.3.3.2)

Discontinuous aeration was started first according to the sequence presented in Figure 15. In total, the powder was aerated for 1.5 hours. As the resting periods were long, the powder was removed from the fluid bed to prevent moisture uptake from ambient air and stored in a closed container in the climate chamber at 20°C and 30% RH.

During the second resting time, another sample of the same powder was continuously aerated for 1.5 hours.

After aeration, all samples were stored in the same conditions and the evolution of RH during storage was compared.

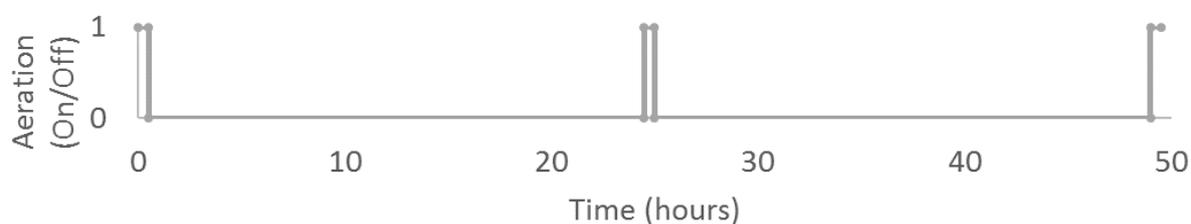


Figure 15: Sequence of 30 minutes aerations followed by 24 hours resting time used for the discontinuous aeration of powder.

3.3.2.3. Effect of a discontinuous aeration with a short resting time (section 7.3.3.3)

Discontinuous aeration was performed first according to the sequence presented in Figure 16. In total, the powder was aerated for four hours. During the resting periods, the powder was left in the closed fluid bed.

Another sample of the same powder was then continuously aerated for four hours.

After aeration, all samples were stored for seven days and the evolution of RH during storage was compared.

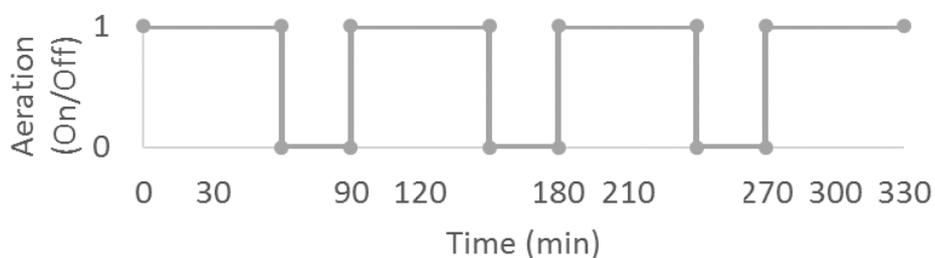


Figure 16: Sequence of 1 hour aerations followed by 30 minutes resting time used for the discontinuous aeration of powder.

3.4. Characterization of the powder intrinsic properties

3.4.1. Chemical composition

3.4.1.1 Samples from pilot production

Protein, moisture (i.e. “free water”) and ash content were determined according to the methods described by Schuck et al. (2012a). Total nitrogen content determined by Kjeldahl with a 6.38 conversion factor will be designated as protein content. Given the filtration steps in the lactose process, it is however unlikely that proteins remain in the final powder. Therefore, impurities formally expressed as protein may more likely be smaller nitrogen-containing components such as peptides and amino-acids. Analysis of moisture and ash content was carried out in triplicate and the protein content was determined in duplicate. The lactose content was then calculated by difference.

3.4.1.2. Samples from the process line

The protein content was obtained by the Kjeldahl method (ISO 8968-3/IDF 20-3, 2004), similarly to the method used for the pilot samples. The method to analyze the ash content was also similar to the one described by Schuck et al. (2012a). The sulfated ash content in commercial samples was analyzed as described in the European Pharmacopeia (EDQM, 2008). The moisture content was determined after drying the sample at 87°C for 16 hours. The total water content, which includes both the free moisture content and the water of crystallization, was obtained by the Karl Fischer titration method (ISO 12779/IDF 227, 2011). Lactose in commercial samples was determined by polarimetry. All chemical analyses on commercial samples were conducted in duplicate.

Individual minerals (calcium, phosphorus, sodium, potassium and magnesium) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Optima 2000 DV (PerkinElmer, Waltham, Massachusetts, USA). The limit of quantification was dependent on sample preparation, which was affected by the powder structure and expected amount of minerals. It is therefore specified in the relevant sections of chapters 6 and 8. Chloride was determined by potentiometry. All minerals were analyzed in duplicate.

3.4.2. Measurement of particle size

The particle size distribution of the powders was measured by laser light scattering using a Malvern Mastersizer 2000 equipped with a Scirocco 2000 dry dispersion unit (Malvern Instruments, Worchestershire, UK).

The span of the distribution was calculated as:

$$Span = \frac{(D_{90} - D_{10})}{D_{50}} \quad (3)$$

Where the diameters D_{10} , D_{50} , and D_{90} represent the particle size at 10%, 50%, and 90% in a cumulative size distribution respectively. The specific surface area was calculated from the surface weighted mean diameter $d_{3,2}$.

3.4.3. Moisture sorption measurements

Sorption isotherms of powders were obtained with a Dynamic Vapor Sorption (DVS) Advantage (Surface Measurement Systems Ltd., London, UK) equipped with a Cahn microbalance. The experiments were carried out in duplicate at a constant temperature (25°C) using a nitrogen flow rate of 200 standard $\text{cm}^3 \cdot \text{min}^{-1}$. Approximately 40 mg of powder was subjected to ramping of RH from 0% to 95% in 10% RH steps with water as solvent. Equilibrium was considered to be reached if the rate of change in mass was less than $0.0002\% \cdot \text{min}^{-1}$.

3.4.4. Particle morphology — scanning electron microscopy (SEM)

The surface morphology of the lactose samples was examined using a scanning electron microscope (SEM, JEOL JCM-6000 - NeoScope II, Tokyo, Japan) operating at 15 kV. Samples were mounted on an aluminium stub and coated with a thin layer of gold (JEOL JFC-1300 auto fine coater) prior to analysis. The photomicrographs were taken at $\times 1,000$ and $\times 400$ magnification.

3.4.5. Solid-state Nuclear Magnetic Resonance (NMR)

^{13}C NMR spectra were obtained using proton decoupling, magic angle spinning (MAS) and cross polarization (CP). The spectra were recorded on a Bruker Avance I WB 300 MHz (7T) instrument (Bruker, Billerica, USA) at ambient temperature according to the method described by Gustafsson et al. (1998), with the following parameters: spinning rate 5 kHz, contact time 2 ms, acquisition time 147 ms, sweep widths 2190 ppm and delay between pulses of 3 s. For each spectrum, about 150,000 transients were cumulated with 49k data points. The spectra were referenced to trimethylsilane (TMS).

3.4.6. Amorphous lactose content (Methods investigated in chapter 6)

3.4.6.1. Modulated Temperature Differential Scanning Calorimetry (MTDSC)

MTDSC measurements were conducted according to the method described by Schuck et al. (2012b). The MTDSC samples were prepared using hermetically sealed aluminium pans. An empty pan was used as a reference. For each powder, three samples were analyzed. The samples were heated from -10 to 140°C using a ramp rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ with a 0.48°C modulated signal

every minute using a modulated differential scanning calorimeter (Q-1000, TA Instruments, New Castle, DE, USA) calibrated with indium (melting point 156.6°C).

3.4.6.2. Dynamic Vapor Sorption (DVS)

See section 3.4.3.

3.4.6.3. RH measurements to detect crystallization

Miniature temperature and humidity data loggers (iButton Hygrochron™ data loggers, DS1923, Maxim Integrated, San Jose, CA, U.S.A) were programmed to record temperature and humidity with a measurement every ten minutes. The data logger was placed directly in the powder (Figure 17). Approximately 250g of powder were necessary to fill the polypropylene container up to the top and thereby minimize the headspace. Commercial crystalline unmilled lactose powder was mixed with amorphous powder produced as explained in section 3.2.3, in order to obtain the following content of amorphous powder (w/w): 1%, 2.5%, and 5%.

Samples were then stored in the climate chamber (see 3.3.2). RH was kept constant at 50% while a temperature program was applied with the objective to trigger crystallization. The temperature was increased from 25°C to 60°C at a rate of 1.3°C per hour.

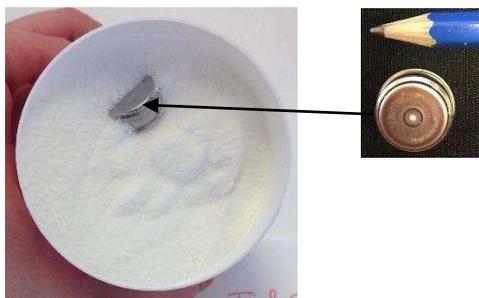


Figure 17: Data logger placed in the lactose powder to record temperature and RH.

3.4.7. Water activity

The water activity was measured with a water activity meter LabMaster-aw (Novasina AG, Switzerland). The temperature in the chamber was set to 25°C for all measurements.

Measurements by data loggers (cf. section 3.4.6.3) were performed by placing the logger directly in the powder in order to record the evolution of RH. Measurements of RH and temperature were automatically taken every ten minutes.

For direct measurements within a powder bag, RH probes (SDL550, Extech instruments, Nashua, USA) were used.

These three instruments use electrical impedance sensors, which consist in a hygroscopic dielectric material placed between a pair of electrodes. Whereas the a_w -meter uses a resistive sensor, data loggers and RH probes use capacitive sensors. The material electrical properties

change when it adsorbs moisture. There is a direct relationship between relative humidity, the amount of moisture present in the sensor, and sensor capacitance or resistance (Rotronic, 2017). Measurements of water activity in section 7.2.2 (Figure 46) were performed on three different batches, which were sampled at the exit of the fluid bed of production site C. The water activity meter was placed in the same room as the fluid bed to minimize delay between production and measurement. For each batch, the powder was sampled directly into the small plastic containers intended for measurement of a_w . Four samples were taken at the same time. The containers were filled completely to minimize headspace and closed. Analysis of the first sample was started right after sampling. The other three samples were analyzed one after another as soon as analysis of the previous sample was finished. The samples were stored at ambient conditions next to the water activity meter until analysis.

Measurements of RH with humidity loggers in section 7.2.2 (Figure 47) were performed on eight samples sampled at the exit of the fluid bed of production site A. For each sample, a data logger was placed at the bottom of a sampling bag which was subsequently filled with minimum 2.5 kg of powder by means of an autosampler. The eight powders came from various crystallizers and were produced over three different days.

3.5. Caking measurement

Caking, also known as time consolidation, was measured with a ring shear tester (RST-XS, Schulze-Schüttgutmesstechnik, Wolfenbüttel, Germany). The measurement procedure has been described in detail by Schulze (2008b).

3.5.1. Primary caking test (chapters 4, 5 and 6)

3.5.1.1. Measurement of the initial yield locus

First, the yield locus of each powder was measured (see Figure 11, section 1.3.4.3) for a normal stress at preshear σ_{pre} estimated as follows:

$$\sigma_{pre} = 0,5 * \sigma_1 \quad (4)$$

With the consolidation stress σ_1 acting on the powder in the Big Bags calculated as follows:

$$\sigma_1 = \rho_b * g * z \quad (5)$$

With ρ_b the bulk density of lactose, g the standard gravity (9.81 m.s^{-2}) and z the height of powder in a Big Bag. Indeed, the consolidation stress was chosen to simulate powder consolidation at the bottom of a Big Bag. The bulk density of commercial lactose was measured in the range $800\text{-}1000 \text{ kg.m}^{-3}$. Thus, for a bag of one meter height, the consolidation stress σ_1 was between 7.8 and 9.8 kPa.

The stress acting on the powder in the shear cells during the consolidation time was mainly induced by the load placed on the lid of the shear cell. In order to obtain the above-mentioned consolidation stress, a load between 1.7 and 2.1 kg had to be applied. Thus, a two kilos load, corresponding to a consolidation stress σ_1 of 9.3 kPa, was considered to be representative of the storage of lactose powder in a Big Bag.

Three points of incipient flow were used to draw the yield locus.

3.5.1.2. Storage

Once the initial yield locus was established, the powder was preconditioned using the same σ_{pre} as above and placed in a closed cabinet in a temperature controlled room at 20°C (Figure 18). Humidity was controlled with saturated salt solutions placed in the cabinet. Sodium bromide was used to obtain 60% RH. Loads of two kilos were applied to the samples through a consolidation bench for the duration of storage. Temperature and humidity data loggers were used to check the storage conditions.

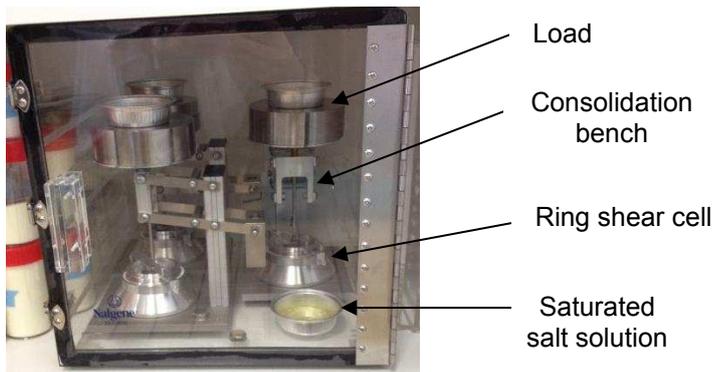


Figure 18: Storage of the shear cells containing lactose powder for measurement of caking.

3.5.1.3. Time yield locus

After storage, the samples were sheared to obtain the time yield locus. From this, the unconfined yield strength σ_c (see Figure 12, section 1.3.4.3) and the ratio of σ_1 to σ_c , called *ffc*, were identified. By definition, a sample with a *ffc* lower than 1 was considered to be caked. Indeed, Jenike (1964) classified powder flowability according to the *ffc* value as follows:

$ffc > 10$: Free-flowing

$4 < ffc < 10$: Easy flowing

$2 < ffc < 4$: Cohesive

$1 < ffc < 2$: Very cohesive

$ffc < 1$: Not flowing

For each powder, the *ffc* was measured in triplicate.

3.5.2. Accelerated caking test (chapter 8)

The initial yield locus was measured as described above (cf. 3.5.1.1). The samples were then stored in a closed cabinet in an oven where temperature was controlled at 50°C. This allowed to control humidity as well, with saturated salt solutions placed in the cabinet. Sodium bromide and potassium iodide were used to obtain 50% and 60% RH, respectively. As for the primary caking test, loads of two kilos were applied on the samples and data loggers were used to check the storage conditions. After storage, the time yield locus was measured as described above (see 3.5.1.3).

3.5.3. Caking test without controlled humidity (chapter 8)

Compared to the primary caking test (see 3.5.1), only the storage conditions were modified. After the preconditioning step, the shear cell was placed in a container which was filled with the same powder as in the shear cell (Figure 19). Temperature and RH in the powder were monitored with a miniature data logger. A two kilos load was applied on the shear cell and the container was closed and wrapped in parafilm. All containers were stored in a temperature controlled room at 20°C.

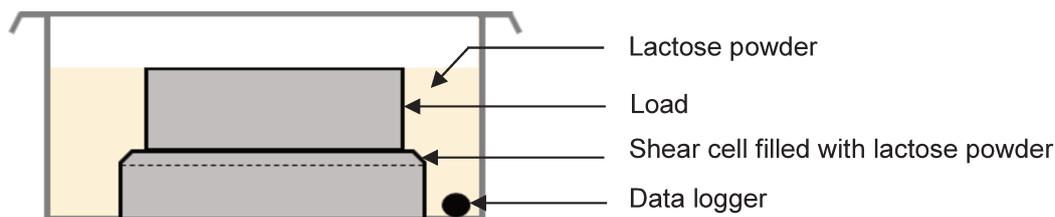


Figure 19: Schematic representation of the experimental setup for the caking test without controlled humidity.

Chapter 4 – Impurities increase caking

Summary

Various lactose grades with different purities can be found on the market. This chapter focuses on the influence of impurities (i.e. non-lactose components) on caking of lactose powder and the mechanisms involved. Lactose powders with different washing grades were produced on a pilot scale by varying the amount of water added to the lactose slurry before separation and washing. The powders were then analyzed for their chemical composition, moisture sorption properties and caking tendency. A higher washing grade was associated with a lower level of impurities and a decreased moisture sorption. Regardless of the washing grade, the amount of amorphous material was below the detection limit of the solid-state NMR analysis. Caking tests with a ring shear tester clearly showed a higher caking tendency for samples with larger amounts of impurities. Besides, the quantitative assessment of caking by ring shear testing is discussed. The results of the different methods suggested that impurities act through a humidity caking mechanism. Considering the application of these results in industrial settings, the crucial role of impurities in the development of caking highlights the need to control the separation and washing processing steps. The results of this chapter have been published in *Journal of Food Engineering*² and the chapter is based on the paper published.

The objectives of this chapter were to:

- Highlight the link between the presence of impurities and caking
- Understand how impurities increase caking

² Published as Carpin, M., Bertelsen, H., Dalberg, A., Roiland, C., Risbo, J., Schuck, P., & Jeantet, R. (2017). Impurities enhance caking in lactose powder. *Journal of Food Engineering*, 198, 91–97. <https://doi.org/10.1016/j.jfoodeng.2016.11.013>

4.1. Introduction

Commercial lactose powder has a very high purity, with a lactose content above 99%. The exact lactose content depends on the lactose grade, i.e. edible, infant, dry blend or pharmaceutical. The remaining fraction consists of different types of impurities. Minerals and proteins present in cow milk are for the major part eliminated by the filtration and washing steps in the lactose powder production process. Ultrafiltration membranes retain practically all the protein and 20-40% of the non-protein nitrogen compounds. Urea and amino acids pass through the membrane as well as the diffusible minerals which are not bound to proteins (Tan et al., 2009). These compounds are then separated from the lactose crystals during the washing step. The efficiency of this processing step will therefore determine the amount of remaining impurities. Edible grade lactose powder usually also contains riboflavin, lactose phosphate and lactic acid (Paterson, 2009).

Pharmaceutical grade lactose has been used in most studies dealing with lactose caking e.g., (Foster, Bronlund, & Paterson, 2005; Lloyd et al., 1996; Paterson & Bronlund, 2009). As it is recrystallized from edible grade lactose, this lactose grade contains a very limited amount of impurities. However, pharmaceutical grade lactose is estimated to account for approximately 20% of the global lactose production only (Affertsholt & Fenger, 2013). Consequently, the vast majority of the lactose powder produced worldwide contains some impurities (no more than 0.3% sulfated ash (Codex Alimentarius, 2001)). As no study on the washing step in lactose processing can be found in the literature, lactose producers could benefit from more investigations in this area (Paterson, 2017). The use of wash water (volume, continuous washing or several dilutions in series) could be optimized depending on the required level of remaining ash. Another focus area could be the loss of fines during the washing process.

A special kind of impurity in crystalline lactose powder is amorphous lactose. As lactose is allowed to crystallize during a slow cooling, the presence of amorphous lactose is not expected in the final product. However, after washing, lactose crystals enter the fluid bed with a free moisture content between 3 and 12%. Drying of the remaining water is fast and due to the content of dissolved lactose in this water, formation of amorphous lactose can occur on the surface of the crystals (Paterson, 2017).

As humidity has a crucial role in both amorphous and humidity caking, any impurity that can enhance lactose hygroscopicity might be detrimental. It would thus be interesting to elucidate the role of impurities in the caking process. As previously mentioned, this parameter has not been investigated to date. The aim of this study was therefore to characterize the influence of impurities on lactose caking. Lactose powders with different levels of impurities were produced on a pilot scale. These powders were characterized for their physicochemical composition, moisture sorption properties and caking tendency.

4.2. How do impurities increase caking?

4.2.1. Chemical composition

The results showed, as expected, that the higher the washing grade (see section 3.2.1.1), the fewer the remaining impurities measured in the final powder (i.e. nitrogen containing components expressed as proteins, free moisture, ash and minerals) (Table 6 and Figure 20). The remaining ash and protein levels were highly correlated ($R^2=0.972$). Moreover, ash and protein levels were found to correlate better with moisture measured by loss on drying at 87°C for 16 hours ($R^2=0.995$ and $R^2=0.972$, respectively) than with moisture measured after drying at 105°C for 5 hours ($R^2=0.709$ and $R^2=0.840$, respectively) (data not shown). The method to measure food moisture by loss on drying has been criticized for the lack of discrimination between the different types of water, distinguished by the extent of binding with solids (Isengard, 2001). “Free” and “bound” water can indeed be difficult to differentiate, and the results at 105 °C may overestimate the “free” water content of the samples.

Table 6: Composition of lactose powders as a function of degree of washing of the crystals. Results are given as average \pm standard deviation. Number of repeats = 3 for moisture and ash and 2 for proteins.

Washing Grade	Protein (g.100g ⁻¹)	Moisture (g.100g ⁻¹)	Ash (g.100g ⁻¹)	Lactose (g.100g ⁻¹)
0	0.640 \pm 0.014	1.12 \pm 0.01	2.14 \pm 0.05	96.09
0.3	0.332 \pm 0.005	0.89 \pm 0.00	0.79 \pm 0.04	97.99
0.5	0.227 \pm 0.006	0.77 \pm 0.02	0.52 \pm 0.02	98.49
1	0.152 \pm 0.006	0.36 \pm 0.02	0.43 \pm 0.04	99.05
2	0.082 \pm 0.001	0.31 \pm 0.01	0.19 \pm 0.00	99.42
Pharmaceutical grade lactose	0.004 \pm 0.002	n.d.	0.01 \pm 0.00	n.d.

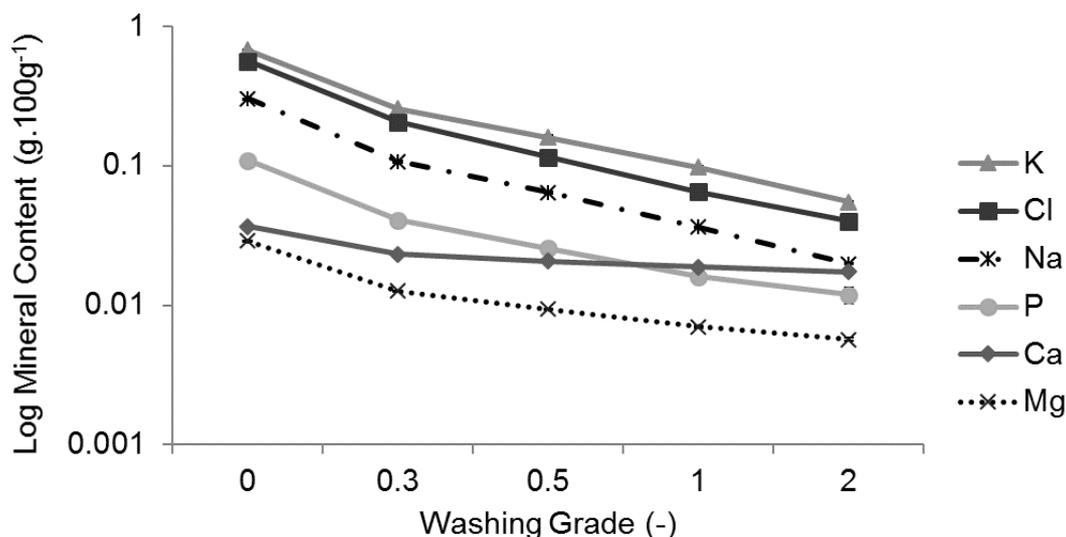


Figure 20: Variations in the mineral content (potassium (K), chloride (Cl), sodium (Na), phosphorus (P), calcium (Ca), and magnesium (Mg)) of lactose powder as a function of degree of washing of the lactose crystals.

The amounts of all minerals decreased with a higher degree of washing, with the exception of calcium (Figure 20). The decalcification and subsequent separation steps applied to the UF permeate reduced the initial calcium and phosphorus content (Hourigan et al., 2013). Thus the starting material for the trial already had low calcium and phosphorus content from the beginning. Figure 20 shows that it was not possible to reduce the calcium content much further by washing the lactose crystals. This suggests that, as mentioned by Guu and Zall (1992), most of the remaining calcium formed strong complexes with lactose. Interestingly, phosphate did not follow the same trend as calcium. Guu and Zall (1991) reported that calcium phosphate precipitates may act as nuclei facilitating lactose crystallization. It was therefore expected that calcium phosphate could be trapped inside the crystals, thereby preventing it from being washed away. This was however not observed in the present study.

Using a basic mass balance with simple assumptions, the expected amount of impurities in the different washing grades after decantation was calculated from the amount measured in Wash 0. The water content in the decanter output was considered the same for all washing grades (i.e. 10%) and it was assumed that no lactose was dissolved during the decantation process. The calculated levels of protein and ash were in general lower than the measured amounts (data not shown). The inclusion of droplets of mother liquor inside the crystals, as suggested by Mathlouthi and Rogé (2003) for sucrose, could explain the limited effect of washing.

4.2.2. Moisture sorption

Sieving the powders led to standardization of particle size distribution (Figure 21). Indeed it has been shown that particle size can have a significant effect on moisture sorption (Stoklosa, Lipasek, Taylor, & Mauer, 2012).

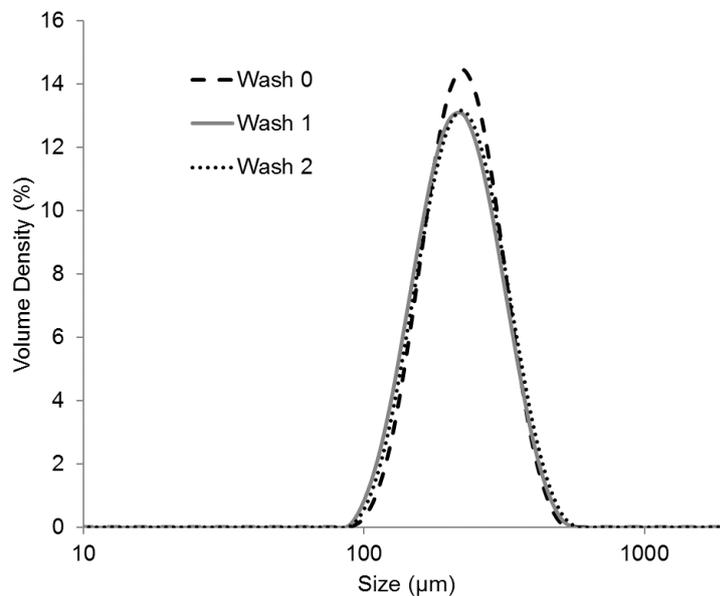


Figure 21: Particle size distributions of lactose powders for three different washing grades (0, 1, 2) but with the same particle size fraction ($160 < x < 250 \mu\text{m}$) (modified from (Carpin et al., 2017)).

Moisture sorption was highly dependent on the washing grade (Figure 22). For the same particle size fraction ($160 < x < 250 \mu\text{m}$), the sorption of the unwashed powder (Wash 0) was dramatically enhanced from 30% RH and the final sorption (at 95% RH) was almost ten times higher than the most washed powders (Wash 1 and Wash 2).

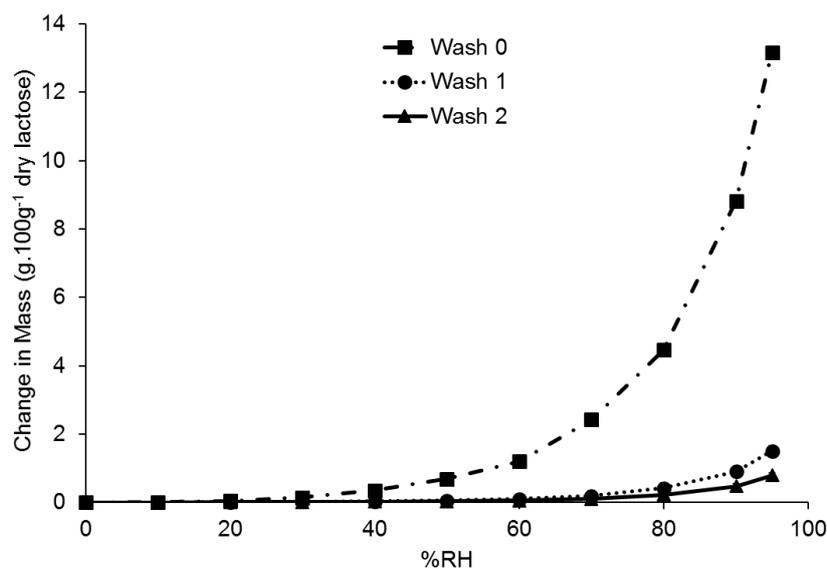


Figure 22: Moisture sorption isotherms of lactose powders with three different washing grades but the same particle size fraction ($160 < x < 250 \mu\text{m}$): Wash 0 (squares), Wash 1 (circles), Wash 2 (triangles).

Crystalline lactose is characterized by a very low hygroscopicity, with a DRH value of 95% (Salameh et al., 2006). However, Tereshchenko (2015) reported that, for a water soluble crystalline solid, moisture sorption below the DRH was due to impurities. Enhanced sorption and reduced DRH due to the presence of low levels of impurities have also been reported in a model deliquescent pharmaceutical salt, in agreement with our results (Guerrieri et al., 2007). The sorption behavior of the different lactose powders is thus likely to originate from differences in impurity contents (Table 6). This was further evidenced by a comparison with pharmaceutical grade lactose. The latter was found to contain about 20 times less ash and proteins than the most washed powder produced during the pilot trial (Table 6). The difference in moisture sorption behavior between Wash 2 and the pharmaceutical grade powder was very clear: indeed, Wash 2 powder adsorbed almost 10 times more moisture than pharmaceutical grade lactose above 50% RH (Figure 23).

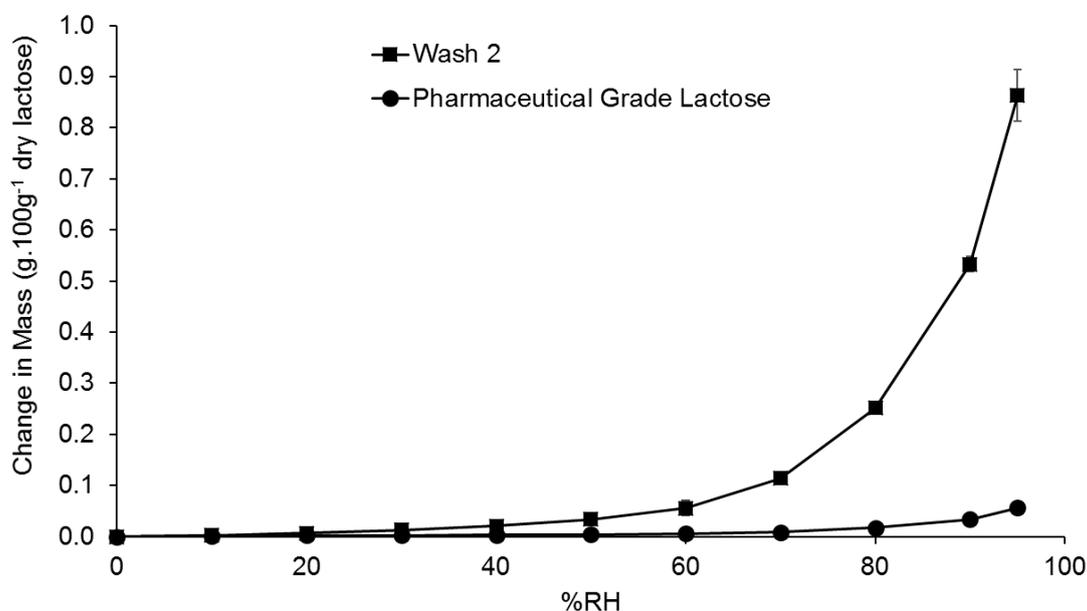


Figure 23: Moisture sorption isotherms of non-sieved pharmaceutical grade lactose (circles) and the most washed lactose from the pilot trial (Wash 2) (squares).

As moisture sorption occurs primarily on the surface of crystals, a comparison of the surface of the different washing grade lactose powders was undertaken by scanning electron microscopy (Figure 24). All samples from the pilot trial (Figure 24A-D) presented a rough surface. Wash 0 powder had many pores (Figure 24A), which would provide greater possibilities for capillary condensation and could therefore partly explain the enhanced moisture sorption previously reported (Figure 22). Compared to pharmaceutical grade lactose, which presented a smooth surface (Figure 24E), Wash 0.5, 1 and 2 powders had significant amounts of fines agglomerated on the surface of their large tomahawk crystals (Figure 24B-D). Mathlouthi and Rogé (2003) showed that the presence of fines in sucrose crystals enhanced moisture sorption and that the

greater the number of fine particles, the closer the sorption behavior of the sample to that of the amorphous state. Their findings are consistent with the moisture sorption isotherms obtained in this study, showing less sorption for pharmaceutical grade lactose (Figure 23).

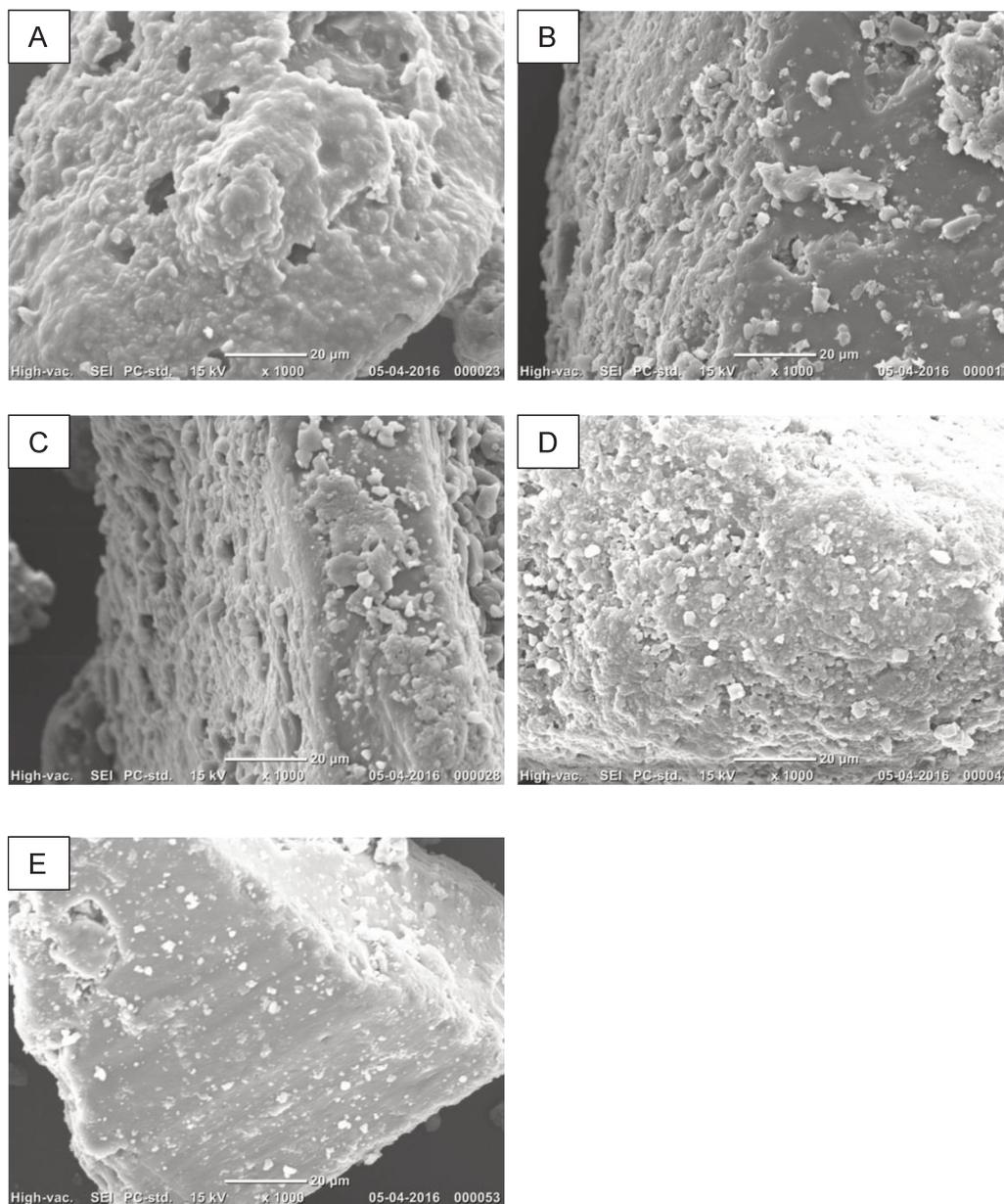


Figure 24: SEM images showing details of particle surface of different washing grade lactose powders: (A) Wash 0; (B) Wash 0.5; (C) Wash 1; (D) Wash 2; (E) Pharmaceutical grade lactose.

Moreover, a higher concentration of impurities on the surface of the crystals would probably lead to enhanced sorption behavior. On the other hand, impurities trapped inside the crystals are not expected to have a significant role in moisture sorption. This point requires further attention to identify which impurities (nature, concentration) are present on the surface of the particles.

4.2.3. Role of amorphous material

One particular kind of impurity is amorphous material, which is well known for its high hygroscopicity compared to the crystalline counterpart. Amorphous lactose can be formed on the surface of lactose particles during rapid drying and milling (Vollenbroek, Hebbink, Ziffels, & Steckel, 2010). As the samples were dried in a spin flash dryer in the present study (see section 3.2.1.1), the possibility of formation of amorphous material due to rapid drying cannot be excluded. The impurities remaining after the washing process (e.g., minerals and protein fractions) were likely to retain some mother liquor which could turn into amorphous lactose upon drying. The presence of increasing, yet very low, amounts of amorphous lactose at lower washing grades could thus be another explanation for the enhanced hygroscopicity of the corresponding powders.

However, no recrystallization event was observed in the moisture sorption curves, contrary to previously reported sorption isotherms of predominantly crystalline materials containing some amorphous content (Sheokand, Modi, & Bansal, 2014). For example, a weight increase and subsequent decrease due to amorphous lactose absorbing moisture and crystallizing has been reported in samples containing between 0.125 and 0.5 w/w % amorphous material (Buckton & Darcy, 1995). However, the presence of amorphous material in our samples cannot be ruled out from the sorption isotherms. Residual amorphous lactose might be present at lower levels than those studied by Buckton and Darcy (1995). Moreover, Buckton and Darcy (1995) used physical mixes of spray-dried lactose and α -lactose monohydrate in their study, which can facilitate the crystallization event compared to a situation where the amorphous material is in close contact with crystalline portions on the same particle.

The samples with different washing grades were therefore analyzed by solid-state NMR. A detection limit of 0.5% amorphous lactose has been reported for this technique (Gustafsson et al., 1998), which is among the lowest levels for the detection of amorphous material in predominantly crystalline materials (Giron et al., 2007). No disorder indicating amorphous material was detected in our samples (Figure 25). It can therefore be concluded that if any amorphous material was present in the samples, the amorphous content was probably below 0.5%. However, the analysis of very low levels of amorphous material is always challenging in terms of sample storage and sampling. Indeed, amorphous material can crystallize during storage before analysis, thus preventing its identification.

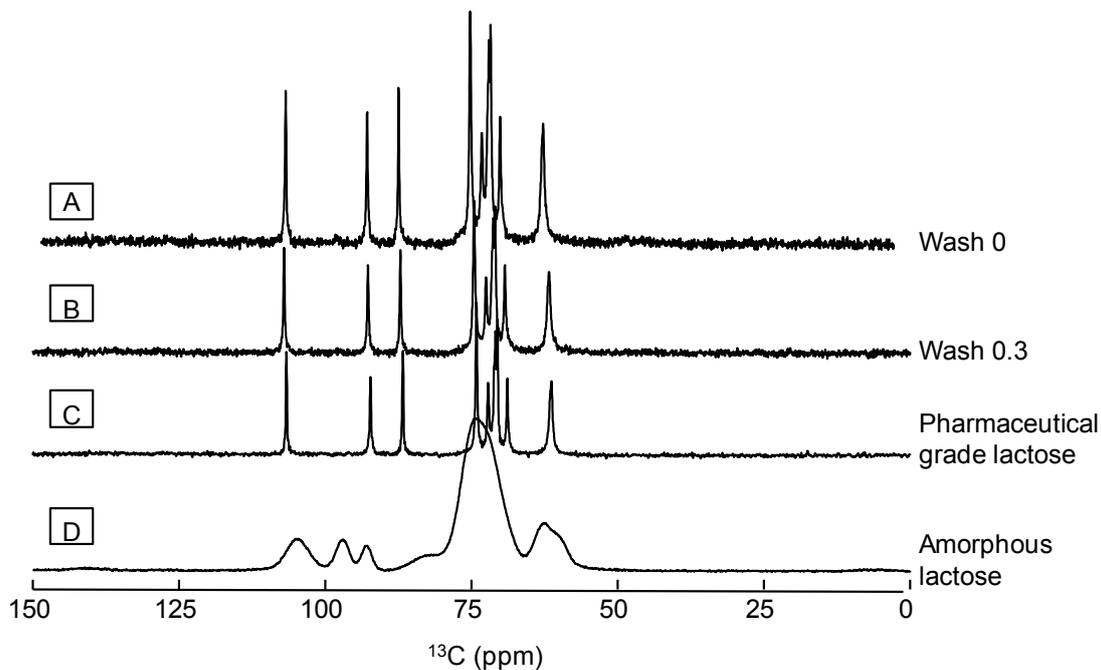


Figure 25: ^{13}C CP/MAS NMR spectra of (A) Wash 0; (B) Wash 0.3; (C) Pharmaceutical grade lactose; (D) Amorphous lactose.

4.2.4. Caking tendency

For the different particle size distributions investigated, the unwashed powder was characterized by a poorer flowability and hence a higher tendency to caking than the washed powders (Figure 26). Moreover, a *ffc* after storage of 0.6 ± 0.1 was obtained for non-sieved Wash 0.3 (data not shown) while non-sieved pharmaceutical grade lactose still flowed easily after the four-day storage. It was not straightforward to discriminate Wash 1 and Wash 2 powders from each other.

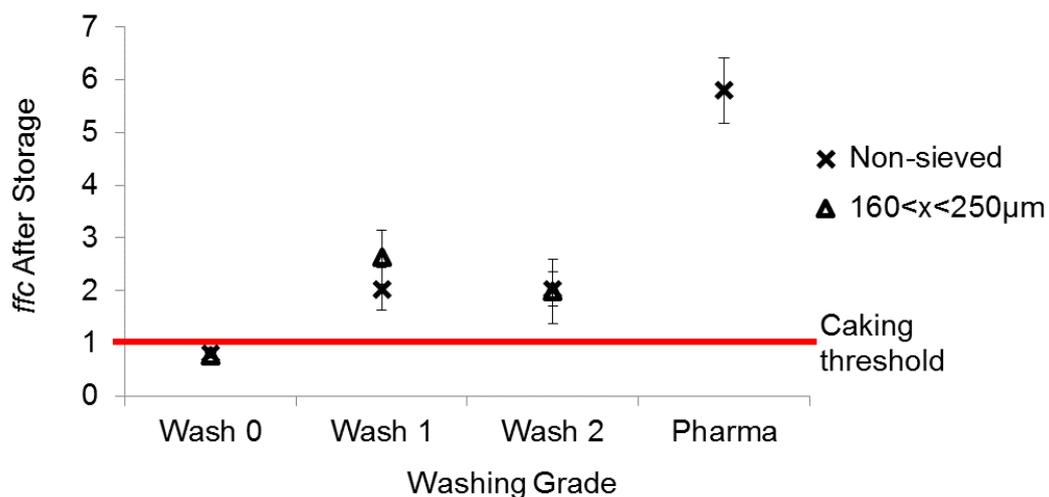


Figure 26: *ffc* of non-sieved (crosses) and sieved (triangles) lactose powders between $160\ \mu\text{m}$ and $250\ \mu\text{m}$ as a function of the washing grade. The *ffc* was measured after storage for four days at 60% RH and $20\ ^\circ\text{C}$. Each sample was consolidated under a pressure of 9.3 kPa. The flowability of pharmaceutical grade lactose after storage is included for comparison purposes.

It is clear from these results that higher levels of impurities lead to greater risk of caking. In the present study, the samples were stored at 20 °C and 60% RH for four days in the ring shear cells before measurement of caking tendency. Amorphous lactose stored at room temperature (20-25 °C) has been reported to crystallize at about 40% RH (Jouppila & Roos, 1994; Thomsen et al., 2005). Amorphous caking was therefore expected to occur if the samples contained amorphous lactose. However, as mentioned in section 4.2.3, the solid-state NMR analysis did not indicate the presence of disordered structures, meaning that the amorphous content of the samples was probably below 0.5%. Thus amorphous caking cannot be considered to be the main mechanism responsible for the caking tendency observed here. In his work on caking of crystalline lactose, Bronlund (1997) also showed that amorphous caking was only marginal for amorphous content below 5%, and that the major contribution to caking from the amorphous material occurred through moisture sorption.

The sorption isotherms of Wash 0, 1, 2 powders and pharmaceutical grade lactose showed that the difference in sorption behavior was important at 60% and room temperature (Figure 22 and Figure 23). During the caking experiments, the samples were given time to equilibrate with ambient air at 60% RH. Due to humidity caking, the caking tendency was therefore expected to be enhanced for samples which could adsorb more moisture. This was confirmed by the flowability results after storage (Figure 26). Only Wash 1 and Wash 2 showed similar flowability values, although Wash 1 was found to adsorb twice as much moisture as Wash 2 at 60% RH according to the DVS measurements. The difference in the impurity levels and thus moisture sorption between these two powders was probably too small for the ring shear tester to detect a difference between the caking tendencies of the two powders.

As humidity caking could be evidenced by the caking measurements with the ring shear tester, the repeatability of the measurement was considered acceptable. In order to discriminate between samples with similar sorption behaviors (such as Wash 1 and Wash 2), it might be helpful to increase the repeatability even further. As pointed out by Hartmann and Palzer (2011), one drawback of the ring shear cells is that they are almost closed, which hampers moisture exchange between the powder and the surrounding atmosphere. If the impurities are not homogeneously distributed in the powder, moisture sorption might be heterogeneous at a local level, leading to various degrees of consolidation. It is however interesting to note the low standard deviation associated with the results for Wash 0 and Wash 0.3. It seems therefore that once humidity caking has reached a certain level, it systematically proceeds to strong and repeatable caking. This level may be associated with the DRH which, as explained in section 4.2.2, can be significantly decreased by the presence of impurities. Moreover, a critical step in the experimental procedure is relieving the shear cells from the consolidation pressure and moving them from the humidity controlled chamber to the ring shear tester. This operation requires care as interactions between

the powder particles can be damaged. It is thus consistent that the stronger the interactions between particles, the better the caking reproducibility.

4.3. Conclusions

This chapter investigated the role of impurities in caking of lactose powder. A higher content of impurities was shown to increase both moisture sorption and caking tendency of the powder. DVS measurements coupled with the characterization of the physicochemical composition, including the amorphous content, suggested that the development of caking could be explained by enhanced humidity caking mechanism.

From an analytical point of view, an important achievement in this study is the quantitative assessment of caking by time consolidation experiments with a ring shear tester. This method was demonstrated to be able to discriminate between samples with different caking tendencies.

Finally, the content of impurities was directly linked to the efficiency of the washing process. This result stresses the importance of controlling the washing step in the manufacturing process of lactose to obtain a powder with a limited caking tendency. How this can be done in practice will be dealt with in chapter 6 as part of the industrial application of the results. As mentioned in chapter 1 (section 1.2.3), the efficiency of the washing and separation process can be dramatically decreased by a large number of fines. Thus, the crystal size distribution should be taken into account. This parameter is also well known to have an effect on the compaction properties of a powder and therefore on mechanical caking. It seems therefore interesting to investigate further how the particle size distribution influences caking.

4.4. Take-home messages

- Impurities in the lactose powder increased moisture sorption and caking.
- The ring shear tester is a valuable tool to assess caking.
- The separation and washing steps should be closely monitored to limit caking.

Chapter 5 – The size target to obtain a non-caking powder: a narrow size distribution with large particles

Summary

Particle size distribution (PSD) is known to influence several product properties such as compressibility and flowability. The aim of this chapter was to investigate how it affects the caking tendency of crystalline lactose and which mechanisms come into play. Lactose powders with various washing grades were sieved to obtain different size classes which were analysed for their chemical composition, PSD, sorption properties and caking tendency. Both the average particle size and the span of the size distribution were shown to have an effect on caking. A decreasing particle size led to increased sorption and stronger caking. Smaller particles indeed contained more impurities and were characterized by a larger specific surface area, promoting moisture sorption. A larger span was also associated with stronger caking, which could be explained by the multiplication of contact points and enhanced capillary condensation. Controlling the PSD of the final product should therefore be a priority of the lactose manufacturers to be able to prevent caking. The results of this chapter have been published in *Journal of Food Engineering*³ and the chapter is based on the paper published.

The objectives of this chapter were to:

- Investigate the influence of PSD on caking
- Understand the mechanisms involved in caking due to a change in PSD
- Highlight the PSD characteristics which need to be controlled in order to prevent caking in the final product

³ Published as Carpin, M., Bertelsen, H., Dalberg, A., Bech, J. K., Risbo, J., Schuck, P., & Jeantet, R. (2017). How does particle size influence caking in lactose powder? *Journal of Food Engineering*, 209, 61–67. <https://doi.org/10.1016/j.jfoodeng.2017.04.006>

5.1. Introduction

Particle size distribution is a very important characteristic as it governs several product properties (Ortega-Rivas, 2008) such as density, compressibility (Barbosa Canovas, Malave-Lopez, & Peleg, 1987), flowability (Juliano & Barbosa-Cánovas, 2010), segregation (Barbosa-Canovas, Malave-Lopez, & Peleg, 1985), rehydration (Gaiani, Schuck, Scher, Desobry, & Banon, 2007), etc. However, obtaining the right PSD is often a challenge. The crystallization step is crucial for this purpose but by no means straightforward given the complex physicochemical processes involved (Schuck, 2011). Downstream, the PSD can be modified unintentionally (e.g. by particle attrition) or intentionally (e.g. by milling).

If the PSD is modified, for example due to changes in the crystallization process, how will the caking tendency of the final powder be impacted? This question frequently arises in the powder handling industries and the answer is not straightforward. Mathlouthi and Rogé (2003) investigated the effect of particle size on moisture sorption and caking of sucrose. The higher the amount of fine particles (<250 μm) added to a standard sugar sample, the more sorption was recorded. The particle cohesiveness was found to increase with a decreasing particle size. Fine particles had moderate flow as measured with a Jenike shear cell. This result was explained by their small size and increased hygroscopicity. In addition, Provent et al. (1993) reported that the main cause for caking of a particular pharmaceutical powder was the particle size. By mixing coarse and fine particles in different ratios, they showed that caking was affected by both the total surface area of the powder and the distribution of particle sizes. However, these studies were performed on powders other than lactose, and one could question if the results are still valid for this latter compound. For example, impurities are known to influence the caking behavior of a given powder (Carpin et al., 2017). It is therefore worth investigating the caking mechanisms specific to the lactose powder.

Listiohadi et al. (2005a) investigated the effect of milling on the caking behavior of lactose. The hardness of the powder cakes was found to increase for a smaller particle size but moisture sorption was not affected by the particle size. More recently, Modugno et al. (2015) published a study on the influence of the PSD on lactose caking. They sieved the lactose powder to obtain different size classes which were subjected to caking tests. They reported that lactose crystals with a D_{50} (median particle size) smaller than 300 μm could cake easily if the water content was higher than 3%: they explained their result by a greater number of liquid bridges in the small size classes compared to the large size classes. However, this result cannot be applied to dried lactose powders for which the water content is usually below 0.5% (Hourigan et al., 2013). Moreover and as in most studies, the span of the size classes was not taken into account, which can greatly affect the packing density of the powder and thereby the number of liquid bridges. Therefore, even

though articles have been published on the subject, it remains difficult to assess how the PSD influences caking of a given powder. The aim of the present study was therefore to investigate the influence of the PSD on caking of crystalline lactose and the mechanisms involved. The expected results should provide a clearer picture of what needs to be measured and controlled in order to limit caking.

The lactose powders with various washing grades were sieved to obtain different size fractions which were analyzed for their PSD, physicochemical composition, moisture sorption properties and caking tendency.

5.2. Why do smaller particles cake more?

5.2.1. Particle size distribution (PSD)

The division between the different size classes obtained by sieving the two extreme washing grades (Wash 0 and Wash 2) was noticeably different (Figure 27). Particles were generally bigger in Wash 0, which can be explained by the presence of agglomerates, visible on the sieve in the fraction above 500 μm . These agglomerates may be structured by liquid bridges, favored by the presence of fines ($x < 80 \mu\text{m}$); the dissolution of the fines upon washing probably limited the formation of agglomerates in Wash 2, and led to a narrowed PSD with very few particles over 355 μm . In line with these observations, the general trend for all washing grades was that a decreasing washing grade led to bigger particles (data not shown). Thus, apart from crystallization (Schuck, 2011), washing is another important processing step that must be controlled in order to obtain a given PSD. Moreover, the particle size should not be neglected when investigating the effect of the washing grade on a given powder parameter, such as for example caking.

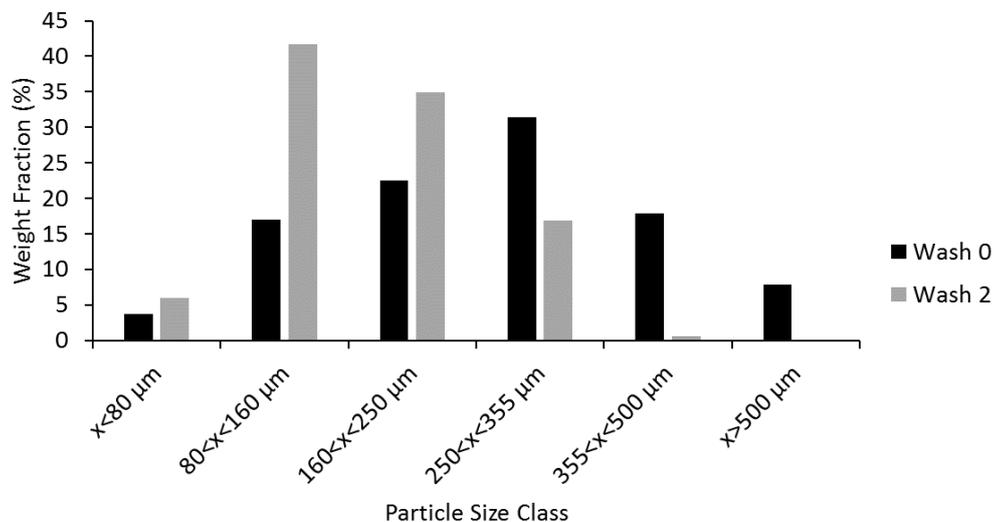


Figure 27: Particle size distributions of Wash 0 and Wash 2 lactose powders sieved to separate 80, 160, 250, 355 and 500 μm fractions.

5.2.2. Chemical composition

The different particle size fractions were analyzed separately for their impurity content. Impurities consisted in non-lactose components, mainly minerals and nitrogen containing components expressed as proteins, remaining in the powder after crystallization and washing. The fines ($x < 80 \mu\text{m}$) showed a higher content of proteins and ash than the bigger particles in Wash 0, Wash 1 and Wash 2 (Figure 28). Wash 0 presented a minimum content of impurities in the size fraction $250 < x < 355 \mu\text{m}$; above this size fraction, increasing the particle size resulted in a higher content of impurities (Figure 28). In Wash 1 and Wash 2, the general trend was a decrease in the impurity content with a larger particle size. Moreover, as expected, a smaller specific surface area was measured for larger particles (Figure 28).

In general, and with the exception of the larger size fractions of Wash 0, the evolution of impurity content with the particle size followed the one of the specific surface area. This indicates that impurities are likely to be located mostly on the surface of the particles. In Wash 0, the agglomeration of impurity containing fines together or on a larger crystal may explain the greater amount of impurities in the size fractions $x > 355 \mu\text{m}$. As these agglomerates were most likely only present in the lowest washing grade Wash 0 (Figure 27), they may explain the different evolution of impurity content with particle size for Wash 0 compared to the other washing grades (Figure 28). The results indicate that the fine fraction should be given attention as it can greatly influence the level of impurities in the powder. Crystallization is an important processing step to control the amount of small crystals. However, small particles are often fragments of bigger crystals which are damaged during processing steps (Mathlouthi & Rogé, 2003) such as rotary drying in a spin flash dryer used in the present study (see section 3.2.1.1). Considering the industrial process for lactose production, air transport between silos can for example be harsh to the particles which may be altered by attrition. In addition, milling is obviously a processing step which affects the particle size distribution of the final product (Hourigan et al., 2013).

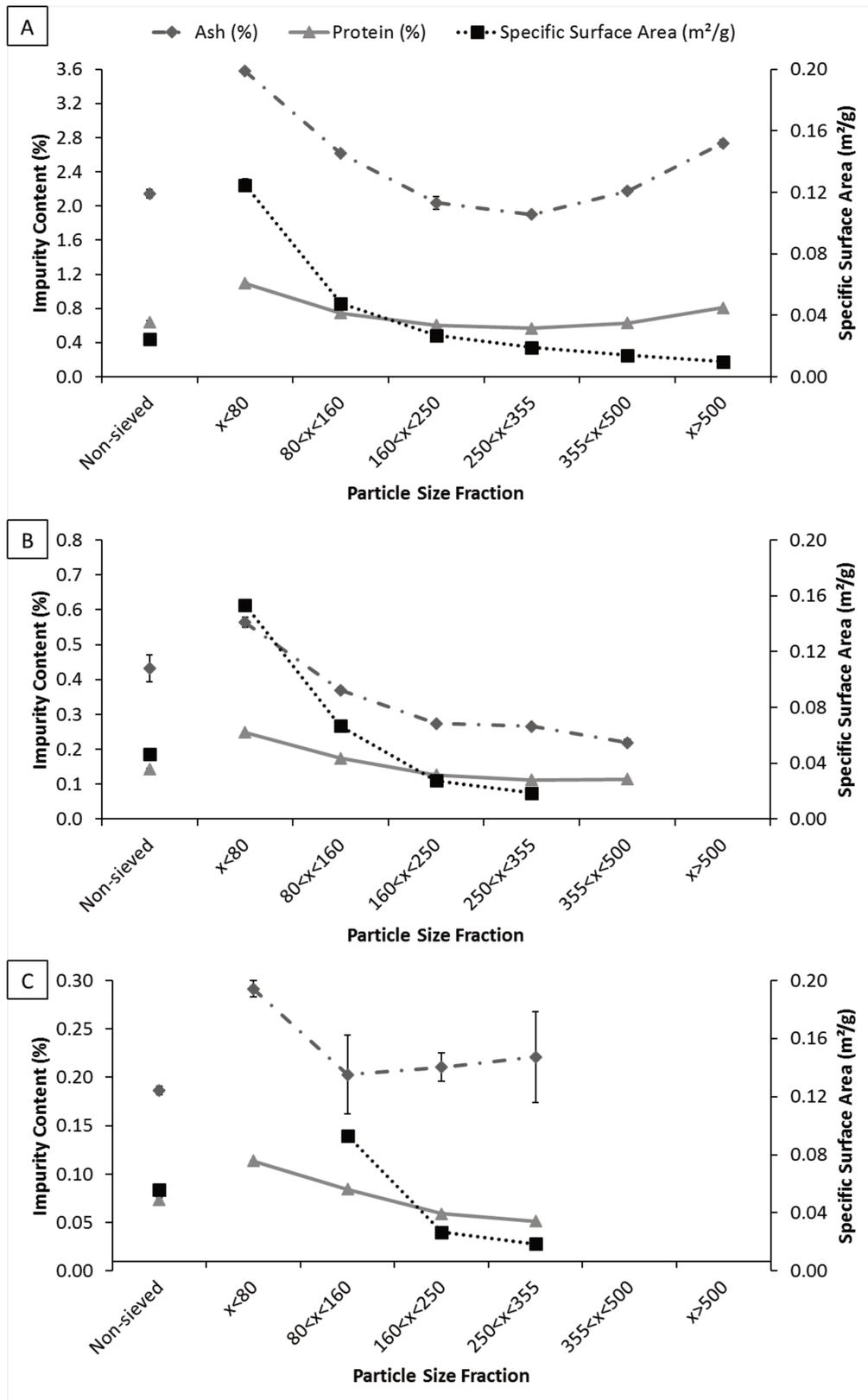


Figure 28: Impurity content (either protein or ash content; left axis) and specific surface area (right axis) of lactose powders as a function of the particle size class: (A) Wash 0; (B) Wash 1; (C) Wash 2. Results are given as average \pm standard deviation (represented by the error bars). Number of repetitions = 4 for specific surface area, 3 for ash, and 2 for proteins.

5.2.3. Aspect of the fines

Microscopic observations of the fine particles can help identify whether these are whole but small crystals or fragments of bigger crystals.

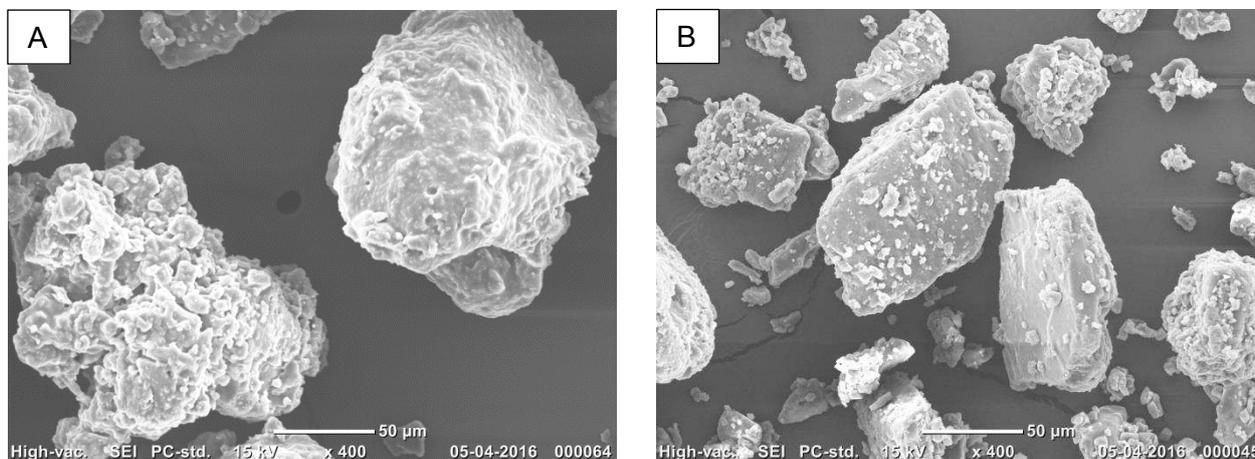


Figure 29: SEM images showing small particles of different washing grade lactose powders: (A) Wash 0; (B) Wash 2.

Scanning electron microscopes of Wash 0 and Wash 2 powders revealed differences in the agglomeration propensity of the fines (Figure 29A&B). Wash 0 showed agglomerated particles (Figure 29A) as expected from the particle size distribution (Figure 27). In contrast, small particles in Wash 2 were a mix of well-formed crystals and agglomerates. Very small fragments were also present (Figure 29B). For both powders, the agglomerated fragments were likely to originate from the surface of bigger crystals. Assuming that impurities were mainly concentrated on the crystal surface, these fragments thereby increased the overall impurity content of the fine fraction. A suitable technique which could distinguish between the composition of the surface and the inner part of a lactose crystal could confirm this hypothesis. For example, the surface composition of several milk powders, characterized by X-ray photoelectron spectroscopy (XPS), was found to differ from their bulk composition in lactose, proteins and fat (Murrieta-Pazos et al., 2012).

5.2.4. Moisture sorption

The difference in moisture sorption behavior depending on the size fraction was significant (Figure 30). The final amount of water adsorbed (at 95% RH) indeed increased for the smaller particles ($80 < x < 160 \mu\text{m}$) compared to the medium ($160 < x < 250 \mu\text{m}$) and bigger ($250 < x < 355 \mu\text{m}$) particles by 40% and 72%, respectively.

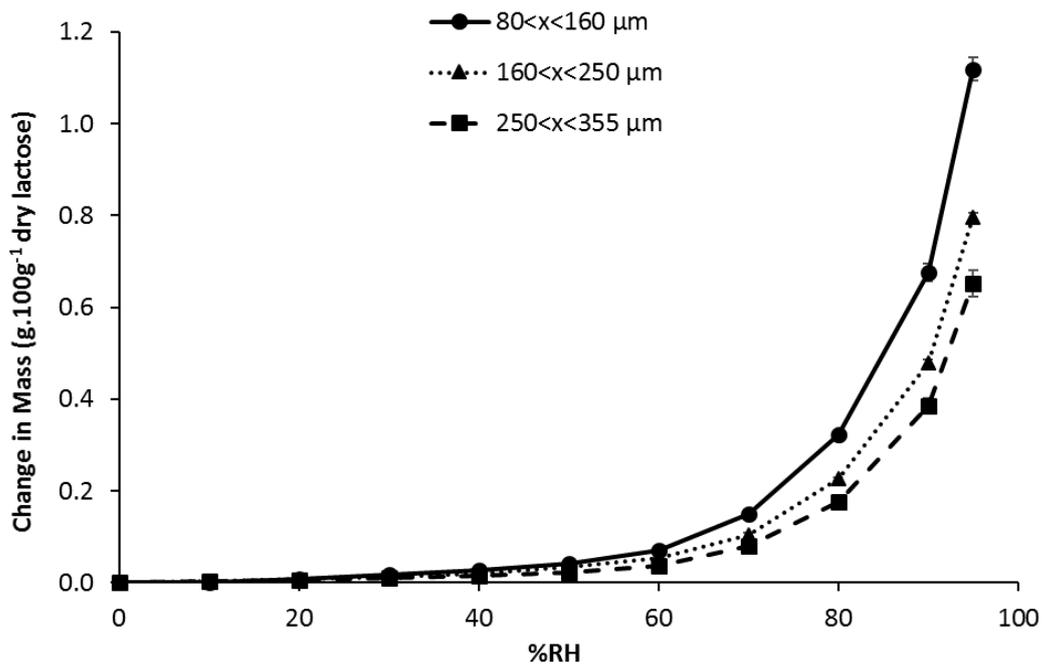


Figure 30: Moisture sorption isotherms of lactose powder Wash 2 for three different particle size fractions: $80 < x < 160 \mu\text{m}$: circles; $160 < x < 250 \mu\text{m}$: triangles; $250 < x < 355 \mu\text{m}$: squares.

When the ambient RH increases, three mechanisms of water-solid interactions can be considered for the crystalline lactose-water system, i.e. adsorption of water molecules on crystal surface, capillary condensation and deliquescence (Mauer & Taylor, 2010). As moisture sorption occurs primarily on the surface, the larger specific surface area associated with smaller particles (Figure 28) is consistent with a higher sorption behavior. Likewise, such an increase in moisture sorption was measured for smaller particles of glass beads (Stoklosa et al., 2012) and sucrose (Mathlouthi & Rogé, 2003) compared to bigger counterparts.

Moreover, capillary condensation occurs in pores between adjacent particles. Using the Kelvin equation, it is possible to predict the critical capillary radius below which all capillaries will be full of water at a given water activity and temperature (Billings et al., 2006). The size distribution of the pores is expected to depend both on the average particle size as smaller particles give smaller pores, but also on the span of the particle size distribution as powders with a larger span can be compacted to a higher packing density and thus a structure with smaller pores (Bronlund & Paterson, 2004). The PSD of the different size fractions of Wash 2 powder showed a broader span value (Eq. (3) in chapter 3) for the fraction $80 < x < 160 \mu\text{m}$ compared to the fractions $160 < x < 250 \mu\text{m}$ and $250 < x < 355 \mu\text{m}$: 1.56, 0.88 and 0.73 respectively. This broader span certainly contributes to the higher moisture sorption of the size class $80 < x < 160 \mu\text{m}$.

Finally, pure crystalline lactose is characterized by a very low hygroscopicity, with a DRH value of 95% (Salameh et al., 2006). However, for water-soluble crystalline solids it has been shown that impurities can increase moisture sorption below DRH and reduce the DRH value (Guerrieri et al.,

2007; Tereshchenko, 2015). The higher content of impurities in the smaller particles (Figure 28), especially if these impurities are located on the surface, is thus likely to influence the shape of the sorption isotherm.

In summary, the observation of increasing moisture sorption for the smaller size fraction can be explained by a larger surface area, a higher level of impurities and smaller capillaries due to a broader span of the size distribution.

5.2.5. Caking tendency

The caking tendency of the different size fractions of the least (Wash 0) and most washed (Wash 2) powders from the pilot trial was measured with a ring shear tester (Figure 31). For both powders, it was clear that the smaller particles showed poorer flowability after storage (i.e. lower *ffc* value) and thus a higher caking tendency. It was even possible to exceed the caking threshold by selecting the right particle size fraction and thereby prevent the powder from caking under the chosen storage conditions. For a given powder, the non-sieved fraction had an intermediate caking tendency compared to the sieved fractions. The results for the caking tendency of the different size fractions of Wash 1 showed the same trend (data not shown).

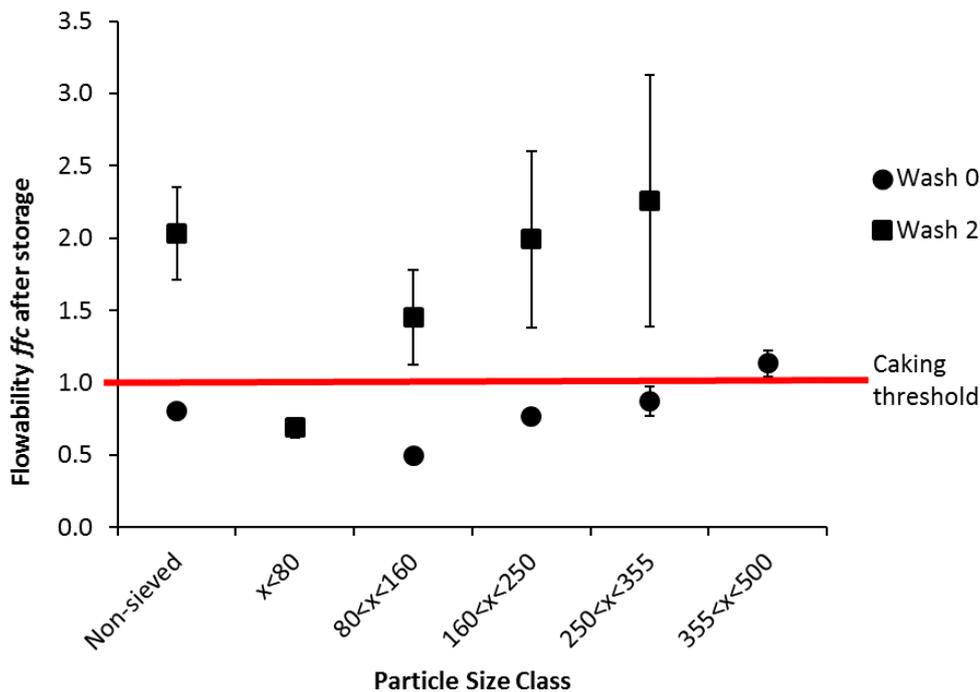


Figure 31: Flowability *ffc* of lactose powders Wash 0 (circles) and Wash 2 (squares) as a function of particle size class after storage for four days at 60% RH and 20°C and under a consolidation stress of 9.3 kPa.

The results for the caking measurements were consistent with the moisture sorption isotherms showing higher sorption for smaller particles. Humidity caking is therefore a critical mechanism to consider for caking in lactose powder under the selected conditions. Similarly, Paterson and

Bronlund (2009) also concluded on a capillary condensation mechanism leading to significant liquid bridging in crystalline lactose powder.

Moreover, sugar dust from a sugar factory has been reported to contain amorphous material originating from the surface of sucrose crystals dried at high temperatures in a short time (Mathlouthi & Rogé, 2003). These fines were shown to adsorb significantly more moisture compared to microcrystals of the same size produced with a special crystallization process. In the present study, different size fractions of Wash 0 powder were analyzed by solid-state NMR but the amount of amorphous material was below detection limit (data not shown). Thus, amorphous material in the fines is probably present at too low levels to trigger amorphous caking, i.e. viscous flow of material to contact points. However, even in low levels, amorphous material can still promote moisture sorption and thus contribute to caking. Fragments of bigger particles surface among the fines, as revealed by SEM images (Figure 29), should therefore be closely controlled as they can contain amorphous material.

The third mechanism reported in the literature for caking in food powders is mechanical caking (Carpin et al., 2016). This mechanism is highly influenced by the PSD of the powder through the number of possible contact points. As smaller particles are known to create more contact points than the bigger counterparts for the same volume of powder, mechanical caking takes part in the greater caking tendency of the smaller particles (Figure 31). However, Bronlund and Paterson (2004) measured more moisture sorption and thereby a greater possibility of caking in unmilled lactose compared to the milled powder; they explained this difference by a wider PSD in unmilled lactose. The D_{50} , i.e. the median particle size of the distribution, is therefore not the only parameter that should be taken into consideration when assessing the effect of a change in the PSD on caking.

5.3. A narrow size distribution to prevent caking

In order to investigate the influence of the span, three different size fractions ($160 < x < 250 \mu\text{m}$, $100 < x < 355 \mu\text{m}$ and non-sieved) of the same lactose powder with very similar D_{50} values ($243 \pm 11 \mu\text{m}$) were subjected to caking measurements. The PSD of the three size fractions was measured to verify that they had different span values but similar D_{50} values (Figure 32). A lactose powder with an intermediate washing grade (i.e. Wash 0.3) was used for these time consolidation experiments. This powder was chosen to allow moderate to strong caking to take place in the powder and thereby a differentiation of the samples while avoiding a strong caking of all samples.

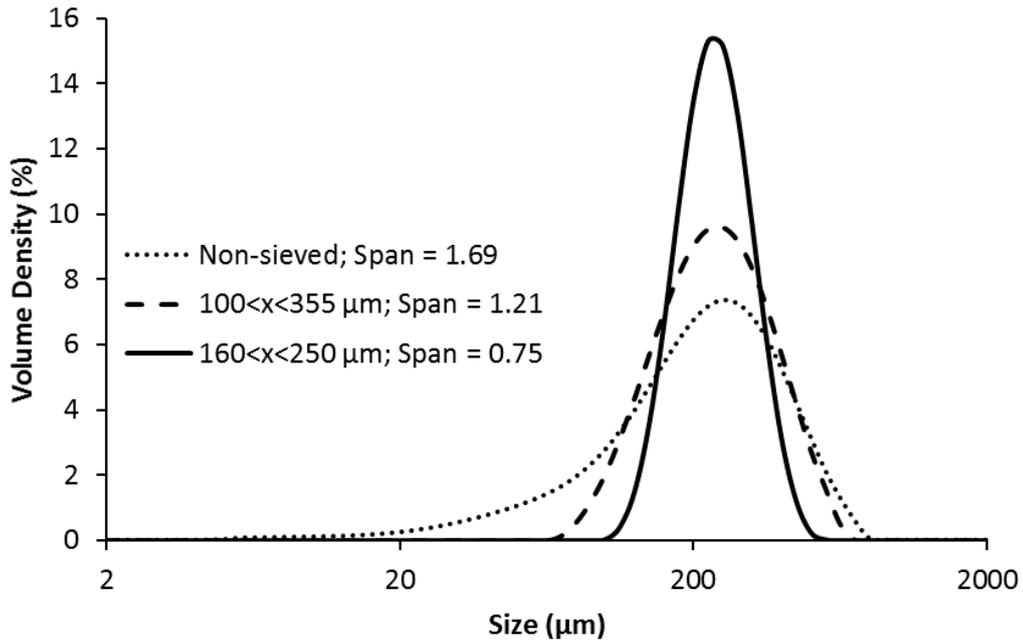


Figure 32: Particle size distributions of different size fractions (non-sieved, $100 < x < 355 \mu\text{m}$ and $160 < x < 250 \mu\text{m}$) of lactose powder Wash 0.3.

Figure 33 shows that for powders with similar D_{50} , a broader span of the size distribution clearly led to a stronger caking tendency, in agreement with the observations of Bronlund and Paterson (2004). The numerous contact points associated with a wider PSD allow more interactions between particles and thereby increase the possibility of mechanical caking and humidity caking by capillary condensation, as explained in section 5.2.4.

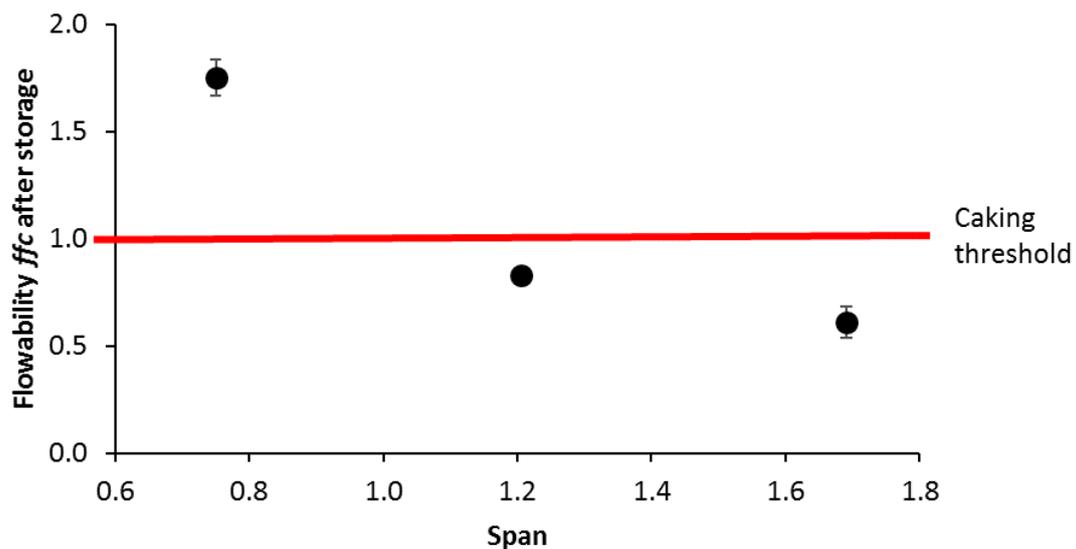


Figure 33: Flowability f_{fc} of different size fractions of lactose powder Wash 0.3 as a function of the span of the particle size distribution. The size fractions were $160 < x < 250 \mu\text{m}$, $100 < x < 355 \mu\text{m}$ and non-sieved, with the span being 0.75, 1.21 and 1.69 respectively. The measured D_{50} were $249 \mu\text{m}$, $249 \mu\text{m}$ and $230 \mu\text{m}$ respectively. The f_{fc} was measured after storage for four days at 60% RH and 20°C and under a consolidation stress of 9.3 kPa.

In order to assess the effect of changes in PSD on the caking tendency of the product, it is crucial to consider both the specific surface area of the powder and the span of the size distribution as they influence caking in different ways. Indeed, Provent et al. (1993) reported that mixing coarse and fine particles in a powder might lead to critical concentrations of fines for which the risk of caking was greatest. It might therefore be helpful to shift the size distribution slightly towards bigger particles in order to remove part of the fines.

5.4. Conclusions

The results of this chapter demonstrate a clear effect of PSD on caking in crystalline lactose. A given crystalline population is usually composed of various particle sizes and the size distribution should be characterized both in terms of mean particle size and span of the distribution. Smaller particles showed increased moisture sorption and greater caking tendency. This can be explained by the larger surface area and amount of impurities measured with a decreasing particle size. Impurities were indeed shown in the previous chapter to increase moisture sorption and caking. Smaller particles combined with a broader span also promoted mechanical caking through the multiplication of contact points. A broader span influenced moisture sorption as well by enhancing capillary condensation.

Considering the methods used in this study on a pilot scale, ring shear testing was able to demonstrate the negative impact of a decreasing particle size and a larger span on caking. It was also successfully used to discriminate samples with different amount of impurities in the previous chapter. This method is therefore suitable to quantitatively assess the effect of various product parameters on the caking tendency of the final product. In addition, moisture sorption isotherms clearly indicated increased sorption in samples with a lower degree of washing or smaller particles. Sorption isotherms are therefore valuable to help predicting the effect of a given product parameter on caking.

PSD of food powders can be difficult to control in industrial settings because of the many processing steps which can affect it. However preventing caking in lactose powder cannot be achieved without a tight control of the PSD, which will therefore be further investigated in the next chapter.

5.5. Take-home messages

- In general, smaller particles presented a larger surface area and more impurities than the larger size fractions.
- Smaller particles showed increased moisture sorption and higher caking tendency.
- Moisture sorption isotherms can help to assess the effect of the particle size on humidity caking.

- For the same mean particle size, a larger span of the size distribution leads to stronger caking.
- When optimizing the PSD in order to prevent caking, industrials should target a narrow span and a large average particle size to minimize the specific surface area.

Part 3

Industrial Development

Chapter 6 – On the process line: how to control the impurity content and the PSD in the final product in order to avoid caking?

Summary

This chapter constitutes the first part of the industrial development of the PhD thesis, where focus is shifted to the process line. It aims at applying the results from the previous chapters obtained on a pilot scale to commercial samples from the factory. Despite the investigation of several methods, amorphous material was not detected in commercial crystalline lactose. A higher amount of the other impurities (e.g. minerals and protein) was demonstrated to increase the hygroscopicity and the caking tendency of the commercial lactose powder, in line with the results from the pilot study (chapter 4). Smaller particles in commercial lactose powder were also found to contain more impurities, indicating that the learnings from the pilot study (chapter 5) are relevant for commercial samples. The first lever to control the amount of impurities is the raw material composition, while the PSD is largely determined during the crystallization step. Downstream, impurities could be significantly lowered by optimization of the separation and washing steps. However, these steps can also modify the PSD of the powder for example by mechanical abrasion or small crystals dissolution. Importantly, the recirculation of fines, either at the washing or at the drying step, should be carefully considered as it can increase the hygroscopicity of the whole bag after packaging. Finally, transport of the powder by pneumatic conveyors can be harsh to the particles and thereby impact the PSD of the powder. Several processing steps were found to have an effect on both the impurity content and the PSD, most often through the amount of fines rich in impurities. The close relationship between these two product parameters highlights the need to consider all product parameters when modifying a processing step to decrease the caking tendency of the final product.

The objectives of this chapter were to:

- Determine if amorphous material is present in commercial crystalline lactose powder
- Investigate whether the results from the pilot study are valid for the commercial samples
- Point out the processing steps where attention is required in order to control the amount of impurities and the PSD of the final product and thereby limit its caking tendency

6.1. Introduction

The previous developments (chapters 4 and 5) provided knowledge on the underlying mechanisms of caking due to variations in impurity content and particle size distribution in pilot samples. These two parameters were indeed found critical with regard to the caking issue in lactose powder. Although the pilot-scale experimental conditions were chosen to mimic the industrial process, they still differ from this latter. For example, pilot samples were dried on a spin-flash dryer as a fluid bed was not available at this scale at the time of the pilot experiments. Consequently, the final products may differ from industrial products to some extent. More generally, it is not straightforward to extrapolate the conclusions of a pilot study to commercial samples given the fact that each processing step can affect several product parameters. The first aim of this chapter was therefore to verify the validity of the results obtained on a pilot scale for commercial samples.

Impurities were shown to increase moisture sorption in the powder and favor humidity caking (chapter 4). Amorphous lactose can play a role in the development of caking, by participating in the increased sorption and even by forming bridges between particles depending on the amount present in the powder. The slow crystallization and subsequent washing utilized in the crystalline lactose production process lead to amorphous material not being expected in commercial samples. However, it has been suggested that amorphous material could be formed on the surface of the crystals during the rapid drying of the wet lactose crystals (Bronlund & Paterson, 2004). The presence of amorphous material in commercial lactose should therefore be investigated. In addition, the overall level of impurities in commercial samples can differ from the levels obtained on the pilot scale, depending on the efficiency of the washing process. Thus, the detrimental effect of impurities on the powder hygroscopicity and caking tendency should be confirmed for the levels present in commercial samples. Moreover, PSD, and more specifically both particle size and span, were found to have a critical effect on caking of crystalline lactose (chapter 5). The amount of impurities increased with a decreasing particle size, leading to larger amounts of adsorbed moisture. This important result should also be confirmed for commercial samples.

The other aim of this chapter was to investigate which processing steps determine the level of impurity and the PSD of the product, and whenever possible, to give recommendations to lactose manufacturers on how to adjust the process in order to limit the caking tendency of the final product. A thorough knowledge of the process was therefore necessary in order to identify relevant sampling points.

6.2. Amorphous lactose in commercial powders

In order to determine the main caking mechanism in commercial samples, the amount or at least the presence of amorphous material should be investigated. A great number of methods have been reported in the literature, driven by the need from the pharmaceutical industry to control the amorphous content in a drug product, as it can affect processing, performance, and stability. Several methods were investigated in the present PhD study. The use of humidity loggers to record crystallization is also reported for the first time.

6.2.1. Modulated Temperature Differential Scanning Calorimetry (MTDSC)

DSC is a popular technique to quantify amorphous material in food powders (Ho, Truong, & Bhandari, 2017). For example, the glass transition and the lactose crystallization peak can clearly be observed on the DSC thermogram of non-crystallized whey powder (Figure 34). A more recent DSC approach developed in the nineties, namely modulated temperature DSC (MTDSC), has been reported to enhance both sensitivity and resolution of the DSC technique (Guinot & Leveiller, 1999).

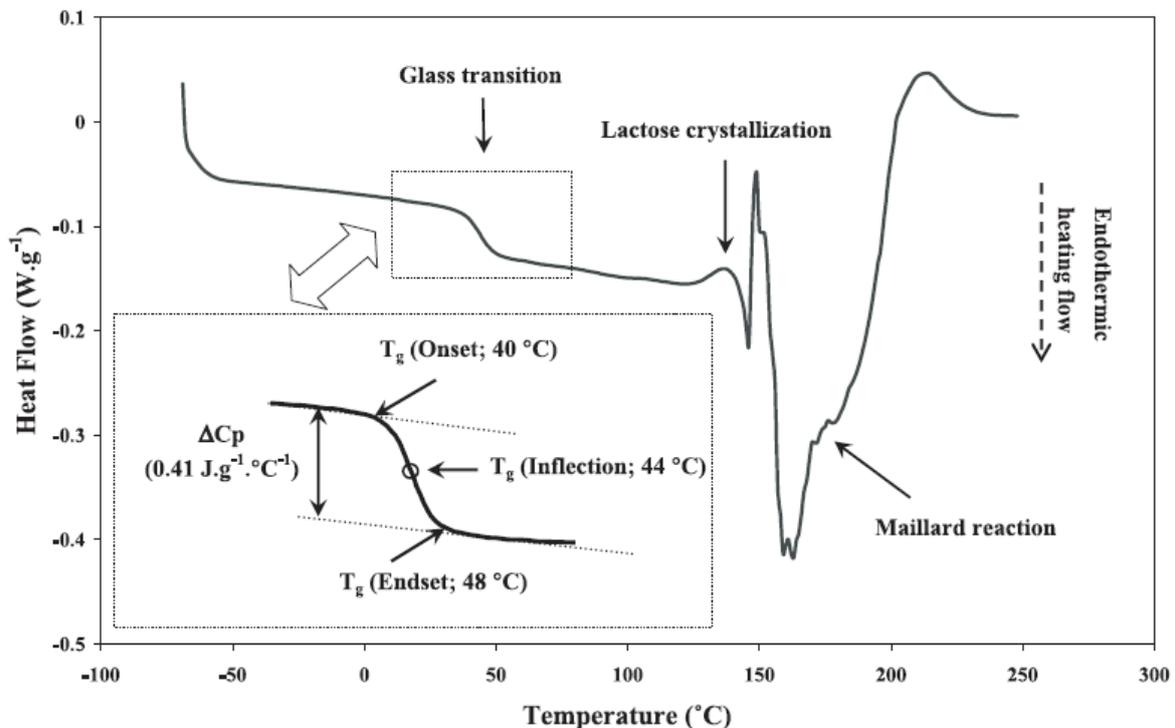


Figure 34: DSC thermogram of non-crystallized whey powder at 0.22 aw (Schuck, Blanchard, Dolivet, Méjean, & Onillon, 2005).

MTDSC thermograms of commercial milled and unmilled α -lactose monohydrate did not show any sign of amorphous content (Figure 35 A&B). Milled powder was included in the analysis as amorphous lactose has been reported to be formed upon milling (Newell et al., 2001b). While

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

detection of amorphous material by conventional DSC is limited to contents above 10% (Saleki-Gerhardt, Ahlneck, & Zograf, 1994), a much lower detection limit has been calculated for MTDSC, around 5% (Müller et al., 2015; Venkatesh, Barnett, Owusu-Fordjour, & Galop, 2001) and even down to 0.9% depending on the experimental conditions (Guinot & Leveiller, 1999). Thus, amorphous material in commercial lactose was not detected by MTDSC but may still be present at a level which requires attention, especially at a local surface scale. Indeed, Newell et al. (2001b) measured a similar surface energy, leading to comparable interfacial interactions, in ball milled lactose containing 1% amorphous material and amorphous lactose prepared by spray drying. Therefore, a more sensitive analytical method was required.

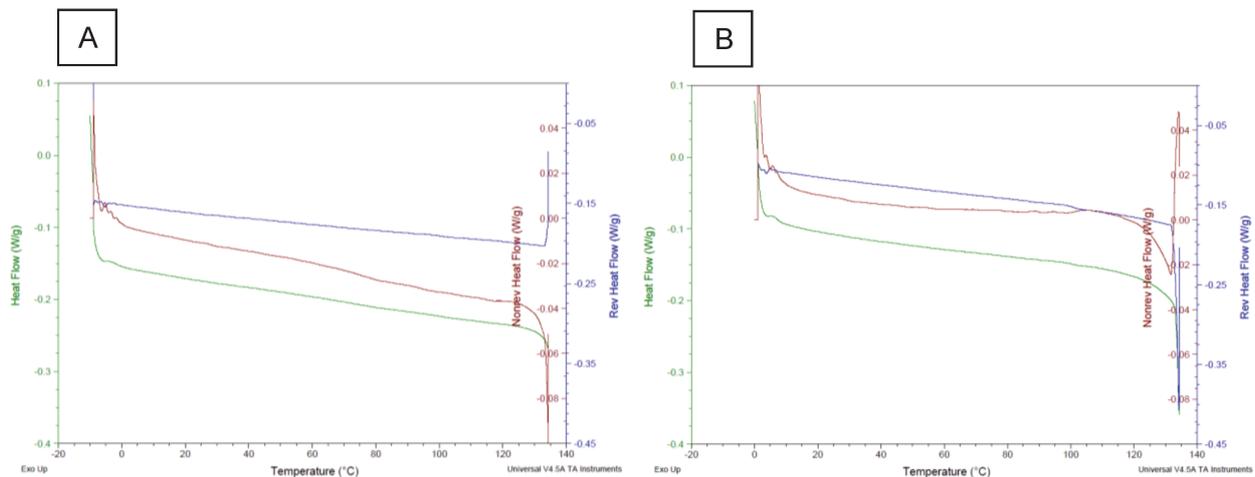


Figure 35: DSC thermogram of commercial α -lactose monohydrate. (A) Unmilled; (B) Milled.

6.2.2. Dynamic Vapor Sorption (DVS)

DVS has been reported to be a powerful method to detect very low levels of amorphous material in crystalline samples. Amorphous levels down to 0.05% could be detected by DVS in lactose powder (Buckton & Darcy, 1995). The analysis focuses on the powder surface, where amorphous material is likely to predominate. Several scientific approaches have been utilized for quantification purposes and they have been classified in three groups by Sheokand et al. (2014): equilibrium moisture uptake method, water uptake method, and residual weight method. The first method relies on the determination of moisture uptake by physical mixtures at a particular temperature and RH before crystallization. The two other methods are based on the plasticization effect of water which induces recrystallization of the amorphous material. In the water uptake method, water uptake at a reference RH before and after vapor induced recrystallization is compared. Finally, correlation between the amorphous content and the residual weight after a sorption-desorption cycle where recrystallization and hydrate formation occur is the basis of the third method (Sheokand et al., 2014).

The moisture sorption isotherm of commercial unmilled lactose was measured (Figure 36). The sample showed very low hygroscopicity with only 0.6% adsorbed moisture at 95% RH. A decrease

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

in sorption at 50% RH was recorded, which can be considered as representative of a recrystallization event. This decrease was not observed when analyzing pharmaceutical grade lactose (data not shown).

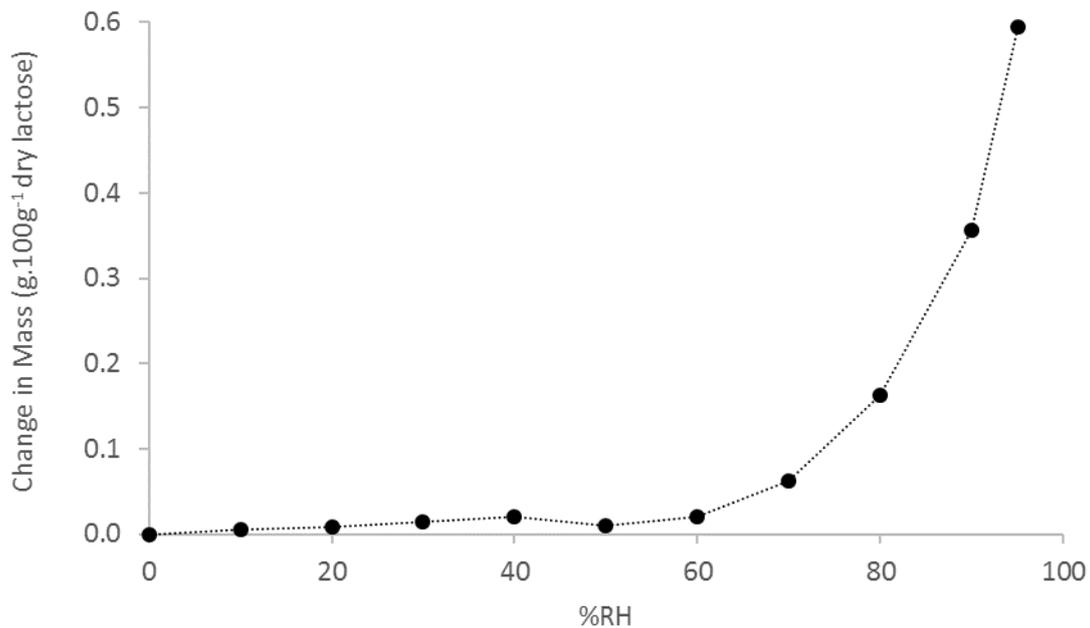


Figure 36: Sorption isotherm of unmilled α -lactose monohydrate

Using the second or third method described by Sheokand et al. (2014), it would theoretically be possible to correlate the weight loss with the amount of amorphous material present in the sample. However, the weight decrease was very difficult to reproduce. Perhaps the amorphous material was not homogeneously distributed in the powder and as the DVS measurement only used approximately 40 mg powder, the amorphous content may vary between samples. The instrument lack of sensitivity at such extremely low content, or onset of crystallization which cannot be achieved during the experimental time scale can also be part of the explanations. Thus, for low amounts, the amorphous material can be present but the crystallization event not seen (Shah, Kakumanu, & Bansal, 2006). Moreover, Listiohadi et al. (2005c) explained the presence of remaining uncrystallized lactose in physical mixes after storage at 75% RH for 3 months by amorphous material being isolated in micro cells or widely distributed in the matrix thereby delaying crystallization. The equilibrium moisture uptake method, which do not rely on crystallization of the amorphous material, could be investigated. However, this method is sensitive to particle size, which has been shown to dramatically influence moisture sorption in lactose (chapter 5).

In addition, in most studies assessing the amount of amorphous material by gravimetric methods and other methods, physical mixes are used to test the method and draw a calibration curve (Buckton & Darcy, 1995; Saleki-Gerhardt et al., 1994; Vollenbroek et al., 2010). This provides a simple and fast experimental setup. Physical mixes can however be very different from real

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

samples where amorphous lactose may be mostly present on the surface of the particles (Newell et al., 2001b). The response of the amorphous material during the analysis may differ depending on whether it is in close contact with crystalline portions on the same particle or if it is present on separate particles. While gravimetric studies are considered to be very useful to detect low amounts of amorphous lactose, there is no consensus on their actual capacity for quantification purposes (Buckton & Darcy, 1999).

6.2.3. RH measurements to detect crystallization

Crystallization of amorphous material triggers the release of water molecules, thereby inducing an increase in water activity. Monitoring the water activity of the powder could therefore be a fast and easy method to detect crystallization. Miniature RH loggers were used to follow the evolution of RH in a powder bed to this end.

The loggers were placed in samples of commercial lactose powder mixed with amorphous lactose (see section 3.4.6.3). The storage temperature was raised continuously at a rate of 1.3°C per hour to 60°C to reach the glass transition temperature and induce crystallization in the samples. Then temperature was lowered again and equilibrated to 35°C. Figure 37 presents the evolution of RH and temperature in the powder samples over time. The RH measurement curves can be divided in three phases. During the first phase, temperature and RH were stable and RH was lower in samples with more amorphous lactose. In the second phase, temperature was raised and RH decreased slightly. However, in all samples with amorphous material added, RH increased sharply when temperature reached about 40°C, namely at a temperature depending on the amorphous content. More precisely, a higher temperature triggering the RH increase was observed for samples with more amorphous lactose. Moreover, a higher initial content of amorphous material led to a higher final RH. A further increase of temperature was associated with a decrease in RH. In the third phase, temperature was lowered again, and RH inversely followed the evolution of temperature.

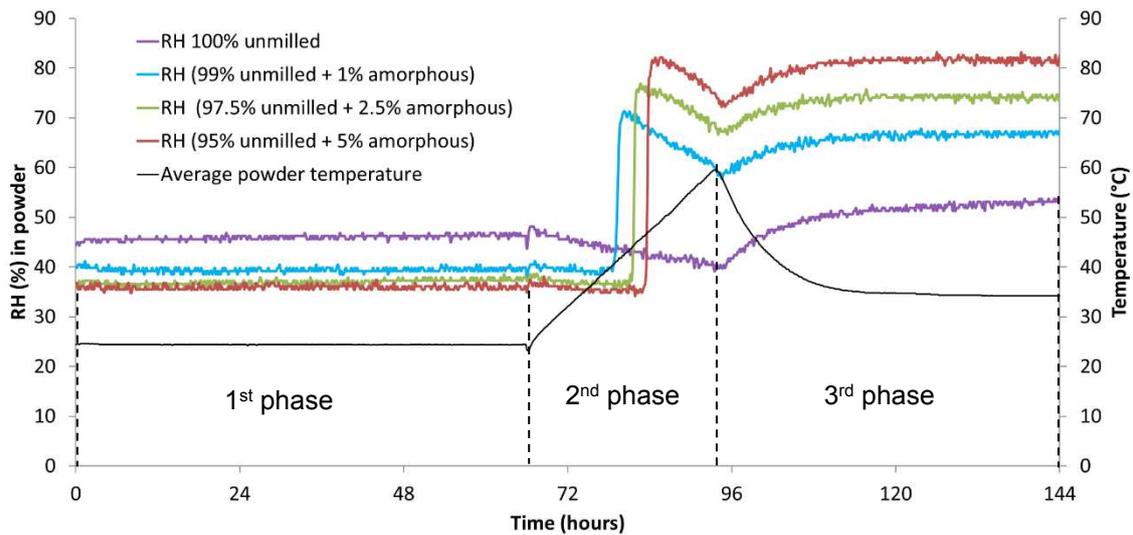


Figure 37: Evolution of RH in crystalline unmilled lactose powder mixed with amorphous lactose stored in closed containers in a climate chamber. Ambient RH was kept constant at 50% and temperature was increased from 25°C to 60°C in 30 hours. 1st phase: stable RH and temperature; RH was lower in samples with more amorphous material. 2nd phase: temperature was raised and RH increased sharply in all samples with amorphous material added. 3rd phase: temperature was lowered again and RH increased.

In the first phase, a new equilibrium was established between the amorphous material (RH=30%) and the crystalline lactose (RH=45%). According to the Salwin equation for the equilibrium water activity of a closed multi-components system, the equilibrium depends on the ratio of the components and the slopes of their respective moisture sorption isotherms (Bhandari & Adhikari, 2009). Thus, the addition of amorphous material led to lowering RH in the powder. Thomsen et al. (2005) showed that a lower RH was associated with less plasticization of amorphous lactose and a higher temperature necessary to induce crystallization.

These findings are consistent with the evolution of RH during the second phase presented here (Figure 37). Indeed, the storage temperature necessary to induce crystallization was higher in samples containing more amorphous material and where the equilibrium RH was lower. When the storage temperature was raised during the experiment, the glass transition temperature was exceeded and crystallization occurred accompanied by a release of water which was seen as a sudden peak in the RH curve.

In order to check that the sudden increase in RH was due to crystallization of amorphous material, 15% amorphous lactose were added to a commercial lactose sample. Then, MTDSC analyses were conducted before and after subjecting the sample to a storage with temperature increasing to values over the glass transition temperature. The crystallization peak visible in the samples before storage was absent from the DSC thermograms after storage (Figure 38). These results confirmed the important decrease in the amount of amorphous material in the sample during storage at temperatures over the glass transition temperature.

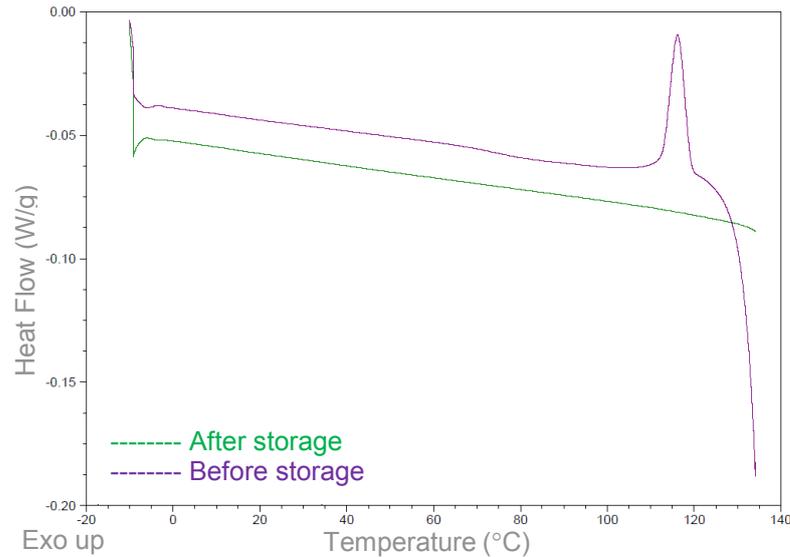


Figure 38: DSC thermogram of crystalline lactose powder mixed with 15% amorphous lactose before and after storage where temperature was raised over the glass transition temperature. The samples were stored in closed containers in a climate chamber, where RH was kept constant at 50%.

RH after crystallization depended on the amount of amorphous material crystallizing (Figure 37). Indeed, a larger amount of amorphous lactose was associated with a larger amount of water bound and subsequently released in the surrounding air during crystallization. This phenomenon can be observed in Figure 39 presenting the effect of small amounts of amorphous lactose on the moisture sorption isotherm of crystalline lactose (Bronlund & Paterson, 2004). In a closed system as a container, the moisture content remains constant and crystallization can be represented as an horizontal line in Figure 39. Clearly, RH can increase from values below 0.4 to values above 0.8 when crystallization occurs. Moreover, even if powders with higher amounts of amorphous material before crystallization had a lower RH, they probably contained more moisture as the difference in RH was small. Moisture bound to amorphous material was then liberated upon crystallization and led to a higher final RH in the crystalline powder for higher initial amorphous contents. It should be noted that the product of amorphous lactose crystallization can be a mixture of anhydrous and hydrous forms, which will impact the shape of the moisture sorption isotherm.

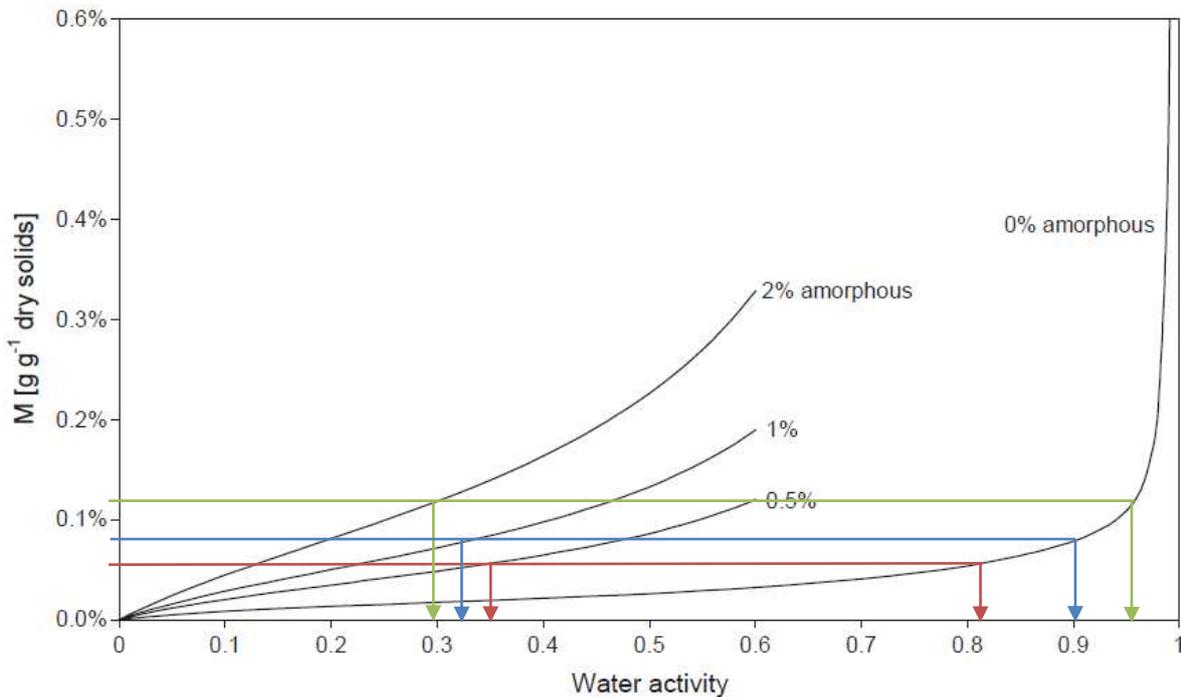


Figure 39: The predicted effect of small amounts of amorphous lactose on the moisture sorption isotherm of crystalline α -lactose monohydrate (modified from (Bronlund & Paterson, 2004)). The horizontal lines represent crystallization at constant moisture content in a closed system. The red, blue and green lines represents crystallization of 0.5, 1 and 2% amorphous lactose respectively.

It is also interesting to note that crystallization was a sudden event (Figure 37). This all-or-nothing event was also reported by Knudsen et al. (2002) and Clark et al. (2016) who failed at measuring the amorphous lactose crystallization kinetics because crystallization was completed too quickly once started.

In the end of the second phase and in the third phase, after crystallization, RH was only affected by variations in temperature, with as expected an increasing RH when temperature decreased. The crystalline powder indeed has a very low binding capacity and probably exchanges moisture with ambient air in a slow and limited fashion. The RH measured in the third phase of the experiment may therefore be mostly influenced by the water holding capacity of ambient air, rather than by moisture movements in the powder.

In the case of commercial crystalline lactose powder, no increase in RH was detected when temperature was raised in the second phase. The amount of amorphous material is thus probably below the detection limit of the method. With this method, a crystallization peak was observed in physical mixes containing down to 0.2% amorphous material (data not shown). However, as already mentioned for the gravimetric methods (cf. 6.2.2), the amorphous material might be less prompt to crystallize when distributed in a crystalline matrix as is most probably the case for commercial samples.

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

Data loggers have been used in studies dealing with food powders to monitor environmental conditions e.g. (Clark et al., 2016; Thomsen et al., 2005; Yazdanpanah & Langrish, 2013). However, using a miniature data logger placed directly in the powder to detect physicochemical changes associated with water has not been reported previously to the best of our knowledge. This method presents obvious advantages for the food industry as it is easy to use, not operator dependent, only requires a relatively small amount of sample and no data treatment. It can also be used at line if a computer is available for data reading. Moreover, as the sorption isotherm of lactose with low levels of amorphous material is flat (Figure 39), a method which detects the RH increase might be more sensitive than gravimetric methods.

The investigation of the presence of amorphous material in commercial crystalline lactose was undertaken using different methods with various detection limits. Measuring amorphous material in commercial samples is challenging because most instruments cannot be used in line. Amorphous lactose is unstable and can readily crystallize under specific conditions such as elevated temperature and RH after sampling. Careful storage of the sample prior to analysis should therefore be considered. In addition to DSC, DVS and RH measurements presented in this thesis, X-ray powder diffraction and spectroscopic analyses (IR, NIR, Raman) were also briefly conducted in collaboration with research groups expert in the field. All the measurements led to conclude that, if amorphous material was actually present, its amount was very limited. However, a very low amount does not mean that the remaining amorphous lactose is not involved in the caking issue. As mentioned in chapter 4, Bronlund (1997) found the amorphous material to play a role in caking by enhancing moisture sorption, when present at levels below 5%. Moreover, if it is concentrated on the surface of the lactose particles, it can greatly increase the interfacial interactions (Newell et al., 2001b). Thus, the presence of amorphous material will participate in the increased sorption observed for lactose powder containing more impurities (chapter 4). Therefore, there is a need for establishing means of controlling the impurity content in lactose powder.

6.3. How to control the impurity content on the process line?

6.3.1. Raw material

Before even considering the process, the type of raw material should be taken into account. For example, lactose is usually produced from sweet whey, a by-product of renneted cheese (mostly hard and semi-hard type) manufacturing, but there are also relatively large amounts of acid whey originating from the production of acid coagulated dairy products (e.g. fresh cheese) available for further processing. In 2015, approximately 10 million MT liquid acid whey and 170 million MT liquid sweet whey were derived from cheese and casein production at a global scale (Affertsholt &

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

Pedersen, 2016). The composition of the two types of whey can vary significantly (Pisecky, 2012) and average values are given in Table 7.

Table 7: Average composition of sweet whey, lactic acid whey and hydrochloric acid whey (modified from (Durham, 2009)).

Whey Component (g/100 g)	Sweet	Acid	
		Lactic Acid Whey	HCl acid Whey
Total solids	6.7	6.0	5.1
Lactose	4.8	3.9	4.4
Protein	0.60	0.72	0.73
Ash	0.54	0.72	0.60
Fat	0.25	0.06	0.05

Acid whey, and especially lactic acid whey, is considered to be a difficult stream to process. The higher mineral load makes it more prone to fouling during heat treatment, separation and evaporation. Acid whey also contains more acid which hampers the separation of lactose from minerals and impacts on the ease of drying (Hourigan et al., 2013), given the very low glass transition temperature of lactic acid. Lactose in lactic acid whey has also been reported to be difficult to crystallize (Chandrapala, Wijayasinghe, & Vasiljevic, 2016).

Another aspect which is often overlooked is the day-to-day and plant-to-plant variations of permeate composition depending on the whey origin and the efficiency of the process. To add to the complexity of the traceability of the product, whey from different cheese factories is often mixed prior to ultrafiltration.

6.3.2. Processing steps impacting on the impurity content

As presented in the process chart for the manufacture of lactose (Figure 9, Chapter 1), several steps, such as calcium phosphate removal, activated carbon treatment and nanofiltration, can be included in order to facilitate evaporation and the subsequent steps (Durham, 2009). Indeed, these pre-evaporation steps aim at reducing the amount of minerals and other impurities like riboflavin in the whey permeate. Minerals can otherwise induce fouling.

The hygroscopicity of a powder which had not been subjected to the calcium removal process was compared with a powder where calcium had been removed. The calcium removal process did not have any effect on the moisture sorption isotherm (data not shown). This suggests that calcium could be trapped inside the crystals, thereby preventing it from participating in moisture adsorption.

6.3.2.1. Separation and washing

Post-evaporation, the crystalline lactose slurry coming out of the crystallizer needs to undergo separation and washing where the mother liquor is removed, so that the crystals can be dried (cf.

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

Figure 9). The efficiency of the separation and washing steps greatly determine the remaining amount of impurities in the final product. Paterson (2017) emphasised the absence of published research work in this area, which might be a consequence of in-house kept knowledge.

Separation of the lactose crystals from the mother liquor is performed continuously in a solid bowl decanter, which is a decanter centrifuge (Durham, 2009). A decanter centrifuge (Figure 40) works by the action of a centrifugal force in an elongated, horizontal rotating bowl (5), which induces continuous sedimentation of suspended solids from a liquid. An axial screw conveyor (6) ensures continuous unloading of separated solids from the rotor. Solids discharge occur from the narrow end (3) while discharge of liquid phase takes place from the wide end (2) by countercurrent flow (Tetra Pak, 2015).

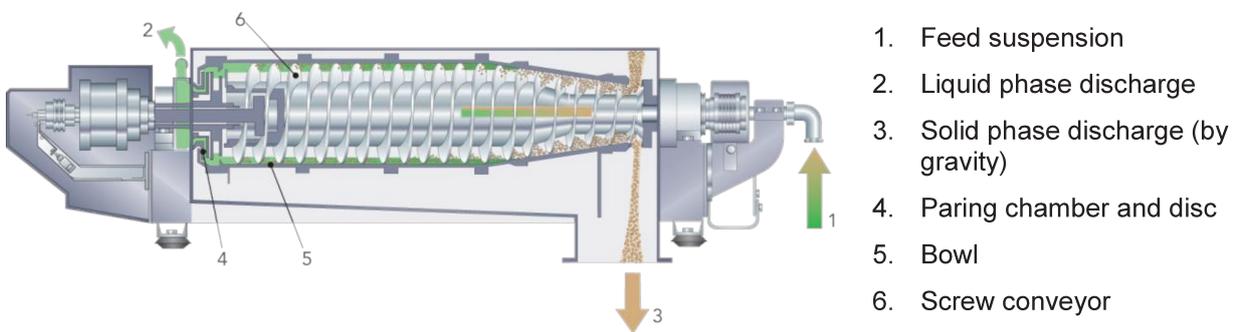


Figure 40: Operating principle of the decanter centrifuge used at the separation step (see Figure 9). Section through the rotor of a solid bowl decanter with pressurized discharge (Tetra Pak, 2015).

Then, the crystal slurry is typically washed by means of screen bowl centrifuges (Figure 41, (Durham, 2009)), that combine the clarifying action of the solid bowl decanter with a screen section allowing efficient dewatering (TEMA, 2017). The dry matter content of the product exiting the screen bowl centrifuge is typically 88-90% (Durham, 2009).

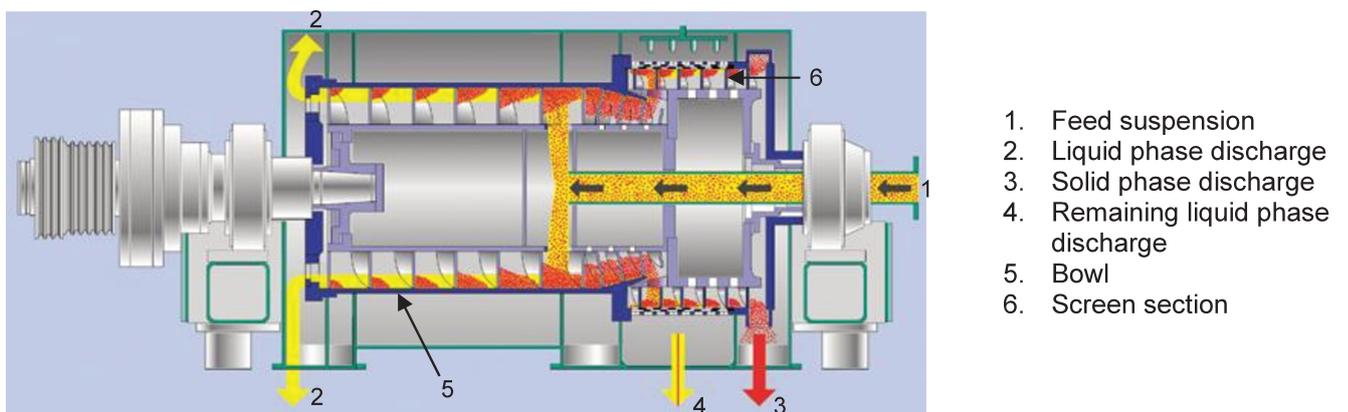


Figure 41: Operating principle of the decanter centrifuge used at the washing step (see Figure 9). An example of screen bowl centrifuge: the Turbo Screen decanter (modified from (TEMA, 2017)).

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

In this PhD project, the impact of the separation and washing steps on caking was investigated. Indeed, these steps greatly determine the final level of impurities, which have been shown to increase caking (chapter 4).

All other process parameters being constant, lactose powder produced without the action of the solid bowl decanter was found to contain about four times more sulfated ash than powder produced with a separation step (Table 8).

Table 8: Composition of lactose powders (fluid bed samples) with or without the separation step included in the production process (see Figure 9). All results are in percentage. The quantification limit was 0.025% for calcium and sodium, and 0.1% for protein and moisture.

Separation step	Lactose	Protein	Moisture	Total Water*	Sulfated Ash	Ca	Mg	P	K	Na
Yes	99.3	<LOQ	<LOQ	5.26	0.16	<LOQ	0.011	0.029	0.061	<LOQ
No	98.2	0.18	<LOQ	5.30	0.68	0.026	0.032	0.067	0.139	0.052

**as determined by the Karl Fischer method*

The dewatering process is less efficient when more impurities are present in the slurry (Durham, 2009). However, the final moisture content was low in the two powders, demonstrating the ability of the fluid bed drying step to remove the excess free water that could not be removed in the screen bowl centrifuge. It can also be seen that the total water content is slightly higher in the powder without the separation step. This can be explained by water bound to peptides and other impurities, which are in larger amounts in this powder.

In line with the results from chapter 4, the separation step was demonstrated to critically affect the hygroscopicity of the final powder (Figure 42). The increased hygroscopicity of the sample containing more impurities led to a higher caking tendency. Indeed, after a storage for 15 days at 20°C and 50% RH, the sample without the separation step was caked ($ffc < 1$) while the sample with the separation step was still easy flowing ($ffc > 4$). These results demonstrate the crucial role of the separation step in obtaining a product with a limited caking tendency.

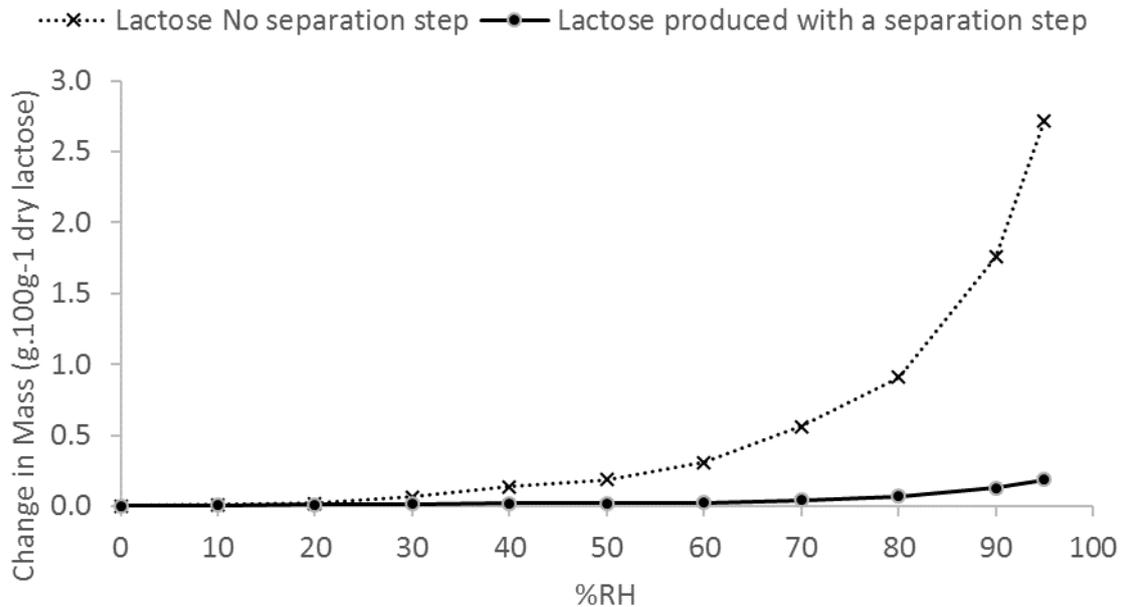


Figure 42: Moisture sorption isotherms of lactose powders (fluid bed samples) with or without the separation step included in the production process (see Figure 9).

Optimization of the washing process was conducted in order to reduce the amount of wash water used while ensuring a sulfated ash level below 0.3% as listed in the AFI specifications for lactose powder (see section 1.2.4). Samples with standard washing and increased washing were subjected to moisture sorption measurements and caking test. In these samples, the sulfated ash content was measured to be 0.2% and 0.1% for the standard and increased washing, respectively. The hygroscopicity of the sample with increased washing was close to the one of pharmaceutical grade lactose (Figure 43). The total sorption (at 95% RH) was four times higher in the sample with standard washing compared to the more washed powder. Wash 1 and Wash 2 powders produced on a pilot scale displayed a factor two difference in total sorption (Figure 22, chapter 4) but were not possible to discriminate in the caking test (Figure 26, chapter 4). Here, on the contrary, the commercial sample with standard washing and increased hygroscopicity was also characterized by a stronger caking tendency (Table 9). In addition, the PSD, which was not measured in these samples, can also affect the results.

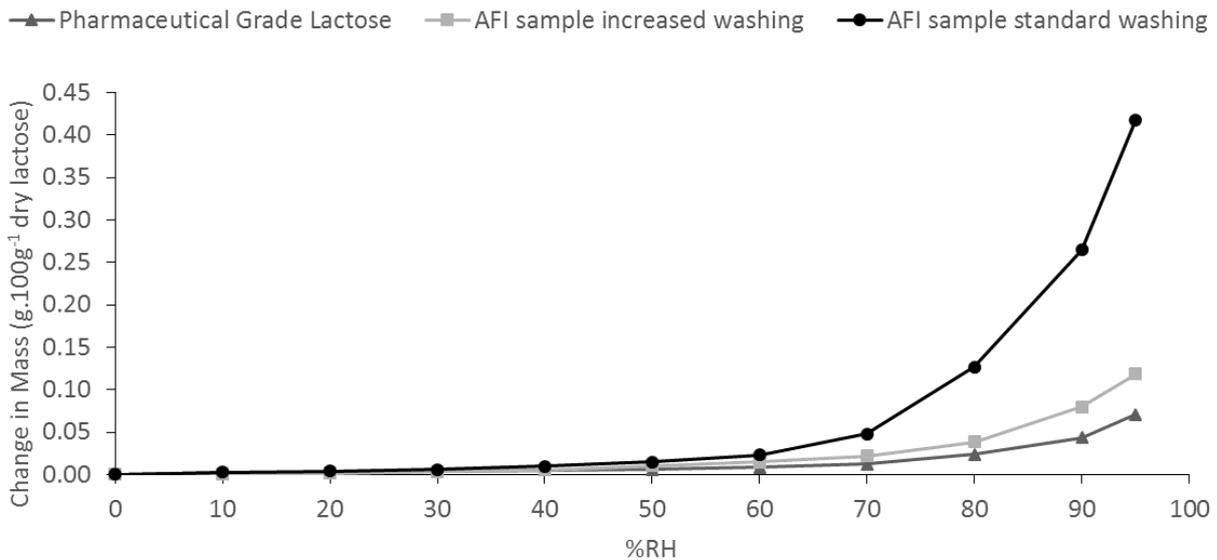


Figure 43: Moisture sorption isotherms of commercial lactose finished goods samples with different washing levels. Pharmaceutical grade lactose is included for comparison purposes.

Table 9: ffc of commercial lactose powders with different washing levels after storage for four days at 60% RH and 20 °C. Each sample was consolidated under a pressure of 9.3 kPa. The flowability of pharmaceutical grade lactose after storage is included for comparison purposes.

Sample	ffc after storage
Pharmaceutical Grade Lactose	5.8 ± 0.6
AFI sample increased washing	5.8 ± 0.8
AFI sample standard washing	1.0 ± 0.1

These results emphasize the importance of optimizing the separation and washing steps as they can significantly influence the caking tendency of the final product through the impurity content. However, lowering the impurity content always involves higher operating costs, in connection with the use of more wash water or longer processing times needed. Recirculation of wash water is a possibility but the fines dissolved in the water contain high levels of impurities which will increase the hygroscopicity of the whole powder. Increased washing can also modify the particle size distribution of the crystals, which has been demonstrated to be a critical parameter for caking (chapter 5). It is therefore impossible to give *a priori* a precise guideline for the amount of impurities that should not be exceeded in order to secure a free-flowing product. Indeed, caking does not depend only on the impurity content and while adjusting this parameter on the process line, other product properties can be changed. For these reasons, a specific study on how (e.g. several successive dilutions rather than a single water addition) and until which point (washing grade value) the washing step should run is needed in the future, in order to provide useful recommendations based on a cost/benefit assessment.

6.3.2.2. Drying

In the present PhD study, amorphous material was not detected in the commercial samples. However, the formation of a layer of amorphous material on the surface of the lactose crystals during rapid drying has been reported and the kinetics of amorphous lactose crystallization at high temperatures have been investigated to ensure complete crystallization of amorphous material in the fluid bed (Clark et al., 2016). The results showed that very little change in the fluid bed operating conditions were required to move from complete crystallization of any amorphous lactose present to no crystallization, leading to an unstable product after drying. Analysis of the optimal drying conditions have not been included in the frame of this PhD project.

However, the amorphous content is not the only product parameter which can be influenced by the fluid bed operating conditions. Indeed, the fluid bed is equipped with filters which capture the fine particles. Results from chapter 5 have shown that the fines in samples produced on a pilot scale contained significantly more impurities than bigger particles. On the production line, powder was sampled at the fluid bed exit, sieved into different size fractions which were analyzed for their chemical composition. The same trend for the commercial samples was observed as for the pilot samples, that is the content of impurities increased with a decreasing particle size (Figure 44). An exception can be noticed for the biggest particles ($x > 500 \mu\text{m}$) which had a higher content of impurities than the particles in the smaller size fraction ($355 \mu\text{m} < x < 500 \mu\text{m}$). This was also the case in the least washed powder from the pilot trial (Wash 0) and was explained by the agglomeration of several fines together or on larger crystals (section 5.2.2). The learnings from chapter 5 therefore applies to commercial samples as well.

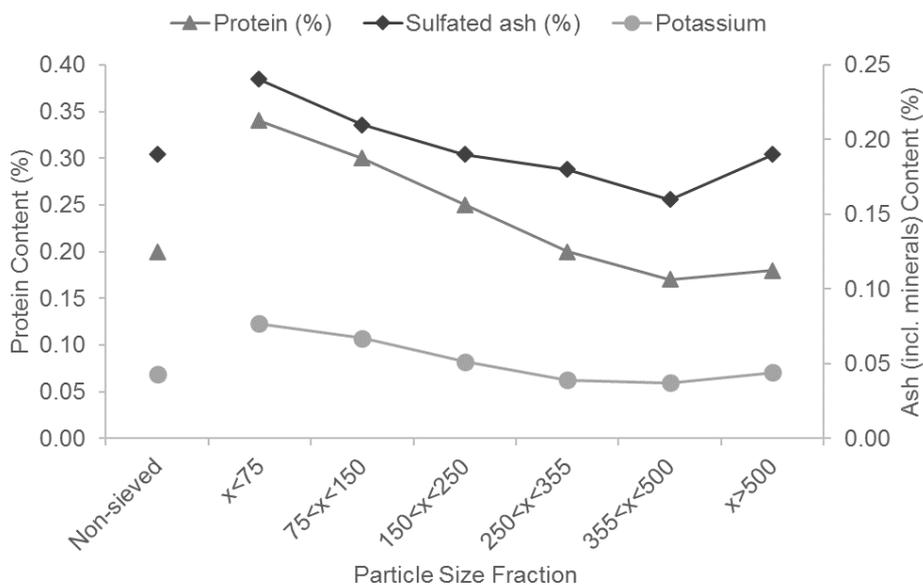


Figure 44: Impurity content (protein on the left axis; sulfated ash and potassium content on the right axis) as a function of the particle size class of a lactose powder sampled at the exit of fluid bed. Other minerals analyzed were below quantification limit.

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

An investigation of the composition of the powder from filter bags equipping the fluid bed was undertaken. The filter powder composed of the fine particles was found to contain up to almost three times more sulfated ash than what is permitted by the Codex standard for sugars (Codex Alimentarius, 2001). The level of protein was also at the maximum of the permitted amount in one of the samples.

Table 10: Composition of two samples of lactose powders from filter bags. The reference composition given by Codex (Codex Alimentarius, 2001) is included for comparison purposes.

Sample	Lactose (%)	Sulfated Ash (%)	Protein (%)
1	99.0	0.6	0.3
2	98.6	0.8	0.5
Codex standard for sugars (Codex Alimentarius, 2001)	min 99	max 0.3	max 0.5

Recirculation of the fines during drying should therefore be done with extreme care. It is not expected to impact the overall ash level of the final powder to a significant extent. However, the fines which will be present in the powder will greatly enhance the hygroscopicity of the whole powder, as shown in chapter 5. This chapter also concluded that there is a need to control the PSD and more specifically the amount of fines and the span of the distribution in the finished powder in order to limit caking.

6.4. How to control the PSD on the process line?

6.4.1. Crystallization

Crystallization is obviously the most important process to consider in order to obtain the right PSD. Batch cooling crystallization is the usual process in the lactose industry (Paterson, 2017). The overall aim is to produce large crystals with few fines, which is not straightforward considering the multiple parameters that can influence both nucleation and growth of the crystals. Some of these parameters are the cooling profile, seeding, mixing and the pH of the solution (Wong & Hartel, 2014). In addition, various impurities commonly found in whey have been shown to impact nucleation, growth and the type of crystal formed (Paterson, 2017). Considering the complexity of the crystallization process, a study on how the different crystallization parameters impact the PSD was outside the scope of this PhD work. According to Wong and Hartel (2014), the crystallization process is far from being optimized and the dairy industry should focus on applying the knowledge obtained from numerous papers to the industrial process.

After exiting the crystallizer, the crystals with a given size distribution will undergo several processing steps. It is difficult to imagine that the PSD will not be modified throughout these subsequent steps.

6.4.2. Separation and washing

The separation and washing steps were demonstrated to dramatically influence powder caking through the impurity content and hygroscopicity (6.3.2.1). In addition, the centrifugal action utilized in these steps is likely to induce mechanical abrasion of the crystals. The amount and temperature of the water introduced in the decanters will also influence the solubility of the small crystals. Recirculation of the wash water containing dissolved fines to an earlier process step is an attractive option as it can increase the yield of the overall process. However, the fines were shown to contain more impurities than the bigger particles (Figure 44, 6.3.2.2) and should therefore be recirculated upstream the separation step in order not to increase the overall impurity content of the final powder.

6.4.3. Drying

Mechanical abrasion can also take place in the fluid bed depending on agitation, fluid bed design and holding time. These parameters together with the fluid bed temperatures will also influence the formation of agglomerates. Moreover and as mentioned in 6.3.2.2., recirculation of the fines in the fluid bed should be done with care. It will impact the PSD of the final powder, either by increasing the amount of fines or by inducing the formation of agglomerates when the fines are redirected into the fluid bed. Indeed, the fines can agglomerate together or promote agglomeration of bigger crystals by acting as a glue in between them (Figure 45). Depending on their friability, the agglomerates can be worn out downstream in the process.

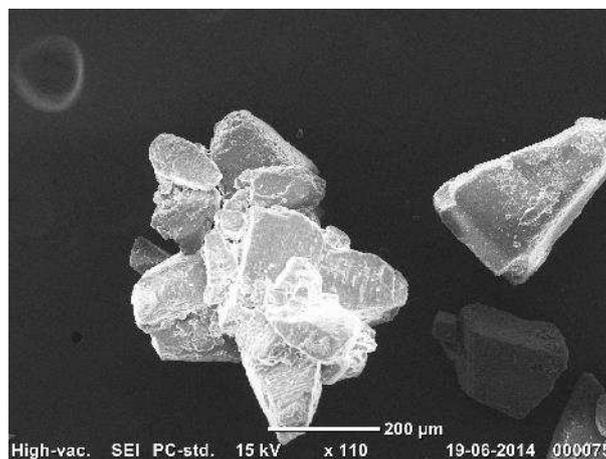


Figure 45: Example of agglomerate constituted of large tomahawks agglomerated together by smaller fragments. Powder was sampled at the exit of the fluid bed.

6.4.4. Transportation and silo system

Pneumatic conveying lines transport the powder to silos and packaging lines (Paterson, 2009). In order to assess the impact of pneumatic transport on PSD, lactose powder was sampled at the exit of the fluid bed and during silo emptying on the packaging line. All samples were analyzed for

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —

their PSD and a clear reduction in size was observed (Table 11). The D_{10} was reduced by a factor two and the span of the distribution was significantly broadened, demonstrating the formation of fines during transport. Pneumatic transport is therefore harsh to the particles, with agglomerates that can be broken into smaller fragments and crystals that can be damaged, leading to smaller particles and an increased amount of fines. The air velocity and the transport path into the pipes should therefore be carefully chosen. Moreover, aeration is often used in the silos in order to fluidize the powder. This process, which can also impact the PSD of the particles, will be in focus in the next chapter (chapter 7) which aims at controlling the powder water activity.

Table 11: Characteristics (D_{10} , D_{50} , D_{90} and span) of the PSD of samples of lactose powder obtained at the exit of the fluid bed and on the packaging line during silo emptying. n corresponds to the number of samples taken at each sampling point.

Sampling Point	Particle Size Distribution			
	D_{10}	D_{50}	D_{90}	Span
Fluid Bed Exit ($n=16$)	165 ± 31	313 ± 51	543 ± 90	1.2 ± 0.1
During Silo Emptying ($n=12$)	81 ± 27	257 ± 41	508 ± 89	1.7 ± 0.2

6.4.5. Milling

The effect of the milling parameters on caking has not been investigated in this PhD project as the focus was on unmilled lactose. Yet, milling is an obvious process which will modify the PSD of the product. The average particle size decreases, which was shown to lead to stronger caking. However, it is also important to evaluate how the span is modified (chapter 5). For example, Bronlund and Paterson (2004) measured less moisture sorption for milled than for unmilled lactose powder and explained this result by a narrower span in the milled powder. In addition, milling can influence the impurity content of the powder. Amorphous material was shown to be formed on the surface of the lactose crystals during milling (Newell et al., 2001b). Breaking the crystals can also expose impurities which were originally trapped inside the crystals.

6.5. Conclusions

This chapter aimed at applying the results from chapter 4 and 5 to the process line. In order to evaluate the influence of impurities on caking in commercial samples, their content was measured. Amorphous material was below the detection limit of all investigated analytical methods. The increased hygroscopicity and stronger caking measured in pilot samples with more impurities (chapter 4) was confirmed in commercial samples with a lower degree of washing. In addition, a higher amount of impurities was measured for smaller particles in the commercial samples,

— Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —
similarly to the pilot samples (chapter 5). The presence of fines can thus lead to increased humidity and mechanical caking. According to the results of the study on a pilot scale, the amount of impurities and the PSD are therefore critical to control in order to limit caking in commercial samples.

Consequently, the control of these two parameters on the process line was another focus point of this chapter. Apart from the raw material origin which determines the nature and the level of impurities in the product, several processing steps were pointed out to influence either the impurity content or the PSD. Interestingly, many steps influenced both. Thus, the levels of impurities and the PSD of the powder are closely related. For example, increased washing would decrease the amount of impurities but may also modify the particle size by mechanical abrasion or partial dissolution. In addition and given the highest amount of impurities in the fines, each step with a recirculation of fines can impact the final purity of the product and the PSD, either by increasing the amount of fines or by agglomeration.

Considering the close relationship between the impurity level and the PSD, it appears difficult to define quantitative thresholds for these two product parameters independently in order to prevent caking. For example, ensuring that the ash level is below 0.3% cannot secure a free-flowing product if there is a large amount of impurity containing fines in the product. Moreover, it is often a challenge to reach precise values for each individual product parameter in industrial settings as food products are complex systems with many interactions that can be easily influenced by the process. The solution for the dairy industry could be to directly evaluate the influence of the different processing steps on caking, instead of trying to achieve specific levels for the product parameters to secure a non-caking product. This solution still requires to know which product parameters are critical for caking in order to focus on the processing steps impacting them.

The investigation of the caking mechanisms in crystalline lactose powder has highlighted the crucial role of humidity. Impurities and fines were shown to increase the interactions of the powder with moisture, which is known to form liquid bridges between particles and thereby lead to caking. The availability of the water contained in the lactose powder is therefore a capital information, which could possibly be used to evaluate the powder caking potential.

6.6. Take-home messages

- The results from the study on a pilot scale (part 2) were confirmed for the commercial powder. Indeed, in commercial samples, smaller particles were found to contain more impurities. Commercial powders containing more impurities also showed increased hygroscopicity and stronger caking.
- The critical processing steps to control the impurity content and the PSD of the final product have been highlighted. Many steps were found to impact both parameters. Therefore,

- Chapter 6: On the process line: how to control the impurity content and the PSD in the final product? —
- optimization of a specific processing step to limit caking should be done by taking both product parameters into account.

Chapter 7 – Monitoring the powder water activity as a mean to prevent caking

Summary

Moisture plays a crucial role in the development of caking. Water activity which represents the availability of the water in the powder, was therefore the focus of this chapter. The first objective was to obtain a reliable measurement of water activity in lactose powder. This was difficult to achieve with an automatic water activity meter, probably because of the very small amount of free water in lactose powder which limits water exchange with the surrounding air. Moreover, the product was observed to be unstable after drying, with the water activity measured with data loggers reaching values up to 0.9 in less than a day of storage. This sharp increase was explained by the crystallization of remaining amorphous material. The same phenomenon was observed in the powder during storage after packaging and a high water activity in the powder was linked to the development of caking in most batches. Thus, the second main objective of this chapter was to investigate the processing steps which impact the water activity of the final product. The washing and fluid bed drying parameters should be optimized in order to obtain a lactose powder with a minimum content of impurities and a low water activity. Alternatively, aerating the lactose powder after drying, either by pneumatic transportation or during storage in silos, should enable to reach a low and stable a_w . Indeed, it was shown that aeration significantly lowered the powder a_w . The optimal aeration mode (i.e. continuous or discontinuous) was dependent on the availability of silos for the powder to rest for a long time between aerations. Finally, after packaging, the powder a_w can still be modified due to variations in temperature and humidity during transportation to the customers.

The objectives of this chapter were to:

- Investigate a method to obtain reliable water activity results in commercial crystalline lactose powder
- Understand how water activity can increase sharply in lactose powder after drying
- Point out the processing steps which can impact the water activity of the final product

7.1. Introduction

The review of the literature (chapter 1) indicated that crystalline lactose can cake whenever relative humidity is high enough for significant liquid bridging to occur. In addition, any amorphous material present would lower the stability of the powder as it can absorb significantly more moisture than the crystalline material. Impurities in general and a smaller particle size were demonstrated to increase moisture sorption and caking in crystalline lactose powder (chapters 4 and 5). Therefore, at this point of the study, the crucial role of humidity in the caking issue has become clear.

In addition, Bronlund (1997) modelled caking in lactose powder due to moisture migration as a result of temperature gradients, and concluded that the product, if fully crystalline, should be packed at a water activity below 0.57 to avoid caking. If amorphous material is present, then he recommended a maximum a_w at 0.25 upon packaging. The water activity of the powder is a measure of the thermodynamical state and the availability of the water for interactions (e.g., solvent) or reactions (e.g., hydrolysis) with constituents or micro-organisms. As such, it gives an indication of the powder stability against humidity caking. Thus, if caking can be avoided by ensuring a low water activity in the powder, then water activity should be measured and the different process steps that can influence the final a_w value should be investigated.

In this PhD study, both off-line measurements in the laboratory after sampling and measurements directly in the powder bag were performed. The first method involves automatic devices which measure the relative humidity of the air above the powder sample in a hermetically closed chamber. When equilibrium between the air and the powder is reached, the water activity of the powder is known. The second method relies on the use of RH probe or humidity loggers, which can measure water activity over a long period and at different places in a bag. An essential difference between the two approaches is that automatic laboratory devices are constructed to give, as fast as possible, the a_w value representing the state of the system once equilibrium between the air and the powder sample has been achieved. However, as noticed when measuring RH to detect crystallization (section 6.2.3), the lactose powder contains very little free water which can limit exchange with ambient air in the measurement chamber of a water activity meter. Equilibrium might therefore establish very slowly, leading to an a_w value only representing a partial equilibrium. On the other hand, measurements with RH probe give instant values of humidity in the air surrounding the powder particles and allow to follow its evolution. Thus, equilibrium might not be achieved at all points, making this approach only partially representative of the water status, that is to say bound or free, in the powder. However, as data loggers can record RH over a long storage time, it is possible to take measurements until equilibrium is achieved. In addition, the measurement is performed directly in a powder bag, where the ratio of powder to air is much larger than in the measurement chamber of a water activity meter. Thus, exchange might be facilitated

and equilibrium achieved faster. In the following, the term water activity (or a_w) will be used to designate the result of an off-line measurement with an automatic device while the term relative humidity (or RH) will refer to measurements with probes or data loggers.

7.2. Evolution of water activity in factory samples

7.2.1. Water activity measured after storage

Water activity measurement with automatic device is nowadays a routine analysis in many laboratories (Mathlouthi, 2001). However, care should be taken in order to obtain reliable results. For example, it was observed that analyzing first a sample with a high a_w could influence the a_w value measured subsequently on a different sample, even if this latter was analyzed on a different day (Table 12). Some moisture might remain in the chamber of the measuring device and as the isotherm of lactose is very flat, the small amount of moisture influences the a_w value. Similarly, a dependency of the results on the room humidity was observed. It is therefore recommended to take at least two measurements on each powder and to control RH in the room where the apparatus is placed. Moreover, measurement times were often long (over ten minutes) when analyzing lactose powder and the a_w value could still vary after a result was given by the apparatus. As explained above (section 7.1), the little free water in the lactose powder might slow down establishment of the thermodynamic equilibrium between the product and the air surrounding it. A stable value can thus be long to obtain. In conclusion, given all the above-mentioned limitations, the water activity of lactose powder measured with a water activity meter should not be used for quality control purposes.

Table 12: Water activity repeatability test performed with a water activity meter. Sample 1 was taken before fluid bed while sample 2 was taken at the exit of the fluid bed. The measurements were performed after storage of the powders at ambient conditions for several days.

	Sample 1 (high a_w)					Sample 2 (low a_w)				
Day 1						0.348	0.386	0.398	0.392	0.386
Day 2	0.972	0.974	0.971	0.972	0.972					
Day 3						0.558	0.397	0.371	0.360	0.351
Day 4	0.972	0.974	0.970	0.975	0.973	0.401	0.374	0.361	0.356	

7.2.2. Water activity measured right after drying

The time delay between sampling and measurement of a_w can possibly also influence the result depending on the storage conditions. To overcome this bias, measurements were performed immediately at the exit of the fluid bed (Figure 46, see section 3.4.7). Lactose powder was sampled

on three different days and for all batches, an increase in a_w with storage time was observed. The product seems therefore to be unstable after drying.

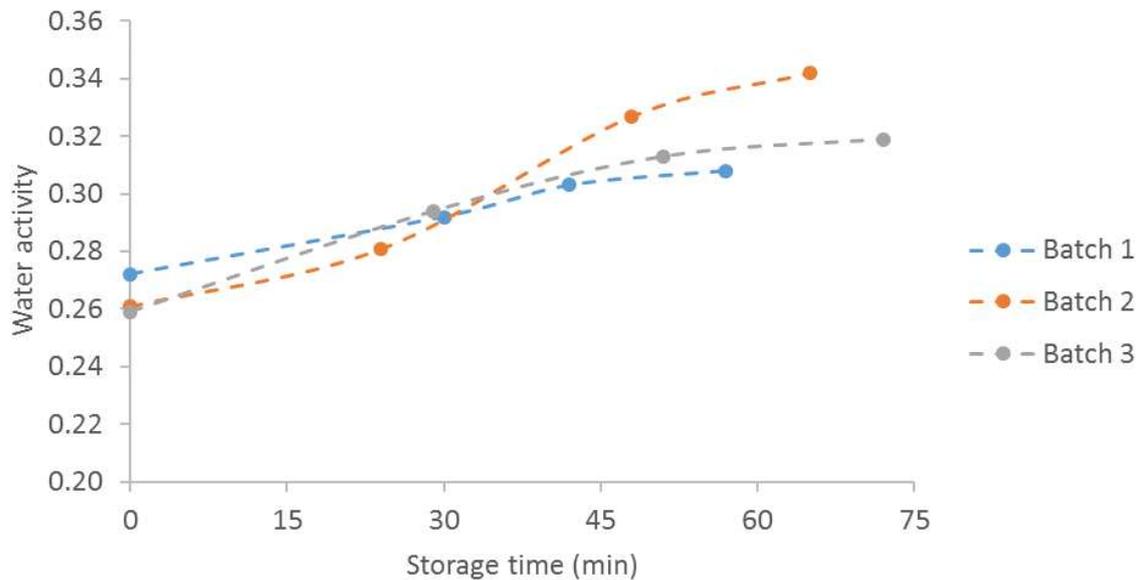


Figure 46: Evolution of water activity with storage time in three batches of lactose powder produced on different days. For each batch, four samples were taken from the exit of the fluid bed at the same time and analyzed one after another with a water activity meter.

A high a_w in a food powder is known to be detrimental not only for the caking tendency but for the whole storage stability, as it will dramatically favor mold and microbial development. It is therefore crucial to be able to monitor the increase in a_w in the powder. The use of miniature temperature and humidity loggers placed directly in the powder is more suitable for this purpose than the water activity meter. The evolution of relative humidity in eight fluid bed samples coming from different crystallizers was followed with this method (Figure 47, see section 3.4.7). It can be observed that RH increased sharply during storage and reached very high values up to 90% in about 9 hours. The moisture content was measured to be below 0.11% in all samples. This increase in RH after drying is an unusual behavior for a powder and this new phenomenon has not been reported in the literature to the best of our knowledge.

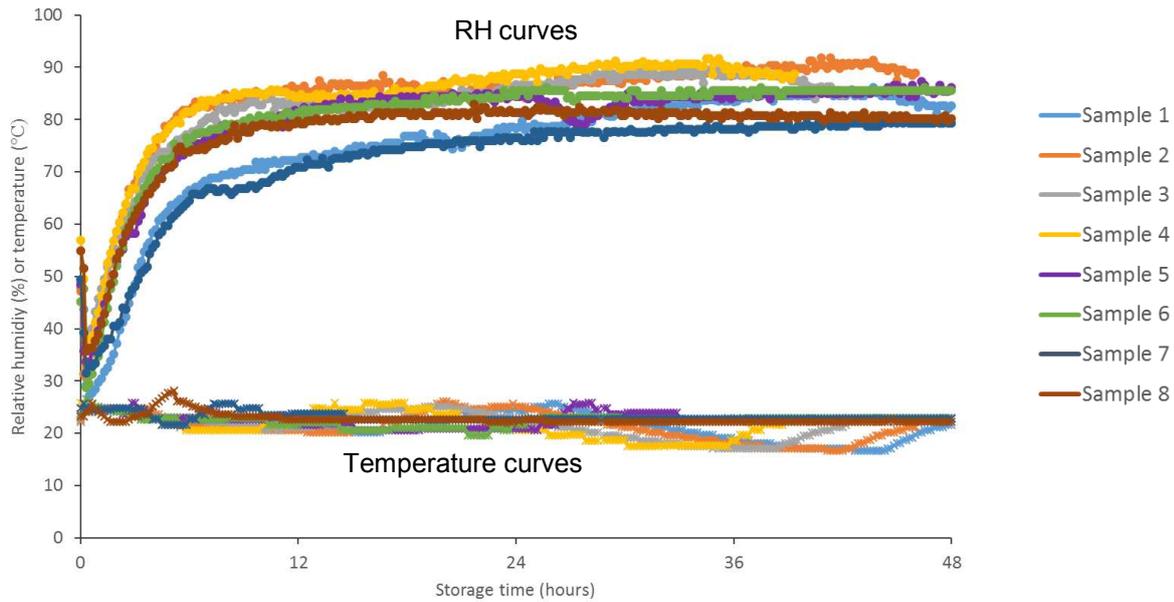


Figure 47: Evolution of relative humidity and temperature with storage time measured with a data logger in eight different fluid bed powders. Powders came from various crystallizers at the same production site.

The sharp increase in RH was also observed on the RH curve obtained during crystallization of the amorphous material added to a lactose sample (section 6.2.3). It suggests therefore the presence of amorphous material in the lactose powder sampled at the exit of the fluid bed. The rapid crystallization after drying could explain the fact that amorphous material was not detected in commercial samples (section 6.2). It would be interesting to estimate the amount of amorphous material needed to trigger such an increase in RH in the powder. Bronlund and Paterson (2004) proposed a simple additive method for predicting isotherms for partially amorphous lactose powders, that is expressed as:

$$M_{\text{mixture}}(a_w) = (1-w) \cdot M_{\text{crystalline}}(a_w) + w \cdot M_{\text{amorphous}}(a_w) \quad (6)$$

where $M(a_w)$ is the moisture sorption isotherm function of the powder (either 100% crystalline, 100% amorphous or a mixture of both) and w represents the mass fraction of the powder that is amorphous. $M_{\text{amorphous}}(a_w)$ can be parametrized using the Guggenheim–Anderson–De Boer (GAB) equation with the GAB parameters reported by Bronlund and Paterson (2004) for example. Using Eq. (6), the moisture content of a powder of a specific a_w containing a mass fraction w of amorphous material can be determined. Out of the fluid bed, RH was between 30 and 40% and increased to about 80% depending on the sample. As the bag with the powder is assumed to be hermetic at least on the time scale of a few days, it is considered a closed system and the moisture content of the powder can be considered as constant. When crystallization occurs, this moisture content moves the system to a new equilibrium RH corresponding to the isotherm of the crystalline lactose. This can be visualized on Figure 48, which represents the measured isotherm of a commercial crystalline lactose and the calculated isotherm using Eq. (6) of a mixture of crystalline

lactose with amorphous material. If the powder initially contained 0.5% amorphous material, its moisture content at 40% RH was 0.039%. After crystallization, this moisture content would correspond to 80% RH according to the crystalline lactose sorption isotherm.

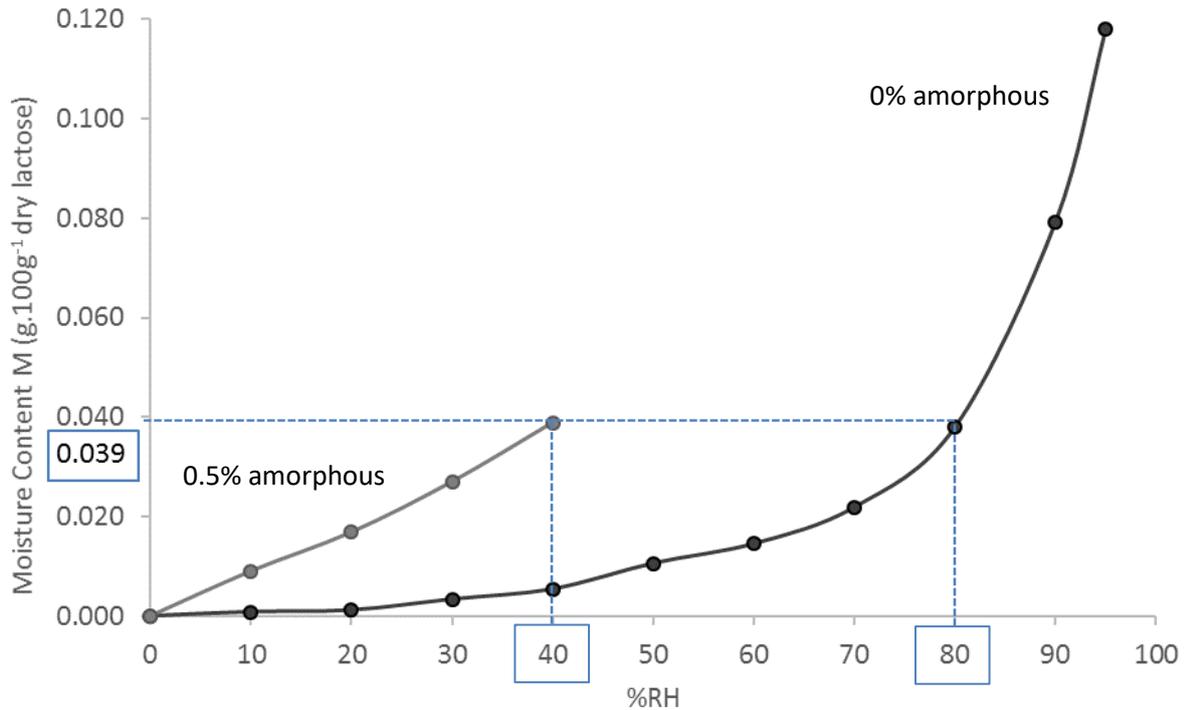


Figure 48: Prediction of an increase in RH from 40 to 80% due to crystallization of 0.5% amorphous material in lactose powder. The moisture sorption isotherm of commercial crystalline lactose was measured and the effect of 0.5% amorphous material on the isotherm was calculated using Eq. (6).

The shape of the isotherm curve of the crystalline sample obviously influences the amount of amorphous material needed to increase RH from 40 to 80% when crystallizing. More precisely, a flat isotherm as represented on Figure 48 leads to a large increase in RH with only 0.5% amorphous material present in the mixture. When the isotherm curve is steeper (Figure 49), 0.5% amorphous material can only trigger an increase in RH to 60%. However, the higher the amorphous material content of the powder (e.g., 3% amorphous), the higher the RH increase (e.g., 82% RH reached after crystallization).

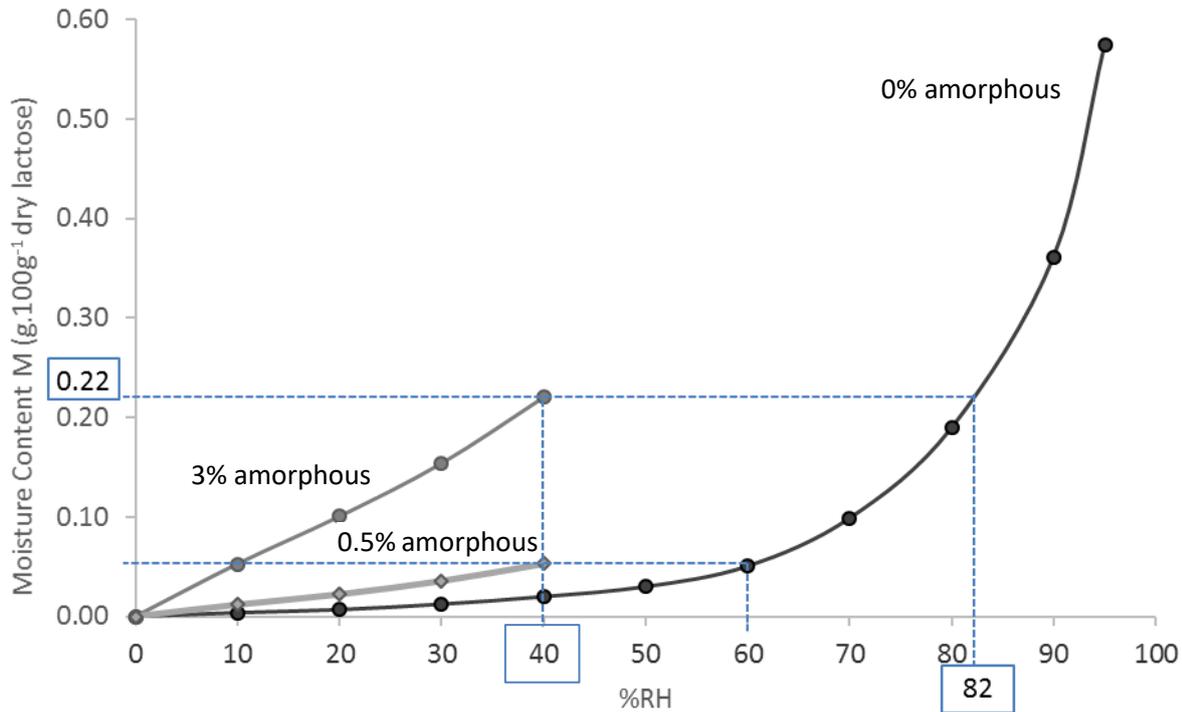


Figure 49: Prediction of an increase in RH from 40 to 82% due to crystallization of 3% amorphous material in another batch of lactose powder. With crystallization of 0.5% amorphous material, RH increases from 40 to 60% only. The moisture sorption isotherm of commercial crystalline lactose was measured and the effect of 0.5% and 3% amorphous material on the isotherm was calculated using Eq. (6).

Important batch to batch variations were observed on the isotherm curves of commercial samples. These differences might be explained by the amount and type of impurities and the PSD, which were both shown to greatly influence the sorption isotherm of lactose powders (chapters 4 and 5). Indeed, depending on the whey composition, the impurities concentrated on the surface of the final lactose powder can vary and adsorb moisture to different extents. Moreover, the sample size was as low as 40 mg for the DVS measurements and the PSD can vary from one sample to another within the same batch of powder, given the difficulty to obtain such a small representative sample. However, the two batches presented in this study (Figure 48 and Figure 49) represent extreme cases. The presence of 0.5 to 3% amorphous material is consistent with the values reported in the literature, which are in the same range, namely 0.9 to 1.6% amorphous lactose present in samples from a dryer discharge (Bronlund, 1997).

A content of amorphous material between 0.5 and 3% is above the detection limit of most analytical methods including the DVS (Giron et al., 2007). However, such measurement constitutes a challenge given the high instability of the amorphous material, which appears to complete crystallization in some hours after the drying step (Figure 47). An in-line and rapid technique should therefore be preferred to have a chance to detect any amorphous material present in the lactose samples. Spectroscopic techniques, such as Raman and NIR, are

increasingly used as process analytical technologies and were demonstrated to be able to quantify the amorphous lactose content in binary mixtures as well as in whey permeate powder (Nørgaard, Hahn, Knudsen, Farhat, & Engelsen, 2005).

Another possibility to quantify the amorphous material in commercial fluid bed samples would be to prevent crystallization from happening by freezing the amorphous lactose in its disordered state until measurement. Two approaches can be considered to this end. The first one consists in lowering the product temperature below its T_g . This could possibly be achieved by freezing the powder in dry ice at the exit of the fluid bed. However, the feasibility of such treatment is limited in industrial settings especially considering the high hygiene requirements in the production. The second approach to prevent crystallization is to increase the T_g so that it is not exceeded at the exit of the fluid bed. Attempts to increase T_g by removing the extra water molecules that could plasticize the product right after drying were made. Fluid bed samples were placed in desiccators containing silica gel for several days and subsequently analyzed on DVS but amorphous material was not detected (data not shown).

Another point to consider is that the amorphous lactose might crystallize inside the fluid bed and cannot be quantified in this case. This is supported by RH measured below 30% in some samples exiting the fluid bed dryer (Figure 47). Amorphous lactose is unlikely to crystallize at such a low RH combined with a temperature of 20°C, as the T_g was reported to drop to 24°C at a water activity of 0.37 (Jouppila & Roos, 1994). However, the slow release of water after crystallization might explain the increase in RH measured in the lactose after drying. On the production line, aeration of the product with cool and dry air in silos after the drying step could be a way to remove the extra water in the product. This will be discussed in greater detail in section 7.3.3.

7.2.3. Water activity measured after packaging

It was seen in chapter 6 that the PSD could be modified downstream, even if it is largely determined at the crystallization step. Likewise, drying is expected to be the determining step for a_w but the subsequent process steps can impact a_w . For this reason, a_w should also be measured in the finished goods. However, as mentioned in section 7.2.1., a_w measurements with a_w -meters were found to have limited reliability. Thus, the use of humidity probes that could be placed directly into the bag was advocated. This method eliminated at the same time any sample handling which could alter a_w . Data from a test production showed that RH could also reach very high values in the product after packaging (Figure 50). It was therefore decided to measure RH in Big Bags from test productions sampled over several months and investigate a possible correlation with the caking tendency. More precisely, selected batches from different test productions with varying process parameters were packed in Big Bags and stored for three weeks before RH was measured with a probe. The bags were then emptied on an automatic emptying station and the presence of powder lumps on the sieve was visually assessed. Lumping was observed in most

batches with a high RH (Figure 51). A RH threshold at 55% could be defined. A relative humidity above this threshold leads to an increased risk of caking. In the numerous batches which did not show any sign of lumping and where RH was below 55%, various PSD and impurity content were measured (data not shown). Therefore, there seems to be a critical value of RH which might ensure a non-caking product, whatever the other product parameters, provided that RH is below this value. There is consequently a need to understand how to control the process in order to ensure a low RH in the lactose bags.

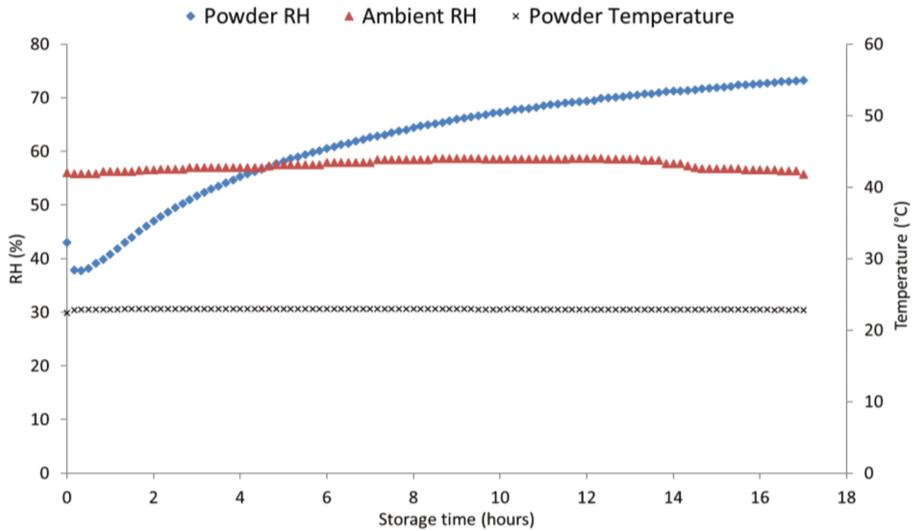


Figure 50: Evolution of relative humidity and temperature measured with a probe stuck into a Big Bag filled with lactose powder from a test production. Ambient humidity was also measured for comparison purposes.

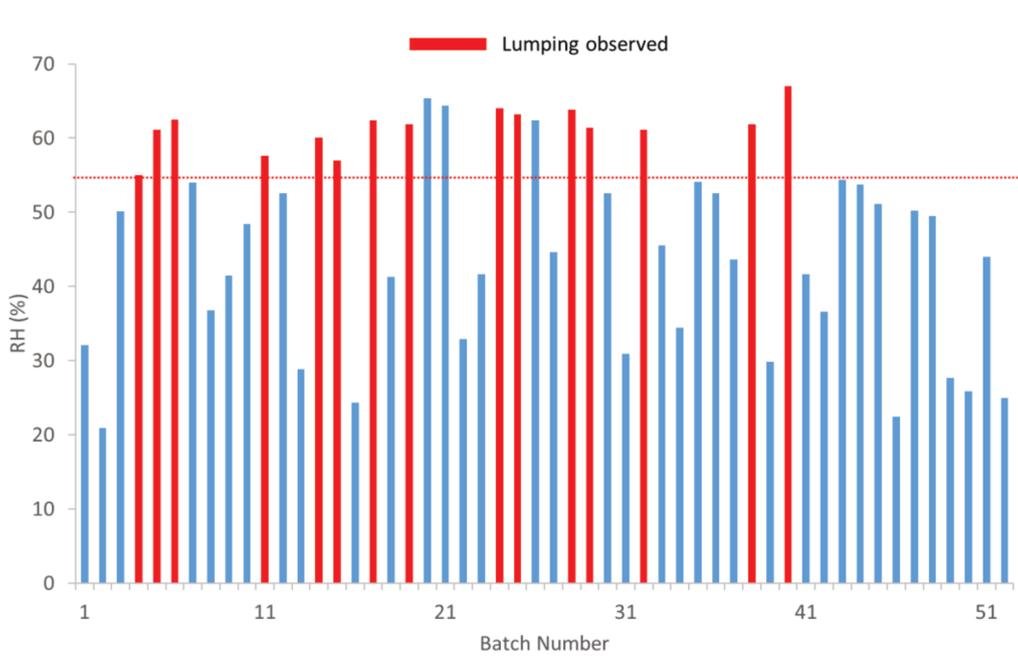


Figure 51: RH measured three weeks after powder bagging with a probe stuck into the Big Bag containing lactose powder. The different batches correspond to productions over ten months. The red bars indicate that lumping was observed when the Big Bag was emptied.

7.3. Controlling the powder water activity

7.3.1. Effect of washing

Impurities have been shown to increase the hygroscopicity of the lactose powder (chapter 4). They can interact with moisture and can be mixed with amorphous lactose thereby impacting on its stability. Water activity measurements were performed on the lactose powders produced on a pilot scale with different washing grades (cf. chapters 4 and 5), after storage for several weeks. The level of washing had a clear effect on the a_w of the powder after drying, with the drying parameters kept constant for all washing grades (Table 13). More precisely, a higher washing grade led to an increase in a_w . Interestingly, the measurement of a_w with an a_w -meter and a RH probe led to similar results for powders with low washing grades but seemed to deviate for higher washing grades, consistently with the measurements on commercial powders.

As demonstrated in chapter 4 (Figure 22, section 4.2.2), a higher washing grade leads to a decreased hygroscopicity and a flatter moisture sorption isotherm. Thus, for a constant moisture content, the water activity would be higher in a powder with a higher washing grade. Although for higher washing grades the moisture content was lower in the present powders (Table 13), a higher water activity was also observed. In addition, as can be seen in Figure 48, the amount of moisture to be removed in order to lower the a_w is very small in this case.

Consequently, even if a higher impurity content in the powder could help to keep a low a_w , it is not recommended to follow this direction as lactose powder containing more impurities showed enhanced hygroscopicity and higher risk of caking. Optimizing both the washing and fluid bed drying parameters should allow to obtain a lactose powder with a minimum content of impurities and a low water activity.

Table 13: Water activity measured with a RH probe and an a_w -meter and moisture content of lactose powders produced on a pilot scale with different washing grades after storage for several weeks.

Washing Grade	RH	a_w	Moisture (%)
0	0.33	0.34	1.12 ± 0.01
0.5	0.44	0.44 ± 0.02	0.77 ± 0.02
1	0.55	0.52 ± 0.00	0.36 ± 0.02
2	0.62	0.56 ± 0.03	0.31 ± 0.01

7.3.2. Effect of the drying step

Drying in the fluid bed serves to remove as much water as possible without impacting on the water of crystallization of α -lactose monohydrate. Free water in commercial lactose powder usually amounts to around 0.1% out of the fluid bed. The powder RH was measured to be between 30

and 40% but was observed to increase very quickly during the first hours after drying (Figure 47). Assuming that the increase in RH observed in fluid bed samples is mainly due to crystallization of amorphous lactose, it would be beneficial to investigate the drying conditions that prevent the formation of a layer of amorphous material or alternatively, allow its crystallization within the fluid bed. Indeed, Clark et al. (2016) reported that only a small change in the fluid bed operating conditions could help to produce completely crystalline lactose. The optimal temperature in the different sections and holding time for this purpose should therefore be investigated.

Another point worth investigation is the rate of RH increasing. If RH can be lowered again in the product by a subsequent processing step, it would indeed be beneficial to accelerate the liberation of water in order to shorten the storage time before further processing. The cooling temperature in the last section of the fluid bed could be varied to increase $T-T_g$, i.e. the difference between the product temperature T within the process and the onset T_g of amorphous material, and thereby accelerate crystallization (Roos & Karel, 1992). It is however important to keep in mind that crystallization might be challenging to follow. Indeed, as already observed in chapter 6 and by other authors (Clark et al., 2016; Knudsen et al., 2002), crystallization tends to be an all-or-nothing event. Moreover, when measuring humidity with data loggers, equilibrium between the sample and the air is a prerequisite to be able to follow crystallization. This equilibrium may be slower than crystallization itself and may only be reached after some time once crystallization completed. Wang and Langrish (2007) also reported that it took more time for all the water to diffuse out of the matrix than for crystallization to complete.

In this PhD study, the optimal fluid bed operating conditions were investigated on a pilot scale. Lactose slurry was sampled at the exit of the crystallizer on the process line. Decantation and drying were then performed on pilot equipment. The drying process was divided in different time sections with various duration and air temperature to simulate the different sections in the fluid bed on the process line. Thus, the effect of an increasing drying temperature in the first section or an increasing cooling temperature in the last section were studied. However, no increase in RH similar to the one observed in fluid bed samples could be measured in the pilot samples (data not shown). This process-related phenomenon is thus very difficult to reproduce on a pilot scale, which makes it challenging to investigate as any test should be performed on the production scale.

Varying the drying conditions on the production line was outside the scope of this PhD study. Nevertheless, the recommendations for necessary investigations presented above should help the industrials to prevent the formation of amorphous material during drying. However, the optimal drying conditions to achieve this goal might be difficult to find as they depend on the fluid bed design and probably on the impurities in the powder. Thus, a better insight in the effect of the subsequent processing steps on water activity would be valuable.

7.3.3. Powder transportation and storage in silo

At the exit of the fluid bed, the powder is transported to a silo. This transportation is generally done by means of pneumatic transportation with dry air (maximum 12% RH, dew point -3°C or even lower), which can therefore be useful to lower and stabilize the powder a_w before packaging. This kind of aeration can be done either between fluid bed and silo, between silos if several silos are available or even inside the silos. Indeed, silos are often equipped with pneumatic discharge aids such as aeration pads or nozzles to help avoiding bridging and ratholing and facilitate powder discharge from silos. They can operate either continuously or by sending air pulses (Schulze, 2008a). Various possibilities are therefore associated with aeration of the powder in the transportation and storage system. The following question arises: how can aeration be optimized to ensure a low a_w at the powder packaging step? In this PhD study, several parameters were investigated on a pilot scale, using the pilot fluid bed where air can be sent through the powder mass from the bottom (see section 3.3.2). Focus was made on the influence of the aeration step duration (continuous aeration), on the aeration mode (discontinuous vs continuous aeration) and on the resting time in between two successive aeration steps (discontinuous aeration).

7.3.3.1. Effect of aeration time on RH of fluid bed samples

Continuous aeration with dry air at about 10% RH and 20°C (corresponding to -12°C dew point) between three and nine hours significantly lowered RH in the powder, which was at 80% without aeration (Figure 52). As expected, increasing the aeration time led to a lower RH, though the decrease in RH was not proportional to the aeration time. Right after aeration, RH was lowered to values between 17% for a three-hours aeration and 10% for a nine-hours aeration. However, RH increased again over several days at a rate depending on the aeration time. After three hours aeration, a fast increase in RH was observed and a stable value at 62% was reached after about four days. The RH increase was slower for longer aeration times but RH was already at 47%, and clearly not stable at the end of the five-day storage in the powder aerated for nine hours.

On the production site, if aeration is done continuously, the aeration time should be as short as possible as storage in silos for long periods will negatively impact the total production time and lead to more constraints on the production schedule. Considering that in this pilot study, RH increased during storage and stabilized at approximately the same value after aeration for three and six hours, the benefit of aerating the powder for a longer time seems limited. It should also be kept in mind that the aeration can modify the PSD of the powder by attrition. Indeed, for most fluid bed samples analyzed in this study, the sieving results showed that the size fraction $x > 500 \mu\text{m}$ was reduced while the number of particles smaller than $250 \mu\text{m}$ increased for longer aeration times (data not shown).

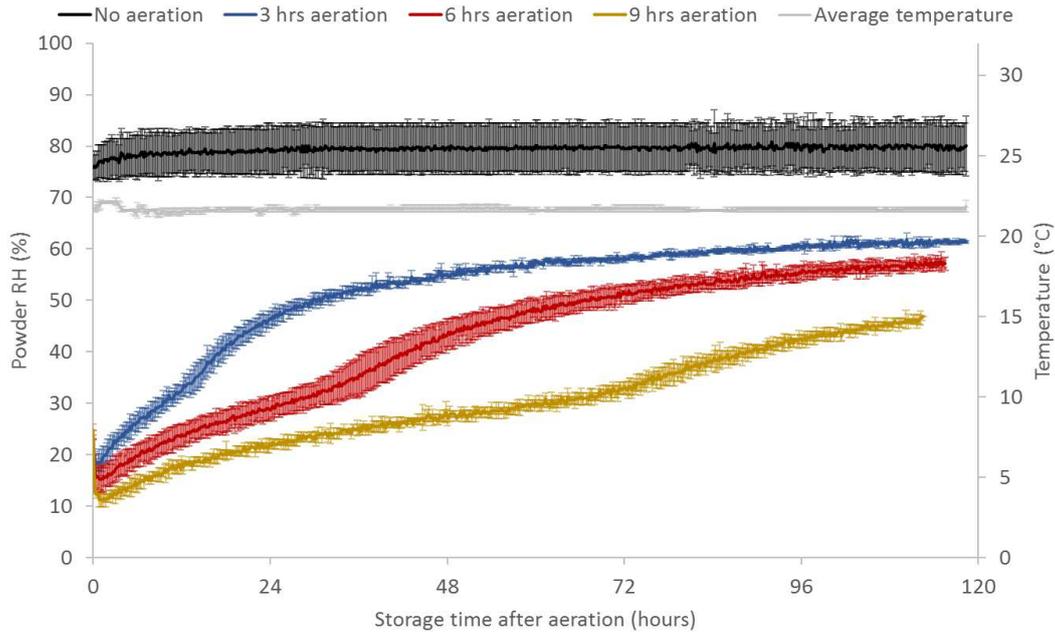


Figure 52: Evolution of RH in lactose powders subjected to various aeration times after drying. Aeration was performed with dry air at 20°C and about 10% RH. The error bars, represented in transparent colors, are calculated from the standard deviation of two measurements for each data point of the curves. Temperature is given as the average of all samples.

In this PhD study, an increase in RH after aeration was systematically observed even after continuous aeration for up to 12 hours. This behavior indicates the difficulty to remove all the water which will eventually come out of the powder at a later stage. Similarly, Paterson et al. (2003) failed at drying lactose powder after conditioning inducing crystallization of amorphous material in spray dried and milled lactose. They explained the slow desorption of moisture by a micro porous crystalline structure at the surface of the crystals, resulting from crystallization of amorphous material and inhibiting moisture release.

The increase in RH after aeration indicates the establishment of a new equilibrium between the air and the powder. Measurements of water activity on lactose powder showed that equilibrium may require a long time to be reached (chapter 6). This equilibrium does not seem to depend much on the aeration time as the RH value after storage was almost the same in samples aerated for three and six hours. Thus, while the first hours of aeration removed some moisture and thereby lowered the RH, it seems that extended aeration time over three hours failed at drying the powder further. Performing aeration in a discontinuous fashion could allow more time for equilibrium between the powder and the air to be reached before the next aeration step. More moisture could possibly be removed this way.

7.3.3.2. Effect of continuous aeration vs. discontinuous aeration

A 1.5-hour continuous aeration was compared to a discontinuous aeration divided in 3 aerations of 30 minutes each with 24 hours resting time in between (see Figure 15, chapter 3). For both

aeration modes, the powder RH after aeration was lower than in the control (not aerated sample; Figure 53). Stability was not completely reached in the aerated samples at the end of storage for at least four days but RH increased very slowly. At that point, RH was lowest in the powder subjected to discontinuous aeration.

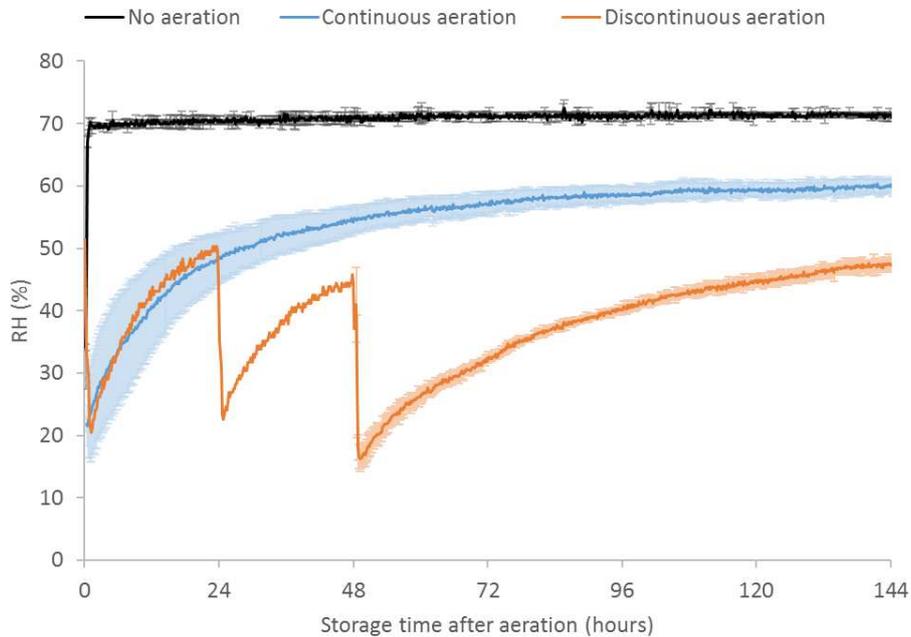


Figure 53: Evolution of RH in lactose powders subjected to various aeration regimes after drying: no aeration, continuous aeration for 1.5 hours and a discontinuous aeration performed as three aerations of 30 minutes each with 24 hours resting time in between. Aeration was performed with dry air at 20°C and about 10% RH. The error bars, represented in transparent colors, are calculated from the standard deviation of four and two measurements for the aerated and non-aerated powders respectively for each data point of the curves. Temperature varied between 22 and 23°C in all samples.

According to these results, a discontinuous aeration seems more effective in lowering RH in the powder. However, a holding time of 24 hours between aerations is difficult to implement on the production line where lactose powder is produced continuously, as it would require several more silos for storage of the powder before packaging. Thus, it would be interesting to investigate if the same effect can be obtained with a shorter resting time between aerations.

7.3.3.3. Effect of a discontinuous aeration with a short resting time

According to the results presented on Figure 52, RH increased faster after aeration when the powder was aerated for a shorter time. Thus, if the powder is aerated for only one hour, a very short resting time might be enough to allow equilibrium to be established at least partly, so that most moisture would be possibly removed on the next aeration step.

A discontinuous aeration was performed with 30 minutes resting time in between four aerations of one hour each and compared to a continuous aeration for four hours (see Figure 16, chapter 3).

For both aeration modes, the powder RH after aeration was lower than in the control (Figure 54). However, a continuous and a discontinuous aeration led to the same RH in the powder, which was still increasing seven days after aeration.

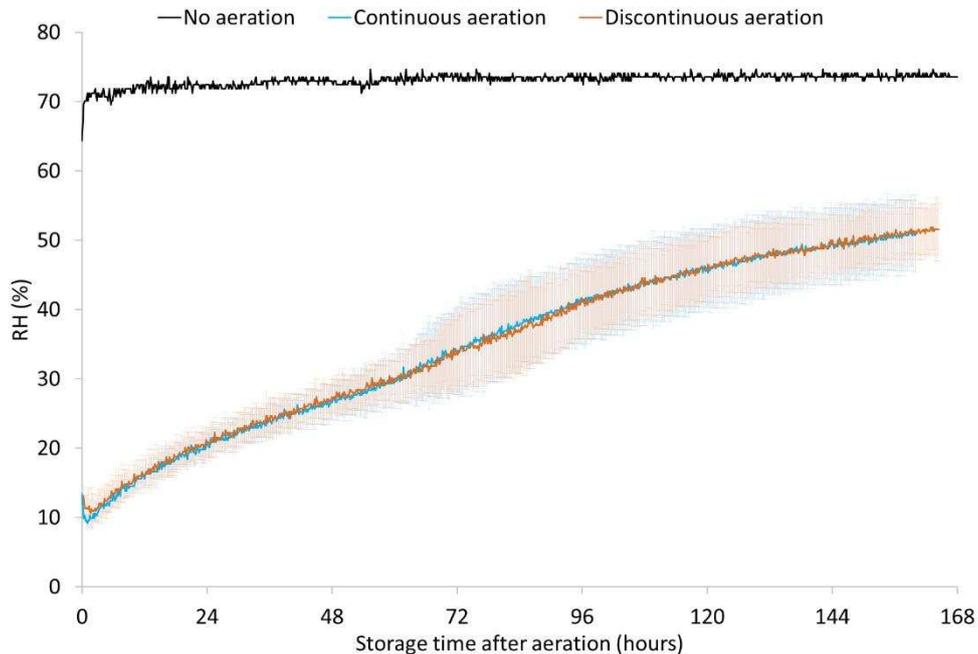


Figure 54: Evolution of RH in lactose powders subjected to various aeration regimes after drying: no aeration, continuous aeration for 4 hours and a discontinuous aeration performed as 4 aerations of 1 hour each with 30 minutes resting time in between. Aeration was performed with dry air at 20°C and about 10% RH. The error bars, represented in transparent colors, are calculated from the standard deviation of two measurements for each data point of the curves. Temperature varied between 21 and 23°C after aeration in all samples.

Though aeration had a positive effect on the powder RH, the discontinuous regime did not allow to lower it further than the continuous aeration. A continuous aeration should therefore be preferred if the resting time can only be very short due to a tight production schedule. If more silos are available and a long resting time can be considered, a discontinuous aeration would lead to a lower RH in the powder before packaging.

7.3.4. Storage of the powder after packaging

Extensive work has been conducted by Bronlund and Paterson (2011, 2008; Paterson & Bronlund, 2009) on caking of lactose due to temperature-induced moisture migration during storage of the powder bags. If the powder is bagged off while it is still hot, and then placed in a cool warehouse, the bag edges will start to cool down. Relative humidity in the air in this part of the bag will thus increase, leading to more moisture adsorbed on the lactose particles. Thus, absolute humidity in the air will decrease, which will trigger moisture movement from the hotter regions of the bag to the cool surface. This process leads to a local increase in water activity in the bag. Provided that

the temperature difference and the moisture content in the powder are large enough at packaging, relative humidity would be high enough for capillary condensation and liquid bridging to occur. Even if the powder is packed at a low temperature (e.g., 20°C), moisture migration in the bag should still be considered. Indeed, during transportation to the customers, it is not rare that the product encounters large temperature variations, up to 20 or even 30°C difference between day and night, especially when it is shipped to Asia.

Paterson and Bronlund (2009) have constructed a graph (Figure 55) which represents the target powder water activity below which the powder must be dried to avoid caking due to temperature gradients in the bag. In order to construct the graph, significant bridging was considered to occur if the RH of the air surrounding the lactose powder exceeded 80%. However, in the present study, significant caking was obtained in the smallest particle size fraction ($x < 80 \mu\text{m}$) of the most washed powder produced on a pilot scale, after storage for 4 days at 60% RH and 20°C and under a consolidation stress corresponding to the bottom of a bag (Figure 31, chapter 5). Thus, the target water activity presented in Figure 55 might actually be too high to prevent the formation of soft lumps in the product depending on the particle size of the powder.

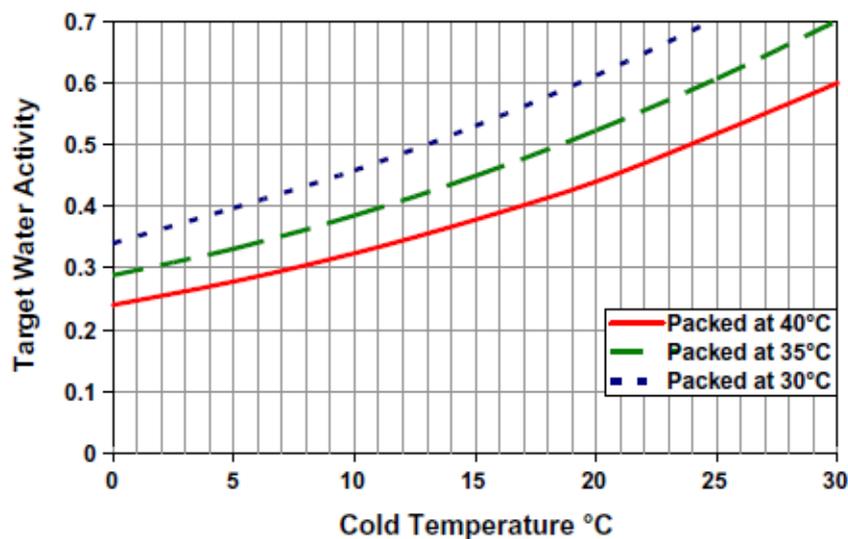


Figure 55: Lines representing the maximum water activity for the powder at packaging to avoid caking due to temperature gradients, when the product is packaged and subsequently cooled at the temperatures indicated. The figure is based on experiments and calculations (Paterson & Bronlund, 2009).

The graph presenting the target a_w to avoid caking (Figure 55; (Paterson & Bronlund, 2009)) is only valid if no amorphous material is present in the powder. Moreover, it was constructed assuming that the powder a_w remains stable in the absence of temperature gradients. Consequently, the increase in RH observed in the powder after drying (Figure 47) or even after packaging (Figure 50) in the present study makes this graph impossible to use. It should be noted that the RH increase cannot be due to temperature gradients as the powder is cooled down in the

last section of the fluid bed and the temperature difference between the product and the warehouse is usually very small.

Finally, another point worth consideration to control the product a_w after packaging is the permeability of the packaging material. Lactose powder is packaged either in small bags of 25 kg or in Big Bags of one metric ton. The small bags are composed of a paper bag and a plastic inner liner, which should act as a barrier against moisture. Indeed, the protective effect of the plastic inner liner depends on its moisture permeability, which can be calculated from the thickness of the material and the water vapor transfer rate through the film. These data should be given by the supplier, in order to choose a packaging material so as to ensure that moisture ingress is prevented even when the product is transported to areas where it can be subjected to large variations in humidity.

7.4. Conclusions

Water activity is a crucial parameter given the importance of water in the caking mechanisms. Measurement of a_w in lactose powder was therefore the first aim of this chapter. The reliability of the results obtained with the usual automatic analytical devices was questioned. The very small amount of free water in lactose powder might explain this limitation as it hampers exchange with surrounding air. Measurements performed with humidity loggers in powder sampled right after the drying step revealed the instability of the water activity, which could increase up to 0.9 in less than a day. This sharp increase might be the result of amorphous lactose crystallization. The same phenomenon was observed in the powder after packaging and a high RH in the powder was linked to the development of caking in most batches.

Investigating the impact of different processing steps on water activity was therefore another objective of this chapter. Although more washing led to a higher a_w in the final product, it should be easy to lower it again in the drying step as the sorption isotherm curve was shown to be flat. Moreover, optimal drying conditions should be investigated in order to prevent post-crystallization of any amorphous material produced during drying and ensure a low and stable a_w . This work should be done on the production site as it was not possible to reproduce the increase in RH in the powder on a pilot scale. An alternative route to obtain a low a_w after packaging is to optimize the aeration parameters either during pneumatic transportation or storage in silo. It was shown that the choice of a continuous or discontinuous aeration depends on the possibility, with regard to the production schedule, to let the powder rest for a long time between aerations. Indeed, a short resting time led to the same RH in the powder after a continuous or a discontinuous aeration. Finally, it should be kept in mind that the product may be subjected to large variations of temperature and humidity during transportation to the customers and this can increase its water activity and caking tendency.

Together with the amount of impurities and the PSD, the water activity should be controlled in order to secure a non-caking lactose powder. However, for none of these parameters it is a simple task as they can be impacted by several processing steps and the process parameters which can be varied are numerous. As mentioned in the previous chapter (chapter 6), it would be highly beneficial for the dairy industry to investigate how a change in these process parameters would influence the caking tendency of the final product. In order to do that, a rapid caking test is needed and is therefore the focus of the next and last chapter.

7.5. Take-home messages

- The water activity value measured in lactose powder with a water-activity meter was found unreliable.
- A new phenomenon was revealed by measuring RH with data loggers placed directly into the powder: RH increased to very high values right after drying of the powder.
- The phenomenon was explained by crystallization of amorphous material formed during rapid drying of the lactose crystals in the fluid bed.
- As a high RH in the commercial powder was linked to an increased risk of caking in the bags after storage, the critical processing steps to obtain a low and stable a_w have been determined.
- Optimization of the fluid bed parameters should allow to produce a powder with a low and stable a_w . Alternatively, aeration of the powder after drying, in silos or during pneumatic transportation, was shown to lower its water activity significantly. However, attempts to stabilize the powder RH after aeration were unsuccessful.

Chapter 8 – Development of an accelerated test to quantify the caking tendency

Summary

The aim of this chapter was to adapt the caking measurement with the ring shear tester developed in the previous experiments (chapters 4, 5 and 6) in order to obtain an accelerated caking test. Appropriate environmental conditions were therefore investigated. Temperature was controlled at 50°C and tests were performed at 50% and 60% RH. Both combinations could discriminate two lactose powders with different characteristics in terms of their caking tendency. The second test, at 60% RH, was preferred for its better repeatability and applied successfully to discriminate commercial lactose powders from different factories. It is recommended to implement a similar test at all production sites, with the exact storage conditions adapted to the powder produced at a specific site, in order to rapidly identify batches with high risk of caking. However, such a test does not take the powder RH into account as RH is controlled by saturated salt solutions. Thus, an alternative test was proposed, where the effect on caking of aerating the powder after drying (cf. section 7.3.3) could be assessed. Aeration was shown to significantly delay the development of caking. This second test could therefore be useful to optimize the aeration process in order to ensure a stable and low a_w and thereby prevent caking. For powders with intermediate a_w values, the critical effect of the PSD on caking can be assessed with an accelerated caking test.

The objectives of this chapter were to:

- Investigate appropriate experimental conditions for an accelerated caking test
- Perform a screening of commercial samples using the newly developed accelerated caking test
- Assess the effect of aeration on caking

8.1. Introduction

Ring shear testing has been shown in the previous developments (chapters 4, 5 and 6) to be able to discriminate samples according to their caking tendency. The development of an analytical method to quantitatively assess caking is a major achievement. Using this method, the influence of crucial product parameters on caking was investigated. However, samples were stored for four days before analysis, which can be too long to wait for a result in industrial settings. The dairy industry needs a fast method to evaluate the caking potential of a sample before it is shipped to a customer. This would allow to classify the batches depending on the quality requirements of the customers.

Research on the development of an accelerated caking test started as early as in the 1940's, driven by the fertilizer industry (Gilbert & Knapp, 1970). Numerous accelerated caking tests have been published since then for application on different powders (Albadarin, Lewis, & Walker, 2017; Calvert et al., 2013; Cleaver et al., 2004; Walker, Holland, Ahmad, Fox, & Kells, 1999). All tests involve the use of either high mechanical pressure, high humidity or high temperature. However, the experimental conditions should be realistic to involve the same caking mechanisms as the ones occurring in the powder bags during real storage and transportation to the customers. A thorough knowledge of the powder characteristics and its caking mechanisms is therefore critical. As powders generally differ in composition and behavior in terms of glass transition, moisture sorption and compressibility among others, it is impossible to develop a universal test which can be used on any powder.

The primary objective of this chapter was to adapt the caking measurement with the ring shear tester developed in the previous experiments to obtain an accelerated caking test. Experimental conditions (temperature, humidity, mechanical pressure and time) should be chosen carefully in order to be able to discriminate commercial lactose powders in terms of their caking tendency during shipping, storage and up to use. Indeed, too harsh conditions might lead to strong caking of all powders indifferently while too mild conditions would not induce any caking within the experimental storage time.

8.2. Development of the method

The development of an accelerated method was performed on two finished good samples, obtained from test productions. According to the process parameters used during these tests, the samples were expected to be relatively different in terms of impurity content and PSD, while still being representative of AFI lactose powders. Pharmaceutical grade lactose was included in the study for comparison purposes, as it is generally acknowledged to have a better physical stability than the other lactose grades.

8.2.1. Characterization of the finished good samples

As the PSD and impurity content have been shown to critically influence caking, the samples were analyzed for these two parameters. The sample finished good 1 (FG1) presented a narrower size distribution with a larger average particle size than the sample finished good 2 (FG2) (Figure 56). Both FG1 and FG2 were characterized by the presence of fines, as shown by the “long tail” of the PSD curve. The D_{10} of FG1 and FG2 were calculated to be 105 μm and 45 μm , respectively. Interestingly, pharmaceutical grade lactose presented the same D_{10} value as FG2, while the D_{50} was smaller and the span narrower.

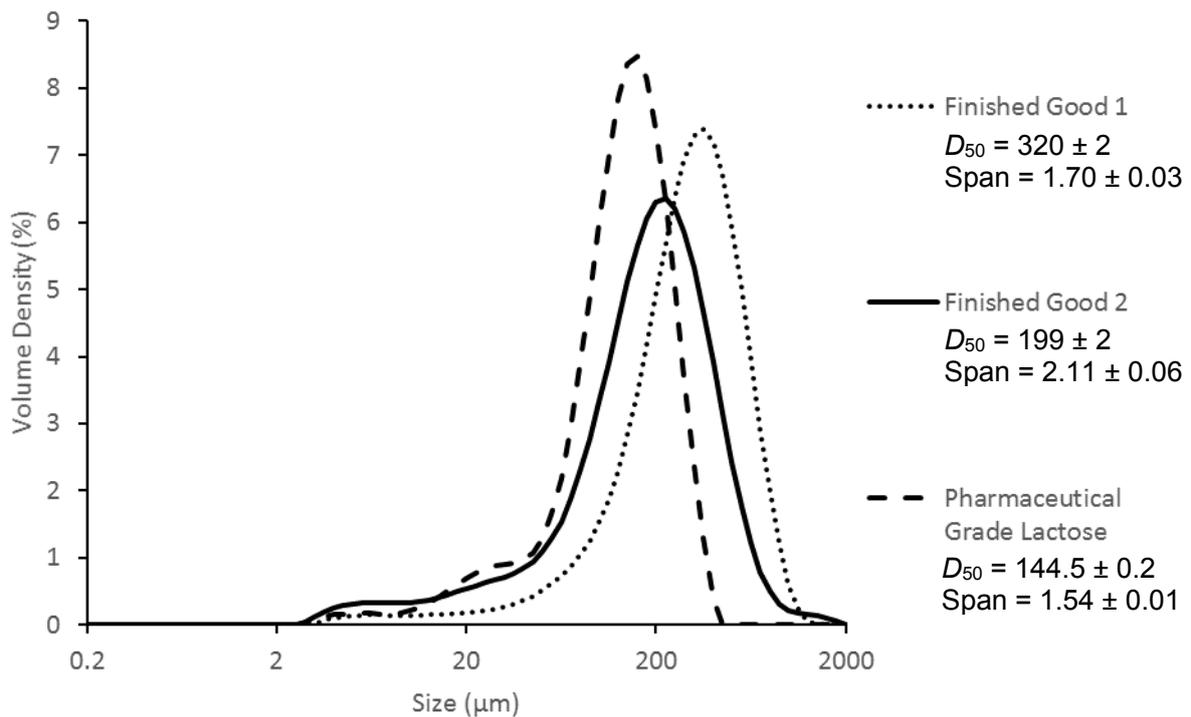


Figure 56: Particle size distributions of two finished good samples of commercial lactose powder and a sample of pharmaceutical grade lactose. The D_{50} and the span of each distribution, indicated in the figure legend, are means of at least two replicates.

The impurity content was similarly low in both finished good powders (Table 14). As expected, pharmaceutical grade lactose did not contain any of the impurity analyzed. FG2 contained significantly more ash and potassium than FG1. These differences were representative of the limited variations in impurity content that can be observed in most commercial powders. Moreover, RH was measured three weeks after packaging, and was 58 and 25% in FG1 and FG2, respectively. Thus, extreme batch to batch variations in PSD and impurity content and large differences in powder RH were accounted for when using these two finished good powders to develop the caking test. This allowed to investigate relevant test conditions which would induce slight to strong caking in the powders, and finally obtain a suitable method for powders with a large range of industrial settings.

Table 14: Impurity content of two finished good samples of commercial lactose powder and a sample of pharmaceutical grade lactose. None of the impurities analyzed was detected in the pharmaceutical grade lactose. The quantification limit for sulfated ash, ash and proteins was 0.1%. Other minerals (calcium, sodium, magnesium, phosphorus) than potassium were below quantification limit, which was 0.025% for calcium, potassium, sodium and phosphorus, and 0.001% for magnesium.

Powder	Sulfated Ash (%)	Ash (%)	Potassium (%)	Proteins (%)
Finished Good 1	0.14 ± 0.00	0.11 ± 0.01	0.031 ± 0.001	0.16 ± 0.02
Finished Good 2	0.14 ± 0.04	0.14 ± 0.00	0.045 ± 0.000	0.19 ± 0.01
Pharmaceutical Grade Lactose	<LOQ	< LOQ	< LOQ	< LOQ

8.2.2. Investigation of appropriate experimental conditions

In the previous experiments (chapters 4, 5 and 6), samples were stored at 20°C and 60% RH for 4 days with a consolidation stress of 9.3 kPa before caking measurement. Samples with different impurity content or various particle size could be discriminated in terms of caking tendency. However, a four-days delay before the result of the caking test can be obtained is too long in industrial settings. Indeed, depending on the results, the ability of the different batches to withstand important variations in humidity and temperature during transportation would determine which customer they are shipped to. In order to ease logistics, the caking tendency of the powder should be known as soon as possible, ideally in a day.

8.2.2.1. Test at high temperature (50°C) and high humidity (60% RH)

The results of the study on a pilot scale suggested that humidity caking was the principal caking mechanism in lactose powder under the conditions of the test (chapters 4 and 5). Thus, in order to accelerate the development of caking, a possible approach was to enhance moisture movement within the sample by increasing the storage temperature. With the consolidation stress and RH unchanged (9.3 kPa and 60% respectively), the powders were stored at 50°C for up to 24 hours and caking was regularly assessed (Figure 57).

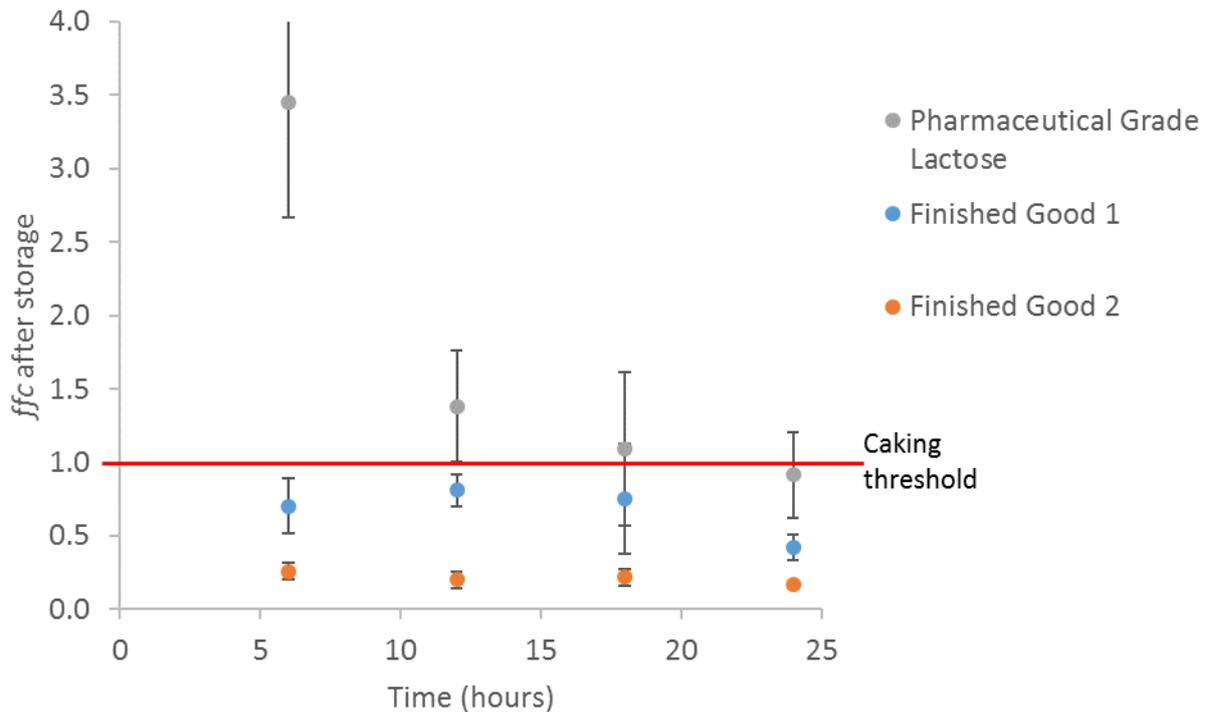


Figure 57: Flowability ffc of two samples of finished good commercial lactose powder as a function of storage time. Samples were stored at 50°C and 60% RH and under a consolidation stress of 9.3 kPa. The flowability of pharmaceutical grade lactose is included for comparison purposes.

Under these conditions, the development of caking was extremely rapid in the finished good samples. Both samples were caked already at the first measurement point after six hours storage. Pharmaceutical grade lactose was still free-flowing at that point but became consolidated during the next six hours and finally caked after 24 hours storage. At each measurement point, FG2 showed stronger caking than FG1. The repeatability of the measurement, as shown by the error bars in Figure 57, was better when the powder was caked (measurement points below the red line) than when it was easy flowing or consolidated as pharmaceutical grade lactose. This was also observed previously (section 4.2.4) when measuring caking in samples with different washing grades.

The higher caking tendency measured in FG2 than in FG1 was consistent with the results from chapter 5, where it was demonstrated that a powder with a broader span and a smaller particle size caked more. Yet, pharmaceutical grade lactose was composed of even smaller particles (Figure 56) but was much less prone to cake (Figure 57). This result can be explained by a combination of a narrower span (Figure 56) and a significantly lower amount of impurities (Table 14) than for the finished good samples. These two parameters would also lead to a limited agglomeration of fines on the crystals surface and a well-defined crystal morphology with fewer impurities affecting crystallization. Thus, pharmaceutical grade lactose is likely to present a smoother surface which decrease the possibility of capillary condensation. This hypothesis could

be investigated by microscopy, for example by comparing scanning electrons micrographs of commercial powders and pharmaceutical grade lactose as it was done on the lactose powders with different washing grades (Figure 24, chapter 4).

Increasing the storage temperature also affected the amount of moisture in the system. Indeed, relative humidity is defined as:

$$\%RH = \frac{p_{H_2O}}{p_0} \times 100 \quad (7)$$

with p_{H_2O} is the partial vapor pressure of water in the air and p_0 is the saturation vapor pressure of pure water, that is the vapor pressure which is created at the same temperature when the air is totally saturated with water vapor (Bell & LaBuza, 2000). At 20°C and 50°C, p_0 is equal to 2.3 and 12.3 kPa respectively (Lide, 2004). Thus, a relative humidity of 60% is equivalent to a vapor pressure five times higher at 50°C than at 20°C. The strong caking observed in the finished good samples is therefore most likely due to the high amount of moisture available to form liquid bridges. However, according to data logger measurements in the closed cabinet, it was noted that the time required for RH to equilibrate at 60% was approximately 12 hours. Thus, 60% RH was not required to obtain strong caking in the first 6 hours.

In order to assess the influence of a high humidity in the development of caking when temperature is high, the finished good samples were stored at 50°C without controlling humidity (i.e. without saturated salt solution, see section 3.5.2) for six hours and caking was measured. The caking tendency of both powders was affected by the presence of a saturated salt solution, though to various extents (Figure 58). Indeed, humidity markedly influenced caking in FG1, which was still easy-flowing after storage without saturated salt but caked after storage in presence of saturated salt. While FG2 was strongly caked after a storage with controlled humidity, the powder was only close to the caking threshold after storage without saturated salt.



Figure 58: Flowability ffc of two samples of finished good commercial lactose powder after storage for six hours at 50°C and controlled or uncontrolled RH. Controlled humidity was achieved with a saturated salt at $a_w=0.6$ at 50°C . Uncontrolled humidity was the humidity in the oven, measured as about 40% RH. Each sample was consolidated under a consolidation stress of 9.3 kPa.

The combination of high temperature and high pressure on the powder is therefore not enough to induce caking or even consolidation in a few hours in powders with similar characteristics as FG1, if humidity is kept at a low level. Powders with similar PSD and impurity levels as FG1 will probably not be discriminated in a test at low humidity. A humidity higher than 40% is therefore required for a fast caking method. However, as both finished good powders were caked after six hours storage (Figure 57), the experimental conditions with 60% RH seem too severe to enable a discrimination of the samples. A test with milder conditions was therefore conducted.

8.2.2.2. Test at high temperature (50°C) and lower humidity (50% RH)

With the other storage parameters left unchanged, a lower humidity (50% RH, see section 3.5.2) was experimented in order to allow a more gradual development of caking in the powder. Under these conditions, it was possible to discriminate the two finished good samples as caked vs. non-caked during the first days of storage (Figure 59). Allowing more time, both samples eventually caked. Interestingly, the development of caking with time could be followed. The caking strength of FG2 indeed increased by 61% between 18 and 110 hours of storage. FG1 approached the caking threshold and then caked after 68 hours and 110 hours storage, respectively. On the contrary, these storage conditions were too mild for pharmaceutical grade lactose to cake in the course of a little less than five days.

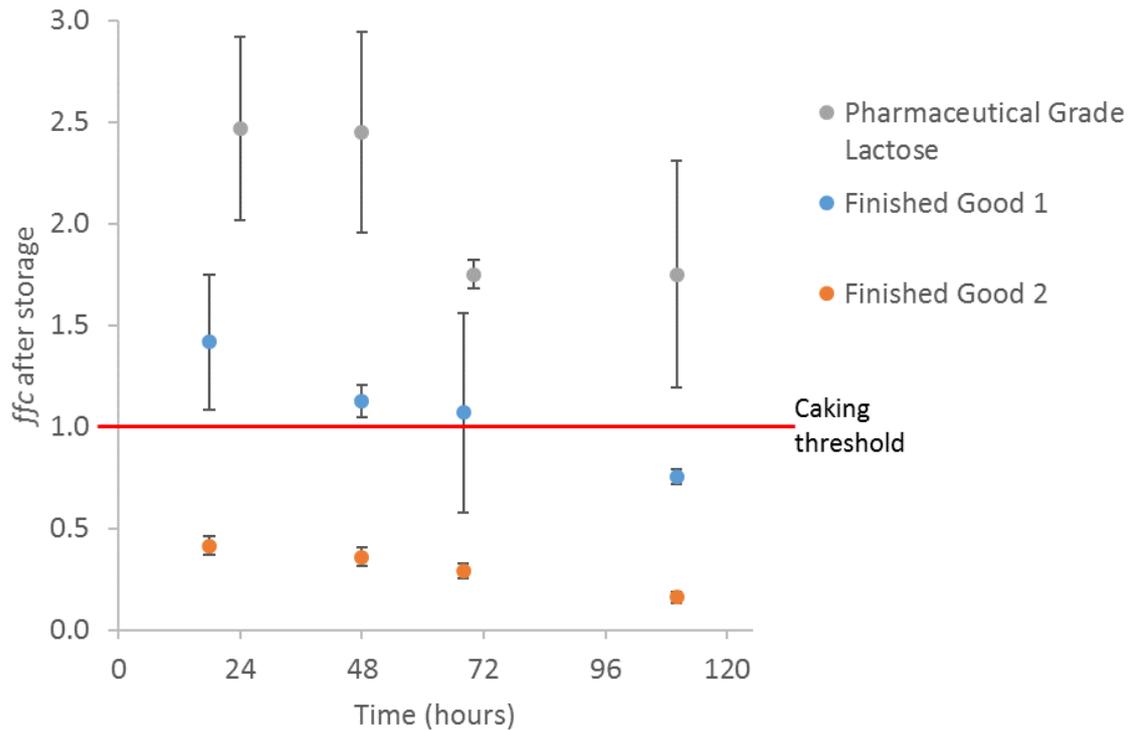


Figure 59: Flowability ffc of two samples of finished good commercial lactose powder as a function of storage time. Samples were stored at 50°C and $50\% \text{RH}$ and under a consolidation stress of 9.3 kPa . The flowability of pharmaceutical grade lactose is included for comparison purposes.

This test seems more suitable than the test at $60\% \text{RH}$ to classify powders into the two categories “caking” ($ffc < 1$) vs. “not caking” ($ffc > 1$). However, as mentioned above (section 8.2.2.1), the flowability values of samples which fall into the category “not caking” are associated with large error bars. There might therefore be more uncertainty on the results from this test with more mild conditions than with the one at $60\% \text{RH}$ where the powders are more likely to cake. Moreover, the experimental time is extended compared to the test at $60\% \text{RH}$, which might be an issue if the test is to be used as quality control, given the many samples that have to be tested.

Several approaches can be considered in order to shorten the experimental time. Temperature could be increased further. However, as lactose is a reducing sugar with the powder containing small amounts of protein most probably in the form of peptides and amino acids, Maillard reactions should be considered. Indeed, their reaction rate increases at higher temperatures and reaches a maximum at a_w values in the range $0.6\text{--}0.7$ (BeMiller & Huber, 2008). More generally, to ensure relevant results, the product composition should not be modified during storage before the caking test. Thus, the maximum temperature that can be used for the test could be investigated. This study was outside the scope of this PhD project.

Another approach could consist in increasing the consolidation stress that is applied on the powder during storage (Albadarin et al., 2017). In order to remain within the range of realistic levels, the

following questions about the transport conditions should be answered: is pallet stacking common practice? If so, how many pallets is a stack composed of? Then, the maximum compressive stress acting on the bottom of the stack can be applied during the accelerated test.

Increasing humidity has been shown in the first test at 60% RH to accelerate caking, with all powders being caked in 24 hours (Figure 57). The minimum RH required to induce significant liquid bridging in a short time could be investigated for each temperature of interest. Alternatively, water can be added directly to the powder in order to diffuse through the sample (Cleaver et al., 2004). In this case, it is important to ensure a homogeneous distribution of the water in the sample. The amount of water to add was proposed to be determined by measuring the water sorption isotherm of the powder, where it corresponds to the RH where a significant increase in moisture sorption is observed (Cleaver et al., 2004).

Finally, humidity and temperature cycling can be performed to simulate diurnal variations (Gilbert & Knapp, 1970). This can accelerate the development of strong caking as liquid bridges will be formed at high humidity and subsequently dried out during the low humidity periods.

As mentioned in section 1.3.4.6, Calvert et al. (2013) developed a caking tester where rapid conditioning of the powder is performed and consolidation is applied while recording the powder bed height. Finally, cake strength is assessed. Conditioning is achieved by means of air at a desired RH percolating through the powder sample. The whole tester is placed in a temperature controlled chamber. Thus, temperature, RH and consolidation stress can be varied. The usefulness of the tester was demonstrated by measuring the caking tendency of a hygroscopic powder. The strength of the test is the rapid conditioning of the powder, which ensures that the equilibrium moisture content is reached in the experimental time scale. Its limitation is the removal of the powder cake from the caking rig prior to cake strength measurement. For powders with limited hygroscopicity as crystalline lactose, high values of RH, temperature or consolidation stress would be necessary to induce sufficient caking strength to allow the sample removal without breaking the cake.

Thus, in any method reported in the literature so far, the challenge lies in defining realistic environmental conditions which would not induce chemical or physical modifications of the sample beyond the scope of what is expected from normal operation. As highlighted by Zafar et al. (2017), detailed knowledge of the material properties in relation to moisture sorption and variations in temperature and consolidation stress is a prerequisite to the development of an accelerated caking test. Consequently, a universal test for application on any powder is not feasible.

Considering lactose powder, both accelerated tests developed in this PhD study were able to discriminate the samples in terms of their caking tendency. The first test with harsh conditions (50°C and 60% RH) led to a rapid caking of all samples, though to various extents. The second test with more mild conditions (50°C and 50% RH) was able to classify the powders in “caking”

and “non-caking” categories. In order to further evaluate the applicability of the method, a screening of lactose powder samples from different AFI production sites was performed. As the first test exhibited better repeatability of the measurement in a shorter time, it was chosen to perform the screening at 50°C and 60% RH.

8.3. Screening of production samples

The screening was performed both on fluid bed and finished good samples (see section 3.2.2).

8.3.1. Fluid bed samples

In order to test the method on samples representative of the variety that can be found in commercial lactose powders, three different production sites were included in the screening. For each site, two different batches were analyzed. In total, six samples were characterized in terms of impurities and PSD and subjected to accelerated caking tests (Table 15).

Table 15: Flowability ffc of fluid bed lactose samples from different production sites after storage at 50°C and 60% RH for 6 hours under a consolidation stress of 9.3 kPa. The PSD characteristics and impurity contents of each sample are also presented. The maximum standard deviation associated with the results for the D_{10} , D_{50} and the span were 1, 2 and 0.02 respectively. The quantification limit was 0.01% for sodium, phosphorus and calcium. The quantification limit for sulfated ash and protein was 0.1%.

Prod. Site	Batch	ffc after storage	D_{10}	D_{50}	Span	K	Mg	Na	P	Ca	Protein	Sulf. Ash
A	1	6.53 ± 0.86	104	247	1.54	0.04	0.003	<LOQ	<LOQ	0.01	0.19	0.15
A	2	4.07 ± 1.95	115	246	1.43	0.03	0.003	<LOQ	<LOQ	0.02	0.15	0.16
B	1	0.26 ± 0.02	83	245	1.71	0.02	0.002	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
B	2	0.20 ± 0.04	81	233	1.79	0.03	0.003	<LOQ	<LOQ	<LOQ	0.10	0.10
C	1	7.45 ± 1.34	178	362	1.36	0.19	0.045	0.07	0.28	0.38	<LOQ	0.37
C	2	2.16 ± 1.08	134	265	1.30	0.03	0.006	<LOQ	0.04	0.06	<LOQ	0.27

The results of the caking test were dependent on the production site. The samples from site B were strongly caked at the end of the six hours storage whereas the samples from sites A and C were still easy flowing. Within production sites, the two samples from sites A and B gave similar results. On the contrary, the samples from site C showed markedly different caking tendency (i.e. different ffc values), with C1 being easy flowing after storage while C2 was cohesive, according to Jenike’s classification of powder flowability ((1964); see section 3.5.1.3).

Powders from sites A and B presented a similar D_{50} values but the span was narrower in samples from production site A. Site C produced powders with an even narrower span. The D_{50} was different for the two samples: batch C1 had bigger particles than all other samples analyzed while batch C2 was similar to the samples from the other production sites. In terms of impurities, the

levels were lowest in powders from production site B, followed by site A. The ash and minerals levels were in general highest in samples from production site C, with a large difference between the two batches for this site.

The screening led to unexpected results as most samples were not caked after the six hours storage at 50°C and 60% RH. This result was opposite to the strong caking observed for the two finished goods samples used for method development (cf. 8.2.2.1). Compared to FG1 (Table 14 and Figure 56), powders from production site A and C presented similar or higher impurity contents and a lower average particle size (except for production site C, batch 2) which are known to increase the caking tendency. However, the narrower span of these powders (Table 15) seems to compensate for the effect of the other parameters and prevent or at least delay caking.

The accelerated caking test was able to discriminate samples from the different factories. Site B produced lactose powders with a broader span than the other factories, which led to an increased caking tendency. The difference in caking tendency between the two samples of production site C could also be explained by the PSD. For a similar span, particles were indeed bigger in C1, resulting in reduced caking. However, this batch contained significantly more impurities than C2. Its free-flowing state after the six hours storage under harsh conditions demonstrates that at the low levels of impurities found in commercial lactose powder, a large particle size and a relatively narrow span overrule the effect of impurities and limit caking.

In order to be able to assess the combined effect of particle size and span of the distribution on caking, the ratio D_{50}/span could be useful. Bigger particles and a narrower span, which are known to lower the caking tendency, lead to a larger ratio. Thus, the larger the ratio D_{50}/span , the higher the expected ffc value and therefore the lower the caking tendency.

8.3.2. Finished goods samples

Previous results showed that PSD can be modified after the fluid bed drying step (chapter 5). As this parameter has a large influence on caking, it would probably be more relevant to assess the caking tendency of the powder at the packaging step (finished goods samples). One batch from each production site was subjected to the same caking test as the samples from fluid bed (6 hours at 50°C and 60% RH).

Powders from production sites B and C were caked and consolidated, respectively (Table 16), hence giving the same caking results as the fluid bed samples from the same factory (Table 15). On the contrary, the sample from site A was caked while powder from this site was easy flowing when sampled from the fluid bed.

These results should be confirmed by sampling a large number of batches both at the exit of the fluid bed and at the packaging station and subjecting them to the accelerated caking test. Optimally, the same powder should be followed along the process line and sampled at both places.

However, this task is challenging as in practice, the fluid bed is operated continuously and the silo at the packaging station is composed of a mix of powders dried over several hours.

Table 16: Flowability ffc of finished goods lactose samples from different production sites after storage at 50°C and 60% RH for six hours under a consolidation stress of 9.3 kPa. The PSD characteristics and impurity contents of each sample are also presented. The maximum standard deviation associated with the results for D_{10} , D_{50} and the span was 2, 2 and 0.01 respectively. The quantification limit for sodium was 0.01% at sites A and B and 0.025% at site C. The quantification limit for protein was 0.1%.

Prod. Site	ffc after storage	D_{10}	D_{50}	Span	D_{50}/Span	K	Mg	Na	P	Ca	Protein	Sulf. Ash
A	0.51 ± 0.18	82	314	1.74	181	0.04	0.002	<LOQ	0.01	0.01	0.16	0.16
B	0.20 ± 0.01	63	205	1.82	112	0.02	0.003	<LOQ	0.01	0.01	0.10	0.15
C	2.40 ± 0.99	154	309	1.30	238	0.03	0.008	<LOQ	0.05	0.09	<LOQ	0.35

It would be beneficial to extrapolate directly the results from caking tests on fluid bed samples to finished goods. This would allow to save time as the powders with high risk of caking would be identified at an early stage. The present results (Table 15 and Table 16) suggest that the processing steps downstream the fluid bed impact the product properties and the caking tendency to various extents depending on the factory. Powders from production site B are in general finer than the other production sites right after fluid bed and their PSD is only slightly modified during pneumatic transportation. Therefore, powders from the three production sites can be ranked differently in terms of caking tendency whether they are tested right after fluid bed or at the packaging step. Extrapolating the results from fluid bed samples to finished goods should thus only be done to compare samples produced at the same factory. For a defined factory, this also requires that the variations of the process parameters downstream the fluid bed are limited. For example, the pneumatic transportation and silo system can affect the PSD (section 6.4.4) and prevent extrapolation of the results.

The ranking of the three samples in terms of caking (Table 16) was the one expected from the ratio D_{50}/span . The caking tendency of the powders was therefore largely determined by their PSD. This can be explained by large differences in PSD, which outweigh the differences in impurity content. This would probably not be the case if the caking results were used to compare samples from the same factory, where the PSD is expected to be more stable between batches. Indeed, a similar PSD was observed in the two fluid bed samples from production sites A and B, respectively (Table 15). However, as observed for production site C, large batch to batch variations can also occur and should be accounted for in the caking test.

In conclusion, the results of the caking tests at high temperature and controlled humidity illustrate the difficulty associated with the development of a single accelerated caking test which can be used on all batches with good repeatability. The solution probably lies in a similar caking test

implemented on all production sites but where the experimental conditions are adapted to the powder produced at the specific site. It should also be kept in mind that the lactose powders produced at different production sites can vary in quality and might not be intended for the same markets. Powders to be shipped across continents would have to withstand harsher environmental conditions, which should be reflected in the caking test.

In the previous experiments, the combination of PSD and impurity content determined the caking tendency of the samples. In addition, the development of caking largely depended on the ambient humidity, which is imposed in the accelerated caking test. As it was shown that RH in lactose powder sampled at the exit of the fluid bed can reach extremely high values (Figure 47, section 7.2.2), it would be interesting to take this parameter into account in a caking test.

8.4. Assessing the effect of aeration

In order to assess the influence of the powder RH on caking, lactose powder was aerated on a pilot scale to modify its RH (section 3.3.2). Indeed, aeration in silo with dry air was demonstrated to lower the powder RH (section 7.3.3). Powder was sampled before aeration (the control) and after aeration, and subjected to both the accelerated caking test developed previously (section 8.2.2.1) and a test without controlled humidity.

8.4.1. Characterization of the powders

The relative humidity in the powders was recorded with a humidity logger over several days after aeration and reached 61% and 75% in the aerated powder and in the control, respectively, when stability was achieved. As expected, aeration did not impact the content of impurities (Table 17). Moreover, the PSD was very similar for the two powders of batch 1 (Table 17).

Table 17: PSD characteristics and impurity content of the aerated and non-aerated powders of batch 1 from production site A. The powder was sampled at the exit of the fluid bed on the production line and aerated continuously for three hours on a pilot scale. Sodium and phosphorus were below quantification limit, which was 0.025%.

Powder Batch 1	RH	D_{10}	D_{50}	Span	D_{50} / Span	K	Mg	Ca	Prot.	Sulf. Ash
With aeration	61%	185 ± 27	383 ± 30	1.41 ± 0.08	270	0.03	0.005	0.03	0.14	0.18
Control	75%	164 ± 12	375 ± 20	1.50 ± 0.03	251	0.04	0.005	0.03	0.14	0.18

The powder was aerated for three hours as a longer aeration was found to have a limited effect on the powder RH, when performed continuously (section 7.3.3.1). A short aeration was also favored to limit the impact of aeration on PSD. However, in other batches from the same production site, significant modifications were observed after a three-hours aeration (Table 18).

The extent of changes in PSD seems therefore to depend on the powder, probably because of differences in friability between batches.

Table 18: PSD characteristics of the aerated and non-aerated powders of batch 2 from production site A. The powder was sampled at the exit of the fluid bed on the production line and aerated continuously for three hours on a pilot scale.

Powder Batch 2	RH	D_{10}	D_{50}	Span	D_{50} / Span
With aeration	68%	153 ± 9	437 ± 11	1.63 ± 0.03	268
Control	77%	231 ± 12	492 ± 25	1.47 ± 0.04	335

8.4.2. Accelerated caking test

The caking tendency of batch 1 with and without aeration was assessed in an accelerated caking test and no significant difference was observed (Figure 60).

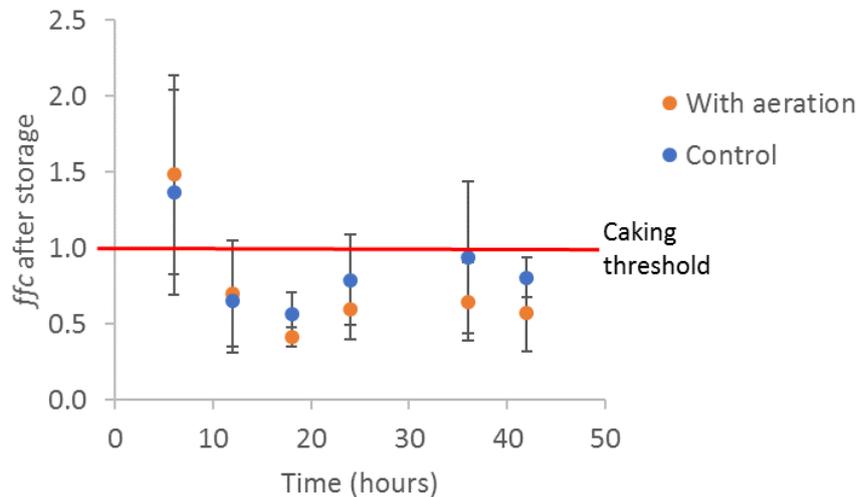


Figure 60: Flowability ffc of lactose powder sampled before and after aeration as a function of storage time. Samples were stored at 50°C and 60% RH and under a consolidation stress of 9.3 kPa.

This result was expected given the similarities in PSD and impurity content between the two powders (Table 17). The same caking test was performed on batch 2 and the aerated sample caked more than the control (ffc value of 2.2 ± 0.7 and 0.8 ± 0.2 for the control and the aerated sample after 24 hours storage, respectively). In this case, the large difference in PSD between the two powders, as shown by the ratio D_{50} / span (Table 18), determines the caking potential when humidity is imposed and is the same for all samples in the test.

8.4.3. Test without controlled humidity

As humidity is regulated with saturated salt solutions in the accelerated caking test, it is not possible to evaluate the effect of the powder RH on caking. Thus, an experimental setup was

developed where the storage container with the shear cell filled with the sample, was itself half-filled with the same powder, so that the humidity in the container could be imposed by this latter (see section 3.5.3 for greater detail). In order to simulate storage in the warehouse, temperature was controlled at 20°C. Caking was regularly assessed.

The aerated powder and the control (non-aerated powder) showed marked difference in caking tendency in the first ten days of storage (Figure 61). The control was close to the caking threshold already after 5 days of storage and caking became strong in the first 20 days. On the contrary, the aerated powder was still free-flowing during the first ten days of storage. Then, caking developed and the powder was close to the caking threshold after 20 days.

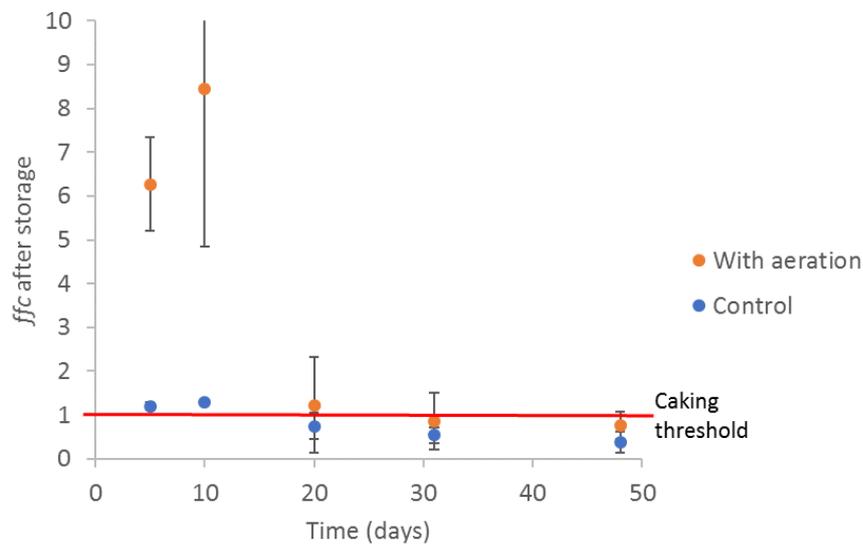


Figure 61: Flowability ffc of lactose powder sampled before and after aeration as a function of storage time. Samples were stored at 20°C and under a consolidation stress of 9.3 kPa. Humidity was not imposed.

Whereas it was impossible to observe the impact of aeration on caking in the accelerated caking test (see 8.4.2), the test performed without imposing a constant humidity highlighted the enhanced stability of the aerated powder. However, it can be observed that the beneficial effect of aeration was limited as both samples eventually caked (Figure 61). As developed in chapter 7 (section 7.3.3), aeration can be optimized, for example by being performed discontinuously, to lower the powder RH further. The advantage of the test proposed here is to allow to assess the effect of different aeration modes on caking on a lab scale. Its limitation is the longer storage time required compared to the accelerated caking test. The relatively high consolidation stress imposed on the powder probably already accelerates the development of caking compared to the real storage conditions. Experimental time could be further reduced by applying the maximum consolidation stress in case of pallet stacking or by increasing temperature. Optimization of aeration could then be performed until caking is not observed in the aerated samples in such a test.

If the effect of the powder RH on caking overweighs the effect of all other product parameters, the accelerated caking test at imposed RH will give misleading results. Consequently, it appears necessary to focus future research on assessing the relative weight of PSD and powder RH, as these have been shown to be the most critical parameters for caking in the commercial powders containing low levels of impurities (i.e. sulfated ash and proteins). The results could be represented as in Figure 62, where the values of X and Y have to be determined. For powders classified in the orange category, the accelerated test developed above (see 8.2.2) would be extremely useful. The limit between the green and orange areas would also provide a target for the optimization of the aeration process.

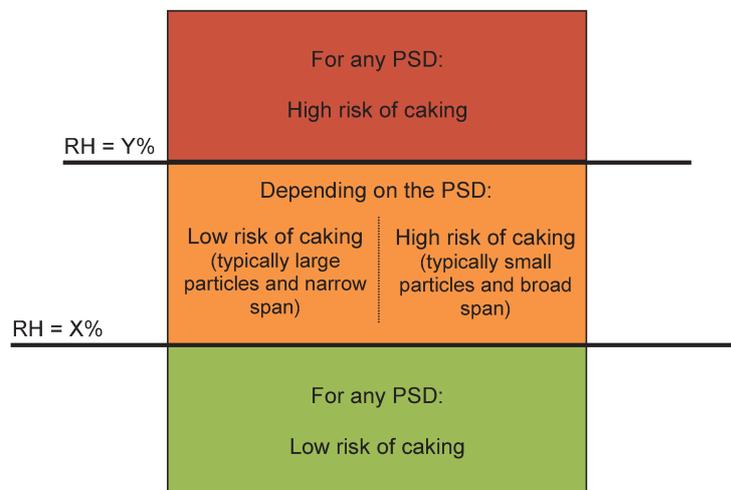


Figure 62: Assessment of the risk of caking of commercial lactose powder as a function of the powder RH and the PSD. X and Y are RH limits to be determined.

8.5. Conclusions

Appropriate storage conditions to discriminate commercial lactose powders in an accelerated caking test were investigated. High temperature (50°C) was used to increase water mobility, and combined with a high RH (60%). Under these conditions, caking developed very rapidly (in less than six hours) in the two batches used for the method development, though to different extents. On the contrary, a lower RH (50%) allowed to separate the two batches in “caking” and “non-caking” categories after a storage for 18 hours.

As the measurement was associated with a better repeatability at 60% RH, this humidity was chosen to perform a screening of commercial lactose powder produced at different factories. Surprisingly, most fluid bed powders were not caked after the six hours storage at 50°C and 60% RH, which was explained by a narrow span in these powders. The accelerated test was able to discriminate both fluid bed and finished goods samples from different factories. The differences in terms of caking tendency could be explained by the PSD, which was observed to be more determining than the impurity content at the low levels characterizing commercial lactose.

Extrapolation of results from measurements on fluid bed samples to finished good samples could save time to categorize the batches and ease logistics. However, this can only be done to compare samples produced at the same factory as the processing steps downstream the fluid bed drying can impact the characteristics of the powder and thereby its caking tendency in different ways. It is recommended to implement a similar accelerated caking test at all factories, with the exact experimental conditions adapted to the powder produced at the specific site. This would allow to increase the repeatability of the measurement and rapidly identify the powders with high risk of caking.

However, the accelerated caking test is only useful if the effect of the powder RH does not outweigh the effect of the other parameters on caking. Indeed, the effect of aerating the powder after the fluid bed drying step could not be assessed due to RH being regulated by saturated salt solutions in the accelerated caking test. Another test where RH is imposed by the powder itself was designed and revealed the enhanced stability of the aerated powder. Indeed, aeration significantly reduced the caking tendency during the first ten days of storage at 20°C. However, its effect was limited as caking developed in the aerated powder after 20 days of storage. This alternative test could be used to optimize aeration so that the powder RH is lowered enough to prevent caking. However, as suggested in Figure 62, the PSD should also be considered to assess the risk of caking.

8.6. Take-home messages

- An accelerated caking test, which can discriminate lactose samples in terms of caking in less than a day, has been developed.
- The test should be implemented at all production sites as part of the quality control, in order to target the batches with high risk of caking. The storage conditions (temperature, RH, mechanical pressure) imposed on the samples before caking measurement should be adapted to the powder produced at the specific production site.
- For powders where the increase in RH after drying is an issue, an alternative test was proposed. In this caking test, the powder RH is a test parameter. Indeed, the RH used to store the samples is imposed by the powder itself.
- Using this latter test, aeration was shown to significantly delay caking in lactose powder.

General Conclusion

Lactose caking is a costly issue in the dairy industry. In order to find means to prevent it, it is necessary to understand the caking mechanisms. According to the review of the literature (chapter 1), these latter can be impacted by numerous parameters. A strict control of the product parameters is therefore a prerequisite to a non-caking product, and this cannot be achieved without a detailed knowledge of the process. Thus, the strategy developed in the present PhD study focused on the relationship between the production process and the product properties.

The first part of the work aimed at investigating the caking mechanisms in lactose powder. It consisted first in reviewing the literature and characterizing lactose powder sampled at different points on the production line. Then, lactose powders with a controlled variation of critical product parameters were produced on a pilot scale and analyzed for their physicochemical characteristics including caking tendency. The following scientific objectives, presented in chapter 2, were addressed:

Objective 1: Develop a method which can discriminate samples according to their caking tendency.

As described in chapter 1, various methods to characterize caking can be found in the literature. In this PhD work, ring shear testing was successfully used to investigate the effect of different parameters on caking. Suitable environmental conditions for storage of the samples before caking measurement were proposed so as various degrees of caking were obtained, thus enabling a discrimination of the powders.

Objective 2: Highlight the most important intrinsic parameters in relation to caking in lactose powder.

The first part of the work, namely the literature review combined with the product sampling, led to identify two critical parameters for lactose caking: the impurity content and the particle size. Indeed, these two parameters can largely influence the three main caking mechanisms in lactose powder, which are amorphous caking, humidity caking and mechanical caking. Moreover, large batch to batch variations of the two parameters were observed. Characterization of the lactose samples also highlighted the difficulty to measure water activity in lactose powder, especially with a water activity meter. Further investigation revealed a process-related phenomenon, namely a large increase in the powder water activity during storage right after drying of the powder. Thus, as part of the applied objectives (4, 5 and 6) of the PhD, it was necessary to point out which steps can alter the impurity content and particle size along the process line and how a low and stable water activity can be obtained.

Objective 3: Understand the mechanisms behind caking due to variations in the key intrinsic parameters in relation to caking, as highlighted in point 2.

On a pilot scale, it was possible to vary the washing grade in order to produce lactose powders with increasing level of impurities. A higher impurity content led to increased hygroscopicity and stronger caking. As amorphous lactose was not detected in the powder, it was suggested that humidity caking was the principal caking mechanism, whereby moisture sorption was increased by the presence of impurities.

In addition, the lactose powders were sieved to obtain various size fractions. Caking measurements revealed that both the particle size and span of the size distribution were crucial to control in order to prevent caking. Indeed, smaller particles showed increased hygroscopicity as they presented a larger surface area and were found to contain more impurities than bigger particles. Moreover, the multiplication of contact points with smaller particles favors mechanical caking. In the same manner, a broader span leads to enhanced mechanical caking and also increases humidity caking through capillary condensation.

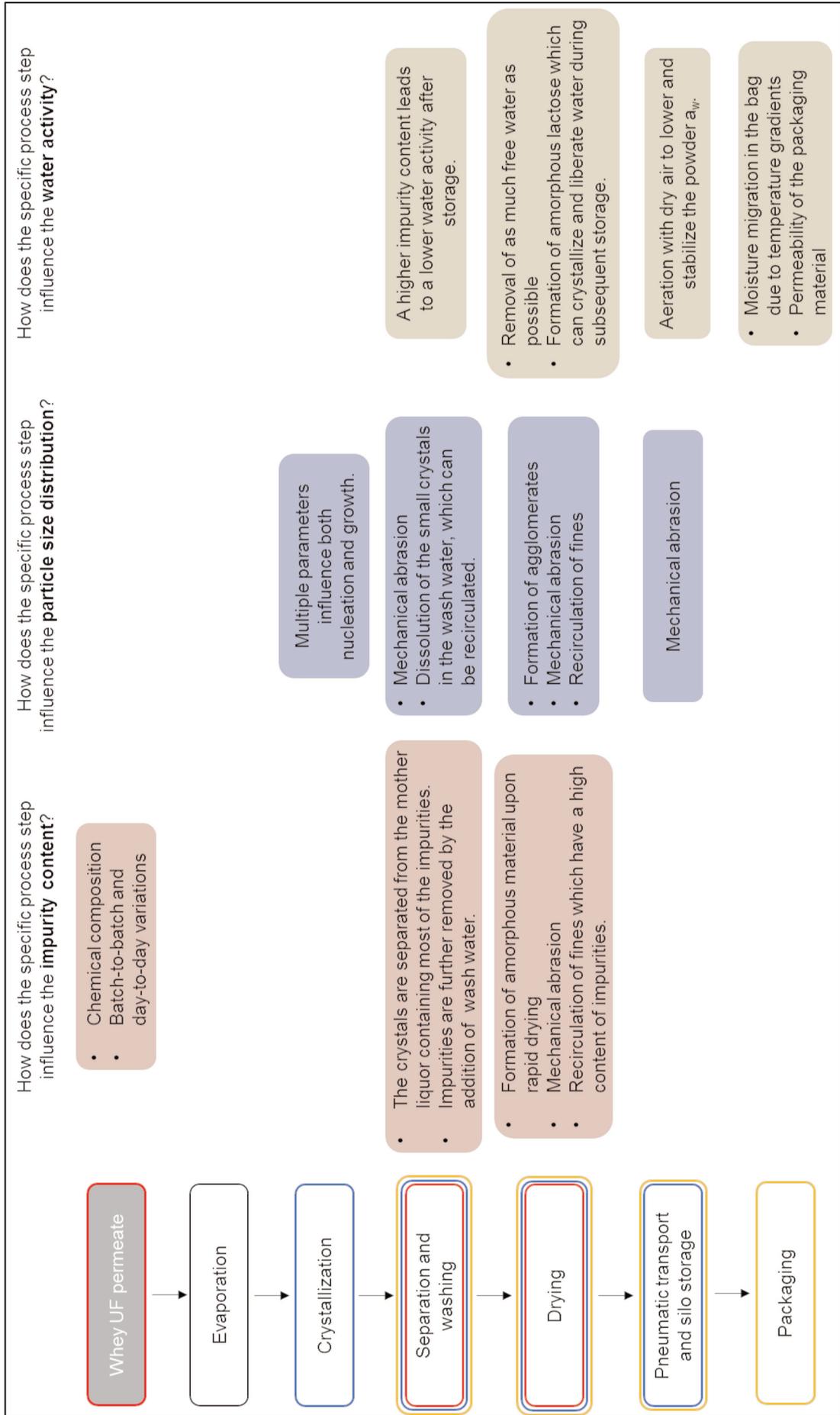
Considering the large increase in water activity during storage after fluid bed drying, it was explained by the crystallization of residual amorphous lactose. The drying parameters were varied on a pilot scale but the increase in water activity in the lactose samples during storage was very limited. Therefore, it was concluded that the effect of the drying parameters on the increase in water activity has to be investigated on the production line.

The third part of the work aimed at applying the results to the commercial product in industrial settings. Focus was on the following applied objectives:

Objective 4: Investigate the process steps which are key to control the main product parameters responsible for caking in lactose powder (in relation to point 2).

There is usually at least one processing step that is determining for each product parameter. For example, crystallization, washing and drying critically influence the PSD, impurity content and water activity of the final product, respectively. However, several other steps, both upstream and downstream can impact the different product parameters. Figure 63 summarizes the important steps to control for the three product parameters which were found critical in relation to caking of lactose powder.

Figure 63: The main process steps impacting the critical product parameters for caking, namely the impurity content (red blocks), the particle size distribution (blue blocks) and the water activity (yellow blocks) and summary of their effect. Compared to the production process presented in Figure 9 (section 1.2.3) the purification steps before evaporation have been removed for simplification but they obviously influence the impurity content. In addition, pneumatic transportation and silo storage have been added as a process step given their importance to control the water activity of the final product.



Objective 5: Give recommendations to the dairy industry on how to control the critical process steps in order to limit the caking tendency of the final product (in relation to points 2 and 3).

Once the critical processing steps were identified (see above), focus was made on investigating how the process parameters at this particular steps would influence the final product properties and thereby its caking tendency (Figure 63). It was found that different product parameters were often related and that a modification of the process could impact several product parameters at the same time. Guidelines for a specific product parameter to prevent caking can therefore not be established without taking the other parameters into account.

Objective 6: Develop a method to predict the caking tendency of a lactose sample before it is shipped to a customer.

A urgent need of the dairy industry is to be able to categorize different batches in terms of their caking tendency in order to ensure that a defined batch will withstand the temperature and humidity conditions during transportation and arrive as free-flowing powder at the customer. Thus, an accelerated caking test based on ring shear testing has been developed as part of this PhD thesis, which allows to discriminate batches according to the caking tendency in less than a day. The results showed that, even if the impurity content is at the highest level permitted in commercial lactose powder, a large particle size overrules the effect of impurities and limits caking. As the lactose powders can have different characteristics from one production site to another, it was proposed to implement a similar test at all sites with the precise test conditions adapted to the powder produced at the site under consideration. Thus, the accelerated caking test would also allow to directly assess the effect of a process modification on caking. Finally, an alternative caking test was developed for powders with unstable water activity. This test, where RH is imposed by the powder itself, showed that aeration can significantly delay caking in lactose powder.

The PhD work flow and the main results obtained at each step are summarized in Figure 64.

General Conclusion

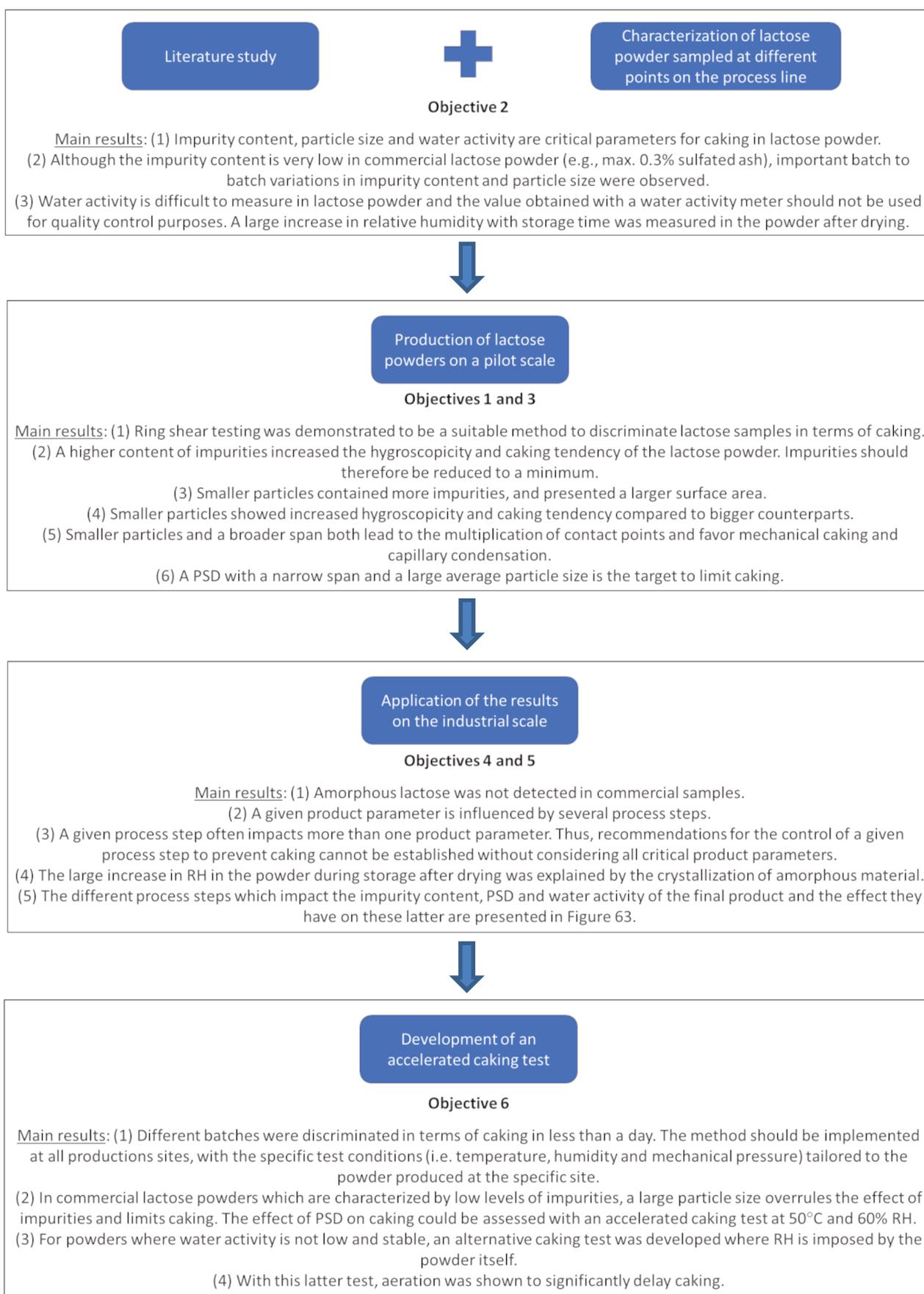


Figure 64: PhD work flow with the objectives and main results for each work package. The objectives refer to the ones presented in the text (pg 131,132 and 134).

Recommendations for Future Work

This PhD project has highlighted the importance of taking the effect of the processing steps into account when investigating means to limit caking. Thus, following the strategy employed, future work should include purely scientific research on a laboratory scale and investigations of the process-related phenomena on a production scale.

1. Understanding the effect of the critical parameters on lactose caking

The crucial effect of the impurity content and the PSD on caking was demonstrated, while a correlation between unstable water activity during storage and development of caking in commercial lactose powder was shown. Some aspects remain to be considered in order to fully understand caking due to a variation of these parameters in lactose powder.

First, experimental results suggested that impurities were mostly present on the surface of the lactose crystals. This point should be verified by analyzing the surface composition. Some attempts were made in this PhD project in collaboration with the department of chemistry at the University of Copenhagen. For example, lactose crystals with different washing grades were analyzed by atomic force microscopy coupled with IR spectroscopy in order to investigate local differences in the surface composition at the nanoscale. Measurements at different depths in the crystal structure were also performed by micro-Raman spectroscopy. More research is needed for a thorough investigation of the potential of these methods on dairy powders. Alternatively, XPS measurements could give insight in the powder surface composition in lactose, protein and lipids through the elementary content, which could then be compared to the bulk composition (Gaiani et al., 2006). Analysis of dairy powders with the XPS technique is well-established. However, inorganic components, which are of great importance in lactose powders, are often neglected in the XPS analysis because of their low content (Murrieta-Pazos et al., 2012).

Another point to focus further research on is the instability of the powder water activity. The increase in water activity after drying of the powder was explained theoretically by the crystallization of amorphous lactose. However, it was not possible to demonstrate experimentally the presence of amorphous lactose in the powder as it was not detected by any of the method investigated. There is a need for a fast analysis with a portable device so that the powder can be analyzed right after drying and before the onset of crystallization. This could for example be achieved by NIR spectroscopy, providing a good sensitivity of the instrument to detect the low amount of amorphous material. Moreover, a new indirect method was proposed in this PhD project, namely the use of humidity loggers to detect the presence of amorphous material by inducing crystallization and following the release of moisture. The method is particularly relevant

in industrial settings as it is very easy to use and only requires minimal equipment. The results were promising and more work should be done to investigate the detection limit of the method.

Moreover, the higher caking exhibited by smaller particles was explained by a larger surface area and number of contact points among others. Beside particle size, particle shape and surface roughness could thus also give useful information about the risk of increased moisture sorption and mechanical caking. As particle size, particle shape is largely determined at the crystallization step but can be modified downstream, for example by attrition. To capture particle shape and analyze surface roughness, microscope images can be useful. Automated image analysis is also a powerful tool as it allows the automated measure of a great number of particles in a short time.

2. Control of the process

The process steps which are critical to control to prevent caking have been identified (Figure 63) and recommendations have been given for their optimization. As a high water activity was shown to correlate with caking in the powder bags (Figure 51), producing a powder with a low and stable a_w should be the first priority of lactose manufacturers. This task involves the optimization of the drying parameters to prevent the formation of amorphous lactose that can subsequently crystallize and release water during storage. Alternatively, aeration in silos could be used to lower the water activity. However, the aeration conditions which would ensure that water activity does not increase again after aeration remain to be determined.

In order to control the PSD of the powder, crystallization is a process which requires full attention but which is also particularly complex. For example, much research has already been performed on a laboratory scale on the effect of impurities on lactose crystallization (Chandrapala et al., 2016; Gernigon et al., 2013; Guu & Zall, 1991). However, model solutions are often used. Thus, studies of crystallization of the complex slurry on the process line are also needed. On this occasion, it could be interesting to investigate the formation of lactose polymorphs other than α -lactose monohydrate depending on the operational parameters and the impurities. Indeed, the different lactose polymorphs were shown to present different moisture sorption behaviors and caking characteristics (Listiohadi et al., 2008).

Commercial lactose powder contains a very low amount of impurities. Due to environmental and economic concerns, the washing process could be optimized regarding the consumption of wash water, while ensuring the impurity content remains low. In addition, the effect on PSD and especially the production of fines should be evaluated. Thus, a specific study should be conducted investigating how (e.g. several successive dilutions rather than a single water addition) and until which point (washing grade value) the washing step should run.

On top of the processing steps, the raw material entering the process should also be a focus point. The whey composition is crucial as it determines the impurities which should be washed away in the process. In addition, these impurities impact the crystallization and drying processes and

therefore the PSD and water activity of the final product. Many routes for optimization of the production process have been suggested in this PhD thesis, in order to limit caking. However, the efficiency of the different processing steps largely depends on the incoming material. Thus, a full control of the raw material and especially its composition is crucial.

3. *Investigation of the relative effect of process parameters and product parameters on caking*

It should be kept in mind that numerous process parameters can be modified at each step on the process line. In order to investigate which process parameters have the largest influence on caking, multivariate data analysis should thus be used. This work requires a systematic evaluation of the caking behavior of the lactose powder produced. Indeed, customer complaints about caking would depend on the location of the customer in the world and the transport conditions but also on the intended application of the powder. Depending on their process, some customers might accept a powder with soft lumps while others would not handle it. Thus, customer complaints do not provide a reliable assessment of caking. It is therefore recommended to implement the accelerated caking test (chapter 8) in order to measure the caking tendency of the different batches under the same conditions. The result of the test can then be linked to the process parameters in a statistical analysis.

However, the knowledge of the batches which caked during transportation to the customer can be used to adjust the parameters in the caking test. Indeed, a batch which was reported as caked by the customer should also cake in the accelerated caking test. This way, the caking test could be used as a predictive test.

RH measurements in the finished goods suggested the existence of a zone at intermediate values of RH, where PSD largely determines the development of caking. It was also shown that at the low levels of impurities found in the commercial powder, significant differences in PSD are more determining for caking than differences in impurity content. However, precise threshold values delimiting the different zones where a specific parameter has the preponderant effect on caking are still to be defined. This could be achieved by characterizing the powders in terms of impurity content, PSD and water activity and investigating possible correlations with caking by statistical analysis. Representative parameters are required for the impurity content and the PSD. Sulfated ash and potassium are suggested as representative parameters of the impurity content. Indeed, the potassium content in commercial samples was found to be usually above the quantification limit of the ICP-OES method. For the PSD, the ratio D_{50} / span would allow to consider the combined effect of the particle size and the span. If the relative effect of these two parameters is needed, both the span and the D_{50} should be included in the analysis. Finally, for all batches, water activity should be measured after a defined storage time after packaging as it was shown that the product water activity can be unstable during storage.

The results obtained in this PhD thesis can also help to set the directions of search to investigate caking in other dairy powders. However, as mentioned in chapter 1, the caking mechanisms are often specific to the product under consideration, and the critical product parameters can differ between dairy powders. In any case, as caking is influenced by multiple product parameters which are determined by the process conditions, applying the strategy developed in this PhD study to investigate caking in any product can only be a strength.

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Table of Figures

Figure 1: USA export growth from 2009 to 2016 for several dairy products.	6
Figure 2: Share of announced finalized investments between 2012 and 2014 in the EU.	6
Figure 3: Range of whey based products according to the added-value level.....	9
Figure 4: The different applications of whey based ingredients.....	9
Figure 5: Lactose structure in α and β forms.	11
Figure 6: Typical tomahawk and prism shapes of α -lactose monohydrate.	12
Figure 7: Typical uneven-sided diamond shape of anhydrous β -lactose crystallised from water.	13
Figure 8: Relationships between glass transition temperature (T_g), water content and water activity for amorphous lactose.....	14
Figure 9: Process chart for the manufacture of edible grade lactose.	16
Figure 10: Lactose powder caked in a bag.	18
Figure 11: Measurement of a yield locus by preshear and shear to failure with a ring shear tester.	29
Figure 12: Output of a test for the measurement of flowability of α -lactose monohydrate with a Schulze ring shear tester.....	30
Figure 13: Overview of the three caking mechanisms together with the internal and external parameters which can influence caking in lactose.....	34
Figure 14: Aeration of lactose powder in a pilot fluid bed.....	43
Figure 15: Sequence of 30 minutes aerations followed by 24 hours resting time used for the discontinuous aeration of powder.....	44
Figure 16: Sequence of 1 hour aerations followed by 30 minutes resting time used for the discontinuous aeration of powder.	44
Figure 17: Data logger placed in the lactose powder to record temperature and RH.	47
Figure 18: Storage of the shear cells containing lactose powder for measurement of caking. ...	49
Figure 19: Schematic representation of the experimental setup for the caking test without controlled humidity.	50
Figure 20: Variations in the mineral content (K, Cl, Na, P, Ca, Mg) of lactose powder as a function of degree of washing of the lactose crystals.	54

Figure 21: Particle size distributions of lactose powders for three different washing grades (0, 1, 2) but with the same particle size fraction ($160 < x < 250 \mu\text{m}$).....	55
Figure 22: Moisture sorption isotherms of lactose powders with three different washing grades but the same particle size fraction ($160 < x < 250 \mu\text{m}$): Wash 0, Wash 1, Wash 2.	55
Figure 23: Moisture sorption isotherms of non-sieved pharmaceutical grade lactose and the most washed lactose from the pilot trial (Wash 2).....	56
Figure 24: SEM images showing details of particle surface of different washing grade lactose powders.	57
Figure 25: ^{13}C CP/MAS NMR spectra of (A) Wash 0; (B) Wash 0.3; (C) Pharmaceutical grade lactose; (D) Amorphous lactose.	59
Figure 26: ffc of non-sieved and sieved lactose powders between $160 \mu\text{m}$ and $250 \mu\text{m}$ as a function of the washing grade.....	59
Figure 27: Particle size distributions of Wash 0 and Wash 2 lactose powders sieved to separate 80, 160, 250, 355 and $500 \mu\text{m}$ fractions.	64
Figure 28: Impurity content and specific surface area of lactose powders as a function of the particle size class: (A) Wash 0; (B) Wash 1; (C) Wash 2.	66
Figure 29: SEM images showing small particles of different washing grade lactose powders: (A) Wash 0; (B) Wash 2.	67
Figure 30: Moisture sorption isotherms of lactose powder Wash 2 for three different particle size fractions: $80 < x < 160 \mu\text{m}$; $160 < x < 250 \mu\text{m}$; $250 < x < 355 \mu\text{m}$	68
Figure 31: Flowability ffc of lactose powders Wash 0 and Wash 2 as a function of particle size class after storage for four days at 60% RH and 20°C and under a consolidation stress of 9.3 kPa.	69
Figure 32: Particle size distributions of different size fractions (non-sieved, $100 < x < 355 \mu\text{m}$ and $160 < x < 250 \mu\text{m}$) of lactose powder Wash 0.3.	71
Figure 33: Flowability ffc of different size fractions of lactose powder Wash 0.3 as a function of the span of the particle size distribution.....	71
Figure 34: DSC thermogram of non-crystallized whey powder at 0.22 aw.	77
Figure 35: DSC thermogram of commercial α -lactose monohydrate.....	78
Figure 36: Sorption isotherm of unmilled α -lactose monohydrate	79
Figure 37: Evolution of RH in crystalline unmilled lactose powder mixed with amorphous lactose stored in closed containers in a climate chamber.	81

Figure 38: DSC thermogram of crystalline lactose powder mixed with 15% amorphous lactose before and after storage in closed containers in a climate chamber.. 82

Figure 39: The predicted effect of small amounts of amorphous lactose on the moisture sorption isotherm of crystalline α -lactose monohydrate..... 83

Figure 40: Operating principle of the decanter centrifuge used at the separation step..... 86

Figure 41: Operating principle of the decanter centrifuge used at the washing step. 86

Figure 42: Moisture sorption isotherms of lactose powders (fluid bed samples) with or without the separation step included in the production process. 88

Figure 43: Moisture sorption isotherms of commercial lactose finished goods samples with different washing levels. 89

Figure 44: Impurity content as a function of the particle size class of a lactose powder sampled at the exit of fluid bed. 90

Figure 45: Example of agglomerate constituted of large tomahawks agglomerated together by smaller fragments..... 92

Figure 46: Evolution of water activity with storage time in three batches of lactose powder produced on different days..... 99

Figure 47: Evolution of relative humidity and temperature with storage time measured with a data logger in eight different fluid bed powders. 100

Figure 48: Prediction of an increase in RH from 40 to 80% due to crystallization of 0.5% amorphous material in lactose powder..... 101

Figure 49: Prediction of an increase in RH from 40 to 82% due to crystallization of 3% amorphous material in another batch of lactose powder. 102

Figure 50: Evolution of relative humidity and temperature measured with a probe stuck into a Big Bag filled with lactose powder from a test production.. 104

Figure 51: RH measured three weeks after powder bagging with a probe stuck into the Big Bag containing lactose powder..... 104

Figure 52: Evolution of RH in lactose powders subjected to various aeration times after drying. 108

Figure 53: Evolution of RH in lactose powders subjected to various aeration regimes after drying: no aeration, continuous aeration for 1.5 hours and a discontinuous aeration performed as three aerations of 30 minutes each with 24 hours resting time in between. 109

Figure 54: Evolution of RH in lactose powders subjected to various aeration regimes after drying: no aeration, continuous aeration for 4 hours and a discontinuous aeration performed as 4 aerations of 1 hour each with 30 minutes resting time in between. 110

Figure 55: Lines representing the maximum water activity for the powder at bagging to avoid caking due to temperature gradients, when the product is packed and subsequently cooled at the temperatures indicated. 111

Figure 56: Particle size distributions of two finished good samples of commercial lactose powder and a sample of pharmaceutical grade lactose. 116

Figure 57: Flowability ffc of two samples of finished good commercial lactose powder as a function of storage time. 118

Figure 58: Flowability ffc of two samples of finished good commercial lactose powder after storage for six hours at 50°C and controlled or uncontrolled RH. 120

Figure 59: Flowability ffc of two samples of finished good commercial lactose powder as a function of storage time. 121

Figure 60: Flowability ffc of lactose powder sampled before and after aeration as a function of storage time. 127

Figure 61: Flowability ffc of lactose powder sampled before and after aeration as a function of storage time. 128

Figure 62: Assessment of the risk of caking of commercial lactose powder as a function of the powder RH and the PSD. 129

Figure 63: The main process steps impacting the critical product parameters for caking, namely the impurity content, the particle size distribution and the water activity and summary of their effect. 133

Figure 64: PhD work flow with the objectives and main results for each work package. 135

Table of Tables

Table 1: Typical composition of human milk and milk of the major producer domesticated mammals.	5
Table 2: Production of lactose by region between 2011 and 2015 together with the Compound Annual Growth Rate (CAGR) and forecast for 2020	10
Table 3: Currently known forms of lactose.	11
Table 4: Specifications for the composition of pharmaceutical and edible grade lactose.....	17
Table 5: AFI chemical and physical specifications for food grade lactose powder.....	17
Table 6: Composition of lactose powders as a function of degree of washing of the crystals. ...	53
Table 7: Average composition of sweet whey, lactic acid whey and hydrochloric acid whey.	85
Table 8: Composition of lactose powders (fluid bed samples) with or without the separation step included in the production process.	87
Table 9: ffc of commercial lactose powders with different washing levels.	89
Table 10: Composition of two samples of lactose powders from filter bags.....	91
Table 11: Characteristics (D_{10} , D_{50} , D_{90} and span) of the PSD of samples of lactose powder obtained at the exit of the fluid bed and on the packaging line during silo emptying.	93
Table 12: Water activity repeatability test performed with a water activity meter.	98
Table 13: Water activity measured with a RH probe and an a_w -meter and moisture content of lactose powders produced on a pilot scale with different washing grades after storage for several weeks.....	105
Table 14: Impurity content of two finished good samples of commercial lactose powder and a sample of pharmaceutical grade lactose.	117
Table 15: Flowability ffc of fluid bed lactose samples from different production sites after storage at 50°C and 60% RH for 6 hours under a consolidation stress of 9.3 kPa.	123
Table 16: Flowability ffc of finished goods lactose samples from different production sites after storage at 50°C and 60% RH for six hours under a consolidation stress of 9.3 kPa.	125
Table 17: PSD characteristics and impurity content of the aerated and non-aerated powders of batch 1.	126
Table 18: PSD characteristics of the aerated and non-aerated powders of batch 2.	127

Résumé de la Thèse en Version Longue

Introduction générale

Pour approcher la composition du lait maternel, la formulation des laits infantiles implique le mélange précis de plusieurs dizaines d'ingrédients. Le lactose, premier constituant en masse du lait maternel, est également l'ingrédient principal des poudres de laits infantiles. Pour satisfaire la forte croissance de la demande en lait infantile depuis 2007, la production mondiale de lactose a augmenté de 50% depuis 2009 pour atteindre 1,5 millions de tonnes en 2017 (Affertsholt & Fenger, 2013). L'utilisation du lactose dans la fabrication des laits infantiles, mais aussi des confiseries et produits pharmaceutiques, requiert un niveau de qualité élevé tant sur le plan microbiologique que physico-chimique. Cependant, l'usage des poudres de lactose peut être entravé par le phénomène de mottage qui consiste en leur prise en masse en agglomérats de taille variable. Leurs propriétés d'écoulement et d'usage sont dans ce cas dégradées, affectant transport et dosage de ces poudres, et engendrant de coûteuses réclamations de la part des clients.

Le mottage a fait l'objet de nombreuses études sur les aspects suivants : mécanismes de mottage, caractérisation du mottage à l'échelle particulaire et à l'échelle du lit de poudre, modélisation du mottage, agents anti-mottants. Cependant, le mottage est un phénomène complexe, avec des mécanismes propres à la poudre étudiée. Malgré une recherche intensive, le mottage des poudres persiste donc en tant que problème récurrent dans de multiples industries. Dans l'industrie laitière, le mottage de la poudre de lactose est assez fréquemment constaté. Pourtant, le lactose en poudre est généralement considéré comme un produit stable, avec une durée de conservation jusqu'à deux ans. Pour prévenir le mottage et assurer une qualité optimale du produit, Arla Foods Ingredients (AFI) souhaite acquérir une meilleure connaissance du sujet.

Pour aborder la problématique du mottage du lactose, une collaboration entre AFI, l'unité mixte de recherche INRA-Agrocampus Ouest Science et Technologie du Lait et de l'œuf (STLO) et l'Université de Copenhague a été initiée. Au cours de la thèse, des périodes de durée variable ont été réalisées successivement au sein des trois structures. Ce projet de thèse a donc bénéficié de la combinaison d'expertises variées et de l'accès à de multiples équipements à l'échelle du laboratoire et du pilote. De plus, des données de production ainsi que d'expériences réalisées sur la ligne de production ont pu être obtenues.

Ce manuscrit de thèse présente d'abord le contexte économique et scientifique du projet. Un aperçu général du marché laitier et de la poudre de lactose en particulier, une présentation des caractéristiques physicochimiques du lactose et des mécanismes de mottage ainsi qu'une revue

des méthodes de caractérisation du mottage (chapitre 1) ouvrent sur la question de recherche et la stratégie mise en œuvre pour y répondre (chapitre 2).

L'objectif général de l'étude consiste en la compréhension des mécanismes de mottage de la poudre de lactose, afin de proposer des moyens de prévention du mottage. Pour cela, des études à l'échelle pilote ainsi que des échantillonnages sur la ligne de production ont été réalisés. Différentes propriétés physicochimiques des poudres ainsi que leur tendance au mottage ont ensuite été analysés (chapitre 3). Dans la première partie de l'étude, à l'échelle pilote, des poudres de lactose ont été produites avec une variabilité contrôlée de la teneur en impuretés (chapitre 4) et de la taille des particules (chapitre 5), tous deux des paramètres critiques pour le mottage. Les leviers de contrôle de ces paramètres sur la ligne de production sont également présentés (chapitre 6). En outre, l'échantillonnage sur la ligne de fabrication a démontré l'importance du contrôle de l'activité d'eau de la poudre pour prévenir le mottage. Différents moyens pour y parvenir ont été étudiés (chapitre 7). Enfin, le projet de thèse s'intéresse à un besoin crucial du fabricant de lactose, à savoir le développement d'un test de mottage accéléré (chapitre 8).

Contexte économique et scientifique

1. Aperçu du marché laitier mondial

Le lait, premier aliment de l'homme en tant que mammifère, est consommé depuis des millénaires. La composition du lait dépend de l'espèce productrice mais aussi de la race, de l'âge, du stade de lactation, etc. Les produits dérivés du lait comme le yaourt, le beurre et le fromage existent également depuis des millénaires. Leur production était historiquement très locale, avec des caractéristiques sensorielles propres à chaque produit. Aujourd'hui, une grande partie des consommateurs a accès à un choix très varié de produits laitiers et la consommation augmente. Les prévisions tablent sur une augmentation globale de 22% entre 2015 et 2025 (International Dairy Federation, 2016). De plus, la part de la production exportée au-delà des frontières est aussi en augmentation.

Dans ce contexte, les produits en poudre prennent une importance croissante, de par leur facilité de traitement, stockage et transport. La technique de séchage par atomisation est la plus couramment employée pour la déshydratation des produits laitiers (Knipschildt & Andersen, 1994). Il existe une grande variété de produits laitiers en poudre, du lait écrémé ou lait entier aux produits intermédiaires pour l'industrie agroalimentaire en passant par les biens de consommation courante comme la poudre pour boisson cacao ou aromatisée (Pisecky, 2012). De plus, la séparation du lait en ses différents constituants s'est accentuée ces 20 dernières années, dû entre autres à l'intérêt économique des poudres riches en protéines de lait.

De nouveaux ingrédients, issus du lactosérum, ont également émergé dans les années soixante-dix. En effet, le lactosérum, produit dérivé de la fabrication de fromage, était traditionnellement éliminé (effluent traité en station, épandage) ou utilisé pour l'alimentation du bétail (Lifran, Hourigan, Sleigh, & Johnson, 2000). Cependant, pour des raisons économiques et environnementales, les fabricants de fromage ont été contraints de trouver progressivement de nouveaux modes de valorisation du lactosérum. La filtration membranaire permet ainsi de séparer le lactosérum en ses différents constituants et d'obtenir des produits à haute valeur ajoutée, comme la poudre de lactose.

2. Zoom sur la poudre de lactose

Parmi les ingrédients issus du lactosérum, la poudre de lactose est le deuxième ingrédient en volume après la poudre de lactosérum. La production de lactose est en constante augmentation, d'environ 5% par an. La valeur marchande globale du lactose était de 1.2 milliard de dollars en 2015 et devrait atteindre 1.5 milliard en 2020. L'industrie agroalimentaire et la fabrication de laits infantiles sont les deux principaux utilisateurs de poudre de lactose (Affertsholt & Pedersen, 2016).

2.1. Les différentes formes de lactose¹

La lactose est un disaccharide composé de galactose et glucose (Figure 65). La molécule de lactose peut se trouver sous forme α ou β , les deux formes étant des stéréoisomères. La transformation d'un anomère à l'autre est appelée mutarotation. A l'état solide, le lactose peut être cristallin, amorphe ou un mélange des deux. Le lactose est également polymorphe, ce qui signifie qu'il peut cristalliser sous différentes formes : α -lactose monohydraté, α -lactose anhydre stable ou instable, β -lactose anhydre (Holsinger, 1988).

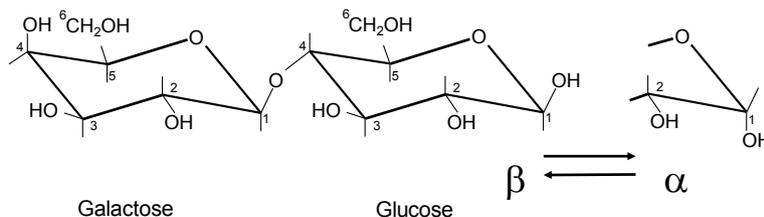


Figure 65: Structure de la molécule de lactose sous forme β et α (Schuck, 2011).

Le lactose alpha monohydraté est la forme la plus courante et la plus stable dans des conditions normales de température et d'humidité. En effet, sa structure est stabilisée par la présence d'une molécule d'eau par molécule de lactose. Cette forme de lactose est également peu hygroscopique, par opposition aux formes stable et instable de lactose alpha anhydre. Ces deux

¹Carpin, M., Bertelsen, H., Bech, J. K., Jeantet, R., Risbo, J., & Schuck, P. (2016). Caking of lactose: A critical review. *Trends in Food Science & Technology*, 53, 1–12. <https://doi.org/10.1016/j.tifs.2016.04.002>

formes sont dérivées du lactose alpha monohydraté par élimination de la molécule d'eau de cristallisation. Pour ce faire, un chauffage à une température supérieure à 100°C, de préférence sous vide, est nécessaire (Listiohadi, Hourigan, Sleight, & Steele, 2005a). Par ailleurs, le lactose beta anhydre est la seule forme cristalline de l'anomère beta. Elle est relativement stable et présente une faible hygroscopicité. En solution, la forme beta devient la moins soluble quand la température dépasse 93.5°C (Hudson, 1904). Le lactose beta anhydre peut donc être cristallisé à partir d'une solution de lactose concentrée à haute température.

Le lactose amorphe se caractérise par une structure désordonnée constituée d'un mélange de molécules de lactose alpha et beta. Le lactose amorphe apparaît solide de par sa forte viscosité. Cette forme de lactose est thermodynamiquement instable et très hygroscopique. Elle se forme quand les conditions de séchage d'une solution de lactose concentrée entraînent une augmentation rapide de la viscosité et empêchent ainsi la cristallisation (Holsinger, 1997). Un solide amorphe se caractérise par une température de transition vitreuse (T_g) au-delà de laquelle il passe d'un état vitreux et rigide à un état caoutchouteux. La T_g du lactose amorphe anhydre est de 101°C (Roos & Karel, 1990) mais elle diminue quand la teneur en eau augmente (Roos & Karel, 1991). Quand la T_g est atteinte, la cristallisation a lieu et s'accompagne de l'expulsion de l'eau absorbée par la structure amorphe (Buckton & Darcy, 1999).

2.2. Le procédé industriel de fabrication de la poudre de lactose

Dans l'industrie laitière, le lactose alpha monohydraté est la forme de lactose la plus couramment produite. La matière première, le lactosérum, est en général ultrafiltré pour séparer les protéines (rétentat) du lactose et des minéraux (perméat). Le perméat d'ultrafiltration est ensuite soumis à différents traitements présentés en

Figure 66. Les deux premières étapes permettent de déminéraliser le perméat et ainsi d'augmenter l'efficacité du procédé de séparation. Le perméat est ensuite concentré par évaporation avant d'être pompé dans des cristallisoirs où la cristallisation se fait par refroidissement. Les cristaux de lactose sont ensuite lavés par centrifugation et décantation pour les débarrasser de leurs impuretés (minéraux, peptides, acides organiques...). Finalement, les cristaux sont séchés sur lit fluidisé jusqu'à une teneur en eau totale de 4.5 - 5.5% puis refroidis avant ensachage.

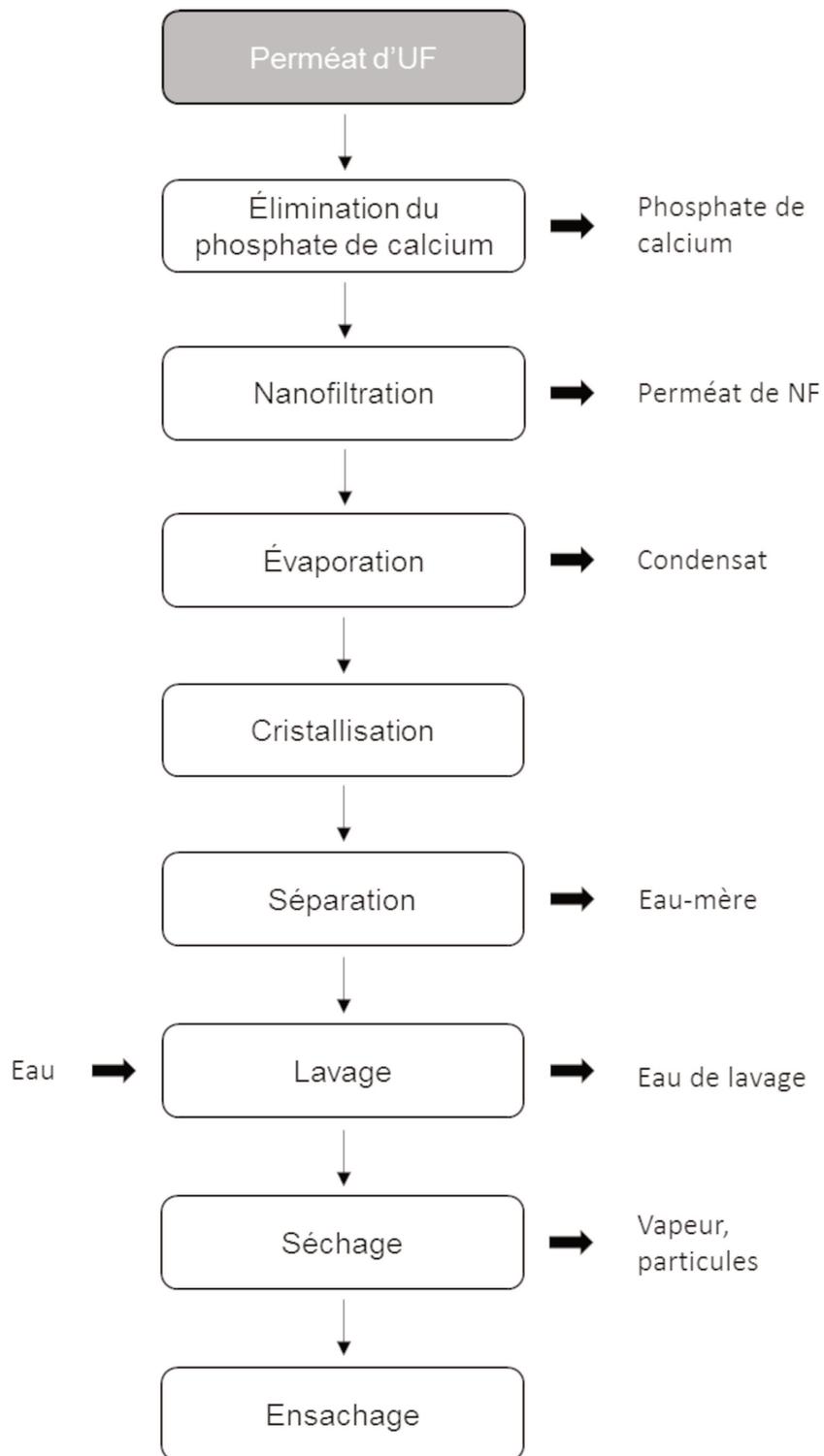


Figure 66: Schéma du procédé de fabrication de la poudre de lactose (modifié à partir de (Durham, 2009)).

3. Le mottage¹

Le mottage de la poudre de lactose fait intervenir trois mécanismes principaux. Le premier implique la présence de matière amorphe tandis que le deuxième prend en compte les interactions de la poudre avec l'humidité ambiante. Le troisième mécanisme découle de l'équilibre des forces entre particules.

3.1. Le mottage amorphe

En permettant la diffusion des molécules aux points de contact entre particules, une augmentation de la température peut entraîner le mottage. Comme expliqué en section 2.1, la viscosité d'un matériau amorphe diminue fortement dans la région de la transition vitreuse. Les particules amorphes deviennent ainsi mobiles et peuvent créer des ponts entre particules. Si les conditions environnementales permettent aux structures amorphes de cristalliser, les ponts se solidifient. Le mottage amorphe a été étudié sous l'angle du procédé d'agglomération entre deux particules, en utilisant des équations issues du procédé de frittage et de la théorie viscoélastique (Haider et al., 2014; Palzer, 2005).

La différence entre la température T du procédé ou de stockage et la T_g du matériau, i.e. $T - T_g$, gouverne la vitesse de cristallisation et l'étendue du mottage (Foster, Bronlund, & Paterson, 2006; Lloyd, Chen, & Hargreaves, 1996; Roos & Karel, 1992, 1993). Cependant, l'humidité ambiante doit également être contrôlée en raison de la plastification de la matière amorphe par l'eau. Ainsi, la cristallisation du lactose amorphe lyophilisé peut avoir lieu à température ambiante quand l'humidité relative est de 43% (Roos & Karel, 1991).

Dans le cas de poudres cristallines contenant seulement une faible quantité de matière amorphe, le transfert de matière amorphe aux points de contact n'est pas le seul mécanisme pouvant entraîner le mottage. En effet, l'absorption d'eau à une humidité relative donnée augmente avec la quantité d'amorphe (Bronlund, 1997; Darcy & Buckton, 1998; Listiohadi, Hourigan, Sleigh, & Steele, 2005b). Si la quantité d'eau absorbée est assez importante pour entraîner la cristallisation de la matière amorphe, cette eau est relarguée et peut interagir avec le reste de la poudre sous forme cristalline par le mécanisme suivant.

3.2. Le mottage hygrique

La plupart des poudres alimentaires sont hygroscopiques, à différents degrés en fonction des conditions de température et d'humidité (Mauer & Taylor, 2010). Aux faibles humidités, les molécules d'eau sont adsorbées à la surface des particules (Dupas-Langlet, 2013). Quand

¹Carpin, M., Bertelsen, H., Bech, J. K., Jeantet, R., Risbo, J., & Schuck, P. (2016). Caking of lactose: A critical review. *Trends in Food Science & Technology*, 53, 1–12. <https://doi.org/10.1016/j.tifs.2016.04.002>

l'humidité ambiante augmente, la condensation capillaire apparaît due à la tension de surface aux points de contact entre particules. En utilisant l'équation de Kelvin, il est possible de prédire l'activité d'eau pour laquelle le rayon capillaire critique augmente fortement et entraîne ainsi une multiplication des ponts liquides (Billings, Bronlund, & Paterson, 2006). Pour les matériaux solubles, la condensation capillaire s'accompagne d'une dissolution en surface, qui peut être considérée comme le début de la déliquescence.

La déliquescence se caractérise par la transformation d'un solide cristallin en solution aqueuse suite à la prise en eau du solide entouré de vapeur d'eau (Martin, 2000). Cette transition de phase a lieu à une humidité relative bien définie, appelée *humidité relative de déliquescence* (HRD) et caractéristique du solide cristallin considéré. La valeur de HRD dépend de la température et des propriétés du solide (Mauer & Taylor, 2010). Lorsque l'humidité relative ambiante est supérieure à la HRD, les ponts liquides se multiplient. Si elle diminue ensuite en-deçà de la HRD, le processus d'efflorescence conduit à la cristallisation de la matière dans la solution hautement concentrée ; des ponts solides sont alors formés. Cependant, le mottage du à la formation de ponts liquides peut aussi avoir lieu à une humidité inférieure à la HRD, par condensation capillaire (Billings et al., 2006; Scholl & Schmidt, 2014).

Lorsque plusieurs ingrédients déliquescents sont mélangés, la chute de déliquescence est à prendre en compte pour contrôler la stabilité du mélange. En effet, la HRD d'un mélange est inférieure à la HRD de chaque ingrédient (Dupas-Langlet, Benali, Pezron, Saleh, & Metlas-Komunjer, 2013; Wexler & Seinfeld, 1991). Ce phénomène peut donc expliquer le mottage d'un mélange à une humidité inférieure par rapport à ses constituants. Dans le cas du lactose, la présence d'impuretés cristallines déliquescentes pourrait ainsi favoriser le mottage.

Enfin, d'autres facteurs peuvent influencer l'absorption d'eau et la formation de ponts liquides dans la poudre de lactose. La présence de matière amorphe, quoiqu'en faible quantité, modifie la forme de l'isotherme de sorption du lactose alpha monohydraté (Bronlund & Paterson, 2004). Même pour une poudre complètement cristalline, la tendance au mottage et la solidité des ponts formés varient d'un polymorphe à l'autre (Listiohadi, Hourigan, Sleight, & Steele, 2008; Scholl & Schmidt, 2014). En outre, Rogé et Mathlouthi (2003) ont montré pour le sucrose que les petits cristaux ou fragments de cristaux au sein du lit de poudre absorbent davantage d'humidité et jouent le rôle de liant entre les cristaux de taille supérieure. La présence de petits cristaux affecte également la densité de la poudre, qui est un paramètre important pour le mottage, comme expliqué ci-dessous.

3.3. Le mottage mécanique

Le mottage mécanique peut être défini comme la consolidation de la poudre due à la pression auto-exercée par la masse de poudre dans son contenant. L'écoulement d'une poudre dépend

des forces de liaison entre particules. Dans une poudre sèche, les forces de Van der Waals prédominent (Schulze, 2008). Ces forces sont intenses à courte distance et expliquent la forte cohésion de la poudre lorsque les particules se rapprochent. Le réarrangement des particules due à la pression mécanique implique aussi une multiplication des points de contact et une extension de la surface de contact. Ainsi, certaines caractéristiques de la poudre comme la taille et la forme des particules et la déformabilité, influencent grandement la mottage mécanique.

L'étude et la prédiction du mottage mécanique requiert l'estimation de la force de consolidation agissant sur la poudre. Le calcul de cette force diffère selon que le système considéré est un silo ou un sac. En effet, Roberts (Roberts, 1883) et Janssen (Janssen, 1895) ont démontré il y a plus d'un siècle qu'à partir d'un certain niveau de remplissage du silo, la force s'exerçant sur une tranche du lit de poudre est indépendante de la hauteur, car les parois du silo supportent le poids de la poudre par friction. Dans le cas d'un sac, les parois sont flexibles et la pression augmente de façon linéaire avec la profondeur du lit de poudre. Le bas du sac est donc la partie la plus consolidée.

En conclusion, la mottage mécanique peut expliquer l'apparition du mottage au cours du stockage dans un endroit sec et tempéré. Cependant, la pression est souvent davantage un facteur aggravant que la principale cause de mottage. Elle reste donc importante à prendre en compte pour prévenir le mottage d'une poudre. De multiples facteurs doivent également être considérés. Un aperçu de ces facteurs et des mécanismes de mottage sur lesquels ils agissent est donné en Figure 67.

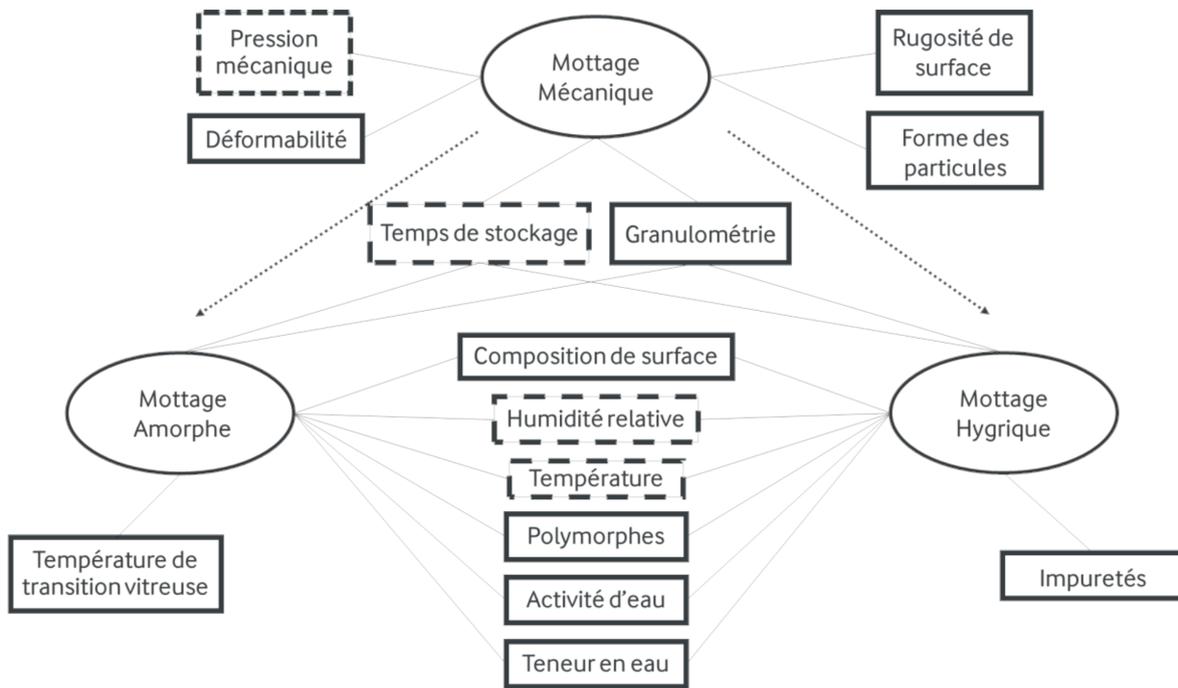


Figure 67: Aperçu des trois mécanismes principaux de mottage (ovales) ainsi que des paramètres intrinsèques (rectangles avec contours plein) et extrinsèques (rectangles avec contours en pointillés) pouvant influencer le mottage du lactose.

3.4. Comment caractériser le mottage ?

Le mottage peut se présenter sous la forme d'agglomérats de différentes tailles et différentes compacités où le reste du sac est non motté mais aussi sous forme d'un sac entier motté en bloc. Compte tenu de la vaste étendue d'applications, il est difficile de développer un test universel de caractérisation du mottage. De plus, le mottage est souvent un processus lent. Cependant, l'industrie alimentaire a besoin d'une méthode rapide d'évaluation du mottage, qui puisse être utilisée par exemple en contrôle qualité. De nombreuses méthodes ont été mises en œuvre, de la simple évaluation visuelle (Scholl & Schmidt, 2014) à l'analyse des propriétés rhéologiques de la poudre (Descamps, Palzer, Roos, & Fitzpatrick, 2013). Listiohadi et al. (2005a) ont catégorisé les méthodes présentées dans la littérature scientifique en cinq groupes : mesures de coulabilité, mesure de force à la compression, mesure de force de cisaillement, examens morphologiques et autres méthodes. Ce manuscrit de thèse présente les méthodes les plus pertinentes pour l'industrie alimentaire ainsi que les paramètres à considérer pour guider dans le choix d'une méthode. Pour notre étude, la mesure de la force de cisaillement après stockage des échantillons dans des conditions contrôlées de température, humidité et pression mécanique a été choisie pour évaluer le mottage.

Résultats

1. Les impuretés augmentent le mottage².

La poudre de lactose est un produit comportant peu d'impuretés, avec une teneur en lactose supérieure à 99%. La valeur précise de cette dernière dépend du type de lactose considéré. Les protéines issues du lait sont en grande partie éliminées à l'étape d'ultrafiltration au cours de la fabrication du lactose. Les composés plus petits, peptides et minéraux, passent à travers les membranes et doivent être séparés des cristaux de lactose à l'étape de lavage. L'efficacité de cette étape détermine donc la pureté finale du produit. Cette étude vise à comprendre le rôle des impuretés dans le processus du mottage du lactose. Pour ce faire, des poudres de lactose avec une teneur en impuretés variable ont été produites à l'échelle pilote et analysées pour leur composition physicochimique, leurs propriétés d'absorption d'eau et leur tendance au mottage.

Comme attendu, il a été montré qu'un degré de lavage des cristaux plus important conduit à une diminution de la teneur en protéines, cendres, eau libre et minéraux dans la poudre après séchage. Seule la teneur en calcium reste quasiment stable, sans doute parce que la fraction résiduelle de cet élément est fortement liée et incluse au sein des cristaux de lactose (

Figure 66).

Pour une distribution de tailles de particules donnée, la sorption d'eau dépend fortement du degré de lavage. En effet, le lactose monohydraté pur est très peu hygroscopique. Cependant, notre étude a montré qu'une augmentation de la teneur en impuretés d'un facteur 10 implique une sorption accrue dès 30% d'HR et une sorption totale (à 95% d'HR) presque 10 fois supérieure. Cet effet a également été observé pour d'autres composés (Guerrieri, Salameh, & Taylor, 2007). Des observations au microscope électronique à balayage (MEB) ont révélé des différences à la surface des cristaux de lactose, comme la présence de particules fines voire de pores. L'adsorption d'eau étant principalement un phénomène de surface, ces hétérogénéités de surface peuvent expliquer les différences de comportement à la sorption.

La sorption est aussi largement influencée par la présence de matériel amorphe, qui peut se former à la surface des cristaux suite à un séchage rapide (Vollenbroek, Hebbink, Ziffels, & Steckel, 2010). Après l'étape de lavage, les impuretés peuvent retenir une certaine quantité d'eau contenant du lactose dissout qui, lors du séchage, pourrait ainsi conduire à la présence de matériel

²Carpin, M., Bertelsen, H., Dalberg, A., Roiland, C., Risbo, J., Schuck, P., & Jeantet, R. (2017). Impurities enhance caking in lactose powder. *Journal of Food Engineering*, 198, 91–97. <https://doi.org/10.1016/j.jfoodeng.2016.11.013>

amorphe. Cependant, ni les isothermes de sorption, ni les spectres de RMN du solide n'ont confirmé la présence d'amorphe.

Enfin, les mesures de mottage ont montré la forte tendance au mottage de la poudre peu lavée par rapport aux poudres avec un degré de lavage élevé. Une teneur en impuretés plus élevée accroît donc le risque de mottage, en favorisant l'adsorption d'eau au sein de la poudre. L'étape de lavage des cristaux de lactose est donc un levier important pour limiter le mottage du produit fini.

2. Une distribution de taille resserrée avec de gros cristaux améliore la résistance au mottage³.

La distribution de tailles de particules ou granulométrie est une caractéristique importante car elle gouverne de nombreuses propriétés de la poudre. Cependant, obtenir la distribution souhaitée est souvent compliqué. L'étape de cristallisation est déterminante mais requiert de nombreux essais pour contrôler les phénomènes physicochimiques complexes mis en jeu dans l'évolution de taille des particules. En cas de modification du procédé impactant la granulométrie, il est important de savoir comment la tendance au mottage du produit fini évoluera. Dans ce but, les poudres à teneur en impuretés variable ont été tamisées pour obtenir différentes distributions de tailles. Ces fractions ont ensuite été soumises à des analyses physicochimiques, granulométriques, d'absorption d'eau et de tendance au mottage.

Les résultats de notre étude ont montré qu'une variation du degré de lavage conduit à une modification de la granulométrie dans la poudre après séchage. De plus, les différentes fractions présentent une teneur en impuretés variable. En général, une augmentation de la taille des particules va de pair avec une diminution de la teneur en impuretés ainsi que de la surface spécifique. Les impuretés sont donc sans doute majoritairement présentes en surface. Les particules les plus fines observées au MEB apparaissent comme un mélange de cristaux bien définis et de fragments agglomérés ou non. Ces fragments provenant sans doute de la surface de cristaux plus gros, ils contribuent ainsi à augmenter la teneur en impuretés de la fraction des particules fines. Il serait donc intéressant de limiter leur formation.

A degré de lavage constant, un effet significatif de la taille des cristaux sur la sorption d'eau a été démontré. En effet, les cristaux plus petits absorbent davantage, ce qui s'explique par une surface spécifique et une teneur en impuretés plus importantes. Par ailleurs, l'étendue de la distribution de taille doit être considérée. Une étendue plus large permet un meilleur réarrangement des

³Carpin, M., Bertelsen, H., Dalberg, A., Bech, J. K., Risbo, J., Schuck, P., & Jeantet, R. (2017). How does particle size influence caking in lactose powder? *Journal of Food Engineering*, 209, 61–67. <https://doi.org/10.1016/j.jfoodeng.2017.04.006>

particules et donc une structure avec des pores plus petits (Bronlund & Paterson, 2004). La condensation capillaire et l'adsorption d'eau sont ainsi facilitées.

Les mesures de mottage sur les différentes fractions ont montré une augmentation de la tendance au mottage lorsque la taille des particules diminue. Ces résultats sont cohérents avec une adsorption d'eau plus élevée mesurée pour des particules plus petites. Le mottage hygrique apparaît particulièrement important. Au contraire, le mottage amorphe est peu probable ici puisque aucune matière amorphe n'a été détecté par les analyses de RMN du solide. En outre, le mottage mécanique est également favorisé par une diminution de la taille des particules en raison d'un nombre croissant de points de contact. En outre, notre étude a montré que l'étendue de la distribution est un autre paramètre crucial pour le mottage, de par sa large influence sur le nombre de points de contact au sein de la poudre. Bien que difficile à contrôler dans une production à grande échelle, la distribution de taille des cristaux peut donc être déterminante pour le mottage du produit fini. Idéalement, la poudre doit être constituée de cristaux de taille homogène et la plus large possible pour limiter le mottage.

3. En pratique : comment contrôler la teneur en impuretés et la granulométrie de la poudre pour limiter le mottage ?

Ce chapitre inaugure l'application industrielle de la thèse. L'objectif est d'abord de vérifier la validité des résultats obtenus dans les chapitres précédents à l'échelle pilote sur des échantillons commerciaux produits en usine. Par ailleurs, une étude des étapes du procédé pouvant influencer la teneur en impuretés et la granulométrie a été menée.

Afin de déterminer le mécanisme de mottage principal dans le lactose issu de l'usine, la poudre a été analysée par de multiples méthodes pour détecter la matière amorphe. Une méthode nouvelle basée sur l'enregistrement de l'humidité relative au sein de la poudre pour suivre la cristallisation a été testée. Cependant, aucune méthode n'a montré la présence de lactose amorphe. Considérant la grande instabilité de ce dernier, il serait intéressant de tester une méthode intégrée à la ligne de fabrication.

Les autres impuretés, comme les minéraux et les peptides, se trouvent généralement en quantité très faible dans la poudre de lactose commerciale. Notre étude a montré que les étapes de séparation et de lavage (

Figure 66) sont déterminantes pour assurer une faible hygroscopicité de la poudre et limiter sa tendance au mottage. Comme pour les échantillons issus de la production pilote, les différentes fractions d'une poudre de lactose commerciale tamisée contiennent des teneurs en impuretés différentes. De manière générale, plus la taille diminue, plus les impuretés augmentent. La

recirculation des particules fines, souvent opérée pour améliorer le rendement, doit donc être considérée avec précaution. En effet, ces particules fines, plus riches en impuretés, peuvent augmenter sensiblement l'hygroscopicité de la poudre.

Concernant la granulométrie, l'étape de cristallisation est sans aucun doute la plus importante à maîtriser. Le procédé est cependant complexe et loin d'être optimisé dans l'industrie laitière selon Wong et Hartel (2014). En outre, les étapes ultérieures lors de la fabrication de la poudre de lactose peuvent modifier la taille des cristaux obtenus. Par exemple, la formation d'agglomérats et l'abrasion mécanique peuvent se produire pendant le lavage, le séchage ou le transport pneumatique jusqu'aux silos. Il est donc essentiel de considérer l'ensemble du procédé de fabrication pour assurer un contrôle optimal des deux facteurs critiques pour le mottage, i.e. la teneur en impuretés et la taille des particules.

4. Suivre l'évolution de l'activité d'eau de la poudre de lactose pour prévenir le mottage.

Comme indiqué dans la revue de la littérature, l'humidité joue un rôle crucial dans l'apparition du mottage. L'activité d'eau (a_w), qui représente la disponibilité de l'eau au sein de la poudre, est donc un paramètre crucial. D'après Bronlund (1997), le mottage du lactose peut être évité en s'assurant que l'activité d'eau de la poudre ne dépasse pas un seuil donné. L'objectif de ce chapitre est donc de définir une méthode fiable de mesure de l'activité d'eau et d'étudier les étapes du procédé qui peuvent influencer l'activité d'eau du produit fini.

Au cours de cette thèse, des mesures d'activité d'eau ont été effectuées avec un a_w -mètre après échantillonnage mais aussi directement dans un sac de poudre à l'aide d'une sonde d'humidité. Les résultats obtenus avec l' a_w -mètre doivent être considérés avec précaution en raison de la très faible quantité d'eau libre contenue dans la poudre de lactose. Les échanges d'eau entre la poudre et l'air environnant dans la chambre de mesure sont en effet limités. L'utilisation de sondes d'humidité permet de réaliser la mesure directement dans un sac, où le ratio poudre/air est supérieur et les échanges d'eau facilités. De plus, l'évolution de l'activité d'eau peut être suivie au cours du stockage. Les résultats ont ainsi montré une forte instabilité du produit après séchage, avec une humidité relative mesurée dans la poudre augmentant jusqu'à des valeurs très élevées en quelques heures de stockage (Figure 68).

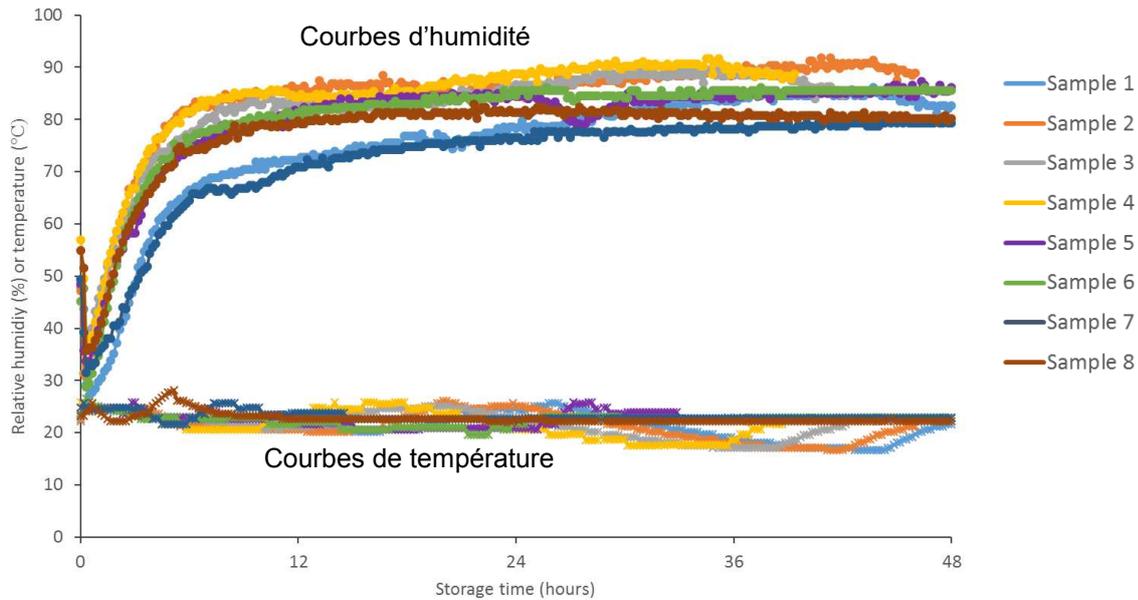


Figure 68: Evolution de l'humidité relative et de la température au cours du stockage de huit poudres échantillonnées en sortie du lit fluidisé. Les poudres proviennent de différents cristalliseurs sur le même site de production. Ces courbes ont été obtenues grâce à un enregistreur de données placé directement dans la poudre.

Cette augmentation rapide de l'activité d'eau de la poudre suggère la présence de matière amorphe qui cristallise et relargue de l'eau. Grâce à une méthode additive de prédiction d'isotherme d'une poudre de lactose partiellement amorphe (Bronlund & Paterson, 2004), il a été montré qu'une teneur en amorphe aussi faible que 0.5% peut conduire à une augmentation de l'humidité de 40% à 80% dans un sac. Des mesures réalisées sur une cinquantaine de lots différents après ensachage ont montré que l'activité d'eau varie considérablement entre lots. De plus, une valeur supérieure à 55% mesurée 3 semaines après ensachage conduit à un risque accru de mottage, comme l'a montré la présence de mottes à l'ouverture du sac après stockage. Un contrôle de l'activité d'eau est donc essentiel.

Pour ce faire, plusieurs étapes sont à considérer. D'abord, une poudre mieux lavée présente une activité d'eau plus élevée après séchage. Cependant, nous avons montré que les impuretés favorisent l'absorption d'eau et le mottage. Il paraît donc plus opportun d'optimiser le lavage et le séchage simultanément pour obtenir une poudre avec une teneur en impuretés et une activité d'eau faibles. A l'étape de séchage, l'objectif est d'éviter la formation de matière amorphe ou bien de la faire cristalliser au sein du lit fluidisé pour éliminer l'eau relarguée. Une stratégie alternative a également été étudiée au cours de cette thèse. Elle consiste à aérer la poudre avec de l'air froid et sec après séchage, à la faveur du transport pneumatique jusqu'aux silos, voire directement dans les silos. Plusieurs modes d'aération (i.e. continu vs. discontinu) ont été testés à l'échelle

pilote. Après aération, l'activité d'eau de la poudre avait diminué de façon significative. Cependant, il n'a pas été possible de la stabiliser. Des recherches futures devront donc se focaliser sur ce point. Par ailleurs, il faut noter qu'une fois mise en sacs, la poudre peut être soumise à d'importantes variations de température et d'humidité pendant le transport ou le stockage. L'activité d'eau et la tendance au mottage peuvent de ce fait être impactées.

5. Développement d'un test de mottage accéléré

L'objectif de ce chapitre est d'adapter la méthode de mesure de mottage avec la cellule de cisaillement de Schulze utilisée dans les chapitres précédents pour obtenir un test de mottage accéléré. Ce test doit permettre de discriminer différents échantillons de lactose en fonction de leur tendance au mottage et ainsi d'établir un contrôle qualité pour détecter les lots peu résistants au mottage. Le défi réside dans le fait de définir des conditions expérimentales de stockage qui accélèrent le mottage et conduisent à des degrés de mottage variés. Cependant, les conditions de température, humidité et pression mécanique utilisées doivent être réalistes pour susciter des mécanismes de mottage analogues à ceux impliqués dans les conditions de stockage et de transport réelles.

En maintenant la température à 50°C, des tests ont été réalisés à 50 et 60% d'HR. Dans les deux cas, des poudres de lactose différant par leur granulométrie et dans une moindre mesure par leur teneur en impuretés ont montré des tendances au mottage différentes. En cohérence avec les résultats obtenus dans les chapitres précédents, le lot aux particules les plus fines mottait le plus fortement. A l'HR la plus élevée, les échantillons étaient mottés après seulement six heures de stockage, à des degrés divers. En comparaison, le test à 50% d'HR a permis, en quelques jours de stockage, de séparer les lots en deux classes, « motté » et « non motté ». Ce deuxième test se distingue cependant par une faible répétabilité qui pourrait limiter son application à des poudres avec des tendances au mottage similaires. Pour cette raison, le test à 50°C et 50% d'HR a été préféré pour une comparaison à plus grande échelle.

Grâce à ce test accéléré, des poudres de trois usines différentes prélevées lors de l'ensachage en sortie du lit fluidisé ont pu être classés selon leur tendance au mottage, après seulement six heures de stockage. Aux faibles niveaux d'impuretés présents dans les poudres commerciales, la granulométrie est le paramètre déterminant. Comme indiqué précédemment, celle-ci peut être modifiée après séchage. Il est donc conseillé de réaliser le test de mottage sur le produit fini.

Nous avons également montré dans le chapitre précédent que l'activité d'eau de la poudre joue un rôle crucial dans le mottage. Cependant, dans le test de mottage accéléré à 50°C et 50% d'HR, l'humidité est fixée et supplante ainsi l'effet de l'activité d'eau de la poudre. Pour prendre cet effet

en compte, un test complémentaire a été développé, où la poudre s'auto-impose l'humidité pendant le stockage. L'effet positif de l'aération après séchage a ainsi pu être mis en évidence. Le mottage apparaît en effet significativement plus tard dans la poudre aérée.

Le choix du test de mottage à réaliser nécessite de connaître le poids relatif des deux paramètres qui apparaissent critiques pour limiter le mottage du lactose, i.e. la granulométrie et l'activité d'eau. Plus généralement, il serait avantageux de focaliser des recherches futures sur ce point pour permettre de classer les lots quant à leur susceptibilité au mottage et de prendre des mesures appropriées avant envoi au client (Figure 69).

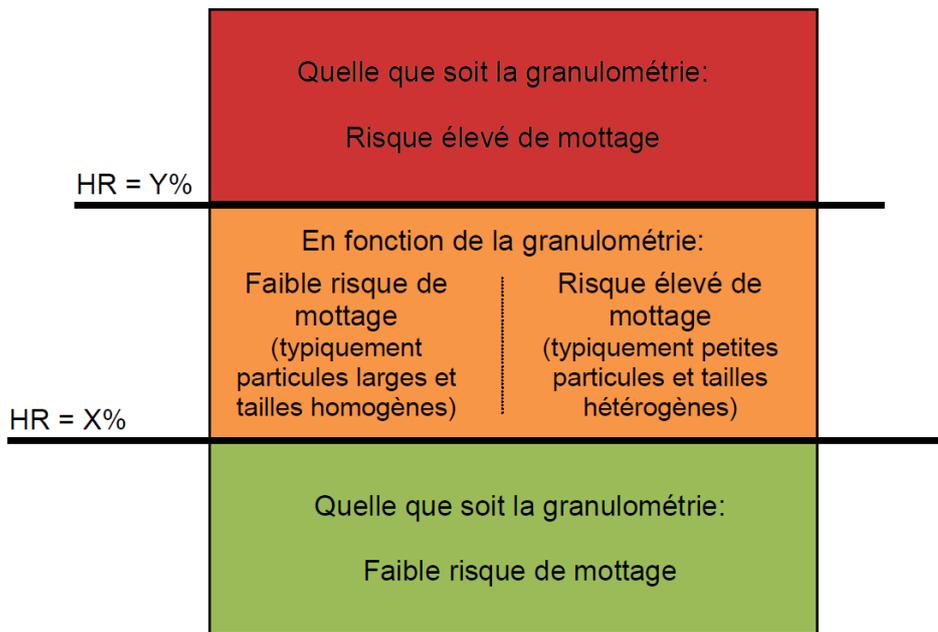


Figure 69: Evaluation du risque de mottage de la poudre de lactose commerciale en fonction de la granulométrie et de l'activité d'eau. X et Y sont des seuils à déterminer.

Conclusion générale et perspectives

La stratégie mise en place dans ce travail de thèse a permis d'atteindre des objectifs divers et complémentaires. Tout d'abord, les objectifs scientifiques qui étaient le développement d'une méthode de mesure du mottage et l'identification des paramètres produits critiques et des mécanismes de mottage ont été atteints. Puis, l'application des résultats aux poudres industrielles a permis de cibler les étapes clés du procédé pour contrôler les paramètres produits déterminants pour le mottage. Des leviers de contrôle du mottage ont ainsi pu être proposés. Enfin, un test accéléré de mottage a été développé pour répondre à un besoin critique des industriels.

Plus précisément, cette étude a montré que les impuretés résiduelles dans la poudre de lactose ainsi que la taille des cristaux sont des facteurs déterminants pour le mottage. Les impuretés ainsi que les petits cristaux favorisent en effet l'absorption d'eau. Le lavage des cristaux doit donc être suffisant pour garantir un niveau d'impuretés faible, comme cela est le cas dans la poudre commerciale. De plus, les étapes influençant la taille des cristaux, en premier lieu la cristallisation, doivent être contrôlées pour obtenir des cristaux larges et de taille homogène et ainsi limiter le mottage. En outre, des mesures d'activité d'eau dans la poudre commerciale ont montré que des valeurs très élevées, jusqu'à 0.9, peuvent être atteintes en quelques heures de stockage après séchage. Une étude systématique a révélé une corrélation entre une activité d'eau élevée dans les sacs et l'apparition du mottage. L'activité d'eau de la poudre doit donc être basse et stable avant mise en sacs pour éviter le mottage pendant le stockage et transport jusqu'au client.

Le contrôle de l'activité d'eau, soit pendant l'étape de séchage, soit en traitement post-séchage requiert des recherches complémentaires. En effet, ce travail de thèse présente plusieurs pistes comme la prévention de la formation de lactose amorphe et l'aération post-séchage de la poudre. Cependant, le développement d'une méthode de mesure appropriée du lactose amorphe permettrait d'optimiser les conditions de séchage pour limiter sa formation. Par ailleurs, les résultats des tests de post traitement par séchage ont montré qu'il est possible de faire diminuer l'activité d'eau et ainsi le mottage. Toutefois, il n'a pas été possible de stabiliser l'activité d'eau par les différents modes d'aération testés. Le mottage n'est donc que retardé. L'aération reste donc à optimiser.

Enfin, comme le montre la Figure 69, les seuils définissant les zones où chaque paramètre a un effet prépondérant sur le mottage restent à déterminer. Pour cela, l'implémentation du test accéléré de mottage sur les différents sites de production permettrait d'évaluer de façon systématique la tendance au mottage. Ce résultat pourrait ensuite être corrélé aux paramètres produits comme la granulométrie et l'activité d'eau, et permettrait *in fine* de mieux cibler les paramètres procédés à modifier pour prévenir le mottage du produit.

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RÉSUMÉ ABSTRACT

Le mottage du lactose : compréhension des mécanismes et prévention

L'augmentation de la demande en lait infantile génère une forte croissance de la production mondiale de lactose. En raison d'exigences accrues sur la qualité du produit, le mottage, ou prise en masse spontanée de la poudre, est une non-conformité pouvant s'avérer très coûteuse. En utilisant une approche procédé – produit, ce projet vise à identifier les paramètres critiques et comprendre les mécanismes de mottage du lactose, pour donner les moyens aux industriels de prévenir le mottage. Les résultats obtenus sur des poudres produites à l'échelle pilote montrent le rôle déterminant des impuretés (i.e. composés autres que le lactose) et de la granulométrie. En effet, les impuretés renforcent l'hygroscopicité et le mottage. De plus, en augmentant la teneur en impuretés, la surface spécifique et le nombre de points de contact, une diminution de la taille des particules et une hétérogénéité de tailles accrue intensifient le mottage. L'analyse des poudres commerciales a confirmé ces résultats mais aussi révélé une augmentation rapide de l'activité d'eau pendant le stockage après séchage de la poudre. Une forte activité d'eau entraîne du mottage dans la majorité des lots concernés. Un autre résultat marquant de ce travail est le développement d'un test de mottage accéléré, qui permet de classer des poudres de lactose en fonction de leur tendance au mottage en moins d'une journée, après un stockage à 50 °C et 60% d'HR. Un test similaire implémenté sur chaque site de production permettrait l'identification rapide des lots à risque avant expédition. Grâce à la meilleure compréhension des mécanismes de mottage fourni par ce travail, les industriels peuvent cibler les étapes critiques du procédé à optimiser pour prévenir le mottage du lactose.

Mots-clés : poudre de lactose, mottage, procédé de fabrication, humidité

Lactose caking: Understanding the mechanisms as a route to prevention

Driven by the growth in the infant formula market, lactose production is increasing worldwide, and the requirements for the product quality are becoming stricter. Caking, or the unwanted agglomeration of lactose powder particles, is synonym of poor quality for the customers and should therefore be prevented to avoid large economic loss. Focusing on the process-product relationship, this PhD project aimed at finding the critical parameters and understanding the caking mechanisms in lactose powder in order to establish means to limit caking. In samples from pilot production, impurities (i.e. non-lactose components) were shown to increase moisture sorption and caking. The particle size distribution of the powder also exhibited a large effect on caking. Indeed, smaller particles and a broader distribution were characterized by enhanced moisture sorption and stronger caking, which were explained by a larger impurity content and surface area and more contact points. Analyses on the commercial powder confirmed these results and revealed the instability of the water activity during storage of the powder after drying, which was linked to caking in the bags. This PhD project also addressed an essential need in the dairy industry, i.e. the development of an accelerated caking test. Samples from different production sites were discriminated in terms of caking in less than a day, using appropriate test conditions (50 °C and 60% RH). A similar test implemented at all sites would highlight batches with a high caking tendency before shipment to the customers. The better understanding of the caking mechanisms provided by this PhD work enables industrials to target the critical processing steps requiring optimization to avoid caking in the finished product.

Keywords: Lactose powder, caking, production process, moisture



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